Examination of the properties of the interface of a-SiNx:H/Si in crystalline silicon solar cells and its effect on cell efficiency

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ABSTRACT

Nitridation is the process in which, during the initial growth of a-SiNx:H layers on Si surfaces, nitrogen (N) is incorporated into Si lattice near its surface. We show that this nitridation process affects the density of interface states (D_{it}) and fixed charges (Q_f) at the interface. These parameters determine the effective surface passivation quality of the layers. The nitridation can be tuned independently of the growth of a-SiNx:H layers by using a plasma treatment prior to actual a-SiNx:H layer deposition. It is shown that the Q_f can be varied from $2 \cdot 10^{12}$ to $15 \cdot 10^{12}$ cm^{-2} without changing the a-SiNx:H deposition process. It is demonstrated that in our case and processing window, Q_f is the determining factor in surface passivation quality in the range of $2 \cdot 10^{12}$ to $8 \cdot 10^{12}$ cm^{-2}. For higher values of Q_f, D_{it} has increased significantly and has become dominant thereby reducing the passivation quality. It is shown that the passivation can be controlled independently of the a-SiNx:H deposition process. On completed solar cells this variation in Q_f due to nitridation results in a change in open-circuit voltage, V_{oc}, of almost 20mV.

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. Commonly, the layer is deposited using plasma-enhanced chemical vapor deposition (PECVD). The physical properties of the layer have previously been correlated to cell output properties like the open-circuit voltage V_{oc} [1,2]. In general, the optimized a-SiNx:H layer is a compromise of optical (antireflection and absorption) properties, and bulk and surface passivation. Si-rich a-SiNx:H layers show good surface passivation, but are highly absorbing and cannot be used for solar cell application. N-rich layers show good optical properties, but are less effective in surface passivation. In this paper our aim is to better understand the surface passivating properties and open ways to de-couple the surface passivating properties from the other properties (bulk passivation and optical) that should finally result in better solar cells.

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 by 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]. For lightly doped material a high Q_f will increase the field-effect contribution to the surface passivation. For dopant types with opposite polarity than the fixed charges, the field effect is governed by accumulation. For doped material with the same polarity the field effect is governed by inversion. For highly doped materials with opposite polarity as the fixed charges, a higher Q_f can (slightly) improve the surface passivation by accumulation. For highly doped materials with the same polarity as Q_f the

surface passivating quality will decrease because of depletion. More information can be found in [3]. Q_f and D_{it} are determined by the physical properties of the a-SiN$_x$:H layers. The general rule is that a lower Q_f and D_{it} are related to more Si-rich layers while a higher Q_f and D_{it} are related to more N-rich layers as also shown this paper. Note that it means that these parameters are competing with respect to the surface passivating quality and an optimum needs to be found.

As Q_f and D_{it} are properties of the interface of Si/a-SiN$_x$:H, this indicates that they are determined by the initial growth of the a-SiN$_x$:H layer. More profoundly, 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 [4]. This local field depends on the different polarizabilities within each material and the variation of these polarizabilities over distance at the interface. The different polarizations in a-SiN$_x$:H, which can be charged have been linked to the so-called K- and N-centers [5]. These centers are respectively *Si≡N$_3$ and *N=Si$_2$. * indicates that these centers can be neutral, positive, negative or bonded to H. 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. The number of K-centers that is bonded to H can be estimated from the Si-H peak in an FTIR [6] spectrum and is correlated to Q_f and D_{it}. A peak location close to 2220 cm^{-1} indicates relatively more K-centers. Both the K- and N-centers have also been described as the origins of the dangling bonds at the interface and therefore related to D_{it} [5]. Therefore, when the (charged) K- and/or N-centers are increased in volume fraction, Q_f will increase. Simultaneously, as the volume fraction of the centers is increased, the amount of (unpassivated) dangling bonds also increases and, therefore, D_{it} increases as well.

During the initial growth of a-SiN$_x$:H the surface is nitridated, which can be described as N-diffusion into the Si surface and is found to be 1-3 nm within the Si bulk. Depending on the deposition temperature and gas flow different bonds and diffusion characteristics of the nitridation are obtained [7]. Up to temperatures of 300°C no effect was observed. Above 350°C it is observed that NH$_2$ starts to adhere to the Si surface. Above 400°C N begins to be inserted into the Si-Si bonds. Above 425 °C Silicon Nitride is formed inside the Si surface which continues to increase with temperature. That this nitridation has indeed a direct relation with Q_f was shown by Takakura, though he observes no difference in D_{it} [8].

In this article we will demonstrate the variations in Q_f and D_{it} by different plasma pretreatments causing different nitridation profiles and thus different surface passivating properties while applying the same a-SiN$_x$:H layer. The effect of the nitridation on the surface passivating properties for completed solar cells are shown as well. This indicates that separate control of bulk and interface properties of a-SiN$_x$:H is possible.

LAYER STUDY

General a-SiN$_x$:H

During a-SiN$_x$:H deposition, different gas ratios and temperatures determine both the initial growth conditions and bulk properties [1,9]. As the initial growth of the a-SiN$_x$:H layer determines both nitridation and the Q_f and D_{it} values, a clear correlation is found between the properties of the layer and Q_f and D_{it}. To show this, samples were prepared using 275 μm thin p-type FZ <100> wafers, which were double side mirror polished with a base resistivity of 2.5 Ωcm. Remote PECVD was used to deposit 80-100 nm a-SiN$_x$:H layers with different composition on one side of the wafer. Bond densities were calculated from FTIR data, and after

300 nm aluminum deposition on the samples to create MOS structures, Q_f and D_{it} were determined using CV-MOS analysis. The relationship between Si-H bond density and Si-H peak position with Q_f and D_{it} are shown in figure 1A and 1B. It can be seen that Q_f and D_{it} show the same trend. This can be explained since, as the number of charged K- and N-centers increases, the neutral dangling bonds (uncharged and non-passivated K- and N-centers) increase as well. A higher N-content within the layer corresponds to a higher Q_f and D_{it}. Even more, it can be seen that Q_f and D_{it} increment with increasing Si-H peak position, but with decreasing Si-H bond density. This leads to the conclusion that the number of K-centers in a-SiN$_x$:H are more pronounced in N-rich material. It should be noted that in this case bulk properties are used to explain surface effects, which is not a trivial relation..
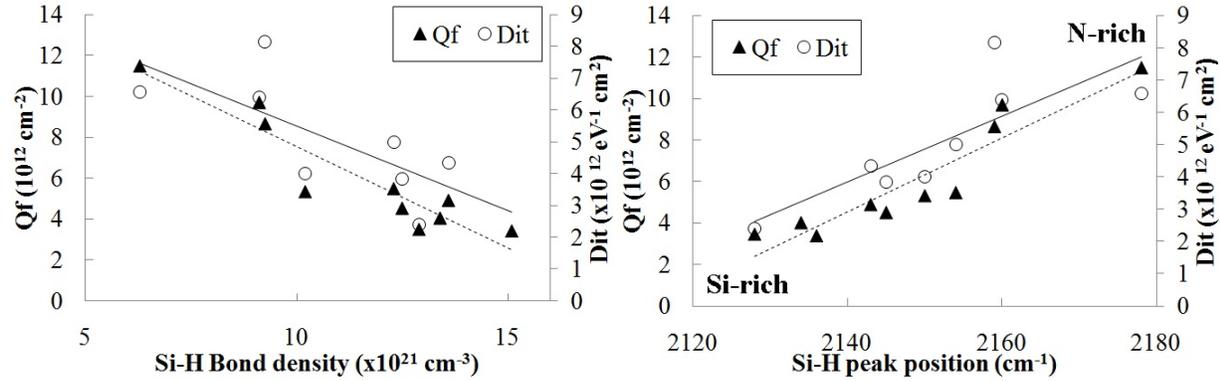

Figure 1: A: The relationship between Q_f and D_{it} and A: Si-H bond density. B: Si-H peak position.

Nitridation of the Si surface

To study the effect of nitridation on passivation in more detail, various plasma (pre-) treatments prior to a-SiN$_x$:H layer deposition were done. To study possible dependence on dopant type and crystal orientation, two different materials were used: 275 µm thin p-type FZ <100> wafers, which were double side mirror polished with a base resistivity of 2.5 Ωcm, and 275 µm thin n-type FZ <111> wafers, which were double side mirror polished too, but with a base resistivity of 3.5 Ωcm. Half of the wafers were diffused on both sides with an industrial boron emitter used in n-type processing and cleaned to remove the boron glass and organic particles. This step was taken to differentiate between influences of p-type and n-type on one hand and the crystal orientation on the other. Shortly before nitridation, the wafers received an HF dip to remove the surface oxide. As mention above the total process consisted of a plasma pretreatment to vary nitridation followed by a-SiN$_x$:H layer deposition. The latter was the same for all pre-treatments. Both steps in the process were performed using a remote PECVD system. The effective lifetime, which is determined by the bulk lifetime and surface passivating quality, of the minority carriers was measured using symmetric test structures with nitridation and a-SiN$_x$:H coating on both sides. Samples with nitridation and coating on one side were used to determine Q_f and D_{it} using CV-MOS. Plasma treatments were carried out at temperatures between 300 and 500°C.

In figure 2A the effect of the temperature of a NH$_3$ plasma on Q_f is shown. It can be seen that already at 300°C a small effect can be seen, which suggests that the onset of nitridation might start at somewhat lower temperature than suggested by Dai et al. [7]. The nitridation effect can be seen by the increase in Q_f. In figure 2B, the effect on the effective lifetime is shown. A higher lifetime, thus better passivation, is obtained when the surface is slightly

nitridated and so Q_f values up to about $8 \cdot 10^{12}$ cm^{-2} corresponding to pre-treatment temperatures of 400 °C. In this case and according to Dai et al. [7], NH$_2$ starts to grow on the surface, but no insertion of N in the Si-Si bonds takes place. The improvement in lifetime compared to samples without plasma pre-treatment (nitridation) might be related to improved hydrogenation of the surface which lower D_{it}. A too large increase in Q_f lowers the surface passivation since D_{it} now also significantly increases. An optimum was found at 400°C for n-type <111> and at 300°C for p-type <100>. A similar trend as for the p-type <100> was found for the boron diffused samples (not shown), which suggests that the effect is dopant related and not depending on the crystal orientation.
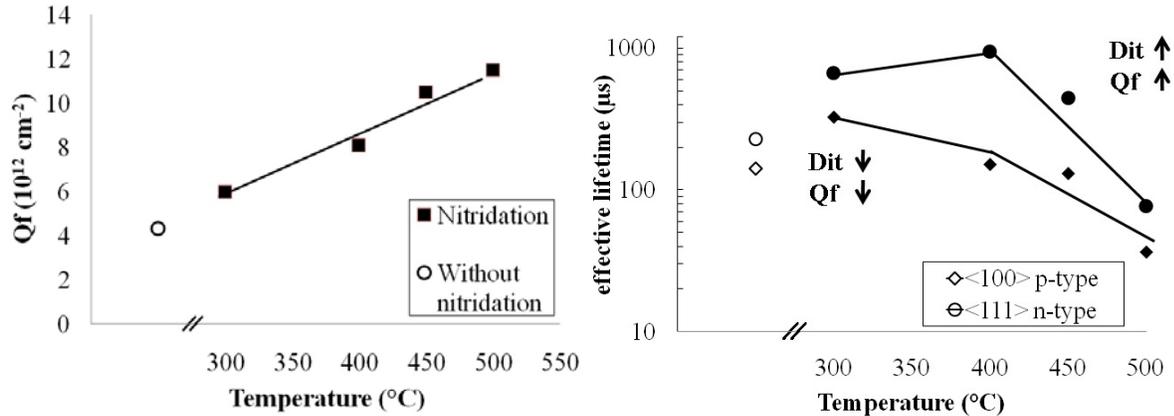

Figure 2: A: The effect of the temperature of a NH$_3$ plasma treatment on Q_f as measured on p-type <100>. B: The effect of the temperature of a NH$_3$ plasma treatment on the effective lifetime determined for a minority carrier density of 1.10^{15} cm^{-3}. Open symbols are samples without nitridation (pre-treatment), the closed ones with. The lines are guides to the eye.

SOLAR CELL STUDY

For p-type silicon solar cells the emitter is n-type and a higher Q_f can have a positive contribution to the surface passivating quality due to accumulation. Since in our case higher Q_f will result in higher D_{it}, these effects can be competing. For n-type solar cells the emitter is highly doped p-type and a higher Q_f will have a negative effect on the passivating quality due to depletion. Since Q_f and D_{it} have the same trend, a stronger (and negative) effect is expected to be seen for n-type solar cells. Therefore, we decided to use n-type solar cells to the study this effect on completed cells.

The structure of the fabricated n-type cells is illustrated in Figure 3 and the processing is described in [10]. Prior to the a-SiN$_x$:H layer deposition on the front side, the cells are given a plasma pre-treatment to alter Q_f and D_{it}. The same a-SiN$_x$:H layer was used for all solar cells.

The variation in plasma treatments consisted of a response curve matrix where the temperature was varied between 300 and 500°C and the gas flow ratio, NH$_3$/(H$_2$+NH$_3$), between 0 and 1. Q_f and D_{it} were determined using the same method and material as described above.
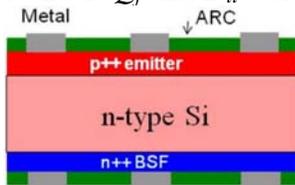

Figure 3: Structure of a bifacial n-type cell.

In figure 4, V_{oc} is given as a function of Q_f. As Q_f and D_{it} increase simultaneously with increased nitridation, as shown in figure 5, the trend in V_{oc} is due to the combined effect of increased D_{it} and increased depletion caused by higher Q_f. Also the effect in other cell parameters like the J_{sc}, FF and cell efficiency were very significant (not shown). This strong effect, independent of the a-SiN$_x$:H deposited, indicates that separate control of bulk and interface properties is possible to optimize the efficiency of solar cells.
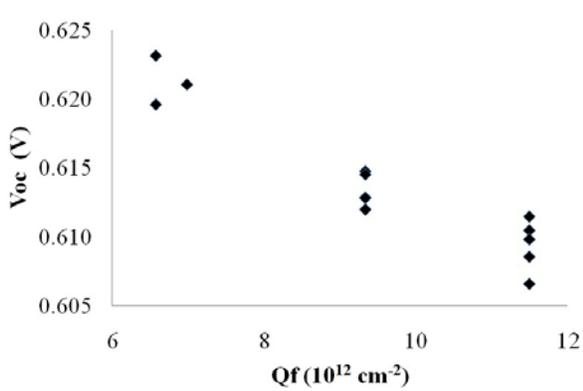

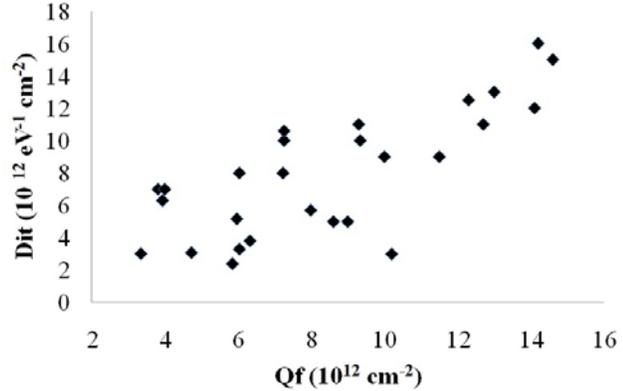Figure 4: The V_{oc} of the solar cell as function of Q_f.

Figure 5: The relationship between Q_f and D_{it} due to nitridation.

MODELLING STUDY

Molecular dynamics simulations confirm the influence of nitridation profile on the concentration of defects at the interface between the a-SiN$_x$:H and the Si bulk [11]. Heavier nitridation increases the recombination inside the Si crystal. This recombination then occurs with increasing distance from the interface in the range of a few nm. This confirms the expected increase in dangling bonds and related K- and N-centers. In figures 6A and 6B the dependence of interface defect centers concentration on the nitridation profile are shown. The plots show a clear increase in volume and fraction of both the K- and N-centers, which correlate to the experimentally found increase in Q_f and D_{it}.
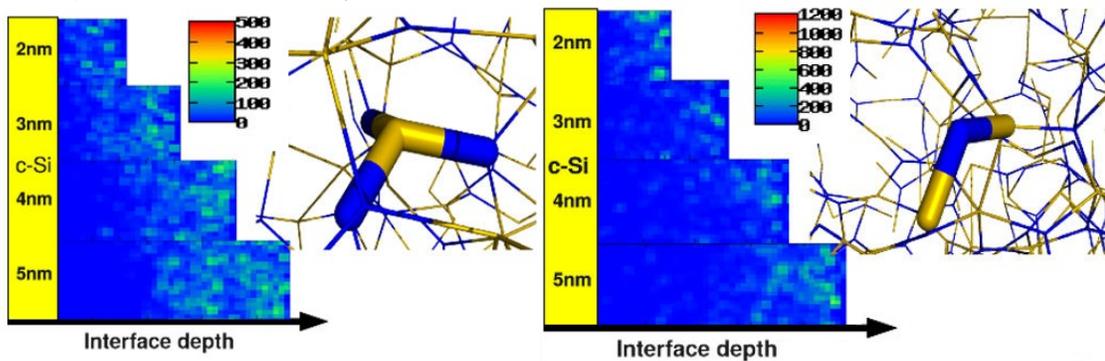

Figure 6. Molecular Dynamics Simulations of nitridation on: A: K-centers; B: N-centers. In the figures the interface lies right, the c-Si bulk left.

CONCLUSIONS

The incorporation of N into the Si surface during the initial growth of a-SiN$_x$:H is a process called nitridation. This nitridation is closely related to the density of interface states (D_{it}) and fixed charges (Q_f), which are parameters that determine the surface passivation quality in a solar cell. Increasing the nitridation by use of a plasma treatment prior to a-SiN$_x$:H deposition alters Q_f from $2 \cdot 10^{12}$ to $15 \cdot 10^{12}$ cm^{-2} and the correlated D_{it} from $2 \cdot 10^{12}$ to $16 \cdot 10^{12}$ eV^{-1} cm^{-2}. It is demonstrated that in our case and processing window, values of Q_f till about 8.10^{12} cm^{-2} determines the quality of the passivation. For values of Q_f between $6\text{-}8 \cdot 10^{12}$ cm^{-2} optimal passivation is found on lightly doped samples.

Molecular dynamics modeling of the nitridation effect shows that with increased nitridation the volume and fraction of the K- and N-centers in the Si bulk increase and are located in the first few nm from the interface. This correlates to the experimentally found increase in both Q_f and D_{it}. On completed solar cells this variation in Q_f due to nitridation results in a change in open-circuit voltage, V_{oc}, of almost 20mV. This shows that separate control of interface and bulk properties of a-SiN$_x$:H is possible.

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