



Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb



Compensation of decreased ion energy by increased hydrogen dilution in plasma deposition of thin film silicon solar cells at low substrate temperatures

A.D. Verkerk^a, M.M. de Jong^a, J.K. Rath^{a,*}, M. Brinza^a, R.E.I. Schropp^a, W.J. Goedheer^b, V.V. Krzhizhanovskaya^{c,d}, Y.E. Gorbachev^c, K.E. Orlov^e, E.M. Khilkevitch^e, A.S. Smirnov^e

^a Utrecht University, Faculty of Sciences, SID-Physics of Devices, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

^b FOM-Institute for Plasma Physics, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands

^c Faculty of Materials Research and Technology, St. Petersburg State Polytechnic University, Polytechnicheskaya, 29, 195251 St. Petersburg, Russia

^d University of Amsterdam, Section Computational Science, Kruislaan 403, 1098 SJ Amsterdam, The Netherlands

^e Plasma Physics Department, St. Petersburg State Polytechnic University, Polytechnicheskaya 29, 195251 St. Petersburg, Russia

ARTICLE INFO

Article history:

Received 1 May 2008

Received in revised form 30 October 2008

Accepted 10 November 2008

Keywords:

Solar cells

Silane

Amorphous silicon

Thin films

Ion energy distribution function

VHF PECVD

ABSTRACT

In order to deposit thin film silicon solar cells on plastics and papers, the deposition process needs to be adapted for low deposition temperatures. In a very high frequency plasma-enhanced chemical vapor deposition (VHF PECVD) process, both the gas phase and the surface processes are affected by low process temperature. Using an electrostatic ion energy analyzer the effect of deposition temperature on the energies of ions reaching the substrate was measured. The ion energy decreases with decreasing temperature, but this can be compensated by diluting the silane source gas by hydrogen.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The share of solar energy on the global energy market will definitely grow explosively in the coming years. Thin film silicon based solar cells, although presently sharing for less than 10% in the photovoltaic market, are heading for a rapid growth, due to the availability of equipment manufacturers, the already proven high cell efficiencies and the choice of substrates: robust (glass) or flexible (metal foil or plastic). Whereas record efficiencies have reached 15% with triple junction concepts [1,2], the efficiency of the tandem “micromorph” (a-Si/nc-Si) cell concept is not too far behind with 14.7% [3]. Further developments have taken place in fabricating such type of cells on light-weight, flexible and cheap plastic substrates, which can be applied in roll to roll processes. This has been achieved by either a lift-off process from a high-temperature-resistant temporary substrate (an efficiency of 9.4% achieved by the Helianthos concept [4]), or direct deposition on plastics. For the latter type, a wide efficiency range has been achieved depending on the process temperature. Whereas thin film silicon tandem solar cells on high temperature resistant (expensive) poly-imide type plastics have delivered efficiencies comparable to the state-of-the-art cells on glass (initial

conversion efficiency 10.1% [5]), the efficiency of cells on cheap plastics (such as PET) with a low processing temperature of around 100 °C deposited with plasma-enhanced chemical vapor deposition (PECVD) has so far reached only 4.9% [6]. The above results clearly show that the substrate temperature plays a crucial role in the quality of the thin film silicon layer and a detailed understanding the growth process at low temperature is necessary for improving the film quality. The effect of depositing the films at a lower substrate temperature is a decrease in material quality, mainly because the film is less compact and more porous [7]. This negative trend can partially be ascribed to the decreased surface mobility of SiH₃ molecules at the growing surface [8]. One of the benefits from PECVD is that it takes advantage of the energy and flux of ions so that the amount of extra energy arriving at the growing film can be controlled. The effect of changes in substrate temperature on these important plasma properties has not been studied very well. This paper shows that these key figures in the plasma process are significantly affected by changes in the substrate temperature. At the same time a method to compensate the negative effect of low substrate temperatures on the material quality is presented.

2. Experimental

Thin amorphous silicon films have been deposited in a p-i-n configuration on glass using VHF PECVD at 50 MHz in the ASTER [9] high

* Corresponding author. Tel.: +31 30 253 2961; fax: +31 30 254 3165.
E-mail address: j.k.rath@uu.nl (J.K. Rath).

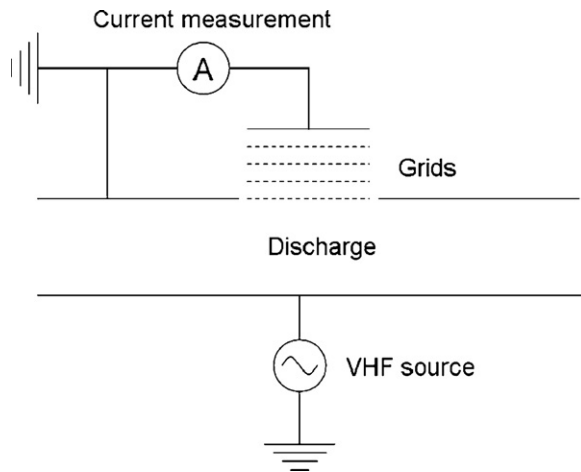


Fig. 1. Ion analyzer principle of operation.

vacuum multichamber deposition system at different substrate temperatures using a mixture of silane and hydrogen. The heater temperatures used were 280 °C, 157 °C and 50 °C, calibrated to achieve substrate temperatures of 200 °C, 100 °C and 39 °C, respectively. It was found that the silane concentration, defined as the ratio of the SiH₄ flow to the total flow, has to be decreased from 50% to 6.3% and to 2.4%, going from high to low substrate temperature, in order to obtain optimal device quality material for that particular substrate temperature.

The a-Si:H material with the highest quality in the series deposited at 100 °C had a photo-response of 10⁶. This material has been used as the absorber layer in a test solar cell deposited on stainless steel substrate with a smooth Ag/ZnO back reflector in an n-i-p configuration to confirm its quality. The solar cell showed a conversion efficiency of 5.3%.

In a separate reactor (in the high vacuum system ATLAS) that has a design similar to the reactor in ASTER where the films for the solar cells are deposited, an electrostatic ion energy analyzer (Fig. 1) was installed in order to measure in situ the ion energy distribution function (IEDF) and the ion current in relation to the deposition temperature and silane concentration. The spacing between the grids in the analyzer was 1 mm and the diameter of the aperture was 1 cm. The first grid, as seen from the discharge, was grounded to leave the plasma unaffected. To the next grid a potential of about -50V is applied, repelling electrons and negatively charged particles. The potential of the third grid is varied to allow ions with sufficient energies to pass. The last grid is kept at a constant negative voltage of -15 V to prevent any secondary electrons from contributing to the measured current. The current is converted to a voltage by a current amplifier and subsequently measured by a computer controlled digital multimeter. The IEDF is obtained by differentiating the measured ion current with respect to the voltage applied to the third grid. The experiments with the analyzer were performed using both 50 and 60 MHz excitation frequencies. The deposition pressure was 0.10 mbar, the electrode distance was 27 mm, the VHF power was 12 W and the total gas flow was 50 sccm. A series of layers has been deposited with these parameters at all the three substrate temperatures mentioned above, to determine the deposition rate of the material at a silane concentration of 0.2. fitting the interband transition model of O'Leary et al. [10] to the measured reflection and transmission spectra, the thickness and refractive index of the material is found.

3. Results

Experimental results were compared with 2D discharge simulations based on a fluid model [11] to verify the reliability of the ion

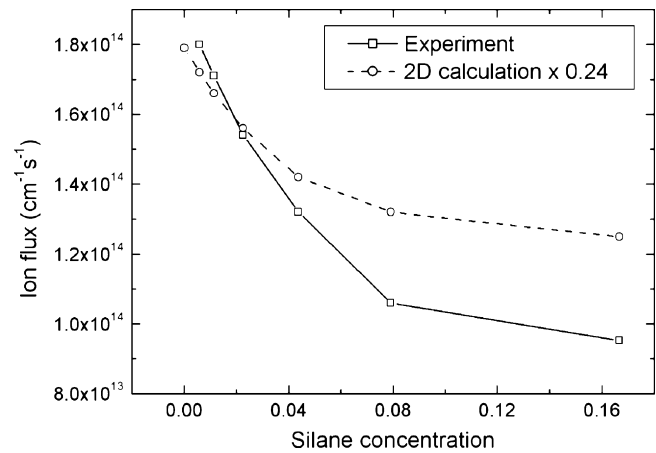


Fig. 2. Dependence of measured and calculated ion flux on the silane concentration. The gas temperature was 550 K, the pressure was 0.16 mbar, discharge power was 13 mW/cm², the inter-electrode distance is 27 mm and the discharge frequency was 50 MHz.

analysis. A comparison of the experimental data with the simulated plasma parameters is presented in Fig. 2, where the dependence of the ion flux on the silane concentration is presented. The simulations predict the correct ion flux dependencies on discharge parameters, though the simulated flux values exceed the measured flux values by a factor of 4. The fluid model approach used in the simulation provides a good agreement of the sheath voltage drop with the decrease of the measured ion energy, although it does not provide the ion energy distribution function. Typical IEDFs measured using the ion energy analyzer are presented in Fig. 3 for several values of silane concentration. Both the peak and the average ion energy and the ion flux are highest for a pure hydrogen discharge. If the dilution is decreased, the peaks get less pronounced and eventually the IEDFs get a collision-dominated character where the peak ion energy can no longer be identified. The total ion flux can nevertheless be determined, as well as the average ion energy. Fig. 4 shows the measured ion flux towards the substrate as a function of the silane fraction in the process gas. Going from a hydrogen dominated discharge to a silane dominated discharge, the flux of ions vanishes almost completely, especially for the lowest temperature series. This indicates that the beneficial effect of ions to the film growth is drastically reduced in a low substrate temperature deposition when the process solely relies on the use of pure

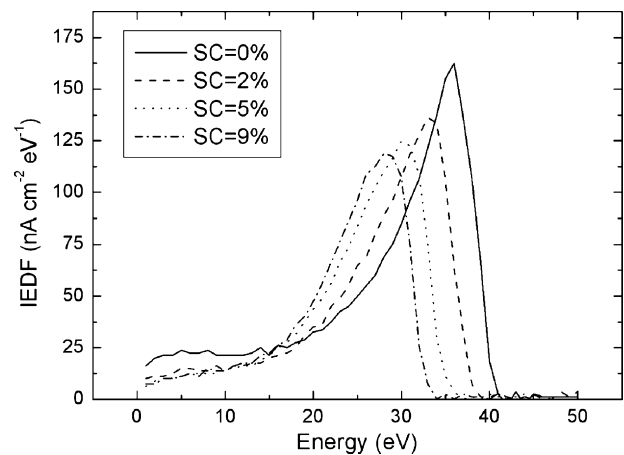


Fig. 3. Examples of IEDFs recorded in discharges with the indicated silane concentration. The substrate temperature was 200 °C, the pressure was 0.10 mbar, the discharge power was 80 mW/cm², the inter-electrode distance was 27 mm and the discharge frequency was 60 MHz.

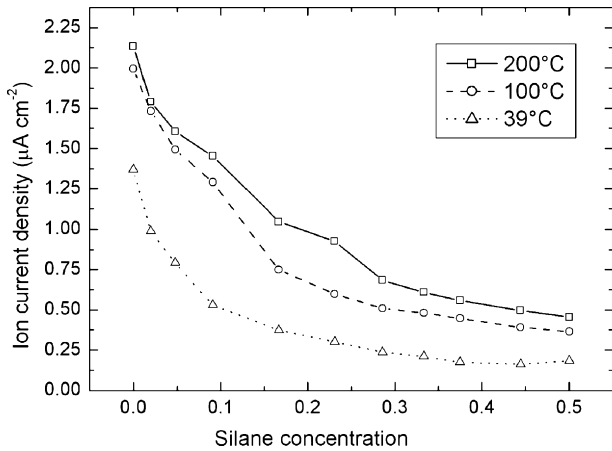


Fig. 4. Ion current density as a function of the silane concentration at the indicated substrate temperatures. Other parameters are equal to those of Fig. 3.

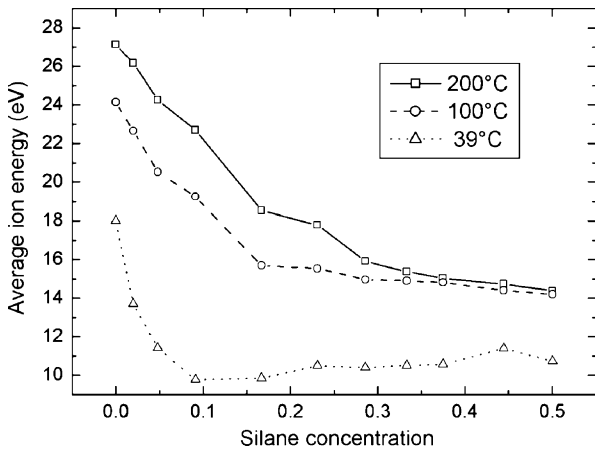


Fig. 5. Average ion energy as a function of the silane concentration at the indicated substrate temperatures. Other parameters are equal to those of Fig. 3.

silane or a source gas with a high silane concentration. Furthermore, Fig. 5 shows how the average ion energy is also significantly reduced. Figs. 4 and 5 may be combined to obtain the average ion energy density (Fig. 6). It can be concluded that the total ion energy carried to the growing silicon film is strongly reduced when the deposition temperature is lowered from 200 °C to 39 °C at a constant silane concentration. Therefore, in order to restore the original

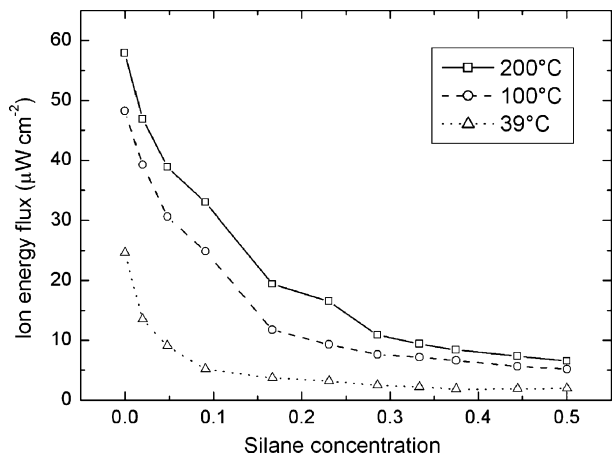


Fig. 6. Ion energy flux as function of the silane concentration at the indicated substrate temperatures. Other parameters are equal to those of Fig. 3.

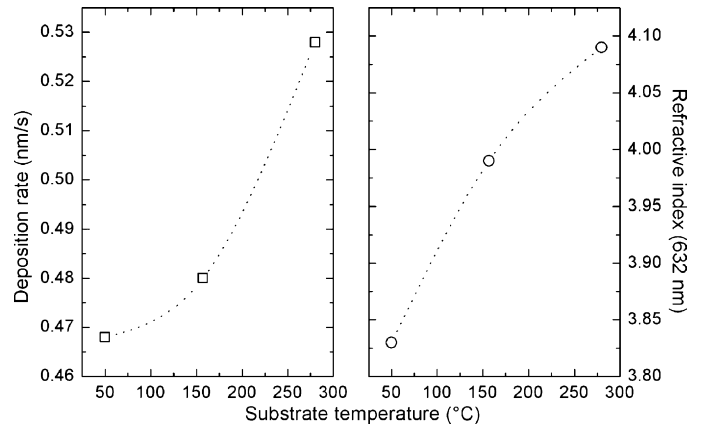


Fig. 7. Deposition rate and refractive index as function of substrate temperatures. The silane concentration was 0.2. Other parameters are equal to those of Fig. 3. The dotted lines are a guide to the eye.

optimum ion energy condition of 200 °C, it is a reasonable solution to decrease the silane concentration. This is in agreement with the experimentally found requirement of higher hydrogen dilution to achieve device-quality thin films when decreasing the substrate temperature.

Fig. 7 shows the deposition rate and refractive index as a function of substrate temperature. Both the deposition rate and the refractive index increase with increasing substrate temperature.

4. Discussion

A reasonable explanation for the effect of decreasing temperature on the ion energy originates from the increase in the gas density that accompanies the decrease in gas temperature. This increases the ion energy loss due to the increased rate of collisions. This is in agreement with the observation that the shape of the IEDFs is becoming more and more collisional, not only when the pressure is increased, but also when the temperature is lowered at a constant pressure.

We investigated whether the effect of temperature on the deposition rate and the compactness of the material can provide an additional explanation. Since every silane molecule deposited yields roughly two extra hydrogen molecules in the gas phase, a decrease in the deposition rate may cause a significant shift in the actual gas mixture towards higher silane concentration, resulting in lower ion current and energy. Since the fraction of the silane actually used in deposition in this regime is estimated to be 20% at most, and the deposition rate decreases by 11% according to Fig. 7, this would give an increase of the ‘effective’ silane concentration of about 3% within the temperature range investigated. Moreover, from the refractive index, the material compactness appears to increase at higher temperatures as expected, resulting in an extra shift towards a higher effective silane concentration. The changes in both the deposition rate and the refractive index shift the energy curves in the correct direction to partially account for the observed effects.

The observation that the ion energy is restored with increasing hydrogen dilution can be explained via the electron temperature: In order to generate the H* excited species from electron impact dissociation an electron energy of at least 16.6 eV is required for the reaction:



whereas for the dissociation reaction of silane resulting in excited Si, such as:



an electron energy of 10.5 eV [12] is sufficient. To sustain a discharge in a gas with a low silane concentration, a higher electron temperature is necessary, resulting in a higher plasma potential and consequently higher ion energies compared to a pure SiH₄ discharge.

Another method of compensation for the effects of low temperature may be found in the adjustment of the gas density by tuning the pressure. Although such a solution could restore the gas phase conditions (as far as ion energies are concerned) of a higher temperature process, it would lack the additional positive effects of the atomic hydrogen on the surface processes [13].

5. Conclusions

The plasma properties depend significantly on the substrate temperature during the deposition of amorphous silicon using a low pressure PECVD deposition process. The experiments show that both the ion flux and the average ion energy decrease with decreasing deposition temperature. On the other hand, the experiments also indicate that a solution exists in compensating the temperature effect by proper adjustment of the silane concentration.

Acknowledgements

The authors gratefully acknowledge Caspar van Bommel for depositions and Ruurd Lof for technical support. This research was financially supported by the Netherlands Agency for Energy and the

Environment (SenterNovem) of the Ministry of Economic Affairs: regeling 'Energie Onderzoek Subsidie: lange termijn' (EOS LT) and The Netherlands Organisation for Scientific Research (NWO).

References

- [1] K. Yamamoto, A. Nakajima, M. Yoshimi, T. Sawada, S. Fukuda, T. Suezaki, M. Ichikawa, Y. Koi, M. Goto, T. Meguro, T. Matsuda, T. Sasaki, Y. Tawada, Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion, WCPEC-4, 2 (2007) 1489.
- [2] B. Yan, G. Yue, J.M. Owens, J. Yang, S. Guha, Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion, WCPEC-4, 2 (2007) 1461.
- [3] K. Yamamoto, A. Nakajima, M. Yoshimi, T. Sawada, S. Fukuda, T. Suezaki, M. Ichikawa, Y. Koi, M. Goto, H. Takata, T. Sasaki, Y. Tawada, Proceedings of the 3rd World Conference on Photovoltaic Energy Conversion, vol. C, 2003, p. 2789.
- [4] A. Gordijn, M.N. van den Donker, F. Finger, E.A.G. Hamers, G.J. Jongerden, W.M.M. Kessels, R. Bartl, A.M.B. van Mol, J.K. Rath, B. Rech, R. Schlatmann, R.E.I. Schropp, B. Stannowski, H. Stiebig, M.C.M. van de Sanden, R.A.C.M.M. van Swaaij, M. Zeman, Proceedings of 4th World PVSEC, Hawaii, 2006, p. 1716.
- [5] Y. Ichikawa, T. Yoshida, T. Hama, H. Sakai, K. Harashima, Sol. Energy Mater. Sol. Cells 66 (2001) 107.
- [6] Y. Ishikawa, M.B. Schubert, Jpn. J. Appl. Phys. 45 (2006) 6812.
- [7] W. Beyer, Phys. B: Cond. Matter 170 (1991) 105.
- [8] P.C.P. Bronsveld, J.K. Rath, R.E.I. Schropp, T. Mates, A. Fejfar, B. Rezek, J. Kočka, Appl. Phys. Lett. 89 (2006) 051922.
- [9] C.A.M. Stap, H. Meiling, G. Landweer, J. Bezemer, W.F. van der Weg, Proceedings of the Ninth E.C. Photovoltaic Solar Energy Conference, Freiburg, 1989, p. 74.
- [10] S.K. O'Leary, S.R. Johnson, P.K. Lim, J. Appl. Phys. 82 (1997) 3334.
- [11] G.J. Nienhuis, W.J. Goedheer, Plasma Sources Sci. Technol. 8 (1999) 295.
- [12] A. Matsuda, M. Takai, T. Nishimoto, M. Kondo, Sol. Energy Mater. Sol. Cells 78 (2003) 3.
- [13] Jérôme Perrin, J. Non-Cryst. Solids 137–138 (1991) 639.