

# STATE-OF-THE-ART SURFACE PASSIVATION BY HYDROGENATED AMORPHOUS SILICON DEPOSITED AT RATES > 1 NM/S BY THE EXPANDING THERMAL PLASMA TECHNIQUE

B.Hoex<sup>1,2</sup>, W.M.M. Kessels<sup>1</sup>, M.D. Bijker<sup>2</sup> and M.C.M. van de Sanden<sup>1</sup>

<sup>1</sup> Dept. of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

<sup>2</sup> OTB Solar B.V., P.O. Box 7108, 5605 JC, Eindhoven, The Netherlands

**ABSTRACT:** State-of-the-art surface passivation of crystalline silicon can be obtained by hydrogenated amorphous silicon (a-Si:H) films deposited by the expanding thermal plasma technique. These a-Si:H films can be deposited at significantly higher deposition temperatures (400 °C) and deposition rates (>1 nm/s) compared to conventional rf-PECVD. Surface recombination velocities in the order of 7-15 cm/s can be obtained on low resistivity *n*-type c-Si.

**Keywords:** hydrogenated amorphous silicon, surface passivation, high-rate deposition, crystalline silicon

## 1 INTRODUCTION

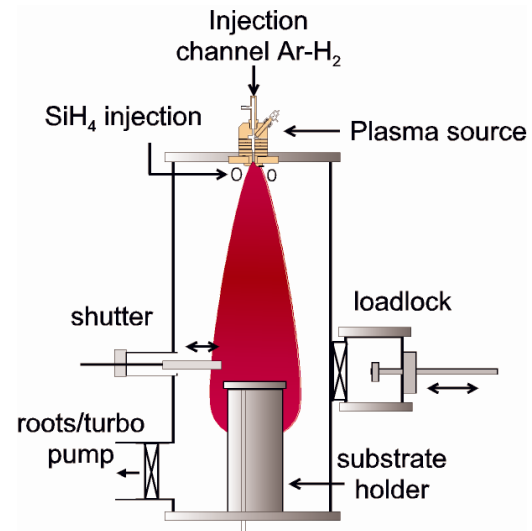
An excellent level of surface passivation for crystalline silicon solar cells is essential when the wafer thickness decreases and high conversion efficiencies are desired. Traditionally thermally grown oxides were successfully used for this purpose. However, for a broad industrial application both the high process temperature and long time necessary to grow thermal oxide are less suitable. Consequently, there is a continuous search for other materials that exhibit a high level of surface passivation on crystalline silicon. Hydrogenated amorphous silicon (a-Si:H) is an example of such a material [1]. A-Si:H does not only yield an excellent level of surface passivation on crystalline silicon solar cells with a diffused emitter [2], but is also of prime importance for a-Si:H/c-Si heterojunction (e.g. HIT) solar cells [3]. Previous studies have shown an excellent surface passivation for a-Si:H films deposited at 200-250°C at rates well below 1 nm/s. Both deposition and annealing temperatures >350°C showed a severe decrease in the level of surface passivation of the a-Si:H films, indicating a poor thermal stability of the films. On the other hand it is known from previous experiments that a high deposition temperature is necessary to deposited good quality a-Si:H films at high rates.[4] For industrial application a higher deposition rate, a broader process window and higher thermal stability are desired.

In this paper we show that it is possible to deposit a-Si:H films at a deposition temperature of 400 °C and at deposition rates >1 nm/s using the expanding thermal plasma (ETP) technique, while maintaining a sufficiently high level of surface passivation.

## 2 EXPERIMENT

### 2.1 Experimental setup

The a-Si:H films were deposited using a lab-scale reactor employing the ETP technique, as shown in Fig. 1. This setup is already described extensively in the literature (see e.g. Kessels *et al.* [4]) and will, therefore, only be addressed briefly here. An Ar-H<sub>2</sub> plasma is created at sub-atmospheric pressures (typically 0.3-0.5 bar) in the ETP source and then expands supersonically through a nozzle into the deposition chamber, which is kept at a low pressure of 0.2 mbar by a two-stage roots



**Figure 1:** Schematic representation of the lab scale setup employing the expanding thermal plasma (ETP) technique used for the deposition of the a-Si:H films.

blower system. The SiH<sub>4</sub> is injected in the plasma expansion via an injection ring 5 cm from the plasma source. The substrates are inserted into the reactor via a loadlock system. The substrate holder can be heated up to 500 °C by resistive heating. Good temperature control is assured by a small (1 standard cm<sup>3</sup> per second (sccs)) He flow. The heating time prior to deposition is at least 20 minutes to ensure that the c-Si samples are at thermal equilibrium.

### 2.2 Analysis of film properties

The films analyzed in this study were deposited on single side polished 10-20 Ω cm *p*-type Cz c-Si substrates with a <100> orientation. The substrates were ultrasonically cleaned in ethanol for 20 minutes and blown dry with N<sub>2</sub> prior to deposition. The films were measured *ex situ* by means of spectroscopic ellipsometry (Woollam M2000) in the 250-1000 nm range. The data was analyzed by a three layer model consisting of a crystalline silicon substrate with native oxide, the a-Si:H with the dielectric function described by the Cody-Lorentz formalism [5] and a surface roughness layer

described by the Bruggemann effective medium approach (50% bulk and 50 % voids). The Tauc band gap is determined from the intersect of the linear extrapolation (in the 2-2.5 eV photon energy range) of  $(E^2\varepsilon_2(E))^{1/2}$ .

Infrared absorption spectra were measured by Fourier transform infrared spectroscopy (FTIR, Bruker Vector 22) in the 370-8000  $\text{cm}^{-1}$  range with a resolution of 4  $\text{cm}^{-1}$ . The measurements were taken at normal incidence both prior to and after a-Si:H deposition to obtain a reliable background of the transmission spectrum. At least 20 spectra were averaged to obtain a sufficiently high signal-to-noise ratio. The absorption spectrum of the a-Si:H film was deduced by taken into account interference effects in the films.[6] The H content of the films was determined by the absorption intensity of the Si-H bonds using the well known proportionality constant from Langford *et al.*[7] The microstructure parameter  $R^*$  is calculated from the SiH stretching mode and is defined as  $I_{2100}/(I_{2000}+I_{2100})$ . The SiH stretching mode at 2100  $\text{cm}^{-1}$  is associated to either  $\text{SiH}_2$  or SiH in voids. The SiH stretching mode at 2000  $\text{cm}^{-1}$  is associated to isolated SiH in the a-Si:H bulk.

### 2.3 Surface passivation experiments

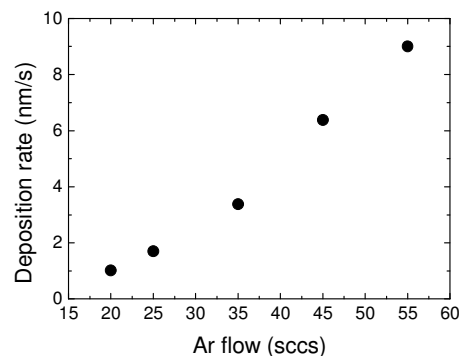
The surface passivation of the a-Si:H films was tested on double-side polished float zone 1.9  $\Omega$  cm *n*-type FZ c-Si substrates with a thickness of 275  $\mu\text{m}$ . The c-Si substrates were cleaned using a conventional RCA1 & RCA2 clean and received a final cleaning step in diluted HF (2%) prior to the deposition. An a-Si:H film was deposited on both sides of the c-Si wafer and the effective lifetime of the charge carriers in the lifetime sample was determined by means of the photo conductance decay method (Sinton WCT100). These measurements were performed both in transient and quasi-steady-state mode and the reflectivity of the wafer was taken into account.[8] The effective surface recombination velocity was calculated by assuming an infinite bulk lifetime in the float zone c-Si substrates.

## 3 RESULTS & DISCUSSION

### 3.1 a-Si:H material properties as a function of the Ar flow rate.

As already mentioned in the experimental setup Ar is used as a non-depositing carrier gas in the ETP source. Usually a rather high Ar flow of 55 sccs is used together with a  $\text{H}_2$  flow of 10 sccs to deposit the a-Si:H films [4]. In this study it was identified that the a-Si:H material quality was significantly improved by the addition of  $\text{H}_2$  gas in the ETP source. This improvement was associated to the increase role of H radicals in the deposition plasma chemistry[4]. In this study we will investigate the impact of a lower Ar flow rate, hence increasing the  $\text{H}_2/\text{Ar}$  ratio, on the a-Si:H material properties. A-Si:H films were deposited for Ar flows in the range of 20-55 sccs, while the  $\text{H}_2$  flow (10 sccs),  $\text{SiH}_4$  flow (10 sccs), deposition temperature (400  $^\circ\text{C}$ ) and reactor pressure (0.2 mbar) were kept constant.

The deposition rate of a-Si:H as a function of the Ar flow is shown in Fig. 1. It can be seen that the deposition

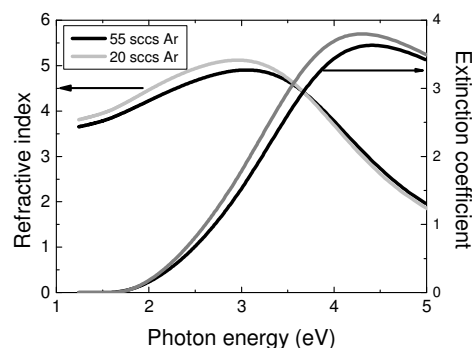


**Figure 2:** a-Si:H deposition rate as a function of the Ar flow rate. The other process conditions, e.g. gas flows and deposition temperature were kept constant.

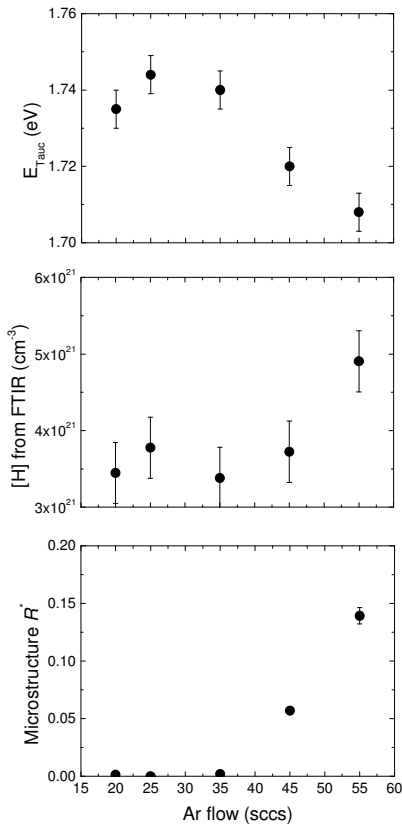
rate almost scales linearly in the 1-9 nm/s range with the Ar flow rate in the range of 20-55 sccs. The deposition rate, for these process conditions, is mainly determined by the amount of reactive particles (Ar ions and H radicals) emanating from the ETP source. By lowering the Ar flow from 55 sccs to 20 sccs the pressure in the ETP source decreases from ~350 mbar to 160 mbar, and this lower pressure will lead to a plasma with a lower dissociation/ionization degree.

In Figure 3 the refractive index and extinction coefficient as a function of the photon energy of two a-Si:H films are shown in the 1.2-5 eV range. It can be seen that both the refractive index and the extinction coefficient are significantly higher for the a-Si:H film deposited with an 20 Ar flow, compared to the a-Si:H film deposited with an Ar flow of 55 sccs. Also the refractive index in the infrared (not shown) is higher for the film deposited with a low Ar flow. A higher refractive index in the infrared is associated with a higher mass density of the film [9].

In Figure 4 the Tauc band gap, bonded hydrogen content (determined from FTIR) and the microstructure of the a-Si:H films are shown as a function of the Ar flow rate. The microstructure significantly improves from 0.15 to almost 0 when the Ar flow rate is lowered from 55 to



**Figure 3:** Refractive index and extinction coefficient as a function of the photon energy for an a-Si:H film deposited for an argon flow of 20 sccs (grey) and 55 sccs (black).

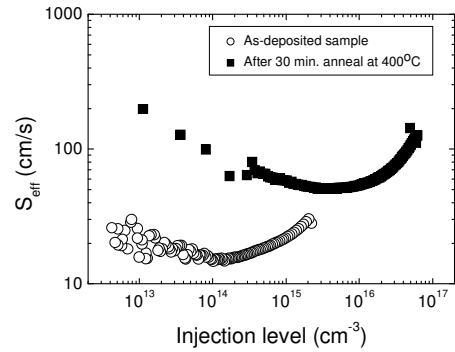


**Figure 4:** Tauc band gap (from ellipsometry), hydrogen content (from FTIR) and microstructure as a function of the Ar flow.

35 sccs, while the bonded hydrogen content shows a decrease from approximately 10 at.% to 7 at.% when the Ar flow is lowered from 55 sccs to 45 sccs. It is interesting to note that the Tauc band gap is the highest at 1.74 eV for the films with the lowest bonded hydrogen content, whereas a higher hydrogen content normally yields a higher Tauc band gap.

### 3.2 Surface passivation induced by ETP deposited a-Si:H.

The conditions yielding the a-Si:H films with the lowest microstructure and an optical bandgap of 1.6 eV were selected to test the surface passivation on c-Si. In Fig. 5 the resulting effective surface recombination velocity (SRV) is shown for a c-Si wafer coated on two sides with a 30 nm a-Si:H film grown at 400 °C with an Ar flow of 25 sccs. In contrast to previous studies on conventional rf-PECVD reactors [1], it is still possible to obtain effective SRV in the order of 15 cm/s for films deposited at a substrate temperature of 400 °C. While the effective SRV was ~100 cm/s for a film deposited at 350 °C in the study presented by Dauwe *et al.* [1]. Despite the fact that the a-Si:H film deposited at the first side of the c-Si wafer had to withstand a temperature in the range of 300-400 °C for approximately 15 minutes during the thermal stabilization for the deposition of the second side

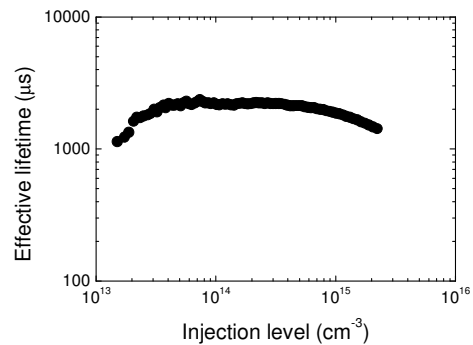


**Figure 5:** Injection level dependence of the effective surface recombination velocity of a 1.9 Ω cm *n*-type wafers passivated by a 80 nm a-Si:H film deposited at 400 °C before and after a 30 minute anneal at 400 °C.

of the c-Si wafer.

The thermal stability is further investigated by annealing the double sided coated c-Si wafer at 400 °C for 30 minutes in a rapid thermal anneal oven. A factor of three decrease in level of surface passivation is observed after the anneal, as shown in Fig. 5. This decrease is comparable as demonstrated by Dauwe *et al.* [1]. Remarkably, this result shows that even though the a-Si:H film is deposited at 400 °C, this does not imply that the a-Si:H is thermally stable at 400 °C. Hence, prolonged high temperatures should be avoided during lifetime testing and in the process flow of an industrial process when using a-Si:H as a surface passivation layer.

In order to obtain an indication of the real level of surface passivation of the *as deposited* a-Si:H films grown at a substrate temperature of 400 °C, the c-Si wafer was immersed in an iodine/ethanol solution directly after the first a-Si:H deposition [10]. The effective lifetime of this c-Si is shown in Fig. 6. Immersion of identical wafers directly after cleaning yields effective lifetimes in the order of 3-4 ms. Hence, in this case the measured effective lifetime will probably be limited by the a-Si:H film, corresponding to effective SRV in the order of 6 cm/s. This effective SRV is



**Figure 6:** Effective lifetime of a 275 μm 1.9 Ω cm *n*-type c-Si wafer coated with a single layer of a-Si:H in an iodine/ethanol solution [10].

comparable to films grown by the ETP technique at 250 °C [11].

#### 4 CONCLUSIONS

In this paper we have shown that a-Si:H with an excellent level of surface passivation can be deposited with a deposition rate > 1 nm/s at a substrate temperature of 400 °C by the expanding thermal plasma technique. In our process optimization of a-Si:H deposition at a substrate temperature of 400 °C we have focused on the impact of the Ar flow rate on the a-Si:H material properties. For low Ar flow rates (20-35 sccs) a-Si:H films with a low hydrogen content and microstructure can be deposited at deposition rates in the range of 1-3.5 nm/s. An effective surface recombination velocity of 15 cm/s was obtained for c-Si wafer that was passivated on both sides with a 80 nm thick a-Si:H film. However, a single side deposited c-Si:H yielded effective surface recombination velocities in the order of 6 cm/s, indicating thermal degradation of the a-Si:H film. Remarkably, the a-Si:H is not thermally stable at the deposition temperature of 400 °C as further confirmed by post-deposition thermal annealing.

#### 4 ACKNOWLEDGEMENTS

M.J.F. van de Sande and J.F.C. Jansen are thanked for their skillful technical assistance. P.H.W. Robeerst and J.M. Goud are thanked for their help during the experiments. This study has been carried out within the E.E.T. "HR-CEL" program funded by the Netherlands Ministry of Economic Affairs, the Ministry of Education, Culture and Science and the Ministry of Public Housing, Physical planning and Environment. The research of W.K. is made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

#### REFERENCES

1. Dauwe, S., J. Schmidt, and R. Hezel. *29th IEEE Photovoltaic Specialist Conference*. 2002. New Orleans, 1246.
2. Schaper, M., J. Schmidt, H. Plagwitz, and R. Brendel. *Progress in Photovoltaics*, **13**, 2005, pp. 381.
3. Taguchi, M., K. Kawamoto, S. Tsuge, T. Baba, H. Sakata, M. Morizane, K. Uchihashi, N. Nakamura, S. Kiyama, and O. Oota, *Progress in Photovoltaics*, **8**, 2000, pp. 503.
4. Kessels, W.M.M., R.J. Severens, A.H.M. Smets, B.A. Korevaar, G.J. Adriaenssens, D.C. Schram, and M.C.M. van de Sanden, *Journal of Applied Physics*, **89**, 2001, pp. 2404.
5. Ferlauto, A.S., G.M. Ferreira, J.M. Pearce, C.R. Wronski, R.W. Collins, X. Deng, and G. Ganguly, *Thin Solid Films*, **455-56**, 2004, pp. 388-392.
6. Gielen, J.W.A.M., M.C.M. van de Sanden, and D.C. Schram, *Thin Solid Films*, **271**, 1995, pp. 56.
7. Langford, A.A., M.L. Fleet, B.P. Nelson, W.A. Lanford, and N. Maley, *Physical Review B*, **45**, 1992, pp. 13367-13377.
8. Sinton, R.A. and A. Cuevas, *Applied Physics Letters*, **69**, 1996, pp. 2510.
9. Remes, Z., M. Vanecek, P. Torres, U. Kroll, A.H. Mahan, and R.S. Crandall, *Journal of Non-Crystalline Solids*, **230**, 1998, pp. 876-879.
10. Horanyi, T.S., T. Pavelka, and P. Tutto, *Applied Surface Science*, **63**, 1993, pp. 306-311.
11. Hoex, B., F.J.J. Peeters, A.J.M.v. Erven, M.D. Bijker, W.M.M. Kessels, and M.C.M.v.d. Sanden. *4th WCPEC*. 2006. Hawaii,