COMPARISON OF VHF, RF AND DC PLASMA EXCITATION FOR a-Si:H DEPOSITION WITH HYDROGEN DILUTION

R. PLATZ, C. HOF[‡], S. WIEDER[†], B. RECH[†], D. FISCHER[‡], A. SHAH[‡],
A. PAYNE and S. WAGNER

Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA

[‡] Institut de Microtechnique, Université de Neuchâtel, Switzerland

[†] Institut für Schicht- und Ionentechnik - PV, Forschungszentrum Jülich, Germany

ABSTRACT

A comparative study of DC, RF and VHF excitation for the plasma enhanced chemical vapor deposition (PECVD) of intrinsic layers of a-Si:H is presented, with special emphasis on the effects of hydrogen dilution. Growth rates at comparable plasma power, for substrate temperatures between 100°C and 300°C and for various H₂ dilution ratios are presented, along with optical bandgap, H content, and electronic transport properties in the light-soaked state.

H₂ strongly reduces the growth rate for all techniques. The growth rate for the highest H₂ dilution ratio is approximately four times higher for VHF than for DC or RF excitation. In all three cases increasing the substrate temperature reduces the optical gap and the H content C_H. Raising the substrate temperature slightly enhances the stability of undiluted films. H₂ dilution increases the optical gap for all three techniques. The H content of RF- and VHF-deposited samples increases with increasing H₂ dilution ratio, while in DC deposition it produces an initial drop of the H content, followed by an increase.

In all three cases, H₂ dilution improves the electronic transport properties of the material by roughly a factor of two. The gain in stability is most pronounced for relatively small dilution; in the case of DC deposition, too strong a dilution even has an adverse effect on stability.

INTRODUCTION

Since the first observation of enhanced stability of a-Si:H films deposited with H₂ dilution [1] this technique has become the only tool available at the production level proven to result in a-Si:H solar cells with improved stability against light-soaking. However, the proper choice of plasma excitation frequency in combination with H₂ dilution has not yet been resolved satisfactorily.

In the present paper, we directly compare standard radio frequency (RF, 13.56 MHz) deposition to very high frequency (VHF) deposition at 70 MHz and deposition using a direct current (DC) excitation, all with special emphasis on the influence of H₂ dilution. All three methods have shown potential for producing solar cells with high stabilized efficiency (e.g., [2,3] for RF, [4] for VHF and [5] for DC).

EXPERIMENTS

Three different deposition systems were used for the deposition of the a-Si:H films. Each of the three systems was built and optimized for a given excitation frequency. The DC-deposited films were made in the i-chamber of a three-chamber PECVD system with load-lock at Princeton. We also deposited a few layers using RF excitation in this reactor (referred to as RF(P)). All other intrinsic layers using RF excitation were deposited in the i-chamber of a three-chamber system with load-lock at Jülich. Depositions using the VHF excitation technique at

70 MHz were performed in a load-locked single chamber reactor at Neuchâtel, designed especially for the VHF-GD technique. Table 1 gives an overview of the deposition conditions used for the three techniques.

	Electrode dimensions	Electrode area [cm ²]	El.-substr. distance [cm]	Pressure undiluted films [mbar]	Pressure diluted films [mbar]	Power density [mW/cm ²]
DC	15×15 cm ²	225	1.6	0.67	0.93	44 ($\times^{1/2}$)
RF	Ø 13.5 cm	143	1.2	1.33	2.66	30
RF(P)	15×15 cm ²	225	1.6	0.67	-	22
VHF	Ø 13.0 cm	133	1.6	0.35	0.5	30

Table 1: Geometrical dimensions of the electrodes, and deposition conditions.

The temperatures given throughout this work are true substrate temperatures, determined by calibration for conditions corresponding to those during deposition. The plasma excitation power was chosen to be comparable in all three cases. For the DC-deposited films, the plasma burns towards both sides of the powered electrode, due to the triode-configuration of the reactor. The effective electrode surface is therefore doubled. The value of 44 mW/cm² given in the table is the value of the input power divided by the single electrode surface. The input power given for RF and VHF deposition was measured by a power meter between the generator and the matching network, and the value for DC deposition is given by current and voltage of the discharge.

Corning 7059 glass, and crystalline silicon substrates for infrared (IR) spectroscopy, were used in parallel for all depositions.

The optical absorption coefficient was measured by transmission, and C_H by integration of the 640 cm⁻¹ absorption peak in the IR absorption spectrum, using $C_H[\text{at.}\%] = 2.1 \cdot 10^{19} \text{ cm}^{-2} / 5 \cdot 10^{22} \text{ cm}^{-3} \int \alpha(\omega)/\omega d\omega$.

DC- and VHF-deposited films were degraded to saturation by a combination of pulsed dye laser degradation and HeNe laser illumination [6]. The transport properties were characterized using the mobility-lifetime product $\mu_0\tau_0$, which combines information on the majority carriers (from photo-conductivity measurements) and the minority carriers (from the steady-state photo-carrier grating, SSPG, technique); $\mu_0\tau_0$ correlates with the performance of a-Si:H p-i-n solar cells [7]. RF-deposited films were light-soaked for 600 h using 100 mW/cm² white light and characterized by photo-conductivity and constant photo-current method (CPM) measurements [3].

GROWTH RATE

The growth rate of the a-Si:H films is plotted in Figure 1 as a function of the H₂ dilution ratio ($=[\text{H}_2]/[\text{SiH}_4]$) for the three excitation techniques and a substrate temperature of ~200°C. For undiluted films, VHF deposition yields the highest growth rate of over 4 Å/s; however, the growth rate obtained with DC excitation is only slightly lower. The growth rate of RF-deposited films without H₂ dilution is ~2 Å/s. The influence of H₂ dilution is quite different for the three excitation frequencies. We observe a roughly linear dependence of the growth rate on the H₂

Figure 1: Growth rate for VHF, RF and DC deposition as a function of the H₂ dilution ratio ($=[\text{H}_2]/[\text{SiH}_4]$). Input power is 30 mW/cm² (VHF, RF) and 44($\times^{1/2}$) mW/cm² (DC). $T_s \sim 200^\circ\text{C}$.

dilution ratio in the case of VHF excitation. The range of H_2 dilution is very limited for the VHF technique as microcrystalline growth starts already at a dilution ratio of ~ 12 . Above 200°C microcrystalline growth sets in at even lower H_2 dilution ratios. The RF growth rate is lower and also a smooth function of H_2 dilution. Microcrystalline growth sets in at dilution ratios exceeding 30. The growth rate of the DC-deposited films drops by a factor of three between H_2 dilution ratios of zero and eight, almost parallel to VHF deposition. More H_2 in the plasma reduces the growth rate further, but with a smaller slope and similar to RF deposition. We observe the onset of microcrystalline growth at 190°C for H_2 dilution ratios of ≤ 30 . We conclude that VHF clearly favors microcrystalline growth, which starts at very low H_2 dilution ratios. DC and RF deposition both require much higher H_2 dilution ratios to yield microcrystals. The amount of H_2 dilution to obtain microcrystalline films appears lower for DC than for RF excitation.

OPTICAL GAP AND HYDROGEN CONTENT

Influence of the substrate temperature

In all three cases the substrate temperature has a relatively small influence on the growth rate. The growth rate increases slightly with increasing substrate temperature and at any temperature follows the same dependence on the H_2 dilution ratio as plotted in Figure 1. The optical gap and the material properties of the a-Si:H films, in contrast, are strongly influenced by the substrate temperature. We varied the substrate temperature between $\sim 100^\circ\text{C}$ and $\sim 300^\circ\text{C}$. The optical gap of intrinsic a-Si:H films deposited without H_2 dilution decreases approximately linearly with increasing substrate temperature (Figure 2a) for all three excitation techniques.

The decrease in the optical gap of the a-Si:H films correlates with a decrease in the H content in the films (Figure 2b). C_H is an approximately linear function of the substrate temperature in the investigated temperature range. All excitation frequencies yield comparable values for the optical gap and the H content.

Influence of hydrogen dilution

The influence of H_2 dilution depends on the excitation frequency. In all three cases, the optical gap E_{04} increases with H_2 dilution (Figure 3a). For VHF and RF excitation techniques, the increase is monotonic and almost linear. In the case of RF excitation, a H_2 dilution ratio of 30 results in approximately the same increase in E_{04} as a dilution of ten for VHF (~ 0.05 - 0.1 eV).

Figure 2a): Optical gap E_{04} as a function of the deposition temperature for films deposited without H_2 dilution and VHF, RF (Jülich and Princeton) or DC excitation.

b): Hydrogen content as a function of the deposition temperature for films deposited without H_2 dilution by VHF, RF or DC excitation.

DC deposition exhibits a different response to H_2 dilution. For low H_2 dilution ratios, the optical gap increases moderately and similarly to VHF and RF. Between a dilution ratio of four and six, however, the increase in the optical gap is very steep, followed by an increase to >2.05 eV with further dilution. Sub-bandgap absorption spectra and UV reflectance measurements [8] indicate that these samples still are purely amorphous.

The H content of the RF and VHF films increases with increasing H_2 dilution ratio (Figure 3b). The increase in C_H is much more pronounced for the VHF than for the RF samples, and C_H exceeds 20 at.% for the highest dilution. However, we find again for both, RF- and VHF-deposited samples, a correlation between the optical gap and the H content.

The DC samples exhibit an anomaly in the influence of H_2 dilution on the H content. The optical gap increases with H_2 dilution, though not monotonically. The H content, in contrast, initially decreases and reaches a minimum at a H_2 dilution ratio of ~ 4 . For still higher H_2 dilution ratios the H content increases as it does for VHF and RF deposition. Bennett et al. [9] also reported a decrease in the H content and a moderately increased optical gap for DC samples deposited with H_2 dilution ratios of up to ten.

TRANSPORT PROPERTIES AND STABILITY

The primary goal of H_2 dilution is to enhance the stability of a-Si:H against light-induced degradation.

Figure 4 shows the $\mu_0\tau_0$ product in the degraded state for VHF-deposited samples as a function of the H_2 dilution ratio for deposition temperatures between 195°C and 280°C . The $\mu_0\tau_0$ product for samples deposited without H_2 dilution improves slightly with increasing substrate temperature, and considerably with H_2 dilution. A H_2 dilution ratio of two raises $\mu_0\tau_0$ by a factor of two. A further increase in the H_2 dilution ratio does not raise $\mu_0\tau_0$, whereas the optical gap continues to increase.

In RF-deposited films (Figure 5), higher deposition temperatures similarly result in higher photo-conductivity and lower defect density in the degraded state for films deposited without H_2 dilution. H_2 dilution also raises σ_{ph} and reduces the defect density, both by up to a factor of 2-3. The improvement is more pronounced for samples deposited at lower temperature. The material quality continuously increases with increasing H_2 dilution, even though most of the improvement is achieved already for a H_2 dilution ratio of ten.

Likewise, the stabilized $\mu_0\tau_0$ product in the DC films improves with increasing substrate temperature (Figure 6). H_2 dilution has a beneficial effect at low dilution ratios: the degraded $\mu_0\tau_0$ product is roughly a factor of two higher for samples deposited with a dilution ratio of 2-4

Figure 3a): Optical gap E_{04} for VHF, RF and DC deposition at a substrate temperature $\sim 200^\circ\text{C}$ as a function of the H_2 dilution ratio of the plasma. All samples in the figure are purely amorphous.

b): Hydrogen content for VHF-, RF- and DC-deposited samples as a function of the H_2 dilution ratio.

Figure 4: $\mu_0\tau_0$ product in the degraded state for VHF-deposited films as a function of the H_2 dilution ratio.

Figure 5: Defect density and photo-conductivity values in the degraded state for RF-deposited films as a function of the H_2 dilution ratio [3].

Figure 6: $\mu_0\tau_0$ product in the degraded state for DC-deposited films as a function of the H_2 dilution ratio.

than for undiluted films, which is comparable to the improvement achieved for VHF-deposited samples (Figure 4). For high dilution ratios, in contrast to the observations for VHF and RF deposition, the quality of the films decreases again, even to below the value for undiluted films. It is interesting to note that the improvement of the stability correlates with the decrease in the hydrogen content (Figure 3b) for small H_2 dilution ratios. In the case of DC excitation, material with enhanced stability is therefore equivalent to material containing less hydrogen, whereas for RF and VHF deposition the gain in stability is achieved for material containing more hydrogen than material deposited without H_2 dilution.

DISCUSSION

H_2 dilution enhances the electronic transport properties of a-Si:H in the light-soaked state for all the investigated excitation methods. For the DC deposition technique we observe an optimum H_2 dilution ratio whereas VHF and RF exhibit a pronounced improvement for small H_2 dilutions followed by a rather small additional effect for still higher H_2 dilution ratios. For application as an intrinsic layer in a-Si:H solar cells, the stability of the material is only one issue. All three excitation techniques result in a more or less pronounced increase in the optical gap of a-Si:H deposited with H_2 dilution. This in turn requires thicker i-layers to obtain a given current density, thus affecting the stability of the device. However, this effect is an advantage for the thin a-Si:H top cells in tandem or triple junctions. For these wide-gap cells the necessary thickness adjustment is generally small, resulting in an overall efficiency gain from the enhanced stability coupled with the higher V_{oc} that results from the higher optical gap of the i-layer. In other applications, such as in the top cell of a micromorph tandem cell [10] the increase in the optical gap due to H_2 dilution is unwanted and undiluted i-layers are required [11].

The reduced growth rate under H₂ dilution may become an important issue in industrial production. For VHF deposition we observe the best stabilized electronic properties for a H₂ dilution ratio of two ($\sim 4 \text{ \AA/s}$). DC deposition yields comparable values for the degraded $\mu_0\tau_0$ product for a H₂ dilution ratio of four ($\sim 2.9 \text{ \AA/s}$). RF deposition yields considerably lower growth rates ($\sim 1 \text{ \AA/s}$ at a H₂ dilution ratio of ten and $\sim 0.5 \text{ \AA/s}$ at a dilution of 30). Therefore, as intrinsic a-Si:H material of more or less equal quality can be obtained by all three deposition techniques, the growth rate may become the decisive factor for the choice of excitation frequency.

CONCLUSIONS

Hydrogen dilution is a well-suited tool to all three excitation techniques, DC, RF and VHF, for obtaining a-Si:H with improved stability. H₂ dilution results in an increase in the optical gap for all three techniques. The hydrogen content of RF- and VHF-deposited samples increases with increasing H₂ dilution ratio. DC deposition with increasing H₂ dilution first lowers and then raises the hydrogen content. Raising the substrate temperature in all three cases reduces the optical gap and the H content. The stability of samples deposited at higher substrate temperature is slightly enhanced.

In all three cases of excitation, the electronic quality of light-soaked material is improved by roughly a factor of two upon H₂ dilution. Optimum H₂ dilution ratios are ~ 4 for DC, 10-30 for RF and ~ 2 for VHF excitation. H₂ dilution strongly reduces the growth rate for all techniques. The growth rate for the best VHF-deposited material is $\sim 4 \text{ \AA/s}$, which is 35 % higher than for the equivalent DC-deposited sample ($2.9 \text{ \AA/s}$), and 4-8 times the value for the best RF-deposited film ($0.5\text{-}1 \text{ \AA/s}$).

ACKNOWLEDGEMENTS

R. Platz thanks the Arthur u. Aenne Feindt Stiftung, Hamburg (Germany), the Fondation Charles-Edouard Guillaume, Bienne (Switzerland), and the Electric Power Research Institute for providing support for his stay at Princeton University. The authors thank S. Dubail for his technical assistance, as well as C. Beneking and F. Siebke for helpful discussions.

REFERENCES

- 1 S. Guha, K.L. Narasimhan and S.M. Pietruszko, J. Appl. Phys. 52 (1981) 859.
- 2 S. Guha, Proc. 25th IEEE PVSC (1996) 1017.
- 3 B. Rech, S. Wieder, F. Siebke, C. Beneking, H. Wagner, MRS Symp. Proc. 420 (1996) 33.
- 4 R. Platz, D. Fischer, S. Dubail and A. Shah, Solar Energy Materials and Solar Cells 46 (1997) 157.
- 5 L. Yang, M. Bennett, L. Chen, K. Jansen, J. Kessler, Y. Li, J. Newtown, K. Rajan, F. Willing, R. Arya, D. Carlson, MRS Symp. Proc. 420 (1996) 839.
- 6 C. Hof, Y. Ziegler, R. Platz, N. Wyrsh and A. Shah, Proc. ICAMS-7 (Budapest 1997), in print.
- 7 N. Beck, N. Wyrsh, C. Hof and A. Shah, J. Appl. Phys. 79 (1996) 9361.
- 8 T.I. Kamins, Polycrystalline silicon for integrated circuit applications, Kluwer Academic Publishers 1988, p.68.
- 9 M. Bennett, K. Rajan, K. Kritikson, Proc. 23rd IEEE PVSC (1993) 845.
- 10 R. Platz, J. Meier, D. Fischer, S. Dubail, A. Shah, MRS Symp. Proc. 467 (1997) 699.
- 11 R. Platz, C. Hof, D. Fischer, J. Meier, A. Shah, Solar Energy Materials and Solar Cells, in print.