

a-Si:H-based Triple-Junction Cells Prepared at i-layer Deposition Rates of 10 Å/s using a 70 MHz PECVD Technique

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ABSTRACT

Using a 70 MHz VHF PECVD technique to prepare all of the i-layers at deposition rates near 10 Å/s, a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells have been fabricated and initial active area AM1.5 efficiencies of 11% (total area efficiencies of 10-10.3%) have been achieved. After 700 hrs. of light soaking of one sun light soaking, the cell efficiencies degrade to 9.6% with a percentage of degradation of 10-14%, a percentage typical of what is obtained for high efficiency triple-junction cells prepared using i-layer deposition rates near 1 Å/s. A major challenge toward further improving the efficiencies is the fabrication of a-SiGe:H i-layers at 10 Å/s with the quality of those made using the standard 13.56 MHz, 1 Å/s method. Deposition conditions that lead to less polyhydride formation during a-SiGe:H growth would likely lead to improved performance for the triple-junction cells.

INTRODUCTION

The production costs of amorphous silicon (a-Si:H) photovoltaic technology is presently limited by a few factors including the low deposition rates (1-3 Å/s) required to make high quality i-layers for high efficiency a-Si:H multi-junction devices. The lower rates lead to limited machine throughput as well as poor gas utilization and thus high production gas costs. Extensive attempts to increase these rates, in particular for the i-layer growth, using the standard PECVD process with a 13.56 MHz rf frequency signal has led to enhanced powder and polyhydride formation in the plasma and poorer stable cell efficiencies. At present, the outlook for achieving higher deposition rates calls for the development of an alternative thin film deposition technique.

Of the alternative high deposition rate techniques tested, the Very High Frequency (VHF) PECVD technique is presently one of the most promising. Several research groups [1-4] have reported higher efficiencies for a-Si:H cells made using frequencies of 70-100 MHz at i-layer deposition rates between 5 and 10 Å/s than for those prepared at the same rates using the 13.56 MHz deposition technique. Also, Chatham et. al. [1] and Shah et. al. [2] 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 [5],

the feasibility of using the VHF technique to prepare small area high efficiency a-Si:H/a-SiGe:H/a-SiGe:H triple-junction solar cells is presently being studied with the ultimate goal of preparing high efficiency large area multi-junction solar modules. The VHF technique is particularly desirable because of the ability to apply the technique to ECD's existing roll-to-roll process with relatively few hardware changes. Here, the recent progress in preparing small area (0.265 cm²) cells with R&D size deposition systems using high i-layer deposition rates with the VHF technique are reported. The focus of these studies has been on preparing high performance a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells with i-layer deposition rates near 10 Å/s in order to achieve an order of magnitude increase in the deposition rate over the state-of-the-art cells. To achieve this ultimate goal, a-Si:H and a-SiGe:H single-junction component cells have also been fabricated separately in order to optimize the i-layer deposition conditions.

EXPERIMENTAL

The a-Si:H/a-SiGe:H/a-SiGe:H triple-junction solar cell structures were fabricated using a research scale, multi-chamber load locked deposition system. Stainless steel substrates coated with current enhancing Ag/ZnO back reflectors were used as the substrates for preparation of the semiconductor structures. Both the thin doped layers and the thin a-Si:H buffer layers, grown between the VHF deposited a-SiGe:H i-layers and the doped layers, were prepared using the conventional 13.56 MHz PECVD process since these thin layers are not rate limiting in a production process. 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, buffer layer and i-layer deposition conditions were altered including substrate temperature, hydrogen dilution, active gas flows, chamber pressure and applied power. After fabrication of the triple-junction structure, the devices were completed by depositing Indium Tin Oxide (ITO) conductive layers and then Aluminum collection grids. Both the ITO and Al layers were prepared using standard evaporation techniques.

To characterize the cells, standard IV and spectral response (quantum efficiency) measurements were made. For optimization of the a-Si:H cells, standard white AM1.5 light was used to obtain the IV data. For optimization of the a-SiGe:H cells for the green-red light absorbing middle

and the red light absorbing bottom structures, the AM1.5 light for the IV measurements was filtered using a 530 nm cutoff filter to simulate the absorption due to a top a-Si:H cell for the middle cells and a 630 nm cutoff filter for the bottom cells. During optimization of the component cells, top and middle single-junction cells were fabricated without Ag/ZnO back reflectors while the bottom nip cells were. This was done because in the triple-junction structure, the bottom cell reaps almost all of the benefit of the back reflector layers. 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 capacitance techniques.

RESULTS

Using the VHF technique to prepare all of the i-layers at deposition rates near 10 Å/s, several a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells with initial active area AM1.5 efficiencies of 11% and initial total area efficiencies of 10-10.3% have been fabricated. Figure 1 displays an IV curve for such a cell. Also, representative active area cell properties are shown in Table I. After 700 hrs. of light soaking, the active area cell efficiencies degrade to values near 9.5% with a 10-14% degradation from the initial value. This amount of degradation is typical of what is obtained for high efficiency triple-junction cells prepared using i-layer deposition rates near 1 Å/s.

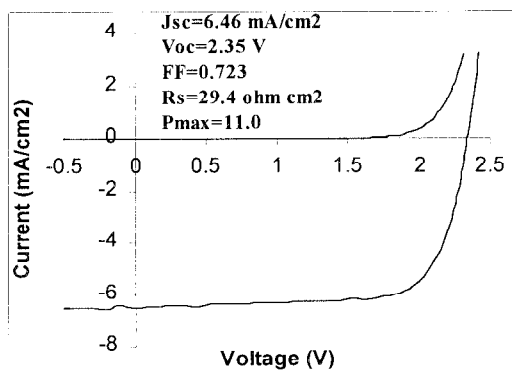


Figure 1. IV data for triple-junction cell made using VHF technique and i-layer deposition rates near 10 Å/s.

Table I. Representative active area properties for triple-junction cells.

Light Soak Time (hrs.)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	P _{max} (mW/cm ²)	% of Degr. with Light Soaking
0	2.35	6.46	0.723	11.0	-
700	2.25	6.45	0.661	9.59	12.8

The fact that stable efficiencies of 9.5% are obtainable using 10 Å/s i-layer deposition rates is encouraging and demonstrates that the VHF technique is desirable over the standard 13.56 MHz technique for high speed production of a-Si:H based modules. Although this

performance of VHF triple cell is approximately the same as the performance of rf triple cells produced with i-layer deposition rates of 1 Å/s with the same deposition system, we recognize that this performance does not match the 13% active area stable efficiency record obtained for cells made using the 1 Å/s rate in R&D[6]. In looking towards improving the cells made using the high rates, the short circuit currents are significantly lower for the cells prepared at the high rates as compared with those for the cells prepared at the low rates. Considering the results of measurements of single-junction a-Si:H and a-SiGe:H cells prepared using the high rate technique, it is apparent that the small currents for the triple-junction cells are related to small currents obtained for the a-SiGe:H bottom cells.

Table II displays cell data for a-Si:H based cells with similar i-layer thicknesses (1500 Å) prepared by the VHF technique at different deposition rates. These cells were made without current enhancing Ag/ZnO back reflectors and the data listed in the table was obtained prior to light soaking. The amount of degradation in the cell efficiency after 700 hrs. of light soaking is also listed in the table. Little change in the cell properties is observed with increasing deposition rate for the cells without back reflectors prepared using the VHF technique. Also, the cell properties are similar to those for a cell of similar i-layer thickness prepared using the conventional 1 Å/s, 13.56 MHz process. In contrast, fill factors for a-Si:H cells whose i-layers are prepared using the standard 13.56 MHz technique degrade almost linearly with increasing i-layer deposition rate as is shown in Figure 2. Thus, the triple-junction cells are not mainly limited by the a-Si:H top cell performance.

Table II. Cell properties for a-Si:H cells prepared without back reflectors.

Freq. (MHz)	Dep. Rate (Å/s)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	P _{max} (mW/cm ²)	% of Degr with light soak
70	2.1	0.946	9.38	0.728	6.46	-
70	6.1	0.934	9.51	0.726	6.45	13.4
70	10.9	0.939	9.63	0.733	6.63	12.1
13.56	0.9	0.930	9.52	0.732	6.47	12.5

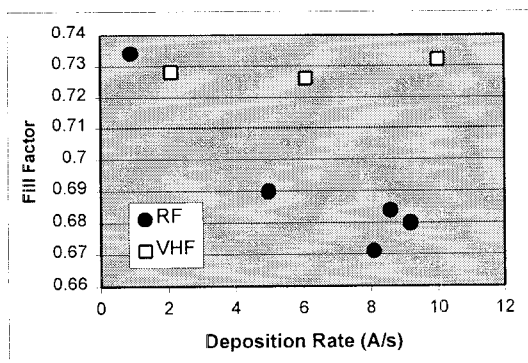


Figure 2. Fill Factor vs. deposition rate for a-Si:H cells prepared using the RF and VHF techniques.

In contrast to the a-Si:H cells, the a-SiGe:H cells prepared at the higher deposition rates are significantly inferior to the cells made at the lower rates. In Table III, data for a-SiGe:H cells whose i-layers were prepared using the VHF technique and the 10 Å/s i-layer deposition rate are compared with cells prepared using the standard 13.56 MHz, 1 Å/s conditions. The data was obtained using 630 nm filtered light in order to simulate absorption due to a top a-Si:H and middle a-SiGe:H cells. While the cells made using the VHF technique have respectable efficiencies that are larger than those obtained for cells made using the same 10 Å/s rate and the 13.56 MHz frequency, the efficiencies obtained thus far are lower than those obtained using the standard 13.56 MHz, 1 Å/s conditions. Comparing cells with similar V_{oc} , those made using the VHF technique have lower efficiencies due in most part to lower J_{sc} values. Increasing the currents further by using higher substrate temperatures and/or higher Ge contents leads to a loss in V_{oc} due to lower bandgaps and lower FF due to poorer material quality, as is shown in the third row of the table.

Table III. Properties for a-SiGe:H cells with similar i-layer thicknesses.

Freq. (MHz)	Dep. Rate (Å/s)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	P_{max} (mW/cm ²)
70	10	0.631	8.31	0.606	3.18
70	10	0.627	8.46	0.601	3.19
70	10	0.588	8.84	0.544	2.83
13.56	0.9	0.628	9.09	0.615	3.52
13.56	0.9	0.611	9.21	0.611	3.50

Considering the findings from a number of film property studies of a-SiGe:H materials made using the conventional PECVD method, the poorer performance for the VHF, high rate a-SiGe:H cells is likely related to low surface mobilities for the Ge atoms. The low surface mobilities have previously been identified as the cause of the void-rich microstructures detected in a-SiGe:H alloys[7]. Use of higher rates further minimizes the area of motion of adatoms on the growing surface leading to an increase probability of void formation. In terms of increasing the surface mobility or eliminating the void-rich microstructure, the suggested possible solutions include the use of increased ion bombardment of the growing film surface and/or the use of etchant gases. It has been suggested that ion bombardment can increase the atom surface mobilities and the etchant gases would remove weakly bound materials that lead to void formation leaving only the high density, good quality material.

In order to test the effect of ion bombardment and etching, the use of plasma treatments after 30-50 Å of a-SiGe:H deposition at 10 Å/s has been studied. It is thought that a plasma treatment might remove low density, weakly bound material from the growing surface leaving only high quality, high density material. In using these treatments, the idea is to see if the material deposited by the VHF method at high rates can be altered by a treatment to achieve the desired cell performance. In the study, the conditions used for the deposition periods for all

of the cells were fixed at the same values. Thus, the cells had no Ge grading and thus the efficiencies were slightly below the optimum values. The deposits were made such that the i-layer thicknesses were similar for all of the cells in the study.

Table IV summarizes the data for cells prepared using the different plasma treatments. Again, the data was obtained using 630 nm filtered light in order to simulate absorption due to a top a-Si:H cell and a middle a-SiGe:H cell. The data in the second row of the table is for a control cell whose i-layer deposition was uninterrupted, i.e. no plasma treatments were done. Again, the efficiency for this cell does not meet the best efficiencies obtained thus far (3.2%) due to the fact that Ge content is not graded. A hydrogen plasma treatment was tested to observe the effects of a moderate etching of the film surface. Fixing the deposit period to 5s, use of a 10s hydrogen plasma leads to a small decrease in cell efficiency due to a lower fill factor while increasing the plasma treatment time to 30s does not lead to a significant change in the cell properties. However, these decreases were noted even when the plasma was just turned off during the treatment time (see the data in the sixth row of the table). Thus, the decreases are not an artifact of the hydrogen plasma but are related to some other artifact such as heating. Shortening the deposition time to 3s with a 10s plasma treatment time leads to even lower FF. Thus, use of a hydrogen plasma treatment does not lead to improvements in the cell efficiencies.

Table IV. Properties for a-SiGe:H cells made using different plasma treatments.

Plasma	Dep. time (s)	Treat. Time (s)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	P_{max} (mW/cm ²)
None	All	-	0.634	7.81	0.607	3.01
H ₂	5	10	0.642	7.86	0.585	2.95
H ₂	5	30	0.639	7.66	0.587	2.87
H ₂	3	10	0.643	7.56	0.557	2.71
No Plasma	5	10	0.639	7.80	0.585	2.92
Ar	5	10	0.538	5.77	0.406	1.30
Ar	5	30	0.473	4.59	0.328	0.74
He	5	10	0.652	6.90	0.567	2.55
He	5	30	0.525	4.11	0.321	0.69

In contrast to the hydrogen plasma treatments, use of argon and helium as the treatment gases leads to large changes in the cell data. All of the cell properties (V_{oc} , J_{sc} , FF) are significantly lower when Ar and He plasma treatments are used and their values degrade further with longer treatments. These poorer properties are likely related to the increased bombardment of the growing surface and are consistent with our previous findings with Ar and He dilution of the plasma. It is clear that ion bombardment leads to deterioration in the cell performance. This deterioration may be related to the formation of voids, dangling bonds and/or microcrystals.

From these results, it is clear that our attempts to alter the a-SiGe:H material prepared at 10 Å/s has yet to lead to improved cell performance. Moderate etching or ion bombarding of the surface in order to modify the film

microstructure does not improve the cell efficiencies. While a heavier etching of the film surface using fluorine-based gases has yet to be tested, it is unlikely that any treatment of the high rate materials will lead to an improvement in the cell performance. It should be noted that the use of Ar and He dilution of the plasma during a-SiGe:H growth has also been tested in these studies. In both cases, the added dilution led to a deterioration in the cell performance.

DISCUSSION AND CONCLUSIONS

The achievement of stable efficiencies of 9.5% for triple-junction cells whose i-layers are prepared at rates of 10 Å/s is encouraging and demonstrates that the VHF technique is desirable over the standard 13.56 MHz technique in terms of a high rate deposition process. However, improvements to these efficiency values are needed before the high rate process can be considered for large scale production. It is clear from these studies that in order to achieve the required improvements in cell performance, the quality of a-SiGe:H materials prepared at the high rates must be improved.

The ability to obtain high red-light cell efficiencies for a-SiGe:H cells is a difficult task even when low deposition rates and the standard 13.56 MHz PECVD technique is used. Raising the deposition rate leads to even more difficulties in maintaining high cell efficiencies. These difficulties include; 1) the ability to achieve high surface mobilities for the adatoms while the time for diffusion is less due to the high rate of adatom addition to the growing film surface, 2) less time for etchant gases (H_2) to remove undesired weakly bound material, and 3) the need for high powers or lower dilution levels to achieve high deposition rates which lead to enhanced particle/powder formation in the plasma. While the use of the higher frequencies allows for the ability to overcome these obstacles in the case of a-Si:H, the benefits are not large enough to achieve the desired performance for the a-SiGe:H alloys.

In the case of rf plasmas, it has been suggested that the addition of GeH_4 to a SiH_4 plasma leads to lower average adatom surface mobilities and a greater chance of powder formation. Both the low mobilities and powder formation led to void-rich, low density films with poor electrical performance. Attempts to improve the surface mobility or to change the film microstructure through increases in the substrate temperature, hydrogen dilution, ion bombardment and etching of the growth film surface have led to small improvements, no changes or detrimental effects. While a higher degree of etching through the use of different gases may lead to more significant improvements, it does not seem likely that a modification of the surface growth kinetics without a change in the plasma chemistry will lead to the desired device properties. A change in the plasma chemistry will likely be required to prepare high quality a-SiGe:H alloys at high deposition rates.

There is strong evidence that the improvements in the a-Si:H alloys with increased plasma frequency are related to changes in that plasma chemistry. Takagi et. al. [8] have found that at higher frequencies, there is less trisilane in the $SiH_4 + H_2$ plasma and have correlated this

decrease in multi-hydride species with higher fill factors. The smaller amount of multihydride species is consistent with the earlier discovery by Shah et. al. [2] of less powder formation in the higher frequency hydrogen diluted silane plasmas in high growth rate regime. While few studies of a-SiGe:H plasmas generated using VHF have been made, the fact that a-SiGe:H cells with even moderate efficiencies can be prepared at the 10 Å/s using the VHF technique is probably related to lower amounts of multihydride and powder formation with the higher frequency. Use of the 13.56 MHz frequency and the 10 Å/s rate leads to high rates of powder production and a-SiGe:H cells with very poor fill factors. In addition to the improvements with increased plasma frequency, further changes in the plasma chemistry that minimize polyhydride and powder formation further will likely be required to achieve the desired a-SiGe:H device performance and high i-layer growth rates.

In summary, a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells have been fabricated with initial active area AM1.5 efficiencies of 11% and initial total area efficiencies of 10-10.3%. After 700 hrs. of light soaking, the cell efficiencies degrade to 9.0% with a percentage of degradation from the initial value of 10-14%. The efficiencies are presently limited by the performance of the a-SiGe:H cells whose currents are lower than those obtained for cells of similar Ge contents prepared using the standard 13.56 MHz, 1 Å/s conditions. In addition to the improvements with increased plasma frequency, changes in the plasma chemistry that further limit polyhydride and powder formation will likely be required to achieve the desired a-SiGe:H and triple-junction cell performance.

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