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a-Si:H Grown by Hot-Wire CVD at Ultra-High Deposition Rates

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ABSTRACT

We increase the deposition rate of growing hydrogenated amorphous-silicon (a-Si:H) by the hot-wire chemical vapor deposition (HWCVD) technique by adding filaments (two) and decreasing the filament(s) to substrate distance. Increasing the deposition pressure, silane flow rate, and filament current also increases the deposition rate. However, an optimization procedure of these parameters, including the substrate temperature, is necessary to yield films with good electronic properties. We grow a-Si:H with photo-to-dark conductivity ratios exceeding 10^5 at deposition rates up to 130 Å/s. However, other electronic properties drop off at lower deposition rates. There is also a sharp increase in the void density, as measured by small-angle X-ray scattering (SAXS), when going from one to two filaments. However, both Raman and X-ray diffraction (XRD) measurements show no change in film structure with increasing deposition rates.

1. Introduction

Typical deposition rates of a-Si:H grown in commercial applications is normally less than 3 Å/s, below 10 Å/s. Increasing the deposition rate is important in order to decrease the manufacturing costs of a-Si:H devices. Increasing the deposition rates decreases the manufacturing time, which translates directly into reducing costs. Typical a-Si:H devices are based a p-i-n structure [1] where the intrinsic layer is much thicker than the doped layers. To accommodate this in an inline manufacturing process, the chambers where the i-layers are grown are usually made longer to allow for the requisite longer deposition times. Increasing the deposition rate of the i-layer growth can also lead to shorter deposition chamber length which translates into reduced capital equipment costs.

Since one early work in using HWCVD to grow a-Si:H [2] we have used the technique to grow films that have less light-induced degradation than similar films grown by plasma-enhanced CVD (PECVD) [3]. However, it is the ability to grow quality a-Si:H at very high deposition rates relative to PECVD-grown films that prompted this work.

2. Experimental Procedures

We grow a-Si:H by HWCVD in two types of reactors; a cross reactor and a tube reactor [4]. The cross reactor consists of a standard vacuum, six-way cross with an external substrate heater, room temperature chamber walls, and the filament perpendicular to the direction of gas flow. The tube reactor consists of a resistively-heated tube in a vacuum chamber that provides an isothermal heating zone at the substrate/deposition region, with the filament parallel to the direction of gas flow. Substrates must be loaded into the cross reactor by breaking vacuum each time. The tube reactors are equipped with a load lock to prevent exposing the chamber to air upon substrate loading.

The work reported in this paper was done entirely in one of our tube reactors. Our standard tube-reactor configuration has a single tungsten filament, 0.5 mm in diameter and approximately 16 cm long, in the center of the deposition region [4]. We can increase the deposition rate of this configuration by decreasing the filament to substrate distance (L) from 5 cm to 3 cm. By making this change, and increasing the silane flow rate and the chamber pressure we are able to obtain deposition rates up to 50 Å/s. However, to increase the deposition rate beyond 50 Å/s, we had to install a second filament. These filaments sit physically parallel and the current passes through them in parallel circuit. To maximize the thickness uniformity of the films, we try to keep the spacing between the filaments equal to L, but this was not physically possible for larger L. The two filaments are symmetric along the long axis of the tube-reactor. For this study, we have grown a-Si:H from pure silane, without dilution by hydrogen or other gases. More details of the chamber configuration and deposition conditions are in reference[5].

Deposition Parameter	Range
L—filament to substrate	5 to 3.2 cm
chamber pressure	10 to 75 mT
silane flow	10 to 75 sccm
filament current	14 to 16 amps/filament
substrate temperature	300 to 400°C

Table 1: Range of deposition conditions used to grow the a-Si:H reported on in this paper.

3. Results

Figure 1 shows how the photo-to-dark conductivity ratio of these films decreases as the deposition rate increases. The ambipolar diffusion length—as measured by the steady-state photo-grating technique—shows a similar decrease with increasing deposition rate from over 1,400 Å

at 17 Å/s to ~1,000 Å at 110 Å/s. The defect density (Nd_{CPM}) and Urbach energies (E_U) as measured by the constant photo-current method (CPM) do not reflect such a monotonic trend with deposition rate. Those films grown at <40 Å/s have similar Nd_{CPM} ($3\text{-}5 \times 10^{15}$ cm^{-3})and E_U (45-47 meV). There is then a big change and all the films grown at >40 Å/s also have similar Nd_{CPM} ($1\text{-}1.5 \times 10^{16}$ cm^{-3}) and E_U (52 meV). Rather than a monotonic change with deposition rate, these parameters seem to be in two groupings with the break being at 40 Å/s. For more details on the electrical properties of these materials, see reference [5].

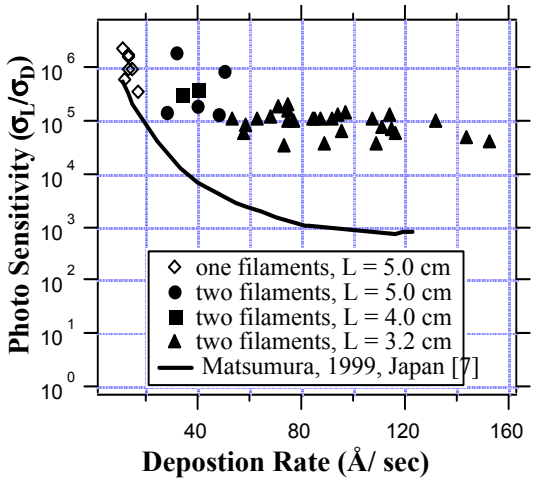

Figure 1: Changes in the photo response of a-Si:H grown at increasing deposition rates.

The degree of heterogeneity on nanometer scale as determined by SAXS follows a similar trend to the CPM measurements. That is, all films grown with two-filaments have an increase in the integrated-SAXS intensity by about a factor of 50 greater than those grown with a single filament at ~10 Å/s (from 0.05 to $\sim 2.5 \times 10^{24}$ eu/cm^3). Again, there is a clustering of the data in this range rather than a monotonic change with deposition rate. The degree of heterogeneity is associated with voids in the material; the larger the integrated SAXS intensity, the larger the void fraction of the film. Increasing the substrate temperature to 415°C can reduce the degree of heterogeneity in these high deposition-rate films by a factor of five, but does not reduce the single filament values. The void density of these high deposition-rate films amounts to about one percent.

The structural measurements as determined by other measurements do not show this trend of having a significant change when going to two filaments. Both XRD and Raman measurements show almost no change between films grown with one filament at deposition rates below 20 Å/s and those grown with two filaments at deposition rates over 130 Å/s. The full width at half maximum (FWHM) of the X-ray peak is related to the degree of medium-range order in the film. These films have a FWHM peak of 5.44° ± 0.05 of 2θ from 17 all the way up to 144 Å/s. These values are about 15% lower than those for state-of-the-art a-Si:H films grown by PECVD; indicating that these films have a higher degree of medium-range order. For more details on how the increase in deposition rate influences the structural properties of the resulting films, see reference [6].

4. Discussion

The dramatic change in some film properties at relatively low deposition rates (over the range investigated) indicates that there are significant differences in film growth below 40 Å/s and above that rate. However, these differences may not significantly limit the use of these high deposition rate materials in devices. The relatively small changes in some electronic properties (especially in the photo response) with increasing deposition rate is extremely encouraging.

The increase in void density as measured by SAXS does not correlate with the relatively small changes in the structure of the material as measured by both XRD and Raman. It may be that the growth mechanism responsible for void formation may not necessarily affect the tissue growth, giving rise to films with a high degree of medium-range order that have a high void density. If the tissue around the voids is of sufficient electronic quality, this technique may yield films adequate for device applications.

5. Conclusion

The results of this work are very encouraging. To maintain a photo-to-dark conductivity ratio in excess of 10^5 at deposition rates up to 130 Å/s is remarkable and far exceeds the results of any high deposition-rate research of which we are aware (see reference in Figure 1). Our future work will include further optimization of a-Si:H grown under these conditions as well as incorporating these materials into solar cells.

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7. References

[1] D.E. Carlson and C.R. Wronski, *Appl. Phys. Lett.* **28**, 671 (1976)
[2] A.H. Mahan, J. Carapella, B.P. Nelson, R.S. Crandall, and I. Balberg, Journ. Appl. Phys., 69, 6728 (1991)
[3] A.H. Mahan and M. Vanecek, Amer. Inst. of Phys. Conf. Proc. 234, (AIP, New York, 1991), p.195. .
[4] B.P. Nelson, R.S. Crandall, E. Iwaniczko, A.H. Mahan, Q. Wang, Y. Xu, and W. Gao, , *Mat. Res. Soc. Symp. Proc*. Vol. 557, MRS, Warrendale, PA, (April, 1999).
[5] B.P. Nelson, Y. Xu, A.H. Mahan, R.S. Crandall, E. Iwaniczko, and Q. Wang, Mat. Res. Soc. Symp. Proc. in press, MRS, Warrendale, PA, (April, 2000).
[6] A.H. Mahan, B.P. Nelson, Y. Xu, D.L. Williamson, M. Vanecek, R.S. Crandall, being submitted to Appl. Phy. Rev. Letters.
[7] Matsumura, CAT-CVD PVSEC satellite pre-workshop, Sept. 1999, unpublished.