PREPARATION OF a-Si:H AND a-SiGe:H I-LAYERS FOR NIP SOLAR CELLS AT HIGH DEPOSITION RATES USING A VERY HIGH FREQUENCY TECHNIQUE

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ABSTRACT

The 70 MHz Plasma Enhance Chemical Vapor Deposition (PECVD) technique has been tested as a high deposition rate (10 Å/s) process for the fabrication of a-Si:H and a-SiGe:H alloy i-layers for high efficiency nip solar cells. As a prelude to multi-junction cell fabrication, the deposition conditions used to make single-junction a-Si:H and a-SiGe:H cells using this Very High Frequency (VHF) method have been varied to optimize the material quality and the cell efficiencies. It was found that the efficiencies and the light stability for a-Si:H single-junction cells can be made to remain relatively constant as the i-layer deposition rate is varied from 1 to 10 Å/s. Also these stable efficiencies are similar to those for cells made at low deposition rates (1 Å/s) using the standard 13.56 MHz PECVD technique. For the a-SiGe:H cells of the same i-layer thickness, use of the VHF technique leads to cells with higher currents and an ability to more easily current match triple-junction cells prepared at high deposition rates which should lead to higher multi-junction efficiencies. Thus, use of this VHF method in the production of large area a-Si:H based multi-junction solar modules will allow for higher i-layer deposition rates, higher manufacturing throughput and reduced module cost.

INTRODUCTION

The further advancement of the a-Si:H manufacturing technology has been hindered by the relatively low deposition rates (1-3 Å/s) required to make high quality i-layers for high efficiency multi-junction solar panels using the standard 13.56 MHz PECVD technique. These low deposition rate conditions impede machine throughput, limit machine hardware costs to relatively high values as well as restrict material utilization costs. There is a clear need for a deposition technique that will allow for the deposition of films at higher rates without the detrimental effects of powder and polyhydride formation in the plasma and poor film microstructure observed when high deposition rates are used with the 13.56 MHz PECVD technique.

Of the alternative high deposition techniques tested, the Very High Frequency (VHF) PECVD technique is presently one of the most promising. Chatham et. al.[1] have used VHF frequencies to prepare **pin** a-Si:H devices at i-layer deposition rates of 18 Å/s with respectable 9.7% initial efficiencies. More recently, Shah et. al.[2] have made **pin** a-Si:H cells with efficiencies above 9% at i-layer deposition rates of 5 Å/s. In both cases, it was found that the deposition rate of a-Si:H films could be increased to 10-15 Å/s without an observable deterioration in the film properties.

In order to incorporate a new high deposition rate technique into ECD's roll-to-roll manufacturing process[3], we have chosen to test the feasibility of using the VHF technique to prepare high efficiency a-Si:H and a-SiGe:H **nip** solar cells with the ultimate goal of preparing high efficiency large area multi-junction solar modules. The VHF technique is desirable because of the ability to apply the technique to ECD's present roll-to-roll process with relatively little hardware changes. Here, we discuss the results from our feasibility study for a-Si:H and a-SiGe:H small area cells prepared in R&D size deposition systems using high i-layer deposition rates.

Mat. Res. Soc. Symp. Proc. Vol. 507 © 1998 Materials Research Society

EXPERIMENT

The nip solar cell structures with stainless steel substrates were fabricated using a research scale, multi-chamber load locked deposition system. Both the doped layers and the a-Si:H buffer layers, grown between the VHF deposited a-SiGe:H i-layers and the 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 and a-SiGe:H i-layers, a fixed VHF frequency of 70 MHz was used. To improve the cell properties, several buffer layer and i-layer deposition conditions were altered including the substrate temperature, the hydrogen dilution and active gas flows, and the applied power.

After fabrication of the nip structure, the devices were completed by depositing Indium Tin Oxide (ITO) conductive layers and then Al collection grids. Both the ITO and Al layers were prepared using standard evaporation techniques. In some cases, Ag/ZnO back reflectors were deposited on the stainless steel substrates prior to nip fabrication in order to enhance the collected current and improve the overall efficiency. The Ag/ZnO back reflectors were prepared in a roll-to-roll manufacturing machine using a DC sputtering technique.

To characterize the cells, standard J-V and spectral response (quantum efficiency) measurements were made. For the a-Si:H cells, standard white AM1.5 light was used to obtain the J-V data. Since our goal is to use the a-SiGe:H cells as middle and bottom cells for triple-junction cells, the AM1.5 light for the J-V measurements of the a-SiGe:H cells was filtered using a 530 nm cutoff filter to simulate the absorption due to a top a-Si:H cell. To complete light soaking studies, the cells were subjected to 600-1000 hrs. of one sun light with the cell temperature fixed at 50°C. The i-layer thicknesses were determined using standard capacitance techniques.

RESULTS AND DISCUSSION

a-Si:H

An earlier publication outlines much of the work completed on a-Si:H cells prepared at high i-layer deposition rates by the VHF technique[4]. The general conclusion from these studies was that by using the VHF technique and careful selection of deposition conditions, the initial and stable cell efficiencies could be made to remain relatively constant with varying i-layer deposition rate up to 10 Å/s. Figure 1 demonstrates this result where the initial and stable efficiencies for a number of cells prepared under a variety of conditions are plotted as a function of deposition rate. All of the cells whose data is shown in the figure had J_{sc} near 10 mA/cm^2, i-layers which were roughly 2300 Å thick and had no current-enhancing Ag/ZnO back reflectors. The stable efficiencies were obtained by light soaking the cells for 1000 hrs. Below a deposition rate of 10 Å/s, the initial and stable cell efficiencies are relatively insensitive to the deposition rate with average values of 6.6 and 5.5%, respectively. The small amount of scatter (±5%) is related to experimental measurement procedures and variations in a few deposition parameters. Beyond 15 Å/s, the efficiencies are lower. Preparing the VHF a-Si:H cells on back reflector, we have achieved efficiencies greater than 10%[4].

To truly demonstrate the advantage of using the VHF technique to prepare a-Si:H i-layers at high rates, we compare in Table I data for cells whose i-layers were prepared using the same deposition hardware by either the standard 13.56 MHz frequency or the VHF 70 MHz frequency at different deposition rates. At low deposition rates of ≤ 1 Å/s, the cells prepared using the 13.56 MHz frequency had efficiencies between 6.5 and 6.6 % which degraded by about 15% after 1000 hrs. of light soaking. These efficiencies and the amounts of degradation are similar to what were found for the cells prepared at 10 Å/s by the VHF method. Thus, we can indeed use the VHF

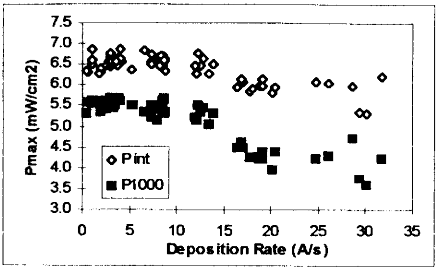

Figure 1. Cell efficiencies for VHF a-Si:H devices with Jsc = 10 ± 0.5 mA/cm^2.

Table I.
Data for a-Si:H nip cells whose i-layers were made using 13.56 or 70MHz frequencies.

Plasma Freq. (MHz)	Dep. Rate (Å/s)	Initial Pmax (mW/cm^2)	Light Degradation (%)
13.56	0.61	6.65	14.3
70	9.9	6.51	11.8
13.56	16.0	5.30	36.2
70	24.8	6.04	21.9

technique to prepare cells at a high rate of 10 Å/s with similar quality to those prepared at 13.56 MHz. Comparing cells made at even higher rates, the cells prepared with the 13.56 MHz frequency have significantly lower efficiencies than the cells produced at the low rates while the efficiencies for the cells made by the VHF method are not as low and are more stable. It is clear that for high deposition rates, the VHF is superior to the standard 13.56 MHz method for a-Si:H.

a-SiGe:H

Since the ratio of Si/Ge in the a-SiGe:H i-layers, and thus the V_{oc}, depends strongly on the deposition conditions used, we initially explored the a-SiGe:H cell properties over a wide range of parameter space using a Design of Experiments (DOE) approach. An overview of the DOE technique and how we typically use it to complete research studies was previously given[5]. Use of the DOE approach allowed us to map the tendencies of V_{oc} over a parameter space in a minimum amount of deposition runs and time. An effort was made to keep the i-layer deposition rates near 10 Å/s and the i-layer thickness near 1500 Å.

Figures 2 and 3 show the dependence of V_{oc} on various parameters. V_{oc} depends strongly on the temperature, the applied power and the SiH_4 flow. With increasing SiH_4 flow, V_{oc} increases due to the widening of the i-layer bandgap with the addition of more Si to the lattice. The increase in V_{oc} with increasing applied power is likely related to a combination of three effects,

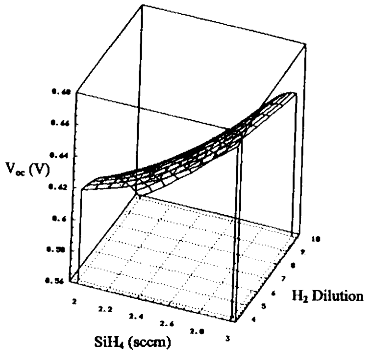

Figure 2. Dependence of V_{oc} on the SiH_4 flow and H_2 dilution.

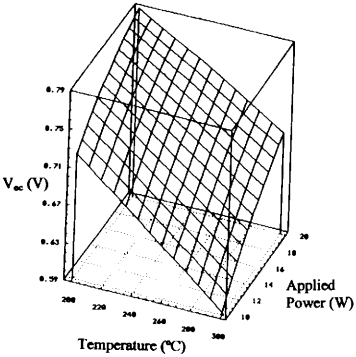

Figure 3. Dependence of V_{oc} on the substrate temperature and applied power.

1) an increased amount of hydrogen in the i-layers, 2) an increased amount of preferential etching of Ge from the film surface, and 3) an increased amount of silane decomposition. As the substrate temperature is increased, the hydrogen content decreases causing the observed decrease in V_{oc}.

With these DOE generated maps of V_{oc}, we selected the conditions which would give V_{oc}=0.75 V and focused our cell optimization in these regions of parameter space. Table II compares J-V data taken using AM1.5 white light for cells whose i-layers were made at deposition rates near 10 Å/s and different substrate temperatures while all other deposition conditions were fixed. While V_{oc} decreases with increasing substrate temperature, the increase in J_{sc} while maintaining a relatively constant FF outweigh this loss in V_{oc} and lead to higher efficiencies. To compensate for the loss in V_{oc}, we later decreased our GeH_4 flow slightly to obtain the desired V_{oc}=0.75 V. This led to a slight decrease in J_{sc} and an improvement in FF and cell efficiency. The improvement with increasing substrate temperature was not a surprise since high substrate temperatures have previously been found to be beneficial when either GeH_4 is added to the plasma[6] or the deposition rate is increased[7]. Table III compares J-V data taken using AM1.5 white light for cells made with and without grading of the Ge content through the i-layer. By altering the Ge profile, we were able to obtain significantly higher currents as well as improved FF.

Table II.
Data for a-SiGe:H cells made <u>without a back reflector</u> using deposition rates of 10 Å/s and different substrate temperatures.

Sub. Temp. (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	R_s (Ωcm^2)	P_{max} (mW/cm^2)
250	11.6	0.761	0.597	9.4	5.29
300	12.7	0.747	0.594	8.6	5.66
350	14.1	0.718	0.598	6.8	6.05

Table III.
Data for a-SiGe:H cells made <u>without a back reflector</u> using deposition rates of 10 Å/s and different Ge grading profiles.

Grad. Profile	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	R_s (Ωcm^2)	P_{max} (mW/cm^2)
No	16.5	0.759	0.573	7.2	7.15
Yes	18.1	0.739	0.595	6.3	7.96

In TableIV, we compare cells prepared with the same deposition equipment using the VHF technique with those made using the standard 13.56 MHz. To judge the potential use of the VHF technique as a method to prepare middle and/or bottom cells for triple-junction structures, we compare in the table J-V data obtained using 530 nm filtered AM1.5 light. The 530 nm filter eliminates light typically absorbed by the a-Si:H top cell. Comparing cells with similar i-layer thicknesses and V_{oc}, independent of the deposition rate, cells prepared using the VHF technique have larger J_{sc} than those prepared using the standard technique. The cause of the higher currents is not understood but it could be related to a combination of an increased incorporation of Ge into the film which would explain the higher J_{sc} as well as an improvement in the film quality, which would explain why the VHF cells do not have lower V_{oc} values because of the additional Ge.

The higher currents for the VHF cells will have a significant effect on the triple-junction cell efficiencies. To obtain high stable efficiencies, one matches the currents in each of the three components cells such that the middle and bottom cells have more current than the top a-Si:H cell. To obtain the correct currents for the middle and bottom cells, the Ge content and/or the i-layer thickness are varied. Since the cells prepared by the VHF method have higher currents, less Ge and/or thinner layers are required to obtain the desired currents. With lower Ge contents, higher FF and higher V_{oc} values will be obtained for the triple-junction cells. Thinner i-layers will lead to higher FF. Thus, use of the VHF method to prepare the a-SiGe:H layers will lead to higher efficiencies for the triple-junction cells. This is particularly important when one uses higher a-SiGe:H i-layer deposition rates. As can be seen from the data in TableIV, as the deposition rate

TableIV.

Data for a-SiGe:H cells prepared at different deposition rates using a 13.56 or 70 MHz frequency.

Frequency (MHz)	Deposition Rate (Å/s)	i-layer thickness (Å)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	R_s (Ωcm^2)	P_{max} (mW/cm^2)
13.56	0.79	1790	7.66	0.765	0.570	13.3	3.34
13.56	1.2	1490	6.66	0.770	0.605	17.8	3.10
70	2.0	1460	7.34	0.771	0.618	15.6	3.50
13.56	5.7	1480	5.54	0.749	0.597	14.3	2.48
70	6.2	1540	6.51	0.753	0.590	10.9	2.89
13.56	9.9	1350	5.30	0.757	0.600	13.6	2.41
70	9.9	1490	6.28	0.760	0.590	14.9	2.82

increases, the J_{sc} for cells with similar i-layer thicknesses decreases significantly, independent of the plasma frequency used. Thus at higher deposition rates, the addition of more Ge or thicker i-layers are needed to current match the triple-junction cells. For the cells made using the standard frequencies where the currents are extremely low, such a large amount of Ge or such large thicknesses are required that a significant drop in the triple-junction cell efficiency is observed. Again, in using the VHF technique, less Ge and/or thinner layers will be required and thus higher efficiencies should be obtained.

For the a-SiGe:H cells made with Ag/ZnO back reflectors at i-layer deposition rates of 10 Å/s, our best efficiency obtained to date is just over 9.0%. The J-V curve for such a device is shown in Figure 4 and the spectral response trace for the device is shown Figure 5.

A number of cells whose i-layers were made at 10 Å/s using the VHF method have been light soaked for 600 hrs. along with a-SiGe:H cells made at 1 Å/s. The VHF cells were not made under our optimum conditions which have just recently been obtained. All of the cells had i-layer thicknesses between 1700 and 1900 Å. Both types of cells degraded by a similar amount suggesting that the stability of the cells deposited at 10 Å/s is reasonably good. However, a more comprehensive light soaking study using our optimum cells made at 10 Å/s using VHF as well as with cells made at 1 and 10 Å/s using the standard 13.56 MHz technique must be completed before a true assessment of the light stability of the high deposition rate cells can be made.

In terms of determining the cause for the beneficial effects of increased frequency, the VHF technique may be desirable for high growth rate processes due to an increased amount of low

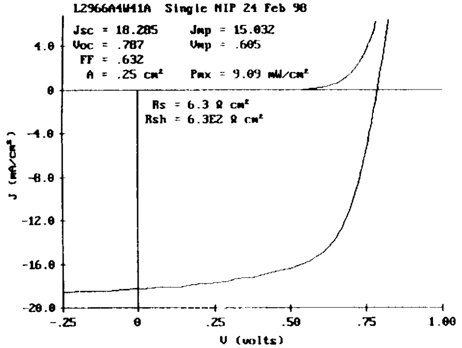

Figure 4. J-V plot for a-SiGe:H cell prepared at 10 Å /s.

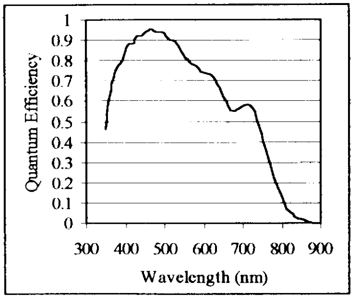

Figure 5. Quantum efficiency plot for cell whose J-V data is shown in Figure 4.

energy ion bombardment, as has been suggested previously[8]. With the use of higher frequencies, it is known that average energy of the ions striking the growing surface is lower while the flux of ions is higher[8]. It has been argued that while high energy ion bombardment leads to sputtering effects and the creation of undesirable defects, low energy ions increase the surface mobility of adatoms on the growing surface and also eliminate unfavorably placed species which would eventually lead to the formation of low density material.

Assuming that low energy ion bombardment is a key to improving the high rate process, we plan on further altering the low energy ion bombardment through variation of the frequency and the substrate bias in an attempt to improve the a-Si:H as well as the a-SiGe:H materials.

CONCLUSIONS

When using deposition rates near 10 Å/s, there is a clear advantage to using the VHF technique instead of the standard 13.56 MHz technique. For the a-Si:H cells, higher stable efficiencies are obtained at this deposition rate due to the fact that, with proper optimization of deposition conditions, one can obtain similar solar cell efficiencies for cells made at 1 and 10 Å/s. While more complete light soaking studies need to be completed before an overall conclusion can be made concerning the a-SiGe:H alloy cells, initial results show that, for cells with similar i-layer thicknesses and V_{oc}, J_{sc} values are higher for cells prepared using the VHF technique than for those prepared using the standard 13.56 MHz frequency. These higher currents become important at high deposition rates where it becomes difficult to obtain the currents needed to properly current match the triple-junction structures to obtain high efficiencies. Thus, there is likely a benefit in using the VHF technique to prepare all i-layers made at high rates for triple-junction structures.

ACKNOWLEDGEMENTS

We would like to thank Dr. H. Fritzsche and Mr. S. R. Ovshinsky for important discussions which helped further advance this work. We would also like to acknowledge B. Viers for her efforts in completing ITO and Al depositions. The work was funded by NREL under the Thin Film Partnership contracts ZAN-4-13318-11 and ZAK-8-17619-18.

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