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High-quality a-Si:H grown at high rate using an expanding thermal plasma

M.C.M. van de Sanden *, R.J. Severens, J. Bastiaanssen, D.C. Schram

Department of Applied Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Abstract

An expanding thermal arc plasma is used to deposit amorphous hydrogenated silicon films. The thermal arc is operated in an argon–hydrogen mixture and SiH₄ is injected downstream in the plasma jet. In this contribution, we report the results of substrate temperature variation keeping the arc settings constant. It is observed that the growth rate is more or less independent of the substrate temperature at a value of 7 nm s⁻¹ and that the hydrogen content decreases with increasing substrate temperature to a value around 7% at 350 °C. The defect density decreases with increasing substrate temperature to a solar grade quality value of around 5 × 10¹⁵ cm⁻³. These results are compared with results obtained using a classical RF glow discharge and are interpreted through a deposition model based on the SiH₃ radical which is first physisorbed on the hydrogenated surface, diffuses to a dangling bond and then sticks. © 1997 Elsevier Science S.A.

Keywords: Expanding thermal plasma; a-Si:H; Fast deposition

1. Introduction

The deposition mechanism of amorphous hydrogenated silicon has been the subject of much research. By understanding the growth mechanism and its dependence on material quality, better material at possibly higher growth rates can be obtained. It is imperative that the growth rate of intrinsic a-Si:H for photovoltaic applications is increased above the value of 0.3–0.5 nm s⁻¹ usually reached by plasma enhanced chemical vapour deposition (PECVD) as this will eventually decrease the cost of solar cells produced. Many techniques have been investigated in the past. Although high growth rates were obtained, none of the alternative techniques showed a quality similar or better than that of the PECVD process. In this contribution, we will describe an expanding thermal plasma based on a cascaded arc [1,2], which improves the growth rate by more than one order of magnitude without compromising the quality. A deposition model will be presented which describes the results, both the growth rate and the quality of a-Si:H, quantitatively.

2. Expanding thermal plasma (ETP) set-up

The set-up consists of a DC thermal arc plasma source and a low-pressure chamber (Fig. 1): plasma production and deposition are spatially separated and in this way, the method can be classified as remote plasma deposition [1,2]. The plasma is generated by a DC discharge (typically 50 A, 100 V) between three cathodes and one anode. As the arc is operated at a typical pressure of 0.5 bar, the plasma is close to local thermal equilibrium and is characterized by a high electron density and low electron temperature ($n_e \approx 10^{22}$ m⁻³, $T_e \approx 1$ eV). It expands into the deposition chamber through a parabolically shaped nozzle in the anode plate. Usually, a gas mixture of argon and hydrogen is used, leading to a flux of atomic hydrogen which is much larger than the ion flux. The plasma expands supersonically into the deposition chamber (pressure typically 20 Pa), shocks and flows subsonically towards the substrate with a typical transport velocity of 10³ m s⁻¹. At the substrate (32 cm downstream from the nozzle), the plasma beam has a diameter of about 30 cm. In the argon–hydrogen plasma jet, typical downstream plasma parameters are an electron density of about 10¹⁷ m⁻³ and an electron temperature of about 0.2 eV. Pure silane is injected into the jet just behind the expansion nozzle.

* Corresponding author.

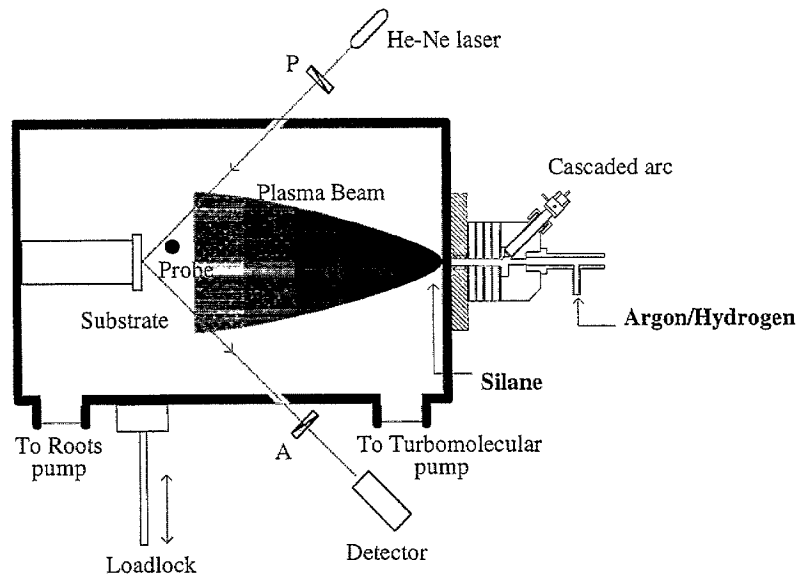


Fig. 1. The expanding thermal plasma (ETP) set-up.

Due to the low electron temperature, the substrate self-bias is less than 2 V; consequently, ion bombardment is negligible. It also rules out the dissociation of silane by electron collisions; this is mainly attributed to hydrogen abstraction — primarily generating SiH_3 — and to a sequence of dissociative charge exchanges and consecutive dissociative recombinations. When a gas flow ratio of $\text{Ar}:\text{H}_2:\text{SiH}_4=55:10:10$ is used, the first process dominates.

Substrate temperature is determined using an empirical model of the heat balance in which all necessary parameters such as the plasma heat fluxes, emissivities and conduction coefficients have been determined experimentally. Assuming the temperature of the substrate holder on which the substrate is clamped, this model yields the substrate temperature as a function of time. During the actual deposition the substrate temperature did not vary more than 25 °C.

The substrates used are silicon and Corning 7059 glass. Growth rates are measured using in-situ HeNe ellipsometry. The hydrogen content, refractive index and optical bandgap are determined using UV-VIS-IR transmission-reflection spectrometry. The defect density is measured ex-situ using dual beam photoconductivity spectrometry.

3. Results

In the following, we discuss results obtained using the ETP set-up. We have only varied the substrate temperature and have kept the plasma conditions fixed. Under these conditions, the creation of the SiH_3 radical is dominant. We will compare our results with the results of Matsuda et al. [3] obtained by PECVD using a triode

reactor, also under conditions where SiH_3 is dominant. In our case, the influence of ions is negligible as they are quenched efficiently by the hydrogen molecules which are formed on the wall of the vacuum vessel [4].

Fig. 2 shows the growth rate as a function of inverse substrate temperature using the expanding thermal arc plasma. The results of Matsuda et al. [3] are shown for comparison. It is seen that the growth rate is more or less independent of the substrate temperature. Apart from this, the growth rate obtained in the ETP set-up is about 20 times higher. Above 350 °C, the growth rate in case of Matsuda et al. [3] increases owing to the fact that the thermal desorption of hydrogen from the hydrogenated silicon surface becomes effective in creating dangling bonds and resulting in additional growth sites. In our case, the highest substrate temperature studied

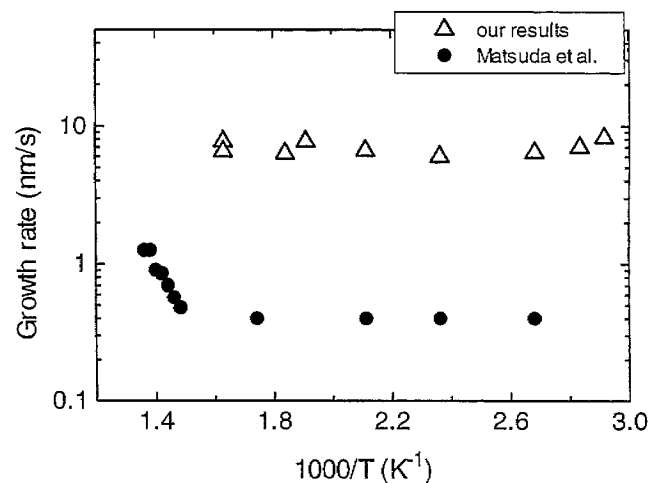


Fig. 2. Growth rate of a-Si:H versus inverse substrate temperature.

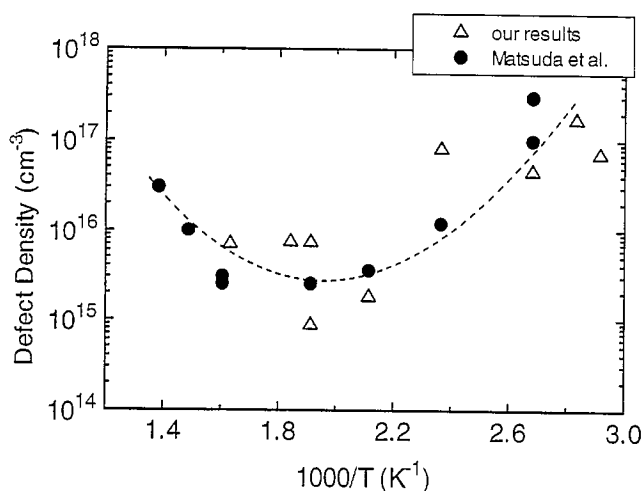


Fig. 3. Defect density of a-Si:H versus inverse substrate temperature.

so far is 350 °C. The defect density given in Fig. 3 is an important parameter quantifying the quality of a-Si:H and is shown as a function of inverse substrate temperature. Again, a comparison is made with the results of Matsuda et al. [3]. The temperature trend of our results is similar to that observed for the capacitively coupled RF plasma up to the point where the growth rate starts to increase, i.e. the growth rate is more or less independent of the substrate temperature. This is rather remarkable as our results were obtained at growth rate which was a higher by a factor of 20. Other properties, such as the hydrogen content, refractive index and optical bandgap are shown in Fig. 4 as a function of the inverse substrate temperature. It can be concluded that the properties of our material are very similar to the PECVD process. Moreover, we conclude from Figs. 2–4 that hydrogen and defect incorporation in a-Si:H under

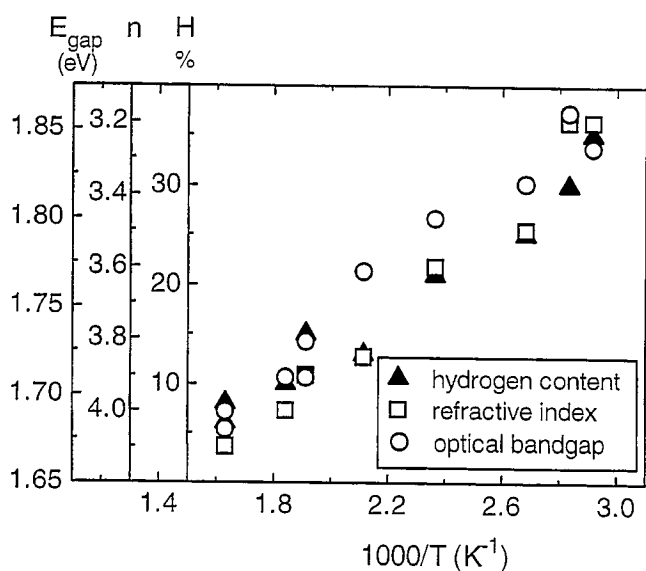


Fig. 4. Hydrogen content H (▲), refractive index n at 632.8 nm (□) and Tauc optical bandgap E_{gap} (○) versus inverse substrate temperature.

conditions of dominant SiH_3 flux towards the growth surface is independent of the growth rate. As these two properties are linked to other opto-electronic properties of a-Si:H, it follows that these properties are independent of growth rate too. The results presented in Figs. 2–4 can be explained qualitatively with the model as original proposed by Matsuda et al. [3]. However, some changes to the model should be made.

The model of Matsuda et al. [3] and others [5] is based on the observation that during growth the surface is hydrogenated [6]. This fact is closely related to the low defect density of smaller than 10^{16} m^{-3} , which corresponds to a fractional density of smaller than 10^{-7} . Since the surface is hydrogenated, direct incorporation of SiH_3 is unlikely. However, the reactive sticking probability of SiH_3 is measured to be around 10% [3], a value in contradiction to the hydrogen surface coverage which must be very close to 1 owing to the small defect density observed. This apparent paradox has been solved by the introduction of a so-called physisorbed state. This intermediate state acts as a reservoir. The growth sites are created by hydrogen abstraction due to SiH_3 . In the model of Matsuda et al. [3] and others [5], this abstraction occurs by SiH_3 radicals which are physisorbed and which hop from site to site. Apart from abstraction, the SiH_3 sticks on a dangling bond or it recombines with another SiH_3 to form Si_2H_6 . Since the (macroscopic) number of hops per unit of time, which is proportional to the number of physisorbed SiH_3 radicals, is orders of magnitude higher than the number of incoming radicals per unit of time, the effective sticking probability is enhanced by that same factor. As long as the amount of physisorbed radicals remains proportional to the incoming radical flux, i.e. the surface coverage is much smaller than unity, the effective sticking probability is not affected by the radical flux and therefore the growth rate is directly proportional to the incoming flux.

The recombination process of two physisorbed SiH_3 radicals on the hydrogenated surface is a quadratic process in the physisorbed SiH_3 density and is therefore incompatible with the observed constant growth rate as a function of substrate temperature and with the fact that both the hydrogen content and defect density do not depend on the growth rate [7]. Therefore, we propose that the abstraction reaction occurs on impact, i.e. an Eley–Rideal type reaction, similar to the hydrogen abstraction on a crystalline surface by atomic hydrogen [8]. These reactions usually have a weak temperature dependence consistent with the observed constant growth rate. The next step is to explain the growth rate independence of the hydrogen content and defect density. To explain this, we introduce a so-called activated hydrogen site, a site which is created after the SiH_3 has chemisorbed on a dangling bond. The 2–3 eV released during this chemisorption is used, with a large prob-

ability, to overcome the activation energy for molecular hydrogen formation and cross-linking of the remaining two silicon bonds. This explains the small amount of hydrogen incorporated in a-Si:H and the usually small activation energy observed (around 0.1 eV) for the hydrogen content as a function of inverse substrate temperature. However, there is a probability, which decreases with substrate temperature, that hydrogen is incorporated, which one can tentatively visualize as two Si–H bonds opposite to each other. The formation of Si₂H₆ in our model is due to the re-etching of SiH₃ by means of surface diffusing SiH₃. The defect incorporation is similar to the hydrogen incorporation. Therefore, the defect density depends on this re-etching process, which has a probability which is exponentially dependent on the inverse substrate temperature [7].

The described model remains valid up to the point where the surface is kept passivated with hydrogen. Dehydrogenation occurs at a point when hydrogen desorption becomes effective. The latter depends on the flux of SiH₃: higher fluxes of SiH₃ shift the dehydrogenation temperature to higher values. This implies that since the defect density is proportional to the dangling bonds on the growth surface, a higher growth rate and higher substrate temperature lead to lower defect density and lower hydrogen content.

4. Conclusions

Most a-Si:H material characteristics depend sensitively on the substrate temperature during deposition. The dependence of the dangling bond density can be explained using a surface kinetic growth model and is basically determined by a hydrogen surface coverage equilibrium between direct abstraction, re-etching, deposition and thermal desorption. In addition, we propose that the hydrogen content — and bonding

configuration — is essentially determined by a thermally activated cross-linking step immediately subsequent to sticking.

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References

- [1] R.J. Severens, G.J.H. Brussaard, H.J.M. Verhoeven, M.C.M. van de Sanden, D.C. Schram, *Mater. Res. Soc. Symp. Proc.* 377 (1995) 33.
- [2] R.J. Severens, G.J.H. Brussaard, M.C.M. van de Sanden, D.C. Schram, *Appl. Phys. Lett.* 67 (1995) 491.
- [3] G. Ganguly, A. Matsuda, *J. Non-Cryst. Solids* 164–166 (1993) 31; *Jap. J. Appl. Phys.* 31 (1992) L1269; *Mater. Res. Soc. Symp. Proc.* 258 (1992); A. Matsuda, K. Nomoto, Y. Takeuchi, A. Suzuki, A. Yuuki, J. Perrin, *Surf. Sci.* 227 (1990) 50.
- [4] M.C.M. van de Sanden, R.J. Severens, R.F.G. Meulenbroeks, M.J. de Graaf, Qing Zhou, D.K. Otorbaev, R.A.H. Engeln, J.W.A.M. Gielen, J.A.M. van der Mullen, D.C. Schram, *Surf. Coat. Technol.* 74/75 (1995) 1.
- [5] A. Gallagher, *Mater. Res. Soc. Symp. Proc.* 70 (1986) 3; J. Perrin, Y. Takeda, N. Hirano, Y. Takeuchi, A. Matsuda, *Surf. Sci.* 210 (1989) 114.
- [6] Y. Toyoshima, K. Arai, A. Matsuda, K. Tanaka, *J. Non-Cryst. Solids* 137/138 (1991) 765.
- [7] M.C.M. van de Sanden, R.J. Severens, D.C. Schram, to be published.
- [8] D.D. Koleske, S.M. Gates, B. Jackson, *J. Chem. Phys.* 101 (1994) 3301; W. Widdra, S.I. Yi, R. Maboudian, G.A.D. Briggs, Weinberg, *Phys. Rev. Lett.* 74 (1995) 2074.