

Chemical and structural study of electrically passivating Al₂O₃/Si interfaces prepared by atomic layer deposition

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Aluminum oxide (Al₂O₃) layers, prepared by atomic layer deposition (ALD), provide excellent surface passivation properties on crystalline Si surfaces, which are of major importance for photovoltaic applications. Beyond the chemical passivation by reduction of the electronic surface state density, a supportive field effect passivation mechanism emerges at the Al₂O₃/Si interface. The atomic origin of the fixed negative charges that are responsible for the field effect is currently under discussion. In this contribution, thin layers of Al₂O₃ with thicknesses ranging from the submonolayer region to several nanometers have been grown on Si substrates by means of thermal ALD. The principle elements of the samples have been quantified by x-ray photoelectron spectroscopy as a function of the film thickness. Changes at the interface upon thermal annealing have been investigated in detail. After the first few ALD cycles an imperfect Al₂O₃ layer is found together with the formation of an ultrathin SiO_x interlayer. Continued deposition leads to stoichiometric Al₂O₃ growth. Within the first ~1 nm from the Si interface, additional O (“excess O”), surpassing the Al₂O₃ and SiO₂ stoichiometry, is observed. The excess O does not completely react with the Si surface to SiO₂ during thermal annealing. Therefore, interstitial O in near-interface Al₂O₃ is suggested to provide the fixed negatively charged states. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4704601]

I. INTRODUCTION

The properties of aluminum oxide (Al₂O₃) layers grown by atomic layer deposition (ALD) are of major scientific interest due to their various applications. The ALD process itself for Al₂O₃ films on Si has been widely investigated with a strong focus on the initial growth.^{1,2} The structural properties of the Al₂O₃/Si interface have been studied in detail by surface analytical methods for the application of high-k materials in microelectronics.^{3,4} Lately, it has been found that Al₂O₃ may provide excellent surface passivation on Si for photovoltaic applications.^{5,6}

The level of electrical surface passivation has a high impact on the efficiency of crystalline Si solar cells. This is because the surface remains a limiting factor to the effective charge carrier lifetime as thin Si wafers with comparatively good material quality are used for current state-of-the-art solar cells.⁷ Beyond the chemical passivation by reduction of the electronic surface state density,⁸ the superior surface passivation properties of Al₂O₃ are explained by an additional field effect.^{9,10} This electric field is caused by a high fixed negative charge density within ~1 nm from the Si interface.¹¹ The structural interface properties leading to the

formation of negatively charged states at the interface are the subject of the actual scientific discussion.

The formation of a thin SiO₂ interlayer that occurs during thermal annealing of Al₂O₃ is known to play a key role for the passivation mechanism. Until now, different theories for the physical origin of the near-interface fixed charges have been developed, ranging from Al–O–Si dipoles¹² to the proposition that interstitial O atoms or Al vacancies may be responsible for the field effect.¹³ In a recent paper, Werner *et al.* have proposed a high O/Al ratio to be related to the high negative charge density at the interface.¹⁴ However, the atomic location, i.e., nature of the charge, is not addressed sufficiently yet.

Within the present paper we target the question of stoichiometry and O coordination at the interface as a function of the layer thickness and annealing procedure. For this purpose we apply a particular combination of subsequent thermal ALD and x-ray photoelectron spectroscopy (XPS). The chemical and structural interface properties are deduced from the thickness-dependent elemental XPS intensities and chemical shifts. Based on these results, a model for the formation of the charges within the atomic structure is presented.

II. EXPERIMENT

Pieces from a polished 350 μm thick Czochralski, (100), 4 Ω cm *p*-type Si wafer (as manufactured) were used as

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substrates. Native silicon oxides were individually stripped by hydrofluoric acid (HF) directly before insertion into the ALD chamber. Al_2O_3 films were grown in a TFS 200 ALD system from Beneq. The thermal ALD process was cycled with 200 ms H_2O and 200 ms trimethylaluminum (TMA) precursor pulses and N_2 purge times of 3 s after each pulse at a reactor temperature of 220°C , which yields a constant growth rate of $1.02 \text{ \AA}$ per ALD cycle after initial growth stabilization.^{1,3} We coated two samples each by 125, 50, 30, 15, 10, 7, 5, 3, 2, and 1 full ALD cycles. Two similarly treated Si pieces without coating serve as reference samples (0 ALD cycles). One of the two obtained sample series was thermally annealed for 30 min at 400°C in low pressure Ar atmosphere directly after the last ALD run. All samples were temporarily stored in a sample box at atmosphere and introduced into high vacuum within 40 min after the last preparation step. We performed XPS measurements at a Kratos Axis Ultra instrument, equipped with a monochromatic Al $K\alpha$ x-ray source. High-resolution photoelectron spectra of O $1s$, C $1s$, Si $2p$, and Al $2p$ peaks were acquired with a pass energy of 5 eV under variation of the sample tilt angle (0° , 45° , and 60° with respect to the sample normal). Additionally, survey spectra of each sample were recorded with a pass energy of 40 eV before and after a short sputter step (500 eV Ar^+ , $\sim 10^{-2} \text{ As/cm}^2$) with the intention to evaluate the effect of surface contaminations. Shirley background subtraction was applied for determination of the peak areas.

III. RESULTS

A. XPS characterization of thin Al_2O_3 films on Si

The specific characteristics of the XPS method (such as adjustable surface sensitivity, information depths up to 10 nm for common inorganic materials, quantitative elemental composition, and information about chemical bonds) allow for its use for investigations of the interface between thin layers and Si substrates. [The term “information depth” refers to the depth range from which significant XPS intensity can be collected. The number of photoelectrons (“signal”) that can be collected from a certain depth is determined by the Beer–Lambert attenuation law, i.e., it is not constant over the whole information depth.] The sample preparation (ALD and thermal annealing) took place in separate rooms. Therefore, a possible environmental influence was monitored by means of reference Si samples without any coating. These samples ran alongside the coated. Figure 1 shows the Si $2p$ spectra of both reference samples. The black curve is representative of the sample without coating and annealing, introduced into the XPS high vacuum about 40 min after the HF dip. There is no (“chemically”) shifted peak of Si species within higher oxidation states (Si_{ox}) measurable, indicating vanishing bonding between Si and O at the surface. Even at higher emission angles up to 60° from surface normal, there is no Si_{ox} feature visible. In contrast, the annealed Si sample shows a distinct feature attributed to the Si^{4+} oxidized state of Si (dashed curve).¹⁵ This surface oxidation must have occurred during the annealing process while the hot sample was briefly exposed to air due to sample handling.

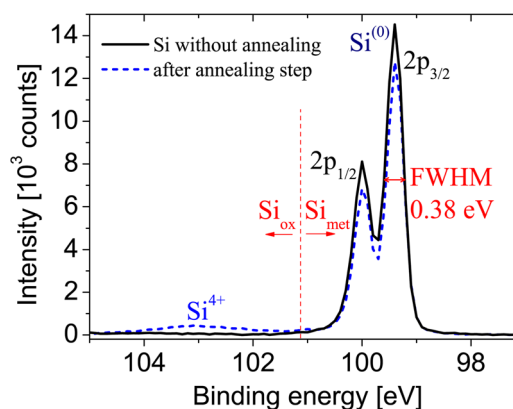


FIG. 1. (Color online) High-resolution XPS spectra of the Si $2p$ photoelectron peak (after background subtraction) at blank Si substrates after HF dip, without further treatment (black, solid line) and after standard annealing step (blue, dashed line).

Nevertheless, both samples exhibit distinct O and C peaks (not shown here), yielding that surface contaminations are present. The measured intensities of O and C were reduced to about 25% (samples without ALD film) after 30 s sputtering (500 eV Ar^+ , $\sim 1 \times 10^{17} \text{ ions/cm}^2$). It is deduced that mainly physisorbed H_2O and organic residuals are responsible for these apparent surface contaminants. (H cannot be measured by means of XPS.)

The XPS data were acquired under the same conditions for all samples. The elemental composition of the layer structures is evaluated as a function of the number of ALD cycles from survey spectra using the peak areas of O $1s$, C $1s$, Si $2p$, and Al $2p$ photoelectrons. The spectra in Fig. 2 show Si $2p$ and Al $2p$ peaks exemplarily for 30 and 15 Al_2O_3 ALD cycles (without annealing). In contrast to Fig. 1, these are sections from wide scan survey spectra with less resolution and higher count rates. It is clearly visible that an increase of the Al signal is correlated with a decrease of the Si signal when the ALD cycle number is scaled from 15 to 30. The Si signal includes the shifted Si oxide (Si_{ox}) peak that must arise from the interface between Al_2O_3 and Si substrate. The Si_{ox} peak is much more pronounced for the sample with the thinner Al_2O_3 layer. Since the Al $2p$ signal

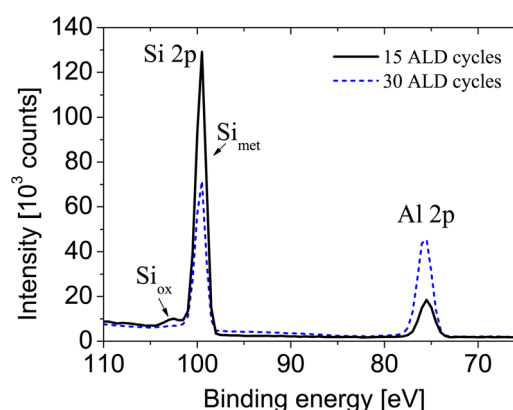


FIG. 2. (Color online) Raw XPS spectra in the energy range of Si $2p$ and Al $2p$, acquired at samples with 15 (black, solid line) and 30 (blue, dashed line) ALD cycles without subsequent annealing.

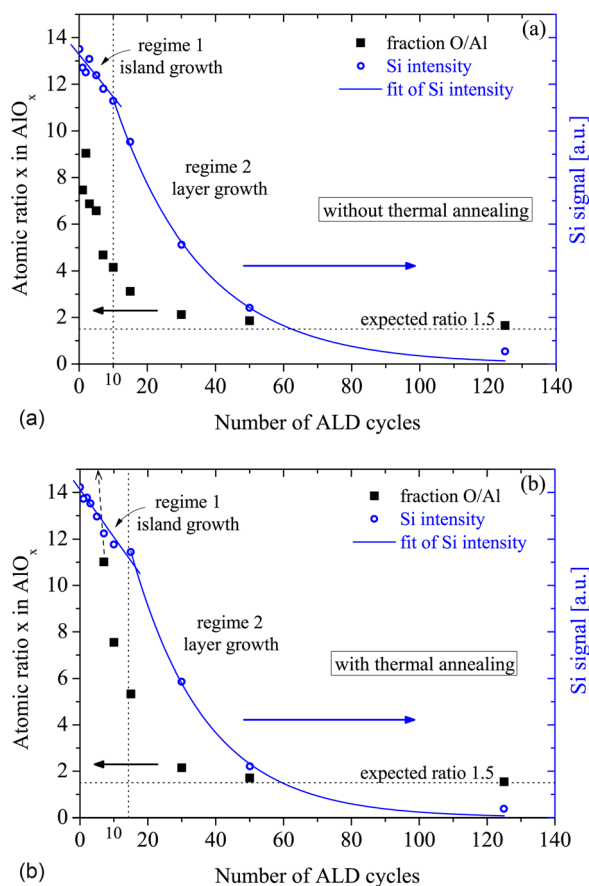


Fig. 3. (Color online) Atomic ratio O/Al (black solid squares), the theoretical limit value expected for stoichiometric bulk Al_2O_3 (dashed horizontal line), and the relative Si signal (blue open circles) as functions of the ALD cycle number for as-grown (a), and annealed (b) Al_2O_3 samples. Two growth regimes are identified and separated by the vertical dashed line.

shows no resolvable double peak we conclude that Al exists only in the oxidized state within the whole Al_2O_3 layer and at the interface to Si.^{3,4,14}

B. Stoichiometry of the layers

The graphs in Fig. 3 show the Si substrate signal damping (open circles) as a function of ALD cycle numbers for the preparation conditions without annealing (a) and with annealing (b). For 125 ALD cycles almost no Si $2p$ intensity can be collected, because the major part of Si $2p$ photoelectrons has suffered energy loss due to inelastic collisions within the Al_2O_3 overlayer. With decreasing ALD cycle number the Si signal increases exponentially, as expected for homogeneous layers (regime 2). At cycle numbers of 10 and 15 a sudden break of this exponential behavior occurs for the samples without and with annealing, respectively. At lower coverages, the Si intensity increases linearly with a shallower slope (regime 1). It is easy to understand that this linear relation between the Si XPS intensity and the ALD cycle number can most likely be explained by an islandlike growth mode of the first 1–2 Al_2O_3 monolayers. The Si signal damping correlates to the area fraction of Si covered by Al_2O_3 , which in turn depends roughly linearly on the ALD cycle number for the assumed island growth.^{1,2}

Moreover, these graphs show the O/Al ratio (black solid squares). At the thick film limit (125 ALD cycles) an O/Al ratio close to 1.5 is measured, corresponding to a stoichiometric Al_2O_3 layer within the information depth. The constant O/Al ratio above the Si-interface region is qualitatively proven by means of angle dependent XPS. Samples with more than 30 ALD cycles show no significant difference of the measured O/Al ratios between emission angles of 45° and 60° with respect to the surface normal (photoelectron escape depth varied). This indicates a constant O/Al ratio from ~ 1 nm above the interface region for all layer thicknesses. For thinner Al_2O_3 layers the O/Al ratio deviates from the stoichiometric values, increasing to roughly 8 (without annealing) and >20 (after annealing) for samples with one ALD cycle. In Fig. 3 the influence of surficial adsorbed H_2O and contamination by carbonates on the measured O/Al ratio is not considered separately. Additional XPS measurements after Ar sputtering (not shown) exhibit only a slight decrease of the O/Al ratio for films without annealing where the maximum decrease is 10% for cycle numbers below 10. At the same moment the C $1s$ signal as an indicator for surficial adsorbates is reduced by at least 75% and even by 90% for cycle numbers >15 . The thermally annealed samples still show O/Al ratios larger than 6 for cycle numbers of 10 and below after sputtering. These observations are assigned to O-containing compounds close to the Si interface increasing the apparent O content of the Al_2O_3 . However, in Ref. 14, 75% and 85% higher O/Al ratios have been reported for 30 and 125 ALD cycles, respectively. Because of the inherent perfect stoichiometry of ALD-deposited Al_2O_3 films,^{3,16} it has to be concluded that the observation of too high O/Al ratios is caused by incorrect sensitivity factors for Al or O.

The increasing O/Al ratio for thinner Al_2O_3 layer thicknesses is initially supposed to arise mainly from the interfacial SiO_x layer.^{5,9,14} Therefore, we use the XPS data to roughly determine the excess O amount (i.e., the amount of nonstoichiometric bound O atoms) within the information depth, assuming the following:

- (1) A ratio of two O atoms per Si atom within the SiO_x inter-layer ($x = 2$).
- (2) A ratio of 1.5 O atoms per Al atom within the Al_2O_3 layer, as measured for the thick layer limit.
- (3) Relative errors of XPS intensities of 1%, and an error of 1% absolute for the fraction of the Si_{ox} peak area (with respect to total Si peak area).

According to this model, the fraction of excess O ($r_{\text{O,ex}}$) is calculated from

$$r_{\text{O,ex}} = \frac{A_{\text{O}} - 2A_{\text{Si,ox}} - 1.5A_{\text{Al}}}{A_{\text{O}}}, \quad (1)$$

where A_i is the measured XPS signal of element i divided by the element specific relative sensitivity factor.

The graph in Fig. 4 shows the calculated fraction of excess O (weighted over the information depth) as a function of the ALD cycle numbers for both as-grown and annealed samples. In both cases, for low Al_2O_3 coverage with 3–10

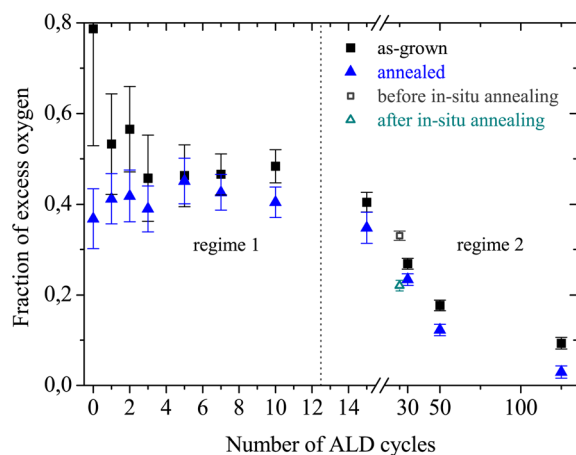


FIG. 4. (Color online) Calculated atomic excess O fraction for both as-grown (squares) and annealed (triangles) samples as a function of the ALD cycle number [according to Eq. (1)]; the open symbols represent similar calculations for an *in situ* annealing experiment at an extra sample with 25 ALD cycles.

ALD cycles (regime 1), roughly half of the detected O is neither stoichiometrically bound to Si (presumed SiO_2) nor Al (Al_2O_3). For thicker Al_2O_3 layers, at >15 cycles (regime 2), this fraction decreases monotonically. Values lower than 0.1 are measured at the thick layer limit after 125 ALD cycles. At as-grown samples, very low Al_2O_3 coverages with <3 ALD cycles lead to an increase of the excess O fraction (up to 0.8 for the reference sample without any ALD cycle). The annealed samples exhibit a decrease to the range of 0.4 for decreasing cycle numbers <3. At higher ALD cycle numbers the annealed samples generally have values of 0.05–0.1 below that of the as-grown samples. The influence of surficial adsorbates from atmosphere such as organics and H_2O before sample introduction into XPS, which would of course contribute to the observed excess O, is examined by additional sputtering. The C 1s signal, attributed to adsorbates, is significantly reduced due to sputtering as already stated while referring to Fig. 3. Nevertheless, from the observed small amount of reduction of the absolute O 1s intensity after sputtering, it is concluded that O-containing adsorbates make only a partial contribution to the excess O amount. The largest effect is found for 10 and 15 ALD cycles, where only half of the excess O is removed due to the sputtering. A second estimation for the influence of adsorbates is derived from an *in situ* heating procedure that forced desorption at an extra sample with 25 ALD cycles (open symbols in Fig. 4). This verifies the result of the sputtering experiments that at least half of the totally measured excess O exists near the interface for all samples. As a cause for the observed excess O we propose surficial OH groups and postdeposition-physisorbed H_2O on bare Si for coverages up to a closed Al_2O_3 layer (~ 10 ALD cycles). Furthermore, before annealing there may be OH groups at the interface and inside the Al_2O_3 (Refs. 2 and 4) that convert into an O-rich interlayer during annealing under release of H_2 ,⁸ which is further treated in the following sections. An interfacial accumulation of excess O would also explain the observed decline with

increasing Al_2O_3 layer thickness due to the limited XPS information depth.

C. Thickness and O coordination of the interfacial oxide layer

The thickness and O coordination of interfacial SiO_x layers can be extracted from high-resolution Si 2p spectra. The peak area ratio of the Si oxide (Si_{ox}) state to the metallic Si (Si_{met}) state corresponds to an effective thickness of an SiO_x layer on Si substrate. Thus,

$$d_{\text{SiO}_x} = \lambda_{\text{SiO}_x} \cos \beta \ln \left(\frac{I_{\text{Si,ox}}}{I_{\text{Si,met}} R} + 1 \right). \quad (2)$$

with given values for the effective attenuation length of Si 2p photoelectrons in Si oxide (λ_{SiO_x}) and the intensity ratio for bulk samples (R) from Ref. 17 allows one to calculate SiO_x thickness values (d_{SiO_x}) from measured peak area ratios ($I_{\text{Si,ox}}/I_{\text{Si,met}}$). The angle between surface normal and emitted photoelectrons (β) is set to 0° , 30° , and 60° , respectively. According to Eq. (2), effective thicknesses of 1 Å, corresponding to only a few O–Si–O sites at the Si surface, are obtained for samples without annealing. After annealing, the effective SiO_x interlayer thickness has increased to 3–5 Å for all samples, which is still in the monolayer range. This is also concluded from comparable XPS data as well as from the TEM image in Ref. 14. Despite (angle resolved) XPS being an appropriate method to determine very small layer thicknesses, these values are quite rough estimations because the minimum layer thickness of the underlying model is at 3 Å.¹⁷ Furthermore, chemical properties can be obtained from the high-resolution Si 2p spectra. An indication for the average oxidation state of Si (i.e., coordination of Si to O) within this layer can be derived from the measured high-resolution spectra. This is performed by measuring the shift between the metallic Si $2p_{3/2}$ peak and the Si_{ox} peak (see Fig. 1). An evaluation of the measured, so-called, chemical shift as a function of the ALD cycle number is shown in Fig. 5 for samples without and with annealing at different emission angles.

Obviously, the O coordination of Si within the ultrathin oxide layers increases during the annealing step. The constant chemical shift of 3.6 eV at the annealed samples corresponds to well coordinated SiO_2 , where Si is in the 4+ oxidation state.^{15,17} Especially for low Al_2O_3 coverages, when the Si is only partially covered, this oxidation must be attributed to air (e.g., entering the oven chamber at the end of the annealing step) as the source of O. In contrast, for as-grown Al_2O_3 the measured chemical shift of the Si_{ox} peak is not constant over the number of ALD cycles. It decreases to 2.5–3.0 eV for cycle numbers below 5. Above, it remains constant at a value of roughly 3.2 eV. The corresponding lower coordination is due to the reduced thermal energy budget during the ALD process. Only a few chemical bonds between O (which is indeed present at the interface) and Si are formed, compared to the situation after thermal annealing.

To determine the formation of the SiO_x interlayer as a function of the annealing temperature, an *in situ* annealing

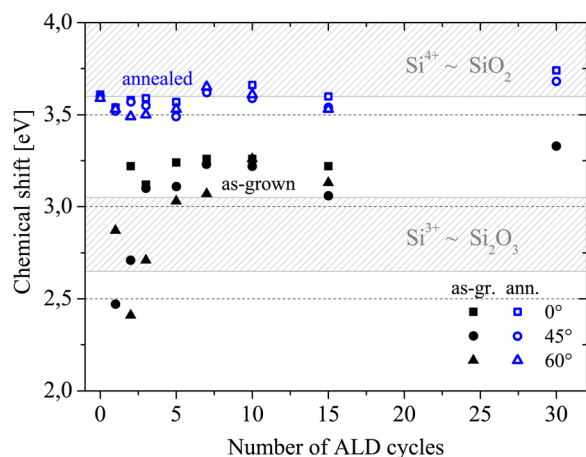


FIG. 5. (Color online) Chemical shift of the Si $2p$ oxide peak with respect to the $\text{Si}^{(0)} 2p_{3/2}$ peak as a function of the ALD cycle number for as-grown Al_2O_3 samples (solid symbols) and after annealing (open symbols), measured for different sample tilt angles; the chemical shift corresponds to the degree of O coordination of Si.

experiment was performed within the XPS instrument. The Si_{ox} peak fraction is evaluated from Si $2p$ high-resolution spectra using

$$r_{\text{SiO}_x} = \frac{I_{\text{Si,ox}}}{I_{\text{Si,met}} + I_{\text{Si,ox}}} \quad (3)$$

A plot of this fraction as a function of the temperature is shown in Fig. 6 for a sample prepared with 25 ALD cycles. The data were acquired over a period of 13 h while the sample temperature was increased from 110 to 500 °C at a rate of 0.5 K/min. The maximum temperature was held for an additional 30 min.

From Fig. 6 it can be deduced that the amount of (interfacial) SiO_x ($1.5 < x < 2$), measured through the fraction of the Si $2p$ oxide peak, does not increase until 300 °C. Obviously, the growth of the SiO_x interlayer does not saturate before 500 °C.

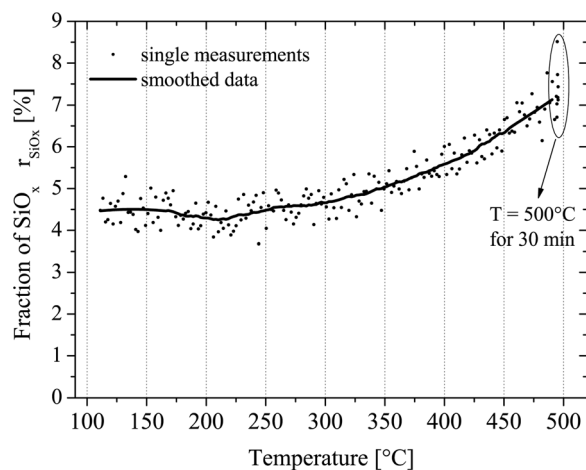


FIG. 6. Fraction of SiO_x peak area [after Eq. (3)] measured *in situ* as a function of the slowly increased temperature (constant rate of +0.5 °C/min) at a sample prepared with 25 ALD cycles on HF dipped Si substrate; smoothed data were calculated over 50 points by the Savitzky–Golay method.

The O $1s$ peak component attributed to O–H bindings as in OH groups is found to decrease significantly due to annealing.⁴ This is a strong indication for the rearrangement of the atomic bindings under release of H during annealing.^{8,18}

D. Structural model of ALD growth and annealing

A rough model for the first few nanometers above the Si surface during deposition and annealing of ALD- Al_2O_3 is provided in Fig. 7. The following steps are visualized from left to right:

- (1) Si substrate after HF dip with low surface coverage with physisorbed H_2O , OH groups and organic contaminants.
- (2) Initial island growth of Al_2O_3 through the first 10 ALD cycles (top); conformal layer by layer growth for more than 10 cycles (bottom) (referring to Ref. 1 and references therein); The interface to Si is loaded with residual OH groups, leading to a low Si–O coordination (“ SiO_x ” with $x < 2$), as it is shown in Fig. 5. From the linear drop in signal intensity due to partial Al_2O_3 coverage observed in Fig. 3 (regime 1) we deduce that the film follows an island growth mode until at least 10 ALD cycles are completed. During the following cycles, linear film growth with a constant growth per cycle causes the exponential decrease of the Si $2p$ signal intensity. This behavior is in very good accordance with the results reported by Puurunen and Vandervorst, who investigated the growth mode during the first ALD cycles using the TMA/ H_2O process.¹
- (3) The formation and growth of an interlayer with enhanced Si–O coordination (“ SiO_2 ”) and concomitant reduction of the excess O fraction due to rearrangement of Al–O–Si bonds during annealing leads to an enhanced chemical passivation. An O-rich layer as a possible source of the measured excess O is proposed at the interface between SiO_2 and Al_2O_3 , according to proposals for the origin of the prominent field effect passivation.^{9,12}

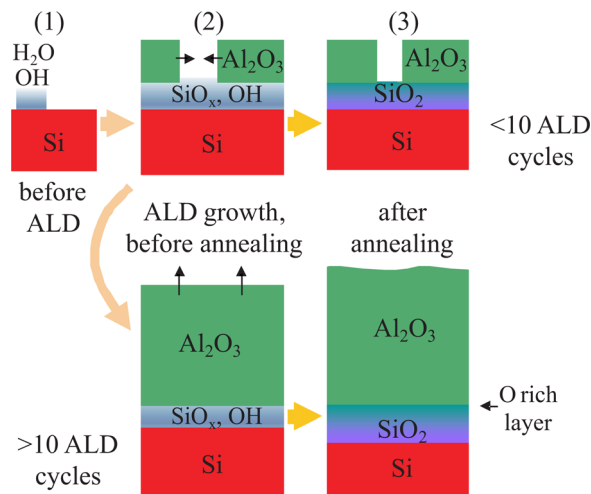


FIG. 7. (Color online) Model for the chemical structure near the Al_2O_3 –Si interface: (1) before ALD, (2) during ALD cycling, and (3) after ALD and annealing step.

IV. DISCUSSION

We deduce from our XPS measurements and following excess O calculations that the elevated O/Al ratios for thinner Al₂O₃ layers can only partially be explained by the presence of the SiO_x. For the as-grown samples, in addition to the very small O signal from the SiO_x at the interface, we determined a clear level of excess O. Several experiments, namely the above-mentioned sputtering experiments, angle dependent XPS, and *in situ* annealing, reveal only a minor contribution of surface adsorbates to this excess O. Therefore, most of the found excess O has to be incorporated during the first ALD cycles. In our model it is concluded that OH groups at the Si-interface are the principal source of excess O before annealing.⁴ We measured a significant increase of the SiO_x thickness and, in addition, an increase in the Si–O coordination during the postdeposition anneal. This is assigned to the oxidation of Si by OH groups under release of H.³ Gas evolution experiments, reported by Zhu *et al.*¹⁹ for the thermal treatment of SiO_x, show an effusion of H₂ for temperatures >300 °C. The effusion of H₂O does not begin until 500 °C for Al₂O₃,⁸ which leads to the assumption that the mobility of O in Al₂O₃ is low at the considered annealing temperatures. With this applied to ultrathin SiO_x and its interface to the Al₂O₃ film, we can explain the retention of interfacial excess O. In particular, we still observe excess O at a reduced level after annealing, which we interpret as O atoms that are not consumed in the oxidation of Si. It is deduced that the excess O atoms are incorporated as interstitials^{13,20} (O_i) in the Al₂O₃ close to the interface. Accordingly, we propose the following global chemical reaction, taking place at the Si interface:



From the electronic point of view, OH groups at the interface seem to be the essential source for the enhanced chemical passivation after annealing¹⁰ due to the formation of new Si–O and Si–H bonds at the surface of the Si crystal. As for the field effect passivation, fixed negative charges are expected at the SiO_x–Al₂O₃ interface.¹³ Interestingly, this is in agreement with density functional theory calculations that revealed preferably negative charged states for O_i in Al₂O₃.²⁰ Al vacancies that may arise alternatively after relaxation of an O-rich aluminum oxide network would also yield fixed negative charges.

V. SUMMARY

Based on coverage dependent XPS examinations of nanometer-thin Al₂O₃ layers, grown by thermal ALD with H₂O as O source, we have distinguished two growth regimes – island growth and conformal layer growth. The island growth mode is found in conjunction with the detection of excess O, which is assigned to residual OH at the Si

surface. A subsequent thermal annealing step is characterized by reducing the amount of excess O at the interface between Si and Al₂O₃, leading to an SiO₂ interlayer with enhanced O coordination of Si. XPS has also been employed to observe the process of binding rearrangement *in situ* during thermal annealing. It has been measured to begin at about 300 °C and apparently proceeds above 500 °C. Therefore, excess O is still measured after standard annealing. It is assigned to an O-rich layer close to the interface. In consequence, interstitial O within 1 nm above the Si/SiO₂/Al₂O₃ interface is recognized as the origin of the high fixed negative charge density. The presented structural model is constituted as a basis for more detailed structural investigations and complementary measurements of electronic properties.

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