IMPROVED μc-Si p-LAYER AND a-Si i-LAYER MATERIALS USING VHF PLASMA DEPOSITION

X. Deng, S. J. Jones, T. Liu, M. Izu and S. R. Ovshinsky
Energy Conversion Devices, Inc., 1675 West Maple Road, Troy, Michigan 48084

ABSTRACT

Microcrystalline Si p-layers have been widely used in a-Si solar cell technology to achieve high efficiency. To further improve the solar cell performance, we have studied the deposition of high quality μc-Si p-layer material using a modified very high frequency (VHF) plasma enhanced CVD process and consequently have improved the solar cell current. This improvement was primarily in the blue response which leads to a 6-10% improvement in the overall solar cell efficiency. In addition, we have explored the deposition of a-Si at high rates using VHF plasma, and compared these VHF i-layers with RF plasma deposited i-layers. With improved deposition conditions, VHF intrinsic layers deposited at a rate up to 15 Å/s show similar device performance and light stability to VHF and RF i-layers deposited at low rates, and show higher stability than RF i-layers deposited at high rates in the same deposition system. A 10.9% single-junction solar cell was fabricated using a VHF deposited i-layer.

INTRODUCTION

Microcrystalline silicon (μc-Si) p-layer materials have been widely used in amorphous silicon (a-Si) solar cell research and manufacturing to achieve record high solar cell efficiencies [1,2], in particular in the recent 14.6% initial and 13% stable efficiencies for small area a-Si solar cells [3]. However, using conventional RF (13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) process, the window in deposition parameter space to produce a high performance p-layer is relatively narrow so that high quality p materials can not be easily reproduced at different laboratories or in different manufacturing machines. To address this issue, we have investigated the deposition of μc-Si p materials using a 70 MHz Very High Frequency (VHF) PECVD process with the objectives of 1) further enhancing the performance of a-Si solar cells by improving their p-layers, and 2) establishing a wider process window for the deposition of high quality p-materials.

The high rate deposition of a-Si using VHF has been studied by many groups [4,5]. However, most of these studies were focused on the thin film properties of the VHF deposited materials. Few studies were carried out using solar cell devices to characterize the VHF material and those that were used the glass superstrate structure [5]. In this study, we have investigated the application of VHF plasma deposited a-Si material in substrate type solar cells deposited on stainless steel (SS) substrates. It is generally found that the deposition rate of a-Si on a conductive substrate such as SS is often sizably higher than that on glass under otherwise identical deposition conditions. Therefore, the study in a substrate type solar cell structure is important for the high rate a-Si material deposited using a VHF plasma.

EXPERIMENT

We deposited μc-Si p-layer and a-Si i-layer materials using a VHF plasma enhanced CVD process in a research scale multi-chamber load-locked solar cell deposition system (LL2). The substrate is 5 mill thick stainless steel. For the p-layer study, the substrates that we typically used were semi-finished devices SS/a-Si-n^+/a-Si-i-layer in which the doped n-layer and the undoped a-Si intrinsic layer were deposited previously in a large area roll-to-roll process [2]. Such SS/n-i substrates have high uniformity in terms of film thickness and quality.

After the semiconductor deposition, ITO/Ag top contacts were deposited using evaporative processes to complete the solar cell structures. The solar cells were characterized using standard J-V and spectral response (quantum efficiency) measurements. Particular attention was paid to the blue light section of the spectral response curves for the p-layer study since the response in this section depends strongly on the transmission properties of the p-layer.

RESULTS AND DISCUSSIONS

μc-Si p-layer using a modified VHF plasma deposition

To further improve the performance of p-layers in solar cells, we have investigated the application of a modified VHF plasma process for the μc-Si p-layer deposition [6]. In Table 1, we compare the results of solar cells with p-layers deposited using this modified VHF process with those deposited in the same deposition system by conventional RF (13.56 MHz) and conventional VHF (70 MHz) plasma CVD processes. Three types of devices are listed in the table corresponding to the use of different plasma frequencies for the p-layer deposition. Each type of device is individually optimized for optimum performance. Besides the use of the same substrates, the ITO layers for these three devices were made in the same

0-7803-3767-0/97/$10.00 © 1997 IEEE

Table 1 Results of solar cells whose p-layers were deposited using different processes: conventional RF, conventional VHF and a modified VHF process.

Sample No.	p-layer Run#	p process	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s (Ω•cm^2)	P_{max} (mW/cm^2)	J_{sc} from QE (mA/cm^2)	QE@400nm (%)
1	L2523	Modified VHF	0.959	10.39	0.664	11.5	6.62	10.71	0.655
2	L2525	Conventional RF	0.948	9.82	0.63	14.8	5.86	10.09	0.591
3	L2526	Conventional VHF	0.933	8.78	0.651	12.2	5.33	10.04	0.56

deposition run (ITO4408) to ensure consistency. The data listed in Table 1 is the average of data for many small area devices on the same sample. J-V curves for the best solar cell device in each sample are show in Figure 1. Note that the J-V performance is largely determined by the SS/n-i substrates. However, the differences in the J-V curves are due to the different p-layers.

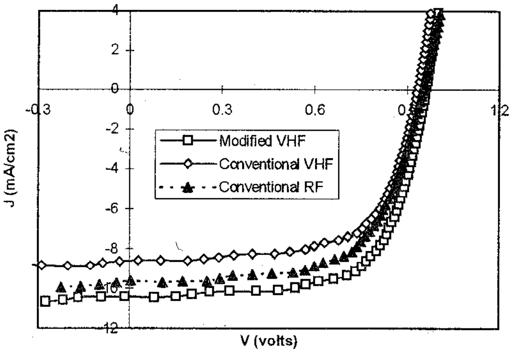

Fig. 1. J-V curved for solar cells having p-layer deposited using a modified VHF process, a conventional RF process, and a conventional VHF process.

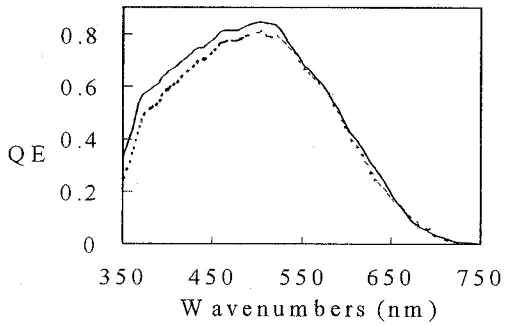

Fig. 2. Quantum efficiency curves for an a-Si n-i-p devices with p-layer deposited using the modified VHF PECVD (Sample L2523, solid curve) and conventional RF PECVD (Sample L2525, dashed curve).

As we can see from these data, the device with p-layer deposited using the modified VHF process (Sample L2523) shows the highest performance. The V_{oc} and FF are the highest among the group. The largest amount of improvement is in J_{sc}, about a 6% increase in J_{sc} compared with the value for the conventional RF sample (L2525). Figures 2 shows the quantum efficiency curves for the modified VHF device (L2523) and the conventional RF device (L2525). The improvement in J_{sc} in the modified VHF device is mainly due to the 11% increase in the blue response. The lower absorption loss in the blue indicates that a modified-VHF p-layer is more transparent most likely due to enhanced microcrystallinity.

The improved microcrystallinity using the VHF deposition process is also supported by the RHEED measurement. Figure 3 shows a RHEED pattern of a device with the VHF p-layer on the top. The sharp lines in the 220 and 311 rings and the dark background in between these rings indicate that the VHF p-layer is a microcrystalline material with a high degree of microcrystallinity.

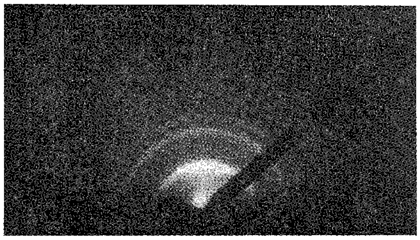

Fig. 3. RHEED pattern of a device with VHF p-layer, showing a high volume fraction of microcrystalline phase in the p-layer.

High-rate deposition of a-Si for solar cells on SS substrates using a VHF plasma

We investigated the deposition of a-Si for SS substrate type solar cells using a VHF plasma under various deposition conditions. Table 2 shows the device performance for five groups of solar cells having the i-layer deposited at different VHF powers, silane flows, and/or pressures, therefore, different deposition rates. The deposition times for the i-layer were adjusted so that the thickness is around 2500 Å. All of these solar cells were deposited on bare SS substrate without the use of back-reflectors. The data in Table 2 is an average for many solar cells on the same sample piece. The hydrogen flow in the gas mixture is the same for all these samples. Let us first look at samples in group 1 (Samples 4 to 11) for which the deposition pressure was 0.5 Torr. As we see from the table, with increasing power from 2 W up to 15 W, the deposition rate increases from 1.4 Å/s up to 5.3 Å/s as expected. However, the device performance as indicated by V_{oc}, J_{sc} and FF and maximum power output P_{max} remain approximately the same. This result is important since higher rate deposition of a-Si with the same device quality would result in a significant reduction

Table 2 Intrinsic layer growth conditions and the performance of solar cells with VHF i-layers.

Sample No.	Group No.	Ref. No.	SiH4 (sccm)	H2 (sccm)	Power (W)	P (Torr)	Dep. time (min)	d (A)	Dep. rate (A/s)	Voc (V)	Jsc (mA/cm2)	FF	Pmax (mW/cm2)	Stability 1000hrs (%)
Sample 4	1	L2636	5	Std	2	0.5	30	2530	1.4	0.938	10.14	0.67	6.37	
Sample 5	1	L2638	5	Std	4	0.5	15	2600	2.89	0.956	9.97	0.676	6.44	
Sample 6	1	L2697	5	Std	4	0.5	13.5	2360	2.9	0.95	10.4	0.692	6.88	86.7
Sample 7	1	L2652	5	Std	6	0.5	11.5	2540	3.68	0.963	9.97	0.695	6.67	
Sample 8	1	L2699	5	Std	6	0.5	10	2550	4.3	0.961	10.27	0.686	6.77	86.2
Sample 9	1	L2644	5	Std	10	0.5	8.17	2400	5	0.966	9.55	0.68	6.28	
Sample 10	1	L2653	5	Std	15	0.5	8	2530	5.26	0.957	10.02	0.677	6.49	
Sample 11	1	L2654	5	Std	30	0.5	5.83	2340	6.67	0.973	8.44	0.64	5.25	
Sample 12	2	L2701	5	Std	4	1	21	2190	1.74	0.926	9.65	0.687	6.14	83.8
Sample 13	2	L2711	5	Std	6	1	14.5	2520	2.9	0.941	11.27	0.673	7.14	78.9
Sample 14	2	L2707	5	Std	10	1	5.83	2940	8.4	0.957	10.04	0.679	6.52	81.8
Sample 15	2	L2706	5	Std	15	1	3.83	2340	10.2	0.956	8.46	0.69	5.58	85.5
Sample 16	2	L2656	5	Std	15	1	4.5	2670	9.9	0.977	9.58	0.696	6.51	90
Sample 17	2	L2694	5	Std	15	1	4	2800	10.93	0.965	9.65	0.67	6.12	
Sample 18	2	L2702	5	Std	20	1	3.5	2480	11.8	0.956	9.2	0.674	5.93	87.7
Sample 19	3	L2698	10	Std	15	1	2.5	2220	14.8	0.963	8.96	0.69	5.96	
Sample 20	3	L2655	10	Std	15	1	3	2600	14.5	0.957	9.36	0.702	6.19	81
Sample 21	3	L2712	10	Std	20	1	2.5	2560	17	0.961	9.6	0.67	6.18	
Sample 22	3	L2704	12	Std	20	1	2.33	2480	17.7	0.954	9.33	0.68	6.05	74.2
Sample 23	3	L2662	12	Std	20	1	2.5	2680	17.89	0.957	9.46	0.675	6.1	
Sample 24	3	L2708	12	Std	40	1	1.5	2230	24.8	0.943	9.56	0.671	6.04	78.1
Sample 25	3	L2674	12	Std	40	1	1.58	2460	25.9	0.957	9.16	0.678	5.95	
Sample 26	4	L2661	10	Std	15	1.5	3.67	2480	11.29	0.954	9.12	0.675	5.9	
Sample 27	4	L2660	10	Std	15	2	2.33	1110	7.94	0.949	5.4	0.672	3.45	
Sample 28	5	L2688	2.5	Std	15	1	7.33	2280	5.18	1.01	8.65	0.668	5.83	
Sample 29	5	L2690	1	Std	15	1	42	3000	1.19	0.405	8.09	0.585	1.92	

in manufacturing cost. With the VHF power further increased to 30 W, the further increase in deposition rate was small, yet the a-Si material quality experienced a sizable deterioration.

Another way to increase the deposition rate is by increasing the chamber pressure. Samples 12-18 (group 2) have i-layers deposited at 1 Torr. Compared with Sample 10, Sample 16 showed an 88% increase in deposition rate when the pressure was increased from 0.5 to 1 Torr. Samples deposited under 1 Torr showed similar trend as those deposited under 0.5Torr, i.e., a higher VHF power leads to a higher deposition rate, yet no apparent deterioration was observed in the device performance.

To further increase the deposition rate, i-layers were deposited with higher SiH_4 flows and power, as shown in Samples 19-25. Essentially no apparent deterioration in device performance was observed when the deposition rate was around or below 15 Å/s. When the deposition rate approached 25 Å/s, P_{max} started to decrease.

Further increase in chamber pressure beyond 1 Torr does not enhance the deposition rate, as we see from the result of Sample 26. Comparing Samples 26 and 27 with Samples 19 and 20, we found that the deposition rate decreases when the chamber pressure is above 1 Torr.

Besides using VHF plasma to search for high rate deposition, we also used a VHF plasma to deposit intrinsic a-Si with wider bandgap at relatively lower substrate temperatures. This wider bandgap leads in turn to a higher V_{oc}. A high hydrogen dilution approach was used for depositing wider bandgap a-Si material [7]. As we can see from Samples 28 in Table 2, a two fold reduction in SiH_4 flow, therefore a two fold increase in hydrogen dilution, leads to an increase of V_{oc} up to 1.01 V. Further increase in hydrogen dilution causes the formation of microcrystalline, therefore, results in a significant drop in V_{oc} and FF (See Sample29 in Table 2).

An important issue regarding high rate deposition of a-Si materials is its light stability. We selected some representative samples with various deposition rates and conducted light soaking under 1 sun light at 50 °C for 1000 hours. The column in Table 2 under "stability" shows the ratio of the degraded P_{max} and the initial P_{max} for samples gone through light soaking test for 1000 hours. From the light soaking data in Table 2 and those re-plotted in Figure 4, we found that there is a small increase in light degradation for samples with deposition rates higher than 15 Å/s. Devices with deposition rates less than 15 Å/s show approximately the same light degradation, which is low. Figure 5 shows the time dependence of P_{max} upon light soaking for a VHF device (Sample 16). We see that the device performance have come to an equilibrium within 100 hours of light exposure. In fact, the majority of degradation occurred during the initial 3 hours of light soaking.

The a-Si solar cell investigated in this study is to be used as the top cell in a triple-junction solar cell. A top-cell is usually deposited directly on the middle component cell rather than directly on a back-reflector. The majority of the i-layer optimization was therefore performed on SS substrates without the use of a back-reflector. However, we have also deposited a VHF device on a textured Ag/ZnO back-reflector for an evaluation purpose. Figure 6 shows an I-V curve of a single-junction a-Si solar cell with the i-layer deposited using VHF plasma deposition, showing an initial solar cell efficiency of 10.9%, which is comparable, if not better, than what we usually obtained for a-Si solar cells deposited using RF plasma deposition in the same deposition system.

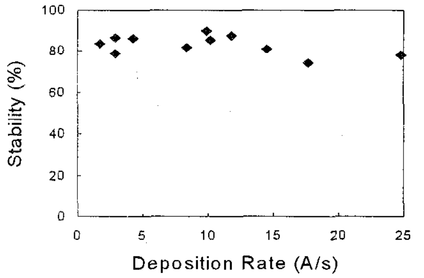

Fig. 4. Stability, P_{max}(degraded)/P_{max}(initial), after 1000 hours of one sun light soaking for devices having VHF i-layers deposited at different deposition rate.

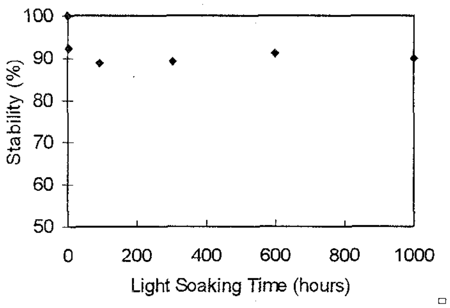

Fig. 5. Light soaking degradation of a VHF device as a function of light soaking time.

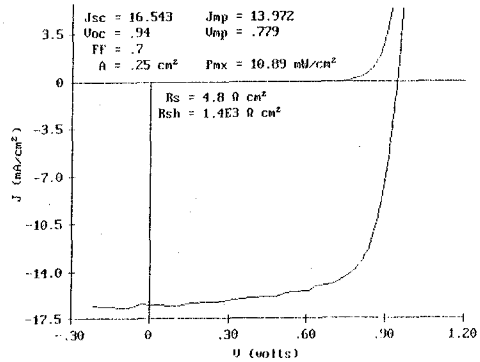

Fig. 6. I-V curve of a single-junction a-Si solar cell with i-layer deposited using VHF plasma, showing η=10.9%.

In Table 3, we compare the light stability of a-Si solar cells with i-layers deposited using VHF and RF at both high and low deposition rates. All devices in Table 3 have i-layer thicknesses around 2500 Å and were deposited on bare stainless steel without back-reflectors. After 1000 hours of light soaking under one sun light at 50 °C, optimized i-layers deposited in the same system using an RF plasma at low deposition rate (0.61 Å/s) lead to a light degradation of 14.3% while i-layers deposited using VHF at 10 Å/s lead to a light degradation of only 10% for otherwise identical devices. Although the degradation of a VHF device with i-layer deposited at 24.8 Å/s increased to around 22%, that of an RF device with i-layer deposited at 16 Å/s (a lower rate) showed a degradation of 36% (a higher degradation). Therefore, VHF deposited i-layers show superior stability properties compared to RF i-layers when deposited at high rates.

SUMMARY

VHF PECVD is used to deposit µc-Si p-layer and a-Si i-layer materials. The use of a modified VHF process for the p-layer deposition result in a-Si solar cells with increased J_{sc}, V_{oc} and FF, most likely due to the improved µc-Si formation in the p-layer. For the deposition of i-layers at high rate using a VHF plasma, we were able to fabricate solar cells with a-Si i-layer deposited at up to 15 Å/s yet with similar device performance and light stability as the low-rate deposited samples. i-layers deposited using a VHF plasma at high rates show superior performance and stability than i-layers deposited in the same deposition system at high rate using a conventional RF plasma. As an additional benefit, the VHF process can be easily incorporated into a large scale production process such as ECD's continuous roll-to-roll a-Si PV production line.

ACKNOWLEDGMENTS

We would like to thank Drs. H. Fritzsche, S. Guha and J. Yang for the helpful discussions and experimental helps throughout this research. This work was partially supported NREL under Thin Film Partnership Program (Contract No. ZAN-4-13318-11).

REFERENCES

[1] S. Guha, J. Yang, P. Nath, and M. Hack, Appl. Phys. Lett. **49**, 1986, p. 218.
[2] S. Guha, J. Yang, A. Banerjee, T. Glatfelter, K. Hoffman, S.R. Ovshinsky, M. Izu, H.C. Ovshinsky, and X. Deng, Mat. Res. Soc. Proc. **336**, 1994, p. 645.
[3] J. Yang, A. Banerjee, T. Glatfelter, S. Sugiyama, and S. Guha, this conference.
[4] M. Heintze, R. Zedlitz and S.H. Bauer, Mat. Res. Soc. Proc. **297**, 1993, p. 49.
[5] J. Meier, et. al, Proc. of 1st WCPEC, 1994, p. 409.
[6] X. Deng, S. Jones, T. Liu, M. Izu, S. R. Ovshinsky and K. Hoffman, Mat. Res. Soc. Proc. **467**, 1997.
[7] X. Deng, K.L. Narasimhan, J. Evans, M. Izu and S.R. Ovshinsky, Proc. of 1st WCPEC, 1994, p. 678.

Table 3 Comparison of light soaking stability between devices with i-layers deposited using RF and VHF.

Sample No.	Ref. No.	Plasma Frequency (MHz)	Dep. Rate (Å/s)	Initial P_{max} (mW/cm^2)	Light degrad. (%)
Sample 30	L2710	RF (13.56)	0.61	6.65	14.3
Sample 16	L2656	VHF (70)	9.9	6.51	10
Sample 31	L2715	RF (13.56)	16	5.3	36.2
Sample 24	L2708	VHF (70)	24.8	6.04	21.9