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## Comparison of Structural Properties and Solar Cell Performance of a-Si:H Films Prepared at Various Deposition Rates using 13.56 and 70 MHz PECVD Methods

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### ABSTRACT

The advantage of using very high frequencies for preparation of a-Si:H materials at high rates (above 5 Å/s) for intrinsic layers (i-layer) of solar cells has been well documented. In an effort to identify film properties which may be related to this superior device performance, a study of the structural, optical and electrical properties of films made at various deposition rates between 1 and 15 Å/s using rf frequencies of 13.56 and 70 MHz has been made. The films were characterized using a number of techniques including small-angle x-ray scattering, infrared absorption spectroscopy, and scanning electron microscopy. For the films made using the 70 MHz frequency, the amount of nanovoids with sizes of  $< 100\text{Å}$  increases systematically as the deposition rates increases beyond 5 Å/s. Accompanying the increase in void fraction in the films are increases in the hydrogen content and the amount of  $2070\text{ cm}^{-1}$  mode in the infrared absorption spectra. In addition to an increase in the amount of nanovoids in the films as the deposition rate exceeds 5 Å/s, the films made using the 13.56 MHz and high deposition rates have large amounts of SAXS related to scattering features with sizes  $> 200\text{Å}$ . This scattering is associated with large bulk density fluctuations and/or enhanced surface roughness. None of the films in the study displayed signs of having columnar-like microstructures. The nanovoids are not related to changes in the solar cells with increasing i-layer deposition rate for both fabrication processes, perhaps due to the relatively small volume fractions of less than 0.2% and/or good void-surface passivation. However, the larger-scale structures detected in the films made using the 13.56 MHz technique could cause poorer performance in cells prepared at high growth rates.

### INTRODUCTION

The advantage of using very high frequencies (70-100 MHz) to prepare i-layers for a-Si:H solar cells at deposition rates between 5 and 10 Å/s has been reported by several research groups[1-4]. As the deposition rate for the a-Si:H i-layer growth is increased from 1 to 10 Å/s, virtually no change is observed in the solar cell properties, such as the fill factor (FF), the open circuit voltage ( $V_{oc}$ ) and the short circuit current ( $J_{sc}$ ). Only a 5% drop in  $J_{sc}$  is noted for a-Si:H cell with the same thickness prepared with current-enhancing Ag/ZnO backreflectors. In contrast, extensive attempts to increase the i-layer deposition rates using the standard 13.56 MHz PECVD process has led to cells with poor fill factors and cell efficiencies. This poorer performance is usually attributed to enhanced powder and polyhydride formation in the plasma that leads to i-layers with defect ridden, heterogeneous microstructures.

Here, optical and structural properties for single-layer films prepared at a variety of deposition rates using either a 13.56 or a 70 MHz frequency are compared with the performance of nip solar cells whose intrinsic layers were prepared under identical conditions to those for the single-layer films. The measurements include small-angle x-ray scattering (SAXS), infrared absorption

spectroscopy (IR), optical absorption spectroscopy and scanning electron microscopy (SEM). With these comparisons, a determination of which film properties play a role in determining the device performance can be made.

## EXPERIMENT

The a-Si:H films and nip solar cells were fabricated using a research-scale, multi-chamber, load-locked deposition system. The system has three separate chambers for deposition of n-type, p-type and intrinsic layers. For preparation of the single-junction solar cells, stainless steel substrates without current-enhancing Ag/ZnO backreflectors were used for preparation of the semiconductor structures. The thin doped layers were prepared using the conventional PECVD process in which a 13.56 MHz RF signal is used. To fabricate the a-Si:H i-layers, either the standard 13.56 MHz frequency or a fixed VHF frequency of 70 MHz was used. In this study of the general effects of deposition rate on film and device performance, a large set of parameters was altered to look for systematic trends with deposition rate. After fabrication of the nip structure, the devices were completed by evaporative deposition of indium tin oxide (ITO) conductive layers and then aluminum (Al) collection grids.

To characterize the cells, current vs. voltage (IV) and spectral response (quantum efficiency) measurements were made. For the IV measurements, white AM1.5 light was used to obtain the IV data. For light soaking studies, the cells were subjected to 600 h. of one Sun light with the cell temperature fixed at 50°C. The i-layer thicknesses were determined using capacitance techniques.

For the SAXS [5] and SIMS measurements, 1  $\mu\text{m}$  a-Si:H films were deposited on 10- $\mu\text{m}$ -thick, 99.999% Al substrates with both types of measurements performed with the same samples. IR and SEM measurements were made using 1  $\mu\text{m}$  a-Si:H films deposited on crystalline Si substrates while 1  $\mu\text{m}$  a-Si:H films on 7059 glass were used for optical absorption analysis.

## RESULTS

To study the heterogeneity of the films as the deposition rate was varied, films were prepared under a variety of conditions for SAXS analysis using both plasma frequencies. It was found that for films made using either the RF (13.56 MHz) or VHF (70 MHz) methods, the amount of SAXS increased as larger deposition rates were used. Figures 1 and 2 compare SAXS data for films prepared at 1-3 and 9-10  $\text{\AA}/\text{s}$  for a-Si:H films made using the 70 and 13.56 MHz frequencies. While the total amount of scattering increased for the films using both frequencies, detailed analysis of the SAXS data demonstrated that there are differences in the microstructural changes between the films made using the two different techniques. Through this analysis, the SAXS from a-Si:H films can be attributed to three different sources [5] ; 1) nanovoids with sizes less than 100 $\text{\AA}$ , 2) larger scale structures having sizes greater than 200 $\text{\AA}$ , and 3) diffuse scattering due to atomic-scale density fluctuations. For both deposition techniques, the volume fraction of nanovoids increases as the deposition rate goes beyond 5  $\text{\AA}/\text{s}$  as is shown in Fig. 3 where the integrated SAXS related to the nanovoid fraction ( $Q_n$ ) [5] is plotted as a function of deposition rate. As can be seen from the data in the figure, at the higher deposition rates (6-10  $\text{\AA}/\text{s}$ ), the samples made using the RF method typically have a larger percentage of nanovoids. In terms of

larger-scale structures, the amount of related SAXS is also larger for the films prepared by the lower frequency technique. The Porod slope, calculated from the SAXS data in the small  $q$  range

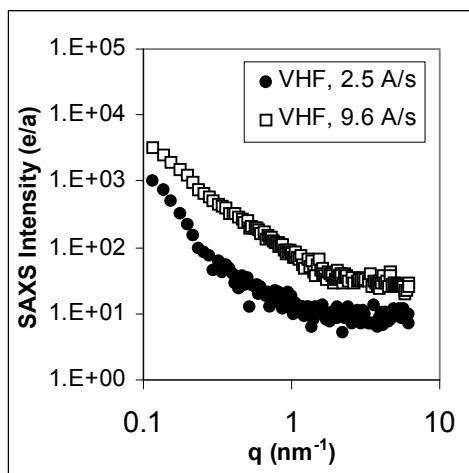


Fig. 1. SAXS for VHF prepared films.

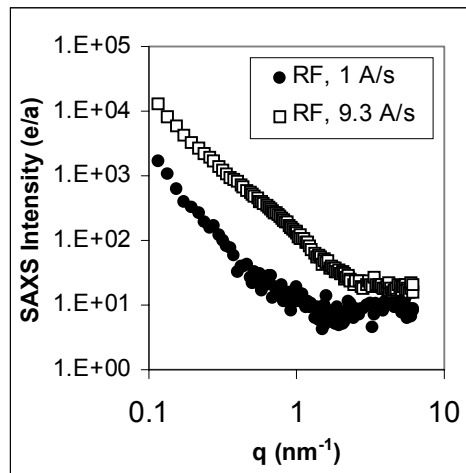


Fig. 2. SAXS for RF prepared films.

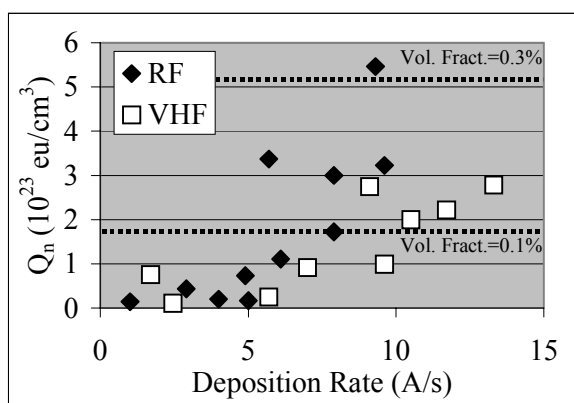


Fig. 3. SAXS signal (nanovoids) versus rate. deposition rate.

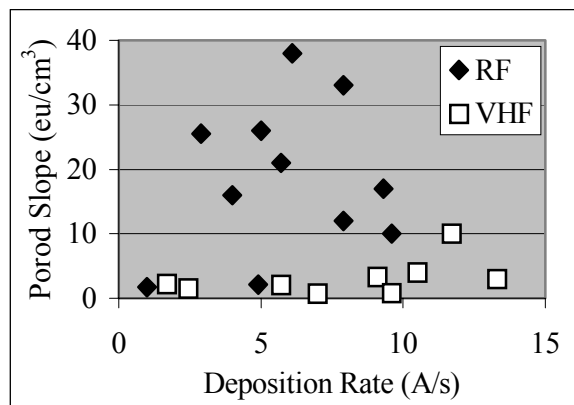


Fig 4. Porod slope versus

[5], is related to the scattering from larger-scale heterogeneity (sizes  $>200 \text{ \AA}$ ) such as density fluctuations from non-uniform hydrogen distributions or from a significant amount of surface roughness. Fig. 4 shows that the Porod slopes for the films made using the 13.56 MHz and deposition rates above the standard  $1 \text{ \AA/s}$  are typically much higher than those for the 70MHz produced films which remain low independent of deposition rate in the range studied. Thus, the RF films made at the higher rates have enhanced larger-scale internal heterogeneity and/or rougher surfaces. Preliminary atomic force microscope (AFM) analysis of films deposited at a  $10 \text{ \AA/s}$  rate demonstrate that the film surfaces are rougher when using the RF technique instead of the VHF method. However, more analysis of this data is needed in order to prove that the larger Porod slopes are entirely due to enhanced surface roughness. For both the RF and VHF-produced films, the diffuse scattering generally increases with increasing deposition rate consistent with an increase in H content [5] and supported by some IR results presented below.

By measuring the SAXS at different tilt angles, one can determine if the scattering centers which cause the SAXS are highly oriented relative to the film surface as they are for films which

have columnar-like microstructures [5]. For all of the films measured in this study, relatively small changes in the SAXS were noted as the samples were measured at different tilt angles. This is demonstrated in Figs. 5 and 6 where SAXS data measured at 0 and 35° tilt angles are compared for a film prepared with the 70 MHz technique at a deposition rate of 10 Å/s (Fig. 5) and a film prepared with the 13.56 MHz method at a 7 Å/s rate (Fig. 6). Only the data at small  $q$  for the sample prepared with the 13.56 MHz frequency decreases slightly with varying angle. The lack of a substantial tilt dependence suggests that all of the films have little in the way of a columnar-like microstructure and that the scattering features detected by SAXS is spherical in nature and/or randomly oriented. The lack of columnar-like structures in the films was confirmed by SEM analysis of the cross-sections of 1  $\mu\text{m}$ -thick films prepared by both techniques at 8-12 Å/s rates. Fig. 7 displays a representative SEM photograph taken at 60,000x of such a 1  $\mu\text{m}$ -thick film demonstrating the lack of any discernable microstructure.

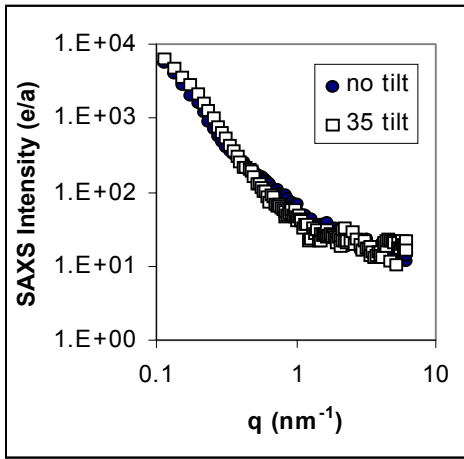


Fig. 5. SAXS data for a film prepared by the VHF method at a 10 Å/s rate.

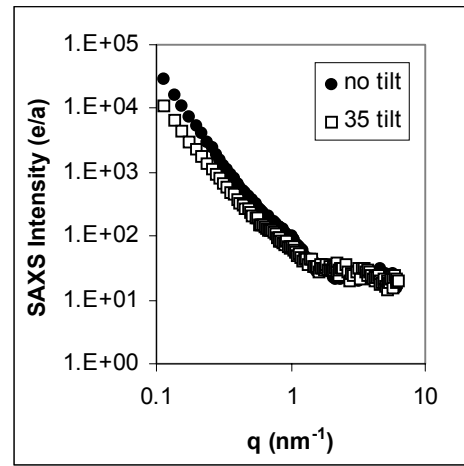


Fig. 6. SAXS data for film prepared by the RF method at a 7 Å/s rate.

Table I compares the SAXS data with data from IR, SIMS and optical absorption measurements of films made at similar deposition conditions. As the amount of SAXS detected nanovoids ( $Q_n$ ) increases with increasing deposition rate for films made using the VHF technique, the hydrogen content determined by IR measurements increases as does the microstructure factor  $(2070 \text{ cm}^{-1})/(1970 \text{ cm}^{-1} + 2070 \text{ cm}^{-1})$  determined by the integrated areas under the 1970  $\text{cm}^{-1}$  and 2070  $\text{cm}^{-1}$  IR peaks. With the increase in hydrogen content, the bandgap also increases. In contrast to these systematic trends for the films produced by the VHF technique, no correlation between the SAXS data and the hydrogen content or the microstructure factor could be made for the samples prepared using the RF method. Besides the trends for the SAXS data, the only systematic observation in the material properties for the films made using the RF technique was an increase in bandgap energy as the deposition rate increased beyond the 5-6 Å/s range.

For comparison of the film properties with device performance, Table II lists properties for a-Si:H nip cells whose i-layers were made using conditions identical to those used to prepared certain SAXS samples. All of the cells were made without current-enhancing backreflectors and have i-layer thickness of  $1500 \pm 150 \text{ \AA}$ . While several measurements suggest that there are structural differences (nanovoids, microstructure factors, and hydrogen contents) for the films

made by the VHF technique using the low (1-3 Å/s) and high (8-10 Å/s) rates, little variations are observed for the cell properties. The FF and the amount of cell degradation with light soaking were found to remain constant in this range of deposition rate while only a drop in the  $J_{sc}$  value

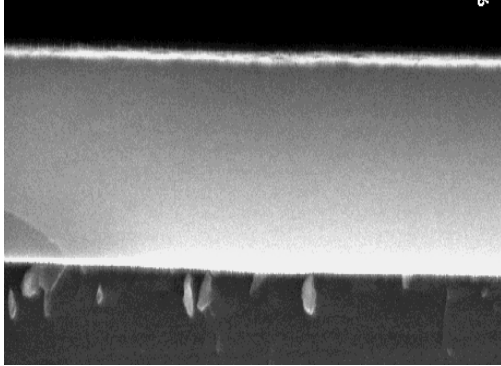


Fig. 7. SEM photograph of the cross section of a RF film made at a 9 Å/s rate.

Table I.  
Data from SAXS, IR, and optical absorption measurements for films prepared by VHF method.

Dep. Rate (Å/s)	$Q_n$ ( $10^{23}$ eu/cm <sup>3</sup> )	Vol. Fract. (%)	$C_H$ from IR (at. %)	Microstr. Factor R	$E_{gap}$ (eV)
2.1	0.11	0.01	9.3	0.14	1.76
6.1	0.92	0.05	13.9	0.16	1.79
10.0	2.00	0.12	16.4	0.22	1.86
10.9	2.54	0.15	-	-	1.83

from 9.5 to 8.9 mA/cm<sup>2</sup> lead to a drop in the cell efficiency. An alternative set of deposition conditions lead to the achievement of the 9.6 mA/cm<sup>2</sup> value and a high efficiency without a large change in the  $Q_n$  value or the bandgap energy (see the data in Table I for the for the films made at rates of 10 and 10.9 Å/s). In contrast, lower FF values and large amounts of degradation with light soaking are found for the films prepared using the RF method and deposition rates of 5 Å/s or higher. Also, the  $J_{sc}$  values are lower at the highest rates, likely due to the same reason that under certain deposition conditions the VHF films prepared at the 10 Å/s also have low currents.

From careful measurements of the high wavelength region of the quantum efficiency spectra, one is able to calculate Urbach energies ( $E_0$ ) for the i-layer materials using the single-junction cells. In contrast to the  $J_{sc}$ , FF and  $P_{max}$ , values listed in the table, the  $E_0$  values were obtained after light soaking of the cells. As can be seen from the data listed in the table, no systematic change in  $E_0$  was observed with increasing deposition rate demonstrating that the changes in cell properties are not related to variations in the valence band tail.

Table II.  
Properties for a-Si:H cells made using RF and VHF methods.

Freq (MHz)	Deposition Rate (Å/s)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	$P_{max}$ (mW/cm <sup>2</sup> )	% of Degradation with Light Soaking	Urbach Energy $E_0$ (meV)
70	2.1	9.38	0.728	6.46	-	-
70	6.1	9.51	0.726	6.45	13.4	47
70	10	8.87	0.732	6.25	15.4	50
70	10.9	9.63	0.733	6.63	12.1	44
13.56	0.9	9.52	0.732	6.47	12.5	48
13.56	5	9.57	0.690	5.98	20.2	46
13.56	5	9.52	0.674	5.88	23.5	47
13.56	8.1	8.95	0.671	5.43	23.8	59
13.56	8.6	8.27	0.684	5.31	18.8	49
13.56	9.2	8.68	0.680	5.47	19.7	48

## DISCUSSION AND CONCLUSIONS

In terms of the effect of the structural properties on the device performance, it is surprising that some of the structural changes noted by the film measurements do not seem to affect the solar cell performance. For the materials made using the VHF technique, all of the structural measurements suggest that as the deposition rate increases, a larger number of randomly oriented nanovoids appear in the films. It seems likely that the surfaces of the nanovoids are coated with hydrogen, leading to the observed increase in the  $2070\text{ cm}^{-1}$  mode in the IR spectra as the deposition rate increases. Also, it is clear that this increase in void fraction in the films does not correlate with a change in device performance. It is possible that the change in void fraction is just too small (only about 0.1 vol.%) to have a bearing on the i-layer transport properties. Also because the IR results suggest that the void surfaces are likely hydrogen coated, the appearance of the additional voids with increasing deposition rate may not lead to an increase in defect density in the i-layers, which may ultimately prove as the determining factor of the cell properties. Measurements of the defect densities for these materials are presently being made.

For the films made using the RF method, no change in the nanovoid fraction is observed when the deposition rate is changed from 1 to 5 Å/s while in this same range of deposition rate a large change in the cell properties is noted (Table II). Since the SAXS films and the i-layers for the cells were made using nominally the same deposition parameters, this would suggest that, at least for these studies, the nanovoid fraction (well below 0.1 vol.% up to 5 Å/s) does not play a significant role in the determination of the cell properties. However, the larger scale structure ( $>200\text{ Å}$ ) could affect the device performance. While there is not a one-to-one correlation with the Porod slope and the device efficiency, all of the i-layers for cells with FF below 0.7 were prepared under conditions which lead to high Porod slopes ( $>10\text{ eu/nm}^3$ , Fig. 4). Only the cells prepared using the VHF technique and the cell made using the RF method and a rate near 1 Å/s have FF near 0.73 and each of these conditions lead to low Porod slopes. As mentioned previously, these large scatterers could be related to non-uniform hydrogen distributions and/or to surface roughness. While they do not conclusively prove the nature of the larger scatterers, preliminary AFM measurements do suggest that the surfaces for the RF films made at high rates are rougher. Further measurements are planned to confirm the origin of the large-scale scattering.

Beyond the measurements completed in this study, the defect densities for the i-layer material could primarily dictate the cell properties. A continuation of these studies will include measurements of the defect densities and comparisons of the results with cell properties in order to determine what causes the differences in the cell properties for the films prepared using the 13.56 and 70 MHz frequencies.

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## REFERENCES

1. H. Chatam and P.K. Bhat, *Mat. Res. Soc. Symp. Proc.* **149**, 447 (1989).

2. A. Shah, J. Dutta, N. Wyrsh, K. Prasad, H. Curtins, F. Finger, A. Howling, and Ch. Hollenstein, *Mat. Res. Soc. Symp. Proc.* **258**, 15 (1992).
3. S.J. Jones, X. Deng, T. Liu, and M. Izu, *Mat. Res. Soc. Symp. Proc.* **507**, 113 (1998).
4. J. Yang, S. Sugiyama, S. Guha, *Mat. Res. Soc. Symp. Proc.* **507**, 157 (1998).
5. D.L. Williamson, *Mat. Res. Soc. Symp. Proc.* **377**, 251 (1995).