ULTRA HIGH-RATE ETP DEPOSITED SILICON NITRIDE FOR >15% IN-LINE PROCESSED MULTICRYSTALLINE SILICON SOLAR CELLS

A.J.M. van Erven[1], R.C.M. Bosch[1], R. Toelle[2], O. Voigt[3], S. Petri[3], and M.D. Bijker[1]
1) OTB Solar, Luchthavenweg 10, 5657 EB Eindhoven, The Netherlands
phone +31 40 2581 721, fax +31 40 2509 871, e-mail: rob.van.erven@otb.nl
2) Shell Solar GmbH, Otto-Hahn-Ring 6, 81739 München, Germany
3) Shell Solar Deutschland GmbH, Am Dahlbusch 23, 45884 Gelsenkirchen, Germany

ABSTRACT

The DEP_X ,developed by OTB Solar, uses the ETP technique for the deposition of a silicon nitride ARC on silicon solar cells. With this technique very high deposition rates can be achieved and experiments were carried out with Shell Solar to investigate the quality of these ultra high-rate deposited silicon nitride layers. An optimization study which focused on mass density and thermal stability showed that *mc*-Si solar cell efficiencies of >15% can be reached with silicon nitride grown at >5 nm/s.

INTRODUCTION

Plasma deposited amorphous hydrogenated silicon nitride (a-SiN_x:H) is currently the choice-material for antireflection coatings (ARC) on silicon solar cells because of its good optical properties and passivating capabilities. Its tunable refractive index and low absorption makes it a suitable material for an ARC. Furthermore, the hydrogen that it contains can be released during the high temperature “firing of the contacts” step and introduced into the multicrystalline silicon (*mc*-Si) substrate. There the hydrogen can passivate defects like silicon dangling bonds and impurities by neutralizing their electrical activity which otherwise enhances charge carrier recombination. Passivating these defects then increases the open circuit voltage (V_{oc}) and to some extent the short circuit current (I_{sc}) which are the output parameters that together with the fill factor (*FF*) determine the solar cell efficiency. So together with the I_{sc} increase caused by the extra photons that enter the cell, which would have been reflected without the ARC, the silicon nitride layer gives an enormous efficiency boost.

Plasma enhanced chemical vapor deposition (PECVD) is the favored silicon nitride deposition technique for solar cell processing. It provides high quality silicon nitride layers at relatively low deposition temperatures and high deposition rates. This is especially true for deposition by the expanding thermal plasma (ETP) technique [1-3] that can achieve deposition rates well above 20 nm/s. OTB Solar uses this ETP technique on its high-throughput PECVD tool, the DEP_X [3], for in-line or batch-wise processing of silicon solar cells. The DEP_X uses three ETP sources, that can provide a very homogeneous deposition of the silicon nitride layers, by placing them in a configuration that gives the right overlap of the Gausian shaped plasma expansions. The silicon nitride is grown from an Ar-NH_3-SiH_4 plasma on the silicon solar cells at a low pressure of 0.1-0.3 mbar. The wafers are inserted by fast load-locking from atmosphere and placed on magnetically propelled carriers that are operated by a linear motor system. Currently, Shell Solar uses two of these tools for the in-line processing of *mc*-Si solar cells in Gelsenkirchen, Germany. Experiments were carried out with OTB Solar to investigate the passivating capabilities of these high-rate deposited silicon nitride layers and to optimize the deposition process for chemically textured, screen printed *mc*-Si solar cells. Bulk passivation induced by ETP deposited a-SiN_x:H has already been demonstrated [3-9] and key layer properties that determine the amount of passivation were identified [5-9]. The experiments reported in this paper have focused on these layer properties during the optimization and show that the level of passivation achieved by these ultra high-rate deposited a-SiN_x:H films is similar to that of low rate deposited state-of-the-art silicon nitride grown by conventional PECVD reactors. This resulted in *mc*-Si solar cells with >15% efficiencies processed on the DEP_X at deposition rates >5 nm/s.

EXPERIMENTAL

A schematic of the set-up used for the experiments is shown in Fig. 1.

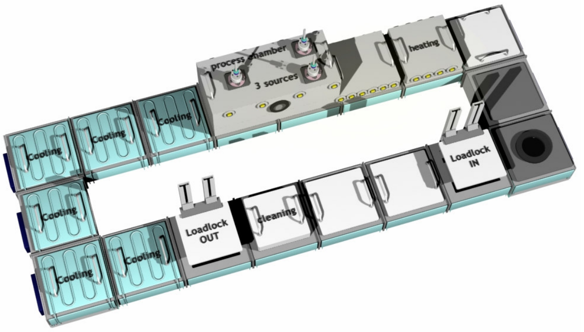

Fig. 1. Schematic layout of the PECVD tool. The carriers travel on a closed track, passing through various modules (load-lock in, pre-heat, deposition, cooling, load-lock out and cleaning).

It is not a laboratory type set-up, but the actual silicon nitride deposition tool that is used for the in-line or batch-wise processing of silicon solar cells, the DEP_X. This modular designed set-up is the result of the industrialization of the ETP concept by OTB Solar and is described more thoroughly elsewhere [3].

The optimization experiments with Shell Solar were carried out under different processing conditions. Total gas flows and gas flow ratio's as well as deposition pressure, temperature, and plasma power were varied in order to obtain clear trends and to find an optimum. For each setting a group of eleven *mc*-Si wafers, that represents a wide range in *mc*-Si wafer quality, was processed. Neighboring cells of the same wafer quality were therefore distributed over the different groups. Monocrystalline substrates were included in each group of eleven wafers and analyzed with spectroscopic ellipsometry (SE) and Fourier transform infrared spectroscopy (FTIR) to determine the relevant layer properties. Also Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) measurements were carried out. As a reference, one group was processed on a conventional PECVD tool (tube oven) which provided an already optimized silicon nitride ARC for comparison and which is capable of producing >15.5% solar cells. The other process steps for the solar cell production were kept identical and were carried out at Shell Solar GmbH in Munich, Germany. As a measure of the amount of passivation achieved by the a-SiN_x:H layers, the relative change in the product of the open circuit voltage and the short circuit current ($V_{oc}\times I_{sc}$) was chosen, measured without encapsulation of the cells.

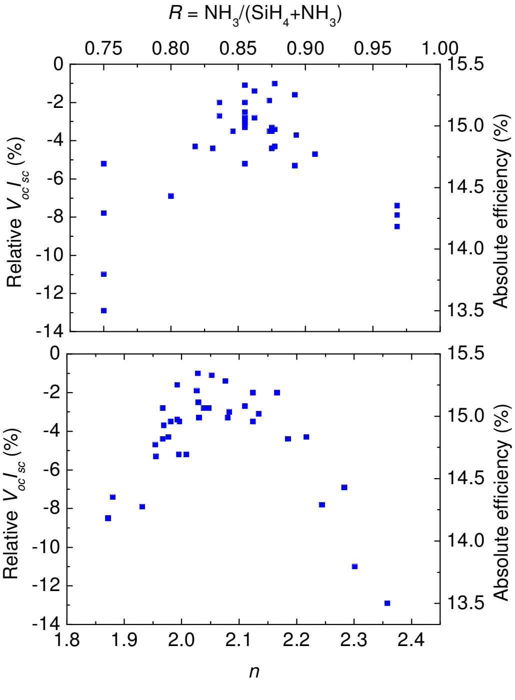

Fig. 2. Solar cell results of the different groups compared with the reference group (15.5% efficiency) as a function of partial ammonia flow and refractive index.

RESULTS

Fig. 2 displays the measured $V_{oc}\times I_{sc}$ relative to the reference group as a function of the partial ammonia flow (R) and refractive index (n). The absolute efficiency obtained using the calculated average fill factor (*FF*) of 0.75 is shown as well. Fill factor values varied in the range from 0.74 to 0.76. Each data point represents the average value of a group of eleven wafers. As can be seen from Fig. 2, a wide range of refractive indices is obtained when the total flow and ammonia to silane flow ratio are varied. An optimum is found around n = 2.05, however, it is also noticed that there still is a rather large spread around this optimum. Only a small process window provides the highest relative $V_{oc}\times I_{sc}$. For example, silicon nitride layers that have a refractive index of ~2.05, however, which were not processed at the optimal deposition pressure and temperature show lower efficiencies.

Furthermore, the best results are very near the optimized reference with only 1% relative behind in $V_{oc}\times I_{sc}$, which results in an absolute efficiency of 15.3%. Moreover, the silicon nitride layers that provide the highest $V_{oc}\times I_{sc}$ are grown at a deposition rate of >5 nm/s and demonstrate that ultra-high rate deposited films can reach an equally high level of passivation as the low-rate deposited layers grown by an optimized conventional reactor.

In the earlier studies [5,7-9] the importance of the mass density of the silicon nitride films for passivation was demonstrated. This is further investigated in Fig. 3 which shows the solar cell results as a function of the mass density. The densities were determined with FTIR spectroscopy and cross-checked with RBS. More information can be found in previous reports [7,8].

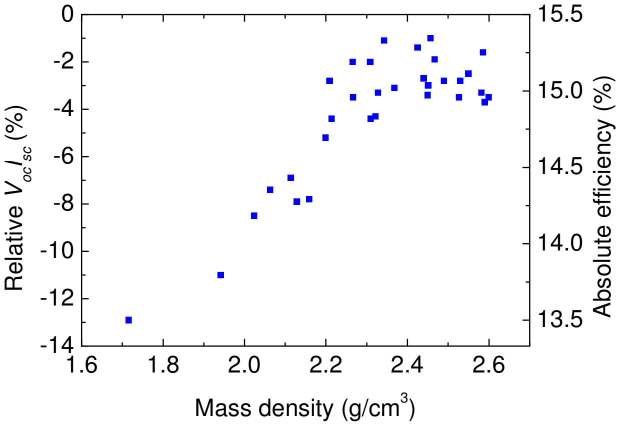

Fig. 3. Solar cell results of the different groups compared with the reference group (15.5% efficiency) as a function of film mass density.

Apparently a minimum density of around 2.3 g/cm^3 is required to obtain good passivating silicon nitride layers. Films that have lower densities show clearly a trend to lower relative $V_{oc}\times I_{sc}$ values. The deposition temperature and layer stoichiometry were the first order parameters that determine the film density.

Analyzing the monocrystalline substrates that were included in the groups with FTIR spectroscopy can also provide information on film stoichiometry and bonded hydrogen. This information can be obtained by measuring the area of the absorption bands caused by Si-H and N-H vibrational modes and also by measuring the wavenumber of the maximum Si-H absorption. The position of this maximum shifts from lower to higher wavenumbers when more or less silicon atoms are present as backbonds of the Si-H bond. This was demonstrated by Bustarret *et al.* [10] and means that the position of this peak maximum is a measure of the N/Si ratio. Thermal stability and the distribution of hydrogen were found to be important layer properties by observing the position of this wavenumber of the Si-H absorption band [7,8]. Fig. 4 demonstrates this by showing the shifting of the Si-H wavenumber to ~2180 cm^{-1} when increasing the annealing temperature, for films with a different stoichiometry varying from silicon rich (N/Si~0.75) to nitrogen rich (N/Si~1.25).

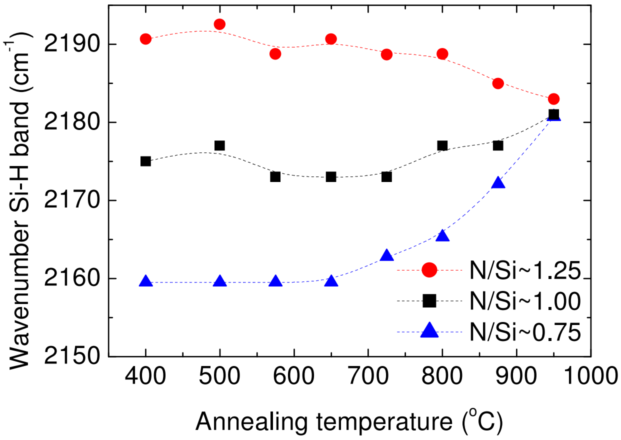

Fig. 4. Wavenumber of the Si-H band as a function of annealing temperature for different stoichiometric films varying from silicon rich to nitrogen rich.

The shifting of three different stoichiometric films to the same Si-H wavenumber indicates that a thermal stable film should have a stoichiometry that corresponds with this wavenumber. This would imply that hydrogen should be equally bonded to silicon as to nitrogen as can be seen from Fig. 5, which shows the bonded hydrogen as a function of the wavenumber of the Si-H band.

At lower wavenumbers more silicon atoms are present as backbonds because of a lower N/Si ratio and hydrogen is more bonded to silicon. Higher wavenumbers correspond with a higher N/Si ratio and hydrogen is more bonded to nitrogen. At the cross-over the hydrogen is equally bonded to silicon as it is to nitrogen and this corresponds with a wavenumber of the Si-H absorption band of ~2180 cm^{-1}. These data points were obtained from the groups that were grown with a varying ammonia to silane ratio (*n* varies from ~1.9 to ~2.4, see Fig. 2).

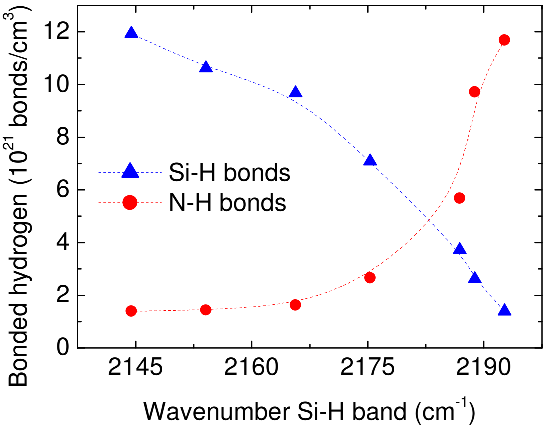

Fig. 5. Hydrogen bonded to silicon and hydrogen bonded to nitrogen as a function of the wavenumber of the Si-H band.

The importance of a thermal stable silicon nitride layer can be deduced from Fig. 6 which displays the solar cell results as a function of the wavenumber of the Si-H band.

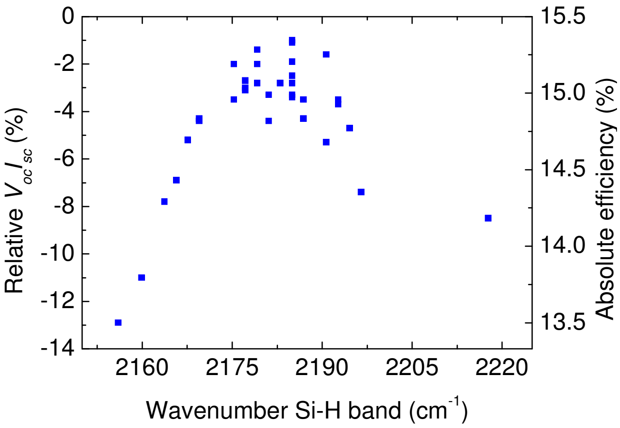

Fig. 6. Solar cell results of the different groups compared with the reference group (15.5% efficiency) as a function of the wavenumber of the Si-H band.

It shows that the optimum in relative $V_{oc}I_{sc}$ is indeed found at a Si-H wavenumber of 2180 cm^{-1}, which demonstrates that thermal stable layers provide the highest degree of passivation.

DISCUSSION AND CONCLUSIONS

From Fig. 2 is was found that silicon nitride layers with a refractive index of 2.05 provide the highest efficiency. However, the spread of the results showed that not every silicon nitride film with this refractive index will give the same result. Also the mass density of the a-SiN_x:H films should be higher than a critical value, found to be ~2.3 g/cm^3 in Fig. 3. This is caused by the fact that the optical properties of the silicon nitride film determine for a large part the efficiency. The product of layer thickness and refractive index should be at the right optical thickness that creates interference, but also the absorption should be as low as possible. The extinction coefficient (*k*) of a silicon nitride film (measured at 3.44 eV) increases with more Si-Si bonds and can start to become larger than zero at a refractive index higher than ~1.9. The optimal refractive index for antireflection, however, lies at higher values so the challenge is to increase *n* while keeping *k* as low as possible. This can be achieved by increasing the mass density of the silicon nitride film which causes a higher *n* at the same *k* [9]. By focusing on this layer property it was found to be possible with the DEP_X to obtain silicon nitride layers with zero *k*-values at refractive indices >2.0.

Silicon nitride films with a higher mass density also provide a higher degree of passivation which could be seen by the also increasing V_{oc} next to I_{sc} (not shown separately). This might be attributed to the fact that denser films are better suited to retain the hydrogen that is released during the firing step. Less voids are present and the hydrogen is then more directed into the substrate instead of lost into the ambient. Silicon nitride films with an even higher mass density than 2.6 g/cm^3 might release not enough hydrogen necessary for the complete passivation of the wafer. This might explain the saturation of the relative $V_{oc}I_{sc}$ increase with higher densities and the slight decrease which can be seen in Fig. 3. Denser films have a lower hydrogen concentration and have a higher thermal stability. Although, the amount of hydrogen normally released during the firing is three orders of magnitude larger than the concentration of deep level traps (like Si dangling bonds) found in polycrystalline silicon [8,11]. Thus only a relative small portion of the released hydrogen would be required.

The distribution of hydrogen and the thermal stability it produces appeared to be other important layer properties according to Fig. 6. Layers with a different stoichiometry showed lower efficiencies. An equal distribution of hydrogen between silicon and nitrogen induces a thermal stable layer which was shown by Fig. 4 and Fig. 5. It has already been shown [8,9] that the optical properties (layer thickness, *n*, and *k*) can change a great deal during the firing step which could partially explain the lower efficiencies. Thermally instable layers would then deviate more from the optimum optical properties after the firing step and this might cause more reflection losses and absorption. Also more hydrogen might be released into the ambient because these instable layers are usually less dense and have more voids incorporated, which results in less passivation.

The necessary equal distribution of hydrogen might suggest that the preferred way of hydrogen release for passivating the *mc*-Si wafer is according to the reaction $\text{Si-H} + \text{N-H} \rightarrow \text{Si-N} + H_2$. The equal distribution of hydrogen would facilitate that all the hydrogen can be released in this manner. This reaction would leave a strong Si-N bond (3.45 eV) behind instead of the weaker Si-Si bond (2.34 eV) or N-N bond (1.70 eV) which would result from other reactions. This would keep the creation of voids to a minimum and forms a dense layer which can retain the hydrogen. Further investigations, however, are necessary to elude the favored mechanism for hydrogen release with respect to silicon passivation.

To conclude, it has been shown which criteria are important for high quality silicon nitride ARC's, deposited with the DEP_X, that provide high efficiency solar cells. And, that these criteria can be met even at a growth rate of >5 nm/s which results in *mc*-Si solar cells with ETP deposited ARC's of an efficiency of 15.3%.

ACKNOWLEDGEMENTS

We would like to thank the Eindhoven University of Technology and especially B. Hoex for performing the spectroscopic ellipsometry measurements.

REFERENCES

[1] D. C. Schram and G. M. W. Kroesen, U.S. Patent No. 4,871,580 (1989); European Patent No. 0297637 (1992)

[2] P.J. van den Oever, W.M.M. Kessels, B. Hoex, R.C.M. Bosch, A.J.M. van Erven, R.L.J.R. Pennings, W.T.M. Stals, M.D. Bijker, and M.C.M. van de Sanden, *Proc. 31st IEEE Photovoltaic Specialists Conf.*, Lake Buena Vista, 2005

[3] R.C.M. Bosch, W.T.M. Stals, A.J.M. van Erven, R.L.J.R. Pennings and M.D. Bijker, *Proc. 19th European Photovoltaic Solar Energy Conference*, Paris, 2CV.2.69, 1098 (2004)

[4] W.M.M. Kessels, J. Hong, F.J.H. van Assche, M.D. Moschner, T. Lauinger, W.J. Soppe, A.W. Weeber, D.C. Schram, and M.C.M. van de Sanden, *J. Vac. Sci. Technol. A*, **20**, 1704 (2002)

[5] J. Hong, W.M.M. Kessels, W. J. Soppe, A.W. Weeber, W.M. Arnoldbik, and M.C.M. van de Sanden, *J. Vac. Sci. Technol. B*, **21**, 2123 (2003)

[6] J. Hong, W.M.M. Kessels, F.J.H. van Assche, H.C. Rieffe, W.J. Soppe, A.W. Weeber, and M.C.M. van de Sanden, *Prog. Photovolt: Res. Appl.* 11, 125 (2003)

[7] A.J.M. van Erven, Master thesis, Eindhoven University of Technology (2004)

[8] A.J.M. van Erven, R.C.M. Bosch, A.W. Weeber, and M.D. Bijker, *Proc. 19th European Photovoltaic Solar Energy Conference*, Paris, 2CV.2.20, 927 (2004)

[9] W.M.M. Kessels, P.J. van den Oever, B. Hoex, R.C.M. Bosch, A.J.M. van Erven, M.D. Bijker, and M.C.M. van de Sanden, *Proc. 31st IEEE Photovoltaic Specialists Conf.*, Lake Buena Vista (2005)

[10] E. Bustarret, M. Bensouda, M.C. Habrard, J.C. Bruyere, S. Poulin and S.C. Gujrathi, *Phys. Rev. B*, **38**, 8171 (1988)

[11] N.H. Nickel, *Hydrogen in Semiconductors II*, p. 113 (1999)