VHF PLASMA DEPOSITION OF μc-Si p-LAYER MATERIALS

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ABSTRACT

Microcrystalline silicon (μc-Si) p-layers have been widely used in amorphous silicon (a-Si) solar cell research and manufacturing to achieve record high solar cell efficiency. In order to further improve the solar cell performance and achieve wider parameter windows for the process conditions, we studied the deposition of high quality μc-Si p-layer material using a very high frequency (VHF) plasma enhanced CVD process. A design of experiment (DOE) approach was used for the exploration and optimization of deposition parameters. The usage of DOE leads to a quick optimization of the deposition process within a short time frame. In addition, by using a modified VHF deposition process, we have improved the solar cell blue response which leads to a 6-10% improvement in the solar cell efficiency. Such an improvement is likely due to an improved microcrystalline formation in the p-layer.

INTRODUCTION

The critical role that p-layer quality plays in determining the solar cell efficiencies for a-Si based devices is well known. The p-layer materials must be highly transparent while still maintaining a relatively high conductance. The research team at Energy Conversion Devices, Inc. (ECD) has previously developed a microcrystalline silicon (μc-Si) p material for use in amorphous silicon solar cell fabrication.[1] Such a p-layer, when used in a-Si solar cell devices, leads to increased solar cell V_{oc}, J_{sc} and FF compared with amorphous p-layers. These μc-Si p-layer materials have been widely used in a-Si solar cell research and manufacturing to achieve record high solar cell efficiencies,[2-4] in particular in the recent 14.6% initial and 13% stable efficiencies for small area a-Si solar cells made by United Solar System Corp. (United Solar).[5] However, using conventional RF PECVD, the process window in 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 on 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[6,7] 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.

EXPERIMENT

We deposited μc-Si p-materials using a VHF plasma enhanced CVD process in a research scale multi-chamber load-locked solar cell deposition system (LL2). The substrate is SS/n-i in which the doped n-layer and the undoped a-Si intrinsic layer were deposited previously in a roll-to-roll process. Thus, these SS/n-i substrates have high uniformity, which is important for optimizing the p-layer with a wide parameter space.

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Table 1 Design parameters and experimental results for the optimization of VHF deposition of μc-Si p-layer using a 4-factor Draper-Lin small composite design with face-centered design characteristics.

Run #	Exp.#	Temp (°C)	BF_3 (sccm)	SiH_4 (sccm)	Time (min)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s (Ω•cm^2)	P_{max} (mW/cm^2)
L2372	1	100	4	0.6	4	0.879	10.02	0.67	9.7	5.76
L2373	2	100	4	0.8	4	0.88	8.91	0.651	10.8	5.1
L2374	3	100	4	0.6	6	0.81	9.39	0.61	10	4.64
L2375	4	60	6	0.8	6	0.864	9.07	0.633	11.1	4.96
L2376	5	100	4	0.4	4	0.868	9.73	0.64	13	5.29
L2377	6	60	2	0.8	2	0.873	9.09	0.619	19.7	4.91
L2378	7	140	2	0.4	6	0.876	9.12	0.678	8.5	5.3
L2379	8	100	4	0.6	2	0.89	9.83	0.657	10.4	5.75
L2380	9	100	2	0.6	4	0.884	10.13	0.643	12.4	5.76
L2381	10	140	4	0.6	4	0.843	8.48	0.661	8.7	4.73
L2382	11	140	6	0.8	2	0.856	8.51	0.671	8.8	4.89
L2383	12	60	6	0.4	6	0.831	10.31	0.56	36	4.71
L2384	13	100	6	0.6	4	0.891	9.28	0.67	10.9	5.44
L2385	14	140	2	0.8	6	0.882	8.89	0.658	7.1	5.16
L2386	15	60	4	0.6	4	0.889	9.74	0.649	11.2	5.52
L2387	16	140	6	0.4	2	0.88	8.91	0.663	8.2	5.2
L2388	17	60	2	0.4	2	0.861	9.31	0.621	23.6	4.98
L2389	18	100	4	0.6	4	0.887	9.48	0.664	8.9	5.47

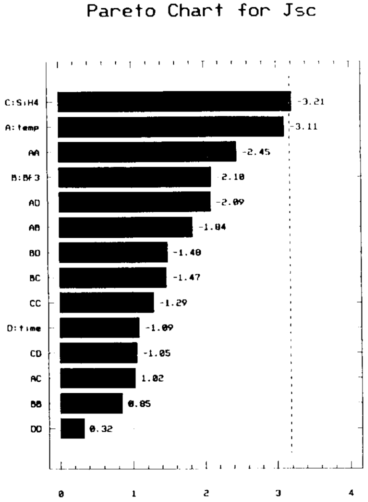
After p-layer deposition, ITO/Ag top contacts were fabricated using evaporative processes to complete the solar cell structures. The solar cells were characterized using standard J-V and spectral response (quantum efficiency) measurements. Particular attention was paid to the blue light section of the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

PROCESS OPTIMIZATION USING DESIGN OF EXPERIMENT

A design of experiments (DOE) approach[8] was used for the exploration and optimization of deposition parameter space. Such statistical analysis is widely used in the semiconductor industry when each experiment is time-consuming and costly, and there are many interacting process conditions that affect the final device performance. By taking advantage of the symmetry and orthogonality of the designed experiments, we were able to obtain, in only a few experiments, the amount of information that otherwise requires a large number of experiments without using DOE. Of even greater importance for the DOE is the ability to sense interactions among experimental variables. One-factor-at-a-time experiments can never uncover information about interactions. Non-statistical methods cannot discern the errors involved and tend to be much less efficient (i.e., a larger number of trials are needed). Thus, the experimenter employing DOE methodologies enjoys several benefits: a more efficient, therefore faster method of experimental discovery, quantitative estimates of the effect of random error, and information about synergies among the variables. The benefit of using DOE would be even greater if more process parameters are involved. The DOE approach has allowed us to quickly optimize a new deposition process covering a broad parameter space.

Table 1 lists the initial deposition parameter space used for the p-layer research. It is a four-factor, five-variable Draper-Lin small composite design with face-centered design characteristic. The limits of the design parameters were carefully selected based on our understanding of the a-Si and μc-Si deposition process. These four parameters were chosen because they should most strongly affect the performance of the p-layer. Other parameters that were not explored and set at constants in this specific set of DOE design include VHF power (75W), Hydrogen flow, and chamber pressure (2 Torr). The solar cell data shown in Table 1 is used to analyze the response of solar cell parameters on the process conditions, as described in the following figures.

Figure 1 is the Pareto chart of J_{sc} of n-i-p solar cells with VHF μc-Si p-layer as a function of temperature, BF_3, SiH_4 and deposition time. The Pareto chart shows how each variable of interest depends on various process parameters, and the degree of sensitivity is reflected by the height of the bar chart. We found that within the above described four dimensional block of parameter space, the J_{sc} is most statistically dependent on the SiH_4 flow and deposition temperature. Figure 2 is the response surface plot of J_{sc} as a function of SiH_4 flow and temperature while keeping the values of BF_3 and deposition time at the center values (average values). Figures 1 and 2 suggest that J_{sc} increases with decreasing SiH_4 flow and temperature within the selected parameter ranges. The increase of J_{sc} at low SiH_4 is most likely due to two reasons: 1) the decreased p-layer thickness when less SiH_4 is used in the gas mixture of SiH_4, BF_3 and H_2; and 2) the increased hydrogen dilution (H_2/SiH_4) could increase the microcrystallinity and hence the transmission through the p-layer. The increase in J_{sc} with lower deposition temperature is likely due to the increased microcrystallinity when the process temperature is lowered. As a reminder, the actual substrate temperatures could be much higher than the temperature values read from the thermal couples reported here due to the heating of intense VHF plasma. The surface plot in Figure 2 suggests that within the selected parameter space, the optimum J_{sc} value could be achieved at a temperature reading of 60 °C and a SiH_4 flow of 0.5 sccm when the BF_3 and deposition time are set at 4 sccm and 4 min, respectively.



Figures 1 Pareto chart for J_{sc} of n-i-p solar cells with VHF μc-Si p-layer as a function of temperature, BF_3, SiH_4 and deposition time.

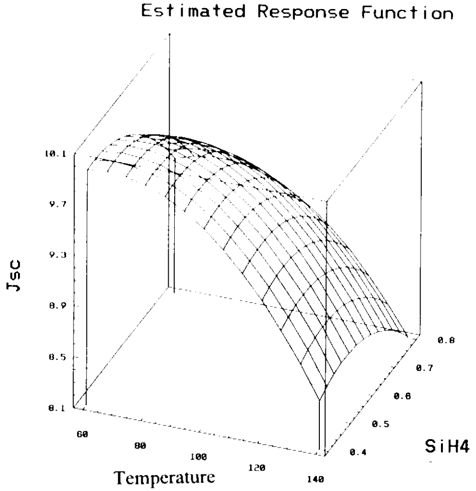


Figure 2 Response surface plot for J_{sc} as a function of SiH_4 and temperature while keeping the values of BF_3 and deposition time at the center values.

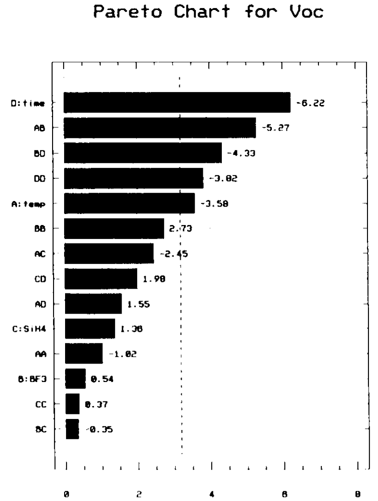


Figure 3 Pareto chart for V_{oc} of n-i-p solar cells with VHF μc-Si p-layer as a function of temperature, BF_3, SiH_4 and deposition time.

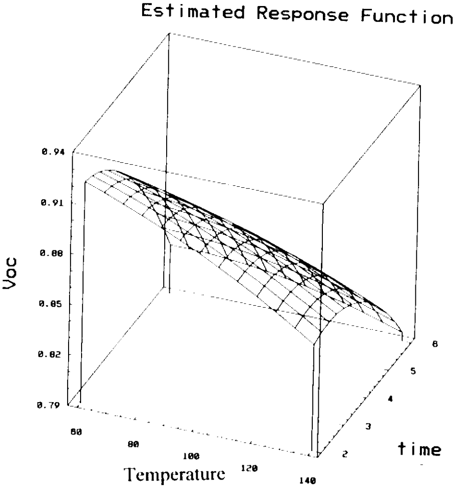


Figure 4 Response surface plot for V_{oc} as a function of deposition time and temperature while keeping the values of BF_3 and SiH_4 at the center values.

Figure 3 is the Pareto chart for V_{oc} in this set of experiments. The V_{oc} is most sensitive to the deposition time and the first order interaction of substrate temperature and BF_3 flow. The surface response plot in Figure 4 also illustrates the dependence of V_{oc} on deposition time and temperature. The decrease in V_{oc} at longer deposition time beyond 3 min could be due to the rapid increase of real substrate temperature during the VHF deposition. Using the design of experiments, we have successfully surveyed the dependence of solar cell performance on these four crucial parameters using 18 experiments. Further improvements in the VHF process from this initial study has led to the deposition of p-layers and solar cells with V_{oc} up to 0.93 V. Figure 5 shows the J-V curve of a representative device having improved VHF p-layer.

μc-Si p-LAYER USING A MODIFIED VHF PLASMA DEPOSITION

In order to further improve the performance of p-layers in solar cells, we have investigated the application of a modified VHF plasma process[9] for the μc-Si p-layer deposition. In Table 2, we compare the results of solar cells with p-layers deposited using this modified VHF process with those deposited in the same load-locked 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 substrate, the ITO layer for these three devices are made in the same run (ITO4408) to ensure consistency. The data listed in Table 2 is the average of data for many small area solar cells on the same sample.

Table 2 Results of solar cells whose p-layers were deposited using different processes: conventional RF, conventional VHF and a modified VHF process

p-layer Run#	ITO Run #	p process	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s	P_{max} (mW/cm^2)	J_{sc} from QE (mA/cm^2)	QE@400nm (%)
L2523	4408	Modified VHF	0.959	10.39	0.664	11.5	6.62	10.71	0.655
L2525	4408	Conventional RF	0.948	9.82	0.63	14.8	5.86	10.09	0.591
L2526	4408	Conventional VHF	0.933	8.78	0.651	12.2	5.33	10.04	0.56
L2527	4409	Modified VHF	0.958	10.4	0.654	13.1	6.52	11.27	0.721

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 conventional RF sample (L2525). To confirm the improvement in the modified VHF configuration, we repeated a modified VHF sample (L2527), with ITO coated in a separate evaporation (ITO4409). The improvement in the J_{sc} as well as V_{oc} and FF over the conventional RF sample was reproduced.

Figures 6 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 indicate that the modified VHF p-layer is more transparent to the sun light, most likely due to enhanced microcrystallinity.

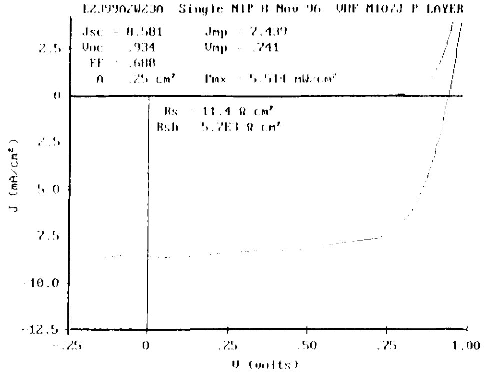


Figure 5 J-V curve for a representative device with VHF p-layer, showing a Voc of 0.93 V.

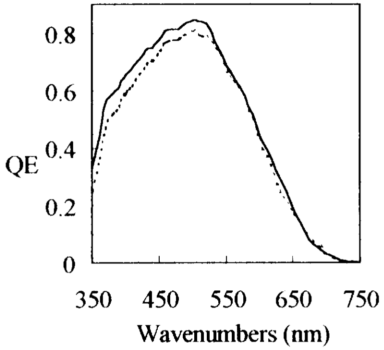


Figure 6 Quantum efficiency curves for an a-Si n-i-p device with p-layer deposited using the modified VHF PECVD (Sample L2523, solid curve) and conventional RF PECVD (Sample L2525, dashed curve).

The improved microcrystallinity using the VHF deposition process is also supported by the RHEED measurement. Figure 7 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.

Figure 7 RHEED pattern of a device with VHF p-layer at the top, showing high volume fraction of microcrystalline phase in the p-layer.

SUMMARY

Very high frequency PECVD is used to deposit μc-Si p-layer material. A design of experiment (DOE) approach was used for the exploration and optimization of deposition parameters. The usage of DOE leads to a quick optimization of the deposition process within a short time frame. The use of the modified VHF p-layer in an a-Si solar cell increases the solar cell J_{sc}, V_{oc} and FF. The increased J_{sc} and V_{oc} are most likely due to the improved microcrystalline formation in the p-layer. As an additional benefit, the new VHF process can be easily incorporated into a large scale production process such as ECD's continuous roll-to-roll amorphous silicon PV production line

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9. Due to the proprietary nature of this process, the details of the modified VHF process is not disclosed at this time while a patent application for the process is being prepared.