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The Interface of a-SiNₓ:H and Si: Linking the nano-scale structure to passivation quality

Machteld Lamers¹, Leif E. Hintzsche², Keith T. Butler³, Per Erik Vullum⁴, Chang-Ming Fang², Martijn Marsman², Gerald Jordan², John H. Harding³, Georg Kresse² and Arthur Weeber¹

¹ ECN Solar Energy, P.O. Box 1, 1755 ZG Petten, the Netherlands, Phone: +31 88 515 56 4718, Fax: + 31 88 515 8214, E-Mail: lamers@ecn.nl
² University of Vienna, Faculty of Physics and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Vienna, Austria.
³ University of Sheffield, Western Bank, Sheffield S10 2TN, United Kingdom.
⁴ SINTEF, Materials and Chemistry, Box 4760 Sluppen, NO-7465 Trondheim, Norway.

Abstract

Surface passivation by hydrogenated amorphous silicon nitride (a-SiNₓ:H) is determined by the combined effect of two mechanisms: so-called chemical passivation by reducing the density of interface states (D_{it}) and field-effect passivation as a result of the number of fixed charges (Q_{f}) at the interface with Si. These are related to the K defect centre: *Si=N₃. Defects near the interface (in both Si as in a-SiNₓ:H), modelled by force field Molecular Dynamics (MD) and ab initio Density Functional Theory (DFT), can be related to Q_{f} and D_{it} measured experimentally using CV-MIS (Capacitance-Voltage Metal Insulator Semiconductor). The compositional build up at the interface as is determined by HRTEM (High Resolution Transmission Electron Microscopy) and modelled by MD correspond to each other; a gradual change from Si to the bulk a-SiNₓ:H composition in the first 2 nm of the a-SiNₓ:H layer. At the c-Si side a highly distorted layer (about 1-3 nm) caused by the insertion of N and/or H is found. The insertion and adhesion of N into and at the Si surface is called nitridation and can be altered by using a NH₃ plasma prior to a-SiNₓ:H deposition. HRTEM image analysis shows that by varying the nitridation of the Si surface the amount and penetration depth of N inside the Si surface is altered. Using MD modeling, it is shown that this process changes the amount of K-centers at the surface, which explains the variation in Q_{f} and D_{it} that is found experimentally. Ab initio DFT studies of a-SiNₓ:H (x=1.17) show that K-centers and Si atoms in distorted configuration, are the dominating defects resulting in a higher D_{it}. For lower x (x=1) the D_{it} caused by K-centers increases, which is observed experimentally too.

Keywords: Silicon Nitride; passivation; interface; nitridation; fixed charge

1. Introduction

Hydrogenated amorphous silicon nitride (a-SiNₓ:H) is the standard antireflection and passivating layer, for both surface and bulk defects, in wafer-based silicon solar cells. The passivating properties of the layer have previously been correlated to cell output properties like the open-circuit voltage V_{oc} [1,2]. The total surface passivation is determined by the combined effect of two mechanisms: so-called chemical passivation by reducing the density of interface states (D_{it}) and field-effect passivation as a result of the number of fixed charges (Q_{f}) at the interface with Si. A low D_{it} reduces the recombination rate at the interface. For Q_{f} the effect on surface passivation depends, besides other parameters, on the doping type and doping density [3]. As Q_{f} and D_{it} are properties of the interface of a-
SiNₓ:H/Si, this indicates that they are determined by the initial growth of the a-SiNₓ:H layer. The relationship between Qᵢ, Dᵣ, and the a-SiNₓ:H layer properties are published elsewhere by the authors [4]. Qᵢ is related to the interface structure between the materials (a-SiNₓ:H and Si) causing a local-field effect as was described by Aspnes [5]. This local field depends on the different polarizabilities of each material and the variation in volume density of these polarizabilities over a certain distance at the interface. The different components in bulk a-SiNₓ:H, which can be charged have been linked to the so-called K- and N-centers [6]. These centers are respectively *Si=≡Nₓ and *N≡Siₓ. * indicates that these centers can be neutral, positive, negative or bonded to H. Assuming that K- and N-centers also occur at the interface, this leads to the conclusion that Qᵢ is determined by the variation and volume fractions of K- and N-centers at the interface region of a-SiNₓ:H/Si.

In this paper our aim is to better understand the surface passivating properties by examining the interface both on electrical and physical properties, and comparing the results to force field Molecular Dynamics (MD) and ab initio Density Functional Theory modeling. We show that the compositional build up at the interface as is measured and modelled correspond to each other; a gradual change from Si to the bulk a-SiNₓ:H composition in the first 2 nm of the a-SiNₓ:H layer. At the c-Si side a highly distorted layer (about 1-3 nm) caused by the insertion of N and/or H is found. The insertion and adhesion of N into and at the Si surface is called nitridation and can be altered by using a NH₃ plasma prior to a-SiNₓ:H deposition. We show by High Resolution Transmission Electron Microscopic (HRTEM) image analysis that by varying the nitridation of the Si surface the amount and penetration depth of N inside the Si surface is altered. Using MD modeling, we show that this process changes the amount of K-centers at the surface, which explains the variation in Qᵢ and Dᵣ that is found experimentally. Furthermore, with ab initio modeling we show that a large amount of H is present at the surface, needed to passivate the dangling Si bonds. Even more, we propose that the location of Qᵢ is stretched over the interface, starting a few nm in the c-Si to around 2 nm in the a-SiNₓ:H, the magnitude can be altered by changing the concentration gradient, more specifically of N in the c-Si. This can be achieved by using a NH₃ plasma prior to a-SiNₓ:H deposition.

2. Results

2.1 A graded interface

a-SiNₓ:H was deposited by remote Plasma Enhanced Chemical Vapour Deposition (PECVD) on a double side mirror-polished <100> 2.5 Ωcm p-type and <111> n-type 3.5 Ωcm FZ Si substrates, 275 μm thick. Cross-section TEM specimens were prepared by mechanical polishing, dimpling and Ar⁺-ion sputtering using liquid nitrogen to cool the sample. The acceleration voltage was progressively reduced to 1.0 keV during the final stage of the Ar⁺-ion sputtering to minimize sample damage. TEM was performed with a JEOL 2010F operated at 200 kV. The HRTEM image of the <100> sample is shown in figure 1.
A white line is drawn over the high amplitude periodic signal. It is observed that the first few atomic layers of c-Si at the surface show a distorted expanded crystal structure and that the high amplitude signal is shifted left and lowered in intensity. This indicates the presence of large strain and the possible insertion of other smaller atoms. A dark band is seen at the interface, which can indicate that light atoms, like N and/or H, are present. Such a dark band is not visible at a SiO₂/c-Si interface [7].

Large strain was also found in the <111> oriented sample as shown in the inverse fast Fourier transformed (FT) image (figure 2c), and corresponds to the dark band in figure 2a. No such strain was found in the c-Si bulk (figure 2b).

On the a-SiNₓ:H side of the interface a 2 nm wide gradient was found in the plasmon loss energy found with Electron Energy Loss Energy Spectroscopy (EELS) as shown in figure 3.
In the figure it can be seen that the plasmon loss energy increases from 17.0 eV to 19.8 eV over 3 nm (from -1 nm to 2 nm). From the high-loss region of the EELS spectrum also the chemical composition can be determined and this is shown in figure 4. Park et al. showed a relation between the plasmon loss energy and the composition of a-SiNx:H [8] and we find that this is also valid for the interface. The relation between plasmon loss energy and composition combined with the increase in plasmon loss energy occurring at the Si side (~1 nm) indicates the presence of N inside Si, besides H. The presence of N was also found inside Si surface by Ikarashi et al. [9]. The composition is determined from the L2,3 peak onset in the high-loss region of EELS (around 99 eV) and it could not be found to change for t<0.5 nm; this indicates that the N content is relatively low.

2.2 Nitridation, Qf, Dit and K-centers

Using remote-PECVD, the gases to deposit a-SiNx:H, typically SiH4 and NH3, are dissociated. Subsequently, a thin film a-SiNx:H can now grow on the substrate surface. During the initial growth of a-SiNx:H the surface is nitridated, which can be described as N adhesion at or insertion into the Si surface. This nitridation is temperature dependent. Typically, adhesion of -NH2 to the Si surface starts above 350°C, N insertion into the Si-Si bonds begins above 400°C and this increases with temperature [10]. To study the effect of
nitridation on passivation in more detail, NH$_3$ plasma pre-treatments prior to a-SiN$_x$:H layer deposition were performed on 275 µm thick p-type FZ <100> wafers, which were double side mirror polished with a base resistivity of 2.5 Ωcm. Shortly before nitridation, the wafers received a short HF dip to remove the surface oxide. Samples with nitridation and coating on one side were used to determine $Q_f$ and $D_{it}$ using CV-MIS. CV-MIS samples were prepared by evaporating 300 nm aluminum on the full area of the uncoated rear side and circular dots with varying sizes ($0.1 – 1.91$ mm$^2$) on the coated front side. The thickness of the a-SiN$_x$:H layers was determined using spectroscopic ellipsometry. The method to analyze the CV-MIS curves is described in [11].

NH$_3$ plasma pretreatments were carried out at temperatures between 300 and 500°C. In figure 5 the effect of the temperature of a NH$_3$ plasma on $Q_f$ and $D_{it}$ is shown [4].

![Fig 5. The effect of the temperature of a NH$_3$ plasma treatment on $Q_f$ and $D_{it}$ on p-type <100>. Open and closed symbols are samples without respectively with pre-treatment. The lines are guides to the eye [4].](image)

A positive correlation between $Q_f$ and $D_{it}$ is found. It can be seen that already at 300°C a small effect is visible, which suggests that the onset of nitridation might start at somewhat lower temperature than suggested by Dai [10]. The nitridation effect can be seen by the increase in $Q_f$ and $D_{it}$. The relationship between nitridation, measured lifetime and solar cell efficiency is shown elsewhere by the authors [4].

The nitridation effect is also observed by analyzing the plasmon loss energy as was measured with an EELS line scan on the samples as is shown in figure 6.

![Fig 6. Plasmon loss energy over the interface for different treatments of NH$_3$ prior to a-SiN$_x$:H deposition. Each line represents the averaged value of three line scans.](image)
For NH₃ treatments a rise in plasmon loss energy is found on the c-Si side of the interface, signaling a larger incorporation of N with increasing temperature. This result is confirmed by MD simulation on graded interfaces. It shows a higher amount of N in a-SiNₓ:H at the interface with Si, which leads to a higher defect concentration as is shown in figure 7. This higher defect concentration results in higher Qᵣ. Also, the MD modeling which compares a sharp interface with a graded one, shows that gradual interfaces show significantly lower defects [12].

Fig 7. MD simulations of defect concentrations at gradual interfaces for increasing N concentration at the interface; p refers to passivated meaning the defect has a H atom bonded, np indicates non-passivated.

A clear gradient in the composition of a-SiNₓ:H at the interface is found and also the presence of N is detected at the silicon side of the interface. With the NH₃ plasma pretreatment the nitridation of the Si surface is altered as shown by an increase in plasmon loss energy at the c-Si side of the interface. Experimentally, it is found that this corresponds to an increase in Qᵣ, while MD modeling shows an increase in K-centers. The variation in volume density of the K-centers at the interface creates a local field, which we propose is the cause of the macroscopically detected Qᵣ. The location of Qᵣ is stretched over the interface, starting a few nm’s in the c-Si to around 2 nm in the a-SiNₓ:H. Furthermore, Qᵣ can be altered by changing the concentration gradient, more specifically of N in the c-Si. This can be achieved by using a NH₃ plasma prior to a-SiNₓ:H deposition.

2.3 Hydrogen and Dᵣ

To increase further the understanding of the interface, ab initio density functional theory (DFT) studies for the interface of Si₃N₃.₅H₀.₈ and c-Si were performed. For the modeling 100 atoms of Si₃N₃.₅H₀.₈ and 56 c-Si atoms were used. Si₃N₃.₅H₀.₈ is the configuration of the standard a-SiNₓ:H layer placed on the front side of solar cells, as determined by the authors [13,14], and the orientation of the c-Si part was <111>. The amorphous structures were generated by heating the samples up to about 2500 K and then cooling them down by using two different cooling strategies. For the first strategy, the samples were cooled continuously until the systems are completely frozen. This was typically the case at a temperature of about 1500 K. Afterwards, the structure was relaxed at 0 K. About 30 interfaces structures have been obtained in this way. For the second strategy, about 500 samples were relaxed immediately at ground states. To prevent an intermixture of the c-Si and a-SiNₓ:H part, the degree of freedom of the c-Si atoms during the molecular dynamics simulations were adjusted. While the c-Si atoms in the middle of
the c-Si part stayed always fixed, the c-Si atoms of the two outermost c-Si layers could either move in all directions or only in directions parallel to the interfaces. This led to systems with either gradual or sharp interfaces. Figure 8 shows the averaged concentration of Si, N, and H of quenched samples with sharp interfaces (sharp, quenched), cooled samples with sharp interfaces (sharp, annealed), and cooled samples with gradual interfaces (gradual, annealed). The figure also shows the typical bonding structures of a c-Si/a-SiNₓ:H interface.

Fig 8. Results of ab initio theory studies regarding the structure and concentrations at the Si₃NₓH₀.₈/c-Si interface.

It can be seen that for Si₃NₓH₀.₈ with constant material properties a higher concentration of N and H is found at the interface, while for a gradient interface, the interface mostly consist of H. This might explain the dark band found in the HRTEM results. In contrast to experimental measurements, no N is found in the c-Si due to placed restrictions on the atom movement during the simulations. Moreover, the dimensions of ab initio model structures are still very small compared to real systems. While the models contain about 150 atoms and cover the length scale of a few angstrom, real systems contain about 10²⁵ atoms and demand a description at nanometer-scale. Also, initial growth of a material in a plasma cannot be modeled by ab initio methods.

In figure 9 the Density of States (DOS) of a-Si₃Nₓ (x=1.17) and a-Si₃N₃ (x=1) are shown. For decreasing x, the band gap shrinks, and the DOS increases due to K-centers (solid lines) and distorted Si units (broken lines) [15]. The inclusion of H decreases the density of states in the gap further (compare black and grey lines). The states caused by N-centers were found to lie outside the bandgap and we can conclude that N-centres do not have an effect on the Dᵢᵣ. These observations can be interpreted in several ways. It is for example a well known fact that the optical absorption increases when the band gap shrinks. Therefore, the absorption for Si₃N₃ must be higher than for Si₃N₃₅, which is generally known. We furthermore suppose that the number of defect states, which are mainly K-defects, are directly related to important passivation properties such as Dᵢₑ and Qₑ. The Dᵢₑ is further increased by distorted Si units. Finally, the reduction of defects due to hydrogen
agrees perfectly with experimental findings as shown in [4].

![Graph of Density of States (DOS) of Si$_3$N$_{3.5}$ and Si$_3$N$_3$ close to Fermi-level](image1)

The Density of States (DOS) of Si$_3$N$_{3.5}$ and Si$_3$N$_3$ close to Fermi-level. The total DOS is related to K-centers and distorted Si units (full and broken lines). Additional hydrogen (grey lines) reduces the amount of electronic defect states in the gap [15].

The observations described above correspond to the ones found experimentally on bulk a-SiN$_x$:H. FTIR (Fourier Transform Infra Red) spectroscopy data for layers with different composition are shown in figure 10 [4,13] and it can be seen that the concentration of distorted Si-N bonds increases for x=1 compared to the one for x=1.17. Simultaneously, the H-Si-N$_3$ (passivated K-centers) concentration increases. These increases can be related to higher values for $Q_f$ and $D_{it}$ as shown in figure 11.

![Graph of bond densities of H-Si-N$_3$ and Si-N stretching in local distorted configuration](image2)

The bond densities of H-Si-N$_3$ and Si-N stretching in local distorted configuration [4,13].
2.4 Effect on solar cells
The effect of NH$_3$ plasma treatments and temperature used prior to a-SiN$_x$:H deposition indicate that, depending on the surface doping, a significant effect on solar cells can be expected. As the increase in plasmon loss energy in the c-Si is found to be an indication of N insertion in the c-Si surface and that this insertion is also found for surfaces without an additional NH$_3$ plasma treatment (see figure 3), it is expected that significant nitridation also occurs during standard a-SiN$_x$:H deposition. Therefore, we can conclude that both the NH$_3$ flow and temperature used in the standard a-SiN$_x$:H deposition will determine the final Q$_f$ and D$_{it}$.

However, for p-type cells with highly doped n-type emitter fabricated using an NH$_3$ plasma treatment (300-500°C) prior to front side a-SiN$_x$:H deposition we did not observe a difference in cell performance [4]. This indicates that these variations in surface passivation do not change the effective passivating quality of the front side for this cell design.

Contrarily, in n-type cells with a p-type emitter fabricated using NH$_3$ plasma treatment (300-500°C) prior to front side a-SiN$_x$:H deposition a significant effect on the cell characteristics could be seen [4]. A variation of 20 mV was observed. This indicates that the used temperature and NH$_3$ flow during a-SiN$_x$:H on p-doped surfaces significantly influence cell performance. No cell experiments were performed regarding the rear side of p-type cells as an increase in Q$_f$ and D$_{it}$ has been shown to have a detrimental effect on cell performance [16].

More details and results for p-type and n-type cells together with modeling are published elsewhere by the authors [4].

3. Conclusions
The atomistic structure of SiN$_x$:H layers is linked to the passivation quality of these layers, expressed by Q$_f$ and D$_{it}$. Both parameters can be measured by using CV-MIS and they can be related to defect states on both sides of the c-Si/a-SiN$_x$:H interface, which is confirmed by using molecular dynamics simulations. Dependent on the modeling technique this can be done at nanometer-scale as well as at atomistic scale. There is a good agreement between HRTEM observations of the silicon nitride interface and corresponding different model structures. We find a gradual change from c-Si to bulk a-SiN$_x$:H within the first 2 nm of the amorphous part. This change is associated with highly strained and distorted c-Si layers (within 1-3 nm) and with the insertion of N and H. The insertion and adhesion of N into and at the Si surface is called nitridation and can be altered by using a NH$_3$ plasma prior to a-SiN$_x$:H deposition. HRTEM image analysis shows that by varying
the nitridation of the Si surface the amount and penetration depth of N inside the Si surface is altered. Using MD modeling, it is shown that this process changes the amount of K-centers, which explains the variation in $Q_f$ and $D_{it}$ that is found experimentally. Based on experimental and modeling results, it is proposed that the change in the volume density of K-centers is the origin of $Q_f$. Consequently, the location of $Q_f$ is stretched over the interface, starting a few nm in the c-Si to around 2 nm in the a-SiN$_x$:H. $Q_f$ can be altered by changing the concentration gradient of N in c-Si. This can be achieved by using a NH$_3$ plasma prior to a-SiN$_x$:H deposition. Ab initio DFT studies of a-SiN$_x$:H ($x=1.17$) show that K-centers are the dominating defects and that its amount increases for lower $x$ ($x=1$). The $D_{it}$ is further increased by distorted Si units. This observation is also in good agreement with experimental results.

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**4. References**