

PASSIVATION MECHANISMS OF AMORPHOUS $\text{Si}_x\text{C}_{1-x}$ LAYERS ON HIGHLY DOPED AND TEXTURED Si SURFACES

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ABSTRACT: Lifetime measurements by means of the Quasi Steady State Photo Conductance technique (QSS-PC) were carried out in order to gather further insight into the passivation performance of amorphous $\text{Si}_x\text{C}_{1-x}\text{:H}$ on textured and highly doped silicon surfaces. The set of lifetime samples used in this experiment consisted of shiny etched p-FZ, $1\ \Omega\text{cm}$ wafers with $\langle 100 \rangle$ crystallographic orientation, that were either textured (random pyramid structure) and/or phosphorous diffused ($120\ \Omega/\text{sq}$) on both sides. A comparison of flat and textured emitter samples shows a constant shift to lower effective lifetimes for textured surfaces independently of the thickness of the a- $\text{Si}_x\text{C}_{1-x}$ layer. Different growth times of native oxide on silicon surfaces after treatment in HF solution (5%) prior to deposition of the a- $\text{Si}_x\text{C}_{1-x}$ layer reveal to have major impact on the effective lifetime of the samples. This uncertainty was sought to be cancelled out by applying an in-situ plasma pre-cleaning process to wafers that were taken directly out of box (shiny etched) and thereby abandoning any wet-chemical pre-treatment. In fact, very high lifetimes exceeding 1 ms on $1\ \Omega\text{cm}$ for an injection level of $5 \cdot 10^{14}\ \text{cm}^{-3}$ were achieved on flat samples whereas plasma pre-treatment showed hardly any effect on textured surfaces. Finally, first tests using a $\text{Si}_x\text{C}_{1-x}$ double layer system consisting of an excellent passivating Si-rich and a robust stoichiometric SiC layer were performed. Although the second layer deposition involves high microwave and high-frequency power densities, hardly any degradation in the performance of the passivating layer could be observed.

Keywords: silicon carbide, passivation, textured surface, native oxide

1 INTRODUCTION

Amorphous $\text{Si}_x\text{C}_{1-x}\text{:H}$ layers deposited by plasma enhanced chemical vapour deposition (PECVD) have shown excellent passivation quality on p- as well as on n-type Si-bulk material with surface recombination velocities less than 5 and $54\ \text{cm s}^{-1}$, respectively [1, 2]. Solar cells using a single $\text{Si}_x\text{C}_{1-x}$ layer and laser-fired contacts as rear surface structure achieved efficiencies exceeding 20% [3] and also considerable progress as regards the front side of the cell has been made proving the applicability of $\text{Si}_x\text{C}_{1-x}$ to highly doped p^+ and n^+ Si-surfaces [4, 5]. As solar cells normally exhibit textured front surfaces, one mayor concern of this work is the passivation performance on random pyramid structures and the dependence on thickness of the $\text{Si}_x\text{C}_{1-x}$ layer.

Basic requirement for good passivation performance of the $\text{Si}_x\text{C}_{1-x}$ layer is a careful preconditioning of the Si-surface. The ideal starting point for subsequent deposition seems to be a hydrogen terminated surface [6]. At Fraunhofer ISE this is normally realised by an HF-dip (5%) and a short in-situ plasma-cleaning that accounts for the removal of the instantly growing native oxide. Other authors [1] report a pre-treatment of the wafers in a $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ (2:1) mixture, HF-dipping (5%) and an immediate introduction into the PECVD reactor, again with the objective to avoid an increasing interface state density due to native oxide. In terms of industrial feasibility an in-situ plasma cleaning prior to deposition of the passivating $\text{Si}_x\text{C}_{1-x}$ layer would be extremely attractive. Having this issue in mind we performed experiments with wafers taken out of box without any wet-chemical pre-cleaning.

Due to remarkable features in terms of chemical and thermal stability of SiC an introduction of the rear side passivation process to an earlier stage of the fabrication sequence of a solar cell is considered [3]. Regarding e.g.

the deposition of the rear-side passivation before texturing and emitter diffusion, the set of requisites of the layer is extended. In addition to a good thermal stability it is necessary to achieve high chemical stability and excellent diffusion barrier properties. These demands are met by a stoichiometric $\text{Si}_x\text{C}_{1-x}$ layer used at Fraunhofer ISE as intermediate layers in c-Si thin film solar cells. Therefore a two layer system consisting of a good passivating Si-rich and a second stoichiometric layer constitutes a straightforward approach to this application. A first deposition of this stack system on lifetime samples should reveal to what extend the passivation quality suffers by virtue of energetic ion bombardment during the deposition of the stoichiometric SiC layer.

2 EXPERIMENTAL DETAILS

2.1 Sample preparation

For our experiments we used p-doped, $1\ \Omega\text{cm}$, FZ wafers with $\langle 100 \rangle$ crystallographic orientation. The lifetime samples were either shiny etched (manufacturer) or textured by etching the samples in a solution of KOH (1%) and isopropanol. By means of anisotropic etch rates of KOH the resulting surface structure exhibits random pyramids with $\langle 111 \rangle$ orientated planes [7]. After a $\text{HNO}_3 + \text{HF}$ cleaning step, some of the flat and textured samples were phosphorous diffused resulting in a sheet resistance of approximately $120\ \Omega/\text{sq}$. Before introducing the samples into the PECVD reactor the standard procedure consisted in wet-chemical removal of the native oxide and H-termination of the Si-surface by HF (5%) treatment. The following rinsing procedure prevents HF diversion and has no effect on the passivation performance. Since the interface between wafer and $\text{Si}_x\text{C}_{1-x}$ layer is the decisive feature of surface passivation, the effective lifetime (τ_{eff}) of minority

carriers is most sensitive to the time of exposure to air between HF treatment and deposition: The immediate onset of growing native oxide replaces gradually the Si-H bondings at the surface and effects passivation quality by altering the growth conditions in the first monolayers of $\text{Si}_x\text{C}_{1-x}$ as well as by increasing defect density with increasing oxide thickness at the interface [6]. Table 1 illustrates this trend in terms of decreasing effective lifetimes of an uncoated, shiny etched p-FZ ($1\ \Omega\text{cm}$) wafer after HF-dipping, rinsing and exposure to air.

Table 1: Decreasing effective lifetime of uncoated, shiny etched p-FZ ($1\ \Omega\text{cm}$) wafer after HF-Dip and rinsing in water.

Time after HF-Dip	1 h	3 h	48 h
$\tau_{\text{eff}} @ 5 \cdot 10^{14}\ \text{cm}^{-3}$	17 μs	7 μs	2 μs

A short in-situ preconditioning process prior to the actual deposition by means of a low power H_2 -Ar plasma accounts for removal of the grown oxide and probably for a re-hydrogenation of the Si-surface. However, as the growth rate of native oxide not only depends on crystallographic orientation but also on aspects like micro-roughness of the surface and storage atmosphere, slightly different starting points for subsequent $\text{Si}_x\text{C}_{1-x}$ growth cannot be avoided by adjusting the duration of the in-situ cleaning either. In order to overcome this element of uncertainty and in view of industrial feasibility some of the lifetime samples were taken out of box and directly introduced into the PECVD reactor without any preceding wet-chemical treatment.

All $\text{Si}_x\text{C}_{1-x}$ layers were deposited by PECVD in an AK400M reactor from Roth&Rau that provides two plasma sources, one microwave (2.45 GHz) and one high frequency (13.65 MHz) generator. In this work we focused on two different $\text{Si}_x\text{C}_{1-x}$ passivation layers that have to be distinguished in the following discussion: The first one is labelled 'intrinsic' and is made up by silane (SiH_4) and methane (CH_4) as precursor gases, the second one is labelled 'doped' and features phosphine (PH_3) as additional precursor gas. The samples were coated on both sides in two subsequent identical processes.

Resulting thicknesses of the $\text{Si}_x\text{C}_{1-x}$ layer were measured by means of spectroscopic ellipsometry on a J.A. Woollam Co. M-2000 in the spectral range between 245 and 2000 nm.

2.2 Lifetime measurement

The effective minority carrier lifetime was measured using the Quasi Steady State Photo Conductance technique (QSS-PC) with a WCT-100 Photoconductance tool from Sinton Consulting, Inc. For comparison of the lifetime samples among each other, an injection level of $5 \cdot 10^{14}\ \text{cm}^{-3}$ was chosen for base material as well as for emitter samples. Transient Photo Conductance Decay (PCD) was applied in order to calibrate the fraction of light absorbed within the samples during QSS-PC. It should be noted that by this method an adequate determination of the absorption coefficient is only possible for lifetimes exceeding 100 μs . Therefore a constant absorption coefficient was assumed for very thin passivation layers.

3 RESULTS AND DISCUSSION

3.1 Plasma preconditioning

The first experiments aimed at determining the appropriate gas ratio for the in-situ plasma preconditioning of Si-wafers. Since non-diffused surfaces are more sensitive to the cleaning process, shiny etched and textured uniformly doped samples ($1\ \Omega\text{cm}$) were introduced into the PECVD reactor where they were plasma cleaned and then coated by a standard Si_xC_x passivation layer. Fig. 1 shows the effective lifetimes of flat wafers depending on the gas ratio Ar/H_2 during the cleaning step for intrinsic and doped $\text{Si}_x\text{C}_{1-x}$. For a subsequent deposition of an intrinsic layer a maximum occurs at a gas ratio of $\text{Ar}/\text{H}_2=30/70$ showing overall only a small dependence of the employed gas. However, hydrogen during the preconditioning process seems to be of paramount importance for the passivation quality of a subsequently deposited phosphorous doped $\text{Si}_x\text{C}_{1-x}$ layer. The pronounced maximum at pure hydrogen disposal points to a rather unfavourable role of Ar in this case.

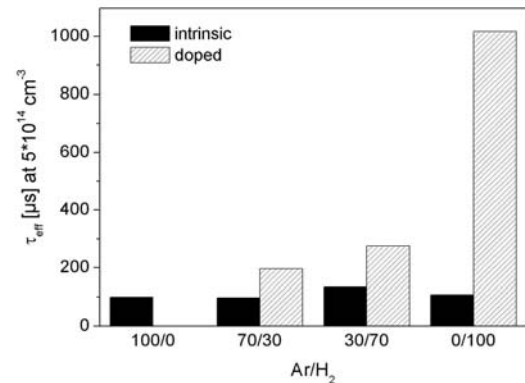


Fig. 1: Effective lifetimes of shiny etched samples depending on the gas ratio Ar/H_2 used in the plasma-cleaning process.

We assume that under the given plasma conditions Ar^+ as well as H^+ -ions remove the native grown oxide layer – the first species by mechanical means constituting a smooth sputtering process whereas the second species rather undergoes a reaction with the oxygen atoms forming water molecules. The major difference between the two ways of surface preconditioning is probably the additional H-termination of Si-surface atoms when using H_2 . For developing a field-effect passivation effect in the case of phosphorous doped $\text{Si}_x\text{C}_{1-x}$ layers the forming of fixed positive charges nearby the interface is crucial and H-saturated Si bonds seem to state a most favourable starting point for this action. However, for a mere saturation of surface bonds by Si- or C-atoms H-termination does not seem to have significant impact.

The influence of duration of the preconditioning process on effective lifetime is shown in Fig. 2 for gas ratios of $\text{Ar}/\text{H}_2=30/70$ and $0/100$ for intrinsic and doped $\text{Si}_x\text{C}_{1-x}$ layers, respectively. The virtually constant passivation quality for prolonged plasma-cleaning in the intrinsic case confirms the softness of the process due to an equilibrium between surface damage and healing of defects due to hydrogen. In the doped case a degradation of the effective lifetimes occurs in the range between 60-120 s pointing to defect generation due to proton

bombardment that takes effect at an elevated lifetime level.

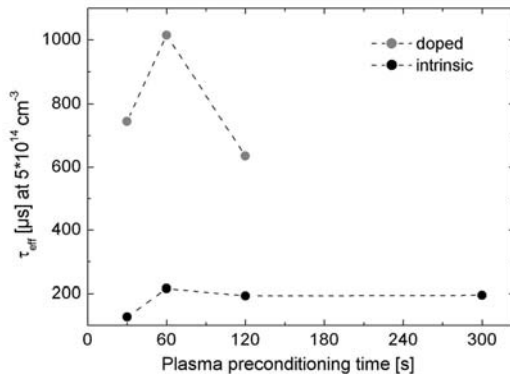


Fig. 2: Effective lifetimes of shiny etched samples depending on the duration of the plasma-cleaning process.

On the other hand plasma-cleaning under the same conditions as applied for flat samples does not work on their textured counterparts. Independently of the Ar/H₂ gas ratio no substantial improvement of the passivation quality could be stated and no impact of prolonged process duration up to 5 min was observed (Fig. 3). Two reasons might account for this outcome: One is associated with the pyramid geometry exhibiting vertices and edges. The other aspect might concern the <111> crystallographic orientation of the pyramid planes and the implicit slightly distinct native oxide growth. We think that this effect does not have a significant impact on plasma-cleaning but could not yet carry out clarifying experiments on plan <111> orientated wafers due to current unavailability of the material.

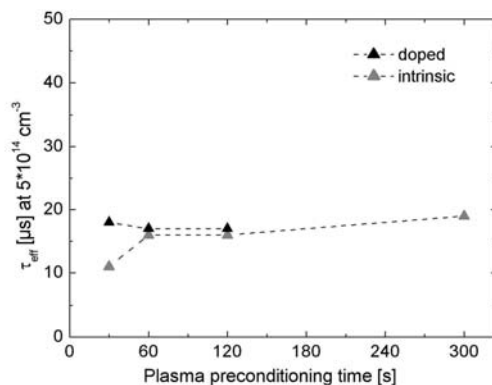


Fig. 3: Effective lifetimes of textured samples depending on the duration of the plasma-cleaning process.

3.2 Passivation of flat and textured n⁺ emitter

When used as an emitter passivation layer on the illuminated front of a solar cell, the optical properties such as refractive index and absorption coefficient of the dielectric layer play a prominent role. Two-layer stacks consisting of a well-passivating Si-rich and a second C-rich Si_{1-x}C_x layer on top of it with antireflection properties are currently under investigation [5]. As Si-rich layers exhibit high absorption in the relevant wavelength region, this first layer should be kept as thin as possible. We investigated the dependence of

passivation quality of phosphorous diffused flat and textured samples applying HF-treatment and plasma preconditioning to the samples prior to depositing Si_xC_{1-x} layers of different thicknesses. Concerning growth rate in our PECVD process on Si-substrate we state an elevated increase in thickness during the first minute of deposition and thenceforth a moderate constant growth. This phenomenon can be explained by the increased amount of energetically more preferable positions on a crystalline Si surface. After some atomic layers of coverage this effects diminishes and a slower growth process on the amorphous network takes its advantage.

Fig. 4 shows that passivation quality improves with increasing layer thickness in all cases within the examined range up to approximately 50 nm from where on a saturation seems to occur. At low thicknesses intrinsic and doped cases present comparable values for the effective lifetime suggesting that the passivation due to field effect only becomes apparent after a certain film thickness. Besides the increasing total amount of fixed charges in the Si_xC_{1-x} layer with process time also an "activation" of the relevant charge centres by diffusing hydrogen might account for this fact.

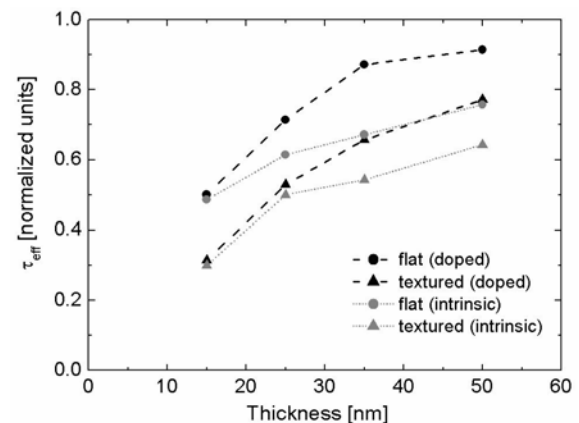


Fig. 4: Effective lifetimes of phosphorous diffused samples depending on Si_xC_{1-x} thickness showing a constant shift between flat and textured surfaces.

For both intrinsic and doped Si_xC_{1-x} films a constant shift in lifetime between flat and textured surfaces can be stated. This means that for emitter passivation on a lower lifetime level the difference in passivation quality between flat and textured surfaces is made up by not or poorly passivated vertices and edges of the random pyramids rather than by area-related effects as the different crystallographic orientation of the pyramid planes. Probably due to electric field effects an adequate passivation of defects is not possible at exposed sites of the texture and the decrease in overall lifetime compared to flat surfaces is therefore independent of deposition time.

3.3 Robust double layer system for solar cell rear side

In order to introduce the Si_xC_{1-x} passivation into the process chain as early as possible (see Fig. 5), the passivation layer has to satisfy some challenging and sometimes conflicting requirements [3]. One solution to overcome this problem is to apply a Si_xC_{1-x}/SiC layer stack which can help to cumulate the necessary physical and chemical properties [8]. We run first tests with an excellent 80 nm thick Si_xC_{1-x} passivation layer and an

additional 50 nm in-situ deposited C-rich, and therefore chemically resistant and temperature stable, second layer on top of it. Comparing the single layer and the layer stack passivation by minority carrier lifetimes measurements (QSS-PC) on a 1 Ωcm p-FZ wafer we found a small reduction from 1370 to 1230 μs . After reducing the thickness of the passivation layer down to 15 nm the losses could still be limited, though on a lower lifetime level, to 10%.

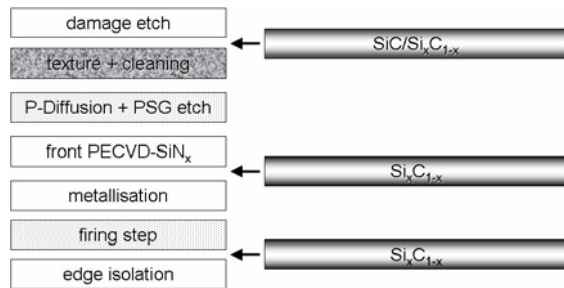


Fig. 5: Process chain for an industrially feasible high efficiency process and possible opportunities to introduce the rear-side passivation layer.

These results clearly show, that the in-situ deposition of a second stoichiometric SiC layer, which acts as a diffusion barrier and an etch stop layer, only slightly reduces the passivation surface performance. This leads to the conclusion, that no significant plasma generated defects are introduced into the solar cell bulk or that they can be healed by the offered hydrogen. Besides the already mentioned advantages of a second SiC layer for the solar cell processing this layer could furthermore act as an additional hydrogen source or generate a field effect passivation through incorporated dopants.

4 CONCLUSIONS AND OUTLOOK

Lifetime measurements by means of the Quasi Steady State Photo Conductance technique (QSS-PC) were carried out in order to gather further insight into the passivation performance of a-Si_xC_{1-x}:H layers on both side textured (random pyramids) and/or phosphorous diffused (120 Ω/sq) silicon p-FZ wafers (p, 1 Ωcm). A comparison of flat and textured emitter samples shows a constant shift to lower effective lifetimes for textured surfaces. This effect occurs independently of the thickness of the a-Si_xC_{1-x} layer which points to inefficiently passivated edges of the pyramids rather than to area-related effects as $\langle 111 \rangle$ planes. Nevertheless, additional investigations on flat $\langle 111 \rangle$ Si wafer will be necessary to confirm this observation. As the time of exposure to air (native oxide) after treatment in HF solution (5%) prior to deposition of the a-Si_xC_{1-x} layer reveals to have major impact on the effective lifetime of the samples we applied an in-situ plasma pre-cleaning process to wafers that were taken directly out of box (shiny etched) and thereby abandoned any wet-chemical pre-treatment. Very high lifetimes exceeding 1 ms for an injection level of $5 \cdot 10^{14} \text{ cm}^{-3}$ were achieved on flat samples whereas plasma pre-treatment showed hardly any effect on textured surfaces. Finally, first tests using a Si_xC_{1-x}/SiC double layer stack consisting of an excellent passivating Si-rich and a robust stoichiometric SiC layer were performed. Although the second layer deposition involves high microwave and high-frequency power

densities, we found a small reduction of minority carrier lifetimes from 1370 to 1230 μs . Such a stack system has the potential of a significant reduction of cost due to an advanced passivation performance and a simplification of the process itself.

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