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Preparation of Microcrystalline Silicon Based Solar Cells at High i-layer Deposition Rates Using a Gas Jet Technique

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ABSTRACT

A Gas Jet technique has been used to prepare microcrystalline silicon (μc-Si) thin films at deposition rates as high as 20 Å/s. The films have microcrystal sizes between 80 and 120 Å with a heterogeneous microstructure containing regions with columnar growth and other regions with a more randomly oriented microstructure. These materials have been used as i-layers for nip single-junction solar cells. The high deposition rates allow for fabrication of the required thicker μc-Si i-layers in a similar amount of time to those used for high quality a-SiGe:H i-layers (rates of 1-3 Å/s). Using a 610nm cutoff filter which only allows red light to strike the device, pre-light soaked short circuit currents of 8-10 mA/cm^2 and 2.7% red-light efficiencies have been obtained while AM1.5 white light efficiencies are above 7%. These efficiencies are higher than those typically obtained for μc-Si cells prepared at the high i-layer growth rates using other deposition techniques. After 1000 h. of light soaking, the efficiencies on average degrade only by 2-5% (stabilized efficiencies of 2.6%) consistent with the expected high stability with the microcrystalline materials. The small amount of degradation compares with the 15-17% degradation in efficiencies for a-SiGe:H cells subjected to similar irradiation treatments (final light-soaked red light efficiencies of 3.2%). Improvements in the cell efficiencies may come through an understanding of the role that columnar microstructure and void structure plays in determining the device performance.

INTRODUCTION

μc-Si-based solar cells are an intriguing alternative to other cost effective, thin film photovoltaic devices. Absorbing a significant portion of the solar spectrum, reasonably high stable efficiencies can be obtained with single-junction device structures. For example, Shah et. al.[1] have shown that high quality μc-Si pin devices with 8.5% efficiencies that absorb a significant amount of the red light and do not degrade with long term light exposure can be made using the Very High Frequency (VHF) PECVD technique. As another alternative, the μc-Si material could replace amorphous silicon germanium alloy (a-SiGe:H) layers as the red-light absorbing structures in amorphous silicon-based multi-junction structures. The a-SiGe:H alloys have historically been more defective and of poorer quality than the a-Si:H materials and in many respects limit the efficiencies of the multi-junction devices. The μc-Si cells do not significantly degrade (<5%) with long term light exposure as do the amorphous silicon-based devices (>10%). Also use of the μc-Si cells as red-light absorbing structures in multi-junction cell with blue-green light absorbing a-Si:H top cells would lead to the elimination of costly germane gas from the fabrication process. The present major disadvantage in using the μc-Si devices instead of amorphous silicon cells is the required thick i-layers (1 μm) due to the indirect bandgap of the

material. This is of particular concern since deposition rates of 1 Å/s or less are required to prepare high quality μc-Si material using conventional PECVD techniques.

Reported here are results from a study of a new technique to prepare μc-Si films and solar cell devices at high growth rates. With this Gas Jet deposition technique [2], a high-speed gas source is subjected to microwaves that decompose the gas, forming a plasma close to the Gas Jet nozzle. After gas dissociation, radicals, ions and neutral species generated in the plasma quickly reach a heated substrate surface due to the high-speed gas flows. The use of microwaves allows for high silane decomposition rates and the large amount of hydrogen etching of the film growth surface required for microcrystalline formation.

EXPERIMENT

The μc-Si materials were prepared using a fixed 2.54 GHz microwave frequency to dissociate the feed gases that included silane, hydrogen and various fluorine-based etching gases. To fabricate nip solar cell structures, doped layers were prepared using the standard PECVD process and deposition rates near 1 Å/s. Also, current enhancing Ag/ZnO back reflectors were deposited on the stainless steel substrates prior to fabrication of the nip semiconductor structures. Because of equipment limitations, the doped layers were prepared in a separate deposition system so that the n/i and i/p interfaces were exposed to the atmosphere and are likely oxidized. The authors recognize that this oxidation could limit the cell efficiencies. The devices were completed by evaporating indium tin oxide (ITO) conductive layers and then Al collection grids.

To characterize the cells, standard current vs. voltage (IV) and spectral response (quantum efficiency) measurements were made. Since our goal is to use the μc-Si cells as the red light absorbing components of multi-junction cells, IV measurements were completed using not only the direct AM1.5 white light but also the while light filtered with a 610 nm low band pass filter to simulate the absorption due to higher bandgap, blue-green light absorbing top layers. To complete light soaking studies, the cells were subjected to 1000 hrs. of one sun light with the cell temperature fixed at 50ºC. The i-layer thicknesses were determined using capacitance techniques.

To classify the structural bonding, degree of microcrystallinity, and film microstructure, a number of structural measurements including scanning electron microscopy (SEM), x-ray diffraction and small-angle x-ray scattering (SAXS) measurements were utilized.

RESULTS AND DISCUSSION

Material Properties

The ability to prepare microcrystalline materials at high rates using this Gas Jet technique has previously been reported [2]. Fig. 1 displays Raman data for two films made using the Gas Jet technique and SiH_4 flows of 20 and 40 sccm. The sharp peaks near 530 and 560 cm^{-1} are Ar Laser lines and are not related to the measured film microstructure. The presence of only the broad peak in the spectra for the film made using the 40 sccm of silane demonstrates that the film is amorphous while the sharper peak near 520 cm^{-1} for the film made using the lower flow shows that there are microcrystals in the film. Fig. 2 demonstrates that as the material becomes μc-Si with the lower SiH_4 flow, the deposition rate decrease. However, when a SiH_4 flow between 15 and 25 sccm is used, the films are microcrystalline and deposition rates between 10 and 20 Å/s

are obtained. The degree of microcrystallinity can further be enhanced while maintaining high rates

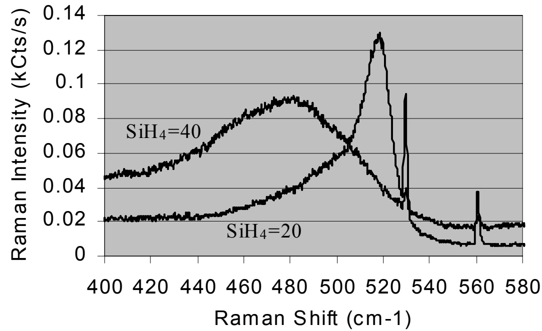


Fig. 1. Raman Spectra for films made using different SiH_4 flows.

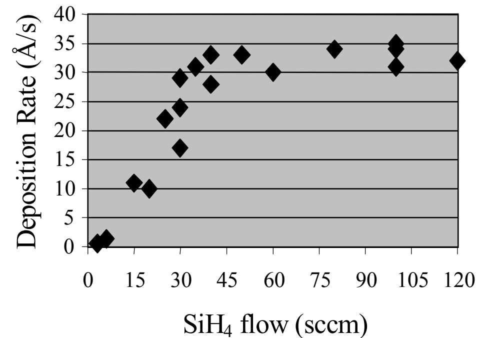


Fig. 2. Deposition rates for films made using different SiH_4 flows.

through proper selection of hydrogen dilution, gas flows and applied microwave power.

Glancing angle x-ray diffraction (XRD) measurements have been made on 1 μm thick μc-Si films prepared at rates of 10-20 Å/s. Samples for these measurements were prepared by depositing a 300 Å a-Si:H n-type layer on a crystalline Si substrate prior to depositing the 1 μm thick layer to be characterized. The thin a-Si:H layer minimizes the effect of the crystalline Si substrate on the microstructure of the 1 μm thick film. A spectra for one of these μc-Si films is compared with that for an amorphous film prepared at a higher silane flow in Fig. 3. Average microcrystal sizes of 80 and 120 Å were calculated from the 220 and 111 peaks, respectively.

In Fig. 4, SAXS data for films prepared at different silane flows are compared. As was done in the XRD measurements, a thin a-Si:H:P layer was deposited on the Al substrate used for the SAXS measurements prior to depositing the 1 μm thick films to be measured. The a-Si:H films prepared at SiH_4= 35 and 45 sccm have similar and relatively high SAXS signals as compared to those for a-Si:H films prepared by the conventional 1 Å/s, 13.56 MHz PECVD method [3] likely due to the fact that the films were prepared by a microwave technique and at high deposition rates of 30-40 Å/s. As the SiH_4 flow is decreased from 35 sccm and the films become microcrystalline, the amount of SAXS dramatically increases and further increases as the flow is reduced and the films have higher microcrystalline fractions. From modeling of the SAXS data, the average sizes of the scattering features have been determined to be 20-30 Å. Since XRD measurements have shown the microcrystal sizes to be 80-120 Å, the increased scattering with microcrystal formation is likely related to density fluctuations near the grain boundaries.

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 a-SiGe:H films which have columnar-like microstructures [3,4]. The films prepared using SiH_4 flows of 15 and 45 sccm were measured at a tilt angle of 35° and a comparison of the data taken with and without the tilt angle for the SiH_4=15 sccm film is shown in Fig. 5. For both samples, some decrease in the SAXS data was observed as the samples were tilted suggesting that some scatterers (voids or low density regions) are elongated with their long dimension preferentially oriented parallel to the growth direction. This phenomenon is typically associated with columnar growth. However, the amount of change with varying tilt angle is not nearly as great as what is

typically observed for the a-SiGe:H films [3,4] suggesting that a significant amount of the scattering centers are spherical in shape and/or randomly oriented. SEM photographs taken of

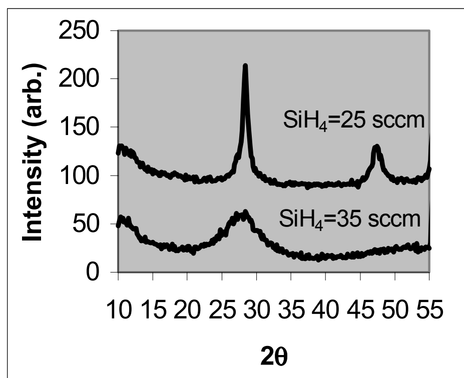


Fig. 3. X-ray Diffraction patterns for films prepared using different silane flows.

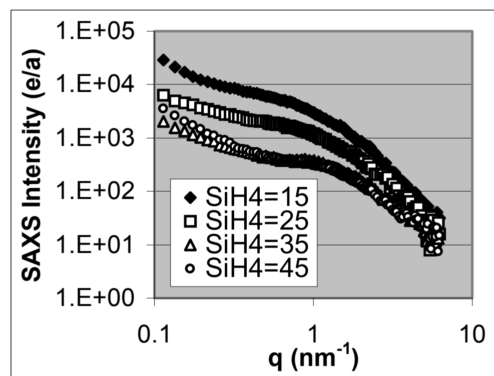


Fig. 4. SAXS data for films prepared using different silane flows.

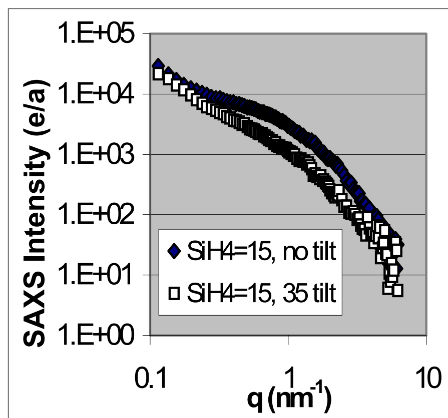
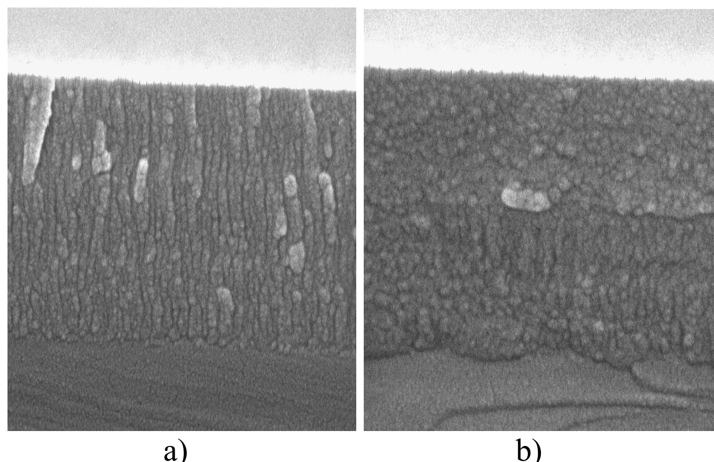


Fig. 5.Tilt angle dependence of SAXS.



a) b)

Fig. 6. SEM photographs of a μc-Si film cross section.

the cross section of the μc-Si films display regions with columnar-like growth (Fig. 6a) and other regions with a more randomly oriented growth (Fi. 6b). Thus, both the SAXS and SEM results suggest that microstructure of the μc-Si films is highly heterogeneous.

Cell Properties

Listed in Table I are the properties for representative μc-Si cells prior to and after 1000 h. of light soaking under one sun conditions at a fixed temperature of 50ºC. The average i-layer deposition rate for these cells was 16 Å/s. To demonstrate the potential use of the μc-Si cell as the red light absorbing component of multi-junction cell structure, the table lists the results of IV measurements using AM1.5 white light filtered with a 610 nm low band pass filter to simulate the absorption due to higher bandgap, blue-green light absorbing top layers. Under these measurement conditions, the μc-Si cells typically have V_{oc} values of 0.49-0.52 V, J_{sc} values between 8.5 and 9.5 mA/cm^2 and FF of 0.58-0.62. These data can be compared with those listed in the same table for a high quality a-SiGe:H cell typically used as a bottom cell for a triple-

junction a-Si:H/a-Si(Ge):H/a-SiGe:H solar cell. This cell was prepared using the standard PECVD technique and an i-layer deposition rate near 1 Å/s. From the data it is clear that the a-SiGe:H cells are presently superior, particularly in terms of pre-light soaked V_{oc} and FF. The smaller V_{oc} for the μc-Si cells is for the most part due to the smaller bandgap for the material. Some improvements in the V_{oc} for the μc-Si cells should come with optimization of the doped layer deposition conditions. The deposition conditions used for doped layers in these devices were optimized for amorphous Si based i-layers but have yet to be optimized for μc-Si i-layers. Presently, the J_{sc} values for the μc-Si cells are also smaller than those for the a-SiGe:H cells. Improvement of the J_{sc} should come through larger fractions of crystalline material in the i-layers and overall improved i-layer material quality.

Table I.
Data for μc-Si cells made by the Gas Jet technique.
IV data taken using AM1.5 light filtered with 610nm cutoff filter (red light).

Cell Type	Light Soak Time (h.)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s ($ohmcm^2$)	P_{max} (mW/cm^2)	% of Degr.
Gas Jet μc-Si cell 1	0	0.521	8.69	0.617	8.3	2.80	-
	1000	0.515	8.49	0.610	9.3	2.67	4.6
Gas Jet μc-Si cell 2	0	0.502	9.35	0.584	8.6	2.74	-
	1000	0.500	9.35	0.576	9.3	2.69	1.8
Gas Jet μc-Si cell 3	0	0.501	8.99	0.598	8.5	2.69	-
	1000	0.498	8.69	0.604	9.0	2.61	3.0
PECVD a-SiGe:H	0	0.615	10.5	0.595	14.1	3.84	-
	1000	0.595	10.3	0.522	24.4	3.18	17.2

These cells were light soaked along with the a-SiGe:H cell to directly compare the stability of the two types of cells. In order to test the feasibility of using these cells as bottom cells for the triple-junction structure, light soaking was completed using white light that was filtered using a low bandpass filter to simulate the light absorbed by the top and middle cells. As can be seen from the data in the table, the P_{max} values for the μc-Si devices degrade by less than 5%, values close to the measurement error. This low amount of degradation was also observed even when the μc-Si devices were light soaked with unfiltered white light. In comparison, the P_{max} value for the a-SiGe:H cell degrades by 17% under the filtered light conditions demonstrating the enhanced stability for the μc-Si cells. Comparing the stabilized efficiencies, the relative difference in the efficiencies for the two types of cells is less than 20%.

Under AM1.5 white light conditions, stable efficiencies of 7% have been achieved for the μc-Si cells made using the i-layer growth rates of 16 Å/s. An IV plot for such a device is shown in Fig. 7. Spectral response curves taken with and without an applied bias have shown that the current can be enhanced by nearly 1 mA/cm^2 by reverse biasing the cells by 1V. The enhancement of the quantum efficiency in the green and red portions of the spectrum demonstrates that the current for these cells is partially limited by carrier collection and not entirely by absorption.

μc-Si cells with red-light currents as high as 10.5 mA/cm^2 have been obtained in these studies as is shown in Fig. 8 where the quantum efficiency curve for such a device is compared with the

one for the PECVD a-SiGe:H cell. It is clear that the μc-Si cell absorbs a significant amount of red light in the 750-950 nm region of the spectrum.

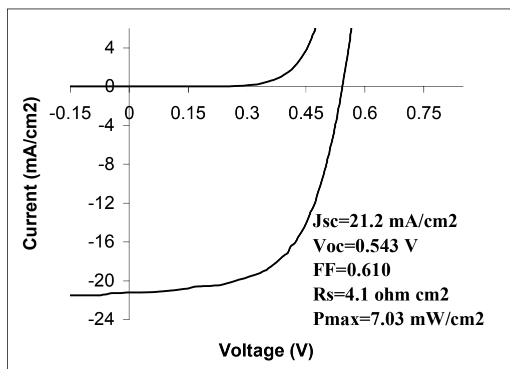


Fig. 7. IV data using AM1.5 white light.

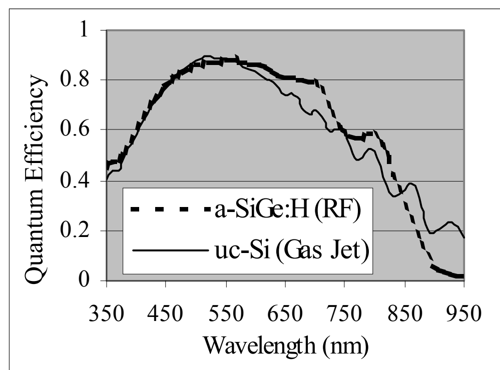


Fig. 8. Quantum Efficiency plots.

SUMMARY AND CONCLUSIONS

The 7.0% white light efficiencies for the cells compare favorably with the values obtained for μc-Si cells prepared at high rates using other deposition techniques. An effort to expand the VHF technique to deposition rates of 11 and 14 Å/s, yielded lower efficiencies of 5.2 and 3.6%, respectively [5]. The 7.0% efficiency is also larger than the 5-6.5% values obtained by Saito et. al. [6] using VHF deposition rates near 15 Å/s. Thus in terms of high growth rate methods, the Gas Jet technique is a promising technique for the fabrication of μc-Si cells. However, the efficiencies for the Gas Jet-produced cells do not yet match the 8.5% AM1.5 efficiency for the μc-Si cells made at 1 Å/s using the VHF method [1].

In looking towards improving the cell efficiencies, determining the effects of the presence of columnar-like microstructure could be important. The presence of this microstructure could be associated with high void densities at the grain boundaries and poorer cell performance. However, if the columns are entirely microcrystalline and contain a low number of defects, they may provide high mobility paths for the carriers to move to the doped layers with little impediment. Thus attempts will be made to alter the deposition conditions in order to vary the degree of columnar microstructure in the film and note its effect on the solar cell performance.

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