

APPLICATION OF ULTRA HIGH-RATE ETP DEPOSITED SILICON NITRIDE FOR SCREEN PRINTED CRYSTALLINE SILICON SOLAR CELLS

A.J.M. van Erven¹, R.C.M. Bosch¹, B. Hoex¹, M Bennett², B. Kumar², S. Narayanan², T. Koval², and M.D. Bijker¹
¹OTB 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
²BP Solar, 630 Solarex Court, Frederick, MD 21703 USA

ABSTRACT: OTB Solar uses the expanding thermal plasma technique on its high throughput PECVD tool, the DEP_x, for the deposition of a silicon nitride antireflection coating on silicon solar cells. These films are deposited at very high rates (>5 nm/s) from an Ar-NH₃-SiH₄ plasma at a substrate temperature of around 400 degrees Celsius. From analyzing these layers it was found that certain layer properties like mass density and bonded hydrogen have predictive capabilities regarding the quality of the silicon nitride films which must have its origin in the fact that they are at least for a part responsible for passivation of the silicon wafer.

Keywords: Silicon-Nitride, PECVD, Passivation

1 INTRODUCTION

Silicon nitride deposited by plasma enhanced chemical vapor deposition (PECVD) is currently the material of choice for antireflection coatings (ARC's) on crystalline silicon solar cells. Next to serving as ARC, silicon nitride can also passivate the surface of monocrystalline silicon solar cells as well as providing both surface and bulk passivation for multicrystalline silicon solar cells.

Usually these layers are deposited with a plasma that is ignited and maintained with an alternating electromagnetic field which normally results in deposition rates ≤ 1 nm/s.

OTB Solar uses the expanding thermal plasma (ETP) technique [1,2] on its high throughput in-line PECVD tool for the deposition of a silicon nitride ARC from an Ar-NH₃-SiH₄ plasma. The ETP technique allows for very high deposition rates (>5 nm/s) and provides an excellent uniformity regarding layer thickness (t) and refractive index (n) when multiple ETP sources are used. Next to a high throughput this results in visually attractive monochrome solar cells.

The quality of these high rate deposited layers regarding the bulk passivating capability at optimal ARC-conditions (i.e., a high refractive index at an acceptable low absorption) has already been demonstrated [3]. This research focuses more on the layer properties that can identify high or low quality silicon nitride antireflection coatings. For this purpose experiments were carried out with BP Solar to investigate various silicon nitride layers by correlating solar cell results with silicon nitride layer properties.

2 EXPERIMENTAL

The silicon nitride layers were deposited on multicrystalline silicon solar cells by multiple ETP sources with a plasma power of ~3500 W for each source. Argon is used as a carrier gas and ammonia and silane as the precursors gasses for the silicon nitride deposition. The depositions were performed on an industrial production machine, OTB Solar's silicon nitride deposition tool, the DEP_x [4], at around 400°C. For the experiments six groups of 20 multicrystalline silicon wafers were processed at two different total reactant flows with varying flow ratio's resulting in

silicon nitride layers with different refractive indices. These films were analyzed by means off spectroscopic ellipsometry on monocrystalline substrates that were processed along with the solar cells. The silicon nitride films on these substrates were also analyzed with Fourier Transform Infrared Spectroscopy (FTIR), Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD). The deposition pressure and temperature were kept constant for the different reactant flow settings as well as the argon flow.

Another group of 20 wafers was processed at BP Solar on a conventional plasma tool (tube oven, direct plasma) which acted as a reference. This provided an optimized low-rate deposition process which resulted in high quality silicon nitride layers for comparison.

3 RESULTS AND DISCUSSION

Figure 1 shows the different refractive indices obtained as a function of the partial ammonia flow (R , normalized to 1.00) for the different groups. The two total reactant flows used for ammonia and silane were 0.55 slm and 0.65 slm and are indicated in the figure. As can be seen in the figure, varying the ammonia to silane flow ratio resulted in a range from around 1.95 to 2.15 for the refractive index. The deposition rates varied in a range of 3.3 to 5.5 nm/s depending on the flow ratio's, with higher partial silane flows resulting in higher deposition rates.

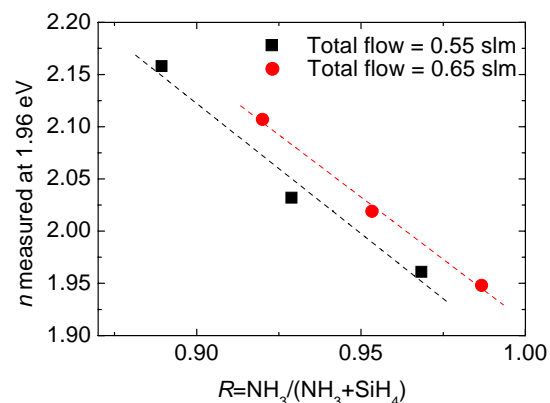


Figure 1: Refractive index of ETP deposited silicon nitride at different conditions

Even higher refractive indices would result in silicon nitride layers that have a high value for the extinction coefficient (k) and consequently absorb much of the sunlight which makes them less interesting for solar cell applications.

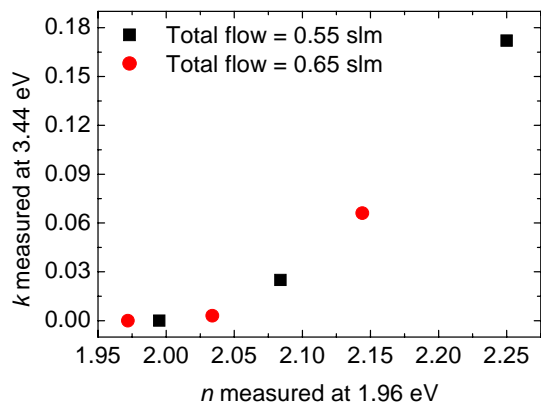


Figure 2: Plot of n versus k for different deposition conditions

Figure 2 shows a plot of the extinction coefficients that correspond with the obtained refractive indices. The k -values were measured at 3.44 eV which corresponds with a wavelength of 360 nm.

The extinction coefficient rises quickly for higher refractive indices (more Si-Si bonds), however, as can be seen from the figure it is still possible to have $k = 0$ at a refractive index >2.00 . This is significantly lower compared with other values that can be found in literature [5, 6].

These optical layer properties can be used to predict the performance of the ARC regarding both reflection and absorption losses. Layers with the same refractive index can have different values for k , so optimizing on a refractive index with a low k -value results in less absorption and thus a higher quality ARC meaning a higher short circuit I_{SC} for the solar cell. Obtaining a lower k at the same refractive index means increasing the mass density (ρ) of the silicon nitride layer which also results in higher quality silicon nitride films regarding both bulk and surface passivation [3,7-9]. Measuring n and k can thus help to predict the performance of the silicon nitride coating.

The fact that film density is an important parameter for silicon nitride acting as an ARC can also be seen by comparing figure 3 with figure 4. Figure 3 shows the film density of the silicon nitride films as obtained by means of FTIR as a function of the refractive index and figure 4 displays the corresponding relative efficiencies for the solar cells processed with these layers. The relative efficiencies shown are averaged over 20 solar cells. The film density is calculated from fitting the amount of Si-N bonds obtained with FTIR with results from RBS measurements [3] which is a good way to monitor the trend of mass density as a function of gas flow or refractive index. However, this method is less suitable for obtaining absolute values which might explain the rather high mass densities in figure 3.

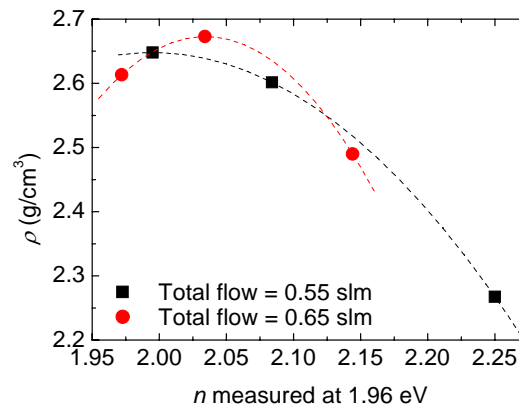


Figure 3: Film density obtained by FTIR as a function of the refractive index

Figure 3 and 4 show similar trends indicating a correspondence of film density with solar cell efficiency. This can be for a part attributed to the higher I_{SC} obtained because of the lower k -values (figure 2), however, also an increase in V_{OC} with film density is observed (not separately shown). This indicates a higher degree of bulk passivation which might be achieved by a better hydrogen diffusion into the substrate which could occur for higher density films. The hydrogen is then easier retained in the silicon nitride (less voids) and directed towards the substrate instead of lost into the ambient.

The efficiency is displayed as a relative efficiency with respect to the low-rate reference process which is normalized to 1.00. When excluding fill factor (FF) effects, a relative $V_{OC} \times I_{SC}$ of 0.995 is obtained compared with the reference process, which demonstrates the passivation capability of these high rate deposited layers again.

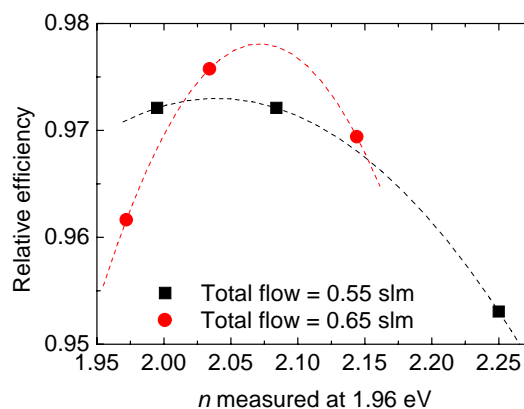


Figure 4: Relative efficiency as a function of the refractive index

So apparently the silicon nitride film mass density can be a measure for the resulting solar cell efficiency or might be a property that can be used to predict the quality of the silicon nitride when serving as an antireflection coating. However, in this case the highest density films might also be approaching the layer properties of the reference layer more than lower density films and the firing profile that was used for processing the solar cells has been optimized for this reference silicon nitride. So increasing the density then means approaching the film

density of the reference layer. Although, the relative $V_{oc} \times I_{sc}$ of the solar cells showed a similar trend as the film density and this parameter normally excludes firing effects.

Silicon nitride films with an even higher mass density might result in lower quality silicon nitride regarding passivation [10]. An optimum in film density can be expected because very high density films might contain not enough hydrogen anymore or have a hydrogen diffusion rate that is too slow. The upper limit has not yet been investigated.

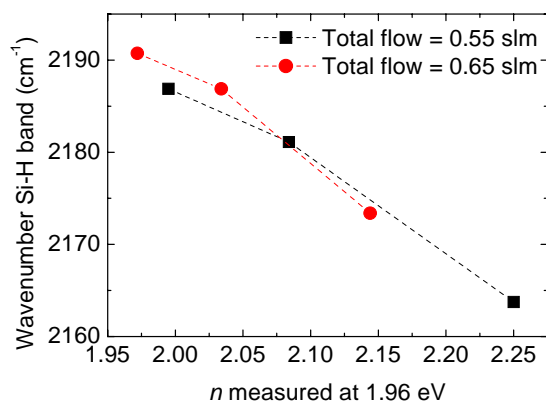


Figure 5: Wavenumber of the Si-H band as a function of the refractive index

In an earlier study it has been shown that the wavenumber of the Si-H band in a FTIR spectrum can also be used to predict the quality of a silicon nitride layer for the purpose of an ARC [3]. The best performing silicon nitride layers had the position of this peak around 2180 cm^{-1} and it can be seen here again by comparing figure 5 with figure 4 that the highest efficiencies are obtained for silicon nitride films with a wavenumber around this same peak position of $\sim 2180 \text{ cm}^{-1}$. It corresponds with a Si/N ratio of ~ 0.95 which produces a refractive index of ~ 2.05 as can be seen in figure 6.

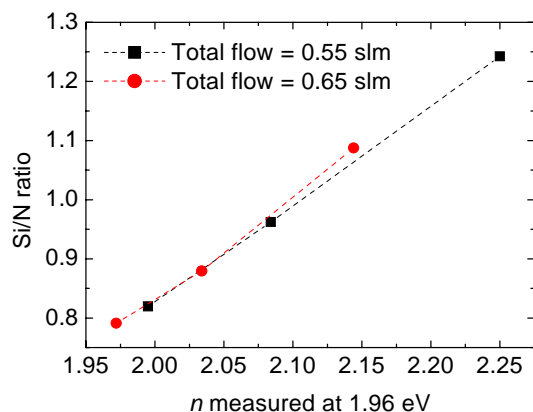


Figure 6: Si/N ratio as a function of the refractive index

Stoichiometric silicon nitride films have a Si/N ratio of 0.75, so slightly silicon rich films appear to be needed for higher efficiencies. Of course, only then a more optimum refractive index of ~ 2.05 is achieved, but also for a higher degree of bulk passivation this seems to be required. A reason might be that hydrogen diffusion in

the silicon wafer occurs via the Si-Si bond-centers, so if hydrogen can diffuse from Si-Si bonds present in the silicon nitride layer (more present with higher Si/N ratio's) towards the Si-Si bond-centers from the substrate it might be beneficial.

Also the distribution of hydrogen was found to be an important layer property. Hydrogen is bonded mostly to silicon for silicon rich films and visa versa for nitrogen rich films, so there is a silicon to nitrogen ratio that has an equal amount of hydrogen bonded to silicon as to nitrogen. This is the case at the cross-over of N-H bonds with Si-H bonds shown in figure 7 which displays the hydrogen bonds as a function of refractive index measured with FTIR.

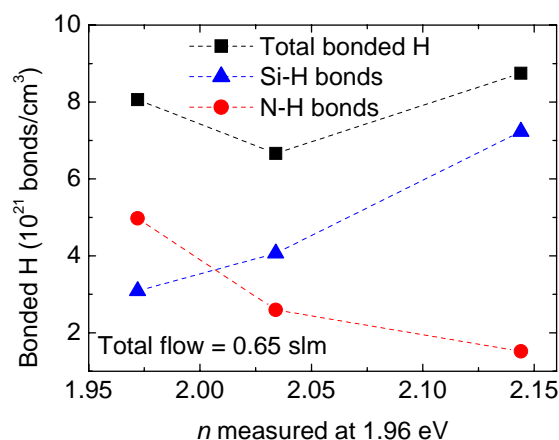


Figure 7: Bonded hydrogen as a function of the refractive index for a total reactant flow of 0.65 slm

Also the value for the total bonded hydrogen is displayed which can be calculated by adding the hydrogen bonded to silicon to the hydrogen bonded to nitrogen.

The highest degree of bulk passivation is obtained near the cross-over of hydrogen bonds which can be seen by comparing figure 6 with figure 4. This cross-over is also near the minimum of the total bonded hydrogen (which becomes clearer if more points are added left and right of the figure). A minimum concentration of hydrogen atoms means that most of the silicon and nitrogen atoms are bonded to each other instead of bonded to hydrogen and this results in a higher mass per bond. Hydrogen bonds are thus replaced by Si-N or Si-Si bonds (there is no evidence found that N-N bonds can exist), so a minimum in bonded hydrogen then results in a maximum in mass density, which was shown to be important for a high silicon nitride quality. An equal distribution and a minimum of bonded hydrogen, which correspond with a wavenumber of the Si-H band of ~ 2180 and with a maximum in film density, also contribute to the thermal stability of a silicon nitride layer [3,11]. Hydrogen then might be released without leaving dangling Si or N bonds because they can form a strong Si-N bond and this bond formation should be easier for higher density films (atoms nearby) and for films with an equal amount of Si-H and N-H bonds.

Thermal stability is very important for silicon nitride coatings applied on screen printed silicon solar cells because they need a high temperature firing step to make

metal contacts. So even though the wafers are passivated by hydrogen, a minimum amount of bonded hydrogen in a silicon nitride film which results in a higher mass density can in this case provide a higher quality ARC.

4 CONCLUSIONS

It has been shown that certain silicon nitride layer properties like n and k , mass density, Si-H wavenumber, Si/N ratio and hydrogen bonding can be used to predict if a silicon nitride layer has a high or low quality when acting as a single layer antireflection coating. A high quality means in this case providing sufficient surface (shown in [7-9]) and bulk passivation as well as having low reflection and absorption losses and thus a high transmittance. So by optimizing these layer properties, already high quality silicon nitride layers can be obtained even without processing any solar cells. Fine-tuning of the process (i.e., matching the silicon nitride deposition process with the firing profile used) is, however, still necessary.

Of course the predictive capability of these layer properties lies in the fact that a good passivating silicon nitride layer should have the shown characteristics. This means that the mechanism of passivation must depend for a part on these properties. Optimizing on the optical properties, high n with a low k -value, provides a higher I_{SC} which has not so much to do with passivation, but when performing this optimization the film density is increased. This is also the case when optimizing on a minimum of bonded hydrogen, or on an equal distribution of hydrogen between silicon and nitrogen, which then again corresponds with a wavenumber of the Si-H stretching band of $\sim 2180\text{ cm}^{-1}$. So by optimizing one layer property always other layer properties change as well and they all end up at a certain value that gives the best results. All the layer properties are interconnected so it is hard to say which one is the most important or responsible for a high degree of passivation when processing solar cells.

What *can* be said is that thermal stability is important for screen printed silicon solar cells and that this is induced by the correlation of a high mass density with an equal distribution of hydrogen and a minimum of total bonded hydrogen (corresponding with a refractive index of ~ 2.05 , Si-H wavenumber of ~ 2180 and a Si/N ratio of ~ 0.95). These properties are probably also determining for the H-diffusion through the silicon nitride layer and consequently for the diffusion of H into the silicon wafer. The fact that these properties are important can help finding a model for the mechanism of passivation. How exactly this mechanism works, however, still has to be elucidated.

5 REFERENCES

- [1] 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, Proceedings of the 31st Photovoltaic Specialists Conference and Exhibition, Lake Buena Vista (2005)
- [2] P.J. van den Oever, W.M.M. Kessels, B. Hoex, R.C.M. Bosch, A.J.M. van Erven, M.D. Bijker, and M.C.M. van de Sanden, This conference
- [3] A.J.M. van Erven, R.C.M. Bosch, R. Toelle, O. Voigt, S. Petri and M.D. Bijker, Proceedings of the 31st Photovoltaic Specialists Conference and Exhibition, Lake Buena Vista (2005)
- [4] R.C.M. Bosch, W.T.M. Stals, A.J.M. van Erven, R.L.J.R. Pennings and M.D. Bijker, Proceedings 19th European Photovoltaic Solar Energy Conference, Paris, 2CV.2.69, 1098 (2004)
- [5] P.Doshi, G.E. Jellison, and A. Rohatgi, Applied Optics, **36**, 7826 (1997)
- [6] G.E. Jellison, F.A. Modine, P. Doshi, and A Rohatgi, Thin Solid Films, **313**, 193 (1998)
- [7] 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, Proceedings of the 31st Photovoltaic Specialists Conference and Exhibition, Lake Buena Vista (2005)
- [8] B. Hoex, A.J.M. van Erven, R.C.M. Bosch, W.T.M. Stals, M.D. Bijker, P.J. van den Oever, W.M.M. Kessels and M.C.M. van de Sanden, accepted for publication in Progress in Photovoltaics: Research and Applications 2005
- [9] B. Hoex, A.J.M. van Erven, R.C.M. Bosch, M.D. Bijker, P.J. van den Oever, W.M.M. Kessels, and M.C.M. van de Sanden, This conference
- [10] A.W. Weeber, H.C. Rieffe, I.G. Romijn, W.C. Sinke, and W.J. Soppe, Proceedings of the 31st Photovoltaic Specialists Conference and Exhibition, Lake Buena Vista (2005)
- [11] A.J.M. van Erven, R.C.M. Bosch, A.W. Weeber and M.D. Bijker, Proceedings 19th European Photovoltaic Solar Energy Conference, Paris, 2CV.2.20, 927 (2004)