CHARACTERIZATION OF STRESS IN HIGH-RATE ETP DEPOSITED SILICON NITRIDE BEFORE AND AFTER ANNEALING

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ABSTRACT: OTB Solar uses the ETP technique on its high throughput PECVD tool the $\mathrm{DEP_X}$ for the deposition of silicon nitride and has investigated the intrinsic stress of these high-rate (>4 nm/s) deposited SiN films before and after annealing. The SiN layers were grown from an Ar-NH_3-SiH_4 plasma expansion and are normally used as ARC and passivation layer on crystalline silicon solar cells. Different SiN films were processed with a wide range of refractive indices (1.88 to 2.44) and characterized by spectroscopic ellipsometry, FTIR and stress measurements before and after a firing anneal step. It appears that ETP deposited SiN layers possess tensile stress which varies with the refractive index. A maximum of 1025 MPa has been observed at a refractive index around 2.0 which corresponds with a minimum of total bonded hydrogen, the point of an equal N-H and Si-H bond distribution and the maximum in Si-N bond density. These results would predict a growth model that favors Si-N bond formation at the surface of the substrate instead of in the plasma. The tensile stress would then be created by sacrificing N-H and Si-H bonds to form Si-N bonds and hydrogen. These layers were also used in a thermal-oxide/SiN passivation stack to determine the extra passivation induced by the SiN. The best performing layers ($J_0 < 20$ fA, $\tau_{eff} > 1$ ms) were obtained at a high refractive index at low levels of stress.

Keywords: Silicon-Nitride, Annealing, Passivation, Lifetime

1 INTRODUCTION

Because the silicon wafer material is still responsible for the largest costs when manufacturing crystalline silicon solar cells the trend is still towards thinner wafers. This will not only present a major challenge in handling these cells but will also affect the currently used standard processing. Wafer bow for example arising after the high temperature firing step due to the differing thermal expansion of silicon and the used aluminum paste when using a screen printed aluminum back surface is one of the problems occurring when moving towards thinner wafers. Therefore, new “low bow” pastes are being developed [1] which are necessary to prevent wafer curvatures that are not acceptable any more. Silicon nitride (SiN) can cause a similar problem for even thinner wafers when the stress in the SiN layer is very high.

OTB Solar uses the expanding thermal plasma (ETP) technique on its high throughput silicon nitride deposition tool the $\mathrm{DEP_X}$ [2] for the deposition of a passivating antireflection coating (ARC) on mono- and multicrystaline silicon solar cells. This ETP technique is a true remote plasma technique (plasma creation in the ETP source, not in the deposition chamber) which has implications for layer properties like the intrinsic stress of the SiN film. The nature of stress occurring in these ETP deposited SiN layers is therefore investigated. The nature of stress in a thin layer is also an important layer property as it can help to understand for example the growth mechanism or annealing behavior.

Good bulk and surface passivation properties of these SiN layers have already been demonstrated [3,4] and here the extra passivation effects obtained when these SiN layers are used within a thermal-oxide/SiN passivation stack are also investigated.

2 EXPERIMENTAL

Silicon nitride layers were grown with varying process parameters in order to obtain a wide range in film properties like Si/N ratio, mass density (ρ), hydrogen content and refractive index (n). The baseline process for the deposition of an antireflection coating on silicon solar cells (n ~ 2.07) was used as the reference silicon nitride. A range from 1.92 to 2.44 for the refractive index was obtained by solely varying the silane flow, and even lower refractive indices (n ~ 1.88) were obtained by also reducing the deposition temperature at the lowest silane flow that was used. The silicon nitride layers were characterized by Fourier Transform Infrared spectroscopy (FTIR, Bruker Vector 22) and spectroscopic ellipsometry (SE, Sentech Senduro). The stress in the silicon nitride films was determined by measuring the curvature (bow) of an 8” CZ silicon wafer by laser reflection before and after SiN deposition. This enables calculating the stress (σ) in the deposited layer by

$$\sigma_{SiN} = \frac{E_{Si}}{6(1-\nu_{Si})} \frac{d_{Si}^2}{d_{SiN}} \left(\frac{1}{R} - \frac{1}{R_0} \right)$$

with:

E_{Si}: Young’s Modulus of silicon (150 Gpa for (100) silicon)
ν_{Si}: Poisson ratio of silicon ($\nu_{Si} = 0.17$)
d_{Si}: thickness of substrate (725 μm)
d_{SiN}: thickness of silicon nitride (80-100 nm)
R: curvature of sample with SiN
R_0: reference curvature (of bare silicon substrate).

The silicon nitride layers were characterized before and after an anneal step that had a temperature profile which mimics the high temperature (~900°C) firing step normally used for processing screen printed solar cells with an in-line belt firing furnace.

The extra passivation effect when these layers are used in a thermal-oxide/SiN passivation stack is determined with a Sinton WCT100 lifetimetester, however, only for as-deposited SiN films and without any forming gas anneal (FGA) treatment.

3 RESULTS AND DISCUSSION

3.1 Silicon nitride film properties

Figure 1 shows the results for the total stress in the silicon nitride layer as a function of the refractive index before and after annealing the SiN films in the in-line firing furnace.

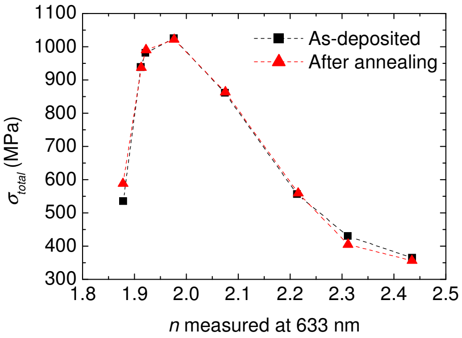

Figure 1: Total stress of ETP deposited silicon nitride before and after annealing as a function of refractive index.

The stress for as deposited silicon nitride is tensile over the complete range of refractive indices and varies from 365 MPa for the highest refractive index that was obtained to a maximum of 1025 MPa at a refractive index of around 2.0. For refractive indices lower than 2.0 the stress is lower with a large reduction of almost 575 MPa when going from a medium deposition temperature of ~300°C (938 MPa) towards a very low deposition temperature of around 200°C (365 MPa).

After the anneal step the stress remains tensile and keeps the same trend as a function of refractive index compared with the as-deposited values. Only the sample processed at the lowest deposition temperature shows a significant increase in stress after annealing of around 50 MPa. The sample at a refractive index around 2.3 shows a decrease of 25 MPa and at the highest refractive index a decrease of 10 MPa is observed. This might be an indication that these silicon nitride layers become less stable at refractive indices higher than 2.2. This corresponds with earlier work [5] which demonstrated that ETP deposited silicon nitride layers with a refractive index of 1.9 and 2.1 are thermally stable while silicon nitride layers with a refractive index of 2.3 proved to be thermally unstable by showing a large increase in refractive index and a change in other layer properties like film thickness and extinction coefficient (*k*) at annealing temperatures higher than 800°C. The results displayed in figure 1 show almost no change in refractive index after the anneal step, even for the highest refractive indices.

This can also be seen in figure 2 which shows the extinction coefficient as a function of the refractive index. Here, almost no change is visible for these optical layer properties before and after annealing which was also the case for the film thickness which did not show any change as well (not shown). This demonstrates that a higher degree of thermal stability is obtained with the currently used process window regarding these optical film properties compared with the earlier work [5]. Figure 2 also demonstrates that these SiN layers have a relatively low UV absorption with values for the extinction coefficient measured at a wavelength of 360 nm being close to zero at a refractive index of around 2.0.

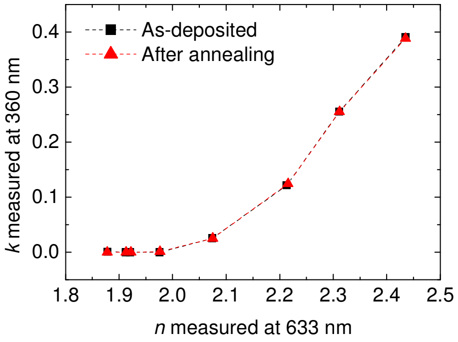

Figure 2: Extinction coefficient measured at 360 nm versus the refractive index.

The hydrogen bonded to nitrogen and silicon in the form of N-H and Si-H bonds has been analyzed by FTIR. The total amount of bonded hydrogen is determined by adding the N-H and Si-H bonds and this is shown in figure 3. It shows when comparing figure 3 with figure 1 that the silicon nitride layers which inhibit the highest degree of tensile stress contain a relative low amount of bonded hydrogen.

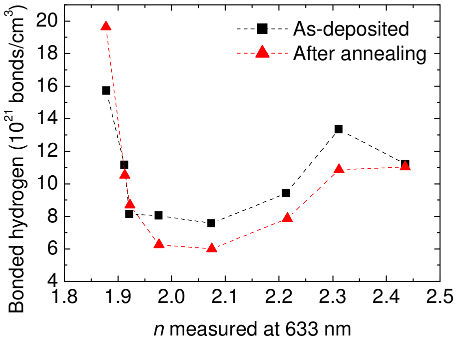

Figure 3: Bonded hydrogen before and after annealing determined by FTIR versus the refractive index.

The samples with the lowest refractive indices were processed at a lower deposition temperature and contain a relatively large amount of bonded hydrogen. The amount of bonded hydrogen as a function of the refractive index first decreases with higher refractive indices and reaches a minimum at around 2.08. At higher refractive indices the amount of bonded hydrogen increases again. After annealing the total amount of bonded hydrogen decreases over almost the complete range of refractive indices that was obtained except for the lowest *n*. This sample is processed at the lowest temperature and has the largest amount of bonded hydrogen in the form of N-H bonds as can be seen in figure 4 which shows the N-H and Si-H bonds before and after annealing as a function of the refractive index. The increase in bonded hydrogen after annealing this sample might be explained by the presence of molecular hydrogen in the SiN layer which bonds with Si or N atoms during the annealing or the extra bonded hydrogen might originate from NH_2 bonds which are not included in the bonded H analysis. It is also possible that the proportionality factors used to determine the N-H and Si-H bonds [6] are not valid for these samples with varying layer properties which has been suggested by [7] and this would give a distorted view of the results. Figures 3 and 4 are obtained by assuming that these proportionality factors are constant.

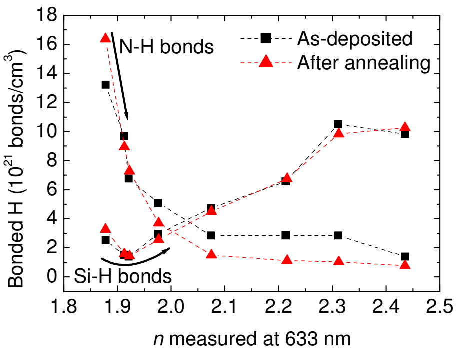

Figure 4: N-H and Si-H bonds before and after annealing versus the refractive index.

The decrease of hydrogen as a function of refractive index for as-deposited layers is caused by an increase in Si-N bonds which can be seen in figure 5. The hydrogen atoms in samples with a low refractive index which are preferably bonded to N are replaced by Si-N bonds until a minimum of bonded hydrogen is obtained around a refractive index of 2.08 in this case. At higher *n* the Si-N bonds are replaced again by Si-H bonds which causes the amount of bonded hydrogen to increase again.

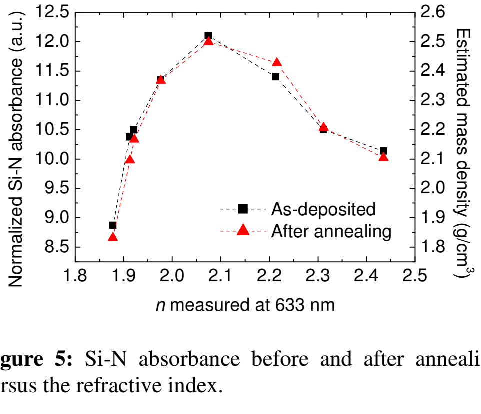

Figure 5: Si-N absorbance before and after annealing versus the refractive index.

The mass density is indicated on the right side of figure 5 as well. When comparing the mass density obtained by Rutherford Backscattering Spectroscopy with the Si-N absorbance determined by FTIR a relationship can be found which links higher mass densities with a higher Si-N absorbance [8].

The maximum of the Si-N absorbance seems to correspond with the maximum of stress in the silicon nitride layer. In fact the overall trend of the Si-N absorbance as a function of the refractive index compared with the stress versus *n* is rather similar. This indicates a correlation between the Si-N absorbance or mass density with the total stress in the SiN film for these samples.

We propose the following mechanism to explain the tensile nature of the stress and the correlation with the Si-N absorbance. It involves the formation of Si-N bonds on the substrate's surface during film growth rather than the formation of Si-N precursors in the plasma. In this mechanism N-H and Si-H bonds on the substrate's surface are sacrificed during film growth to obtain strong Si-N bonds with the release of a hydrogen molecule, or Si and N dangling bonds on the substrate's surface which have lost a hydrogen atom to the plasma link together to form a Si-N bond. Before linking together the Si and N atoms would already have a quasi fixed position in the amorphous layer and are slightly forced together when forming the Si-N bond and therefore increase the tensile stress. A higher amount of bonded hydrogen in the layer would then correspond with less tensile stress because less Si-H and N-H bonds are then forced to Si-N bonds which agrees with figure 3 which shows that the minimum amount of bonded hydrogen corresponds with the refractive index at the maximum of stress in figure 1. Also an equal amount of N-H and Si-H bonds in the layer would then correspond with a maximum of tensile stress because these layers would have the best surface environment for Si-N bond formation during film growth. This seems to be the case when comparing figure 4 with figure 1 which show that the position of the cross-over of the N-H and Si-H bonds for as-deposited layers is located close to the maximum of the tensile stress.

3.2 Passivation results

In order to study the effect of using these SiN layers in a thermal-oxide/SiN passivation stack similar layers were deposited on already thermal oxide passivated solar grade monocrystaline silicon wafers to act as extra passivation layer and as antireflection coating. These test wafers were coated with this SiO/SiN stack on both sides in order to determine the dark saturation current density (J_0) and effective lifetime (τ_{eff}). The dark saturation current density of these wafers when only passivated with a thermal oxide is around 40-60 fA/cm^2.

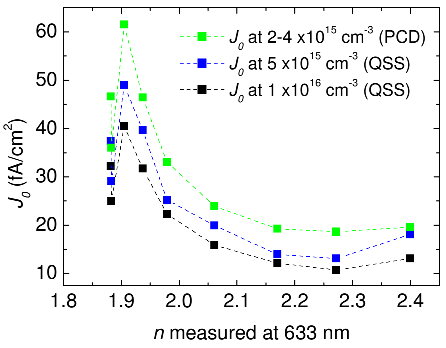

Figure 6: Dark saturation current density versus the refractive index.

Figure 6 shows the dark saturation current density (J_0) displayed as 10^{-15} Ampere/cm^2 as a function of the refractive index and the effective lifetime of the minority charge carriers obtained with these SiN films is shown in figure 7.

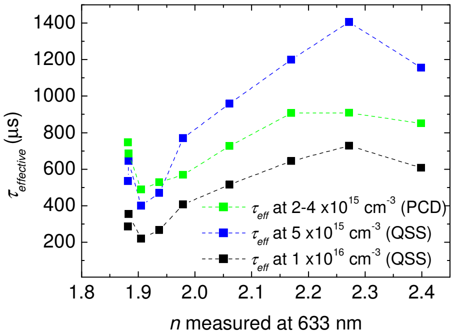

Figure 7: Effective lifetime of charge carriers versus the refractive index.

The J_0 and τ_{eff} were determined with a Sinton WCT100 lifetime tester by the Quasi-Steady State method (QSS) and the Transient Photoconductance Decay method (PCD) [9]. For the QSS measurement the results are displayed at a minority charge carrier density of 5×10^{15} and 1×10^{16} cm^{-3} because the obtained values can vary with the point of choice which is used to execute the linear fit for the J_0 determination. The PCD method gave a less ambiguous dataset for the fit and the point of charge carrier density which was chosen to obtain the best fit (see figure 8) remained in the range of $2\text{-}4\times10^{15}$ cm^{-3}. The obtained J_0 displayed in figure 8 has to be divided by 2 because of the presence of a double emitter (both sides diffused).

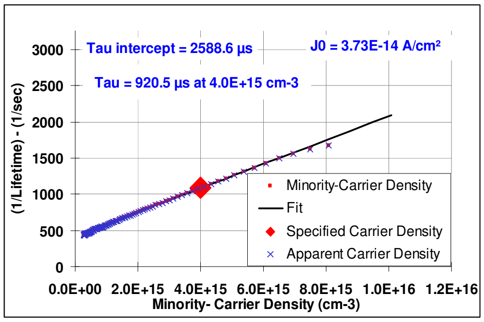

Figure 8: Example of J_0 determination at a charge carrier density of 4×10^{15} with the PCD method

The measured effective lifetime varied with the injection level exponentially so the τ_{eff} is displayed at the same point of charge carrier density which was chosen for the best fit for J_0.

It can be seen that the maximum in stress corresponds with a relatively high J_0 and low effective lifetime of the charge carriers. Tensile stress seems to have a negative effect on the surface passivation of these samples, however, as can be seen in the other figures also other film properties are related with the observed trend. These test wafers are passivated by a double stack with the SiN layer as the top layer which rules out an explanation that stress in the SiN layer causes a negative effect at the silicon interface. The trends in figure 6 and 7 are most likely due to an extra field effect passivation induced by the SiN layer or also by an extra hydrogen passivation at the interface originating from the hydrogen containing silicon nitride film. These effects would then be greater at higher refractive indices creating a very low J_0 of below 20 fA/cm^2 and an effective lifetime >1 ms on solar grade monocrystaline silicon at a refractive index of ~2.3. A silicon nitride layer with a low refractive index deposited at a high deposition temperature seems to have the worst passivation qualities. Decreasing the deposition temperature to ~300°C improves the passivation effect, however, lowering the deposition temperature even more to ~200°C causes a degradation again of the extra passivation.

4 CONCLUSIONS

The stress in ETP deposited SiN layers has been investigated before and after a firing anneal and appears to be tensile at least over a range of *n* from 1.8-2.4 before and after annealing. Furthermore, these SiN layers show a high degree of thermal stability over the complete range of refractive indices used. A growth mechanism that could explain the tensile nature of the stress has been proposed which involves Si-N bond formation on the substrate's surface rather than the formation of precursors with Si-N bonds in the plasma. Moreover, the extra passivation effect has been investigated when these SiN films are used in a SiO/SiN passivation/ARC stack and it has been shown that the highest degree of passivation is obtained at a high *n* accompanied with relatively low levels of stress and that with optimized SiN films a $J_0 <$ 20 fA/cm^2 and $\tau_{eff} >$ 1 ms can be achieved.

5 REFERENCES

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