CONTROLLING THE SILICON NITRIDE FILM DENSITY FOR ULTRAHIGH-RATE DEPOSITION OF TOP QUALITY ANTIREFLECTION COATINGS

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ABSTRACT

In this contribution we address the importance of a high mass density for silicon nitride films used as an antireflection coating on crystalline silicon solar cells. Two approaches for finding the optimized deposition conditions are presented. The outcome of these optimization studies clearly show that both the bulk and surface passivation benefit from a high mass density and that top quality antireflection coatings can be obtained at deposition rates up to 5 nm/s.

INTRODUCTION

Silicon nitride has become the state-of-the-art antireflection coating for crystalline silicon solar cells as, ideally, this coating does not only reduce reflection losses but simultaneously provides surface passivation and, in the case of multicrystalline silicon (mc-Si), a good degree of hydrogen passivation of bulk defects. However, relatively little is known about what controls the degree of passivation reached by the silicon nitride. For example, several studies have been devoted to the understanding of the microscopic mechanism of bulk passivation [1,2,3], but detailed information on the relation between the deposition process parameters and film properties on one hand and the degree of bulk passivation on the other hand is not available. This information is however essential for process optimization such as for the increase in production throughput of the deposition equipment used.

The realization of a high production volume of mc-Si solar cells while keeping the investments in equipment reasonably low has been the main focus of our work in the recent years. The work has been concentrated on inline production processes in which the silicon nitride antireflection coatings can be deposited at (ultra)high deposition rates (1-10 nm/s) while producing top quality mc-Si solar cells [4,5]. In our research efforts, we have found a relation between the degree of bulk passivation induced by the silicon nitride antireflection coating and the mass density of the silicon nitride film [6]. This relation, established by internal quantum efficiency measurements on mc-Si solar cells, is shown in Fig. 1. Obtaining a sufficiently high film density at very high growth rates is not trivial for plasma-enhanced chemical vapor deposition (PECVD) of thin film materials, as the surface processes during growth (such as surface diffusion, relaxation, hydrogen elimination, etc.) have to compete more heavily with the rate of the species arriving at the substrate. Therefore, we have aimed at the deposition of high mass density a-SiN$_x$:H films in our optimization studies while we have also addressed this issue from a more academic perspective. In other words, obtaining a high mass density has been our technological and scientific guideline for depositing silicon nitride at ultrahigh deposition rates for top quality antireflection coating performance. In this contribution, we present our approaches for finding the optimized film density using the films' optical properties as well by monitoring the surface roughness evolution as a function of film thickness. Finally, we will present the cell efficiencies obtained for ultrahigh-rate deposited silicon nitride with optimized, high film densities as well as some preliminary surface passivation data.

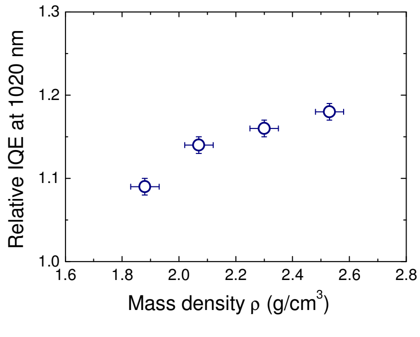

Fig. 1. The relation between degree of bulk passivation of mc-Si solar cells and the mass density of the silicon nitride antireflection coating. The degree of bulk passivation is represented by the solar cells' internal quantum efficiency (IQE) at 1020 nm relative to the IQE of a solar cell without bulk passivation. All solar cells have been produced from mc-Si wafers from adjacent positions of an ingot. The silicon nitride coatings have been deposited at a rate >0.5 nm/s.

EXPERIMENTAL DETAILS

The experiments have been carried out using the expanding thermal plasma (ETP) source as developed at the Eindhoven University of Technology and as employed in the “DEP$_x$” inline PECVD system of OTB Solar [5,7]. With the ETP technique as shown in Fig. 2, a-SiN$_x$:H deposition rates up to 20 nm/s can be reached although generally deposition rates between 3 and 7 nm/s are used. Due to these high deposition rates the DEP$_x$ system reaches nominally a throughput of 960 cells/hour. All a-SiNx:H films in the present study have been deposited from the NH_3-SiH_4 reactant mixture unless otherwise noted. The experiments have been carried out in either a lab-scale reactor (see Fig. 2) or in the DEP$_x$ system (e.g., multicrystalline solar cells and surface passivation experiments) [5].

Spectroscopic ellipsometry measurements have been carried out using a Woollam M2000 ellipsometer with near-infrared extension (250-1700 nm). The ellipsometry data were analyzed by a simple two-layer optical model (bulk film with surface roughness) and using the Tauc-Lorentz parameterization of the dielectric function [8].

FILM DENSITY OPTIMIZATION

In our optimization studies, a wide variety of process parameters and reactor and plasma source design issues have to be studied and determining the film density from traditional methods such as nuclear analysis techniques would be very time consuming. Therefore, we have chosen the all-optical method of spectroscopic ellipsometry that can be used for *ex situ* analysis but also *in situ* and even in real-time during film growth. *In situ* analysis with the substrates/solar cell wafers under vacuum, is very useful as the silicon nitride is prevented from oxidation (oxidation plays a role when depositing low density silicon nitride films in which the oxidation process itself increases the film’s mass density) while real-time analysis yields dynamical information as a function of film thickness (see below). From the spectroscopic ellipsometry data, information on the absorption by the silicon nitride (extinction coefficient, bandgap) is obtained while it gives also insight into the density and stochiometry of the films. This latter insight can be deduced from the combination of refractive index and extinction coefficient of the films as shown in Fig. 3. From literature, it is known that the extinction coefficient of a-SiN$_x$:H films is mainly determined by the amount of Si-Si bonds present in the film and that the refractive index is mainly determined by the N/Si ratio in the film [9,10]. The refractive index and extinction coefficient of silicon nitride are generally related to each other and they both increase when going to more Si-rich films. On the other hand, the refractive index can be increased by depositing films with a higher density, e.g. due to the incorporation of a smaller amount of hydrogen and/or less voids. In this case, the extinction coefficient can be used to verify whether the stochiometry of the films (i.e., N/Si ratio) remains constant. Varying the process conditions and testing different experimental designs, the general relation between refractive index and extinction coefficient shown in Fig. 3 (dashed line) has been established for our high-rate deposited silicon nitride. However, we also found a small optimum process window in which the points in Fig. 3 dropped significantly below the dashed line. These films showed an increased refractive index (i.e., a higher film density) for a constant extinction coefficient (i.e., a constant stochiometry). From these results, we identified our key process parameters governing the film density: substrate temperature and, to somewhat less extent, the plasma power and gas flows (NH_3 and SiH_4) used.

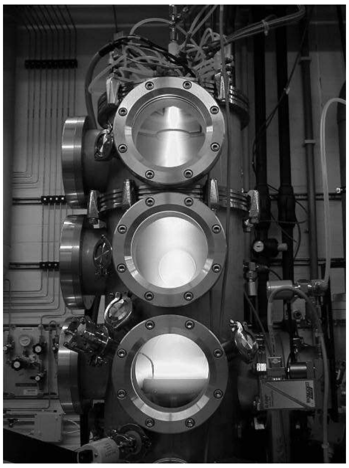

Fig. 2. Lab-scale reactor with the Expanding Thermal Plasma (ETP) technique for ultrahigh-rate deposition of a-SiN$_x$:H antireflection coatings.

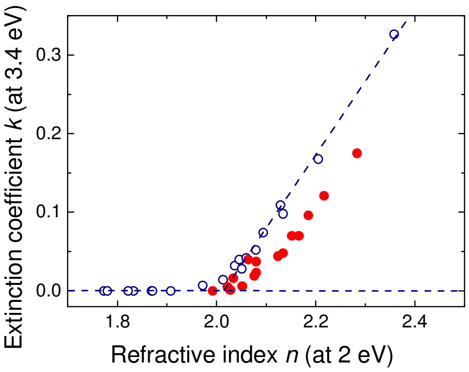

Fig. 3. The relation between the extinction coefficient (at a photon energy of 3.4 eV) and the refractive index (at a photon energy of 2 eV) of the silicon nitride. Silicon nitride films with a high mass density show a relatively low extinction coefficient for a reasonably high refractive index. The extinction coefficient at a photon energy of 3.4 eV has been plotted as it corresponds to the highest photon energy transmitted through the encapsulation material (glass with EVA foil) into the solar cell.

SURFACE ROUGHNESS EVOLUTION

The optimization studies have been supported by more-fundamental experiments in which the initial film growth (probably particularly important for surface passivation) and roughness evolution of the silicon nitride films have been studied [11]. These experiments, carried out using real-time spectroscopic ellipsometry, have been supported by atomic force microscopy measurements on films of varying thickness. As an example, Fig. 4 shows the surface roughness layer thickness for two films having a different mass density. It is generally accepted that a higher surface roughness results in a lower film density but also the evolution of the surface roughness d_s as a function of the film thickness d_b reveals important information. The roughness of the film with the higher mass density increases slower than the roughness of the film with the lower mass density. This is revealed by the value of the growth exponent β when fitting the data with the relation $d_s \sim d_b^{\beta}$ as used in the concept of dynamic scaling [12]. A β value of 0.5 is generally attributed to a random deposition process in which species stick at their position of impact while lower β values are related to surface diffusion and relaxation mechanisms (for more details, see Refs [11,12]). The lower β value can therefore be attributed to a more pronounced surface diffusion mechanism that consequently leads to more compact films. From this, it is evident that analysis of the surface roughness evolution is very helpful to identify conditions yielding a high film density.

CELL EFFICIENCIES FOR ULTRAHIGH-RATE DEPOSITED SILICON NITRIDE

From the aforementioned studies we have determined the optimal process conditions for ultrahigh-rate deposition of top quality high mass density a-SiN_x:H coatings. Under these conditions, multicrystalline silicon solar cells have been produced using a standard industrial process involving contact screen printing, an aluminum back surface field and isotropic surface texturing. The a-SiN_x:H antireflection coating were deposited in the DEP_x inline production tool developed by OTB Solar. In Fig. 5, the influence of the mass density on the solar cell efficiency is shown as obtained by changing the deposition temperature from 300 to 425 ºC under optimized plasma conditions. This figure illustrates that a high film density is important for obtaining top cell efficiencies (the high cell efficiency is determined by the level of bulk passivation and by the relative low UV absorption of the a-SiN_x:H film). Moreover, Fig. 5 shows that an efficiency of 15.3% can be obtained by ultrahigh-rate (~ 5 nm/s) deposited silicon nitride films while the top efficiency obtained using a low-rate (<< 1 nm/s) deposited silicon nitride film used in the same experiment as a reference is 15.5%. These results illustrate the strength of the optimization method used and the high potential of the ultrahigh-rate deposition process of a-SiN_x:H antireflection coatings.

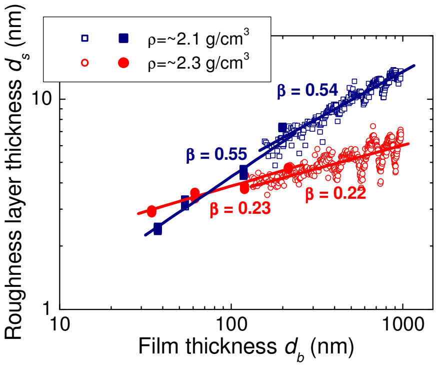

Fig. 4. Roughness layer thickness d_s as a function of the film thickness d_b. Solid symbols represent AFM data (~4× *rms* roughness) while open symbols refer to data obtained by real time spectroscopic ellipsometry. The data with ρ = 2.1 g/cm^3 and ρ = 2.3 g/cm^3 have been deposited from the N_2-SiH_4 and NH_3-SiH_4 reactant mixture, respectively. The data have been fitted with the relation $d_s \sim d_b^{\beta}$.

SURFACE PASSIVATION PROPERTIES OF ULTRAHIGH-RATE DEPOSITED SILICON NITRIDE

Recently, also the surface passivation properties of the a-SiN_x:H deposited by the ETP technique in the DEP_x system has been investigated. Silicon nitride films have been deposited under the optimized plasma conditions for two substrate temperatures on both sides of low-resistivity *p*-type silicon wafers. Figure 6 shows the first results on the effective lifetime of the minority charge carriers in the silicon wafers as determined by the contactless inductively coupled photoconductance tester (Sinton Consulting, WCT100) [13]. The figure reveals immediately the importance of the substrate temperature, and consequently of the film density for the surface passivation properties of the a-SiN_x:H.

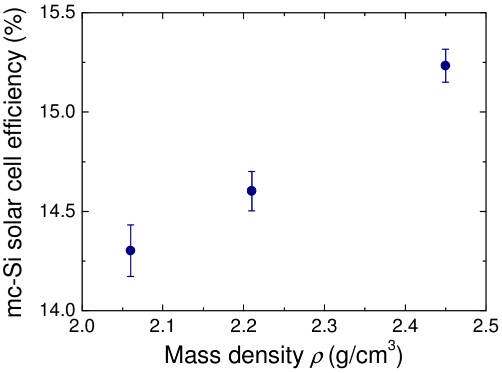

Fig. 5. Cell efficiencies averaged over 10 mc-Si solar cells coated with silicon nitride films with different mass densities deposited at a ultrahigh rate (~5 nm/s). As a reference: the optimum efficiency reached with a low-rate deposited silicon nitride film is 15.5%.

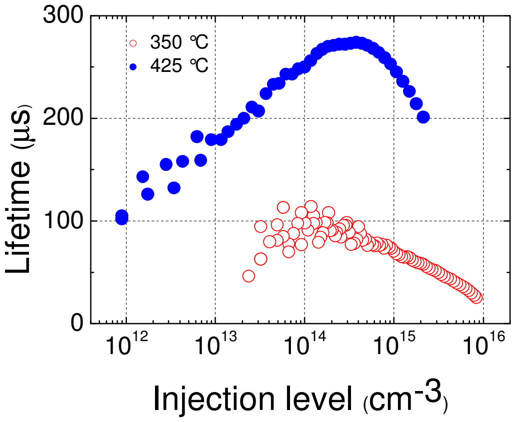

Fig. 6. Effective lifetime of minority charge carriers in low-resistivity (8.4 Ωcm) *p*-type Si wafers coated with a-SiN$_x$:H films (on both sides). The films deposited at 350°C and 425 °C have a refractive index of ~2.2 and ~2.1 respectively, and have been deposited in the DEP$_x$ system

Furthermore, it is clear that the ultrahigh-rate deposited a-SiN$_x$:H can lead to a good level of surface passivation, even for films with a refractive index of ~2.1 [14,15].

CONCLUSIONS

The mass density of silicon nitride films deposited at ultrahigh rate by the ETP technique has been optimized by considering the optical properties of the films and the surface roughness evolution. Results on multicrystalline silicon solar cells and charge carrier lifetime experiments clearly show that the mass density is a key parameter for obtaining a high level of bulk and surface passivation of crystalline silicon solar cells.

ACKNOWLEDGMENTS

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REFERENCES

[1] B.L. Sopori, X. Deng, J.P. Benner, A. Rohatgi, P. Sana, S.K. Estreicher, Y.K. Park, and M.A. Robertson, *Solar Energy Mater. Solar Cells* **41**/**42**, 1996, pp. 159.

[2] R. Lüdemann, *Mater. Sci. Eng. B* **58**, 1999, pp. 86.

[3] F. Duerinckx and J. Szlufcik, *Solar Energy Mater. Solar Cells* **72**, 2002, pp. 231.

[4] 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**, 2003, pp. 125.

[5] 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, 2004, pp. 1098.

[6] 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**, 2003, pp. 2123.

[7] A.J.M. van Erven, R.C.M. Bosch, A.W. Weeber, and M.D. Bijker, *Proc. 19th European Photovoltaic Solar Energy Conference*, Paris, 2004, pp. 927.

[8] G.E. Jellison, and F.A. Modine, *Appl. Phys. Lett.* **69,** 1996, pp. 371.

[9] J. Robertson, *Phil. Mag. B* **69**, 1994, pp. 307.

.

[10] L. Ley, R. Kärcher, R.L. Johnson, *Phys. Rev. Lett.* **53**, 1984. pp.710.

[11] P.J. van den Oever, M.C.M. van de Sanden, and W.M.M. Kessels, *Mater. Res. Soc. Symp. Proc.* **808**, 2004, pp. A9.35.1

[12] A.-L. Barabási, H. E. Stanley, *Fractal Concepts in Surface Growth*, (Cambridge university press, Cambridge, U.K) 1995.

[13] R.A. Sinton, and A. Cuevas, *Appl. Phys. Lett.* **69***,* 1996, pp. 2510.

[14] J.D. Moschner, J. Henze, J. Schmidt, and R. Hezel, *Prog. Photovolt: Res. App.* **12**, 2004, pp. 21.

[15] A.W. Weeber, H.C. Rieffe, W.C. Sinke, and W.J. Soppe. *19th European Photovoltaic Solar Energy Conference*, Paris, 2004, pp. 1005.