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SCIENCE FOR SYSTEMS

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Marius Knapp

GRAPHENE – FROM SYNTHESIS TO THE APPLICATION AS A VIRTUALLY MASSLESS ELECTRODE MATERIAL FOR BULK ACOUSTIC WAVE RESONATORS



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Dissertation zur Erlangung des Doktorgrades der Technischen Fakultät der Albert-Ludwigs-Universität Freiburg im Breisgau

Marius David Knapp

September 2018

Graphene - from Synthesis to the Application as a Virtually Massless Electrode Material for Bulk Acoustic Wave Resonators

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Abstract

Mechanical and electrical losses strongly determine the performance characteristic of Bulk Acoustic Wave resonators. The focus of this work lies in the deeper investigation of extrinsic losses, which are induced by the applied electrode material for the device contacting. Here, mainly viscous and ohmic losses play a role due to an electrode's specific mass and limited conductivity. A conflict of objectives lies here in the requirement of ideally massless and highly conductive materials, which commonly used metal electrodes suffer from due to their comparably high mass density. The chance to overcome this problem lies in the use of graphene as a two-dimensional virtually massless carbonic layer with remarkable electronic properties, which can reduce mass-induced loss mechanisms within the resonator device. This work investigates the first time graphene as an active top electrode material for solidly mounted Bulk Acoustic Wave resonators. Here, a process development from the graphene synthesis via the Chemical Vapor Deposition method on copper foil, a specifically elaborated graphene transfer technique onto Aluminum nitridebased resonator structures and a subsequent successful fabrication of working Bulk Acoustic Wave resonators with an optimized graphene-based electrode design are reported. The obtained results regarding the device characterization are promising with respect to the minimization of mass-induced losses. Both electrical and optical investigations clearly show that graphene enables a significant shift in the device resonance frequency, which corresponds to theoretically electrode-free resonator structures. Furthermore, the resonator's performance characteristic shows significant improvements regarding the quality factor, which is determined with the help of an equivalent circuit parameter fitting, the effective coupling coefficient obtained by group delay data, and the additional device comparison with conventionally applied electrode materials. An elaborated graphene metallization design, which an application for a patent is filed for, enables a homogeneous graphene contacting and results in an enhancement of the effective coupling coefficient by more than 32% as an indicator of the energy efficiency. With these values, State-of-the-Art is achieved with the additional effect of a significant reduction of mass-induced losses. In a nutshell, these findings strongly highlight the advantages of graphene and possibly other 2D materials as an alternative electrode in electroacoustic resonators for radio frequency devices.

Kurzfassung

Mechanische und elektrische Verluste bestimmen und beschränken hauptsächlich die Funktionseigenschaften von Volumenwellen-Resonatoren. Der Fokus dieser Arbeit liegt in einer tiefergehenden Untersuchung der Verlustmechanismen der Elektroden, die für eine erfolgreiche elektrische Kontaktierung der Resonator-Bauteile notwendig sind. Aufgrund der nicht zu vernachlässigbaren Elektrodenmasse und ihrer spezifischen Leitfähigkeit spielen Elektroden-induzierte viskose und elektrische Verluste eine dominierende Rolle bezüglich der Funktionscharakteristik des Resonatorbauteils. Ein vermeintlicher Widerspruch liegt hier in der Anforderung an die Verwendung von sowohl sehr leichten als auch gleichzeitig sehr leitfähigen Elektrodenmaterialien, um diese Verluste möglichst komplett vermeiden zu können. Während hier herkömmliche metallische Elektroden aufgrund ihrer relativ hohen Massendichte an ihr Limit kommen, liegt eine mögliche Lösung in der Verwendung von Graphen, einer zweidimensionalen und sehr gut leitenden Kohlenstoffschicht, die aufgrund ihrer nahezu masselosen Eigenschaft diese viskosen Dämpfungverluste minimieren kann. In dieser Arbeit wird das erste Mal überhaupt Graphen als aktives Elektrodenmaterial für Volumenwellen-Resonatoren untersucht. Dabei beschreibt die Arbeit den erfolgreichen Weg von der Optimierung der Graphen-Synthese mittels der Chemischen Gasphasenabscheidung auf Kupferfolie, über einen eigens weiterentwickelten Transfer dieser Graphenschichten auf die Aluminiumnitrid-basierten Resonatorstrukturen als Zielsubstrat hin zu der letztendlich erfolgreichen Herstellung von funktionsfähigen Volumenwellen-Resonatoren mit einem optimierten Graphen-basierten Elektrodendesign. Die Ergebnisse der Bauteilcharakterisierung sind vielversprechend bezüglich der erfolgreichen Reduzierung von Masse-induzierten Elektrodenverlusten auf das Bauteil. Elektrische als auch optische Untersuchungen zeigen, dass Graphen als Elektrode aufgrund seiner tatsächlich vernachlässigbaren Massendichte eine Frequenzverschiebung hin zu Resonanzfrequenzen liefert, die einem theoretischen Resonator-Bauteil ohne jegliche durch Elektroden verursachte Zusatzmasse entsprechen. Ferner kann für den charakteristischen Gütefaktor, welcher sowohl durch ein theoretisches Ersatzschaltbild als auch durch elektrische Messungen der Gruppenlaufzeit bestimmt wird, eine signifikante Erhöhung erreicht werden. Ein bereits zum Patent angemeldetes Metallisierungsdesign, welches für eine gleichmäßige Graphen-Kontaktierung sorgt, ist zudem in der Lage, den effektiven Kopplungskoeffizienten als Maß für die Energieeffizient des Resonatorsystems signifikant um mehr als 32~% zu erhöhen und damit nahezu Werte zu erreichen, die derzeit von State-of-the-Art Bauteilen vorgegeben werden. Zusammenfassend lässt sich feststellen, dass die in dieser Arbeit erhaltenen Ergebnisse eine klare Bestätigung der theoretischen Überlegungen liefern und gleichzeitig aufzeigen, inwiefern Graphen und andere 2D-Materialien als leitfähige masselose Alternativelektroden für elektromechanische Systeme zukünftig verwendet werden können.

Acronyms

4PP	4-point probes method
AC	alternating current
AFM	atomic force microscopy
AP	atmospheric pressure
APS	ammonium persulfate
BAW	bulk acoustic wave
BL	buffer layer
BLG	bilayer graphene
BS	bar structure
BSE	back-scattered electrons
BVD	Butterworth-van Dyke
CA	contact angle
CAD	computer-aided design
CCD	charge-coupled device
CNT	carbon nanotubes
CVD	chemical vapor deposition
DFT	density functional theory
DI	deionized
DR	double resonance
DUT	device under test
EAR	edge-to-area ratio
EBPVD	electron-beam physical vapor deposition
EDX	energy-dispersive X-ray spectroscopy
EP	electrolytic polishing
FBAR	free-standing Bulk Acoustic Resonator
FEM	finite element method
FIB	focused ion beam
FLG	few-layer graphene
FoM	figure of merit
FWHM	full width at half maximum
GFET	graphene field effect transistor
GR	graphene layer

GSG	ground-signal-ground
hBN	hexagonal boron nitride
HOPG	highly oriented pyrolytic graphite
ІТО	indium tin oxide
KHD	Kramers-Heisenberg-Dirac theory
LDV	laser doppler vibrometry
LP	low-pressure
LPE	liquid-phase exfoliation
MBE	molecular beam epitaxy
mBVD	modified Butterworth-van Dyke
MEMS	microelectromechanical systems
NEMS	nanoelectromechanical systems
NMP	N-Methyl-2-pyrrolidone
NWA	network analyzer
ODCB	1,2-dichlorobenzene
OM	optical microscopy
PMMA	poly(methyl methacrylate)
SE	secondary electrons
SEM	scanning electron microscopy
SLG	single layer graphene
SMR	Solidly Mounted Resonator
SSA	specific surface area
TB	tight binding
TLM	transfer line method
UHV	ultra high vacuum
WLI	white light interferometry
WTT	wet transfer technique

List of Symbols

$ u_{ m L} $ $ ho_{ m n} $	sound velocity nucleation density
$D_0 D_{0,c}$	dissociation energy catalytic dissociation energy
$\begin{array}{c} E^* \\ E^*_{\rm c} \\ E_{\rm ad} \end{array}$	activation energy barrier catalytic activation energy barrier adsorption energy
$f_{\rm n}$ $f_{\rm p}$ $f_{\rm s}$	n-th resonance frequency parallel resonance frequency series resonance frequency
$\Delta H^{\Theta}_{ m r} \ {\cal H}^{ m a}_{ m R}$	standard enthalpy of reaction atomic Hamiltonian operator
$k_{ m eff}^2$ $K_{ m RS}$ $k_{ m T}^2$	effective coupling coefficient Raman biaxial stress conversion factor material coupling coefficient
$L_{\rm C}$ $L_{\rm c}$	carbon solubility coherence length
n	charge carrier density
$egin{array}{c} Q \ Q_{ m p} \ Q_{ m s} \end{array}$	quality factor quality factor at $f_{\rm p}$ quality factor at $f_{\rm s}$
$\begin{array}{l} R_{\rm c,GR} \\ R_{\rm m} \\ R_{\rm p} \\ R_{\rm s} \\ R_{\rm s,GR} \end{array}$	graphene contact resistivity bulk-induced viscous loss resistivity electrode-induced viscous loss resistivity graphene sheet resistivity
$s_{ m q}$	surface roughness parameter
$T_{ m M}$	melting point

$v_{ m F}$	Fermi	velocity

W bar structure width

 $Z_{\rm el}$ electrical impedance

1 Introduction

The current decade undergoes a remarkable transformation in terms of communication and data exchange. At the latest with the release of the first-generation iPhone by Apple Inc. in 2007 smart technologies gain more and more impact on everyman's life. Nowadays the use of smartphones, tablets and computer technology has penetrated almost every imaginable part of society's private and business life regarding e.g. the communication systems, the process automation (e.g. machine-tomachine communication), the Internet of Things (IoT) or the entertainment industry (i.e. video streaming). In a nutshell, the countless application possibilities of smart technologies are all about data transfer. Data transfer means the successful delivery of some sort of digital information from some type of sender to some (other) type of addressee. Each type of communication means the transfer of information data. The most efficient way of data transfer is accomplished by a data transformation into a digital signal. Focusing on the rapidly increasing use of smartphones, which itself impressively shows the impact on the society, the amount of data transferred between devices was soaring within the last decade.

1.1 Motivation of this work

Figure 1.1 reveals an increase of data transfer volume, which follows an exponential growth of more than 800 % within the last five years [1]. At this point, it is remarkable that the originally developed possibility of voice transmission stays on a constant level whereas data in terms of video, music and cloud services highly dominate the total data volume.

Technical communication, i.e. data transfer, uses electromagnetic waves as the carrier medium. The electromagnetic spectrum is divided into different frequency bands, which are nationally and worldwide regulated regarding the bandwidth, the wavelength and the intended use. In a simplified view, a higher data transfer requires more frequency bands towards higher frequencies and a closer positioning of them. Here, some technically highly demanding challenges can be brought into focus by means of the underlying hardware components in terms of filter and duplexer structures. Besides the demand for high-performance filter devices, a larger data transfer is reflected by an increasing number of filters in one smartphone, which increased from around 10 towards about 50 nowadays and which is expected to reach up to 100 filters for future application when keeping in mind the fifth-generation of broadband cellular network (5G) [2]. With this follow up, the actually applied 4G network frequency range will be enlarged from 2.6 GHz up to 26 GHz. In order to overcome the socially arising demand for faster and more efficient filter technologies, the technology itself needs to be reconsidered and adjusted regarding the filter design and its underlying building blocks, i.e. resonators.



Figure 1.1: Plot of the increase in data usage from 2013 to 2018. The data for voice-only services stay constant and play a marginal role compared to other data transfers. Adapted from [1].

A maximization of the provided data rate is achieved by filters, which can define very accurate frequency bands and can provide a sufficiently broad band. The so-called filter bandwidth and insertion loss (IL) are the main characteristics of filters, since these key values determine the width of a band-pass filter (in order to use higher frequency ranges, a higher bandwidth is needed) and its steepness (in order to push filters as close as possible to each other regarding the filtered frequency range). These requirements are directly determined by the quality factor Q and the effective coupling coefficient k_{eff}^2 . In Figure 1.2 the principle effect of Q and k_{eff}^2 is shown schematically in a sketch. Q directly affects the insertion loss by influencing the total signal amplitude, i.e. the height of the passband. For both a low Q and k_{eff}^2 (a), the insertion loss is increased and the passbands cannot be located close to each other due to a relatively flat slope of the admittance curve. A high Q reduces the insertion loss (IL = 0 dB would mean no loss of energy) and a high k_{eff}^2 enables to locate different filters very close to each other without any interfering of the passbands (b).

In terms of technology, so-called bulk acoustic wave (BAW) resonators turned out to be promising to reach such high frequencies with a sufficient low insertion loss [3]. In principle, the underlying effect of piezoelectricity, which enables the conversion of electrical energy into mechanical energy, results in the creation of acoustic waves within the resonator material. Due to sound velocities much lower than the speed of light, very thin piezoelectric layers result in much smaller device sizes and comply with the desired frequencies as they are highly demanded for the future smart technologies. Competing structures here are the free-standing Bulk Acoustic Resonator (FBAR) and the Solidly Mounted Resonator (SMR) designs, which will be elucidated in more detail in Chapter 2. The performance characteristic of a resonator depends on the applied piezoelectric material itself and the chosen geometry on the one hand and on the additional influence of the electrode material, which is used in order to electrically contact the device on the other hand. Technologically, BAW resonators are quite well understood



Figure 1.2: Schematic drawing of the influence of Q and k²_{eff} on the passband shape of filter structures. (a) Low Q and k²_{eff} lead to a high insertion loss and a large cut-off frequency area. (b) High Q and k²_{eff} lead to a low insertion loss and closer positioning possibility of the filters.

and the fabrication already reaches mass market. Generally, the performance of every resonator device is limited due to different loss mechanisms, which can be separated into bulk-induced and electrode-induced ones. Improvements on the bulk material side lie in the field of developing new materials (i.e. Aluminum scandium nitride (AlScN) [4] with a higher piezoelectrical coefficient compared to commonly used AlN) and the improvement of synthesis methods enabling an excellent crystal quality of the piezomaterial. On the electrode side, the potential in optimization lies in a mass reduction with a simultaneously sufficient conductivity of the electrode material. Commonly used electrode materials are metals such as gold (Au), molybdenum (Mo), tungsten (W) or aluminum (Al). Despite their excellent conductivity, damping losses are induced due to their high mass density. It is expected and theoretically predicted that the electrode mass has a main influence on the resonator's quality factor at the so-called parallel resonance frequency. An ideal device would use a massless and conductive electrode in order to reduce these additional viscous losses. The trade-off between a thickness reduction and a simultaneously decreasing conductivity due to surface scattering effects (described by the Fuchs-Sondheimer-Model) make the commonly applied electrode materials being inappropriate. Therefore, the focus of this work lies in the development of a new electrode approach where graphene as a virtually massless conductive material comes into play.

At the latest in 2010, the Nobel prize for the graphene exfoliation set off an avalanche regarding graphene research activities, which reveal the industrial use of graphene in several fields, i.e. graphene in supercapacitors [5, 6], as a transparent electrode material for tablets/smartphones [7], in photovoltaics [8] as a replacement for the transparent but expensive and rare indium tin oxide (ITO) or in other solar cell applications as the photovoltaic layer itself [9]. With respect to micro- and nanoelectromechanical systems, MEMS and NEMS, the focus lies on graphene as an extremely light and conductive material which could strongly reduce mass-induced damping effects on resonator structures. Qian et al. [10–12] successfully applied graphene as a floating potential electrode on AlN based NEMS used as infrared detectors. Here, the massless character of graphene is evaluated, however, its conductivity is not a limiting factor since it is only used as a *passive* conductive electrical field confinement layer, i.e. serving as a floating potential pote

tential with no applied voltage signal. In this work, high-quality graphene is developed in order to use it as an *active* electrode material. For this purpose, the already known chemical vapor deposition (CVD) synthesis method is developed for the specific laboratory reactor *BlackMagic 6inch*, and a modified wet transfer technique is engineered. In the following, the novel approach of this thesis is presented shortly.

1.2 Novel approach of this thesis

In the field of synthesis optimization, the CVD process development and the parameter adjustment for the laboratory reactor *BlackMagic 6inch* is presented. A process parameter optimization enables high-quality graphene growth on up to $40 \times 40 \text{ mm}^2$ copper (Cu) foil substrates with a reproducibly high characteristic 2D/G > 2.5 Raman signal ratio and low Raman defect peak, which reveals the high layer quality of large-area graphene.

With respect to the transfer onto target substrates of interest, the successful transfer of $40 \times 40 \text{ mm}^2$ graphene from its Cu foil growth substrate onto AlN based SMR resonator structures is introduced. The focus here lies in a specific surface pretreatment regarding surface's wettability of the target substrate. With the findings of this work graphene sheet resistances ($R_{\rm s,GR}$) can be achieved, which are comparable to graphene on standardly used silicon dioxide (SiO₂), i.e. $R_{\rm s,GR}$ reproducibly lie in the range of $1 \text{ k}\Omega/\text{sq}$ and below with the best value of $R_{\rm s,GR} = 350 \Omega/\text{sq}$.

The successful graphene synthesis and transfer technique result in a novel investigation of graphene-contacted AlN-based SMR resonators. For the first time, graphene is used as an *active* electrode material and the obtained results comply with the predicted theoretical assumptions, i.e. a tremendous reduction in mass-induced losses. With a significant frequency shift due to the massless character of graphene and triplication of the quality factor at parallel resonance Q_p , the coupling coefficient k_{eff}^2 is increased compared to commonly used state-of-the-art resonator devices. As a result of this, our findings open a new field of applications for graphene as an alternative to commonly used electrode materials.

1.3 Outline of this thesis

Due to the complexity of the topic and due to the fact that both material development regarding the graphene synthesis and the fabrication of working devices are within the focus of this work, the thesis manuscript is structured in the following way:

In Chapter 2 a short introduction to the state-of-the-art concepts of BAW resonators and their working principle are presented. An equivalent circuit model is introduced, which enables a proper description of electrode induced damping effects. The outlook ends with the suggestion of using graphene as an alternative electrode material.

The physical properties of graphene and its two-dimensional appearance are derived in Chapter 3, leading to an explanation of its virtually massless character and its good conductivity. Furthermore, the main experimental characterization methods are presented and a summary about commonly used graphene synthesis methods is given. The chapter ends with a focus on the CVD process which is the applied method for the graphene synthesis in this work.

Chapter 4 presents experimental results regarding the graphene synthesis via CVD. The laboratory reactor is introduced together with its possibility of a proper process parameter study. An optimized synthesis process is developed and established, which is the basis for all following fabrication steps towards electrodes for BAW resonators.

In the next Chapter 5 the wet transfer technique is introduced and an optimized adaption for graphene on AlN is presented. The key step here is a surface termination via a plasma pretreatment which enables the crack-free graphene transfer from the Cu foil growth substrate to the AlN target substrate.

The findings in the previous two chapters are the basis for Chapter 6, in which the fabrication and characterization of graphene-electrode based working BAW devices are presented. The experimental results are very promising with respect to the avoidance of additional electrode mass-induced losses. A sophisticated metal structure for contacting graphene is presented, which successfully juggles both viscous and ohmic losses.

In a summary in Chapter 7, the main findings of this work are highlighted again and conclusions for future work are drawn. It is worth to foreclose that graphene is successfully used as an *active* electrode material for BAW resonator devices for the first time within the framework of this thesis.

2 Basics about Bulk Acoustic Wave resonators

Bulk acoustic wave resonators serve as the key building blocks for radio frequency filters commonly used in wireless communication devices. With a theoretical description of the underlying piezoelectric effect by the acoustic transmission line model, the scope of this chapter is the explanation of the basic working principle of the so called Solidly Mounted Resonator (SMR) type resonators. By thinking of the energy conversion from an electrical signal into a mechanical resonant vibration of a resonator device, the electrode induced losses, both mechanical and electrical, are brought into focus of a deeper explanation and filter description. The overall goal is a maximization of the quality factor as the main performance characteristic of a resonator. The Butterworth-van Dyke model as a description of the underlying electrical circuit allows extensive implications about an optimization procedure. According to the deduced formulas regarding the characteristic admittance behavior, graphene is presented as a suitable candidate for an alternative electrode material. This chapter serves as the framework of this thesis since the motivation lies in an optimization of the resonator's performance. In Chapter 6, the developed electrode material, i.e. graphene, is applied and compared to the theoretical implementations here.

2.1 The working principle of a Bulk Acoustic Wave resonator

The underlying principle of every BAW device is the conversion of electrical energy into mechanical energy and vice versa. This is accomplished by the use of so called piezoelectric materials. A simple BAW structure is the free-standing Bulk Acoustic Resonator (FBAR), which only consists of a thin (normally several μ m) piezoelectric material layer with a double-sided metallization in order to apply an exciting alternating current (AC) signal, as schematically depicted in Figure 2.1 (a). The layer starts resonating at a certain *n*-th resonance frequency (f_n), which is given as

$$f_n = \frac{\nu_L n}{2t},\tag{2.1}$$

with the layer thickness t, the material specific sound velocity $\nu_{\rm L}$ and an integer multiple n of half the acoustic wavelength. Equation (2.1) describes a standing wave frequency whose acoustic energy is mainly stored in the thickness extensional mode TE1, i.e n = 1,



Figure 2.1: (a) Schematic working principle of a theoretically free-standing FBAR with the layer thickness t. An applied AC signal leads to a resonant excitation at f_n . (b) 2D finite element method (FEM) simulation (obtained by COMSOL Multiphysics) at the resonance frequency for an exemplary FBAR structure (AlN as the piezoelectric material, $t = 2 \mu m$), revealing the TE1 mode at time t' = 0 (1) and t' = T/2 (2), with the oscillation period T.

as depicted in Figure 2.1 (b). As a result of this, the BAW is described as a longitudinal/compressive wave with the piezoelectric material as the propagation medium. The resonator's performance is mainly characterized by the quality factor (Q) and the effective coupling coefficient k_{eff}^2 [13], which are defined as

$$Q = \frac{Energy \ stored \ (\omega)}{Energy \ dissipated \ per \ cycle},$$

$$k_{\text{eff}}^2 = \frac{Electrical \ energy \ converted \ into \ mechanical \ energy}{Dl \ t \ into \ mechanical \ energy}.$$
(2.2)

Q is a dimensionless number, which describes the energy efficiency of the resonator in terms of energy dissipation within one oscillation period T, also called insertion loss, whereas k_{eff}^2 stands for the conversion efficiency from electrical into mechanical energy. Thereby, both serve as performance indicators of every resonator device, which is explicated more detailed in the course of this chapter.

Electrical input energy

2.1.1 It is all about coupling – the Solidly Mounted Resonator

The FBAR structure is the far easiest BAW resonator design, since the BAW is perfectly coupled within the piezoelectric AlN due to the strong impedance mismatch between AlN and air or vacuum. As a result of this, FBAR devices do stand out due to their low insertion loss. A proper wave coupling means the maximum reflection of the energy of an acoustic wave into the piezomaterial, which ensures the formation of a standing wave with minimized energy loss. For FBAR structures the AlN is a free-standing membrane-like layer with thin top and bottom electrodes, TE and BE, respectively, as depicted in Figure 2.2 (a). Practically, due to technological reasons, the fabrication of ultrathin piezoelectric layers is not trivial regarding the material requirements and its later application, since the ongoing push towards higher frequencies results in thinner and thinner piezo-layers.



Figure 2.2: (a) Schematic drawing of the FBAR device design (SolidWorks 2014). The resonating AlN membrane is coupled within a top (TE) and a bottom electrode (BE). An air gap leads to a free-standing layer, which is mounted on silicon (Si) on the resonator edges. The corresponding acoustic energy storage is illustrated for the strain amplitude distribution in (b) (red line). The free-standing character ensures a perfect coupling within the resonating layer. (c) Schematic drawing of the SMR device design. The complete resonating system is mounted on a Si substrate. A Bragg reflector (BR) ensures the proper coupling of the BE. (d) Corresponding acoustic energy storage similar to (b). Within the Bragg reflector layers the strain distribution is minimized and vanishes rapidly in vertical direction.

According to Equation (2.1), an FBAR performing at 2 GHz requires an AlN layer thickness of only 2.5 µm, given the sound velocity $\nu_{AlN} = 10\,130\,\mathrm{m/s}$ for longitudinal waves [14]. Although its carried fragility does not provoke problems yet - FBAR are commonly used in electronic devices in filters, e.g. as duplexers - for higher frequencies the thinner layers become more and more fragile and the material quality turns out to be limited in terms of intrinsic and electrode induced stress and of a degrading crystal quality. The SMR approach overcomes the stress issue by mounting the whole resonator structure on a solid substrate, usually Si. The wave coupling is achieved by a stack of materials with changing acoustic impedances in order to ensure a maximum reflection of the acoustic energy [15]. A layer thickness of approx. one quarter of the wavelength leads to destructive interference between incident and reflected wave fronts due to a 180° phase shift. The working principle compared to the FBAR design is shortly depicted in Figure 2.2 (c). In (b) and (d) the corresponding strain amplitude distributions within the piezo-layer are depicted for the FBAR and SMR type, respectively. The exact amplitude slope can be calculated and directly depends on the acoustic impedance of the used layer material. For the FBAR device, the strain attenuates within the electrodes, whereas the desired attenuation within the SMR Bragg reflector is only obtained by multiple reflections and interferences within the layer stack. Thereby strain within the underlying substrate is prevented. Otherwise the acoustic wave would travel into the

substrate leading to a significant energy loss in terms of heat. Commonly used stack materials are alternating oxide and metal layers [16, 17] in order to enforce the acoustic phase shift.

Apart from the consideration of the performance indicators [17], the SMR design has one major advantage compared to the FBAR structure. The SMR approach exhibits a more robust handling regarding the electrode fabrication. This advantage is used to fuller capacity by a further simplification of the design geometry, which is obtained by the adoption of a ground (G) and signal (S) electrode on the top side of the resonator structure. Thereby the fabrication of metal contacts is a strict bottom-up process. In this case the BE only serves as a floating potential which confines the acoustic wave within the piezo-layer. A more detailed description of this applied resonator design is mentioned in Chapter 6, see Figure 6.1. Since the focus of this work lies in the investigation of graphene as an electrode material, this selected SMR design with its bottom-up structure is essential due to technological reasons regarding the wet transfer technique (Chapter 5). In the following section, the underlying piezoelectric effect, which is responsible for the formation of the standing wave, is first described more detailed.

2.1.2 The piezoelectric effect

Generally, solids are made up of atoms or molecules with a certain order and orientation relative to each other. They are characterized by their structural rigidity regarding the change in their shape or volume, which is determined by their specific bond strength and electron configuration. If the atomic constituents are ordered periodically in a microscopic structure, the solid is called a crystal. In order to change the shape of a crystal, an external force F needs to be applied. External stress T leads to a solid deformation S, which is defined by Hooke's law as

$$\boldsymbol{T} = \boldsymbol{cS},\tag{2.3}$$

with the so called stiffness c, which is a specific property of the investigated material.

The formation of bonds within the crystal possibly lead to a charge dislocation within the atomic structure, whereas the crystal in its entirety appears neutral, i.e. no net charge. These dislocation of electrical charges also exhibit a certain order. An electrical charge displacement D within the crystal arrangement is achieved via an externally applied electrical field E, which leads to a charge displacement within the solid, defined as

$$\boldsymbol{D} = \boldsymbol{\epsilon} \boldsymbol{E},\tag{2.4}$$

with the material specific electrical permittivity $\boldsymbol{\epsilon}$.

By combining the mechanical and polarization effect, the piezoelectric effect is a phenomenon, which describes a change in the electrical polarization P of a certain material due to externally induced stress and results in the occurrence of a voltage within the material. The basic principle is depicted in Figure 2.3 (a). Depending on the material's crystal structure and orientation, here a hexagonal arrangement of atoms with an alternating charge distribution, an applied stress T leads to a crystal deformation



Figure 2.3: (a) Schematic drawing of the direct piezoelectric effect for an exemplary hexagonal crystal structure. An externally applied force *F* results in a deformation of the material leading to a polarization *P*, i.e. a net voltage drop within the crystal. (b) Atomic structure of c-axis oriented AlN, used as the piezoelectric material in this work. From [18]. (c) Cutout of the AlN crystal in order to focus on the piezoelectrically relevant mechanism. Due to its crystal structure, the material is piezoelectrically active only in z-direction.

and simultaneously to the formation of microscopic dipoles, which itself can be measured as a macroscopic voltage drop. This is called the direct piezoelectric effect, whereas at once an externally applied voltage results in a crystal deformation (inverse piezoelectric effect). For piezoelectric materials a deformation S influences the electrical displacement D and vice versa, both under the regulation of an electrical field E, which results in a coupling of Equation (2.3) and (2.4) as the constitutive equations [19]

$$T = c^{E}S - eE,$$

$$D = e^{T}S + \epsilon^{S}E,$$
(2.5)

with the electromechanical coupling coefficient \boldsymbol{e} . The exponents in $\boldsymbol{\epsilon}^S$ and \boldsymbol{c}^E stand for a constant strain and electrical field, respectively, under which \boldsymbol{T} and \boldsymbol{D} can be determined. Both $\boldsymbol{\epsilon}$, \boldsymbol{e} and \boldsymbol{c} have a tensor structure (3×3, 3×6 and 6×6, respectively) due to the effect of strain and electrical displacement in 3D and the consideration of both longitudinal and shear mode components [13, 20].

2.1.3 AIN as a piezoelectric bulk material

The successful excitation of bulk acoustic wave resonances with piezoelectric materials was first demonstrated in the 1980s [21, 22], using zinc oxide (ZnO) since it owns a high electromechanical coupling coefficient. The high electrical resistance, low dielectric losses and a high breakdown voltage make AlN as a wide-band-gap material (6.2 eV, [23]) being a suitable piezoelectric alternative. In this work, AlN is used as the piezoelectric layer, as introduced in Chapter 5, cp. also Figure 2.1. Its hexagonal structure, as depicted in Figure 2.3 (b), leads to a much simplified description of the piezoelectric effect within the material regarding the tensor entries of the coupling coefficient e and the stiffness c. Due to the AlN symmetry regarding 60° and 120° rotations, the stiffness and the electromechanical coupling matrices reduce to the constitutive equations as

$$\begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{21} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{31} & c_{32} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} - \begin{bmatrix} 0 & 0 & e_{31} \\ 0 & 0 & e_{31} \\ 0 & 0 & e_{33} \\ 0 & e_{51} & 0 \\ e_{51} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix},$$
(2.6)

$$\begin{bmatrix} D_x \\ D_y \\ D_z \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} + \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}.$$
(2.7)

In BAW devices, the bulk acoustic wave is coupled in the piezo-layer vertically in z-direction. For c-axis oriented AlN, the piezoelectric effect in z-direction results in a strong polarization [24], as schematically depicted in Figure 2.3 (c). For waves propagating in z-direction the sound velocity $\nu_{\rm L}$ within a crystal is generally defined as

$$\nu_{\rm L} = \sqrt{\frac{c_{33}}{\rho}},\tag{2.8}$$

with the stiffness coefficient c_{33} and the mass density ρ of the specific material. Regarding $\nu_{\rm L}$, the piezoelectric effect leads to an additional stiffening of the material. In case of a piezoelectric material, such as AlN, the sound velocity is corrected by the influence of a net potential induced by the polarization change as

$$\nu_{\rm L,p} = \sqrt{\frac{c_{33} + \frac{e_{23}^2}{\epsilon_{zz}}}{\rho}}.$$
(2.9)

In the following, the bulk acoustic wave is mathematically described in terms the electrical impedance in order to state predictions about the resonating behavior of a BAW device regarding the quality factor Q and the coupling coefficient k_{eff}^2 . For simplification, a one-dimensional model is applied, the so called acoustic transmission line model.

2.1.4 The Acoustic Transmission Line Model – a 1D theoretical picture of a resonator

The impedance behavior of a specific material is derived from a simplified onedimensional (1D) view of the resonating structure. Assuming an "air - piezoelectric material - air" layer stack, an acoustic wave within the piezoelectric material can be described mathematically. Here, this layer is labelled as layer II, whereas the indices I and III represent the adjacent "layers" of air. By regarding only a wave propagation in z-direction, the calculus simplifies strongly and will be elucidated roughly in dependence



Figure 2.4: Schematic drawing of the 1D transmission line model. The piezoelectric layer II with a thickness t, i.e. AlN, is considered as a free-standing layer, where the BAW propagates back and forth. Specific boundary conditions at the interfaces with air (layer I and III) lead to the theoretical calculation of the electrical impedance $Z_{\rm el}$.

on the considerations of Mason [25] and Rosenbaum [13]. With the incorporation of the piezoelectric response, a model of the acoustic behavior can be deduced.

From elastic wave theory by solving the wave equation, the general form of the particle displacement within a crystal, i.e. the piezoelectric material layer II, is given as

$$u_{z,II} = A_{II}e^{-jk_z z} + B_{II}e^{jk_z z}, (2.10)$$

with the wave propagation in z and -z direction, which is represented by $e^{jk_z z}$ and $e^{-jk_z z}$, respectively. The wave amplitudes A_{II} and B_{II} stand for the impedance mismatch. The concept of the back- and forward propagating waves at the interfaces of the piezoelectric layer are schematically shown in Figure 2.4. The simplification of considering only in-plane strain and excited waves only in z-direction leads to following mathematical consequences, i.e.

$$S_3 = S_{zz} = \frac{\partial u_z}{\partial z}, \quad S_i = 0 \text{ for } i = 1, \dots 6 \text{ and } i \neq 3,$$

which describes the consideration of crystal deformations only in z-direction. According to Equation (2.6), only the stress component T_3 is of interest, which is given together with the resulting reduced electrical displacement component D_z as

$$T_3 = c_{33}S_3 - e_{33}E_z = c_{33}\frac{\partial u_z}{\partial z} - e_{33}E_z, \qquad (2.11)$$

$$D_z = e_{33}S_3 + \epsilon_{zz}E_z = e_{33}\frac{\partial u_z}{\partial z} + \epsilon_{zz}E_z.$$
(2.12)

Newton's law [13] is then cut down on

$$\rho \frac{\partial^2 u_z}{\partial t^2} = \frac{\partial T_3}{\partial z}.$$
(2.13)

According to Ampere's circuital law, the electrical displacement D_z can be described as an oscillating current density J_z as

$$J_z = \frac{\partial}{\partial t} D_z = j\omega D_z. \tag{2.14}$$

Inserting Equation (2.14) in (2.12), the electrical field E_z which arises from the particle displacement D_z , is determined as

$$E_z = \frac{J_z}{j\omega\epsilon_{zz}} - \frac{e_{33}}{\epsilon_{zz}}S_3, \qquad (2.15)$$

with the piezoelectric coefficient $d_{33} = e_{z3}/\epsilon_{zz}$. For c-axis oriented AlN the theoretically calculated d_{33} lies between 5.3 and 6.7 pm/V [26]. Combining this with Equation (2.11) results in a final description of the stress component $T_{3,II}$ in layer II as

$$T_{3,II} = \left(c_{33} + \frac{e_{33}^2}{\epsilon_{zz}}\right) \cdot \frac{\partial u_{z,II}}{\partial z} + j \frac{J_z e_{33}}{\omega \epsilon_{zz}}.$$
(2.16)

Due to the consideration of a free-standing AlN in the air/vacuum, i.e. an FBAR structure, the boundary condition, i.e. $T_3 = 0$ at the boundaries of the piezoelectric layer II, results in

$$T_{3,I}(z=0) = T_{3,II}(0) = 0$$

$$\iff \left(c_{33} + \frac{e_{33}^2}{\epsilon_{zz}}\right) \cdot jk_z \left[-A_{II} + B_{II}\right] + j\frac{J_z e_{33}}{\omega \epsilon_{zz}},$$
(2.17)

$$T_{3,II}(z=t) = T_{3,III}(t) = 0$$

$$\iff \left(c_{33} + \frac{e_{33}^2}{\epsilon_{zz}}\right) \cdot jk_z \left[-A_{II}e^{-jk_z t} + B_{II}e^{jk_z t}\right] + j\frac{J_z e_{33}}{\omega \epsilon_{zz}}.$$
(2.18)

With these two equations, the wave amplitudes A_{II} and B_{II} can be finally determined as

$$A_{II} = \frac{J_z d_{33}}{\omega^2 Z_{\rm L}} \frac{e^{jk_z t} - 1}{e^{jk_z t} - e^{-jk_z t}},$$
$$B_{II} = \frac{J_z d_{33}}{\omega^2 Z_{\rm L}} \frac{e^{-jk_z t} - 1}{e^{jk_z t} - e^{-jk_z t}},$$

with the acoustic impedance $Z_{\rm L} = \nu_{\rm L,p} \cdot \rho$, the layer thickness t and the wave vector $k_z = \omega / \nu_{\rm L,p}$. At this point, $u_{z,II}$ is completely defined.

With these findings, the electrical impedance $Z_{\rm el} = U/I$ of the piezoelectric layer can be calculated. The current I and the voltage U are defined as

$$I = \iint J_z dA = J_z \cdot A, \tag{2.19}$$

$K_{33} = \frac{e_{z3}}{\sqrt{c_{33}\epsilon_{zz}}}$	Electromechanical coupling coefficient
$k_{\rm T}^2 = \frac{d_{33}^2 \epsilon_{zz} k_z}{\omega Z_{\rm L}} = \frac{K_{33}}{1 + K_{33}}$	Material coupling coefficient
$k_{ m eff}^2 = rac{\omega_{ m p}^2 - \omega_{ m s}^2}{\omega_{ m p}^2} = rac{f_{ m p}^2 - f_{ m s}^2}{f_{ m p}^2}$	Effective coupling coefficient
$ u_{\rm L,p} = \sqrt{\frac{c_{33}\left(1+K_{33}^2\right)}{ ho}} $	BAW sound velocity $\left[\frac{m}{s}\right]$
$d_{33} = \frac{e_{z3}}{\epsilon_{zz}}$	Piezoelectric coefficient $\left[\frac{pm}{V}\right]$
$C_0 = \frac{\epsilon_{zz}A}{t}$	Plate capacitance of the piezolayer $\begin{bmatrix} C \\ V \end{bmatrix}$
$Z_{\rm L} = \rho \nu_{\rm L,p}$	Acoustic impedance $\left[\frac{\text{kg}}{\text{s} \cdot \text{m}^2}\right]$
$k_z = \omega / \nu_{\rm L,p}$	Wave number $\left[\frac{1}{m}\right]$
$\omega_{\mathrm{p}} = rac{\pi u_{\mathrm{L,p}}}{t}$	Parallel resonance frequency [Hz]
$\omega_{\rm s} = \omega_{\rm p} \left(1 - k_{\rm T}^2 \cdot \frac{4}{\pi^2} \right)$	Serial resonance frequency [Hz]

Table 2.1: Basic resonator properties deduced from the acoustic transmission line model.

$$U = \int_{0}^{t} E_z dz = \frac{J_z \cdot t}{j\omega\epsilon_{zz}} - d_{33} \left[u_z(t) - u_z(0) \right]$$

= $\frac{J_z \cdot t}{j\omega\epsilon_{zz}} + 2 \cdot \frac{J_z d_{33}^2}{\omega^2 \cdot Z_{\text{el}}} \frac{e^{jk_z t} + e^{-jk_z t} - 2}{e^{jk_z t} - e^{-jk_z t}},$ (2.20)

with the resonating plate area A and the current density J_z as given from Equation (2.14). This finally leads to the equation of the electrical impedance $Z_{\rm el}$ and the corresponding admittance $Y_{\rm el}$

$$Z_{el} = \frac{1}{j\omega C_0} \left(1 - \frac{2 \cdot d_{33}^2 \epsilon_{zz}}{\omega \cdot Z_{\rm L} \cdot t} \tan \frac{k_z t}{2} \right) = \frac{1}{j\omega C_0} \left(1 - k_{\rm T}^2 \frac{\tan \frac{k_z t}{2}}{\frac{k_z t}{2}} \right),$$
(2.21)

$$Y_{\rm el} = \frac{j\omega C_0}{1 - k_{\rm T}^2 \frac{\tan \frac{k_z t}{2}}{\frac{k_z t}{2}}}, \text{ with } C_0 = \frac{\epsilon_{zz} A}{t},$$
(2.22)

with the material coupling coefficient $k_{\rm T}^2$ and the plate capacitance C_0 . From the calculations above several conclusions can be drawn, which are summarized in Table 2.1. The $1 - \tan(k_z)$ behavior of Equation (2.21) requests the consideration of $Z_{\rm el} \to \infty$ and $Z_{\rm el} = 0$, which results in the serial (s) and parallel (p) resonance frequencies



Figure 2.5: (a) Characteristic admittance curve with a serial resonance f_s at $Y_{\rm el} = Y_{\rm max}$ and a parallel resonance $f_{\rm p}$ at $Y_{\rm el} = Y_{\rm min}$. (b) Schematic description of the creation of a band-pass filter by adding up two or more resonator admittance slopes.

$$\omega_{\rm s} = \omega_{\rm p} \left(1 - k_{\rm T}^2 \cdot \frac{4}{\pi^2} \right) = 2\pi f_{\rm s},$$

$$\omega_{\rm p} = \frac{\pi \nu_{\rm L,p}}{t} = 2\pi f_{\rm p}.$$
(2.23)

The electrical admittance of Equation (2.22) is schematically depicted in Figure 2.5 (a), indicating the serial and parallel resonance at the minimum and maximum $Y_{\rm el}$, respectively. The mechanical motion of the piezolayer occurs at $f_{\rm p}$, i.e. $Z_{\rm el} = max/Y_{\rm el} = min$. Here, the electrical energy is converted into mechanical one, whereas at $f_{\rm s}$ an electrical resonance, which only leads to internally resonating electrons, occurs.

The material coupling coefficient $k_{\rm T}^2$ is frequency-dependent and calculated as

$$k_{\rm T}^2 = \frac{d_{33}^2 \epsilon_{zz} k_z}{\omega Z_{\rm L}}.$$
 (2.24)

Regarding "real" resonators, additional effects contribute to the resonating behavior, i.e. electrode-induced, dielectric and viscous losses. In this case, an effective coupling coefficient (k_{eff}^2) depends on the whole resonator structure, whereas k_{T}^2 is the theoretical limit given only by the properties of the piezoelectric material which is determined to lie at around 6.5% [27]. k_{eff}^2 is described by the distance in frequency space between f_{s} and f_{p} . According to the *IEEE Standard on Piezoelectricity* [28] k_{eff}^2 is determined as

$$k_{\rm eff}^2 = \frac{\omega_{\rm p}^2 - \omega_{\rm s}^2}{\omega_{\rm p}^2} = \frac{f_{\rm p}^2 - f_{\rm s}^2}{f_{\rm p}^2}.$$
 (2.25)

With the separation $Z_{\rm el}(\omega) = R(\omega) + X(\omega)$, the quality factor Q from Equation (2.2) is then given as

$$Q_{\rm s,p} = \left[\frac{1}{2} \ \omega \left|\frac{d\phi}{d\omega}\right|\right]_{\omega_{\rm s,p}} = \left[\frac{1}{2} \ \omega \frac{1}{R(\omega)} \left|\frac{dX(\omega)}{d\omega}\right|\right]_{\omega_{\rm s,p}},\tag{2.26}$$

with the phase $\phi = \arg(Z_{\rm el})$ of the input impedance $Z_{\rm el}$ [22, 29, 30]. $|d\phi/d\omega|$ is the so called group delay and describes the rate of change of the total phase shift with respect to the angular frequency ω (electrical signal). Actual filters, as used in all kind of mobile devices, consist of a combination of filter structures with slightly different resonance frequencies, whereby a specific band-pass shape of the total admittance is created, as depicted in Figure 2.5 (b). Here, a high $k_{\rm eff}^2$ enables a wide bandwidth, whereas a high Q is needed for a steep (ideally rectangular) slope of the passband edges. These requirements are needed in order to overcome the demand for higher data frequencies and wider band width due to increasing data transfer rates and volume, as aforementioned in the previous introductory Chapter 1, and are therefore incorporated in the so called figure of merit (FoM), defined as

$$FoM = k_{\text{eff}}^2 \times Q. \tag{2.27}$$

In the following, the considered resonator structure needs to be calculated regarding its specific values, i.e. Q and k_{eff}^2 . One commonly used method is the Butterworth-van Dyke (BVD) model, which represents an equivalent circuit as an electrical description of the resonator.

2.2 The Butterworth-van Dyke equivalent circuit model

The above described SMR resonator design is a so called one-port device, i.e. the incident voltage signal is applied within the same knot as the outgoing signal [31]. In general, a one-port resonating system such as a BAW device (the signal electrode serves as the knot) can be described via an equivalent circuit. A common description is the BVD equivalent circuit, simply consisting of a set of three essential building blocks (the LCC branch), i.e. a plate capacitance C_0 , a motional capacitance C_m and inductance L_m , which represent the mechanical motion of the piezoelectric layer, as depicted in Figure 2.6 (a). As derived already before, C_0 is simply given as

$$C_0 = \frac{\epsilon_0 \epsilon_{\rm r} A}{h},\tag{2.28}$$

which directly depends on the total resonating area A and the layer thickness t, with the vacuum and relative permittivity ϵ_0 and ϵ_r , as already defined in Equation (2.22). At this point no loss mechanisms are considered, which results in an infinite Q. Still, the resonance frequencies of this system can be calculated from impedance considerations. The total circuit impedance for this LCC circuit is a purely imaginary number and given as

$$Z_{\text{tot}} = X_0 + X_{\text{m}} = X_{C_0} + X_{C_{\text{m}}} + X_{L_{\text{m}}} = -\frac{1}{\omega C_0} + \omega L_{\text{m}} - \frac{1}{\omega C_{\text{m}}}, \qquad (2.29)$$



Figure 2.6: (a) BVD equivalent circuit with no attenuation consisting of the main building blocks, i.e., a plate capacitance C_0 , the motional capacitance C_m and the inductance L_m , which represent the mechanical motion of the piezoeelctric layer. (b) Equivalent circuit representation including the influence of the electrodes. Additional R_s and R_p represent electrode induced ohmic and viscous losses, respectively. (c) modified Butterworth-van Dyke (mBVD) equivalent circuit model including dielectric (R_0) and viscous losses (R_m) of the piezo material.

with the specific reactance X for both capacitors C_0 , C_m and the inductor L_m . The resonance frequencies according to Equation (2.19), are referred to as the series resonance ω_s , which is determined at a vanishing reactance X_m of the motional circuit branch as

$$\omega_{\rm s} = \frac{1}{\sqrt{L_{\rm m}C_{\rm m}}} = 2\pi f_{\rm s},\tag{2.30}$$

and the parallel resonance $\omega_{\rm p}$, which can be referred to a vanishing total impedance within the current loop formed by the mechanical and the C_0 -branch as

$$\omega_{\rm p} = \frac{1}{\sqrt{L_{\rm m}C_{\rm m}}} \sqrt{1 + \frac{C_{\rm m}}{C_0}} = 2\pi f_{\rm p}.$$
(2.31)

Realistically, several sorts of losses affect the device performance. As already introduced in the introductionary chapter, the mainly considered losses in this work are the electrode induced ones. Due to a non-zero electrode mass and a still finite conductivity, it is expected that there is a direct effect on the resonator's performance characteristic. Therefore both electrode-induced viscous (damping) losses and ohmic losses (in form of an energy transfer into heat) need to be incorporated in a proper loss consideration. For this purpose, additional resistivities are added to the BVD circuit, i.e. a parallel resistivity $R_{\rm p}$ and a series resistivity $R_{\rm s}$, representing these viscous and ohmic losses, respectively, as described by [32]. In the mBVD model two more parameters are incorporated, namely a motional resistivity $R_{\rm m}$, which represents the motional (viscous) losses within the piezolayer and results from the material-specific stiffness, and an additional R_0 , which stands for dielectric losses due to a possibly non-zero conductivity of the piezoelectric material. The corresponding electrical circuits are depicted in Figure 2.6 (b) and (c). By focusing on the electrode induced losses, the properties of the BAW resonator can be determined according to the equivalent circuit in (b). In the following, a short derivation of Q from the given circuit parameters is presented, the detailed calculations can be found in Section 7.1. The reader needs to be aware of the fact, that $R_{\rm m}$ and R_0 are initially ignored at this point, unless the drawn conclusion stays unaffected. Their influence is discussed more detailed in Figure 2.7 and in the experimental discussion in Chapter 6.

As aforementioned, a resonance occurs only for disappearing reactance $(X(\omega) = 0)$. Since one is interested in the influence of $R_{\rm s}$ and $R_{\rm p}$ on the quality factor Q, the consideration turns back to Equation (2.26). According to the equivalent circuit in Figure 2.6 (b) the total impedance Z is given as

$$Z = R_{\rm s} + \frac{1}{G_{\rm p} + j\omega C_0 + \frac{1}{j\omega L_{\rm m} + \frac{1}{j\omega C_{\rm m}}}}, \quad \text{with} \quad G_{\rm p} = \frac{1}{R_{\rm p}},$$
(2.32)

which leads to a separation into the resistance $R(\omega)$ and the reactance $X(\omega)$ as

$$Z = [R(\omega)] + [X(\omega)] = \left[R_{\rm s} + \frac{\alpha^2 G_{\rm p}}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2} \right] + \left[\frac{-j\omega C_0 \alpha (\alpha + \beta)}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2} \right],$$

with $\alpha = 1 - \omega^2 L_{\rm m} C_{\rm m}$ and $\beta = \frac{C_{\rm m}}{C_0}.$ (2.33)

By inserting $R(\omega)$ and $X(\omega)$ together with Equation (2.30) and (2.31) in (2.26), the quality factor Q is given after some lengthy calculation (detailed mathematical derivation in Section 7.1) as

$$Q_{\rm s} = Q(\omega_{\rm s}) = \left[\frac{1}{2} \; \omega \frac{1}{R(\omega)} \cdot \left| \frac{dX(\omega)}{d\omega} \right| \right]_{\omega = \omega_{\rm s}} = \frac{1}{R_{\rm s}} \sqrt{\frac{L_{\rm m}}{C_{\rm m}}},\tag{2.34}$$

$$Q_{\rm p} = Q(\omega_{\rm p}) = \left[\frac{1}{2} \left.\omega \frac{1}{R(\omega)} \cdot \left|\frac{dX(\omega)}{d\omega}\right|\right]_{\omega=\omega_{\rm p}} = \omega_{\rm p} R_p \frac{C_{\rm m} + C_0}{C_{\rm m}} C_0.$$
(2.35)

It is seen that Q_s is loaded by the electrode induced electrical series resistivity, whereas Q_p is only defined by the electrode induced viscous losses. As a mathematical conclusion, these equations directly show, that a light and conducting electrode both influences Q_s and Q_p in a positive way. In the following, the influence of the resistive circuit parameters is discussed graphically to more detail. Adapted from

2.2.1 Influence of the different resistances on the quality factor

In the performed experiments later on, experimentally obtained admittance curves will be fitted via the so called LARA10k software (Laboratory for Model Assessment Reproduction and Analysis) [33], which was developed at the Fraunhofer Institute for Applied Solid States Physics (IAF) and which is based on a Simplex method fitting algorithm. With the implementation of the associated circuit parameters, the quality factor and other relevant device parameters can be extracted after circuit parameter optimization. In order to give a more practical sense of the interpretation of R_s , R_p and also R_m , exemplary one-port device admittance curves based on a LARA simulation applying the complete mBVD equivalent circuit (cp. Figure 2.6 (c)), are shown in Figure 2.7. The set parameters for comparison are listed in Table 2.2 which were chosen



Figure 2.7: Simulated admittance curves (obtained by LARA10k) in dependence of the three resistivities $R_{\rm m}$, $R_{\rm s}$ and $R_{\rm p}$. The corresponding frequencies at series and parallel resonance are depicted in dashed lines.

close to our experimental device parameters. The figure illustrates the primary effects on the width and the amplitude of the resonance peaks at $f_{\rm s}$ and $f_{\rm p}$. According to Figure 2.7 (a) $R_{\rm m}$ affects both $Q_{\rm s}$ and $Q_{\rm p}$, whose peaks become steeper and more pointed for a decreasing resistivity. Figure 2.7 (b) and (c) directly correspond to Equation (2.34) and (2.35) and simulate their linear and inverse behavior, respectively. Due to both $R_{\rm m}$ and $R_{\rm s}$ ($R_{\rm p}$) influencing $Q_{\rm s}$ ($Q_{\rm p}$), on the first site a precise separation of electrode and piezo-material induced loss effects on Q is unfeasible. However, by focusing on electrode effects and $R_{\rm m}$ being considered as a material-specific constant value, a relative comparison of electrode-induced effects can be performed. For the experimental analysis, $R_{\rm m}$ is set to 0.2 Ω , which will be explicated in Chapter 6.

Table 2.2: Equivalent circuit parameters used for the resistivity variations which are graphically depicted in Figure 2.7 (a), (b) and (c). These values are kept constant, while $R_{\rm m}$, $R_{\rm s}$ and $R_{\rm p}$ are varied from 0.2 to 5.0 Ω , 1 to 10 Ω and 50 to 500 Ω , respectively.

	$oldsymbol{C}_0$	$oldsymbol{R}_0$	$oldsymbol{L}_{ m m}$	$oldsymbol{C}_{\mathrm{m}}$	$oldsymbol{R}_{ m m}$	$oldsymbol{R}_{ m s}$	$oldsymbol{R}_{ m p}$
(a)	$0.00013\mathrm{nF}$	0.0016Ω	$43.3\mathrm{nH}$	$0.00013\mathrm{nF}$	$0.2\text{-}5.0\Omega$	1Ω	200Ω
(b)	$0.00013\mathrm{nF}$	0.0016Ω	$43.3\mathrm{nH}$	$0.00013\mathrm{nF}$	0.2Ω	110Ω	200Ω
(c)	$0.00013\mathrm{nF}$	0.0016Ω	$43.3\mathrm{nH}$	$0.00013\mathrm{nF}$	0.2Ω	1Ω	$50\text{-}500\Omega$

2.3 Electrodes as thin as possible – The Fuchs-Sondheimer Model

According to the requirements of both a high Q_s and Q_p , a conductive and simultaneously thin material would comply an undamped contacting of the resonator device, cp. Equation (2.34) and (2.35). Commonly used metallization materials are titanium (Ti), ruthenium (Ru), W, Mo, Al, Au, Cu and silver (Ag) due to their low specific resistivities, as summarized in Table 2.3. The electrode thicknesses vary from 50 to 200 nm [16, 17, 30], which implies a significant mass-induced effect on viscous losses since a nonnegligible electrode mass acts as an additional damping on the resonating piezoelectric layer. Initially, the reader might draw the conclusion of making the metallization even



Figure 2.8: Schematic drawing of the surface scattering described by the Fuchs-Sondheimer model with the material thickness t and the specularity parameter p.

thinner than the commonly used thicknesses. In macroscopic systems the effect of sample boundaries does not play a considerable role in affecting the material's resistivity, since the electron's mean free path lies several orders of magnitudes below the sample dimensions. However, a thinning of the metals lifts the mean free path in the same order of magnitude as the sample dimensions, in this case the metal film thickness. As already described by [36, 37], in this scenario additional scattering mechanisms occur which contribute to the overall metal resistivity. The Fuchs-Sondheimer model describes the fundamental mechanism of electron scattering at internal surfaces or interfaces. At this point, the resistivity depends on the dimension of the system. The scattering process can be described graphically as in Figure 2.8. The electron scattering depends on the surface morphology, i.e. the surface roughness or the surface charge distribution. This effect is described with the so called specularity parameter p, which ranges from 0 to 1, indicating diffusive and specular scattering, respectively. The probability of an electron to be scattered at the layer surface increases with decreasing layer thickness t. The total film resistivity $\rho_{\rm f}$ can be described mathematically as

$$\rho_{\rm f} = \left(1 + \frac{3}{8} \frac{l_0}{t} \left(1 - p\right)\right) \cdot \rho_0, \quad (t \gg l_0), \tag{2.36}$$

calculated with the consideration of a metal thickness of 100 nm.						
	$oldsymbol{ ho}_{ m el}\ (10^{-6}\Omega{ m cm})$	$oldsymbol{ ho}_{\mathrm{m}}\ (10^{-3}\mathrm{kg/m^3})$	$m{m}_{ ext{GR}}/m{m}_{ ext{metal}}\ (\%)$			
Ti	43.10	4.51	0.17			
Ru	7.40	12.36	0.06			
W	5.30	19.25	0.04			
Mo	5.30	10.22	0.07			
Al	2.74	2.70	0.28			
Au	2.20	19.28	0.04			
Cu	1.70	8.93	0.08			
Ag	1.61	10.50	0.07			
$Graphene^{*}$	1	$7.57 \cdot 10^{-7}$				
$(in kg/m^2)$						

Table 2.3: Specific resistivity $\rho_{\rm el}$, mass density $\rho_{\rm m}$ of selected metals at room temperature (295 K) in comparison with graphene [34, 35]. The mass ratio $m_{\rm GR}/m_{\rm metal}$ is calculated with the consideration of a metal thickness of 100 nm.
1



Figure 2.9: (a) Experimental sheet resistivity $R_{\rm s,Al}$ measurement of Al layers with varying thickness between 10 and 100 nm. The slope reproduces the dominating scattering effect for thin layers. (b) Theoretical sketch of the Fuchs-Sondheimer model with the implication of graphene (blue bar) as a suitable candidate for an ultra-thin conductive electrode material by overruling the scattering problem of decreasing layer thicknesses of metals. For comparison $R_{\rm s,Al}$ (t = 10 nm) is depicted in red.

$$\rho_{\rm f} = \left(1 + \frac{4}{3} \frac{(1-p)}{(1+p)} \frac{l_0}{d \ln \frac{l_0}{t}}\right) \cdot \rho_0, \quad (t \ll l_0), \tag{2.37}$$

with the intrinsic bulk resistivity ρ_0 and the electron mean free path l_0 . Both equations confirm the intuitional thoughts of the sheet resistivity's inverse dependency on the layer thickness t.

By way of example, the sheet resistivity $R_{\rm s,Al}$ of Al for a variation of its thickness was measured. All the investigated Al layers were sputtered onto Si substrates and afterwards were electrically measured via a 4-point probe setup (as described in Chapter 5). The obtained $R_{\rm s,Al}$ values are depicted in Figure 2.9 (a). A thickness variation from 100 nm down to 10 nm shows a strong increase in the specific sheet resistivity from $0.5 \Omega/\text{sq}$ to $156 \Omega/\text{sq}$, corresponding well to the mathematical prediction.

As a first conclusion, very thin metal electrodes would reduce the mechanical damping of a resonator system with a simultaneously rapid increase of the sheet resistivity. Furthermore, the deposition of metals below a thickness of 10 nm results in not fully closed electrode layers due to physical and technological limitations. At this point, graphene comes into play. As it will have been evaluated in the following chapters, its aforementioned virtually massless character combined with a reasonable sheet resistivity $R_{\rm s,GR}$ of several hundred Ohm, overcomes the surface scattering effect, which deteriorates commonly applied conductive materials. Compared to its thickness of 3.35 Å, corresponding metal layers would exhibit sheet resistivities in the range of several k Ω , as shown in Figure 2.9 (b). Therefore, the effect of graphene on the resonator performance is investigated in this work.

3 Basics about graphene and its synthesis

Fabricated the first time in 2004 and honored with the Nobel price in physics in 2010, graphene is regarded as the century's new wonder material. Theoretically predicted phenomena could finally be investigated in the lab and graphene de facto started to attract notice to a wide range of applications. In this chapter graphene and its outstanding properties are introduced. Initially, the reader will get basic information about graphene's mechanical stability, its electrical behavior and bearing on industrial applications. With a subsection about Raman spectroscopy, an essentially applied non-destructive graphene characterization method is presented, which is also intensely employed regarding the quality monitoring of our synthesized graphene samples. Afterwards, the main graphene synthesis methods are briefly examined and presented. By focusing on the graphene synthesis via chemical vapor deposition, in the last section this method is described in more detail in order to pave the way for the subsequent chapter which enlarges upon the experimental procedure and the results of the optimized growth process achieved in this work.

3.1 Structure and material properties of graphene

Already before its actual fabrication, fundamental theoretical research about graphene was done and conclusions for possible applications were drawn. Based on the fact that the atomic structure is a two-dimensional (2D) sheet of a simple honeycomb type, as depicted in Figure 3.1, with a thickness of one atomic layer ($\approx 0.335 \text{ nm}$), several



Figure 3.1: (a) Illustration of the hexagonal honeycomb lattice of graphene. (b) Corresponding skeleton formula depicting the σ -bonds, i.e. covalent single and double bonds. From [38].



Figure 3.2: Carbon in its different forms of appearance according the ground state (a) and to sp³ and sp² hybridisation in (b) and (c), respectively. The hybridisation forms new orbital sp-states with a stronger binding energy compared to the 2porbitals, leading to the ability to form covalent bonds. Orbital graphs adapted from [39].

considerations and physical effects could be already deduced by transforming obtained knowledge about carbon nanotubes (CNT), fullerenes and graphite – the latter consists of several weakly bound graphene sheets. For all these carbon allotropes graphene acts as the building block.

3.1.1 The chemical structure of graphene

Beside its ground state, carbon occurs in several different forms of appearance, both as the pure element and and various compounds, e.g. in carbides, carbonates etc. By holding six electrons, in its ground state, the electron configuration is $1s^22s^22p^2$, which implies a reaction capability of four free electrons in the outer L shell. Beside this ground state, carbon may exist in hybridized states. According to environmental constraints such as pressure and temperature, two main degrees of hybridization occur naturally. Depending on the number of involved 2p-orbital electrons, carbon forms the diamond (sp^3) or graphite structure (sp^2) , depicted in Figure 3.2. In case of the sp^3 hybridization (b), both 2p-orbital electron overlap with the two 2s-electrons resulting in four energetically equal binding states. These states tend to form covalent bonds with neighboring atoms generating a three-dimensional tetrahedral diamond structure. For sp^2 hybridization (c), only one 2p-orbital interacts with the 2s-orbitals, resulting in a trigonal 2D structure. The formed bonds are called σ -bonds, which are stronger than the bonds in the sp^3 case. The leftover third 2p-orbital, aligned orthogonally to the trigonal layer, interacts also with neighboring ones forming so called π -bonds and results in a delocalized electron gas. Several 2D layers are weakly bound via van der Waals bonds, forming a bulk graphite structure. The lack of free electrons in the diamond structure accounts for being an electrical insulator, whereas in case of graphite, the existing weakly bonded π -electrons are responsible for good in-plane conductivity in contrast to the isolating behavior in out-of-plane direction.



Figure 3.3: (a) Graphene lattice structure with its two triangular sublattices (A and B). a_1 and a_2 are the unit vectors of the unit cell, containing two carbon atoms. $\mathbf{R}_{1,2,3}$ are the nearest-neighbor vectors. (b) Corresponding Brillouin zone with the characteristic points, i.e. Γ , **M** and the Dirac points **K** and **K'** corresponding to the related sublattice. (c) Graphene energy band structure of the complete Brillouin zone and a zoom in of the Dirac cones at **K** and **K'**. By courtesy of [40].

3.1.2 Lattice description and band structure calculations

The graphene lattice unit cell and the concept of nearest-neighbor atoms

Talking about the electronic properties of graphene, the crystal structure needs to be elucidated more profoundly. As depicted in Figure 3.3 (a), the honeycomb lattice can be considered of two interpenetrating sublattices, A and B, so that the total crystal lattice is completely described by a unit cell which consists of two neighboring C atoms and the two real-lattice vectors a_1 and a_2 , which are then given as

$$\boldsymbol{a}_1 = \left(\frac{3a}{2}, \frac{\sqrt{3}a}{2}\right), \quad \boldsymbol{a}_2 = \left(\frac{3a}{2}, -\frac{\sqrt{3}a}{2}\right), \quad (3.1)$$

with the carbon-carbon distance $a \approx 1.42$ Å. The reciprocal-lattice vectors are calculated as

$$\boldsymbol{b}_1 = \left(\frac{2\pi}{3a}, \frac{\sqrt{2}\pi}{\sqrt{3}a}\right), \quad \boldsymbol{b}_2 = \left(\frac{2\pi}{3a}, -\frac{\sqrt{2}\pi}{\sqrt{3}a}\right). \tag{3.2}$$

The reciprocal unit cell, also called the first Brillouin zone, features the shape of a hexagon and is shown in Figure 3.3 (b). It includes three significant points, which are relevant referring to the graphene electron band structure. Γ describes the center of the zone, **M** is centered at the zone edge and the most relevant so called Dirac points are **K** and **K**', which lie in each of the three corners of the Brillouin zone of the corresponding sublattice A and B, respectively. The Dirac points are named after Paul Dirac, since near those points the charge carriers satisfy an equation of motion of the same form as the Dirac equation due to the linearity of the electron energy dispersion relation, as it will be shown in the following. The coordinates of **K** and **K**' are determined as

$$\mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right). \tag{3.3}$$

With this geometrical conception, the electronic properties of graphene can be investigated by calculating the electronic band structure. In order to be able to do so, one needs to take into account a quantum mechanical view. The energy state of an electron in a crystal depends on the total interaction of the electron with the crystal, which can be considered as a many-body problem. A single electron, bound to its atom, exhibits a significantly disturbed wave function due to the influence of the overall crystal, i.e. the atomic potential of the other atoms in the crystal lattice. The first simplification comes with the assumption that only nearest-neighbor atoms contribute to the electron wave function, i.e. given a certain C atom on sublattice A, the nearest-neighbor atoms belong to sublattice B and their relative position is described by their corresponding position vectors, which are sketched in Figure 3.3 (a) and given as

$$\boldsymbol{R}_1 = -a \begin{pmatrix} 1\\ 0 \end{pmatrix}, \quad \boldsymbol{R}_2 = \frac{a}{2} \begin{pmatrix} 1\\ \sqrt{3} \end{pmatrix}, \quad \boldsymbol{R}_3 = \frac{a}{2} \begin{pmatrix} 1\\ -\sqrt{3} \end{pmatrix}. \quad (3.4)$$

The electronic band structure – the tight binding model approach for electrons in solids

Theoretically, the band structure for graphene was already calculated in 1947 by Philip Russell Wallace [41], using the tight binding (TB) model. The TB model is a quantum mechanical model, which describes the electronic properties of electrons in a solid. The name "tight binding" arises from the assumption, that the electrons are tightly bound to their atoms, while neighboring atoms act as a perturbance, directly influencing the electronic behavior. Therefore, by representing the electron energy, the resulting Hamiltonian \mathcal{H} for an arbitrary electron l in the crystal becomes

$$\mathcal{H} = \mathcal{H}_{\mathbf{R}}^{\mathrm{a}} + \Delta V = \sum_{\mathbf{R}}^{N} - \frac{\hbar^2}{2m} \Delta_{\mathbf{R}} + V(\mathbf{r} - \mathbf{R}) + \Delta V, \qquad (3.5)$$

with the atomic Hamiltonian operator $\mathcal{H}^{a}_{\mathbf{R}}$ representing an electron bound to an ion at the lattice site \mathbf{R} , and the potential energy contributions ΔV resulting from the other ions at the sites \mathbf{R}' with $\mathbf{R} \neq \mathbf{R}'$.

Generally, the corresponding electron eigenenergies E_j are given by

$$E_j(\mathbf{k}) = \frac{\langle \Psi_j(\mathbf{k}) | \mathcal{H} | \Psi_j(\mathbf{k}) \rangle}{\langle \Psi_j(\mathbf{k}) | \Psi_j(\mathbf{k}) \rangle},\tag{3.6}$$

with the global electron wave function $\Psi_j(\mathbf{k})$ for the *j*-th energy state The overall goal is the finding of a global electron wave function and the corresponding energy states which include the atomic interactions rising from the crystal structure. In general, crystal solids possess a periodic potential due to their periodical atomic arrangement within the crystal layer. In graphene, regarded as a 2D crystal solid layer, this periodicity can also be seen according to its honeycomb lattice. By assuming an infinite solid, a periodic potential leads to a translational invariance within the layer, according to Bloch's theorem [34], which leads to a mathematical description of the electron wave function $\Phi_j(\mathbf{k}, \mathbf{r})$, given by the so called Bloch function

$$\Phi_j(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}}^{N} e^{j\mathbf{k}R} \phi_j(\mathbf{r} - \mathbf{R}), \qquad (j = 1, ..., n), \qquad (3.7)$$

which is described by a periodic function $\phi_j(\mathbf{k}, \mathbf{r})$, representing the *j*-th atomic orbital wave function with the periodicity of the 2D crystal, multiplied by a plane wave $e^{j\mathbf{k}R}$ and summed over all lattice vectors \mathbf{R} . R is the modulus of \mathbf{R} , n is the number of the atomic orbital wave functions (according to the number of atoms in a unit cell) and Nthe total number of unit cells in the crystal. The corresponding electron eigenfunctions $\Psi_j(\mathbf{k}, \mathbf{r})$ are a linear combination of the n Bloch functions, constructed from the atomic orbital wave functions in the crystal, given as

$$\Psi_j(\mathbf{k}, \mathbf{r}) = \sum_{j'=1}^n C_{jj'}(\mathbf{k}) \Phi_{j'}(\mathbf{k}, \mathbf{r}), \qquad (3.8)$$

with $C_{jj'}$ as the coefficients of the linear combination, which need to be calculated or measured experimentally.

By making a change of subscripts and by substituting Equation (3.8) into (3.6), the corresponding energy eigenvalue in the *i*-th energy state according to Schrödinger's equation [42] is given by

$$E_{i}(\mathbf{k}) = \frac{\sum_{j,j'}^{n} \mathcal{H}_{ij'}(\mathbf{k}) C_{ij}^{*} C_{ij'}}{\sum_{j,j'}^{n} \mathcal{S}_{ij'}(\mathbf{k}) C_{ij}^{*} C_{ij'}}, \qquad \mathcal{H}_{ij'}(\mathbf{k}) = \langle \phi_{j} | \mathcal{H} | \phi_{j'} \rangle, \quad \mathcal{S}_{ij'}(\mathbf{k}) = \langle \phi_{j} | \phi_{j'} \rangle, \quad (3.9)$$

with the transfer matrix elements $\mathcal{H}_{jj'}$ and overlap matrix elements $\mathcal{S}_{jj'}$. According to the local minimum condition, this leads to the secular equation

$$det[\mathcal{H} - E\mathcal{S}] = 0, \qquad (3.10)$$

which gives the solution of all eigenvalues E for a given wave vector \mathbf{k} .

Electron band structure of graphene – nearest-neighbor TB approach

Depending on the crystal structure, proper calculations need to adopt some approximations, which integrate the effective lattice potential. Since graphene attracted major interest due to its experimentally proven and surprisingly high electrical conductance, which results from the weakly bond π -electron orbitals (cp. Section 3.1.1), the energy states of those are most of interest. Calculations of 2D graphite were elaborately done by Saito et al. [43] applying the TB model by considering atomic interactions of only nearest-neighbor atoms. This leads to some deviations compared to more exact calculations, as further investigated by Reich et al. [44] by considering third-nearest neighbors (3NN) or even fifth-nearest neighbors (5NN) [45], but still provides the reader with a first insight in the principle calculations and closes with the main finding for the energy dispersion in graphene. In the following, the calculation procedure for graphene is briefly represented by using the nearest-neighbor TB approach as applied in [43], but with different geometric considerations regarding the graphene lattice. A more detailed mathematical derivation can be found in Appendix B.

In case of graphene with two atoms per unit cell (n=2) there are two Bloch functions describing the total electron wave function $\Psi(\mathbf{k}, \mathbf{r})$, one appertaining to each sublattice, A and B, respectively,

$$\Phi_j(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_{\alpha}} e^{j\mathbf{k}R_{\alpha}} \phi_j(\mathbf{r} - \mathbf{R}_{\alpha}), \qquad (\alpha = \mathbf{A}, \mathbf{B}).$$
(3.11)

According to equation 3.9, \mathcal{H} and \mathcal{S} follow as

$$\mathcal{H} = \begin{pmatrix} \epsilon_{2p} & tf(\mathbf{k}) \\ tf^*(\mathbf{k}) & \epsilon_{2p} \end{pmatrix},$$

$$\mathcal{S} = \begin{pmatrix} 1 & sf(\mathbf{k}) \\ sf^*(\mathbf{k}) & 1 \end{pmatrix},$$
(3.12)

where t is also referred to as the electron hopping interaction parameter. Due to these equations and eq. (3.10), the eigenenergies are calculated as

$$det(\mathcal{H} - E\mathcal{S}) = det \begin{pmatrix} \epsilon_{2p} - E & tf - sEf \\ tf^* - sEf^* & \epsilon_{2p} - E \end{pmatrix} \stackrel{!}{=} 0$$
$$\Rightarrow E^{\pm} = \frac{\epsilon_{2p} \mp t\omega(\mathbf{k})}{1 \mp s\omega(\mathbf{k})}.$$
(3.13)

Given the complex function $\omega(\mathbf{k}) = \sqrt{ff^*}$, expanded to second order close to the Dirac points, $\mathbf{k} = \mathbf{K} + \mathbf{q}$, and under the assumption that $s \ll 1$, the eigenenergies can finally be described as

$$E^{\pm}(\mathbf{q}) = \pm \frac{3}{2}taq = \pm v_{\mathrm{F}}q,$$
 (3.14)

where $v_{\rm F}$ is the Fermi velocity of the electron and **q** the measured momentum relatively to the Dirac points **K** and **K'**. Equation 3.14 shows the remarkable linear dependence of the electron dispersion relation, which directly implies that the π -electrons can be considered as relativistic electrons fulfilling the Dirac equation. This finding greatly



Figure 3.4: (a) Comparison of the energy dispersion relation for the π -electrons in graphene shown within the region of the Brillouin zone, by applying the nearest-neighbor (dotted line) and fifth-nearest-neighbor (solid line) tight binding model. The plot path corresponds to the labels in Figure 3.3 (b). Adapted from [45]. (b) Band diagram of graphene including both π - and σ -orbital electrons within the Brillouin zone. Band slope calculated using the nearest-neighbour approximation. The index * represents the anti-bonding electron states, which lie on higher energies and contribute to the valence band. Adapted from [43].

enables further conclusions of the quantum mechanical properties in graphene, such as the Klein-Paradox or the anomalous quantum Hall effect, which results from the ballistic behavior, i.e. the massless electrons in graphene, which goes beyond the subject of this work though. In Figure 3.4 (a), the band structure close to the Dirac points is plotted. As a reminder, the performed calculations are based on the nearest-neighbor approximation. By taking into account the interaction of more distant lattice atoms, the total band structure changes. The main result, namely the linear dependence close to the Dirac cones, stays unchanged. For comparison, the nearest-neighbor and the 5NN tight binding calculations for the π -electron orbitals are shown, which explicitly confirms the linear dispersion relation as an outstanding quantum mechanical property. Since there are six Dirac points in total, namely three **K** for each sublattice A and three **K'** for sublattice B, the π -electron band structure becomes the three-dimensional shape as depicted in Figure 3.3 (c).

The band structure for the remaining in-plane σ -electrons are calculated similarly by applying the TB model for the corresponding six Bloch orbitals per unit cell. This results in additional six electron bands which are shown in the overall graphene band diagram in Figure 3.4 (b).

3.1.3 Electrical and mechanical properties of graphene

Reich et al. [44] calculated in their work both the transfer and the negligible overlap integral as t = -2.7 eV to -3 eV and s < 0.1 eV, respectively. This confirms the form of equation 3.14 and results in a Fermi velocity in the range of $v_{\rm F} \approx 1 \times 10^6 \text{ m/s}$. Additionally, pristine graphene is a zero-bandgap material as the conduction and valence bands converge at the Dirac points according to Equation (3.14). These findings directly imply several impressive conclusions regarding the electronic properties of graphene. Suspended graphene shows carrier mobilities of up to $200\,000\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and a theoretical resistivity of $R_{\rm s,GR} = 1 \times 10^{-5} \,\Omega {\rm m}$ [46]. For graphene on an insulating substrate, e.g. SiO_2 or AlN, these values may be strongly reduced due to electron interactions, doping effects and scattering at the substrate surfaces [47, 48]. Furthermore, graphene as a 2D ultrathin material layer with a layer thickness of $v_{\rm F} = 3.35$ Å exhibits outstanding mechanical properties. The carbon-carbon bond of approx. 1.42 A and graphene's honeycomb lattice results in a Young's modulus of 1 TPa and a tensile strength of approx. 130 GPa, which makes graphene the strongest material known so far. With a specific surface area (SSA) of $2630 \,\mathrm{m^2/g}$ it can be regarded as a virtually massless conductive material. This effect shall be employed in this work in order to reduce mass-induced losses in the resonator devices, as they were explained in the previous chapter. Here, it turns out that the graphene conductivity acts as the limiting factor in terms of a properly functioning resonator device. For this reason, apart from the synthesis optimization, the transfer of graphene on AlN is developed and presented particular with regard to a minimization of its sheet resistivity $R_{s,GR}$, which on the contrary induces ohmic losses. In combination with its high mechanical stability, graphene therefore is a promising candidate as an alternative electrode material for BAW resonators, as motivated in Section 2.2.1.

3.2 Raman spectroscopy – a nondestructive method for the graphene quality control

After both the graphene synthesis and the graphene transfer, a proper graphene quality control needs to be taken into account. Here, the Raman spectroscopy, named after the Indian physicist and Nobel laureate Chandrasekhara Venkata Raman, is the most used characterization method since it is a nondestructive and experimentally easily applicable method to obtain various information about the quality and number of graphene layers, regarding stress and strain distributions and the existence of defect structures within the layer.

Generally, the light-matter interaction offers a large variety of characterization possibilities of matter. In order to properly integrate Raman scattering, a short introduction of three main absorption and scattering principles is given, namely the Rayleigh scattering, the infrared absorption, and the Raman scattering itself.

Rayleigh scattering

The interaction between light and matter can be described as a collision of an incident photon and a vibrating molecule or lattice. In case of an elastic collision, this scattering process is called the Rayleigh scattering. The schematic process is depicted in Figure 3.5 (a). The scattering is described as a transition via an off-resonant virtual energy state (dashed line), leading to an isotropic radiation of the particular photons induced by the electron relaxation. The scattering intensity I is strongly dependent on the specific polarizability α and the incident wavelength λ [49], as

$$I_{\text{Rayleigh}} \propto \frac{\alpha^2}{\lambda^{-4}},$$
 (3.15)



Figure 3.5: Comparison of the three mainly relevant forms of energy absorption in crystals, i.e. Rayleigh scattering as an elastic process (a), and infrared absorption (b) and Raman scattering (c) which are inelastic processes. Depending on the sign of the energy difference between absorbed and emitted photon, Raman scattering is labeled as Stokes (redshift) and anti-Stokes (blueshift) scattering.

which for instance explains the blue of the sky.

Infrared absorption

The infrared absorption (IR) as an inelastic process describes the interaction of infrared radiation with matter. The absorption of an IR photon occurs at certain materialspecific resonant frequencies which correspond to a transition within vibrational or rotational modes of the molecules or crystals. The transition frequencies directly depend on the specific type of chemical bonds [50]. A transition occurs, if a change in the electronic dipole momentum is possible due to a radiative excitation. A schematic transition is depicted in Figure 3.5 (b), with the quantum number ν_i which indicates the energy level of the vibrational state. The intensity $I_{\rm IR}$ of the IR spectrum depends on this change with respect to the normal coordinate q according to

$$I_{\rm IR} \propto \left(\frac{\partial \mu}{\partial q}\right)^2.$$
 (3.16)

A vibrational mode is IR active, if there is a change in the dipole moment μ .

Raman scattering

Raman spectroscopy is a technique, which is used to observe rotational or vibrational mode changes of a system, i.e. a sample of molecules or crystalline structures, via inelastic scattering of monochromatic light, e.g. of lasers. This means in contrast to the IR spectroscopy, that the incident photon energy must not hit the resonant frequency of the vibrational transition, since the process occurs under participation of a virtual energy state, as it holds for the Rayleigh scattering. The schematic effect is described in Figure 3.5 (c). In solids, the inelastic process, i.e. the system's energy is not conserved, results in the creation or annihilation of phonons, i.e. lattice excitations, which



Figure 3.6: (a) Schematic drawing of the building blocks and the working principle of Raman Spectroscopy. (b) Photographic image of the applied Raman spectrometer setup for this work.

correspond to the vibrational excited states. During scattering the incoming photon experiences an energy change according to the change of the molecular vibration mode $\nu_{\rm n}$ as it is also obtained in IR spectroscopy, which in contrast is a resonant transition. Experimentally, the resulting frequency shift between the incident and scattered photons is detected, which leads to a specific Raman spectrum. If the final vibrational state lies at a higher energy level than the initial state, the Raman process is called Stokes scattering, otherwise it is called anti-Stokes scattering. Due to a higher population of the vibrational excited states at room temperature, the Stokes Raman intensity is higher than the anti-Stokes Raman intensity [51]. The obtained spectrum is a distinct fingerprint of the investigated material and depends on its crystal structure and the involved elements forming molecules, respectively. For graphene, the characteristic Raman spectrum involves the so called D, G and 2D bands, which are described more detailed in the following sections. The Raman intensity depends on the polarizability α , as

$$I_{\text{Raman}} \propto \left(\frac{\partial \alpha}{\partial q}\right)^2.$$
 (3.17)

While Rayleigh scattering occurs together with Raman scattering and therefore often needs to be filtered to extract clear Raman spectra, the IR absorption acts as a complementary characterization method. Due to the selection rules, usually Raman-active modes are IR-inactive and vice versa. Here, the active modes are connected to symmetric (Raman active) and anti-symmetric (IR active) vibrations of the measured molecule or lattice.

3.2.1 The experimental setup

A Raman spectrometer consists of mainly four building blocks, as depicted in Figure 3.6 (a), namely of a monochromatic light source (1), i.e. usually a laser (here 532 nm), a sample stage with the optical setup (2), i.e. an optical microscope, a light dispersing unit (3), i.e. an optical grid, and a data collecting system (4), i.e a detector, an amplifier and data processing hard- and software. Most of the scattered photons result



Figure 3.7: (a) Theoretical phonon dispersion relation of graphene. According to the graphene unit cell there are six phonon dispersion bands. According to Kramers-Heisenberg-Dirac theory (KHD) calculations, the D and 2D Raman peaks are related to iTO phonon mode close to the Dirac point \mathbf{K} (blue circle), whereas the G peak results from iTO and iLO modes in the center of the Brillouin zone, i.e. the Γ point. Adapted from [52]. (b) Exemplary measured graphene Raman spectrum on Cu foil after background subtraction obtained with a laser energy of 2.33 eV, i.e. 532 nm, indicating the three fundamental modes, i.e. D, G and 2D peaks at 1359.3 cm⁻¹, 1594.1 cm⁻¹ and 2699.7 cm⁻¹, respectively.

from the elastic Rayleigh scattering, which would dominate the total signal intensity. In order to extract the Raman signal properly, a Notch filter (NF) is installed which oppresses the incident Laser frequency on the one hand and the Rayleigh scattered photons on the other hand. Due to the mentioned higher population of excited states at room temperature, the intensity of Stokes scattering is higher than for anti-Stokes, wherefore the detector is set to collect only Stokes scattered photons. For the Raman spectroscopy measurements a Renishaw setup (inVia spectrometer system, 100 mW Nd:YAG laser, 532 nm) was used, see Figure 3.6 (b). The usage of a laser as the monochromatic light source establishes a high enough photon intensity in order to detect distinct Raman peaks.

3.2.2 The Raman spectrum of graphene

The origin of the D, G and 2D band (which results from the creation of two D phonons) is elaborately described in [53]. The principal mechanisms are shortly explained in this paragraph. Basically, the number of phonon bands depends on the number of atoms in the unit cell. In graphene, the unit cell consists of two carbon atoms, which results in six phonon dispersion bands, namely the optical (O) branches iLO, iTO and oTO, where L and T stand for longitudinal and transversal, respectively. The corresponding acoustic branches are iLA, iTA and oTA – thus both the optical and acoustic branches consist of two in-plane (i) and one out-of-plane (o) phonon modes. Generally, a phonon has a certain momentum \mathbf{q} and a related phonon energy $\mathbf{E}_{\rm ph}$. Due to the interaction with incident light both momentum and energy can be transferred. In Figure 3.7 (a), the phonon dispersion relation for graphene is depicted [52]. According to KHD calculations, the phonon transition momentum for graphene becomes non-zero at the reciprocal lattice vectors $\mathbf{q}_{\rm v} - \mathbf{q}_{\rm c} = 0$ or $\mathbf{q}_{\rm v} - \mathbf{q}_{\rm c} = \mathbf{K}$, with the indices c and v describing the conduction



Figure 3.8: (a) Schematic drawing of the first-order phonon generation principle of the G band phonon at the K point with corresponding phonon emission (red arrow).
(b) Second-order principle of the intervalley phonon creation process resulting in the 2D peak under the creation of two D phonons (dashed arrows, grey).
(c) Second-order double resonance (DR) phonon transition at a defekt. Only one D (2q) phonon is created together with an elastic back-scattering on a defect within the graphene layer. Same scaling of each graph due to a better visualization. Adapted from [53].

and valence band, respectively. Due to periodic undulations, i.e. displacements of the lattices A and B, which result in a lattice distortion, phonons with a so called pseudomomentum $\mathbf{k} = \mathbf{q}_{\rm v} - \mathbf{q}_{\rm c} = \Delta \mathbf{q}$ can be induced. This mechanism is relevant for the existence of the 2D peak. Group theory and symmetry considerations reveal the iTO and iLO phonon branches as being Raman active and responsible for the appearance of the G peak [54, 55], which results from a transition in the center of the Brillouin zone ($\Delta \mathbf{q} = \mathbf{k}$, intravalley transition), whereas the iTO phonon mode results in the Raman D and 2D peaks at the Dirac points ($\Delta \mathbf{q} = \mathbf{k} \pm \mathbf{K}$, intervalley transition) [51]. According to the phonon dispersion relation, the relevant phonon transitions are marked in Figure 3.7 (a) as a red (G peak) and blue (D and a 2D peak) circle. In the following, the origin of the three most relevant Raman peaks in graphene is briefly explained, as depicted in Figure 3.7 (b). In Figure 3.8, the electron transitions are depicted in order to illustrate the theoretical transition description. Since only Stokes scattering is observed experimentally, the anti-Stokes electron-phonon transitions are ignored in the description. The incident laser light is depicted as the blue upward arrow, which excites electrons from the valence to the conduction band at the Dirac point K according to the electron dispersion relation, cp. Figure 3.4 (b).

Origin of the Raman G peak

As aforementioned, the origin of the G peak results from a first-order transition in the Brillouin zone center, i.e. $\Delta \mathbf{q} = \mathbf{0}$ or an intravalley process, since it is an electron-hole generation and recombination process due to incident photons coming from the laser source. In Figure 3.8 (a) the G phonon production at absorption is depicted. The iTO and iLO mode transitions appear at $\approx 1580 \,\mathrm{cm}^{-1}$, see Figure 3.7 (b). The dashed line represents the changed electron and hole energy (virtual state) after the energy transfer $E_{\rm ph}$ to the phonon. Obviously, the created phonon carries almost no momentum (only a slight shift along the phonon dispersion band), but a certain energy $E_{\rm ph}$, which



Figure 3.9: (a) Schematic drawing of the transition sliding principle. A momentum shift of ∂q leads to a superposition of phonon transitions with the same momentum transfer $\mathbf{k} = -2q$ due to the linearity of the Dirac cones. (b) Intervalley DR phonon transition in bilayer graphene, which leads to a broadened 2D peak due to four different two-photon transitions with $\mathbf{k} = q_{1A}$, q_{2A} , q_{1B} with q_{2B} . Adapted from [53, 56].

directly lowers the electron-hole transition energy (1), black arrow, and creates virtual electron-hole states (blank circles, dashed line). According to KHD the changing electron transition energy leads to a phonon creation by directly transferring a part of the photons energy into the G band energy. The recombination of the energy-altered electron-hole pair creates the G band by emission of a photon with lower energy (2). According to this phonon creation mechanism, the G modes suffer from no dispersion, which means that the band position is independent of the applied incident laser wavelength. The G band is a characteristic Raman band related to the C-C stretching mode and therefore also visible for any other carbonic material, i.e. diamond and graphite.

Origin of the Raman 2D peak

The existence of the 2D peak is a DR process, which describes a transition under the formation of two D phonons at $\Delta \mathbf{q} = \mathbf{k} \pm \mathbf{K}$, resulting in a frequency shift of the emitted photon at $\approx 2700 \,\mathrm{cm}^{-1}$. As an intervalley process, the phonon transition is schematically depicted in Figure 3.8 (b). At first, a phonen D(2q) is created. Under the absence of defects no elastic backscattering without an additional D phonon creation is allowed according to the Pauli exclusion principle. Therefore, an additional phonon D(-2q) is generated, leading to a now Pauli allowed recombination of the lower energy electronhole pair. In total, two phonons are created within the whole transition, therefore also called a second-order double-resonance (DR) phonon transition. Generally, a phonon transition is an improbable event regarding electron-photon interactions, which explains the comparably low Raman intensities. In case of the 2D band, the intensity is strongly increased due to the so called transition sliding as described in detail in [53]. Here, the linearity of the electron band structure of graphene at the Dirac points, as given in Equation (3.14) and shown in Figure 3.4, comes into play, which results in a comparably wide range of scattering events, which can contribute to the 2D Raman signal. According to Figure 3.9 (a), a continuum of symmetrical K-q to K+q transitions is possible due to a variation of $q + \partial q$, which lead all to the same phonons with $\mathbf{k} = -2q$ at absorption and $\mathbf{k} = 2q$ at emission. The transition can therefore "slide" along the Dirac cones. With this consideration, the peak intensity ratio 2D/G is a direct indicator regarding the graphene quality, since it directly reveals the cone structure of the energy band at the Dirac point and therewith the defect-free single layer graphene character. As mentioned in the next paragraph, the formation of bi- or multilayer graphene, doping and strain distributions leads to a change in the band structure, which can directly be detected via Raman spectroscopy.

Origin of the Raman D peak

In contrast to the one-phonon process regarding the formation of the G band at $\Delta \mathbf{q} = 0$, the occurance of the D is also related to the second-order intervalley transition as described for the 2D phonon peak. Defects within the graphene structure might avoid the Pauli exclusion principle, which ensures a double resonance in case of the 2D transition. As a result of this, the momentum transfer can be applied within the graphene crystal via elastic back-scattering of a momentum $\mathbf{k} = 2q$ at a defect, as shown principally in Figure 3.8 (c). In this case only one D phonon is created, which leads to a photon emission with half the energy, i.e. a Raman shift at $\approx 1350 \,\mathrm{cm}^{-1}$ according to Figure 3.7 (b). The D peak intensity is therefore a direct indication about the presence of defect structures in the graphene layer, as elaborately described in [57]. Under the absence of defects in graphene, the D band is not visible in the obtained Raman spectrum, whereas the 2D band as an allowed transition exhibits a strong intensity compared to the graphitic G band.

3.2.3 Interpretation of the graphene Raman spectrum and quality implications

The identification of multilayer graphene growth

Raman spectroscopy is highly suitable for the distinction of single layer graphene (SLG), bilayer graphene (BLG) or few-layer graphene (FLG), since there is a strong 2D peak dependency in terms of its full width at half maximum (FWHM). In Figure 3.9 (b), the electron dispersion relation is exemplary depicted for BLG graphene. Compared to the single layer graphene electron band, the cone structure for bilayer graphene is varied in terms of a broadening and additional two π and π^* bands from the second graphene layer due to the GR-GR interaction within both graphene layers. TB model calculations with four instead of two C atoms in the unit cell reveal the twofold appearence of the conduction and valence band [58]. This finding results in four slightly shifted DR phonon bands, named as $2D_{1A}$, $2D_{2A}$, $2D_{1B}$ and $2D_{2B}$ [56]. The different energy transfer to each of these phonons results in a broadened total 2D peak. The number of up to five layers can be distinguished by measuring the 2D FWHM, which lies e.g. for BLG at $\approx 50 \,\mathrm{cm}^{-1}$, using Cu foil as the underlying substrate. Another indicator for FLG is the rapid decrease of the 2D/G ratio. Due to the loss of the strictly linear electron dispersion relation, the aforementioned transition sliding looses ground, which results in a lower 2D phonon contribution. According to [59], a 2D/G ratio > 2.5 clearly identifies SLG. This value might lie significantly lower for present doping concentrations. This theoretical concept serves as a quality control of the transferred graphene layers onto AlN target substrates, as presented in Chapter 5.



Figure 3.10: (a) Comparison of a commonly obtained Raman spectrum (single measurement) of graphene on Cu foil (red) and pristine Cu foil (black). (b) Corresponding comparison of the Raman signal of graphene on AlN (red) and measurement of the pristine AlN target substrate (black).

The characteristic Raman spectrum of graphene on Cu foil and AIN

In order to interpret the obtained Raman spectrum, it is inevitable to keep in mind possible background signals arising from the substrate. In this work, graphene is grown on Cu foil and transferred onto AlN/Si. Regarding an AlN thickness of $2\,\mu\text{m}$ and a laser penetration depth of $2\,\mu\text{m}$ at maximum, a spectrum contribution of the underlying substrate, in this case the Si or the Bragg mirror structure (cp. Chapter 6), can be neglected. Cu foil as a metal does not show certain phonon peaks but a rather continuous background signal, resulting from plasmon assisted photoluminescence [60], which can easily be subtracted. The evaluation of Raman signal of graphene on Cu foil is depicted in Figure 3.10 (a).



Figure 3.11: (a) Comparison of the D (black), G (red) and 2D peak positions (blue) of graphene on Cu foil and AlN for graphene samples fabricated by the already optimized growth and transfer processes. (b) Corresponding comparison of the FWHM. The dotted lines represent literature values for graphene on Cu [56, 61–63].

Regarding graphene on AlN, as shown in (b), there is an additional AlN related Raman peak close to the D peak. According to literature, this peak is not clearly identified. Its position lies at $\approx 1310 \,\mathrm{cm}^{-1}$ with a wide broadening (FWHM $\approx 55 \,\mathrm{cm}^{-1}$) and the Raman shift might arise from DR overtone signals of the known E_2 band in AlN at $\approx 657 \,\mathrm{cm}^{-1}$ [64, 65]. For a proper Raman characterization, a confident AlN background monitoring is essentials, regarding the absolute peak intensity. A wrong background substraction would lead to a false interpretation of the graphene D peak intensity. Additionally, there is a GR-substrate interaction, which might lead to layer doping and a changed stress distribution. In order to get a first impression of the substrate dependency of the graphene Raman signal, a comparison for D, G and 2D peak regarding their position and FWHM of a synthesized graphene sample on Cu and a transferred one on AlN are depicted in Figure 3.11 (a) and (b), respectively. First, it is worth mentioning, that after a proper process parameter adjustment the synthesized graphene practically bears the Raman spectrum, as it is predicted in literature [56, 61–63]. For transferred graphene on AlN, there is a general blueshift of all peaks, especially for the 2D peak. This is an indication of a doping effect by AlN, which is described in detail in Section 5.3.2. The slightly broadened peaks result from some BLG growth on Cu foil and small areas of graphene folding on AlN, as described in Chapter 4 and Chapter 5, respectively.

The *G* and *2D* peak position influence on strain and doping – Investigations via spatially resolved Raman spectroscopy

In terms of the sheet resistivity, both the charge carrier density n and the strain distribution are highly critical properties. Due to a well-known interaction between the 2D layer and the underlying substrate, it is essential to investigate the substrate's influence on the electronic properties and the mechanical deformation. Via a correlation analysis [66] of the G and 2D peak positions, the strain- and hole doping-sensitivity of the graphene layer can be investigated separately, given as

$$\left(\frac{\Delta\omega_{\rm 2D}}{\Delta\omega_{\rm G}}\right)_{\epsilon} = 2.2 \pm 0.2, \tag{3.18}$$

$$\left(\frac{\Delta\omega_{\rm 2D}}{\Delta\omega_{\rm G}}\right)_n^p = 0.70 \pm 0.05. \tag{3.19}$$

Regarding doping, several groups revealed the influence of an increase in n (both holes and electrons) leading to a blueshift and a narrowing of the G peak [67, 68]. Simultaneously, the 2D peak is redshifted with increasing electron concentration [59]. The dependency on hole doping was revealed as $\Delta \omega_{2D}/\Delta n = -1.04 \text{ cm}$, n in terms of 10^{12} cm^{-2} [69]. The effect of external mechanical strain was described in detail by Yoon et al. [70] and leads to a uniaxial strain dependency of the $\omega_{\rm G}$ shift as $\Delta \omega_{\rm G}/\Delta \epsilon = -23.5 \text{ cm}^{-1}/\%$. This explains the comparably strong redshift of the 2D peak for GR on AlN, shown in Figure 3.11 (a, blue bars). These relations are used in Chapter 5 in order to determine the transfer level of graphene on AlN via a direct identification of strain and doping in graphene. As an exemplary representation of Equation (3.18) and (3.19), a plot is given



Figure 3.12: Raman spectroscopy map of graphene on Cu foil (3822 data points, $30 \times 50 \,\mu\text{m}^2$). 2D peak position (ω_{2D}) versus G peak position (ω_G). Level curves for compressive and tensile strain (in %, red line) and for charge carrier density (holes) n (in $10^{11} \,\mathrm{cm}^{-2}$, blue). Graphene on Cu shows only an intrinsic residual charger carrier density of $n = 2 \times 10^{11} \,\mathrm{cm}^{-2}$, and a strain distribution from -0.4 to $0.0 \,\%$.

in Figure 3.12 for graphene grown on Cu foil. Here, the position correlation of G and 2D reveals a rather compressive strain distribution from -0.4 to 0.0% and a constant residual doping level of $n = 2 \times 10^{11} \text{ cm}^{-2}$, which represents a charge neutrality as for freestanding graphene [71]. The slight changes in the strain might correspond to the Cu foil surface roughness, as discussed in Chapter 4.

3.3 Graphene synthesis methods

Not supposed to exist as a stand-alone material

Free-standing 2D graphene cannot be manufactured due to its thermodynamic instability and the tendency to form 3D bulk graphitic structures. This phenomenon was described by Mermin [72] and is supposed to arise due to thermal fluctuation in lowdimensional crystal structures. The more surprisingly was the report about its first manufactoring. Even suspended graphene sheets could be fabricated, although a substrate material was necessary for the initial synthesis process [73]. Generally, as a result of these findings, a template material serving as a mechanical support [74] is needed, which means any kind of substrate material depending on the chosen fabrication method. The main methods are introduced in the following two chapters.

Most wanted: Graphene withhigh quality and as large as possible.

Several graphene growth techniques have been demonstrated since the first successful isolation of graphene by the group of Geim and Novoselov [76]. The overall ambition as its best is the fabrication of large-area graphene layers of perfect, i.e. defect-free quality.



Figure 3.13: Interrelation between graphene quality and production costs (for mass production). Modified by courtesy of [75].

There are two main principal approaches for graphene synthesis. One is a "top-down" approach starting from bulk graphite and a cleavage of the individual graphene layers. The alternative is a "bottom-up" approach starting with carbon atoms or carbonic molecular building blocks to build up 2D graphene layers. All techniques compete with each other regarding the number of synthesized graphene layers, its homogeneous quality and the possible integration into already established industrial processes and applications. Individual benefits and drawbacks of each synthesis technique need to be weighed up properly in order to use the full capacity when it comes to the transition of the fundamental graphene research on actual applications. One focus of this work is the development and optimization of a CVD process for graphene synthesis, which is described more in detail since it guarantees large-area graphene layers at comparably low production costs (cp. in Figure 3.13).

3.3.1 Deserving the Nobel prize – the mechanical exfoliation of graphene flakes

The mechanical exfoliation process, generally known as the Scotch Tape Method, was first developed and reported by Geim and Novoselev [76]. It constitutes a very simple synthesis method for graphene flakes of the size of several nm up to 1 mm in length [74] by using highly oriented pyrolytic graphite (HOPG) as a precursor material. Originally, the HOPG is exposed to oxygen plasma in order to etch mesa structures. These structures are pressed into a photoresist layer and baked afterwards in order to cleave the primary HOPG substrate from the mesas, which attached to the photoresist. Adhesive scotch tape is used to repeatedly peel off FLG flakes from these mesas and then press to the target substrate, usually SiO₂. After peeling off, the graphene layer remains sticking on the substrate. Repeated iteration of this procedure reduces the number of graphitic layers, even SLG areas emerge. A schematic description of this method is shown in Figure 3.14 (a). The SLG and FLG can be made visible via optical microscopy (OM), see Figure 3.14 (b), and scanning electron microscopy (SEM).



Figure 3.14: (a) Schematic illustration of the mechanical exfoliation method. Based on [82]. (b) Mechanically exfoliated graphene monolayer on SiO₂. By courtesy of Graphene Industries [74].

With achieved carrier mobilities at room temperature as high as $15\,000\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ for graphene transferred onto SiO₂ [77] and even 200 000 cm² V⁻¹ s⁻¹ for suspended graphene [73], the mechanical cleavage provides graphene with the best quality graphene compared to all other synthesis methods. However, its major drawback lies in the difficulty to produce large area graphene films. Furthermore, this fabrication technique is challenged by the lack of control regarding the number of graphene layers attached to the substrate after the cleavage. Although many groups concentrated on optimizing the method, e.g. via anodic bonding [78], lathe-like setups with ultrasonic treatment [79, 80] or pretreatments of the substrates [81], the method still has practical difficulties regarding homogeneity and flake size. For this reason, mechanically exfoliated graphene is mainly used for fundamental research about its material properties and the investigation of prototype graphene manufacturing. For the purpose in industrial applications other synthesis methods are preferred.

3.3.2 The liquid-phase exfoliation

As the aforementioned Scotch Tape method, the liquid-phase exfoliation (LPE) is also a "top-down" graphene synthesis method. Here, the exfoliation of graphene occurs in liquids by exploiting ultrasound in order to obtain the individual layers from bulk graphite [83]. Exfoliation means to overcome the van der Waals attractions between the adjacent graphene layers. Usually in a simple setup, a dispersion of graphite powder and organic solvents, e.g. N-Methyl-2-pyrrolidone (NMP) or 1,2-dichlorobenzene (ODCB) is prepared. In the presence of such solvents, the van der Waals attractions are drastically lowered and therefore a successful cleavage is enabled [84]. Furthermore, these liquids ensure that an instant reassembling of the separated layers is avoided. Electrochemically, by using aqueous ionic compounds or acids, e.g. sulfuric acid (H₂SO₄), potassium sulfate (K₂SO₄) or sodium hydroxide (NaOH)(aq.) [85, 86], the exfoliation process is supported by gas forming reactions, if a voltage is applied. Gas molecules intercalate with the graphene layers and therefore facilitate the exfoliation process. The adding of surfactants can promote the exfoliation process as well due to their high energy of adsorption on the graphene basal plane [87]. Other procedures provide bulk graphite with a preliminary oxidation. The resulting graphite oxide enlarges the graphene layer distance from originally 3.4 Å up to 1 nm due to defect structures and functional groups bound to the surfaces [88, 89]. Simultaneously, a re-aggregation of single graphene layers is inhibited due to the electrostatic stability, which alleviates the storage of dispersion solutions. On the whole, the LPE is a mass production version of the mechanical exfoliation technique with the lack of quality. The transfer onto suitable substrates is challenging since the solvents (and process induced functional groups) need to be removed completely in order to avoid detrimental impacts on the favored characteristics of graphene. Despite this, the LPE method becomes interesting in the functionalization of the fabricated graphene layers, which already can be done within the liquid by adding favored chemical additives.

3.3.3 Industrially highly applicable – the thermal decomposition of silicon carbide

Graphene can be synthesized via a thermal decomposition of silicon carbide (SiC). The decomposition process usually takes place at temperatures around 1200 to 1500 °C in ultra high vacuum (UHV) [90] or argon (Ar) atmosphere [91]. At these temperatures the Si atoms selectively sublimate from the surface of the SiC crystal and therefore leave a surplus of carbon atoms behind on the SiC surface, because of the different sublimation temperatures of around 1830 °C and 3640 °C for Si and carbon (C), respectively [92]. A schematic of the graphene formation process is depicted in Figure 3.15. It is worth mentioning that Graphene does not grow directly on the SiC surface. Instead, due to a crystal mismatch between graphene and SiC, there is an insulating carbon-rich buffer layer (BL) in between, which is covalently bonded to the underlying SiC substrate [93]. Depending on the used SiC face for the graphene formation, i.e. silicon- (S-face) or carbon-polar (C-face), the resulting graphene is highly influenced regarding thickness, carrier density, electron mobility and flake size, which varies between 30 and 200 nm [94]. Up to now, in Ar atmosphere, process optimizations led to domain sizes above $2500 \,\mu\text{m}^2$ [91]. By optimizing the sublimation process the BL can also rearrange to graphene [95]. This greatly influences the actual graphene quality regarding the stress and strain distribution within the layer and the doping concentration; with a further adjustment of the total annealing time and cooling rate, the number of graphene layers can be controlled. The mobility lies around $1100 \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$ and $27\,000 \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$ at 4 K for S-face and C-face, respectively [90, 96]. These values are far below the ones obtained via the scotch tape method (cp. Section 3.3.1).

In the field of the semiconductor industry, the thermal decomposition of silicon carbide is a far more interesting synthesis method compared to the mechanical exfoliation, since here graphene is grown directly on the target material and an additional transfer process step can be avoided. Furthermore, SiC is a commercially available and extensively used wafer-scale material for semiconductor applications such as power electronic devices [97]. Its capability of growing wafer-scale graphene layers on an already insulating substrate and therefore its compatibility to industrial fabrication strongly facilitates the industrial integration into already established application processes. However, a major drawback are the comparably high production costs and a layer quality which is achieved or even outperformed with other synthesis methods.



Figure 3.15: Schematic illustration of the SiC decomposition principle. Pristine SiC is shown in (a). Due to a high temperature annealing Si atoms evaporate (b) leaving C atoms in the crystal which form a graphene layer (GR) with a buffer layer (BL) in between (c).

3.3.4 Molecular beam epitaxy

Generally, the molecular beam epitaxy (MBE) is a commonly used method for the growth of epitaxial layers of comparably high quality and homogeneity [98]. Due to its ability to atomic layer control of the thickness because of a very low deposition rate, it is an interesting technique for the graphene synthesis. Epitaxy means a deposition of a crystalline overlayer (in this case graphene) onto a crystalline substrate with at least one common crystallographic direction. As a result of this, the substrate crystal structure directly influences the crystal structure of the epitaxially grown layer in matters of strain and stress within the layer. For graphene growth, substrates such as SiC, sapphire, Cu foil or even hexagonal boron nitride (hBN) flakes are used. Usually, graphite powder or carbon filaments serve as the carbon source. A wide research field here is the development of atomic carbon sources to enable high quality graphene growth [99]. However, due to the achievements in the process development of CVD graphene synthesis regarding cost efficiency and layer quality, MBE plays a decreasing role in graphene fabrication.

3.4 Synthesis method of choice – The Chemical Vapor Deposition

The chemical vapor deposition (CVD) is a widely used technique in the semiconductor industry for the thin film growth of various materials, such as silicon (Si), carbides, nitrides and carbon-based materials such as graphene. The growth species are supplied by a precursor gas, which is in case of graphene growth e.g. methane (CH₄), ethylene or acetylene. As a "bottom-up" process, the aforementioned building blocks are thermally dissociated carbon atoms. These atoms are adsorbed on a growth substrate by the formation of the energetically favored material structure. Basically, the CVD growth process takes place in a reactor chamber under accurately controlled growth parameters, such as ambient pressure, growth temperature, the partial pressures of the gases and the growth substrate material. The CVD process is classified by several categories, such as by the operating pressure or the type of the substrate heating [100]. Apart from the atmospheric pressure (AP)CVD, modern CVD-reactors employ low-pressure (LP)CVD or ultra high vacuum (UHV)CVD. If the entire reactor chamber is heated by an external source which induces a substrate heating by thermal radiation, it is mentioned as *hot* wall CVD. In cold wall CVD only the substrate is heated (via induction or an electrical current), whereas the chamber walls are at room temperatures. Depending on the growth substrate and the operating conditions, the deposition of materials can be achieved in various forms, such as in mono- or multicrystal appearance. The main advantage of CVD is the process scalability towards mass production which makes this synthesis cost-efficient and industry applicable. However, CVD is highly sensitive to the involved process parameters, such as the chamber pressure, the precursor gas concentration and the process temperature. Therefore, an individual process optimization is inevitable.

3.4.1 Graphene synthesis via CVD

CVD is the method of choice for the synthesis of graphene due to its possibility of large-area growth with excellent carrier mobilities at room temperature up to $25000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $50000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on SiO₂ and hBN, respectively [101–103]. In contrast to the thermal decomposition of SiC, where carbon is already present in the substrate material, in CVD the carbon is supplied in a precursor gas mixture, e.g. commonly containing CH_4 , ethylene (C_2H_4) or acetylene (C_2H_2) as a carbon supplier gas. Since it is used for all graphene synthesis processes performed in this work, the following remarks about the reaction principle of CVD graphene are done using the example of CH_4 . The overall CVD graphene growth can be considered as two main separate steps - the precursor pyrolysis (1) and the formation of a graphitic structure (2) from dissociated carbon atoms. For favorable graphene growth, the CH_4 molecules need to decompose completely into C atoms in order to ensure pure graphene without any additional carbonic products. The energy, which is needed for this decomposition/dissociation is called the dissociation energy D_0 or standard enthalpy of reaction $\Delta H_{\rm r}^{\Theta}$ and describes the change in enthalpy when matter is transformed by a chemical reaction. Generally, depending on the products' and the reactants' enthalpy, a decomposition reaction is either endothermic (standard enthalpy of reaction $(\Delta H_r^{\Theta}) > 0$) or exothermic ($\Delta H_r^{\Theta} < 0$). Even if there is a gain in energy for exothermic reactions, for both types of reaction there is the need of an external energy in order to overcome the activation energy barrier E^* and to initiate the chemical reaction.

Former investigations about CH_4 dissociation developed a number of formation methods of CO and H_2 (synthesis gas formation), e.g. the steam reforming process $(CH_4 + H_2O)$ and the partial oxidation $(CH_4 + CO_2)$ [104, 105]. Several research activities on this topic came to the conclusion that a pyrolysis mechanism underlies the oxidation process and also takes place under the absence of oxygen [106]. Although the complete thermochemical decomposition process of CH_4 is not yet fully understood due to intermediate steps in the CH_4 pyrolysis, a possible and commonly accepted reaction path is given by

$$CH_4 \longrightarrow CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow C.$$
 (3.20)

The reaction principle of the CVD graphene process

Regarding graphene growth, two challenges need to be overcome in order to ensure a twodimensional growth of one carbon layer. At first, CH_4 starts completely decomposing and forming graphitic structures at temperatures above 2200 °C [107]. The pyrolysis



Figure 3.16: (a) Schematic illustration of an endothermic reaction. E^* and E_c^* describe the activation energies without (red) and with a catalyst (green). ΔH_r^{Θ} is the standard enthalpy of reaction, which is positive in the endothermic case. (b) Schematic of the process principle of the chemical vapor deposition. The chemical reaction can be divided into distinct reaction steps.

of CH_4 in gas phase is a strongly endothermic reaction [108] with a calculated total bond-dissociation energy D_0 of 17.2 eV - 18.6 eV [109, 110]. Apart from subordinate melting points of considered substrate materials, the growth process would be very much energy consuming. The cost efficiency would be affected negatively by such high process temperatures and the heating and cooling of the substrate would cause additional stress and strain. The reaction principle is schematically shown in Figure 3.16 a). During the chemical reaction the reactant (CH₄, blue line) undergoes a transition state (red) by overcoming the activation barrier before the products (C and H atoms, violet) are formed.

Secondly, the graphene growth needs to be stopped after the deposition of one atomic layer to ensure that graphene growth instead of a graphitic bulk growth is happening. Here, catalytic materials come into play since they can get a grip on these issues by directly influencing the chemical reaction. Depending on the chemical constituent parts of the catalyst, they are able to increase the reaction rate by lowering the activation barrier and even the dissociation energy, such as depicted in green in Figure 3.16 (a). In more detail, metal (M) substrates such as Cu or nickel (Ni) catalyze the CH₄ decomposition by their ability to bind carbon species forming C–M bonds. Due to a charge transfer between adsorbed carbon atoms and the metallic surface, a resulting adsorption energy lowers the activation energy E_c^* and the dissociation energy D_0 of the dehydrogenation. On Cu(111) substrates the adsorption energy E_{ad} for a single carbon atom was calculated as 6.05 eV by Liang et al. [111] using density functional theory (DFT).

In Figure 3.16 (b) the CVD process on a catalytic substrate is schematically illustrated. The complete chemical reaction can be divided into several reaction steps, which individually influence the whole material deposition. First of all, at a process temperature between 800 to 1100 °C the precursor CH_4 (mixed with Ar as a carrier gas) needs to diffuse to the substrate surface (1) via the boundary layer, i.e. the region close to the Cu foil surface, where no net-stream is observed and free atomic motion is of the precursor products is allowed. A dissociation in the gas phase is not expected due to its high dissociation energy. After this diffusion onto the catalyst surface (2) the adsorption of the precursor on the surface occurs forming C–M bonds (the so called chemisorption). Now, adsorbed precursor molecules can dissociate due to the catalysis and the product atoms either create nucleation centers or contribute to some sort of step growth (3). Depending on the solubility a dissolving of C atoms into the bulk of the catalyst will occur. The byproducts, i.e. hydrogen atoms, desorb (4) and diffuse out of the boundary layer back to the main stream of the reaction gases (5) and leaves the reactor.

In a nutshell, the pyrolysis of methane is catalyzed by metallic substrates via the reaction path

$$Cu + CH_{4,g} \longrightarrow Cu + CH_{4,s},$$
 (3.21)

$$CH_{4,s} \longleftrightarrow CH_{x,s} + (4-x)H_s,$$
 (3.22)

with the indices g = gas phase and s = surface. CH_4 dissociates via the cascade in Equation (3.20) resulting in adsorbed carbon species and hydrogen. This is crucial for the subsequent graphene growth. Equation (3.22) occurs with a comparably low reaction rate and the formation of graphene can be greatly enhanced by the catalytic role of present hydrogen [112]. According to the reaction paths

$$Cu + H_2 \iff Cu + 2H_s,$$
 (3.23)

$$CH_{x,s} + H_s \iff CH_{y,s} + (x-y)H_s, \quad x > y,$$

$$(3.24)$$

the presence of hydrogen accelerates the dehydrogenation of methane significantly. A precise adjustment of the partial pressures is therefore essential in order to control the growth velocity and to avoid multilayer growth, since these chemical reactions compete with the graphene etching ability of hydrogen.

Cu rather than Ni as a catalyst substrate

Several different catalyst materials have been investigated, which differ in their catalytic impact regarding the generated byproducts and their strength in lowering the activation energy barrier. For Cu as the catalyst substrate, the dissociation energy $D_{0,c}$ for the complete reaction path of adsorbed CH₄ molecules lies between 4.3 eV and 6.4 eV. The average activation barrier E_c^* for the dissociation of a single H atom (one reaction step, cp. Equation (3.20)) is lowered to 1.4–2.0 eV [110, 113], which points up the catalytic impact of the catalysts on the decomposition reaction. Ni actually changes the CH₄ dissociation energy of $D_{0,c} \approx -1 \,\text{eV}$ with a much lower E_c^* for each dissociation step of 0.4–0.9 eV [114, 115] (cp. Tables 3.1 and 3.2 for review).

Apart from energy considerations, an additional aspect of successful graphene growth arises in terms of the carbon solubility. Ni or Cu are metals, which have a finite carbon solubility $L_{\rm C}$. Due to their difference in $L_{\rm C}$ of > 0.1 and < 0.001 at%, respectively, the graphene synthesis differs fundamentally [116–118]. Since Ni is able to modify the complete chemical reaction from endothermic to exothermic, which enables lower

	Gas phase	Cu	Ni
	$(\mathrm{CH}_{\mathbf{x},\mathbf{g}} \longrightarrow \mathrm{CH}_{\mathbf{x}-1,\mathbf{g}} + \mathrm{H}_{\mathbf{g}})$	$(CH_{x,s} \longrightarrow$	$CH_{x-1,s} + H_s)$
$\overline{\mathrm{CH}_4}$	4.55	-0.09	-0.44
CH_3	4.79	1.91	-0.16
CH_2	4.39	1.93	-0.12
CH	3.51	1.02	-0.23

Table 3.1: Summary of the bond-dissociation energies [in eV] for CH_4 in gas phase, on Cu and on Ni catalyst substrates (g = gas phase, s = surface). Based on [109, 114].

Table 3.2: Total dissociation energy D_0 [109, 110] and activation energy E^* [114, 115] for CH₄ in gas phase, on Cu and on Ni catalyst substrates (c = catalyst). Comparison of literature values of the carbon solubility $L_{\rm C}$ [in at%] [116–118]. Corresponding adsorption energy $E_{\rm ad}$ (in eV) from [113, 114].

	Gas phase		Cu	Ni
	$(CH_{4,g} \longrightarrow C_g + 4 H_g)$		$(\operatorname{CH}_{4,s} \longrightarrow$	$\rm C_s~+~4~H_s)$
$\overline{D_0}$	$17.2 - 18.6 \mathrm{eV}$	$\overline{D_{0,c}}$	$4.3-6.4\mathrm{eV}$	$-0.95\mathrm{eV}$
		$E_{\rm c}^*$	$1.42.0\mathrm{eV}$	$0.40.9\mathrm{eV}$
		$L_{\rm C}$	< 0.001	> 0.1
		$E_{\rm ad}$	6.05	> 7.7

process temperatures ($\approx 600 - 800 \,^{\circ}$ C) than other catalysts. Furthermore, Ni provides a specific growth mechanism. The adsorbed carbon atoms dissolve into the bulk during the high temperature process. With cooling down the substrate a re-dissolving and a precipitation of these carbon atoms occurs on the Ni surface resulting in a formation of carbonic structures. A proper graphene growth is highly sensitive to the heating duration and the cooling rate, which makes a reliable regulation of monolayer growth almost impossible. Using Cu as the catalytic material, the adsorbed carbon atoms migrate along the surface, not dissolving but persistent in an adsorbed state, and form graphitic structures with nearby carbon atoms. Due to the very low solubility, the chemical reaction takes place directly on the catalyst material, which is therefore losing its catalyst capability due to the gradual coverage with carbon atoms forming a graphitic structure. Ideally, the synthesis is a self-limiting process which stops after the deposition of one atomic layer of graphite – graphene. This is not the case for Ni. Here, the graphene growth process consists mainly of a controlled back-precipitation of dissolved carbon atoms during cooling. Therefore, a self-limitation is not achieved. Taking this into account, Cu as a catalyst is more favorable than Ni in CVD graphene growth and therefore it is the catalyst substrate of choice for all the graphene research experiments presented in this work. In the next chapter, a deeper investigation of the relevant process parameters for the CVD synthesis is presented, with an elaborated parameter adjustment with respect to the laboratory reactor *BlackMagic 6 inch*.

4 CVD growth on Cu foil - the graphene fabrication procedure

In the following chapter, the graphene fabrication procedure, as it is done for this work, is presented. Since the experimental work follows some distinct steps, which turned out to highly affect the whole graphene synthesis, these steps are presented chronologically as they are executed in the lab. Starting with a proper pretreatment of the growth substrate and its surface characterization via White Light Interferometry, the laboratory reactor BlackMagic 6 inch and the related process optimization are explicated. Prior to the synthesis of large-area graphene sheets, the nucleation at the very beginning of the CVD process is investigated in order to optimize the initial growth conditions. The process parameter dependencies and growth results are presented by applying the two main commonly used non-destructive characterization tools, i.e. Raman spectroscopy and scanning electron microscopy.

CVD graphene on copper foil – the operational procedure

As aforementioned, for this work graphene was grown via CVD on copper (Cu) foil as the catalytic growth substrate. The CVD synthesis is highly sensitive regarding the process parameters, i.e. pressure, gas flow and growth temperature. Moreover, the copper foil surface conditions regarding the material purity and the surface roughness have a direct impact on the graphene quality [119]. Therefore, an overall graphene synthesis optimization consists of an interplay of parameter adjustments, which includes both a conditioning step of the pristine Cu foil and the accurate monitoring of parameter variations, cp. Figure 4.1.

Process monitoring, which stands for a routinely applied graphene quality characterization, takes place via Raman spectroscopy measurements (see Section 3.2). Information about defects and stress distributions (Section 5.3.2) leads to a parameter adjustment regarding either the substrate pretreatment or the growth conditions. Several groups investigated countless parameter variations and somehow ideal growth conditions could be established. Nevertheless, many of the main reaction principles are still not entirely understood. Additionally, a detailed parameter study for each individual experimental setup is inevitable due to the dependence of quality results on external factors, such as geometric aspects of the utilized substrates, individual hardware components and the research equipment. Fortunately, the interdependency of substrate pretreatment and CVD growth parameters can be considered separately. A clean and smooth Cu foil surface directly enhances the surface nucleation as the initial growth step and therefore also



Figure 4.1: Schematic of the interplay and reciprocity of mainly four steps for the development of a high quality graphene synthesis.

the total graphene growth, which affects the overall layer quality. For this work, these findings imply the following procedure: At first, a functioning polishing process is developed in order to be able to use smooth Cu foil for the graphene synthesis. Afterwards, a substrate independent analysis of the main CVD growth principles is performed, which leads to graphene sheets on Cu foil with a reproducibly good quality.

4.1 Growth substrate pretreatment – the electrolytic polishing of copper foil

Generally, the polishing of a surface is an abrasive operation in which surface asperities are removed. The result is a smoothened surface. In order to characterize and quantify the surface roughness, the surface roughness parameter (s_q) , which is used for the quantification of the polishing quality, is given as

$$s_{\mathbf{q}} = \sqrt{\frac{1}{A} \int \int_{A} \left| \left(z(x,y) - \bar{z} \right)^{2} \right| dx dy}, \tag{4.1}$$

which defines the averaged quadratic surface height within a given area A and describes mathematically the deviation variance of a quantity height z(x, y) to its mean value \bar{z} . In case of Cu foil, several groups already showed that a low roughness of the growth substrate is essential due to the unintentional growth in irregular valleys of the substrate surface [120, 121]. In Figure 4.2 (a), a comparison of the obtained Raman spectrum of graphene on differently pretreated Cu growth samples is depicted. The decrease in s_q from 278 nm to 157 nm shows clearly the positive effect of a sufficiently abraded Cu foil on the graphene quality, which is indicated by a significantly higher 2D/G ratio for polished Cu foil, i.e. ≈ 3.1 compared to ≈ 1.5 . The lower intensity ratio (red and blue line) corresponds to multilayer graphene regions and a strong change in the strain distribution due to both a 2D peak broadening and a significant red-shift of $\approx 9 \,\mathrm{cm}^{-1}$, as shown in Figure 4.2 (b) and summarized in Table 4.1. This results in a layer inhomogeneity and poor electronic transport properties in terms of the sheet



Figure 4.2: (a) Comparison of averaged Raman spectra (line scan, 121 measurement points) of graphene grown via CVD on pristine Cu foil (blue line) with a roughness s_q of 278 nm, and on differently polished Cu foil with a roughness of $s_q = 252$ nm (red) and $s_q = 157$ nm (black). (b) Zoom-in of the same Raman spectra.

resistivity, as measurements of transferred graphene showed (Chapter 5). Additionally, a rough Cu foil surface leads to a comparably larger graphene area, which itself results in crinkles and cracks during the wet transfer [122], see Chapter 5. These findings indicate the strong influence of a flattened surface on the graphene quality and leads to the necessity of an elaborated cleaning and polishing procedure in order to ensure a stable and reproducible graphene growth.

4.1.1 Chemical fundamentals of the electrolytic polishing and experimental setup

The electrolytic polishing (EP) is an electrochemical technique in order to modify the surface of a metal and to obtain a high gloss, which corresponds to a low roughness. The copper's topography change is obtained by an electrochemical process, in which a surface dissolution of the Cu substrate takes place. As originally investigated by Jacquet in 1936 [123], these days EP is a commonly used technique for polishing the surface of copper. The working principle is basically described in Figure 4.3 (a). The Cu foil is anodically connected to a power supply and suspended in aqueous 14 M (85%) phosphoric acid (H₃PO₄). Ideally, also the cathode material consists of Cu foil with the same dimensions and in parallel position in order to obtain an electric field confinement.

\mathbf{EP} (min)	$egin{array}{c} egin{array}{c} egin{array}$	$rac{2D/G}{(\mathrm{cm}^{-1})}$	$\frac{\mathbf{FWHM}}{(\mathrm{cm}^{-1})}$	$egin{array}{llllllllllllllllllllllllllllllllllll$		
no	278	1.53 ± 0.58	50.18 ± 13.52	2691 ± 5		
10	252	2.03 ± 0.64	32.59 ± 4.81	2692 ± 4		
40	157	3.12 ± 0.44	26.55 ± 4.06	2683 ± 6		

 Table 4.1: Summary of Raman spectroscopy data for three different electrochemically polished Cu foil samples after graphene deposition.



Figure 4.3: a) Schematic sketch of the experimental setup for electropolishing of copper foil. Phosphoric acid (H_3PO_4) is used as an electrolyte. b) Schematic drawing of the working principle of the electropolishing due to an electric field gradient along surface bumps. c) Image of the applied experimental setup with the anodic (black) and cathodic (red) electrodes.

 H_3PO_4 serves as the electrolytic solution by ensuring a controlled surface diffusion of the ions due to its comparably high viscosity. This leads to a uniform film-controlled dissolution of Cu [124]. Its appearance as an ionic liquid is given as

$$H_3PO_4 + 3H_2O \longrightarrow 3H_3O^+ + PO_4^{3-}, \qquad (4.2)$$

where the PO_4^{3-} ions mainly contribute to the polishing of copper.

The polishing effect at the anode is based on two main chemical reaction schemes at the anode and cathode, which are strongly assisted by the electrolytic ions and are described as

Anodic reactions

$$Cu \longrightarrow Cu^{2+} + 2e^{-},$$
 (4.3)

$$3 \operatorname{Cu} + 2 \operatorname{PO}_4^{3-} \longrightarrow \operatorname{Cu}_3(\operatorname{PO}_4)_2 + 6 \operatorname{e}^-, \tag{4.4}$$

Cathodic reactions

$$\operatorname{Cu}^{2+} + 2 e^{-} \longrightarrow \operatorname{Cu},$$
 (4.5)

$$2 \operatorname{H}_{3} \operatorname{O}^{+} + 2 \operatorname{e}^{-} \longrightarrow 2 \operatorname{H}_{2} \operatorname{O} + \operatorname{H}_{2}.$$

$$(4.6)$$

An externally applied voltage via the electrodes ensures the ion transport within the electrolyte. According to the chemical reactions, the anode surface dissolves by the formation of Cu^{2+} ions and electrons, which drift to the cathode, where they are discharged and attached. The polishing effect occurs due to an electric field dependency of the ion transport gradient, which results in a higher reaction rate at bumps and surface hillocks due to a higher electric field, cp. Figure 4.3 (b). Basically, the EP is highly sensitive process regarding its polishing effect on the surface and its reproducibility [124, 125]. Anodic reactions mainly depend on geometry aspects, namely on the sample distance, the area to be polished, the electrolytic composition and the current density on which



Figure 4.4: (a) Current density vs. voltage plot for the electropolishing of copper (Cu) in phosphoric acid (H_3PO_4), based on [126]. (b) Experimentally obtained current density vs. voltage for a 40 min process of electropolished Cu foil with a size of $40 \times 40 \text{ mm}^2$. The expected slope and the pitting/polishing zone are marked with dotted line in red and black (V_b), respectively.

the reactions take place. Therefore, it is inevitable to adjust the process parameters for each experimental setup individually. For this work, Cu foil samples with a size of $40 \times 40 \text{ mm}^2$ were used. The EP setup is shown in Figure 4.3 (c). The anodically and cathodically connected Cu foil samples are positioned vertically into a cylindrical teflon shell, which contains the electrolyte, parallel at a distance of 40 mm. In order to ensure a stable experimental setting, a laboratory acrylic glass holder was used to fix the position of the electrodes.

Already in 1949, Jacquet [127] described the polishing process of copper by investigating the polarization curve, i.e. the current density in dependence of the applied voltage during EP, as depicted in Figure 4.4 (a). There are several theoretical explanations for this specific polarization curve, which is characteristical for different anodic metals and also strongly depends on the used electrolyte. According to Jacquet, the I-V characteristic can be divided into three regions, where the electrochemical reactions take place very differently. At first, there is a current increase with increasing applied voltage up to a certain value $V_{\rm b}$. This is the so called pitting zone, where the anodic reactions already occur, but there is rather a pitting than a polishing effect on the Cu foil due to the probable formation of oxidic compounds. For voltages larger than $V_{\rm b}$ the electrolyte forms a liquid film on the metallic surface, i.e. cubric phosphate $Cu_3(PO_4)_2$, which acts as an insulating layer and opposes to the externally applied electric field. The electrolyte's viscosity promotes the formation of this liquid film, and experiments with different electrolytic viscosities show a strong dependence on the polishing results [123]. The accumulation of these phosphate components during the anodic dissolution results in a current density drop and forms a stable plateau-like shape for applied voltages between $V_{\rm b}$ and c. In this region the actual polishing occurs. At higher voltages $(> V_c)$ the established electric field can overcome this viscous insulating film and the reestablished ion transport away from the metallic surface leads to an abrupt increase in current density. This accounts for the evolution of oxygen on the surface, resulting in a high quality polishing with the side effect of inhomogenities due to the influence

of intense gas bubbling. As several groups [126–128] confirmed experimentally for Cu, the pitting zone lies in the range of $V_a = 0.2$ V and $V_b = 1.1$ V. The actual polishing occurs at the plateau of constant current density within 1.1 V and 2.0 V, where the chemical reaction takes place under stable conditions due to this mentioned formation of an insulating electrolytic layer. In order to replicate these findings and to identify the optimal parameters for the laboratory setup used in this work, in Figure 4.4 (b), the experimentally obtained polarization curve for this setup is depicted. The applied voltage was varied between 0.8 - 1.4 V at a constant polishing time of 40 min. Here, the pitting and polishing regions can clearly be identified. A local maximum current density was found at $V_b = 1.15$ V in good agreement with previous works. For voltages above 1.4 V an overload stopped the reaction process. Due to setup restrictions, higher voltages could not be investigated. As it turned out, the voltage range between 1.2 and 1.4 V already ensures stable and satisfying electropolishing results, which made further parameter investigations obsolete.

4.1.2 Substrate characterization

For all CVD synthesis processes commercially available and standardly used Cu foil (AlfaAesar, 99.8% and 99.98% purity, volumetric mass density $\rho_{\rm Cu} = 8.96 \,\mathrm{g/cm^3}$, 25 µm thickness) is used as a growth material and therefore investigated regarding the EP. The surface roughness can be made visible via optical microscopy and white light interferometry (WLI). The roughness parameter $s_{\rm q}$, as defined in Equation (4.1), can be determined from the WLI surface data and gives a parameter for comparison of the surface polishing effect.



Figure 4.5: (a) Schematic experimental setup of WLI with an exemplary Cu sample. The optical path difference between measurement and reference beam results from the vertical position z of the Cu sample. Based on [129]. (b) Exemplary interference pattern obtained from the WLI measurement setup used for this work. The fringes (black-white) result from interference effects on the Cu surface and represent the intensity of the envelope curve.

White light interferometry

The WLI is an optical method to characterize a material's surface topography with a resolution in the range of several nm [130]. Herewidth, the surface character both can be made visible and characteristic surface parameters, e.g. the aforementioned s_q , can simply be extracted. The basic working principle of WLI, as depicted in Figure 4.5 (a), lies in the separation of a short-coherence-length light source in a measurement and reference beam. This setup is principally known as a common Michelson interferometer. The measurement beam is scattered from the test material surface, the reference beam is reflected by the reference mirror [129, 131]. Both beams are then relayed to a charge-coupled device (CCD) image sensor. Their superposition results in an interference pattern, cp. Figure 4.5 (b), if the optical paths of both beams are of the same length constructive interference occurs. By adjusting the sample position height z relative to the reference beam path length, the optical path difference is varied resulting in an interference intensity change of the envelope function up to a maximum value at z_0 . If this adjustment is done for every pixel, a 3D image of the sample surface is obtained.

In contrast to monochromatic light sources, such as the laser interferometry, the white light interferometry ensures an effective elimination of the phase ambiguity problem due to its comparably short coherence length (L_c) [133] which directly depends on the coherence length of the optical light source. In Figure 4.6 (a) and (b), the interferograms for white light and monochromatic interferometry are shown for comparison emphasizing the color effect. For monochromatic measurements the clear identification of the first order interference is not guaranteed, which might lead to misinterpretations of the actual surface profile. In (c) the corresponding envelope function for a white light source is depicted. A shorter coherence length of the light source leads to a higher spatial resolution due to an increased sensitivity of the shape of the envelope function. Therefore, white light sources are commonly used for the surface characterization.



Figure 4.6: (a) White light interferogram. The interference pattern clearly identifies the maximum of the envelope curve (black bar). (b) Monochromatic (red) interferogram. The interference pattern impedes the proper identification of the first maximum. Adapted from [132]. (c) Exemplary envelope function of a white light interference pattern. The maximum intensity is obtained at a horizontal height z_0 .



Figure 4.7: Surface images of pristine Cu foil. (a) Image of a $400 \times 580 \,\mu\text{m}^2$ area taken by WLI. (b) Image taken by optical microscopy at 50x magnification. The undulatory surface structure is clearly visible which results from the manufacturing process. (c) s_q vs. EP time at a constant applied voltage of V = 1.2 V. The errors bars result from a sample statistic of at least four samples for each parameter variation. s_q is obtained via white light interferometry. (d) Roughness parameter s_q in dependence on the applied voltage for a 40 min electropolishing process.

The used WLI setup for this work is a Mirau interferometer (Contour GT-K, Bruker, Billerica, USA) with a 20x objective and a 0.55x multiplier. Both the vertical positioning, which is technically implemented via a piezoelectric steering mechanism, and the data analysis is governed by the manufacturer's software Vision64[®]. From this data, the surface roughness parameter s_q is extracted.

Voltage- and time-dependent electrolytic polishing

During its fabrication process the Cu foil is flattened by steamrollering resulting in a corrugation surface pattern, as depicted in Figure 4.7. Both WLI in (a) and optical microscopy in (b) show a distinct valley-like surface structure arising from the fabrication process. With a peak-to-valley height of almost 3 µm this asperity influences the growth quality, as mentioned before. Therefore, a polishing process is developed in order to



Figure 4.8: (a) Surface image of electropolished Cu foil $(400 \times 580 \,\mu\text{m}^2)$ obtained by WLI (40 min, 0.9 V), representing the pitting regime. (b) Corresponding OM image at 50x magnification. (c) WLI image of electropolished Cu foil $(400 \times 580 \,\mu\text{m}^2)$ at 1.2 V applied voltage, representing the polishing regime. (d) Corresponding OM image at 50x magnification.

ideally remove this corrugation pattern completely. In order to determine the polishing effect on the Cu surface, both time- and voltage-dependent EP processes were performed. First investigations revealed rather a polishing than a pitting at an applied voltage $V > V_{\rm b} = 1.15 \,\mathrm{V}$, as described in Figure 4.4. For the determination of the total polishing time the voltage was therefore set to 1.2 V, while the time was varied between 5 and 50 min. The corresponding calculated $s_{\rm q}$ is plotted in Figure 4.7 (c). In total four Cu foil samples for each time variation were fabricated and five sectors for each of these samples were investigated optically.

In principle, a clear trend of a lower surface roughness for a longer polishing time is observable. It is worth mentioning that the statistical error bar decreases for longer polishing time, which results from a more homogeneous surface dissolution. This can be explained theoretically by the fact, that the formation of a uniform liquid film close to the surface and the stable establishment of a constant electric field, i.e. an initialization of a constant ion flow, takes a certain time, which strongly influences the polishing
used as the selected standard procedure are denoted bold.										
$V_{ m EP}$	no	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
t	no	5	10	15	20	25	30	40	45	50
$oldsymbol{s}_{ ext{q}}$	278	313	252	195	185	219	226	134	158	154
$V_{ m EP}$	no	0.8	0.9	1.0	1.1	1.2	1.3	1.4		
t	no	40	40	40	40	40	40	40		
$m{s}_{ m q}$	278	314	393	382	214	134	177	187		

Table 4.2: Roughness parameter s_q (in nm) for the variation limits of the voltage V_{EP} (in V) and process time t (min), cp. Figure 4.7 (c) and (d). The process parameters used as the selected standard procedure are denoted bold.

result. However, the gain in homogeneous polishing and the resulting material mass loss, conflict with each other and need to be taken into account when a mechanically robust growth substrate shall be achieved. For an exemplary EP process (40 min, 1.2 V), the total mass loss leads to a thinning of the Cu foil from 25 µm to 19 µm. In the next step, the applied voltage is varied between 0.8 and 1.4 V at a constant process time of 40 min. In Figure 4.7 (d) the trend of s_q is depicted and reproduces the pattern of Figure 4.4 with a slight shift to lower voltage. For a voltage below 1.1 V, a clear pitting of the Cu surface occurs, which leads to a higher s_q of up to 393 nm. Corresponding optical images are shown as an example for 0.9 V in Figure 4.8 (a) and (b). The pitting leads to a rough and cragged surface, which makes this substrate inappropriate for graphene growth. According to these findings V_b can be determined, since for higher voltages the roughness explicitly lies below 200 nm, which corresponds to the polishing region. Here, the smoothening effect is clearly visible due to a reduction of s_q down to 134 nm, as depicted with WLI and OM images in Figure 4.8 (c) and (d), respectively.

In summary, the process time has a more linear effect on the polishing of the Cu surface, whereas the applied voltage follows the obtained polarization curve before. Our findings result in standardized EP process parameters of t = 40 min and V = 1.2 V for $40 \times 40 \text{ mm}^2$ in order to overcome the observed instabilities and to be able to guarantee a high polishing effect, see also in Table 4.2. For the CVD graphene process development and especially for the investigations of certain parameter effects, first growth experiments were performed on Cu foil with a smaller size of $10 \times 15 \text{ mm}^2$. In order to obtain the same EP results regarding the surface roughness, the EP process optimization here leads to an optimal applied voltage of 1.4 V. Again, this indicates, that even geometrical changes in the experimental setup, in this case the sample size, lead to changed optimal process conditions. With the optimized EP parameter, a standardly applied surface treatment is applied, before graphene is grown on the Cu foil. Before the results of the CVD process development are presented, the employed *BlackMagic 6 inch* laboratory reactor is described shortly in order to deliver insight in the CVD growth technology.

4.2 *BlackMagic 6 inch* – a cold wall, reaction rate limited CVD graphene laboratory reactor

The *BlackMagic 6 inch* reactor, as shown in Figure 4.9 (a)-(c), is a specifically designed CVD reactor for the purpose of the growth of carbon nanotubes and high quality



Figure 4.9: (a) Photographic image of the BlackMagic 6 inch laboratory reactor. (b) Reactor chamber with the diamond heat spreader and the spiral graphitic top heater. (c) Inside of the reaction chamber during growth process. (d) Zoom-in sketch of the sample setup indicating a reaction-rate limited growth process. (e) Schematic of the CVD reactor chamber with its main assemblies, namely the shower head (A), the spiral graphitic top heater (B), the graphitic bottom heater (C), the diamond heat spreader (D), the copper growth substrate (E), the quartz ring (F) and the quartz disk (G). (c)Fraunhofer IAF

graphene. Due to its ability to handle wafers up to a size of 6-inch, this system is used in semiconductor industry as well as in fundamental research. The *BlackMagic 6 inch* reactor is a low pressure system $(5 \times 10^{-3} \text{ to } 25 \times 10^{-3} \text{ mbar})$ with the facility of a plasma enhanced growth, i.e. low pressure (LP)CVD and plasma enhanced (PE)CVD, respectively. The growth substrate, in this case Cu foil for all growth processes in this work, is positioned on a 6-inch diamond wafer, which acts as a heat spreader due to its high thermal conductivity of approx. 2000 W/(m · K). This ensures a homogeneous temperature distribution within the Cu foil and therefore stable growth conditions.

The precursor gas consists of a specific mixture of hydrogen (H_2) and the carbon source CH_4 . This gas flows into the reactor chamber via a shower head and is optionally heated by a top heater before reaching the growth substrate (cp. Figure 4.9 (b)). Regarding the growth rate the CVD can be classified into three major regimes: the deposition takes place mass transport limited, reactant concentration limited or surface reaction limited [100]. Both the mass transport and the reactant concentration limitation may influence the reaction due to a lack of enough reactants diffusing through the boundary layer. Constrained by external settings, e.g. the gas flux density, the total pressure and the reactor geometry, the deposition can be controlled by an adjustment of these parameters. On the other hand, in a reaction-rate limited regime, the deposition is



Figure 4.10: Process devolution in terms of process temperature (black dashed line) and the gas flows of CH_4 (blue solid line), Ar (black) and H_2 (red). The complete process can be divided into three sections, namely the heating and surface termination (1), the graphene growth (2) and the cooling down process (3). The actual deposition time lies between 1 min and 30 min.

strongly controlled by the process temperature, which directly influences the reaction kinetics, regarding the dissociation rate and the diffusion length of already adsorbed carbon atoms. Furthermore, the total pressure also influences the reaction kinetics due to an inverse dependency on the boundary layer. Considering the gas flow direction in the *BlackMagic 6 inch* system, cp. Figure 4.9 (d) and (e), the precursor impinges the substrate vertically. Although the precursor itself and its chemical byproducts need to be diverted laterally afterwards, this reactor geometry enables a relatively symmetric flow towards the substrate and relieves a more homogeneous diffusion behavior across the boundary layer.

An exemplary growth process evolution is depicted in Figure 4.10. At the very beginning, the reactor chamber needs to be decontaminated in order to avoid impurity induced defects during the graphene synthesis. Specifically, the oxygen content, which is unpreventable due to the open reactor chamber for sample loading, needs to be minimized. This is done by a Ar venting and evacuating cycle right before the sample heating under H₂ atmosphere (depicted in black representing the Ar flow). Afterwards, the heating with a gradually decreased rate from 45 to 15 K/min and a temperature stabilization occurs (1). The actual graphene deposition (2) under Ar/CH₄/H₂ atmosphere standardly takes place at a process temperature of 980 °C and lasts for 30 min. Followed by a controlled cooling (15 K/min) under a low Ar partial pressure (3) in order to provide a protective chemical atmosphere, the Ar flow is increased again after the process temperature dropped below 600 °C to further assist the passive cooling. The complete

Temperature Total pressure Process time		980 °C 16 mbar 30 min
Gas flow	$\begin{array}{c} \operatorname{Ar} \\ \operatorname{H}_2 \\ \operatorname{CH}_4 \end{array}$	960 sccm 40 sccm 10 sccm
	CH_4	

 $\label{eq:table 4.3: Summary of standardly used process parameters for CVD graphene growth in the Aixtron BlackMagic 6 inch reactor. The selected gas flows result in a H_2/CH_4 ratio of 4:1.$

growth process takes 2.5 to 3 h. The process parameters for standardly grown graphene on Cu foil are listed in Table 4.3. For process optimization, these parameter values are varied. This will be mentioned in detail in the following sections of this chapter. The listed values merely shall give the reader a first impression of the process procedure. Graphene growth CVD is usually performed in LP or UHV regimes and low partial pressures in order to make the process reaction-rate limited. This avoids the formation of additional non-graphenic but still carbonic compounds during graphene growth.

In conclusion, the *BlackMagic 6 inch* system operates in a reaction-rate limited regime, where the partial pressure and the process temperature are highly critical regarding the graphene quality. Hence, the cold wall design of the reactor is advantageous in order to minimize an undesired carbonic deposition on the reactor walls. In order to determine the opto-electronic properties of CVD graphene, the graphene layer needs to be transferred onto an insulating substrate, such as AlN. In Section 4.3.4 the Raman spectroscopy, which is introduced in Section 3.2 as a powerful and routinely used characterization tool, reveals the high quality of the fabricated graphene layers.

4.3 CVD graphene growth – Process development and optimization

According to the previous theoretical considerations, the overall goal regarding the graphene synthesis is a minimization of graphene sheet resistivity $(R_{s,GR})$ in order to reduce the ohmic losses in the aforementioned resonator devices. Several determinants affect $R_{s,GR}$, such as crystal defects, an inhomogeneous strain distribution along the graphene layer and the graphene nucleation density ρ_n at the very beginning of the growth process. For the following process development, the major influence of the process parameters on the graphene growth are investigated in order to be able to synthesize high quality graphene. Before that, the SEM as a powerful characterization tool, apart from the already introduced Raman spectroscopy, is shortly described.

4.3.1 Graphene characterization via Scanning Electron Microscopy

The SEM produces sample images by scanning a material's surface with a focused electron beam. Herewith, a topological image of the surface is obtained. The actual image arises due to several electron interactions with atoms close to the surface, which means secondary electrons (SE), back-scattered electrons (BSE) and radiation effects.



Figure 4.11: (a) SEM image of graphene nucleation centers on Cu foil, 5000x magnification, 980 °C, 150 s deposition time. Areas with higher contrast at the edges of the nucleation centers correspond to bi- or multilayer growth. (b) Schematic drawing of the attenuation effect of graphene (GR) on emitted secondary electrons (SE) in Cu. Multilayer graphene blocks the SE resulting in a lower signal intensity. Based on [134].

SEM is a powerful imaging method for the visualization of the morphologies of graphene films. Its nondestructive and quick utilization made SEM to emerge as being highly suitable for a stable process monitoring, especially for the initial growth. With such images it is possible to obtain information about the number of graphene layers, the existence of fissures and crinkles within the layer and even the occurrence of vacancies and crystal defects.

SEM contrast – Graphene on Cu

In Figure 4.11 (a) an exemplary SEM image of a graphene CVD process on Cu foil is presented and shows separate graphene nucleation centers. The growth process was stopped after a deposition time of 150 s in order to see an incomplete coverage of the Cu foil substrate. The image signal results from secondary electrons which are emitted from the Cu substrate. Despite their similar work funktion, i.e. $\Phi_{\rm GR} = 4.26 \, {\rm eV}$ [135] and $\Phi_{\rm Cu} = 4.59 - 4.98 \, {\rm eV}$ [34], the main SE contribution comes from the Cu surface, since the incoming electron beam penetrates the bulk Cu up to 10 nm, as Monte Carlo simulations showed [136]. In this case, graphene acts more as a blocking medium and decreases the number of the emitted SE reaching the signal detector. In Figure 4.11 (b) the blocking effect is shown schematically. An increase in the number of graphene layers leads to a stronger blocking and makes the different layers easy to identify due to their specific difference in signal intensity. Thus, for process monitoring not only the number and size of graphene nucleation centers can be controlled, but also the number of grown layers.

SEM contrast – Graphene on AIN

When graphene is transferred on insulating AlN substrate, SEM images show a strong contrast change for pristine AlN and graphene. The effect is the same as aforementioned. However, the prevention of surface charging and the strong transparency of graphene at



Figure 4.12: (a) Schematic drawing of the contrast change between graphene and the underlying AlN substrate and the corresponding SEM image (c) which shows this edge contrast. (b) Schematic drawing of the roughness contrast resulting from graphene (GR) wrinkles and the corresponding SEM image (d). Holes in the graphene layer excavate the underlying AlN, also BLG island, arised during the CVD growth, are visible. (a) and (b) are based on [134].

high electron energies necessitates low accelerating voltages in the range of 1-3 kV. There is a higher yield in SE on the AlN surface, which is blocked due to the coverage with graphene. This principle is shown in Figure 4.12 (a). The corresponding SEM image is depicted in (c) which identifies directly the graphene coverage and serves therefore as an appropriate characterization tool for the determination of the degree of coverage, cp. Chapter 5. In addition to that, SEM illustrates graphene wrinkles and cracks or holes, as depicted in Figure 4.12 (b). Wrinkles result in a higher intensity of SE coming from graphene, since a wrinkle means more C atoms per a certain area which at the same time do not block SE coming from the AlN surface, as depicted in (d). In the presence of cracks or holes, i.e. the underlying AlN surface is visible, these areas appear brighter. Since AlN is an insulating material, the energy of incident electrons is too low for SE creation and emission, which results in a strongly reduced number of emitted SE. Instead, the surface is charged and therefore very bright in its image appearance compared to graphene covered AlN areas.



Figure 4.13: (a) Optical microscopy (OM) image of graphene grown on Cu foil with 99.8% purity, 50x magnification indicating the hollow/hillocks structure. (b) OM image of graphene grown on Cu foil with 99.98% purity, 50x magnification. Cu grains are referred. (c) SEM image of graphene grown on Cu foil with 99.98% purity. (d) OM image, 100x magnification indicating the step-like structure within a Cu grain.

4.3.2 Recrystallization process and impurity impact on the Cu surface

As mentioned above in Section 4.1, the surface of the growth substrate highly influences the total graphene synthesis process. Since the applied Cu foil is of polycrystalline structure due to its fabrication process, it is worth to note, that apart from a Cu surface pretreatment via EP, the CVD process itself affects a crystal rearrangement of the Cu grains. At process temperatures in the range of 950 to 1000 °C the Cu is suspended very close to its melting point $T_{\rm M} = 1085 \,^{\circ}{\rm C}$ [34]. At this stage, the so called Ostwald ripening, i.e. a spontaneous and thermodynamically-driven process of a crystal rearrangement towards larger crystals, occurs and leads to the formation of differently sized Cu grains. In Figure 4.13, optical images of graphene on Cu are depicted. In (a) and (b), the surface of Cu foil with a 99.8% and 99.98% purity is shown, respectively. The grain formation is clearly visible due to distinct grain boundaries. For the $99.8\,\%$ Cu foil, a hillock/hollow-like structure on the surface is observed in contrast to the comparably smooth surface of the 99.98 % Cu foil. According to Kim et al. [137], this indicates the occurrence of metal impurities, i.e. Fe, Ag or oxidic components, which are initially distributed inside the Cu foil. During the high temperature growth, the Cu surface is supposed to form a liquid-like state, under which the surface is cleaned by the formation of impurity precipitates, which are driven out to the Cu surface and evaporate. which forms the hillock-like structures. Those can be also identified in the SEM image in Figure 4.13 (c) as white circular dots. Here, the Cu grains can be clearly identified due to a contrast depedence on the crystal orientation, according to the channeling contrast as described by [138, 139]. Depending on the crytal orientation, incident electrons can



Figure 4.14: (a) AFM image, $30 \times 30 \,\mu\text{m}^2$, representing an exemplary hillock/hollow structure. The blue and red lines correspond to the profile extraction in (b) which show the height profiles of selected hillock/hollow with a height and width of 100-120 nm and 10-40 nm, respectively.

penetrate the substrate at a varying depth, which results in a change in the secondary electrons, which reach the substrate surface and contribute to the SEM image.

Apart from that, an underlying step-like structure rises up during the graphene growth process, which is clearly indicated in OM image with 100x magnification, as depicted in (d). Obviously, this structure does not correspond to the Cu grains with their different crystal orientation. The shape of several plateaus indicate an emergence different from recrystallization [140]. The underlying formation principles are still not entirely understood. However, very first growth experiments revealed, that this step formation needs to be completed before the graphene deposition, which otherwise would result in a high Raman D peak intensity. In order to characterize the obtained surface structures in more detail regarding the surface roughness, atomic force microscopy (AFM) and WLI measurements are performed. In the following, the AFM method and the obtained surface results are presented.

Surface roughness and morphology characterization via Atomic force microscopy (AFM) and WLI

Atomic force microscopy (AFM) is a surface sensitive scanning probe microscopy technique with a spatial resolution of several nm. A sharp tip, which is attached to an oscillating cantilever, is used to map the sample surface. Topography information is obtained by surface induced resonance frequency shifts of the cantilever. A detailed description of the AFM measurement technique can be found in [141]. In this work, the surface roughness and morphology were investigated using the AFM (NanoWizard 3, JPK Instruments) in tapping mode with a PPP-NCHR AFM probe and tip radius of curvature < 10 nm. The scan area lay between $1 \times 1 \mu m^2$ and $30 \times 30 \mu m^2$. An exemplary Cu foil AFM image $(30 \times 30 \mu m^2)$ is shown in Figure 4.14 (a). In (b), cross section profiles show the lateral width of 5-10 μm for the hillocks/hollows, indicating a much higher height-to-width ratio compared to the grain boundary with a width of 1-2 nm. Despite the influence of impurities, the total surface roughness s_q is decreased for both Cu foils to $s_q < 130$ nm. Apart from that, the image reveal the aforementioned step-like structure.



Figure 4.15: (a) WLI images of Cu foil, 99.8%, after a standard CVD process. Comparison of untreated (no EP) and electropolished (EP) foils reveals the importance of the EP pretreatment. (b) Surface roughness parameter s_q comparison before (black) and after (red) a CVD process. s_q is strongly reduced due to EP, whereas the temperature exposure during the growth process has little impact on it.

In Figure 4.15 the impact of EP on the surface evolution during a CVD process is summarized. WLI measurements in (a) reveal the difference of electropolished Cu foil and untreated foil after high temperature exposure (980 °C). Even the recrystallized Cu surface seems to be unable to change the surface roughness significantly, a slight reduction from 278 (± 14) nm to 265 (± 3) nm is observed, whereas the EP of the Cu foil reduces s_q from 134 (±15) nm to 120 (±12) nm, as depicted in (b). These findings highlight the importance of this pretreatment procedure. Regarding the hillocks and hollows occurring for the Cu foil with 99.8% purity, the reader might get the impression of preferring the cleaner Cu foil with 99.98% purity due to an even smoother surface. cp. Figure 4.13. It is worth mentioning, that at first glance the observed asperities do not influence the total shape of the Cu surface because of there comparably large lateral dimensions. Indeed, further experiments, which focus on the graphene growth, clarify that these hillocks are simply overgrown by the graphene layer. The same applies to the step-like structure, which doesn't determine the shape and size of graphene crystal grains at all, as spatially resolved Raman spectroscopy measurements reveal. In the following chapters, the growth conditions are optimized with the focus on a defect-free closed monolayer of graphene. As it will turn out, these goals are achieved with even the Cu foil of 99.8% purity. Nevertheless, for the reason of comparison, both Cu foil qualities are investigated and the observed differences between both growth substrates are presented.

4.3.3 Reduction of the graphene nucleation density

According to Section 3.4.1, the formation of graphene starts with the diffusion of dissolved C atoms along the Cu surface. Due to surface imperfections, e.g. impurities, crystal dislocations or surface roughness, chemisorption takes place by finding an energetic minimum on the surface. Subsequent C atoms bind to already nucleated atoms with a higher probability and form nucleation centers.



Figure 4.16: SEM images of graphene nucleation centers on Cu foil of 99.8% purity. (a)-(c) Time evolution of the graphene synthesis for 60 s, 90 s and 120 s. (d) Similar nucleation density on different neighboring Cu grains. (e) Strongly different nucleation density on neighboring Cu grains. (f) Graphene overgrowth of Cu grain boundaries.

As already shown, the nucleation flakes on Cu foil can easily be characterized according to their shape and size via SEM due to a strong contrast difference between graphene and the underlying Cu substrate. For this purpose, the obtained SEM images were edited via the freely available image processing program *ImageJ* and a contrast analyzing tool was applied. As a result of this, both the number of flakes per area, the nucleation density (ρ_n) and the total area, which was covered by graphene could be determined. In Figure 4.16 (a)-(c), SEM images depict the time evolution of the graphene nucleation centers for standardly used process parameters, i.e. 980 °C, H₂/CH₄ = 4 : 1, 16 mbar, $10 \times 15 \text{ mm}^2$ Cu foil. With increasing growth time t the flake size increases, while its density decrements. According to [112, 142] the presence of hydrogen not only catalyzes the graphene synthesis, but also serves as a controlling etchant during the growth, according to the chemical reaction

$$H_s + GR \iff (Gr-C) + (CH_x)_s.$$
 (4.7)

Along the graphene edges (GR-C) chemisorbed H atoms form hydrocarbons CH_x which again diffuse on the Cu surface. The etching and synthesis reactions, cp. Equation (3.22), compete with each other and lead to a viability of only large enough nucleation flakes. This leads to the observed reduction of the nucleation density ρ_n , as it is depicted in Figure 4.17 (a). The black bars correspond to 99.8% Cu foil and a nucleation is already recognizable at t = 60 s, which drops from 0.13 µm⁻² to 0.06 µm⁻² after 150 s). For the 99.98% Cu foil (red bars) there is almost no nucleation detectable at t = 60 s. This finding supports the general assumption of an enhanced nucleation based on impurities, which promote the nucleation by lowering the substrate surface energy and lead to a location-specific initial growth. For a higher purity of the growth substrate, the diffusion process takes more time and the total synthesis process is



Figure 4.17: (a) Growth time evolution from 60 to 150s of the nucleation density ρ_n of graphene on Cu foil at 980 °C, $H_2/CH_4 = 4$: 1, 16 mbar. (b) Corresponding graphene (GR) coverage on Cu foil. Comparison between Cu foils with impurity of 99.8% (black bars and line) and 99.98% (red).

delayed. However, the lost growth time is regained after a stable establishment of a sufficient number of graphene flakes, which is clearly indicated in (b). The graphene covered area assimilates for growth times above 90s and increases with increasing growth time. This result shows that there is no significant difference in growth rate detectable at an already very early stage of the deposition process and the growth rate shows a linear dependence on the growth time for both Cu foil purities.

Additionally, the growth rate strongly depends on the crystal orientation of the Cu grains within the substrate. As already depicted in Figure 4.13, the Cu crystal orientation leads to clearly visible grain boundaries and step-like substructures. EBSD measurements, as performed by Jin et al. [143], clearly reveal a random distribution of crystal orientations and grain rotations. Furthermore, in their CVD synthesis experiments they could determine a significant orientation-dependent nucleation and growth quality. During the performed nucleation experiments for this work, exemplary SEM images impressively show the crystal grain dependent graphene growth on Cu. In Figure 4.16 (d), the different Cu grains are visible due to the varying contrast of the individual grains. The flake density is almost constant, which corresponds to a similar crystal orientation. On the contrary, in (e) the density highly varies for two neighboring Cu grains. It is remarkable, that even for differently oriented Cu grains a graphene overgrowth is observable, as depicted in (f). This implies, that despite a strong growth rate dependency on the Cu grain orientation, the grain boundary itself does not influence the occurring graphene grain boundaries.

These findings correspond well to actual research activities about the substrate influences on the graphene growth and reinforce the importance of a proper substrate pretreatment and a specific parameter adjustment for the growth of continuous graphene films. A large nucleation density results in many grain boundaries which alter the electronic transport in graphene and ultimately increase $R_{s,GR}$ [144, 145]. Therefore, a minimization of ρ_n needs to be elaborated. At this point, one needs to keep in mind, that one focus of this work lies in an overall optimization of the graphene synthesis independent of grain orientations, since for large area graphene films graphene growth



Figure 4.18: (a) Growth temperature evolution of ρ_n of graphene on Cu foil (H₂/CH₄ = 4:1, 16 mbar, 120 s). (b) Corresponding graphene (GR) coverage on Cu foil. Comparison between Cu foils with impurity of 99.8% (black bars) and 99.98% (red).

takes place on multicrystalline Cu substrates. Apart from crystal orientations of the Cu grains and substrate imperfections, which are reduced to a minimum, as presented in Section 4.1, the thermodynamics during the CVD growth process influence the nucleation density ρ_n . By focusing on the thermodynamics, the process temperature dependence and the influence of the H₂/CH₄ ratio is examined in order to find the optimal process parameters. In order to ensure a closed layer during the graphene deposition, an adjustment of the total deposition time needs to be done.

Influence of the growth temperature

In the next experiments, the influence of the growth temperature T was investigated. In order to quantify the effect of the temperature, $10 \times 15 \,\mathrm{mm^2}$ Cu foil samples were used for graphene deposition with the aforementioned standard parameters and a deposition time of t = 120 s. A variation of T has two effects on the total graphene synthesis process. On the one hand there is an out-balancing of the etching and synthesis reactions, cp. Equation (4.7) and (3.22), which determine the chemisorption and formation rate of C-C bonds. On the other hand the condition of the liquid phase of the Cu surface is highly sensitive within this temperature range, regarding sublimation, surface thickness and the impurity evaporation. According to literature, depending on the reactor settings, a successful CVD graphene growth occurs in a temperature range between $950\,^{\circ}\mathrm{C}$ and 1000 °C. Due to an indirect pyrometry via an infrared sensor or by the use of a thermocouple, the actual temperature is difficult to determine. Furthermore, the effective substrate surface temperature strongly depends on the underlying heat spreader structure, which is a 4 inch diamond wafer used in the laboratory BlackMagic 6 inch reactor. In Figure 4.18 (a), ρ_n is depicted for an investigated temperature range between 970 °C and 1000 °C. Higher temperatures resulted in a melting of the Cu foil, therefore there was an upper temperature limit given by the growth substrate. Regarding the statistics, at least four graphene/Cu samples were fabricated and 25 measurements on average were applied. The error bars correspond to the statistical standard deviation.



Figure 4.19: (a) Growth time dependency of the graphene coverage on Cu foil at growth temperatures of 950 °C for Cu foils with purity of 99.8 % (black) and 99.98 % (red) (b) Corresponding area growth rate v_n at 950 °C and 980 °C.

Although the error bars are quite large, especially for the 970 °C and 1000 °C, there is a clear minimum in ρ_n at $T = 980 \,^{\circ}\text{C}$ as $\rho_{n,99.8\%} = 0.60 \,\mu\text{m}^{-2}$ and $\rho_{n,99.98\%} = 0.58 \,\mu\text{m}^{-2}$. In (b), the corresponding graphene coverage is depicted and reveals two findings. First, for $T \geq 980$ °C the total graphene coverage lies constantly at approx. 40-45%, despite a significant deviation in ρ_n from $\approx 1.48 \,\mu m^{-2}$ (990 °C) and $\approx 0.97 \,\mu m^{-2}$ (1000 °C) down to $\approx 0.6 \,\mu m^{-2}$ (980 °C). The comparably low ρ_n at 1000 °C might again result from an enhanced hydrogen-induced etching, which positively correlates with the process temperature. Additionally, at 970 °C the comparably low graphene coverage despite the large nucleation density can only be explained in a low growth rate due to a retarded reaction rate. In an additional experiment, the total growth rate v_n is investigated by comparing CVD processes at 950 °C and 980 °C for a varying growth time t. In Figure 4.19 (a), the graphene coverage for a growth temperature of 950 °C at various process times ranging from 60s to 150s is depicted and shows the linear behavior which was already observed for 980 °C, cp. Figure 4.17 (b). This indicates a constant growth rate v_n , which is calculated via a linear fit. The slope determines $v_{\rm n}$, which is shown in (b) for both 99.8 % (black) and 99.98 % (red) and is reduced from $\approx 45 \,\mu m^2/s$ to $\approx 23 \,\mu m^2/s$ for 980 °C and 950 °C, respectively. At first glance, the linear dependency of the growth rate on the process time may be unexpected since there is no dependency on the actual graphene edges observable. Usually one would expect a changing growth rate with changing graphene edges due to the fact, that newly absorbed C atoms tend to bond to already existing graphene areas. Given a circular area, the growth rate would directly be a function of the circumference, which increases quadratically with increasing radius. However, the reader needs to keep in mind, that the opposite reaction, i.e. the etching by H_2 , occurs with the same dependence, which in turn destroys the expected edge-dependency. As a result of this, a constant, edge-independent graphene formation occurs, which is only reaction-rate limited and therefore exhibits the observed linear slope regarding the process time evolution.

In order to characterize the graphene quality, samples with a continuous graphene layer at different growth temperatures were fabricated by a growth time extension to t = 30 min. Raman spectroscopy measurements were done on several samples applying a standard line scan with 121 point measurements (with a distance of 1 µm between



Figure 4.20: (a) Raman spectrum for graphene on Cu foil (99.8 %, $H_2/CH_4 = 4:1$, 16 mbar, 30 min) for different growth temperatures, i.e. 950 °C (black line), 980 °C (red) and 1000 °C (blue) with the characteristic D, G and 2D peak. The inset shows a zoom-in of the D peak intensities. (b) Zoom-in of the corresponding 2D peak intensities, indicating a temperature-dependent shift and broadening. The inset depicts the related 2D/G ratio (grey line) and the 2D FWHM (black, in cm⁻¹) of the 2D peak.

each measurement point). In Figure 4.20 (a), the corresponding Raman spectra for T = 950 °C, 980 °C and 1000 °C are depicted and clearly reveal two effects. At 950 °C (black line), the D peak is explicitly visible and indicates a comparably high defect rate. Despite the increased growth rate 1000 °C (blue), which can be deduced from Figure 4.18 (a) and (b), many additional defects are induced due to the enhanced etching activity. The Raman spectrum shows a lower but still existent D peak and additional multilayer growth is more established. This is seen by a broadening and shift of the 2D peak, as depicted in Figure 4.20 (b). The inset shows that the 2D/G ratio and the FWHM reveal a maximum (3.1) and a minimum (29.2 cm⁻¹, respectively, at T = 980 °C. At this temperature, mainly monolayer growth with a low D/G ratio occurs. The temperature comparison emphasizes the strong sensitivity of the whole synthesis process, since the operating temperature range lies within 20 K and simultaneously very close to the Cu melting point.

Influence H_2/CH_4 ratio

Hydrogen has influence on both the reconstruction of the Cu foil growth sample and on the actual graphene synthesis. Depending on the ambient total pressure during the CVD, the interplay between etching and supporting the synthesis becomes highly dependent on the H_2/CH_4 gas ratio. According to Equation (3.24) and (4.7), the presence of hydrogen is essential for successful graphene growth, whereas the source of hydrogen might vary depending on the growth conditions. Under atmospheric pressure, several groups [143, 146] found beneficial growth under hydrogen annealing, which leads to a H_2 accumulation within the Cu foil, and the strict absence of hydrogen during the graphene deposition. The required H_2 atoms then dissolve from the Cu bulk and enhance the chemical reaction. In low pressure regimes, this is not the case due to a much lower H_2 incorporation and also a high rate of dissolving. Therefore, relatively high H_2/CH_4

$\rm H_2/CH_4$ ratio	H_2	CH_4	Ar
1:1	10	10	990
4:1	40	10	960
10:1	100	10	900
20:1	200	10	800
30:1	300	10	700

 Table 4.4: Variation of the applied gas flow rates (in sccm). Each set ensures a constant pressure in the reactor chamber.

ratios up to 300: 1 are needed to ensure the hydrogen supply [112]. Apart from its role as a graphene etchant and precursor for the catalytic decomposition of hydrocarbons, hydrogen also acts as a passivation of the graphene edges, resulting in a prevention of edge binding onto the Cu foil substrate. For a certain H₂/CH₄ ratio this leads to the growth of graphene multilayers due to an enhanced probability of C atoms to pass onto the graphene-covered Cu surface [147]. These findings altogether demonstrate the sensitivity of the process on the hydrogen partial pressure and causes a proper investigation and adjustment of the H₂/CH₄ influence. Therefore, for adjustment of the CVD process in the *BlackMagic 6 inch* reactor, the partial pressures of H₂ and CH₄ were varied in such a way that the nucleation density for H₂/CH₄ ratios of 1 : 1, 4 : 1, 10 : 1, 20 : 1 and 30 : 1 was characterized, while all other process parameters were kept constant. By ensuring an unchanged gas flow characteristic in the reactor chamber, the total gas flow was kept constant. The flow rates are listed in Table 4.4.

The growth time t was again set to 120 s in order to characterize the graphene flakes, regarding the nucleation density, as performed in the previous section. Since the total chamber pressure, as already mentioned, is set to 16 mbar for all performed growth experiments, which can not yet be regarded as a low pressure regime, the experimental results will differ from the findings mentioned in the paragraph before. In Figure 4.21 (a),



Figure 4.21: (a) Nucleation density ρ_n of graphene on Cu foil in dependence of the H₂/CH₄ precursor gas ratio (980 °C, 16 mbar, 120 s). (b) Corresponding graphene (GR) coverage on Cu foil. Comparison between Cu foils with impurity of 99.8% (black bars) and 99.98% (red).



Figure 4.22: (a) Raman spectrum for graphene on Cu foil (99.80 %, 980 °C, 16 mbar, 30 min) for a H_2/CH_4 ratio of 4 : 1 and 30 : 1, depicted as the red and black solid line, respectively. (b) Zoom-in of the corresponding 2D peak intensities, indicating no change in the peak shape. The inset depicts the related 2D/G ratio (grey line) and the 2D FWHM (black, in cm⁻¹).

 $\rho_{\rm n}$ is demonstrated for the applied H₂/CH₄ ratios. Changing precursor gas ratios have little influence on $\rho_{\rm n}$ with a minimum for H₂/CH₄ = 4 : 1 at $\rho_{\rm n} \approx 0.05 \,\mu {\rm m}^{-2}$, whereas the growth rate, depicted as the graphene coverage in (b), strongly decreases for other ratios than 4 : 1 from $\approx 40 \%$ down to $\approx 15 \%$. This reversed shape for $\rho_{\rm n}$ and the growth rate is also described by Shi et al. [148]. However, they found the minimal $\rho_{\rm n}$ and maximum growth rate at 3 : 1 and an additional turning point for H₂/CH₄ > 40 : 1, which does not entirely correspond with the obtained results here. One reason might be their different reactor geometry in such a way that the precursor gas bypasses horizontally at the Cu sample, which makes the whole reaction more mass transport limited and therefore the growth rate strongly depends on the total gas supply. Furthermore, again the ambient pressure lies with 1 mbar significantly lower than for the *BlackMagic 6 inch* processes.

Keeping these considerations in mind, the findings agree with the assumption of a reaction-rate limited CVD process in the BlackMagic 6 inch reactor. While the initial nucleation depends on the availability of the participating gas species, the following chemical reaction for graphene synthesis is regulated on the actual gas ratios, assuming an infinite mass-transport of the precursor gas. This results in a ratio-independent nucleation density and highly ratio-dependent growth of these nucleation centers, as experimentally reproduced. The graphene coverage decreases for $H_2/CH_4 \geq 10$: 1, indicating the dominating etching effect of H_2 . As for the investigation of the growth temperature influence, 30 min processes were performed in order to characterize the graphene layers via Raman spectroscopy. The Raman spectrum for a H_2/CH_4 ratio of 4:1 (red line) and 30:1 (black) is depicted in Figure 4.22 (a). At first glance, both spectra reveal graphene with a satisfactory quality. The D peak intensity is almost zero. A zoom-in of the 2D peak (b) shows neither a peak shift nor a significant broadening (from $29.3 \,\mathrm{cm}^{-1}$ to $30.2 \,\mathrm{cm}^{-1}$) for the increased hydrogen partial pressure. The 2D/Gratio of 3.1 is reproducibly slightly higher for a precursor gas ratio of 4:1, compared to 2.6 for a ratio of 30 : 1. This might result from the fact of a higher graphene grain density with increasing H_2 partial pressure, as highlighted in Figure 4.21 (a), which may



Figure 4.23: (a) SEM images of graphene on Cu foil. The effect of a proper process optimization leads to a reduction of multilayer domains. (b) CVD process evolution due to process optimization on the basis of the D/G peak intensity ratio. (c) OM image of graphene on Cu foil. Corresponding D/G (d) and 2D/G (e) map obtained by Raman spectroscopy at the same surface position. Exemplary Raman spectra of selected surface domains (black circles) indicate mono-and multilayer growth at 2D/G > 2.4 and 2D/G < 1, respectively.

contribute in folded graphene structures and small areas of BL graphene. Conclusively, still for the 30:1 ratio high quality graphene can be synthesized, while the growth rate for 4:1 is far larger and therefore preferred.

4.3.4 Process optimization summary

The performed CVD experiments lead to the extraction of a set of process parameter, which are used for all future experiments, regarding the transfer onto AlN substrates and the further processing as an electrode material for BAW resonator devices. The obtained findings implicate the standard use of 980 °C as the growth temperature for the fabrication of large area graphene films. A H_2/CH_4 ratio of 4 : 1 turned out to be the most reliable precursor ratio in terms of defect-free growth and the minimization of the nucleation density ρ_n . The optimizations lead to a homogeneous graphene monolayer growth, as depicted in Figure 4.23 (a). The SEM image clearly reveals the reduction of multilaver growth. The further process development results in a reproducibly high quality of graphene, which is ensured by a routinely monitored Raman spectroscopy investigation of all synthesized samples. The required quality in terms of a low ($\ll 0.2$) defect-related D/G ratio can be consequently be achieved, see Figure 4.23 (b). In order to emphasize the high quality for large graphene areas, an OM image is depicted in (c) with its corresponding Raman map images (d) and (e), which illustrate the D/G(turquois) and 2D/G (red) peak ratios, respectively. The D/G ratio lies continuously below 0.2. The same holds for the 2D/G ratio, which shows only at a few sites values < 1.5, as depicted in the exemplary selected Raman single spectra. Even the domains, where still bi- or multilayer appears, the crystal quality does not suffer from defects. With these findings about the overall graphene quality on Cu, CVD processes can be performed in the *BlackMagic 6 inch* growth reactor, which are highly competitive with other research groups. Ultimately, the complete synthesis can further be transformed to a wafer size of up to 6 inch, which, however, was not needed for this work, yet.

Up to here, the graphene synthesis investigations were performed by using Cu foil with both 99.8% and 99.98% purity. For the transfer optimization in Chapter 5 and the fabrication of graphene based resonator devices in Chapter 6, always Cu foil with 99.8% impurity is used. This is easily justified due to several reasons. On the one hand, for scientific reasons, this decision makes sense in terms of a comparability with other research groups, since 99.8% Cu foil is commonly used for synthesis and transfer experiments. Therefore, our results regarding the transfer process and the resulting reduction in the graphene sheet resistance gain even more in importance. On the other hand, the comparison of both foil qualities show no significant deviation in the graphene quality within the process parameter range, which is set as the future standard synthesis procedure. Additionally, it is also a question of expenses, which made the decision in favor of the slightly lower quality. According to the common suppliers, the price for 99.98% Cu exceeds the price of the 99.8% foil by a factor of more than one hundred¹.

With the determination of the optimal process parameters for the graphene synthesis, the first step in the fabrication procedure for graphene as the electrode for BAW resonators is completed and leads to the following development of a proper transfer technology on the piezoelectrical material AlN, as elaborated in the next chapter.

 $^{^1\}mathrm{According}$ to recent price reviews of the commonly used suppliers Sigma Aldrich and Alfa Aesar.

5 The graphene wet transfer on AIN-based SMR-BAW resonators

Although the CVD of graphene enables a scalable synthesis method with a high process stability and a comparably high layer quality, there is one major drawback, which needs to be overcome. Since graphene is synthesized on conductive Cu foil serving as the growth substrate, the two-dimensional layer needs to be transferred on insulating substrates in order to use it as an active material. For this work the already established wet transfer technique, which was originally developed for the graphene transfer onto SiO₂ substrates, is refined for AIN as a target substrate. Regarding its different surface morphology compared to SiO_{2} , the focus in the following chapter lies in an elaborated surface pretreatment and a proper graphene characterization via spatially resolved Raman spectroscopy with respect to stress and strain distributions, which are inevitably induced by the transfer procedure and detrimentally bear on the electric properties of graphene. With these findings, the last section of this chapter concludes with the transfer process adaption to AIN-based bulk acoustic wave (BAW) resonator structures.

5.1 The graphene wet transfer technique

The challenge of every graphene transfer technique is the non-destructive handling of a graphene sheet with the thickness of one atomic layer. Without any sort of mechanical support, the layer cracks immediately, folds up into multilayers or delaminates from the target substrate and therefore looses its requested electrical properties. The challenge, which all transfer methods have in common, lies in the complete removal of the growth substrate. Both dry [149, 150] and wet etching procedures were developed by several groups [151-154], all of them keeping in mind the trade-off between the graphene quality retention and the economies of scale. Apparently, the mechanical transfer of graphene microstructures is far more easy than the transfer of large-area monolayers. The so called wet transfer technique (WTT) led to a profound process development regarding SiO₂ as the target material [155]. In combination with the ability to synthesize large-area graphene via CVD, the WTT enables an industrial-compatible fabrication method of graphene monolayers on insulating substrates [7]. Primarily, in the area of fundamental graphene research, $300 \,\mathrm{nm}$ thick SiO₂ served as an eligible insulating target substrate material because of its easily accessible optical characterization due to interference effects (cp. Figure 3.14 (b)) [156, 157]. The large number of publications in the field of transferred graphene on SiO_2 via WTT clearly indicates this as a technically mature method, which is described schematically in Figure 5.1 (a). After the synthesis of



Figure 5.1: (a) Schematic illustration of the standard wet transfer technique on an arbitrary target substrate after graphene growth via CVD on Cu foil. (b) Schematic description of the wettability concept for hydrophilic and hydrophobic target surfaces during desiccation.

graphene (GR) via CVD on the Cu foil growth substrate, a supporting layer is deposited onto the GR-Cu sheet. An appropriate and commonly used candidate is poly(methyl methacrylate) (PMMA) due to its simple handling regarding its low viscosity, high transparency, its wetting capability and its good dissolubility in organic solvents [158]. In an aqueous etchant solution, i.e. customary used ferric chloride (FeCl₃), the Cu foil is removed. As a result of this and due to surface tensions the graphene (GR)-PMMA film is floating on the surface of the etchant. After a cleaning procedure, which means the replacement of the etching solution with deionized (DI) water, the layer stack is manually transferred to a substrate wafer and smoothly desiccated. Finally, the PMMA is removed via a thermal treatment in an acetone solution. Graphene persists on the substrate surface due to Van der Waals forces.

5.1.1 The desiccation process – the key challenge of the graphene wet transfer

One of the highly critical process steps of the WTT is the desiccation process after the GR-PMMA layer stack is transferred to the target substrate. Here, the surface morphology and the wettability essentially dominate the successfulness of the avoidance of cracks and wrinkles. In order to get a homogeneous desiccation via capillary forces, the substrates surface needs to be highly hydrophilic. This ensures a continuously thin water film between the substrate and the graphene layer, which enables a constant and smooth desiccation, as schematically depicted in Figure 5.1 (b). On the contrary, on hydrophobic surfaces, the water film tends to form water droplets, which lead to a partial adhesion of the graphene film, especially on the layer edges. As a result of this, during further desiccation the gaseous evaporation of the leftover fluid takes place and creates cracks and discontinuities within the graphene sheet. An uncontrolled desiccation occurs and the graphene sheet remains as a discontinuous and possibly folded thin film. Additional strain is applied on the transferred graphene sheets, which altogether



Figure 5.2: (a) OM image of graphene transferred onto SiO₂/Si. (b) OM image of graphene transferred onto AlN/Si shows water droplets between AlN substrate and the graphene layer. (c) Under larger magnification cracks and graphene-free substrate domains are visible. (d) Raman 2D intensity (a. u.) peak mapping of a randomly selected area for graphene on AlN. The scale represents graphene free domains (black, absent 2D peak) and successfully transferred graphene areas (red). Higher 2D peak intensities correspond to graphene folding.

critically influences the electrical properties, i.e. the graphene sheet resistivity $R_{s,GR}$. For this work, SiO_2 and AlN surfaces are compared regarding the graphene transfer, since the former is a well established target material and the latter is the material used for the later BAW device fabrication. SiO₂, grown 300 nm via thermal oxidation on Si, is known to be highly hydrophilic [159, 160], whereas AlN, which was sputtered on Si for the following experiments with a thickness of $2\,\mu m$, tends to be hydrophobic. The very first transfer results are presented in Figure 5.2. The OM image of graphene on SiO_2 (a) shows a homogeneous layer which indicates a virtually crack-free transfer and a completed desiccation of the residual water film. By contrast, as depicted in (b), graphene transferred on a AlN surface at same transfer conditions leads to a strong formation of water droplets. Additionally, some transfer experiments reveal and comparably large uncovered AlN domains of several $100 \,\mu\text{m}^2$ size, as shown in (c). A spatially resolved Raman mapping of the 2D peak intensity, as represented in (d), clearly reveals, that these domains are completely free of graphene (black domains) and at the domain edges a strong layer folding occurs (observable due to a high red intensity). Individual intensity points within the black domains represent "crunched up" graphitic leavings. This monitoring indicates a significantly different surface wettability and an uncontrolled desiccation on AlN compared to SiO_2 and evidently shows that the conventional WTT technique needs to be adjusted for AlN surfaces. In the following, the surface wettability is investigated in more detail. Both the surface roughness and the chemical conditioning of the surface influence the wettability of a certain material due to a differing surface morphology.



Figure 5.3: (a) Schematic illustration of the Wenzel model. Comparison of a rough surface (blue twisting line), which is described by the corrected Young angle θ^* , and a theoretically flat surface (red straight line) with the Young angle θ . (b) OM images of a water droplet on SiO₂ and AlN surfaces. The contact angles CA are obtained via a circular and elliptical fit, as delineated in the top most image, and are 28° and 48° for pristine SiO₂ and AlN, respectively.

5.2 The influence of the surface roughness on the surface wettability

The underlying effect of the wettability itself is the concept of surface and interfacial energies, which can be measured indirectly via contact angle (CA) measurements. Hydrophobic surfaces feature a low surface energy, whereas hydrophilic ones exhibit a high surface energy. Given the high surface energy of water due to its polar character, the AlN surface energy needs to be increased. Generally, the CA between a fluid and a solid depends on the surface tensions γ between the solid (S), the fluid (F) and the gas (G) phase and is described by the Young's equation [161] as

$$\gamma_{\rm SG} - \gamma_{\rm SF} - \gamma_{\rm FG} \times \cos \theta = 0, \tag{5.1}$$

with the so called Young angle θ , which describes the contact angle of a theoretically perfect flat surface. Since the surface roughness plays an important role regarding the wettability of a certain material, the Young angle needs to be adjusted in the theoretical description, including additional surface effects. Several considerations were applied and led to different models, which describe the relation between a surface-specific roughness and its resulting CA. Assuming the surfaces, which were investigated in this work, i.e. SiO₂ and AlN, feature a homogeneous roughness, the situation can be described by the Wenzel model [162, 163], which is given as

$$\cos\theta^* = r \times \cos\theta,\tag{5.2}$$

with the roughness parameter r as the ratio between the real and the projected solid surface area, as depicted in Figure 5.3 (a) as the blue twisting and the red solid line, respectively. The intrinsic material specific Young angle θ is corrected by this factor r, resulting in the so called corrected Young angle θ^* . Both contact angles, θ^* and θ , respectively, result from the surface plane and the edge of the water droplet (black



Figure 5.4: (a) AFM image of thermally oxidized SiO₂ (300 nm) on Si with $s_q = 0.91 \pm 0.43$ nm. (b) Corresponding AFM image of sputtered AlN (2 nm) on Si with $s_q = 3.49 \pm 0.88$ nm. Scale bar refers to both images.

elliptic line). It is worth mentioning, that Equation (5.2) describes only the stationary equilibrium state of the minimum free energy of the surface system, which results in a lack of explanations of hysteresis effects as arising in subsequent experiments.

Nevertheless, according to the Wenzel model, a smoother surface results in a more extensive wettability. In a first step, the actual CA of the SiO_2 and AlN surfaces are determined. The CA measurements were done by applying the sessile drop method [164]. With this technique, very small water droplets $(10 \,\mu)$ are placed directly onto the surface. Practically, the droplet placement needs to be done pretty carefully by slowly approaching the substrate surface with a dropping glass until the droplet adheres. This cautious procedure and the low mass weight ensure that additional mass effects, which might influence the droplet shape, are minimized. Via an optical microscopy setup, the droplet can be imaged and the contact angle is determined via a circular fitting routine. A monitoring and additional elliptical fit reveal that the potential mass weight effects can be neglected. For the pristine SiO_2 and AlN samples the contact angle is 28° and 48°, respectively, as depicted in Figure 5.3 (b). This might be a first indication that the graphene wet transfer is less stable on the rougher AlN surface. In order to prove the theory of Wenzel, pristine SiO_2 and AlN on Si is characterized via AFM analysis. The calculated roughness parameter s_q , as already defined in Equation (4.1), is averaged between 0.91 ± 0.43 nm and 3.49 ± 0.88 nm for SiO₂ and AlN, respectively, as depicted in Figure 5.4 (a) and (b). According to the theory and in conjunction with the obtained CA measurements, these findings can explain the unstable wet transfer on AlN.

5.3 AIN surface plasma pretreatment

To reduce the CA, a plasma pretreatment of the AlN surface was developed in order to decrease its surface roughness and to possibly affect the surface chemistry. On this account, different gases were investigated, namely H_2 , O_2 , N_2 and Ar. The applied plasma was a radio frequency (RF) plasma (no bias) at 2.5×10^{-2} mbar chamber pressure, 50 sccm gas flow, 100 W RF power, 10 min exposure time. The corresponding AFM images after the plasma treatment are depicted in Figure 5.5 (a)-(d). Optically, the reader might notice directly, that H_2 plasma (b) does not effect the surface roughness at all and the AlN surface looks similar to the untreated sample (a), whereas for N_2 (not



Figure 5.5: (a)-(d) AFM image $(1 \times 1 \,\mu\text{m}^2)$ of differently plasma pretreated AlN surface (RF plasma, 2.5×10^{-2} mbar, 50 sccm gas flow, 100 W RF power, 10 min exposure time). All AFM images are normalized to the scale. (a) No plasma pretreatment. (b) H₂ plasma. (c) O₂ plasma. (d) Ar plasma.

shown), O_2 (c) and Ar plasma (d), a significant surface change is observable, keeping in mind that the process conditions are the same for each applied gas. In Figure 5.6 (a), the obtained s_q values are summarized for all plasma pretreatments and compared with pristing SiO_2 and AlN. 2h after the plasma exposure, CA measurements via the sessile drop method were performed. The corresponding CA are depicted in (b). The corresponding error bars in (a) and (b) result from averaged s_q and CA values, respectively, which are obtained from the measurement of 5-8 samples each. While the investigated pristine AlN samples exhibit an s_q in the range of $3.5 \,\mathrm{nm}$, the plasma pretreatments apart from H₂ plasma reduce this value to ≈ 1 and brings it close to pristine Si. The corresponding CA measurements strongly confirm the roughness dependence, predicted by the Wenzel Model. For N_2 , O_2 and Ar plasma, the significantly decreased CA corresponds well with the decrease in surface roughness. While H atoms don't affect the AlN at all due to their low atomic weight, the heavier atoms are able to flatten the surface, which results in a CA θ^* drop from 48° to 18°. With these pretreatments, the wettability is even larger than for pristine SiO_2 , which can also be clearly seen in Figure 5.6 (c) and be compared with the images of Figure 5.3 (b).

5.3.1 The influence of a chemical conditioning on the surface wettability

As aforementioned, a plasma exposure does not only change the surface roughness but also might alter the chemical surface properties. First, there is a cleaning effect on the surface, if it is exposed to a plasma. Contamination atoms, such as carbon or carbonic composites which tend to be hydrophobic, are removed both physically and chemically.



Figure 5.6: (a) Comparison of the s_q values obtained via AFM measurements for pristine SiO₂ and AlN and plasma pretreated AlN surfaces. (b) Corresponding contact angle θ^* of the same surface samples. (c) OM image of a water droplet on AlN pretreated with Ar plasma.

An increasing probability of those atoms re-adsorbing on the AlN surface with increasing time after the plasma pretreatment may indicate a time-dependent recovery effect. The time-dependency of the contact angle θ^* is depicted in Figure 5.7 (a). A general trend is distinguishable, since there is an explicitly noticeable hydrophobic recovery with increasing time after the plasma exposure. For all applied plasma pretreatments, θ^* increases similar to a limited exponential growth. Except for H₂ plasma, including a vertical shift for H₂ plasma pretreatment towards a limit of $\theta^*_{\text{lim}} \approx 48^\circ$, the shape of all obtained time-dependencies resemble each other quite well in appearance and a θ^*_{lim} between 17° and 25°. Therefore, the cleaning turns out to be a dominant effect, since a similar slope is described by a similar growth constant, which represents the re-adsorption probability in the obtained graph. By repeating the plasma pretreatment, the time-dependent change of θ^* can be obtained at every measurement cycle, i.e there is no hysteresis effect apparent.

Apart from that cleaning effect, each plasma exhibits its content specific chemical effect. In case of the O_2 plasma, there is an oxidation effect on the surface. Oxidation leads to a further surface smoothing, as it is also used for the fabrication of stainless steel [165]. Aluminum oxide allotropes in the nanometer range already make the surface becoming more hydrophilic and increase therefore its wettability. Residual O_2 in the reactor chamber enables oxidation as well, but another effect might dominate. The presence of O_2 during a N_2 or H_2 plasma exposure in combination with a physical damage of the surface leads to the formation of nitrate composites [166], such as $Al(NO_3)_3$ and NH_4NO_3 . Besides, hydrogen can form unstable hydroxide compounds with the assistance of background oxygen, such as $Al(OH)_3$, which itself can activate the AlN surface due to the availability of aluminum atoms in the substrate material. Both nitrite components as intermediate products of chemical reactions and as well the formation of oxides



Figure 5.7: (a) Time-dependent θ^* measurements for all the differently pretreated AlN on Si samples, i.e. O₂ (magenta points), Ar (black), N₂ (blue) and H₂ plasma (red). The corresponding dashed lines are given as a guide to the eye as an average θ^* of measurements more than 2h after the plasma exposure. The black dotted line in (a) and (b) represents θ^* for untreated AlN on Si. (b) Detailed comparison of θ^* for measurements after 5 min (dark red bars) and > 2h (red). The black arrow depicts the chemical surface effect, the red arrow shows the physical effect.

increase the surface energy of AlN, i.e. the wettability. Due to their chemical instability nitrate components tend to degrade very soon after their formation, the same applies for dehydrogenation reactions. On the contrary, an oxidized layer on the AlN surface endures. Although, different chemical reactions can explain the experimental findings, the exact mechanism is not yet fully understood. In any case, all of these described effects can strongly influence the total surface wettability and might explain the recovery effect. In summary, a plasma exposure of the AlN surface leads to both a physical and a chemical effect on the wettability. In order to get an impression of those two separately considered effects, in Figure 5.7 (b), the contact angles θ^* for all differently pretreated samples, measured 5 min (red bars) and > 2 h (dark red bars) after the plasma exposure, are depicted in brown and red bars, respectively. The chemical effects result from the difference in CA between both measurement times for each pretreated sample (depicted as the black arrow), whereas the physical damaging/smoothing is a time-independent effect (red arrow). From the obtained results the reader can conclude that O_2 , N_2 and Ar plasma pretreatments lead to a very large wettability, which results from a CA in the range of 4-6°.

5.3.2 Strain and doping investigations of transferred graphene on AIN substrates

In order to fully understand the surface effect of the different plasma pretreatment, a deeper investigation of the transferred graphene layers was performed. As mentioned in Section 3.2.3, the strain and charge carrier density n within graphene can be concluded from the 2D and G peak positions. With the aforementioned strain and carrier density relations from Equation (3.18) and (3.19), the influence of plasma pretreatment can made be visbile, as depicted in Figure 5.8. (a) and (b) show the 2D peak position in



Figure 5.8: Raman spectroscopy measurements of graphene on AlN. 2D peak position (ω_{2D}) versus G peak position (ω_G) . (a) Raman map (3822 data points, $30 \times 50 \,\mu\text{m}^2$) for untreated AlN. (b) Corresponding Raman map for AlN after Ar plasma pretreatment. (c)-(f) Exemplary line scans (121 data points, $60 \,\mu\text{m}$) for graphene on AlN after different plasma pretreaments. (c) H₂ plasma. (d) N₂ plasma. (e) O₂ plasma. (f) Ar plasma. Level curves for compressive and tensile strain (in %, red lines) and for charge carrier density n (in $10^{12} \,\mathrm{cm}^{-2}$, blue) apply for each image and are indicated in image (b).

dependence of the G peak position for untreated and Ar plasma pretreated AlN, respectively. A map with a size of $30 \times 50 \,\mu\text{m}^2$, resulting from 3822 data points, reveals a statistical strain and n distribution. The strain and charge carrier density levels are la-

belled in (b) as red and blue lines and hold for all graphs in the figure. The effect on the plasma is directly visible in a significant reduction of spreading values. In case of untreated AlN, the graphene layer is afflicted with strong strain gradients, varying from -0.5 % to 0.5%. Since there are observable D peak intensities (cp. Figure 5.11) complete information about the actual carrier density cannot be extracted from those measurements due to overlap effects in the Raman shifts. However, a clear reduction in the strain variation is apparent for an Ar plasma pretreatment (b). The lower value distribution indicates also a lower defect rate and reduced cracks and wrinkles in the graphene layer. The same applies for n, which is more concentrated around $n = 10 \times 10^{12} \,\mathrm{cm}^{-2}$. In order to get a deeper insight in the plasma effects, additional line scan measurements (121 data points, $60 \,\mu\text{m}$ were performed for H_2 , N_2 , O_2 and Ar plasma, as shown as an example in (c), (d), (e) and (f), respectively. While a H_2 plasma exposure has almost no impact on the surface, the strain distribution seems to be clearly reduced by N_2 , O_2 and Ar plasma and tensile strain between 0.1-0.2%, 0.0-0.3% and 0.1-0.3%, respectively, is existent. In terms of n, there is a significant difference for N₂ and O₂ plasma pretreated AlN on the one hand and for Ar plasma pretreated AlN on the other hand, i.e. $n_{N_2} = 25 \times 10^{12}$, $n_{O_2} = 25 \times 10^{12} \text{ cm}^{-2}$ and $n_{Ar} = 10 \times 10^{12} \text{ cm}^{-2}$. The formation of oxide compounds on the AlN surface leads to an increased graphene p-type doping, due to the oxygen atoms, which act as a strong electron acceptor [167, 168]. However, an Ar plasma pretreatment only slightly increases the carrier density, which may result from the physical damaging of the surface and the simultaneous formation of dangling bonds or a rather metallic surface. The Raman investigation furthermore reveals a more homogeneous strain and carrier density distribution after an AlN pretreatment with Ar plasma. It can be assumed, that the cleaning effect, which enhances the quality of the transferred graphene at the end, is the limiting factor. Additional a possibly inhomogeneous oxide formation strongly influences both strain and doping distribution. With respect to the overall goal of applying graphene as an electrode material for resonator structures, a homogeneous graphene layer is preferred in order to ensure a laterally homogeneous electrical contacting. This is a first indication for Ar being the chosen gas for future AlN plasma pretreatments.

5.3.3 Adjustment and optimization of the plasma pretreatment for AIN based resonator devices

Apart from the findings above it can be concluded, that for H_2 plasma, both the physical and chemical effect is too low and therefore the minimal θ^* lies above 20°, whereas for N_2 and O_2 plasma the formation of nitrate and hydroxide compounds might influence the electronic characteristics of the transferred graphene layer. Since the formation and decomposition of those compounds and their possibly detrimental factor impact on the transferred graphene layer, regarding the electromechanical coupling to the AlN surface, the interest lies in an as-clean-as-possible surface. Therefore, an increase in the surface's wettability without any change in surface roughness and the avoidance of stable oxide allotropes are preferable to avoid potential restrictions in the device performance and functionality. These requirements also rule out the application of N_2 and O_2 plasma.

With all these experimental findings, an Ar plasma pretreatment of the AlN surface is supposed to be the chosen method to obtain good quality graphene. However, there is one major drawback, as the previous results revealed. Ar atoms colliding with the AlN



Figure 5.9: (a) AFM image of pristine AlN on the BAW resonator structure, $1 \times 1 \,\mu m^2$. (b) Corresponding image, taken 30 min after adjusted Ar plasma pretreatment $(9 \times 10^{-3} \,\text{mbar}, \,100 \,\text{sccm}, \,250 \,\text{W}, \,10 \,\text{min})$. Both AFM images are normalized to the scale. (c) Comparison of AlN/Si and BAW-AlN before (black bars) and 30 min after (red) the adjusted plasma pretreatment. The black arrows indicate the chemical effect on the increased wettability.

surface cause severe changes in the surface structure, as depicted in Figure 5.5 (e). The typically pebble-like structure for sputtered AlN, which represents the columnar structure of the different AlN grains, is destroyed, although the surface is smoother than without any plasma pretreatment. Since graphene needs to be transferred onto AlN based resonator devices, any avoidance of a potentially different performance characteristic of the device due to a changed AlN surface roughness is desired. Structural changes of the surface can influence the future device functionality. For this reason, an adjustment of the plasma pretreatment was performed in order to only obtain the chemical cleaning effect of the plasma. By significantly lowering the operating chamber pressure from 2.5×10^{-2} mbar to 9×10^{-3} mbar and increasing the RF power from 100 W to 250 W, which should result in an increased ion acceleration rather than the plasma generation, the goal is to achieve a minimization of any physical surface damage due to a lower atom collision rate on the surface and still a retention of the surface cleaning effect. An AFM image of the AlN surface of a BAW resonators structure before and after this adjusted Ar plasma pretreatment is depicted in Figure 5.9 (a) and (b), respectively. The s_q value just slightly changes from 2.04 ± 0.09 nm to 1.96 ± 0.07 nm, which implies no physical surface damage anymore. Still, by the determination of the CA, a significant change is observable, indicating the still existent chemical contribution of the surface conditioning. For both the former AlN on Si and the AlN on the resonator structure, the contact angle θ^* reduces from approx. 48° to below 20°, as shown in Figure 5.9 (c), if the transfer is performed within 30 min after the plasma exposure. Furthermore, as presented before, the investigation of the strain distribution and the carrier density n also revealed, that it is minimized by Ar plasma. Therefore, due to further transfer process optimization, Ar plasma with the adjusted parameters is applied for all following experiments. The actual transfer needs to take place as shortly as possible after the plasma exposure due to the aforementioned recovery effect. According to the time-dependent measurements, cp. Figure 5.7 (a), the contact angle θ^* below 20° is ensured for a direct transfer not later than 60 min after the exposure.

5.4 Experimental procedure of the Wet Transfer Technique on AIN

5.4.1 Etching of the Cu foil

Apart from the investigations about the wettability, which turned out to be highly critical regarding the graphene quality, further transfer process parameters have an impact on the transferred graphene monolayer. As shortly depicted in Figure 5.1 (a), the Cu foil needs to be completely etched away before the transfer of the GR-PMMA stack. The most commonly used etchants to remove Cu are aqueous solutions of FeCl₃, ferric nitrate (Fe(NO₃)₃) and ammonium persulfate (APS) (NH₄)₂S₂O₈, of which FeCl₃ is the strongly commanding etchant in literature. The reaction equations [169, 170] for each of the etching solvents are given as

$$2 \operatorname{FeCl}_{3} + \operatorname{Cu} \longrightarrow 2 \operatorname{FeCl}_{2} + \operatorname{CuCl}_{2},$$

$$2 \operatorname{Fe}(\operatorname{NO}_{3})_{3} + \operatorname{Cu} \longrightarrow 2 \operatorname{Fe}(\operatorname{NO}_{3})_{2} + \operatorname{Cu}(\operatorname{NO}_{3})_{2},$$

$$(\operatorname{NH}_{4})_{2}\operatorname{S}_{2}\operatorname{O}_{8} + \operatorname{Cu} \longrightarrow (\operatorname{NH}_{4})_{2}\operatorname{SO}_{4} + \operatorname{CuSO}_{4}.$$
(5.3)

Due to a low dissolved copper capacity of all of those mentioned etchants the solutions need to be replaced after every etching cycle. The chemical products lead to an easily visible color change of the etchant solution, as depicted in Figure 5.10 (a) for the use of APS as the etchant. In the case of $FeCl_3$ and $Fe(NO_3)_3$, the aforementioned iron compounds arise in the form of FeCl_2 and $\text{Fe}(\text{NO}_3)_2$, respectively. Only a few research groups investigated their influence on the graphene properties, in terms of a proper Raman characterization [171]. They come to the conclusion, that both FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ introduce iron compounds, which stack on the graphene sheet and lead to an additional p-type doping. Due to an also very critical solubility, these compounds precipitate and lead to a negative impact on the graphene layer. As shown in Figure 5.10 (b), the precipitation leads to an accreation on the rear side of the graphene surface, resulting in a wermicular structure between AlN and graphene (dark patterns). The OM image indicates a predomination at Cu grain boundaries, which might come from the layer asperities, as already shown in Figure 4.13 (b). These structures are clearly identified by energy-dispersive X-ray spectroscopy (EDX) measurements as ferric and oxide compounds (not shown here). The formation of these cupric and ferric oxides is reported by [172] and is also made visible via SEM imaging (right upper corner of Figure 5.10 (b)). A closer view of this precipitates is presented in (c) via a comparison of an OM image and a corresponding area map obtained via Raman measurements. The D/G ratio clearly reveals the formation of defect structures (strong red intensity) within the graphene layer along these precipitates. The graphene defect structure accurately displays the ferric impurities. An exemplary comparison with a precipitate-free Raman single



Figure 5.10: (a) Photographic image of the ongoing Cu foil etching process in APS. The originally sallow etchant turns into blue during the etching process. (b) OM and SEM image (down left and up right, respectively, with the same magnification) of graphene transferred on AlN after Cu foil etching with FeCl₃. The ferric precipitates are indicated by the wermicular structure (visible in the OM and SEM image in dark and light grey, respectively. (c) OM image (higher magnification than in (b)) and the corresponding Raman mapping of the D/G peak ratio down left and up right, respectively, directly revealing the negative impact of ferric precipitates on the graphene layer structure. (d) Exemplary single Raman measurements of a graphene in the region of precipitates (red line) and far off it (black) in correspondence to (c).

measurement, as shown in (d), reveals a strong deterioration of the graphene layer. The 2D/G ratio is strongly decreased from > 2.5 to ≈ 1 , the D/G ratio is increased from $\ll 0.2$ to ≈ 1 .

In order to reduce the formation of ferric precipitates, variations in the etchant concentration were preformed. The result was a not significant reduction in the number of impurities and a prelonged etching time which increased from approx. 2h up to 24h, wherefore these etchants were finally refused. In contrast to FeCl_3 and $\text{Fe}(\text{NO}_3)_3$, a promising alternative is aqueous APS, which significantly reduces the number of precipitates, as depicted in Figure 5.11 (a). According to Equation (5.3), by the use of APS as the etchant, the production rate of sulfuric compounds is halved compared to the production rate of ferric chlorides and oxides using FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ as the etchant, respectively. Furthermore, APS avoids the existence of detrimental ferric byproducts at all. In conjunction with the developed plasma pretreatment of the AlN



Figure 5.11: (a) Comparison of transferred graphene on AlN, using FeCl₃, as in Figure 5.10 (b), and APS as the etchant solution, down left and up right, respectively. Images obtained via OM. APS leads to a significantly cleaner surface. (b) Corresponding averaged Raman spectrum (line scan, 121 measurement points) for FeCl₃ (red line) and APS (black) as etchant solutions, depicted with the black and red solid line, respectively. The inset shows the Raman spectrum of a graphene-free area for untreated AlN for comparison.

surface, a defect-free closed graphene transfer is achieved. This results in a total graphene quality enhancement, as revealed via Raman spectroscopy. The defect-related D peak (1350 cm⁻¹) almost completely vanishes. A reproducibly high 2D/G peak ratio of > 2.5 is achieved together with a reduction of the D/G peak ratio below 0.15, see Figure 5.11 (b). In combination with the 2D peak position at 2772 cm⁻¹ these findings indicate the presence of mostly monolayer graphene on AlN (black solid line).

As a short summary, the experimental procedure of the complete wet transfer process is described in the following. According to Figure 5.1, the as grown graphene on Cu foil is covered with PMMA which is deposited via spin-coating. The thickness of the PMMA layer directly depends on the spinning velocity, which is set to 3000 rpm and results in a thickness of about 40 nm. Via a baking on a hot plate at 180 °C for a duration of 3 min, the PMMA is hardened in order to serve as protective supporting layer. The etching of the Cu foil is performed with the presented aqueous etchants (0.5 mol/l). The etching time depends on the size of the GR-Cu sample and the amount of etchant and takes 2h on average. For lower etchant concentrations the etching time increases up to 24 h, which leads to an increase in Raman defect peaks within the layer. Afterwards, the etchant is gradually removed and replaced by DI water. The AlN target substrate is cleaned in organic solvents, i.e. acetone and isopropanole and plasma pretreated, before the AlN sample manually collects the floating GR-Cu sample, cp. Figure 5.12 (a). The desiccation process takes place on a hot plate at 40 °C for a duration of 30 min. It turned out that a longer heating treatment results in additional layer cracks. Furthermore, as already mentioned by [173], an additional drop of liquid PMMA solution is spread on the GR sample and a long term desiccation (usually over night) at room temperature is performed. This additional step cures the transferred graphene sheet by reducing the formation of cracks and wrinkles, which itself could result in bilayer and multilayer structures. In a final step, the PMMA layer is removed in an acetone bath at 60 °C for a duration of 30 min. Both the AlN surface plasma pretreatment and the etching with APS



Figure 5.12: (a) Photographic image of the manually transferred PMMA-graphene stack onto the AlN target substrate wafer. (b) SEM image of a direct comparison between pristine and optimized wet transfer revealing a strong reduction of graphene-free areas on the AlN surface.

lead to a significant improvement of the graphene wet transfer. The formerly existent cracks and partially uncovered AlN surface, as depicted as an example in the inset of Figure 5.11 (b) and in the SEM image in Figure 5.12 (b) can now be strongly reduced and a closed homogeneous graphene film without cracks is possible to be transferred. The empirically obtained process parameters directly reveal the strong sensitivity of the whole transfer procedure, wherefore the process recipe should absolutely be complied with respect to the experimental comparability.

5.4.2 Graphene sheet resistivity measurements and summary of the Wet Transfer on AIN

Besides the quick and easily accessible Raman spectroscopy for the graphene quality characterization, an electrical characterization of the transferred layers is inevitable, keeping in mind the use of graphene as an electrode material. The electric properties are usually determined via the fabrication of graphene field effect transistor (GFET) [73, 174] and transfer line method (TLM) [175] structures. With these structures, electrical characterizations are highly suitable for basic graphene research regarding the determination of charge carrier densities, the doping type, the contact and sheet resistivity, $R_{\rm c,GR}$ and $R_{\rm s,GR}$, respectively. The major drawback lies in their time consuming feature and the infeasibility of the characterized graphene sheets for later deployment. An elegant solution as a quality conformance test is the 4-point probes method (4PP) for the determination of the $R_{\rm s,GR}$, since it is easy applicable and a non-destructive measuring method. Four electrodes, each two of them serve as separated voltage (U)and current (I) electrodes, ensure the independency of any contact resistivity. The electrode arrangement is depicted in Figure 5.13 (a), where the electrodes are positioned quadratically. By supplying a current, a voltage drop is generated and according to Ohm's law the corresponding sheet resistivity can be calculated. Assuming large-area graphene sheets with a diameter D >> s, $R_{s,GR}$ is given as



Figure 5.13: (a) Schematic of the 4-point method with the position of the four electrodes on the transferred graphene sheet (grey) on the AlN substrate. Voltage (U)and current (I) electrodes are separated from each other in order to eliminate resistivity effects due to the contacts. (b) Sheet resistivity $R_{s,GR}$ in dependence of the different investigated plasma pretreatments.

$$R_{\rm s,GR} = c \cdot \frac{U}{I} = \frac{\pi}{\log 2} \cdot \frac{U}{I},\tag{5.4}$$

with the geometric correction factor c. The distance s between each of the electrodes must be equal in order to determine the resulting sheet resistivity $R_{s,GR}$ properly. For the resistivity measurements, the 4-point probe setup Loresta-GX, MCP-700 of Mitsubishi Chemical Analytech was used. The 4-pin probe is applied with low pressure on the surface and the measurement is done automatically. In order to avoid edge effects and therefore to obtain reasonable resistivity values, the measurement position needs to be in the center of the whole sample.

The differently plasma pretreated AlN samples with transferred graphene SLG were investigated and the obtained $R_{\rm s,GR}$ are depicted in Figure 5.13 (b). There is a significant reduction of almost one order of magnitude in $R_{\rm s,GR}$ for all plasma pretreated AlN samples (from $22 \,\mathrm{k}\Omega/\mathrm{sq}$ down to $< 5 \,\mathrm{k}\Omega/\mathrm{sq}$). The comparably large error bars, especially in case of the pristine samples, result from the probe distance s of 1 mm.

Process step		Temperature	Duration
CVD graphene on Cu foil		980 °C	$30\mathrm{min}$
PMMA spin-coating on GR	$3000\mathrm{rpm}$		$30 \sec$
PMMA desiccation		$180^{\circ}\mathrm{C}$	$3 \min$
Cu foil etching	APS (0.5 mol/l)		$2\mathrm{h}$
Ar plasma on AlN			$10\mathrm{min}$
GR transfer on AlN			
Graphene desiccation		$40^{\circ}\mathrm{C}$	$30\mathrm{min}$
Additional PMMA		room temp.	$> 12 { m h}$
PMMA removal	Acetone	60 °C	$30\mathrm{min}$

Table 5.1: Summary of the transfer process with optimized process parameters.

This makes the resistivity measurements strongly dependent on the created gaps, cp. Figure 5.12 (b), since for each sample four centered locations were measured. According to Raman spectroscopy measurements, the small graphene domains might have slightly lower $R_{\rm s,GR}$. For a plasma pretreatment, the results are more reliable with lower resistivity variations due to a homogeneous graphene layer. The best results are achieved after an Ar plasma pretreatment in good agreement with the previous graphene characterization. With resistivity values repeatably below $1 \,\mathrm{k}\Omega/\mathrm{sq}$, and even the best lowest value of $R_{\rm s,GR} = 350 \,\Omega/\mathrm{sq}$, Ar plasma turns out to be able to be successfully integrated in the wet transfer procedure.

The aforementioned findings lead to a significant improvement of the wet transferred of graphene on AlN and make the developed process competitive with the already established transfer onto SiO₂. Furthermore, it reveals valuable knowledge about the importance of the target surface wettability and its dependence on pretreatments due to both a physical and a chemical effect on the AlN surface. The summarized process steps in correspondence with the introductory Figure 5.1 (a) are given in Table 5.1. With respect to the graphene transfer onto other substrate materials, these findings can be converted and adjusted. As presented in the next chapter, for the following application of graphene as a novel and alternative electrode material on AlN-based resonator devices, $40 \times 40 \text{ mm}^2$ graphene samples are transferred and the experimental investigations are predicated on the established process procedure as described in this chapter.
6 Graphene as a top electrode for SMR-BAW resonators

After the successful graphene synthesis on Cu foil and its subsequent transfer procedure onto AIN the influence of graphene on SMR devices is investigated. Thereby, theoretical predictions, which were drawn in Chapter 2 can be verified and implications on prospective applications can be highlighted. In this chapter, the fabrication of AIN based SMR devices by focusing on transfer and metallization aspects is described. By an electrical characterization via network analyzer measurements in order to obtain the aforementioned characteristic admittance curves, the device-specific equivalent circuit parameters are determined. Additionally, a visualization of the out-of-plane displacement is performed via Laser Doppler Vibrometry measurements, which impressively reveal the resonator's performance dependency on the metallization design. It is clearly shown, that the obtained findings strengthen the advantage of the virtually massless character of graphene regarding the reduction of mass-induced loss mechanisms.

6.1 Resonator device fabrication and experimental procedure

With regard to the following investigations of the graphene electrode influence on the overall device performance, a suitable reference device with conventional metal electrodes needs to be taken into account. With the focus on a variation of the top electrode material, a device design is needed which is as easy as possible to handle regarding the aforementioned wet transfer technique and the proper electrical contacting of the graphene electrodes. For that purpose, the device structure, as depicted in the chapter about the resonator basics in Figure 2.2, is slightly modified in the way that the complete electrode contacting is sited on top of the piezoelectric AlN layer. Figure 6.1 (a) schematically illustrates an adjusted layout, in which the electrical voltage signal is applied on the resonator structure via the signal (S) and ground (G) electrodes, lying on top of the whole layer stack. The underlying SMR structure still includes the bottom electrode (BE) - the former signal electrode - which now serves as a simple conducting layer. Its floating potential leads to a confinement of the established electrical field within the piezomaterial and enables the required standing bulk acoustic wave. This chosen design approach, which still represents a so called one-port device, strongly simplifies the fabrication process regarding the graphene wet transfer. The reason lies in the metallization process, which is needed for a proper contacting of the resonator device and which can be performed completely after the graphene deposition/transfer. As a result of this, the



Figure 6.1: (a) Schematic drawing of the SMR device design with a ground-signal-ground (GSG) top metallization scheme and the corresponding zoom-in. The different layers correspond to the Bragg reflector (BR), the Si substrate and the bottom electrode (BE) as aforementioned in Figure 2.2. (b) Direct comparison with the SEM image of a cross section profile (obtained via a focused ion beam (FIB) cut) indicating the layered structure of the piezoelectric AlN, BE, BR and Si. The corresponding layer thicknesses are listed in Table 6.1.

electrical connection for the device characterization can be operated completely from the device front side. Similar SMR resonator devices are commercially available and industrially fabricated. This work is based on SMR structures on 3 inch wafers, with and without top electrodes, as provided by project partners within the underlying research project of the *EU flagship* program. Before a detailed characterization of this material is presented, the characterization tools, which are used for the resonator's performance characterization, are described shortly.

Network Analyzer measurements

A network analyzer measures the scattering parameters (S-parameter), i.e. the reflection and transmission of an electrical signal within electrical networks. An interpretation regarding the network performance is done by a direct comparison of the reflected or transmitted electrical signal with respect to the total incoming one. For this purpose, an electrical steady-state signal is applied on the electrical network (i.e. the "device to be measured"). The key performance parameters Q and k_{eff}^2 can be determined with the obtained admittance information, as introduced in Chapter 2. With their (S) and (G) electrode design, the fabricated SMR devices are one-port devices. The corresponding scattering parameter is S_{11} , which is extracted by the use of ground-signal-ground (GSG) measurement probes (Cascade Microtech). The Y_{11} parameter represents the admittance of the one-port device and is extracted from S_{11} for all upcoming measurements in this work mathematically as

$$Y_{11} = \frac{1}{Z_{\rm L}} \frac{1 - S_{11}}{1 + S_{11}},\tag{6.1}$$



Figure 6.2: (a) Photographic image of a device under test (DUT) with the measurement tip contacting the top electrode structure. ©Fraunhofer IAF. (b) Photographic image of the laser doppler vibrometry (LDV) set-up with the XY sample positioning table (1), the LDV measuring head with the included Laser source (2), the oscilloscope (3) and the signal generator (4).

with the input impedance $Z_{\rm L}$, which is normalized to 50 Ω .

The aforementioned characteristic admittance curve Figure 2.5 is obtained by a frequency sweep around the expected resonance frequencies. A device under test (DUT) is shown in Figure 6.2 (a). The device sample is positioned on a micromanipulator probe station (Summit10000, Cascade Microtech, Beaverton, Oregon, USA). The conversion of S_{11} into admittance values is performed by a network analyzer (NWA) (Agilent E5061B, Agilent Technologies). The obtained admittance curve is fitted with the aformentioned software LARA10k, applying a fitting routine with the underlying mBVD equivalent circuit, described in Figure 2.6 (c) to determine all relevant fit parameters. A more detailed theoretical insight in the electrical spectrum analysis is given in [176].

Laser Doppler Vibrometry

In order to visualize the effect of the applied top electrode and its metallization scheme, laser doppler vibrometry (LDV) measurements are performed (Ultra High Frequency Vibrometer UHF-120, Polytec GmbH, Waldbronn, Germany). LDV is an eminent optical characterization technique, which can detect surface vibrations in the pm range. With a spatial resolution of few μ m and a software controlled movable XY sample stage, a visualization of the *TE1* BAW mode at the size of the complete resonator device is accessible and contour plots can be generated. By this, an optical insight in the oscillating behavior of the devices is obtained.

Basically, via the (G) and (S) electrodes an electrical signal around the expected resonance frequency is applied ("Multicarrier Continuous Wave" signal) on the DUT sample. The DUT is exposed to the LDV set-up. In principle, an incident laser beam (test beam) is reflected by the DUT and influenced by the device vibrations. The experimental installation is depicted in Figure 6.2 (b). Basically, the vibrometry set-up consists of a heterodyne interferometer which exhibits a beam splitter where the incident laser beam is divided into a reference and test beam. An acousto-optic modulator (Bragg cell) is additionally applied in order to define a specifically known frequency shift between the reference and incident test beam. The reflected test beam is modulated due to a

vibration-induced Doppler shift. The overlap between reference beam and reflected test beam causes an interference according to the Bragg cell induced carrier frequency and the Doppler induced modulation frequency. The resulting optical signal is collected on a photodetector and demodulated by a commercial software (here provided by Polytec GmbH). From the time-dependent interference pattern conclusions about the resonance behavior of the measured device can be drawn. The detailed operating mode is described in [177–179]. With the applied set-up it is possible to detect frequencies up to 2.4 GHz with an out-of-plane amplitude resolution of 2 pm.

6.1.1 AIN quality control of resonator structures

This thesis is targeted on the successful use of graphene as a massless top electrode material. In order to interpret the following results of graphene-based SMR devices, several prior experiments and investigations regarding the significance of the experimental findings need to be performed. First of all, as already mentioned, the layer thicknesses and their homogeneity along the wafer are investigated. This is required for a proper analysis of the obtained resonance frequencies of the utilized SMR structures with simulations. Therefore, the SMR layer stack is investigated regarding its layer thicknesses via ellipsometry and SEM. A focused ion beam (FIB) cut is performed to visualize the different layers based on their material specific optical contrast, as shown in Figure 6.1 (b). In Table 6.1, the measured individual layer thicknesses are listed and compared to the values specified by the sample supplier.

The obtained values reveal a deviation from predicted and actually measured thicknesses due to a fabrication process induced variance, although a reliable determination via

Layer	Material	d (theor.)	d (meas.)	d (sim.)
Piezolayer	AlN	1700	1710.5 ± 3.5	1710
BE1 BE2 BE3	W AlCu Ti	$135 \\ 188 \\ 32$	$\begin{array}{c} 138.4 \pm 0.1 \\ 179.9 \pm 5.9 \\ 39.7 \pm 4.9 \end{array}$	138 180 39
upper BR1 upper BR2 upper BR3	${ m SiO}_2 \ { m W} \ { m Ti}$	850 540 32	$\begin{array}{c} 792.1 \pm 2.3 \\ 612.1 \pm 8.2 \\ 37.1 \pm 3.5 \end{array}$	790 610 37
lower BR1 lower BR2 lower BR3	${ m SiO}_2 \ { m W} \ { m Ti}$	530 830 32	520.1 ± 2.5 930.1 ± 10.8	520 930 32
Isolation layer	SiO_2	570	535.0 ± 5.0	535
Substrate (in μm)	Si	725		725

Table 6.1: Layer thicknesses (in nm) of the SMR devices, which are utilized for the experiments with graphene as the top electrode material. Comparison between the theoretical (given by the supplier) and the measured (via SEM images) layer thicknesses. For resonance simulations, the layer thicknesses d (sim.) are adjusted from the experimentally obtained ones.



Figure 6.3: (a) Raman E_2 peak position, i.e. the phonon frequency ω_{E_2} in dependence on the measurement position along the 3 inch wafer center line. (b) Corresponding stress distribution calculated via Equation (6.2). For comparison reasons, AlN on W/AlCu/Ti (black data points) and on pristine Si (red) was investigated.

SEM imaging is impeded by charging effects of the oxide layers. With these findings the thickness parameters used for frequency simulations are adjusted (very right column). It can be reasonably assumed that the AlN thickness is homogeneously along the whole wafer, which additional ellipsometry measurements of AlN reference sample sputtered on Si substrates clearly confirm. Regarding the device performance, the stress distribution within the piezoelectric layer directly influences the electromechanical coupling [180]. The in-plane biaxial stress σ can be determined indirectly via Raman spectroscopy, as described in detail in [181], by focusing on the stress-induced characteristic E_2 peak shift in the AlN Raman spectrum. The stress-peak shift dependency is determined via stress dependent curvature measurements of AlN reference samples [182], according to

$$\omega_{E_2} - \omega_0 = K_{\rm RS}\sigma,\tag{6.2}$$

with the measured phonon frequency ω_{E_2} , the strain-free phonon frequency ω_0 at room temperature, and the Raman biaxial stress conversion factor $K_{\rm RS}$. ω_0 and $K_{\rm RS}$ are experimentally determined as $654.39 \,{\rm cm}^{-1}$ and $3.45 \,{\rm cm}^{-1}/{\rm GPa}$, respectively, in good agreement with literature values [183, 184].

In order to get an impression on the stress distribution, AlN layers grown on a pure Si substrate, and on the W/AlCu/Ti BE layer stack were investigated. In Figure 6.3 (a), the measured E_2 peak shift for the two different underlying substrates is shown. Although there is a clear variation in the total peak shift, it is laterally homogeneous along the 3 inch wafer. This results in a homogeneous stress distribution (compressive for Si, tensile on BE), as calculated according to Equation (6.2) and depicted in Figure 6.3 (b). AlN on Si was used for the process development of the wet transfer, as described in the previous chapter, whereas the actual SMR devices presented in this work involve the W/AlCu/Ti bottom electrode. These findings regarding a homogeneous thickness and stress distribution theoretically allow the fabrication of graphene based wafers across the complete wafer surface without expecting performance deviations induced by a change in the AlN layer properties, which otherwise would result in e.g. a significant variation of the resonator's resonance frequency.



Figure 6.4: (a) Ti/AlCu (72 nm/190 nm) metallization design of industrially fabricated SMR devices with an edge length of 200 µm. (b) Corresponding reference device fabricated for this work with a Ti/Au (20 nm/100 nm) electrode metallization. The languet serves as the contacting area for the measuring tips.

Metallization design of reference top electrodes

Once the SMR layer stack is investigated, one needs to take into account that a proper interpretation of the effect of graphene-based resonator devices and following conclusion only can be drawn with respect to a proper reference samples. In this case, a reference sample means a SMR device with a full metallization in order to study directly the mass-induced effects on the resonator performance. In addition to the bare SMR structure without TE, reference samples with metal electrodes were investigated. In order to rule out a deterioration of performance due to potential issues with the electrode fabrication, which is performed for the following experiments, additional reference devices with a metal top electrode are fabricated. This means that two reference samples are compared in a first step - a commercial one and a sample with an in-house developed electrode design. Both ones possess a full metallization. In Figure 6.4 (a) and (b) the metallization geometry of commercially used devices (EPCOS AG, sputtered Ti/AlCu (72 nm/190 nm)) and fabricated devices (sputtered Ti/Au (20 nm/100 nm)), respectively, are shown. Due to technology reasons, the in-house metallization is geometrically simplified. The languet serves as the contacting area for an accurate positioning of the measuring tips which are needed to apply NWA and LDV measurements.

Electrical characterization of the reference devices

Since both the electrode design as well as the chosen electrode metals slightly differ, an electrical characterization will be necessary to be performed. S-parameter measurements reveal a comparability of both metallizations and prove the functionality of the Ti/Au electrode, which is required for a proper evaluation of the actual influence of graphene as a TE, as described in the following sections. As a result of this, all metal contacts described in the following experiments are made of Ti/Au, including the ground electrode (G). The electrode area, which determines the total resonating area is set to $200 \times 200 \,\mu\text{m}^2$.

In Figure 6.5 (a), the obtained admittance curves of the commercial reference (Ti/AlCu) and the IAF reference (Ti/Au) are shown in red and black, respectively. A shift in the resonance frequency from 1.97 ± 0.01 GHz to 1.76 ± 0.01 GHz is clearly



Figure 6.5: (a) Exemplary admittance curve obtained vie network analyzer measurements of the commercial reference with Ti/AlCu electrode (red line) and IAF reference with Ti/Au electrode (black). A resonance frequency shift is clearly visible. (b) Extracted plate capacity C_0 of both reference resonator samples indicate a similar resonance area. (c) Corresponding quality factors Q_s and Q_p at series and parallel resonance frequency, respectively. (d) Corresponding effective coupling coefficient k_{eff}^2 . All parameters are obtained using a fitting procedure of the underlying mBVD equivalent circuit via Lara10k.

visible, which is a direct consequence of the different thicknesses and masses of the used metal electrodes. The shift due to a different mass loading agrees with the much lower mass densities of Al and Cu compared to Au, which are given as $\rho_{\rm Al} = 2.70 \, {\rm g/cm^3}$, $\rho_{\rm Cu} = 8.93 \, {\rm g/cm^3}$ and $\rho_{\rm Au} = 19.28 \, {\rm g/cm^3}$ [34]. The overall spectra show no vertical shift $(Y_{11} \text{ axis})$. The baseline, which is obtained by the horizontal admittance slope far from the resonance frequencies, is electrically determined by C_0 , since here the resonator system acts as a simple capacitor with capacitance C_0 . Therefore, a similar baseline indicates that the total resonating area is of a similar size. The equivalent circuit parameter fitting leads to only a slight deviation in the plate capacity C_0 from approx. 2.1 pF to 2.4 pF, as depicted in (b). With the assumption of $\epsilon \approx 9.8$, valid at the $TE1 \mod [185]$, the resonating area is calculated according to Equation (2.28) as $4.1 \times 10^4 \,\mu\text{m}^2$ and $4.7 \times 10^4 \,\mu\text{m}^2$ in good agreement with the theoretical area of $200 \times 200 \,\mu\text{m}^2 + 115 \times 90 \,\mu\text{m}^2$ (languet) = $5.04 \times 10^4 \,\mu\text{m}^2$. Deviations here may result from fitting errors and be furthermore caused by technological reasons with respect to a proper mask alignment. Regarding the calculated quality factors, there are only slight differences for both $Q_{\rm s}$ and $Q_{\rm p}$, which are within the statistical deviation (c). The same holds for the effective coupling coefficient k_{eff}^2 , which lies in the range of 5% (d) and therefore comes close to the theoretical k_{T}^2 of 6.5%. The obtained statistical error bars result from the characterization of 20 identical SMR resonator devices at minimum. As a first noteworthy result, the reader may come to the conclusion that these findings



Figure 6.6: (a) Schematic illustration of the resonator device fabrication. After the wet transfer of graphene on the AlN side of the SMR, the Ti/Au metallization (ground electrode and graphene contact) is realized. (b) Comparison of the effect of a different laser intensity used for graphene isolation. SEM images show isolation result for low intensity (1) and for an adjusted (higher) intensity (2), which was used for all SMR device fabrications. (c) Exemplary optical image of a deposited metal pad on graphene. The isolation line is depicted as the dashed white line resulting in a total resonating area of the same size as the reference metallization. Lower image shows the corresponding CAD sketch.

prove the functionality of the in-house fabricated full metallized Ti/Au electrode and therefore a proper comparison between metal and graphene electrodes can be drawn in the future experiments.

Fabrication procedure of graphene-based SMR devices

Given the process procedure described in Figure 5.1 (a), the final resonator device fabrication is depicted in Figure 6.6 (a). Graphene is transferred on the AlN-based SMR device according to the previously described wet transfer technique in Chapter 5. In a second step, the metallization structure, i.e. the ground electrode and the metalgraphene contact, is deposited via electron-beam physical vapor deposition (EBPVD) (Ti/Au, 20 nm/100 nm). The metal structure is defined via a Mo mask, which is positioned onto the wafer with the help of crystal bond as an adhesive. Experiments show that the advantage of crystal bond lies in its almost residual free removal from the graphene surface after the EBPVD deposition. In order to isolate the signal and ground electrode, which is essential for the vertical coupling of the BAW mode via the bottom electrode, the graphene covered resonating area is defined via a low-intensity laser treatment. The laser is able to remove graphene locally with a resolution of $\approx 6 \,\mu m$. There is a severe trade-off between a too low laser intensity, which keeps the graphene layer unaffected and a too high intensity, which results in a possible damage of the underlying AlN layer. A moderate adjustment of the laser power is inevitable in order to ensure a proper graphene isolation, as depicted in Figure 6.6 (b). (1) shows a low intensity treatment, which leads to not fully isolated area, i.e. the applied three laser lines are clearly visible and not continuous along the whole isolating structure. For higher laser intensity, a significant isolation is obtained, as seen in (2) where the underlying clean and undamaged AlN surface is visible. In Figure 6.6 (c), the complete isolation structure for an exemplary metal pad is depicted, as it is applied on every resonator device. The structured graphene corresponds to the aforementioned full metallization design, i.e. a



Figure 6.7: Schematic illustration of the investigated SMR structure with different metallization designs (CAD sketch, SolidWorks). The ground electrode (G) consists of a Ti/Au (20 nm/100 nm) layer stack. (a) Signal electrode (S) with Ti/Au (20 nm/100 nm as reference device. (b) Graphene (GR) as signal electrode, which is contacted by a Ti/Au (20 nm/100 nm) pad. (c) Photographic image of a completely fabricated 3 inch SMR wafer with 576 resonator devices, the inset shows a close-up view of the metallization layout [©] Fraunhofer IAF.

 $200 \times 200 \,\mu\text{m}^2$ resonating area with the languet as the contacting region, as depicted in Figure 6.6 (c).

6.2 Experimental results and device characterization

6.2.1 Influence of the metallization design - the metal bar structure

In a first experiment, the already mentioned metal pad (cp. Figure 6.6 (c)) as a metalgraphene contact is investigated. The comparison with the full metallization reference is depicted in Figure 6.7 (a) and (b) in the form of a computer-aided design (CAD) sketch. The metal pad with its area of $50 \times 50 \,\mu\text{m}^2$ is deposited on the graphene languet for a proper contacting of the graphene layer. Its decentralized position ensures a minimization of additional damping effects induced by the measuring tip. This metallization structure including the surrounding ground electrode G is applied along the whole wafer resulting in theoretically 576 devices (c). Due to the limited area of the transferred graphene sheet ($50 \times 50 \,\text{mm}^2$), centered on the AlN surface, the number reduces to approx. 300. Fabrication issues and possible inhomogenities in both the graphene and metallization area lead to a further reduction. For a well-grounded experimental analysis at least 20 working devices for each structure design are investigated. This consideration also holds for the following device measurements.

Network analyzer measurements clearly reveal a change in the resonant properties compared to the Ti/Au reference. In Figure 6.8 (a), the obtained admittance curves are shown. At first, there is a clear shift of the main resonance frequency from 1.76 GHz to 2.14 GHz. With the graphene mass $m_{\rm GR} \approx 0.037 \% m_{\rm Ti/Au}$, this shift impressively shows the achieved mass reduction with 2D graphene. The peak at 1.76 GHz is still existent although its intensity is pretty much lower compared to the reference samples. This implicates that the Ti/Au contact leads to the already known resonance at this lower frequency. FEM simulations predict that the obtained resonance frequency with graphene as the top electrode material corresponds to a device structure without top electrodes. Furthermore, the effect of the additional metal contact can be shown. In Fi-



Figure 6.8: (a) Exemplary admittance curve obtained via network analyzer measurements of a reference full Ti/Au metallization (black line) and a graphene-based top electrode with a metal pad contact (red) with the corresponding resonance frequencies at f_s and f_p . (b) Simulated resonance frequency in dependence of the total top electrode thickness. For comparison reasons, a Ti/Au (solid line, 20 nm and a pure Au electrode (dashed line) was simulated, leading to a shift in resonance frequency. The corresponding resonance frequency f_p of the Ti/Au and Ti/AlCu reference devices at 1.76 GHz and 1.97 GHz, respectively, and the graphene-metal pad at 2.14 GHz are highlighted via the horizontal black and red lines, respectively. (c) Contour plot of the surface displacement obtained via LDV measurements for a Ti/Au reference device. (d) Corresponding plot for a graphene-metal pad based resonator device.

gure 6.8 (b) the simulation results are depicted for a variation of the investigated SMR device structure with respect to the electrode configuration. The parallel resonance frequency f_p (which represents the actual mechanical displacement) decreases with increasing electrode thickness. For a better understanding of the underlying mass effect, both pure Au SE and 20 nm Ti plus Au is simulated, which reveals a slight upshift of f_p . The corresponding resonance frequency f_p of the Ti/Au and Ti/AlCu reference devices at 1.76 GHz and 1.97 GHz, respectively, and the graphene-metal pad at 2.14 GHz are highlighted via the horizontal black and red lines, respectively, and directly describe the obtained resonance frequencies obtained in the admittance curve. The fitting of those is performed according to the aforementioned procedure. A summary of the fitted equivalent circuit parameters is given in Table 6.2. It is worth mentioning, that the motional resistivity R_m is kept constant for all fitting procedures in order to ensure a compara-

	$egin{array}{c} egin{array}{c} egin{array}$	$egin{array}{c} egin{array}{c} egin{array}$	$egin{array}{c} m{C}_0 \ (\mathrm{pF}) \end{array}$	$egin{array}{c} {m{R}_{ m m}}^{*} \ (\Omega) \end{array}$	$oldsymbol{R}_{ m s}\ (\Omega)$	$oldsymbol{R}_{ m p}\ (\Omega)$
${f Ti}/{f Au}$	1.71	1.76	2.38 ± 0.07	0.2	3.1 ± 0.4	366 ± 73
${f Ti}/{f Au}$ pad	2.10	2.12	0.36 ± 0.01	0.2	52.2 ± 7.3	740 ± 124
${f Ti}/{f Au}~{f BS}$	2.10	2.14	2.66 ± 0.08	0.2	4.5 ± 0.4	276 ± 15
Pure graphene	2.12	2.14	0.25 ± 0.06	0.2	171.0 ± 5.8	1090 ± 152

 Table 6.2: Comparison of the the extracted fit parameters according to the mBVD equivalent circuit model fit for different top electrode structures.

* fixed value

bility of all electrode design variations. The reader shall keep in mind, that additional electrode masses directly influence $R_{\rm m}$ as well as $R_{\rm p}$, as mentioned in Section 2.2.1, and an exact separation of the total effect is catchy and out of focus of this work. In the readers interpretation all mass-induced damping effects are compressed in $R_{\rm p}$, since the only change in the resonator structure is based on a change in the electrode design.

The electrical measurements show a strong downshift of the admittance curve for the graphene-metal pad structure. This indicates a tremendous decrease in the plate capacitance C_0 , which indeed reduces from 2.38 pF to 0.36 pF and represents a decrease in the total oscillating area. LDV measurements confirm these findings. In Figure 6.8 (c) and (d), contour plots of the out-of-plane surface displacement are depicted for the reference and the metal pad sample, respectively. The latter one clearly shows a significant deterioriation of the oscillating area, which lies in the range of 7000-8000 μm^2 according to the obtained fit values. Due to the high metal/graphene area ratio, the enormous mass-induced damping has ripple effects on the quality factor $Q_{\rm s}$ $(Q_{\rm p})$, which lie only at 353 (154) - obtained from group delay data - and represents no resonator performance improvement at all. The reason may lie in an insufficient contacting geometry. Since graphene exhibits a comparably high sheet resistivity compared to commonly used metals, a metallization structure on top of the graphene layer seems to be essential in order to increase the electrically contacted graphene area. The comparably high metal conductivity leads to a sufficient electron transfer all across the graphene layer, which itself ensures an undamped oscillation of the resonator structure. This metallic top-structure would act as some sort of an *electron distribution network* with the requirement of a low metal/graphene area ratio in order to avoid additional metal-induced damping effects. Therefore, a bar structure (BS) design is applied in a next level experiment in order to increase the potentially contacted graphene area. The bar structure (BS) consists of an E-shaped comb-like Ti/Au metallization, which is deposited directly on the graphene layer, as depicted schematically in Figure 6.9 (a). The idea behind is a more accurate contacting of the whole graphene area, which corresponds to the aforementioned resonating geometry. The BS is positioned in a way to catch the isolated area, as it is shown in (b). Again, the two characteristic resonance peaks at 2.14 GHz and at 1.76 GHz, the latter one with a slightly lower intensity indicating a reduction of the metal influence on the device resonance. However, in contrast to the previous metal pad approach, the obtained admittance curve reveals an important change. As depicted in (c), the overall admittance is slightly shifted above the reference curve indicating an increase in C_0 which is fitted in the range of 2.6 pF, see Table 6.2.



Figure 6.9: (a) Schematic illustration of the SMR device with a BS design (CAD sketch, SolidWorks). (b) Optical and photographic image of deposited BS on graphene. (c) Comparison of admittance curves of the full metallized reference (black line) and graphene as top electrode with a 15 µm E-shaped Ti/Au BS for contacting (red). The black dotted line shows the admittance curve for directly contacted graphene without any metal contact. (d) Exemplary admittance spectrum (black) for the Ti/Au BS design with the corresponding fitting curve (red) to extract the equivalent circuit parameters. The inset shows a close-up view of the same fit. The fit divergence lies below 1.5 %.

Theoretically, this value stands for a total oscillating area of $5.2 \times 10^4 \,\mu\text{m}^2$, which corresponds well to the technologically fabricated resonating area, i.e. $200 \times 200 \,\mu\text{m}^2 +$ $115 \times 90 \,\mu\text{m}^2 = 5.04 \times 10^4 \,\mu\text{m}^2$. The reason in little deviations result from possible fabrication instabilities regarding inaccuracies during the graphene isolation or effects due to the additional metal-electrode induced damping. As a conclusion from these findings, the device fabrication satisfies the required neatness and stability. As it will be presented in the next section, LDV measurements prove that the oscillating area is absolutely comparable with the reference samples with an area of $200 \times 200 \,\mu\text{m}^2$. The dotted line in the graph represents the admittance curve of an unmetallized resonator device, which means, that the measuring tip is located directly on the graphene layer. The poor electrical contact leads to a low signal, i.e. $R_{\rm s} = 171 \,\Omega$, which results in a strong reduction of C_0 , which drops down to 3.2 pF. This value is comparable with the metal pad contact and indicates, apart from a possible additional damping due to the tip pressure onto the graphene surface, a large graphene contact resistivity $(R_{\rm c.GR})$. Nevertheless, the resonance behavior still can be extracted. This is of special importance since these measurements clearly reveal, that the graphene-related resonance frequency stays



Figure 6.10: (a) Group delay data obtained via network analyzer measurements. Comparison of resonator devices with metal pad electrodes (blue line), 15 μ m BS metallization (black) and pure graphene electrode (red). A strong phase shift is detected at series and parallel resonance frequency (grey box). (b) Corresponding Q in dependence of the applied frequency, indicating precise peaks of Q_s and Q_p .

almost unchanged under the additional influence of metal electrodes on top. Furthermore, the second peak at 1.76 GHz has vanished due to the absence of metal-induced damping.

From the parameter fitting, the quality factors and the effective coupling coefficient can be determined. As aforementioned in Equation (2.26), the quality factor is calculated from the obtained frequency dependent group delay data, i.e. from phase shift information between the applied voltage signal and the induced current flow within the resonator device. This technique ensures a relatively precise determination of Qas long as the measurement set-up is calibrated properly to avoid additional set-up related signal reflections. In Figure 6.10 (a) exemplary group delay data for the three examined metallization structures are depicted, indicating a strong phase shift at both series and parallel resonance, f_s and f_p , respectively. With Equation (2.26) the frequency dependent quality factor is calculated directly from these data. Q_s and Q_p are easily determined from the obtained plot, as presented in Figure 6.10 (b), (grey boxes). For the metal pad contact the signal-to-noise ratio makes a reliable determination of Q_p difficult, whereas for the BS design and even for pure graphene both quality factors clearly can be determined.

With the introduction of the mBVD equivalent circuit model, the second method for a determination of the quality factors results purely from the fitting parameters, as given in Equation (2.34) and (2.35). As already mentioned in Section 2.2, these equations are derived from the simplified equivalent circuit, as depicted in Figure 2.6 (b), whereas the fitting procedure includes added loss parameters by means of a motional (viscous) resistivity $R_{\rm m}$ and a dielectric resistivity R_0 . Obviously, these deviations might lead to a lack of comparison of both methods of Q determination. However, the uncertainties can be minimized by some constraints. First of all, the fittings consistently reveal a vanishing R_0 , which lies below 0.001Ω for all measured resonator sample whatever metallization design was investigated. The critical point is indeed $R_{\rm m}$, which strongly influences the admittance peaks at both series and parallel resonance frequency. In very

Table 6.3: Calculated quality factors at series and parallel resonance frequency and the effective coupling coefficient k_{eff}^2 . Comparison of different top electrode structures. Q_{s} (Q_{p}) is obtained both by the fitted R_{s} (R_{p}) values, cp. Table 6.2 and by phase-measurement data, cp. Equation (2.26) and Figure 6.10. k_{eff}^2 is calculated from f_{s} and f_{p} .

	$oldsymbol{Q}_{ m s,R_s}$	$oldsymbol{Q}_{\mathrm{p,R_p}}$	$oldsymbol{Q}_{\mathrm{s,phase}}$	$oldsymbol{Q}_{\mathrm{p,phase}}$	$oldsymbol{k}_{ ext{eff}}$ (%)
${f Ti}/{f Au}$	243 ± 44	185 ± 36	450 ± 9	248 ± 83	5.14 ± 0.08
${f Ti}/{f Au}~{f pad}$	197 ± 17	161 ± 16	353 ± 23	154 ± 5	2.07 ± 0.22
${f Ti}/{f Au}~{f BS}$	243 ± 17	464 ± 38	234 ± 9	449 ± 18	3.06 ± 0.07
Pure graphene	50 ± 11	157 ± 18	185 ± 19	761 ± 55	2.24 ± 0.41

first fitting procedures $R_{\rm m}$ changed with changing metallization designs indicating a change in viscous losses of the piezoelectric material. In this case, a proper comparison and evaluation of $R_{\rm s}$ and $R_{\rm p}$ was not possible. Keeping in mind, that the physical interpretation of $R_{\rm m}$ lies only in a change of viscosity of the AlN layer, the induced viscous losses should be unaffected by a top electrode variation. For this reason, a fixed value for $R_{\rm m}$ is chosen. This leads to the effect that top electrode damping effects are fully represented in $R_{\rm s}$ and $R_{\rm p}$. The value of $R_{\rm m}$ is determined by several independent measurements of pure graphene in combination with measurements of metal electrode structures. As aforementioned, in Figure 6.9 (c), the admittance curve (dotted line) for unmetallized graphene on AlN is depicted. Despite its low peak intensity, a fitting can be applied. Since there is no electrode induced damping, it can be concluded, that $R_{\rm m}$ fully represents the purely AlN-induced viscous losses. Fitting optimizations lead to $R_{\rm m} = 0.2 \,\Omega$, which is then applied to all fitted resonator structures. With this parameter regulation, all additional damping losses (electrode-induced) are shifted on to $R_{\rm s}$ and $R_{\rm p}$, which directly leads to a good fitting quality with a fit divergence reproducibly below 2%. With this adjustment a direct comparison of the obtained Q values can be drawn, as listed in Table 6.3. Generally, it can be concluded that the graphene based top electrode leads to a significant higher $Q_{\rm p}$, if a supporting metal BS on top is established for a proper graphene contacting. $Q_{\rm p}$ is increased from 248 (Ti/Au) to 449 (Ti/Au BS), considering phase measurements. However, a simple metal pad leads to an unexpected deterioration of the device performance. Q_s is constantly decreasing with changing metal structures from 450 (Ti/Au) and 353 (Ti/Au pad) to 234 (Ti/Au BS). This negative trend can be explained by the comparably poor conductivity of graphene. For a larger oscillating graphene covered area, which is introduced by a BS, the influence of the poor conductivity dominates. Additionally, the BS also affects the effective coupling coefficient of the device by an enhancement from 2.07% to 3.06%. In fact, the reference value is not reached yet, which lies again in the conductivity deficits of graphene. The comparison with a measurement of pure graphene $(R_{\rm s} = 50 \,\Omega)$ emphasizes the importance of an additional metal structure for better electrical graphene contacting.

Influence of the graphene quality

The performed electrode variations reveal an additional effect on the resonance performance regarding the conductivity of graphene since R_s is directly affected by the elec-



Figure 6.11: (a) Comparison of admittance curves with respect to graphene layers with different sheet resistivity $R_{s,GR}$, i.e. $4.0 \,\mathrm{k\Omega}$ (black line), $2.0 \,\mathrm{k\Omega}$ (blue) and $1.0 \,\mathrm{k\Omega}$ (red). (b) Schematic illustration of the principal change of the resonating area, described by the distance L from the Ti/Au bar electrode, depending on $R_{s,GR}$ and the resulting potential drop along L. U represents the applied voltage at the Ti/Au bar.

trode's conductivity. In order to quantify this effect, graphene-based resonators with the aforementioned 15 µm Ti/Au BS with different graphene qualities are investigated. The quality criterion for graphene apart from its spatial dimensions and homogeneity is the electrical conductivity or sheet resistivity $R_{\rm s,GR}$. According to the mBVD equivalent circuit, $R_{\rm s,GR}$ is represented by $R_{\rm s}$. In these experiments, transferred graphene layers with sheet resistivities of approx. $4 k\Omega/sq$, $2 k\Omega/sq$ and $1 k\Omega/sq$ are investigated. The different qualities were achieved by an adjustment of the desiccating process of the transferred graphene layer on the AlN-based SMR device with respect to the hot plate temperature. While the optimized temperature was found to be at 60 °C, higher temperature leads to additional cracks and small holes within the graphene layer. It is supposed, that the spatial homogeneity is still valid as four-point-measurements clearly revealed a spatially constant sheet resistivity. NWA measurements directly prove the resistivity dependence on the resonator's performance. In Figure 6.11 (a), the admittance curves are plotted for the three different sheet resistivities. First, there is a shift upwards visible for decreasing $R_{\rm s,GR}$. The LARA10k fitting reveals an increase of C_0 from $1.76 \,\mathrm{pF}$ (for the $4.0 \,\mathrm{k}\Omega/\mathrm{sq}$ graphene) to $2.66 \,\mathrm{pF}$ ($1.0 \,\mathrm{k}\Omega/\mathrm{sq}$), as listed in Table 6.4, and therefore supports the aforementioned theoretical assumptions. $R_{s,GR}$ represents

Table 6.4: Comparison of the extracted fit parameters for resonators with a 15 µm BS electrode design for different graphene qualities regarding the sheet resistivity $R_{s,GR}$.Parameters are obtained according to the mBVD equivalent circuit model fit.

$oldsymbol{R}_{ m s,GR}\ ({ m k}\Omega/{ m sq})$	$egin{array}{c} egin{array}{c} egin{array}$	$oldsymbol{f}_{ m p}\ (m GHz)$	$egin{array}{c} m{R}_0 \ (\mathrm{pF}) \end{array}$	$oldsymbol{R}_{ m m}^{\ st}$ (Ω)	$oldsymbol{R}_{ m s}\ (\Omega)$	$oldsymbol{R}_{ m p}\ (\Omega)$
4.0	2.11	2.14	1.76 ± 0.16	0.2	18.7 ± 3.5	252 ± 37
2.0	2.10	2.14	2.49 ± 0.13	0.2	5.9 ± 0.6	255 ± 36
1.0	2.10	2.14	2.66 ± 0.08	0.2	4.5 ± 0.4	276 ± 21

* fixed value

according to the obtained in values of Table 0.4 and phase-measurement data.					
$oldsymbol{R}_{ m s,GR}~(m k\Omega/sq)$	$oldsymbol{Q}_{\mathrm{s,R_s}}$	$oldsymbol{Q}_{\mathrm{p,R_p}}$	$oldsymbol{Q}_{ ext{s,phase}}$	$oldsymbol{Q}_{\mathrm{p,phase}}$	$m{k}_{ m eff}~(\%)$
4.0	90 ± 21	218 ± 54	164 ± 10	236 ± 37	2.65 ± 0.49
2.0	214 ± 23	355 ± 90	181 ± 11	334 ± 40	3.01 ± 0.10
1.0	242 ± 17	464 ± 38	234 ± 9	449 ± 18	3.06 ± 0.07

Table 6.5: Calculated quality factors at series and parallel resonance frequency and the
effective coupling coefficient k_{eff}^2 . Comparison of different graphene qualities
according to the obtained fit values of Table 6.4 and phase-measurement data.

ohmic losses of the electrodes and determines directly the voltage drop from the Ti/Au bar along the graphene layer. This means that the resistivity determines the resonating area. The explanation is simple. Assuming a homogeneous graphene quality, an applied voltage signal experiences a linear voltage drop according to Ohm's law. The larger the resistivity the larger is the voltage drop for a given distance L from the Ti/Au bar electrode. By assuming a laterally homogeneous sheet resistivity , the effect is delineated in Figure 6.11 (b), where the different resistivities are described by a linear voltage drop line with a different slope. At the intercept with the x-axis, the maximum distance from the Ti/Au bar is determined. As aforementioned, $R_{\rm s,GR}$ directly bears on the fitted $R_{\rm s}$, which is significantly decreased for high quality graphene from 18.7 Ω to 4.5 Ω .

This significantly affects the obtained quality factors, which are summarized in Table 6.5. The change in $Q_{\rm p}$ originates from the fact that the graphene/metal ratio increases for lower $R_{\rm s,GR}$ leading to weaker metal bar induced mechanical damping effects and leads to a duplication. The same holds for $Q_{\rm p}$, which increases from 164 to 234. These findings show impressively how the overall performance depends on the graphene sheet resistivity with respect to $Q_{\rm s}$, $Q_{\rm p}$ and the total resonating area. The reader can be aware of the fact that both calculations of Q, i.e. by group delay data and by the fitted resistivity parameters, correspond quite well with each other and describe the same tendency in a similar value spectrum. This underlines the experimentally determined fixation of $R_{\rm p} = 0.2 \Omega$. The improved performance characteristic directly influences $k_{\rm eff}^2$, which increases from 2.65% to 3.09%. The improvement here is not that high as expected, which means on the one hand that the graphene quality needs to be further improved ($\ll 1 \, \mathrm{k}\Omega/\mathrm{sq}$) and on the other hand the influence of the overlying Ti/Au BS leads to a significant damping effect. This is clearly visible in the existent second resonance peak at 1.76 GHz.

6.2.2 Variation of the bar structure width

All the previously obtained frequency responses with the comb-like BS electrode design exhibit the metal-induced additional resonance peak at 1.76 GHz. Regarding the fabrication of real filter structures, a double peak admittance shape counteracts e.g. the ladder type filter setups. The resulting passband-filtered signal shape would strongly suffer from resulting side-peaks. For this reason, the metal design has to be rethought in order to minimize this unwanted side effect. Intuitionally, a mass reduction of the Ti/Au BS might lead to that. Therefore, in the following the comb-like structure is varied regarding its width W of each of the Ti/Au fingers. A reduction of W from 21 µm to 1 µm is investigated. In Figure 6.12, optical images of exemplary BS with selected W, i.e. 21 µm, 15 µm and 6 µm, are depicted. The white dashed lines indicate the



Figure 6.12: Optical images of the Ti/Au comb-like bar structure (BS) on graphene with different BS width W. The white dashed line represents the graphene isolation line via Laser cut.

laser-induced graphene isolation in order to define the oscillating area. The frequency response of admittance is shown in Figure 6.13 (a). Applying graphene with a sheet resistivity $R_{\rm s,GR} = 1 \, {\rm k}\Omega/{\rm s}q$, a distinct resonance peak is obtained at the already known resonance frequency of 2.14 GHz. The significant change in the admittance can be seen in the side resonance at 1.76 GHz. The inset of Figure 6.13 (a) shows that the peak amplitude for the series and parallel resonance can be explicitly reduced with smaller W, and almost vanishes for $W = 6 \, \mu$ m. This finding implies that with a minimization of W the double peak frequency response can be avoided leading to the one peak shape at 2.14 GHz at $W = 6 \, \mu$ m or smaller.

This adjustment of the BS design has strong implications on the whole resonator performance. The reduction of W leads to a visible improvement of the peak amplitude at the graphene-induced f_p . The parameter fitting and evaluation shows a direct dependency on W, as depicted in Figure 6.13 (b). While Q_p is almost constant for varying W, whereas Q_p increases in an exponential-like shape with decreasing W. Again, for comparison and proof of validation of Equation (2.26) with R_p set to 0.2Ω , Q_p is



Figure 6.13: (a) Frequency response of admittance obtained via network analyzer measurements obtained for different BS widths, i.e. 21 μm (depicted in black), 15 μm (red) and 6 μm (blue), cp. Figure 6.12. The inset shows a close-up view of the 1.76 GHz resonance. (b) Quality factors in dependence of W. Q_p obtained by both group delay measurements (red) and calculation from the fitted resistivity parameter R_p according to Equation (2.26) (dark red). Q_p (from group delay data) is depicted in black. The dashed lines serve as a guide-to-the-eye.



Figure 6.14: (a) Edge-to-area ratio (EAR) for different W according to the geometrical dimensions of the BS design (red data points). Corresponding fitted $R_{\rm p}$ values (blue). (b) Experimentally determined effective coupling coefficient $k_{\rm eff}^2$ in dependence of the BS width W. The red line serves as a guide-to-the-eye, indicating the exponential slope in correspondence with the slope of the EAR in (a).

calculated from $R_{\rm p}$ (dark red data points) and from group delay data (red), exhibiting a similar slope trend. These calculations reveal a maximum $Q_{\rm p}$ for $W = 1 \,\mu{\rm m}$ of 788, which is in comparison to the 21 $\mu{\rm m}$ width and the metal reference sample an enhancement of a factor of 2 and 3.2, respectively. The dependence of $R_{\rm p}$ on W is depicted in Figure 6.14 (a), which exhibits a similar trend with increasing W as for the obtained Q values. A summary of the obtained and calculated parameter values is given in Table 6.6. Apparently, the geometrical change of the Ti/Au BS influences the motional damping. A reduced bar structure width leads to a reduced damping and a still proper contacting of the graphene sheet, cp. the almost constant $R_{\rm s}$ for different W.

The reason might be the electron injection principle in graphene. Several groups [186, 187] describe the graphene contacting as a *edge-contacted carrier injection*, which significantly reduces the metal-graphene contact resistivity and means, that the metal-

BS width W	$oldsymbol{Q}_{ m s}$	$oldsymbol{R}_{ m p}\left(\Omega ight)$	$oldsymbol{Q}_{\mathrm{p}}$	EAR	$m{k}_{ m eff}~(\%)$
21	242 ± 18	212 ± 8	390 ± 33	0.096	3.06
19	254 ± 18	237 ± 23	451 ± 54	0.107	3.10
17	235 ± 26	243 ± 9	370 ± 19	0.119	2.97
15	234 ± 9	276 ± 21	449 ± 18	0.135	3.06
13	227 ± 19	271 ± 6	404 ± 46	0.156	3.23
11	193 ± 35	292 ± 27	456 ± 71	0.184	3.41
9	228 ± 9	360 ± 22	471 ± 50	0.224	3.39
7	203 ± 20	547 ± 91	626 ± 70	0.287	3.47
5	199 ± 7	630 ± 132	527 ± 43	0.402	3.52
3	216 ± 16	772 ± 135	571 ± 51	0.668	3.71
1	205 ± 23	660 ± 91	788 ± 87	2.002	4.05

Table 6.6: Summary of the obtained and calculated parameter values for different W, whichare plotted in Figure 6.13 and Figure 6.14.



Figure 6.15: Exemplary contour plots of the surface displacement for different BS widths obtained via LDV measurements. Surface displacement depends on the frequency of the applied RF signal. (a) 1.76 GHz at W = 15 µm. (b) 2.14 GHz at W = 15 µm. (c) 1.76 GHz at W = 6 µm.

graphene contact exists rather on graphene edges than on the top of the graphene layer (side-contacted). The reason is the difference of contributing electrons. While for side-contacted graphene only σ -electrons contribute to the cohesion to the metal surface, for edge-contacted graphene unpaired σ -electrons and additional free π -electrons contribute to a stronger cohesion and therefore larger electron transfer. Since the fit parameter R_s integrates all electrode-induced ohmic losses, also the contact resistivity is incorporated. For the investigated resonator samples R_s stays constant for all tested W structures. This finding reveals the assumption, that the electrical contact is mainly dominated by edge-forming defects (little graphene-free areas). Furthermore, the experimentally obtained independence of R_s on W indicates that this edge-contacting occurs either mainly on the BS edge itself or additional metal-covered areas lead to additional contacting, which does not affect the total contact resistivity.

At this point, the edge-to-area ratio (EAR) as a basic geometry parameter comes into play. It simply describes the ration between the total edge length of a metal structure with its coverage area. In order to examine the theoretical considerations from above, the EAR for the investigated resonator samples with varying W are calculated. Due to the chosen metal geometry, the EAR slope describes immaculately the exponential behavior obtained before for R_p and Q_p , cp. Figure 6.14 (a) and Figure 6.13 (b). This finding directly implies that the EAR is a significant key value in describing the efficient contacting of graphene under the requirement of an motionally undamped electrode structure. The effect of a significant change in the resonator performance can be iden-

	1.76 GHz	2.14 GHz
Ti/Au reference	20	_
Ti/Au metal pad	_	10
$15\mu\mathrm{m}~\mathrm{BS}$	20	25
$6\mu\mathrm{m}~\mathrm{BS}$	5	25

Table 6.7: Vibrational out-of-plane surface displacement (in pm, obtained via LDV measurements) for resonant excitations at 1.76 GHz and 2.14 GHz. Comparison of different metallization designs.

tified at the limit of $W = 6 \,\mu m$ for the specific Ti/Au geometry used in this work. The proper contacting together with the minimization of motional losses leads simultaneously to a significant enhancement in the effective coupling coefficient $k_{\rm eff}^2$, which also can be increased exponentially from 3.06% (for $21\,\mu m$ BS) up to 4.05% ($1\,\mu m$), which means an enhancement of 32%. As a result of this, one can conclude that the resonator performance strongly depends on the interplay of the total electrode mass and the proper carrier injection in the graphene layer via edge-contacting. The Ti/Au induced damping effect at $f_{\rm p} = 2.14 \, {\rm GHz}$ is visualized in Figure 6.15, in which contour plots of the surface displacement at an applied RF signal at 1.76 GHz and 2.14 GHz are compared. While still the double excitation at both resonance frequencies is visible for the 15 µm BS, there is a homogeneous surface displacement at only 2.14 GHz for the BS with $W = 6 \,\mu\text{m}$. The same holds for even smaller W. A direct comparison of the actual total surface displacement with the full metallized reference resonators is summarized in Table 6.7. Although, the reference performance with respect to $k_{\text{eff}}^2 = 5.14\%$ cannot be reached yet, these findings directly emphasize the chances of using graphene as a top electrode. Simultaneously, the focus should be brought in a further graphene quality development, regarding the sheet resistivity. With even more conductive graphene sheets, an increasing k_{eff}^2 will outperform the conventional metal electrode. Furthermore, the obtained results clearly open the possibility in a proper adjustment of the on-top metallization structure design, which lifts out even more the properties of graphene as a virtually massless alternative electrode material.

7 Summary of this thesis

The present thesis describes the complete fabrication procedure from the very beginning of the graphene synthesis, the technological optimization and investigation of a reproducible transfer method and finally the characterization of graphene as the top electrode material for SMR-BAW resonators. Due to the main goal of proving the usability of graphene as an ultra light electrode for electroacoustic devices, high-quality requirements exist at every stage of fabrication. Defect-free graphene on a large area is needed during the synthesis procedure, which afterwards needs to be transferred under defect-free conditions onto the AlN target substrate. Finally, the structuring and contacting of the graphene layer needs to be adapted elaborately. Within all three mentioned topics, significant enhancements are achieved, which open a new field of possible applications by a deliberate technology transfer to other research topics. In the following, the main results and findings are summarized in order to give a review to the reader.

With the process optimization of the CVD synthesis method, large-area graphene with a size of $40 \times 40 \text{ mm}^2$ can be grown on Cu foil substrates. Investigations of the influence of the growth parameters reveal optimal conditions, which are strongly reactor specific. The dependence of the graphene quality on the nucleation center density and the growth velocity turned out to be most critical regarding the formation of defects within the graphene layer and multilayer growth. With an adjustment of the process temperature to 980 °C, the H₂/CH₄ flow ratio to 4:1 and the process deposition time to 30 min, homogeneous graphene layers can be synthesized. Raman spectroscopy confirms the high quality by a constantly low D/G peak intensity ratio of below 0.2 and a 2D/G peak ratio of homogeneously larger than 2.0, which indicates single layer growth. These quality criteria are comparable with literature data, however, large-area synthesis is further improved via an elaborated Cu foil pretreatment. In principle, even large graphene layers up to 6 inch could be grown, which was out of focus of this work due to the limited size of the provided SMR structures.

The successful growth process development leads to the next fabrication step, i.e. the wet transfer onto AlN target substrates. For optimal wettability properties of sputtered AlN layers, a plasma pretreatment is applied in order to reduce the contact angle from 48° to 18°. This directly leads to an enhanced desiccating process and bears on the final graphene sheet resistivity $R_{\rm s,GR}$, which can be lowered from several k Ω /sq to constantly below 1 k Ω /sq. With the best value of 350 Ω /sq, which has not been reported before, the graphene transfer on AlN is well comparable with the standardly used Si as the target substrate.

The implementation of a reliable graphene growth and transfer procedure opened the ability of the first ever reported fabrication of AlN-based BAW resonators with graphene-based *active* electrodes. With the replacement of the conventionally applied metal electrodes, the achieved mass reduction of 99.963 % leads to a resonance frequency shift from 1.76 GHz to 2.14 GHz, which is affirmed by simulations as being in accordance to the resonance frequency of pristine undamped AlN for the given resonator geometry. Apart from that, electrical network measurements reveal a parallel quality factor Q_p which is significantly enhanced about a factor of 3.2 compared to the metallized state-of-the-art reference samples. The comb-like metal structure on top of the graphene layer serves as an improved graphene contacting, which results in a maximized total resonator area. The adjustment of the metallization design, i.e. a decrease in the bar structure width, leads to a successful suppression of the metal-induced side resonance at 1.76 GHz and a simultaneous increase of the effective coupling coefficient of about 33%. Here, the edge-to-area ratio (EAR) of the metal structure turned out to be a fundamental indicator, assuming an *edge-contacted carrier injection* which actually dominates the graphene contacting by the metal.

The total experimental procedure clearly reveals the successful usage of graphene as an alternative virtually massless electrode material with the effects of a strong reduction of electrode mass-induced losses, as they were predicted according to the Fuchs-Sondheimer model. The obtained findings highlight the advantages of graphene and also other related conductive 2D materials for alternative electrodes in electroacoustic resonators for radio frequency applications.

7.1 Outlook and future research chances

Apart from the explicit improvements mentioned before, one might think of further improvement potential for future research in the field of resonator and filter structure. With the presented experimental results, the goal of this work, namely the avoidance of electrode mass-induced losses, is achieved. Thinking of the comparably low quality factor at series resonance frequency, which is directly connected to ohmic losses within the graphene layer there are still improvements possible regarding the sheet resistivity of graphene. The reader should keep in mind, the all relevant experiments have been performed with graphene obtaining a $R_{s,GR}$ between 1 and $4 k\Omega$. Lower resistivities, namely $350 \,\Omega/\mathrm{sq}$, were already achieved at a lower scale. In order to further decrease these values, additional graphene doping and the appliance of graphene multistacks can be brought into focus. Some first experiments, which are not reported in detail in the work, reveal promising results, i.e. an additional decrease of the resistivity, by adding gold chloride $AuCl_3$ to the aqueous solution which is used during the graphene wet transfer, elaborated in Chapter 5. Several different approaches are followed, as described in [188]. With some methods, sheet resistivities far below $200 \Omega/\text{sq}$ are achieved [189]. Adopting these results with the presented finding of this work, there is high chance to even improve the obtained effects due to an expected decrease in $R_{\rm s}$.

Another optimization potential lies in the device design, namely in the metallization design of the applied bar structure. Due to technological reasons (EBPVD, using a metal mask), the bar structure width was limited to a minimum of $1 \,\mu$ m. As a promising alternative, the optical lithography rather achieves resolutions below 100 nm, which enables even narrower structure [190]. This leads to the consideration of other more

complex metallization designs, i.e. comb-like structures with narrow bars and a closer positioning to each other. A further increase in $k_{\rm eff}^2$ is expected due to an even better contacting of the underlying graphene layer and a simultaneously low additional metal-induced damping.

Regarding the overall resonator performance, there are research activities ongoing with respect to other piezoelectric materials. A prominent hot topic here is the composite material aluminum scandium nitride (AlScN), which exhibits a much higher piezoelectric coefficient d_{33} , i.e. up to 15%, compared to the AlN [191, 192] used in this work. The chance in this alternative piezoelectric material for electroacoustic devices lies in a resulting higher effective coupling coefficient. Together with a graphene-induced increased quality factor, a novel resonator device structure can be emerged.

Appendix

Appendix A

Determination of the BAW resonance frequencies

In order to determine the quality factor Q according to Equation (2.26), the total impedance Z of the mBVD equivalent circuit needs to be written as $Z = R(\omega) + X(\omega)$. According to Figure 2.6 (b), Z is calculated as

$$Z = R_{\rm s} + \frac{1}{G_{\rm p} + j\omega C_0 + \frac{1}{j\omega L_1 + \frac{1}{j\omega C_1}}} = R_{\rm s} + \frac{1}{G_{\rm p} + j\omega C_0 + \frac{j\omega C_1}{-\omega^2 L_1 C_1 + 1}}$$
$$= R_{\rm s} + \frac{1}{G_{\rm p} + j\omega C_0 + \frac{j\omega C_1}{\alpha}} = R_{\rm s} + \frac{\alpha}{\alpha G_{\rm p} + j\alpha \omega C_0 + j\omega C_1}$$
$$= R_{\rm s} + \frac{\alpha}{\alpha G_{\rm p} + j\alpha \omega C_0 + j\omega \beta C_0} = R_{\rm s} + \frac{\alpha}{\alpha G_{\rm p} + j\omega C_0 (\alpha + \beta)}$$
$$= R_{\rm s} + \frac{\alpha (\alpha G_{\rm p} - j\omega C_0 (\alpha + \beta))}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2} = R_{\rm s} + \frac{\alpha^2 G_{\rm p} - j\omega C_0 \alpha (\alpha + \beta)}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2},$$
(1)

with the real and imaginary parts, $R(\omega)$ and $X(\omega)$, respectively,

$$R(\omega) = R_{\rm s} + \frac{\alpha^2 G_{\rm p}}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2},$$
$$X(\omega) = \frac{-j\omega C_0 \alpha (\alpha + \beta)}{\alpha^2 G_{\rm p}^2 + \omega^2 C_0^2 (\alpha + \beta)^2}.$$

Resonance occurs for $X(\omega) = 0$, resulting in the distinction of two cases

$$\begin{split} X(\omega = \omega_{\rm ph}) &= 0 \Leftrightarrow \omega C_0 \alpha (\alpha + \beta) = 0 \\ 1. \quad \alpha &= 0 \Rightarrow \omega_{\rm s} = \frac{1}{\sqrt{L_1 C_1}} \\ 2. \quad (\alpha + \beta) &= 0 \Rightarrow \omega_{\rm p} \omega_{\rm p} = \frac{1}{\sqrt{L_1 C_1}} \sqrt{1 + \frac{C_1}{C_0}} \Rightarrow \omega_{\rm p} = \omega_{\rm s} \sqrt{1 + \beta} \end{split}$$

Determination of the quality factor Q

The quality factor Q for $\omega_{\rm s}$ and $\omega_{\rm p}$ is defined as in Equation (2.26)

$$Q_{\rm s,p} = \left[\frac{1}{2} \ \omega \left|\frac{d\phi}{d\omega}\right|\right]_{\omega_{\rm s,p}} = \left[\frac{1}{2} \ \omega \frac{1}{R(\omega)} \left|\frac{dX(\omega)}{d\omega}\right|\right]_{\omega_{\rm s,p}},\tag{2}$$

which results in a separate calculation of $R(\omega)$ and $\left|\frac{dX(\omega)}{d\omega}\right|$ with

$$X(\omega) = \frac{-j\omega C_0 \alpha(\alpha + \beta)}{\alpha^2 G_p^2 + \omega^2 C_0^2 (\alpha + \beta)^2} = \frac{u(\omega)}{v(\omega)},$$

$$\frac{dX(\omega)}{d\omega} = \frac{\frac{du(\omega)}{d\omega} \cdot v(\omega) - u(\omega) \cdot \frac{dv(\omega)}{d\omega}}{v(\omega)^2} = \frac{u'(\omega)v(\omega) - u(\omega)v'(\omega)}{v(\omega)^2}.$$
(3)

The respective components $u(\omega)$, $u'(\omega)$ and $v(\omega)$ become

$$\begin{split} u(\omega) &= (-j\omega C_0 + j\omega^3 L_1 C_1 C_0)(1 - \omega^2 L_1 C_1 + \frac{C_1}{C_0}) \\ &= (-j\omega C_0 + j\omega^3 C_0 L_1 C_1) + (j\omega^3 C_0 L_1 C_1 - j\omega^5 C_0 L_1^2 C_1^2) \\ &- j\omega C_0 \frac{C_1}{C_0} + j\omega^3 C_0 L_1 \frac{C_1^2}{C_0} \\ &= -j\omega C_0 + j\omega^3 C_0 L_1 C_1 + j\omega^3 C_0 L_1 C_1 - j\omega^5 C_0 L_1^2 C_1^2 \\ &- j\omega C_1 + j\omega^3 L_1 C_1^2, \end{split}$$

$$u'(\omega) = -jC_0 + 3j\omega^2 C_0 L_1 C_1 + 3j\omega^2 C_0 L_1 C_1 - 5j\omega^4 C_0 L_1^2 C_1^2 - jC_1 + 3j\omega^2 L_1 C_1^2,$$

$$v(\omega) = (1 - \omega^2 L_1 C_1)^2 G_p^2 + \omega^2 C_0^2 (1 - \omega^2 L_1 C_1 + \frac{C_1}{C_0})^2.$$

$Q_{ m s}$ at series resonance $\omega_{ m s}=2\pi f_s$

$$\begin{split} R(\omega = \omega_{\rm s}) &= R_{\rm s} + \frac{\alpha^2 G_{\rm p}}{\alpha^2 G_{\rm p}^2 + \omega_s^2 C_0^2 (\alpha + \beta)^2} \\ &= R_{\rm s} + \frac{(1 - \omega_s^2 L_1 C_1)^2 G_{\rm p}}{(1 - \omega_s^2 L_1 C_1)^2 G_{\rm p}^2 + \omega_s^2 C_0^2 ((1 - \omega_s^2 L_1 C_1) + \frac{C_1}{C_0})^2} \\ &= R_{\rm s} + \frac{(1 - \frac{1}{L_1 C_1} L_1 C_1)^2 G_{\rm p}}{(1 - \omega^2 L_1 C_1)^2 G_{\rm p}^2 + \omega_s^2 C_0^2 ((1 - \omega_s^2 L_1 C_1) + \frac{C_1}{C_0})^2} \\ &= R_{\rm s}, \end{split}$$

$$\begin{split} u(\omega = \omega_{\rm s}) &= -\mathrm{j}\omega_{\rm s}C_0 + \mathrm{j}\omega_{\rm s}C_0 + \mathrm{j}\omega_{\rm s}C_0 - \mathrm{j}\omega_{\rm s}C_1 + \mathrm{j}\omega_{\rm s}C_1, \\ &= 0 \end{split}$$

$$u'(\omega = \omega_{\rm s}) = -jC_0 + 3jC_0 + 3jC_0 - 5jC_0 - jC_1 + 3jC_1$$

= 2jC₁,

$$v(\omega = \omega_{\rm s}) = (1-1)^2 G_{\rm p}^2 + \frac{C_0^2}{L_1 C_1} \left(1 - 1 + \frac{C_1}{C_0}\right)^2 = \frac{C_0^2}{L_1 C_1} \left(\frac{C_1^2}{C_0^2}\right) = \frac{C_1}{C_0}.$$

This leads to

$$\left[\left| \frac{dX(\omega)}{d\omega} \right| \right]_{\omega = \omega_{\mathrm{s}}} = \frac{u'(\omega) \cdot v(\omega) - u(\omega) \cdot v'(\omega)}{v(\omega)^2} = \frac{2\mathrm{j}C_1 \cdot \frac{C_1}{C_0}}{\frac{C_1^2}{C_0^2}} = 2\mathrm{j}L_1 = \frac{2}{\omega_{\mathrm{s}}^2 C_1},$$

and the resulting $Q_{\rm s}$ becomes

$$Q(\omega = \omega_{\rm s}) = \left[\frac{1}{2} \; \omega \frac{1}{R(\omega)} \cdot \left| \frac{dX(\omega)}{d\omega} \right| \right]_{\omega = \omega_{ph}} = \frac{1}{2} \; \frac{1}{\sqrt{L_1 C_1}} \frac{1}{R_{\rm s}} \frac{2}{\frac{1}{L_1 C_1} C_1} = \frac{1}{R_{\rm s}} \sqrt{\frac{L_1}{C_1}}.$$
 (4)

 $Q_{
m p}$ at series resonance $\omega_{
m p}=2\pi f_p$

$$\begin{split} R(\omega = \omega_{\rm p}) &= R_{\rm s} + \frac{\alpha^2 G_{\rm p}}{\alpha^2 G_{\rm p}^2 + \omega_p^2 C_0^2 (\alpha + \beta)^2} \\ &= R_{\rm s} + \frac{(1 - \frac{1}{L_1 C_1} (1 + \beta) L_1 C_1)^2 G_{\rm p}}{(1 - \frac{1}{L_1 C_1} (1 + \beta) L_1 C_1)^2 G_{\rm p}^2 + \omega^2 C_0^2 (1 - (1 + \beta) + \beta)^2} \\ &= R_{\rm s} + \frac{(1 - (1 + \beta))^2 G_{\rm p}}{(1 - (1 + \beta))^2 G_{\rm p}^2 + 0} \\ &= R_{\rm s} + \frac{1}{G_{\rm p}}, \end{split}$$

$$\begin{split} u(\omega = \omega_{\rm p}) &= -j\omega_{\rm p}C_0 + j\omega_{\rm p}C_0(1+\beta) + j\omega_{\rm p}C_0(1+\beta) - j\omega_{\rm p}C_0(1+\beta)^2 - j\omega_{\rm p}C_1 \\ &+ j\omega_{\rm p}C_1(1+\beta) \\ &= -j\omega_{\rm p}C_0 + j\omega_{\rm p}C_0 + j\omega_{\rm p}C_0\beta + j\omega_{\rm p}C_0 + j\omega_{\rm p}C_0\beta \\ &- j\omega_{\rm p}C_0(1+2\beta+\beta^2) - j\omega_{\rm p}C_1 + j\omega_{\rm p}C_1(1+\beta) \\ &= -j\omega_{\rm p}\beta^2 - j\omega_{\rm p}C_1 + j\omega_{\rm p}C_1\beta \\ &= 0, \end{split}$$

$$\begin{split} u'(\omega &= \omega_{\rm p}) = -{\rm j}C_0 + 3{\rm j}(1+\beta)C_0 + 3{\rm j}(1+\beta)C_0 - 5{\rm j}(1+\beta)^2C_0 \\ &- {\rm j}C_1 + 3{\rm j}(1+\beta)C_1 \\ &= -{\rm j}C_0 + 3{\rm j}C_0 + 3{\rm j}C_1 + 3{\rm j}C_0 + 3{\rm j}C_1 - 5{\rm j}C_0 - 10{\rm j}C_1 - 5{\rm j}\frac{C_1^2}{C_0} \\ &- {\rm j}C_1 + 3{\rm j}C_1 + 3{\rm j}\frac{C_1^2}{C_0}, \\ &= -2{\rm j}C_1 - 2{\rm j}\frac{C_1^2}{C_0} \end{split}$$

$$v(\omega = \omega_{\rm p}) = (1 - (1 + \beta))^2 G_{\rm p}^2 + \frac{(1 + \beta)C_0^2}{L_1 C_1} \left(1 - (1 + \beta) + \frac{C_1}{C_0}\right)^2 = \beta^2 G_{\rm p}^2 = \frac{C_1^2}{C_0^2} G_{\rm p}^2.$$

This leads to

$$\begin{split} \left[\left| \frac{dX(\omega)}{d\omega} \right| \right]_{\omega=\omega_{\rm p}} &= \frac{\left(-2\mathrm{j}C_1 - 2\mathrm{j}\frac{C_1^2}{C_0} \right)\frac{C_1^2}{C_0}G_{\rm p}^2}{\left(\frac{C_1^2}{C_0^2}G_{\rm p}^2\right)^2} = \frac{-2\mathrm{j}C_1 - 2\mathrm{j}\frac{C_1^2}{C_0}}{\frac{C_1^2}{C_0^2}G_{\rm p}^2} \\ &= \frac{-2\mathrm{j}C_1\left(1 + \frac{C_1}{C_0}\right)}{\frac{C_1}{C_0}\frac{C_1}{C_0}G_{\rm p}^2} = \frac{2C_0\left(1 + \beta\right)}{\beta G_{\rm p}^2} \end{split}$$

and the resulting $Q_{\rm p}$ becomes

$$Q(\omega = \omega_{\rm p}) = \frac{1}{2} \,\omega_{\rm p} \left(\frac{1}{R_{\rm s} + \frac{1}{G_{\rm p}}}\right) \frac{2C_0}{G_{\rm p}^2} \cdot \frac{\beta + 1}{\beta} = \frac{\omega_{\rm p}}{G_{\rm p}} \frac{C_0 + C_1}{\beta} = \omega_{\rm p} \omega_{\rm p} R_{\rm p} \frac{C_1 + C_0}{C_1} C_0.$$
(5)

Appendix B

Tight binding approach – calculation of the transfer and overlap matrix elements

The transfer and overlap matrices \mathcal{H} and \mathcal{S} , which were introduced already in Chapter 3 Equation (3.9), are given as

$$\begin{aligned} \mathcal{H} &= \begin{pmatrix} \langle \Phi_{\mathrm{A}} | \mathcal{H} | \Phi_{\mathrm{A}} \rangle & \langle \Phi_{\mathrm{A}} | \mathcal{H} | \Phi_{\mathrm{B}} \rangle \\ \langle \Phi_{\mathrm{B}} | \mathcal{H} | \Phi_{\mathrm{A}} \rangle & \langle \Phi_{\mathrm{B}} | \mathcal{H} | \Phi_{\mathrm{B}} \rangle \end{pmatrix} = \begin{pmatrix} \mathcal{H}_{\mathrm{AA}} & \mathcal{H}_{\mathrm{AB}} \\ \mathcal{H}_{\mathrm{BA}} & \mathcal{H}_{\mathrm{BB}} \end{pmatrix}, \\ \mathcal{S} &= \begin{pmatrix} \langle \Phi_{\mathrm{A}} | \Phi_{\mathrm{A}} \rangle & \langle \Phi_{\mathrm{A}} | \Phi_{\mathrm{B}} \rangle \\ \langle \Phi_{\mathrm{B}} | \Phi_{\mathrm{A}} \rangle & \langle \Phi_{\mathrm{B}} | \Phi_{\mathrm{B}} \rangle \end{pmatrix} = \begin{pmatrix} \mathcal{S}_{\mathrm{AA}} & \mathcal{S}_{\mathrm{AB}} \\ \mathcal{S}_{\mathrm{BA}} & \mathcal{S}_{\mathrm{BB}} \end{pmatrix}. \end{aligned}$$

In order to determine the eigenenergies, the matrix elements \mathcal{H} and \mathcal{S} need to be calculated first. According to Equation (3.11), the diagonal transfer and overlap matrix elements are given as

$$\mathcal{H}_{AA}(r) = \frac{1}{N} \sum_{R,R'} e^{j\mathbf{k}(\mathbf{R}-\mathbf{R}')} \langle \phi_{A}(r-R) | \mathcal{H} | \phi_{A}(r-R') \rangle$$

$$= \frac{1}{N} \sum_{R=R'} \epsilon_{2p} + \frac{1}{N} \sum_{R'=R-\sqrt{3}a} e^{\pm jka} \langle \phi_{A}(r-R) | \mathcal{H} | \phi_{A}(r-R+\sqrt{3}a) \rangle$$

$$+ \frac{1}{N} \sum_{R'=R-2\sqrt{3}a} \dots = \epsilon_{2p} = \mathcal{H}_{BB}(r) ,$$

$$\begin{aligned} \mathcal{S}_{\mathrm{AA}}\left(r\right) &= \frac{1}{N} \sum_{R,R'} e^{j\mathbf{k}(\mathbf{R}-\mathbf{R}')} \langle \phi_{\mathrm{A}}(r-R) | \phi_{\mathrm{A}}(r-R') \rangle \\ &= \frac{1}{N} \sum_{R'=R} \epsilon_{2\mathrm{p}} + \frac{1}{N} \sum_{R'=R-\sqrt{3}a} e^{\pm jka} \langle \phi_{\mathrm{A}}(r-R) | \phi_{\mathrm{A}}(r-R+\sqrt{3}a) \rangle \\ &+ \frac{1}{N} \sum_{R'=R-2\sqrt{3}a} \ldots = 1 = \mathcal{S}_{\mathrm{BB}}\left(r\right), \end{aligned}$$

by considering the nearest-neighbor approximation, which means an energy contribution of only one C atom at $\mathbf{R} = \mathbf{R}'$.

The off-diagonal matrix element consists of three nearest-neighbor atoms B relative to an atom A with the vectors (cp. Figure 3.3 (a) and Equation (3.4)) and are calculated as

$$\mathcal{H}_{AB}(r) = \frac{1}{N} \sum_{\mathbf{R},\mathbf{R}'} e^{j\mathbf{k}(\mathbf{R}-\mathbf{R}')} \langle \phi_A(r-R) | \mathcal{H} | \phi_B(r-R') \rangle, \quad (i = 1, 2, 3)$$
$$= \sum_{\mathbf{R}'=\mathbf{R}-\mathbf{R}_i} e^{j\mathbf{k}\mathbf{R}_i} \langle \phi_A(r-R) | \mathcal{H} | \phi_B(r-R-R_i) \rangle$$
$$= (e^{j\mathbf{k}\mathbf{R}_1} + e^{j\mathbf{k}\mathbf{R}_2} + e^{j\mathbf{k}\mathbf{R}_3}) \langle \phi_A(r-R) | \mathcal{H} | \phi_B(r-R+a) \rangle$$
$$= f(\mathbf{k}) \cdot t = \mathcal{H}_{BA}^*(r),$$

$$\mathcal{S}_{AB}(r) = (e^{j\mathbf{kR_1}} + e^{j\mathbf{kR_2}} + e^{j\mathbf{kR_3}}) \quad \langle \phi_A(r-R) | \phi_B(r-R+a) \rangle$$
$$= f(\mathbf{k}) \cdot s = \mathcal{S}^*_{BA}(r) ,$$

with the so called transfer and overlap integrals

$$t = \langle \phi_{\rm A}(r-R) | \mathcal{H} | \phi_{\rm B}(r-R+a) \rangle,$$
$$s = \langle \phi_{\rm A}(r-R) | \phi_{\rm B}(r-R+a) \rangle.$$

The transfer and overlap matrices can then be written as

$$\mathcal{H} = \begin{pmatrix} \epsilon_{2p} & tf(\mathbf{k}) \\ tf^*(\mathbf{k}) & \epsilon_{2p} \end{pmatrix}, \qquad \mathcal{S} = \begin{pmatrix} 1 & sf(\mathbf{k}) \\ sf^*(\mathbf{k}) & 1 \end{pmatrix}.$$
(6)

The solution of the secular equation

With Equation (6), the secular equation appears to be

$$det(\mathcal{H} - E\mathcal{S}) = det\left(\begin{pmatrix}\epsilon_{2p} & t \cdot f(\mathbf{k}) \\ t \cdot f^*(\mathbf{k}) & \epsilon_{2p}\end{pmatrix} - E \cdot \begin{pmatrix}1 & s \cdot f(\mathbf{k}) \\ s \cdot f^*(\mathbf{k}) & 1\end{pmatrix}\right)$$
$$= det\begin{pmatrix}\epsilon_{2p} - E & tf - sEf \\ tf^* - sEf^* & \epsilon_{2p} - E\end{pmatrix} \stackrel{!}{=} 0.$$

By inserting the vector coordinates of Equation (3.4) the complex function $f(\mathbf{k})$ and $f^*(\mathbf{k})$ can be further simplified to

$$\begin{aligned} f(\mathbf{k}) &= e^{j\mathbf{k}\mathbf{R}_{1}} + e^{j\mathbf{k}\mathbf{R}_{2}} + e^{j\mathbf{k}\mathbf{R}_{3}} \\ &= e^{jk_{x}\frac{a}{2}} \cdot e^{jk_{y}\frac{\sqrt{3}a}{2}} + e^{jk_{x}\frac{a}{2}} \cdot e^{-jk_{y}\frac{\sqrt{3}a}{2}} + e^{jk_{x}a} \\ &= 2e^{jk_{x}\frac{a}{2}}\cos\left(k_{y}\frac{\sqrt{3}a}{2}\right) + e^{-jk_{x}a} \\ \iff \quad f^{*}(\mathbf{k}) &= 2e^{-jk_{x}\frac{a}{2}}\cos\left(k_{y}\frac{\sqrt{3}a}{2}\right) + e^{jk_{x}a}. \end{aligned}$$

The solution of the determinant Equation (7) leads to the energy eigenstates as follows

$$det \begin{pmatrix} \epsilon_{2p} - E & tf - sEf \\ tf^* - sEf^* & \epsilon_{2p} - E \end{pmatrix} \stackrel{!}{=} 0$$

$$\iff (\epsilon_{2p} - E)^2 - (t - sE)^2 \cdot ff^* \stackrel{!}{=} 0$$

$$\iff \epsilon_{2p}^2 - 2\epsilon_{2p}E + E^2 - (t^2 - 2tsE + s^2E^2) \cdot ff^* \stackrel{!}{=} 0$$

$$\iff \epsilon_{2p}^2 - 2\epsilon_{2p}E + E^2 - t^2ff^* + 2tsEff^* - s^2E^2ff^* \stackrel{!}{=} 0$$

$$\iff (1 - s^2ff^*)E^2 + (2tsff^* - 2\epsilon_{2p})E + \epsilon_{2p}^2 - t^2ff^* \stackrel{!}{=} 0$$

$$\begin{array}{l} \Longrightarrow \quad E^{\pm} = \frac{-(2tsff^{*} - 2\epsilon_{2p}) \pm \sqrt{(2tsff^{*} - 2\epsilon_{2p})^{2} - 4(1 - s^{2}ff^{*})(\epsilon_{2p}^{2} - t^{2}ff^{*})}}{2(1 - s^{2}ff^{*})} \\ = \frac{-(2tsff^{*} - 2\epsilon_{2p}) \pm \sqrt{-8tsff^{*}\epsilon_{2p} + 4\epsilon_{2p}^{2} - 4\epsilon_{2p}^{2} + 4s^{2}ff^{*}\epsilon_{2p}^{2} + 4t^{2}ff^{*}}}{2(1 - s^{2}ff^{*})} \\ = \frac{-(2tsff^{*} - 2\epsilon_{2p}) \pm 2\sqrt{ff^{*}}\sqrt{(s\epsilon_{2p} - t)^{2}}}{2(1 - s^{2}ff^{*})} = \frac{\epsilon_{2p} - tsff^{*} \pm (s\epsilon_{2p} - t)\sqrt{ff^{*}}}{1 - s^{2}ff^{*}} \\ = \frac{\epsilon_{2p} - tsff^{*} \pm s\epsilon_{2p}\sqrt{ff^{*}} \mp t\sqrt{ff^{*}}}{1 - s^{2}ff^{*}} = \frac{\epsilon_{2p}(1 \pm s\sqrt{ff^{*}}) \mp t\sqrt{ff^{*}}(1 \pm s\sqrt{ff^{*}})}{(1 - \sqrt{ff^{*}})(1 + \sqrt{ff^{*}})} \\ \Longrightarrow \quad E^{\pm} = \frac{\epsilon_{2p} \mp t\sqrt{|f(\mathbf{k})|^{2}}}{1 \mp s\sqrt{|f(\mathbf{k})|^{2}}} = \frac{\epsilon_{2p} \mp t\omega(\mathbf{k})}{1 \mp s\omega(\mathbf{k})}, \end{array}$$

with the complex function

$$\omega\left(\mathbf{k}\right) = \sqrt{|f\left(\mathbf{k}\right)|^{2}} = \left[4e^{jk_{x}\frac{a}{2} - jk_{x}\frac{a}{2}}\cos^{2}\left(k_{y}\frac{\sqrt{3}}{2}a\right) + 2e^{jk_{x}\frac{a}{2}}\cos\left(k_{y}\frac{\sqrt{3}}{2}a\right)e^{jk_{x}a} + e^{-jk_{x}a}\left(2e^{-jk_{x}\frac{a}{2}}\cos\left(k_{y}\frac{\sqrt{3}}{2}a\right)\right) + 1\right]^{\frac{1}{2}} = \sqrt{1 + 4\cos\left(k_{x}\frac{3}{2}a\right)\cos\left(k_{y}\frac{\sqrt{3}}{2}a\right) + 4\cos^{2}\left(k_{y}\frac{\sqrt{3}}{2}a\right)}.$$
(7)

Equation (7) describes the full graphene band structure for the π -electrons. Close to the Dirac points **K** and **K**', ω (**k**) at **k** = **K**[±] + **q** with **K**⁺ = K and **K**⁻ = K' the band structure is calculated as

$$\begin{split} \omega(\mathbf{K}^{\pm} + \mathbf{q}) &= \left[1 + 4\cos\left(\frac{3a}{2}\left(K_x^{\pm} + q_x\right)\right) \cos\left(\frac{\sqrt{3a}}{2}\left(K_y^{\pm} + q_y\right)\right) \right]^{\frac{1}{2}} \\ &+ 4\cos^2\left(\frac{\sqrt{3a}}{2}\left(K_y^{\pm} + q_y\right)\right) \right]^{\frac{1}{2}} \\ &= \left[1 + 4\cos\left(\pi + \frac{3a}{2}q_x\right) \cos\left(\pm\frac{\pi}{3} + \frac{\sqrt{3a}}{2}q_y\right) + 4\cos^2\left(\pm\frac{\pi}{3} + \frac{\sqrt{3a}}{2}q_y\right) \right]^{\frac{1}{2}} \\ &= \left[1 + 4\left[\cos\left(\pi\right)\cos\left(\frac{3a}{2}q_x\right) - \sin\left(\pi\right)\sin\left(\frac{3a}{2}q_x\right) \right]\cos\left(\pm\frac{\pi}{3} + \frac{\sqrt{3a}}{2}q_y\right) \right] \\ &+ 4\left[\cos\left(\frac{\pi}{3}\right)\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \sin\left(\frac{\pi}{3}\right)\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right]^{\frac{1}{2}} \\ &= \left[1 - 4\cos\left(\frac{3a}{2}q_x\right) \left[\cos\left(\frac{\pi}{3}\right)\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \sin\left(\frac{\pi}{3}\right)\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right] \\ &+ 4\left[\frac{1}{2}\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \frac{\sqrt{3}}{2}\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right]^{2} \right]^{\frac{1}{2}} \\ &= \left[1 - 4\cos\left(\frac{3a}{2}q_x\right) \left[\frac{1}{2}\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \frac{\sqrt{3}}{2}\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right] \\ &+ 4\left[\frac{1}{2}\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \frac{\sqrt{3}}{2}\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right]^{2} \right]^{\frac{1}{2}} \\ &= \left[1 - 2\cos\left(\frac{3a}{2}q_x\right)\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \pm 2\sqrt{3}\cos\left(\frac{3a}{2}q_x\right)\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \\ &+ \left[\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \sqrt{3}\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \right]^{2} \right]^{\frac{1}{2}}. \end{split}$$
(8)

For $\mathbf{q} \to 0$ a second order expansion of Equation (8) leads to

$$\begin{bmatrix} 1 - 2\cos\left(\frac{3a}{2}q_x\right)\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \pm 2\sqrt{3}\cos\left(\frac{3a}{2}q_x\right)\sin\left(\frac{\sqrt{3a}}{2}q_y\right) \\ + \left(\cos\left(\frac{\sqrt{3a}}{2}q_y\right) \mp \sqrt{3}\sin\left(\frac{\sqrt{3a}}{2}q_y\right)\right)^2 \right]^{\frac{1}{2}} \\ \approx \left[1 - 2\left(1 - \frac{\left(\frac{3a}{2}q_x\right)^2}{2}\right) \left(1 - \frac{\left(\frac{\sqrt{3a}}{2}q_y\right)^2}{2}\right) \\ \pm 2\sqrt{3}\left(1 - \frac{\left(\frac{3a}{2}q_x\right)^2}{2}\right) - \left(\frac{\sqrt{3}}{2}aq_y - \frac{\left(\frac{\sqrt{3a}}{2}q_y\right)^3}{6}\right) \\ + \left(\left(1 - \frac{\left(\frac{\sqrt{3a}}{2}q_y\right)^2}{2}\right) \mp \sqrt{3}\left(\frac{\sqrt{3a}}{2}q_y - \frac{\left(\frac{\sqrt{3a}}{2}q_y\right)^3}{6}\right)\right)^2 \right]^{\frac{1}{2}} \\ = \left[\left(\frac{\sqrt{3}}{2}aq_y\right)^2 + \left(\frac{3}{2}aq_x\right)^2 \pm 3aq_y - \left(\frac{\sqrt{3}}{2}aq_y\right)^2 \mp 3aq_y + \left(\frac{3}{2}aq_y\right)^2 + \mathcal{O}(q^3) + \dots \right]^{\frac{1}{2}} \\ = \left[\left(\frac{3}{2}aq_x\right)^2 + \left(\frac{3}{2}aq_y\right)^2 + \mathcal{O}(q^3) + \dots \right]^{\frac{1}{2}} \\ = \left[\left(\frac{3}{2}aq_x\right)^2\right]^{\frac{1}{2}} = \frac{3}{2}aq. \tag{9}$$

Given this mathematical description of $\omega(\mathbf{k})$, the final solution of the secular equation, as shown in Equation (3.14), is determined by inserting into Equation (3.13) as

$$E^{\pm}(\mathbf{q}) = \pm \frac{3}{2}taq = \pm v_{\mathrm{F}}q.$$
(10)

This proves the linear dependence on \mathbf{q} , which is the momentum relatively measured to the Dirac points \mathbf{K} and \mathbf{K}' .

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Publications

Some experimental data and figures have appeared previously in the following publications.

Professional journals

Marius Knapp, R. Hoffmann, V. Cimalla and O. Ambacher; Wettability Investigations and Wet Transfer Enhancement of Large-Area CVD-Graphene on Aluminum Nitride Nanomaterials 2017, volume 7, issue 8, p. 226; doi: 10.3390/nano7080226

Marius Knapp, R. Hoffmann, V. Lebedev, V. Cimalla and O. Ambacher,, Graphene as an active virtually massless top electrode for RF solidly mounted bulk acoustic wave (SMR-BAW) resonators Nanotechnology 2018, volume 29, number 10; doi: 10.1088/1361-6528/aaa6bc

Conference contributions

Proceeding paper

Marius Knapp, V. Lebedev, V. Cimalla and O. Ambacher; Metallization Design Investigations for Graphene as a Virtually Massless Electrode Material for 2.1 GHz Solidly Mounted (BAW-SMR) Resonators IEEE International Frequency Control Symposium 2018

Oral presentations

Marius Knapp, V. Cimalla, D. Schwantuschke, V. Lebedev, O. Ambacher and R. Hoffmann;

Graphene as virtually massless top electrode for RF bulk acoustic wave (BAW) resonators Graphene2017 Conference, Barcelona-Spain, March 28-31, 2017

Poster presentations

Marius Knapp, K. Holc, V. Lebedev, O. Ambacher and R. Hoffmann; Floating transfer optimization of large-area CVD graphene on AIN as advanced electrodes for BAW devices Graphene2016 Conference, Genoa-Italy, April 19-22, 2016

Marius Knapp, V. Lebedev, V. Cimalla and O. Ambacher; Metallization Design Investigations for Graphene as a Massless Electrode Material for 2.1 GHz

BAW-SMR

IEEE International Frequency Control Symposium 2018, Squaw Creek-California, May 21-24, 2018

Patents

Funktionsoptimierendes Metallisierungsdesign für Graphenelektroden; Patent in registration process, reference number:

Other publications

Thomas Rachow, Stefan Reber, Stefan Janz, Marius Knapp and Nena Milenkovic; Degradation of silicon wafers at high temperatures for epitaxial deposition Energy Science and Engineering 2016, volume 4, number 5, p. 344-351; doi: 10.1002/ese3.130

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Mechanical and electrical losses strongly determine the performance characteristic of Bulk Acoustic Wave (BAW) resonators. The focus of this work lies in the deeper investigation of extrinsic electrode-induced losses. Here, mainly viscous and ohmic losses play a role due to an electrode's specific mass and limited conductivity. A conflict of objectives lies here in the requirement of ideally massless and highly conductive materials, which commonly used metal electrodes suffer from due to their comparably high mass density. The chance to overcome this problem lies in the use of graphene as a2D virtually massless carbonic layer with remarkable electronic properties. This work investigates the first time graphene as an active top electrode material for solidly mounted Bulk Acoustic Wave resonators. Here, a process development from the graphene synthesis, a specifically elaborated graphene transfer technique and a subsequent successful fabrication of vvorking BAW resonators with an optimized graphene-based electrode design are reported. In a nutshell, the findings of this work strongly highlight the advantages of graphene and possibly other 2D materials as an alternative electrode material in electroacoustic resonators for radio frequency devices.

