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

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Abstract

Surface passivation by hydrogenated amorphous silicon nitride (a-SiN$_x$: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≡N$_3$. Defects near the interface (in both Si as in a-SiN$_x$: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-SiN$_x$:H composition in the first 2 nm of the a-SiN$_x$: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 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 at the surface, which explains the variation in Q$_f$ and D$_{it}$ that is found experimentally. Ab initio DFT studies of a-SiN$_x$: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-SiN$_x$: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-

SiN_x:H/Si, this indicates that they are determined by the initial growth of the a-SiN_x:H layer. The relationship between Q_f, D_{it} and the a-SiN_x:H layer properties are published elsewhere by the authors [4]. Q_f is related to the interface structure between the materials (a-SiN_x: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-SiN_x:H, which can be charged have been linked to the so-called K- and N-centers [6]. These centers are respectively $*Si\equiv N_3$ and $*N{=}Si_2$. * 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 Q_f is determined by the variation and volume fractions of K- and N-centers at the interface region of a-SiN_x: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-SiN_x:H composition in the first 2 nm of the a-SiN_x: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 NH_3 plasma prior to a-SiN_x: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 Q_f and D_{it} 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 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, 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 NH_3 plasma prior to a-SiN_x:H deposition.

2. Results

2.1 A graded interface

a-SiN_x:H was deposited by remote Plasma Enhanced Chemical Vapour Deposition (PECVD) on a double side mirror-polished <100> 2.5 **Ω**cm p-type and <111> n-type 3.5 **Ω**cm 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.

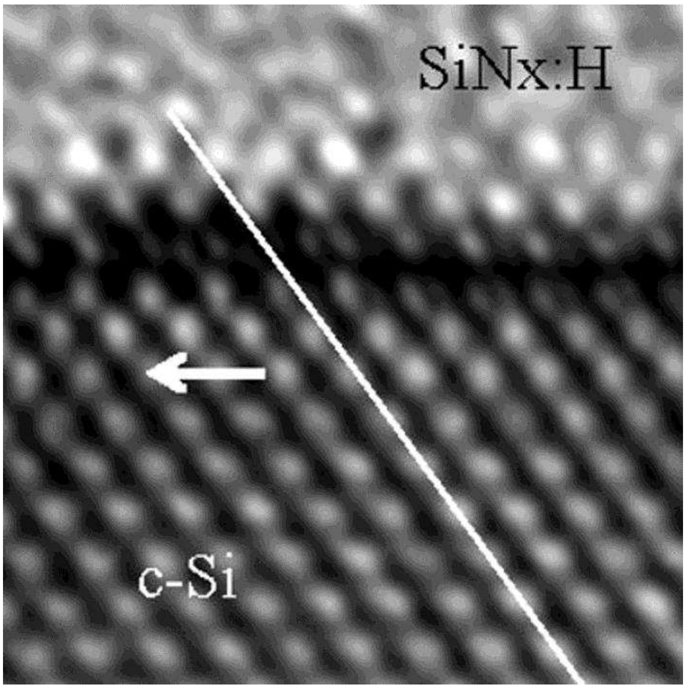

Fig 1. HRTEM image of a-SiN_x:H/c-Si interface of the <100> sample.

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 SiO_2/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).

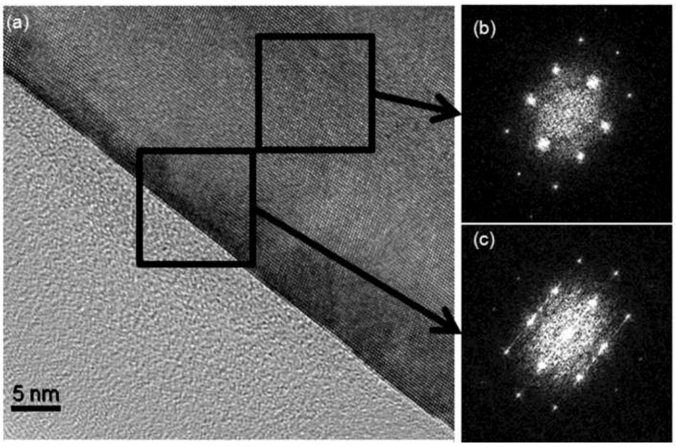

Fig 2. a) HRTEM image of a-SiN_x:H/c-Si interface of the <111> sample; b) FT image of c-Si; c) FT image of the interface of a-SiN_x:H and c-Si.

On the a-SiN_x: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.

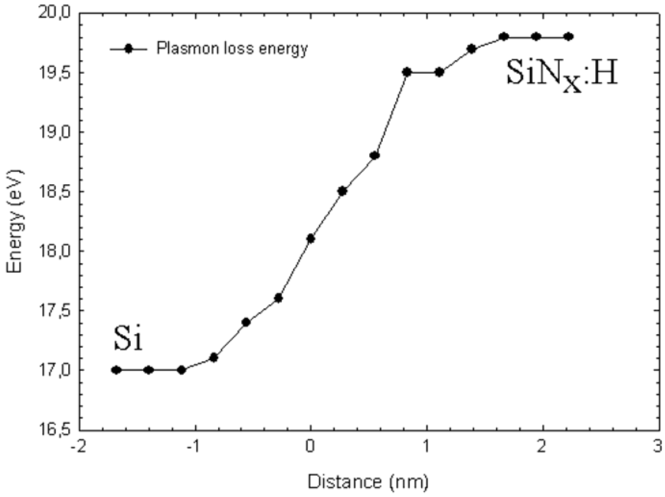

Fig 3. The plasmon loss energy over the interface of the <100> sample.The interface is at 0 nm.

In the figure it can be seen that the plasmon loss energy increases from 17.0eV to 19.8eV over 3 nm (from -1 nm to 2nm). 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-SiN_x: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 occuring at the Si side (~1nm) 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 $L_{2,3}$ 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.

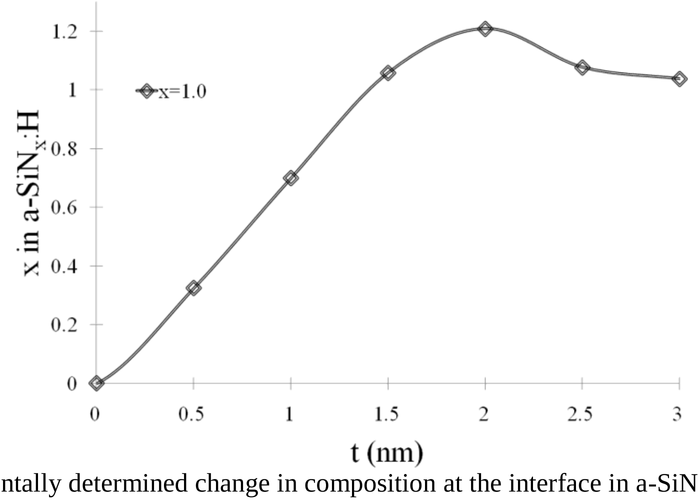

Fig 4. Experimentally determined change in composition at the interface in a-SiN_x:H of the <100> sample.The interface is at 0 nm..

2.2 Nitridation, Q_f, D_{it} and K-centers

Using remote-PECVD, the gasses to deposit a-SiN_x:H, typically SiH_4 and NH_3, are dissociated. Subsequently, a thin film a-SiN_x:H can now grow on the substrate surface. During the initial growth of a-SiN_x: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 -NH_2 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].

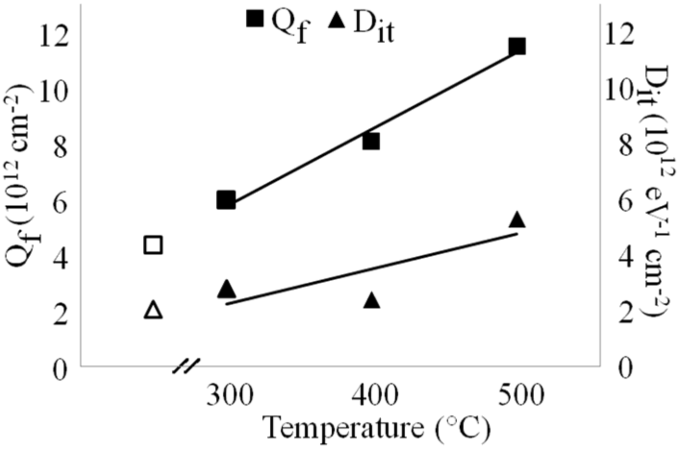

Fig 5. The effect of the temperature of a NH_3 plasma treatment on Q_f and D_{it} on p-type <100>. Open and closed symbols are samples without respectively with pre-treatment. The lines are guides to the eye [4].

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.

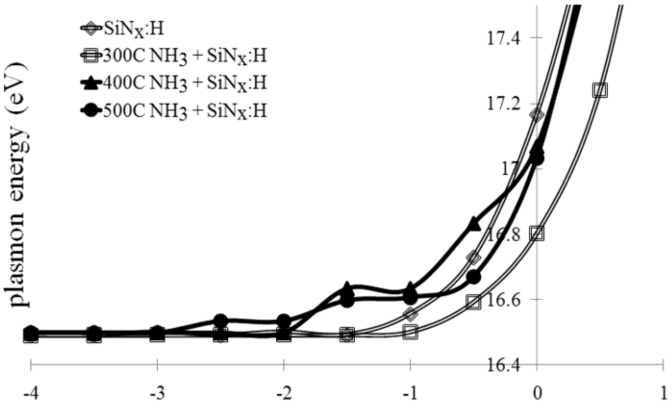

Fig 6. Plasmon loss energy over the interface for different treatments of NH_3 prior to a-SiN_x:H deposition. Each line represents the averaged value of three line scans.

For NH_3 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-SiN_x: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 Q_f. Also, the MD modeling which compares a sharp interface with a graded one, shows that gradual interfaces show significantly lower defects [12].

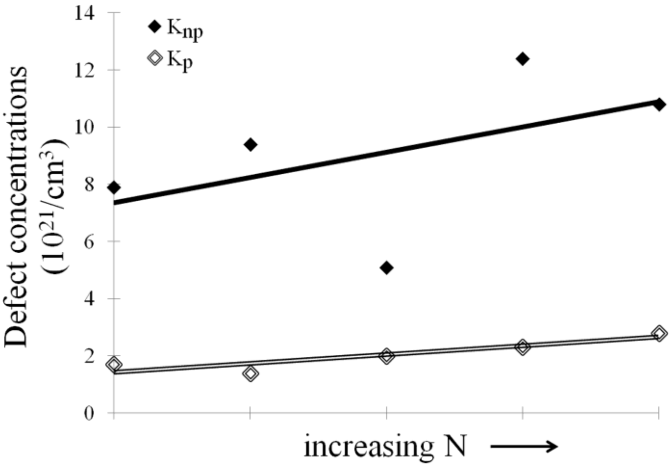

Fig 7. MD simulations of defect concentrations at gradual interfaces for increasing N concentration at the interface; p refers to passivated meaning the defect has a H atom bonded, np indicates non-passivated.

A clear gradient in the composition of a-SiN_x:H at the interface is found and also the presence of N is detected at the silicon side of the interface. With the NH_3 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 Q_f, 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 Q_f. The location of Q_f is stretched over the interface, starting a few nm’s in the c-Si to around 2 nm in the a-SiN_x:H. Furthermore, Q_f can be altered by changing the concentration gradient, more specifically of N in the c-Si. This can be achieved by using a NH_3 plasma prior to a-SiN_x:H deposition.

2.3 Hydrogen and D_{it}

To increase further the understanding of the interface, ab initio density functional theory (DFT) studies for the interface of $Si_3N_{3.5}H_{0.8}$ and c-Si were performed. For the modeling 100 atoms of $Si_3N_{3.5}H_{0.8}$ and 56 c-Si atoms were used. $Si_3N_{3.5}H_{0.8}$ is the configuration of the standard a-SiN_x: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-SiN_x: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-SiN$_x$:H interface.

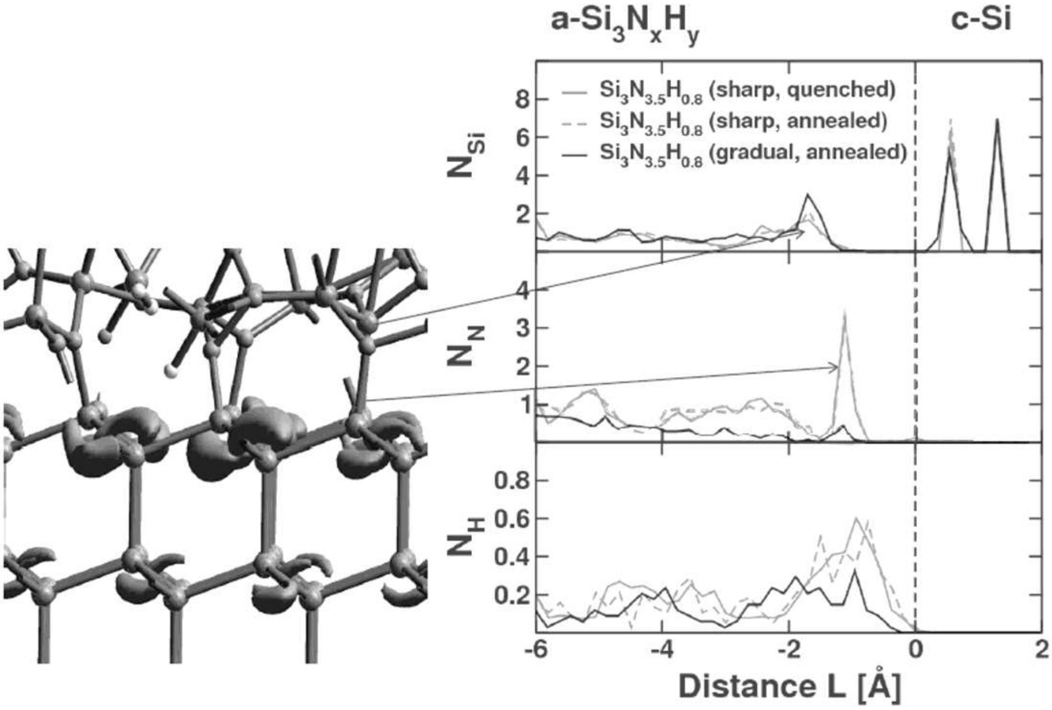

Fig 8. Results of ab initio theory studies regarding the structure and concentrations at the $Si_3N_{3.5}H_{0.8}$/c-Si interface.

It can be seen that for $Si_3N_{3.5}H_{0.8}$ 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 10^{23} 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-$Si_3N_{3.5}$ (x=1.17) and a-Si_3N_3 (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 D_{it}. 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 Si_3N_3 must be higher than for $Si_3N_{3.5}$, 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 D_{it} and Q_f. The D_{it} is further increased by distorted Si units. Finally, the reduction of defects due to hydrogen agrees perfectly with experimental findings as shown in [4].

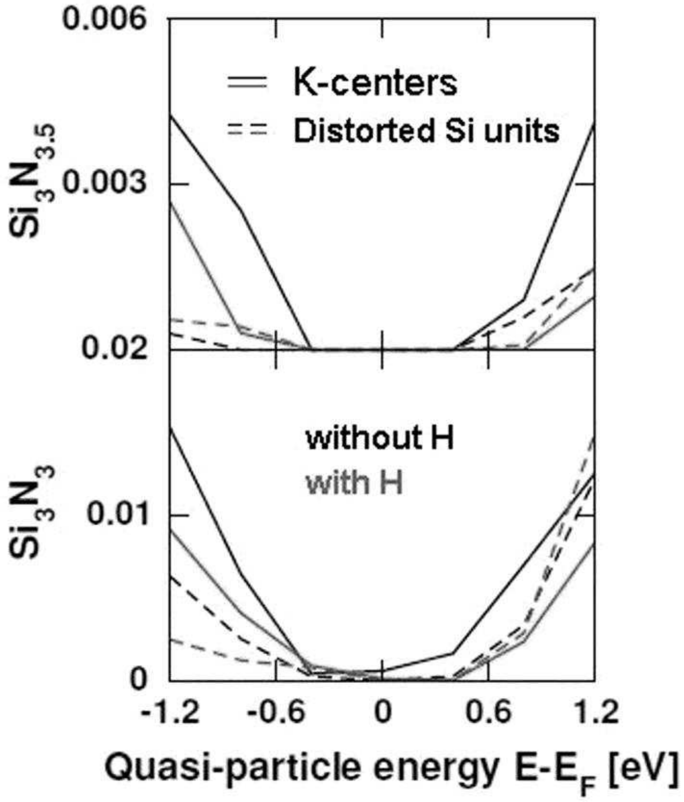

Fig 9. The Density of States (DOS) of $Si_3N_{3.5}$ and Si_3N_3 close to Fermi-level. The total DOS is related to K-centers and distorted Si units (full and broken lines). Additional hydrogen (grey lines) reduces the amount of electronic defect states in the gap [15].

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.

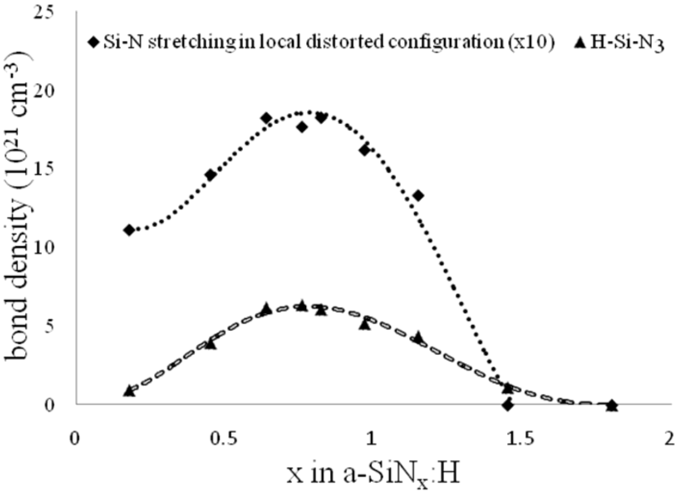

Fig 10. The bond densities of H-Si-N_3 and Si-N stretching in local distorted configuration [4,13].

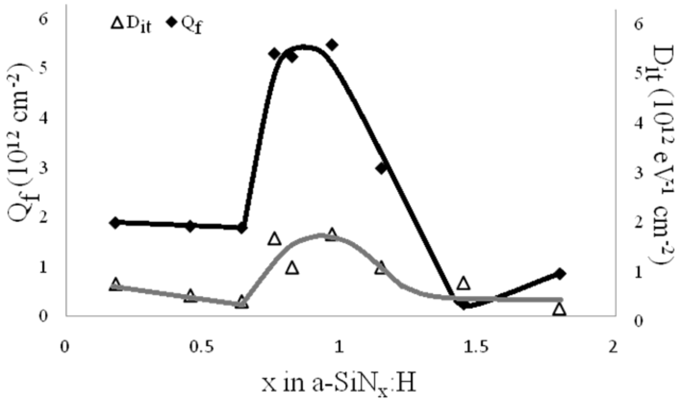

Fig 11. Relationship between Q_f, D_{it} and x. The lines are guides to the eye.

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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