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Microcrystalline Silicon Solar Cells

Final Technical Progress Report
1 July 2001 – 31 August 2004

S. Guha and J. Yang
United Solar Ovonic Corporation
Troy, Michigan

Subcontract Report
NREL/SR-520-38355
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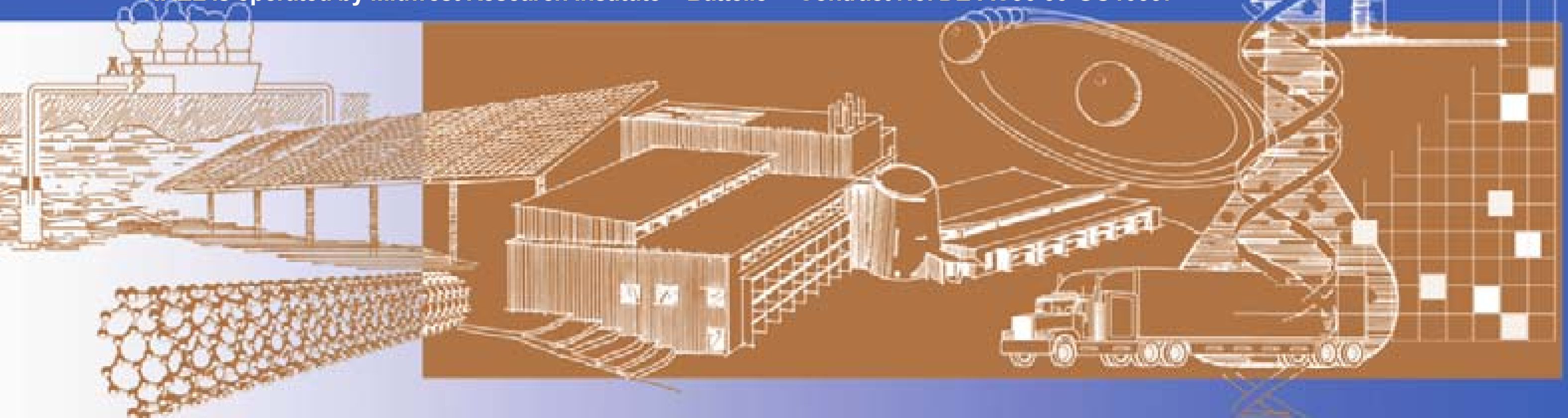

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Prepared under Subcontract No(s). NCQ-1-30619-04

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303-275-3000 • www.nrel.gov

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Contract No. DE-AC36-99-GO10337

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Preface

This final Subcontract report covers the work performed by United Solar Ovonic Corporation for the period from July 1, 2001 to August 31, 2004 under NREL Beyond The Horizon Program Subcontract No. NCQ-1-30619-04. The following personnel participated in this research program.

E. Chen, S. Guha (Principal Investigator), B. Hang, K. Lord, A. Mohsin, T. Nazmee, J. M. Owens, T. Palmer, D. Wolf, B. Yan, J. Yang (Co-Principal Investigator), and K. Younan.

Material characterizations have been made in collaboration with D. Williamson of Colorado School of Mines and D. Han of University of North Carolina.

Executive Summary

Project Objective

The objective of the research under this subcontract is to explore, identify, evaluate, and develop non-conventional photovoltaic technologies capable of making a breakthrough in the production of low cost electricity from sunlight. The specific objectives are to 1) develop microwave glow discharge parameters for the deposition of high quality microcrystalline silicon (μc-Si:H) thin films at high rate, 2) characterize this microcrystalline material, and 3) fabricate high efficiency microcrystalline *nip* solar cells.

Background and Approaches

At United Solar, we use various techniques to explore the possibility of making μc-Si:H solar cells as the bottom cell in multi-junction structures. For example, we have achieved a 14.6% initial active-area efficiency using an a-Si:H/a-SiGe:H/μc-Si:H triple-junction structure deposited with conventional RF glow discharge at a low rate ~1 Å/s. Similarly, we have obtained a 12.5% initial active-area efficiency with an a-Si:H/μc-Si:H double-junction structure, but deposited with Modified Very High Frequency (MVHF) at relatively high rates ~3-5 Å/s. In order to be viable for production, we need to increase the deposition rate further. Microwave glow discharge has been used to deposit a-Si:H and a-SiGe:H alloy solar cells at a very high deposition rate ~100 Å/s. In this project, we use this technique to make μc-Si:H solar cells using the following approaches:

Use of hydrogen dilution: Hydrogen dilution is a key technique in depositing μc-Si:H, but the dilution level for obtaining microcrystalline material depends on the deposition process. Our approach is to optimize the hydrogen dilution level to obtain good quality μc-Si:H material at the desired deposition rate. We find that the required hydrogen dilution strongly depends on several deposition parameters such as substrate temperature, microwave power and substrate material. Therefore, the optimized dilution ratio is found to be different for different choices of parameters.

Control ion bombardment: In general, a certain level of ion bombardment is necessary for making good quality material, but bombardment with high-energy ions is likely to damage the deposited material. The ion energy and flux strongly depend on the chamber pressure and other deposition conditions. The bias voltage between the plasma and substrate also affects the ion bombardment. We have studied the pressure dependence on the cell performance and dilution with different gases such as H_2, Ar and Ne.

Optimize the deposition system: The microwave deposition system used in this study was designed based on the requirements of a-Si:H and a-SiGe:H alloy deposition. In order to obtain high quality μc-Si:H solar cells, we have modified the deposition system according to the special requirements of μc-Si:H deposition such as high hydrogen dilution. We find that under high hydrogen dilution, it is difficult to sustain plasma under low pressure. By changing the hardware, we have expanded the parameter window for obtaining a stable plasma.

Use of strong etchant gases: One mechanism by which hydrogen dilution leads to the improvement of material quality is that hydrogen radicals etch away the less ordered materials from the deposition surface. Use of gases that produce strong etching species in the plasma is expected to lead to more ordered material. It is well known that fluorine has a strong etching effect. In this program, we investigate the effect of fluorine containing gases, such as SiF_4 in the microwave glow discharge.

Optimize cell structure: We have optimized the *n/i* and *i/p* interfaces by inserting suitable buffer layers and found that an initial *n/i* seeding layer can reduce the crossover between the dark and light J-V characteristics and improve fill factor. An optimized *i/p* buffer layer can suppress the shunt current and improve the open-circuit voltage and fill factor.

Status/Accomplishments

During the program, we have worked on the improvement of the microwave glow discharge system to satisfy the requirement of μc-Si:H deposition, and concentrated on the optimization of microwave plasma parameters. We have made comparison studies of the material properties of high rate μc-Si:H using microwave to those made using other techniques such as RF and MVHF. The main areas studied and achievements are as follows:

H_2, Ar and Ne dilution: We have studied the deposition of μc-Si:H solar cells using mixtures of SiH_4 and H_2, SiH_4 and Ar, and SiH_4 and Ne. H_2 dilution promotes the microcrystalline formation, but results in difficulties in sustaining the plasma. Ar dilution leads to stable plasma in a very wide range of pressure, but the material remains amorphous. Ar has relatively low ionization energy, but causes high bombardment due to its large mass. Based on this analysis, we speculated that Ne could help to obtain stable plasma, and at the same time provide moderate ion bombardment. Unfortunately, we found that Ne dilution did not give the desired effect of sustaining the plasma. The best μc-Si:H solar cell was made with moderate H_2 dilution.

Pressure dependence: Pressure is also a critical parameter for microwave plasma deposition. We found that a low pressure is required for low H_2 dilution ratios to reach the amorphous/microcrystalline transition. We can deposit μc-Si:H solar cells with pure SiH_4 under a pressure around 10 mTorr. However, a low pressure requires high power to sustain the plasma.

Microwave power: High microwave power promotes μc-Si:H deposition, but good quality μc-Si:H material is deposited with the lowest power just high enough to sustain the plasma.

Substrate temperature: In the region of 200 to 450 °C studied, it is easy to reach the amorphous/microcrystalline transition. The optimized temperature is around 300 to 350 °C.

Use of F containing gases: We have added a small amount of SiF_4 into the mixture of SiH_4 and H_2, and found that SiF_4 does not improve the cell performance under deposition conditions studied.

Device structure: An optimized initial seed layer is critical for μc-Si:H solar cells. The seed layer can be a μc-Si:H *n* layer, or a high H_2 diluted μc-Si:H intrinsic layer deposited using RF at a low rate.

Material characterization: We studied the μc-Si:H properties using X-Ray diffraction (XRD), Raman, and small angle X-ray scattering (SAXS) and compared the results to the μc-Si:H films deposited using RF and MVHF. We found that the microwave deposited μc-Si:H has a preferential growth direction along (111), which is different from the (220) preferential direction of RF and MVHF deposited μc-Si:H films. We believe that the high-energy ion bombardment resulted in a discontinuous growth of grains and suppressed the (220) preferential orientation. SAXS measurements find that the microwave deposited μc-Si:H film has high microvoid density up to 3% in volume, which is significantly higher than those in the RF and MVHF deposited μc-Si films (around 0.5% in volume).

Solar cell performance: We have achieved a μc-Si:H single-junction cell having an initial active-area efficiency of 4.92%, where the intrinsic μc-Si:H layer was deposited in 210 seconds, corresponding to about 30 Å/sec. Using this recipe in the bottom cell of an a-Si:H/μc-Si:H double-junction structure, we have obtained an initial active-area efficiency of 7.2% with J_{sc}=8.52 mA/cm^2, V_{oc}=1.32 V, and FF=0.642.

Main Conclusions

Microwave plasma can deposit μc-Si:H solar cells at very high rates ~20-30 Å/s. The material quality and solar cell performance are not as good as those deposited using RF and MVHF glow discharge techniques.

The main differences between the microwave plasma deposited μc-Si:H and those deposited with RF and MVHF are (111) orientation instead of (220) orientation based on XRD and high microvoid density based on SAXS measurements.

Major Reports Published

Quarterly reports and annual reports are submitted according to the contract requirements.

Major Articles Published

[1] B. Yan, K. Lord, A. Banerjee, J. Yang, and S. Guha, "High-rate Deposition Hydrogenated Microcrystalline Silicon Solar Cells," National Center for Photovoltaics Program Review Meeting, October, 2001, Colorado.

[2] Baojie Yan, Jeffrey Yang, and Subhendu Guha, "Hydrogenated Microcrystalline Silicon Solar Cells Using Microwave Glow Discharge", NCPV-2003 Review Meeting.

[3] Baojie Yan, Guozhen Yue, Jeffrey Yang, Kenneth Lord, Arindam Banerjee, and Subhendu Guha "Microcrystalline Silicon Solar Cells Made Using RF, MVHF, and Microwave at Various Deposition Rates", 3rd World Conference on Photovoltaic Energy Conversion, Osaka, Japan, 2003 (invited).

[4] Baojie Yan, Guozhen Yue, Jeffrey Yang, and Subhendu Guha, "High Rate Deposition of Hydrogenated Nanocrystalline Silicon Solar Cells", to be presented at NCPV-2004 review meeting.

1. Hydrogen, Argon, and Neon dilution

Hydrogen dilution is the key technique for improving a-Si:H quality [1]. The best a-Si:H and a-SiGe:H alloys are made near the amorphous to microcrystalline transition [2], where nano-structured linear objects were found [3]. On the other hand, the best μc-Si:H solar cells are deposited with a hydrogen dilution ratio close to the microcrystalline/amorphous transition, under which conditions the μc-Si:H material shows a compact structure with low defect density [4]. In this project, we systematically studied the hydrogen dilution effects on solar cell performance. From previous studies, we learned that V_{oc} is a very sensitive parameter with which to measure the phase transition from amorphous to microcrystalline phase. Therefore, we monitored the V_{oc} as a function of H_2 and Ar dilution. The results are shown in Fig. 1, where a series of solar cells made under the same conditions except for the H_2 and Ar flow rates were changed. The results are surprising and unexpected. First, Ar dilution makes the material more amorphous, while H_2 dilution makes the material more microcrystalline. With the decrease of Ar flow, V_{oc} slightly increases from 0.98 V (when Ar flow rate is 100 sccm) to over 1.0 V (when Ar flow rate is 25 sccm). When the Ar flow rate decreases further, the V_{oc} decreases sharply, indicating a transition from an amorphous phase to an amorphous and microcrystalline mixture phase. With no dilution, the solar cell only has V_{oc} around 0.55 V, which means a significant amount of microcrystalline phase has been already included. Compared with RF (or VHF) glow discharge, where very high H_2

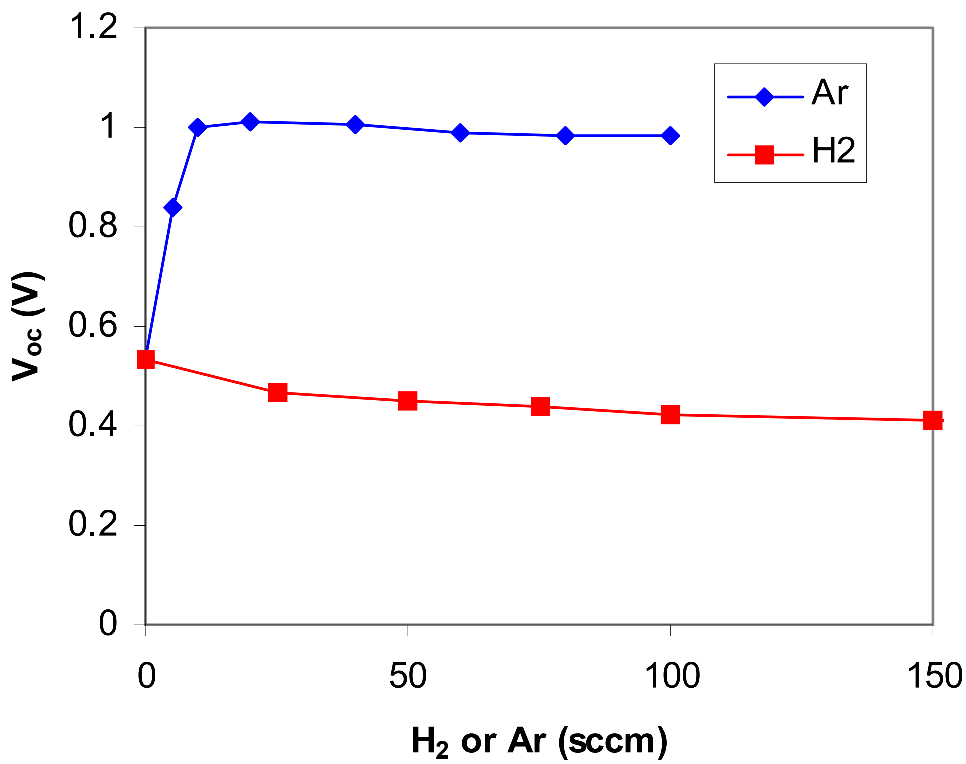

Figure 1. V_{oc} as a function of H_2 and Ar dilution for a fixed SiH_4 flow rate.

dilution is required for making μc-Si:H films, the microwave plasma does not need very high H_2 dilution, which allow us to deposit μc-Si:H solar cells at relatively high deposition rates. Currently, our deposition rate is in the range of 20-40 Å/s. When the H_2 flow rate is increased further, V_{oc} is observed to decrease slightly, along with an increase of long wavelength response obtained from quantum efficiency measurements, indicative of an increase of crystalline volume fraction.

We also scanned other parameters (details are in the following sections) and found that for the microwave low discharge deposition, μc-Si:H is easily obtained under low pressure with high hydrogen dilution, high microwave power, and high temperature. However, good μc-Si:H solar cells were made under low pressure with low microwave power. On the other hand, we have difficulties in sustaining plasma under conditions of low power and low pressure. In this quarter, we have focused on the optimization of plasma conditions including the use of various dilution gases and modification of the plasma chamber to improve the stability of the microwave plasma with low power and under low pressure.

It is known that one can easily obtain plasma with Ar gas due to its low ionization energy. However, as shown in Fig. 1, high Ar dilution tends to make the material amorphous, probably due to high ion bombardment. In contrast, high H_2 dilution easily turns the material microcrystalline. A question then arises that with high H_2 dilution and adding a small amount of Ar as plasma igniter or stabilizer, can we obtain stable plasma under lower pressure with low power? In addition, with Ar under low pressure, can we improve the μc-Si:H cell performance? For this purpose, we have carried out a study on the effect of Ar on plasma stability and cell performance. As expected, a small amount of Ar can significantly improve the stability of the microwave plasma. For example, under a given condition, the lowest pressure was around 20 mTorr. Below this value, plasma could not be sustained. By adding 10 sccm of Ar, we can obtain stable plasma under pressures below 10 mTorr. Table I lists the J-V characteristics of μc-Si:H solar cells made with different Ar flow rates and under different pressures. It appears that we can deposit μc-Si:H under a relatively low pressure with a small amount of Ar flow, but the cell performance is not improved. We repeated similar experiments several times and obtained similar results. By analyzing this result and the nature of Ar in the plasma, we believe that low pressure is desirable for microcrystalline formation by reducing polymerization and increasing ion bombardment. Adding Ar helps by reducing the minimum pressure for sustaining the plasma. However, the Ar atom is probably too large and causes high-energy ion bombardment, which damages the material quality.

As discussed above, Ar can reduce the pressure necessary for sustaining microwave plasma, but does not improve μc-Si:H cell efficiency. High-energy ion bombardment could result in poor material quality. Based on this analysis, we thought Ne could be a candidate. First, Ne also has a low ionization energy, which would help in reducing the minimum pressure for stable plasma. Second, a Ne atom is much lighter than an Ar atom, which may alleviate some of the high-energy ion bombardment. However, we found experimentally that Ne did not reduce the required minimum pressure for stable plasma. Figure 2 shows the minimum microwave power required for sustaining plasma

Table I. List of μc-Si:H solar cell performance and corresponding pressure, Ar flow rate and microwave power. Other deposition parameters are the same for all of the cells.

Sample #	Pressure (mTorr)	Ar (sccm)	Power (W)	Eff (%)	J_{sc} (mW/cm^2)	V_{oc} (V)	FF
7501	25	0	750	3.0	17.7	0.357	0.469
7503	12	1	750	3.3	13.4	0.427	0.477
7502	10	5	750	2.7	16.2	0.372	0.453
7506	22	0	750	3.4	16.7	0.403	0.501
7508	22	1	750	2.5	17.5	0.361	0.397
7533	12	2	650	3.3	17.2	0.380	0.505

under different pressures. We ignited the plasma at a relatively high microwave power, and then reduced the power gradually until the plasma disappeared. The data shown in Fig. 2 were the power values prior to the plasma disappearance. From this figure, one notes that the required power to sustain plasma significantly increases with the decrease of pressure for most of the gas mixtures except for SiH_4 with Ar. Surprisingly, Ne does not reduce the required power. But we still made some solar cells under the lowest pressure for stable plasma. Table II lists a few μc-Si:H solar cells made with Ne dilution. The solar cells show similar performance to the cell made with no Ne in the plasma.

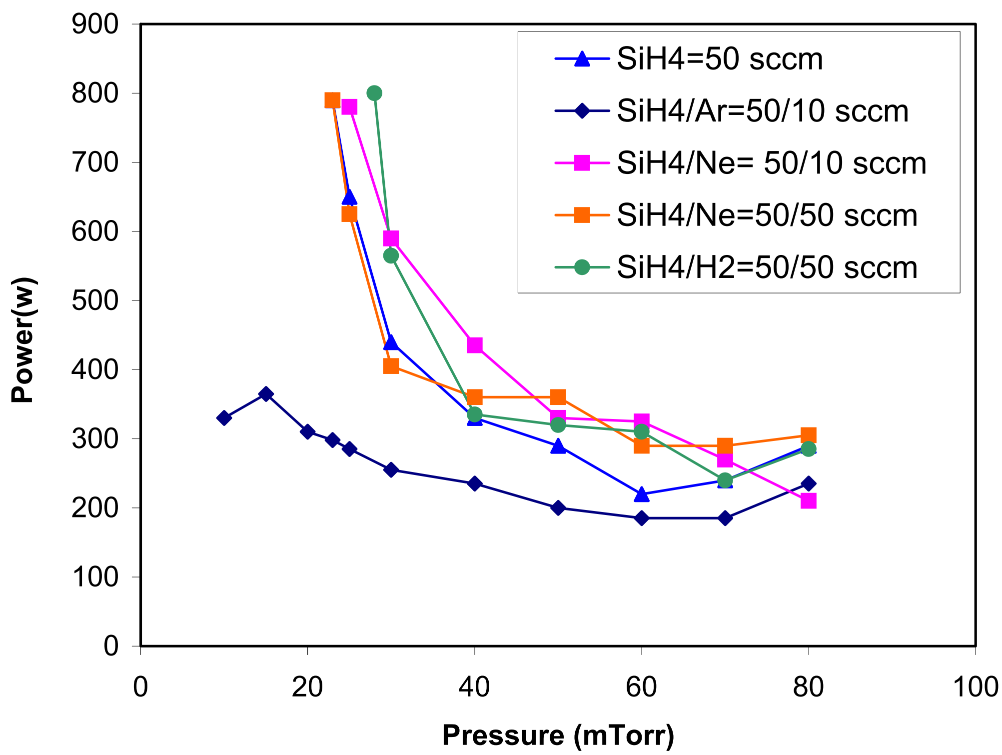

Figure 2. Border curves of microwave power versus pressure at which the plasma can be sustained for various gas mixtures.

Table II. μc-Si:H solar cell performance and corresponding pressure, Ne flow rate and microwave power. Other deposition parameters are the same for all of the cells.

Sample #	Pressure (mTorr)	Ne (sccm)	Power (W)	Eff (%)	J_{sc} (mW/cm^2)	V_{oc} (V)	FF
7630	20	90	800	3.6	16.5	0.425	0.538
7631	18	28	800	3.8	15.6	0.465	0.523
7632	18	90	800	3.4	17.3	0.438	0.450

2. Substrate Temperature Dependence of μc-Si:H Solar Cell Performance

Our previous experience with a-Si:H studies tells us that high substrate temperatures give rise to high diffusion coefficients for radicals on the growing surface and allow for the radicals to find a lower energy position and form compact material. If the substrate temperature is too high, hydrogen will diffuse out of the growing surface and the bulk of the deposited material and leave dangling bonds behind. The optimized temperature also depends on the deposition rate. Normally, high rate depositions require high temperatures. Similarly, an optimized substrate temperature for microcrystalline silicon deposition may depend on the deposition rate. In the literature, researchers found that the optimized substrate temperature is around 200 ºC for μc-Si:H solar cell deposition, at which the defect density is the lowest [4]. It has also been reported that in order to reduce the influence of oxygen, one needs to reduce the substrate temperature to around 150 ºC [5], at which temperature oxygen is not electronically active. Even though the oxygen content could be high, it does not affect the solar cell performance.

In this project, we also systematically studied the effects of substrate temperature on the μc-Si:H cell performance. Figure 3 plots the μc-Si:H solar cell parameters as a function of substrate temperature, where all the other plasma parameters are kept the same. The intrinsic layer is about 700-800 nm thick and deposited in 210 s, which corresponds to a deposition rate of over 30 Å/s. The V_{oc} decreases with the increase of substrate temperature, while FF and J_{sc} are relatively insensitive to temperature for most temperatures. The low J_{sc} and high V_{oc} at 300 ºC indicate a low crystalline volume fraction. With increasing temperature, FF is improved, but V_{oc} continually decreases, indicating the increase of microcrystalline volume fraction. However, J_{sc} does not increase with temperature. Overall, the optimized substrate temperature is around 325 °C, which is higher than the optimized temperature with other deposition parameters such as VHF and RF glow discharge at a high pressure depleting regime.

The optimized substrate temperature depends on other deposition parameters such as pressure, microwave power and hydrogen dilution ratio. We have scanned the substrate temperature over a wide range from 250 °C to 410 °C. In the meantime, we have adjusted other parameters such as the dilution ratio to keep the material microcrystalline. Table III lists a series of μc-Si:H cells made under various conditions. From top to bottom, the data were arranged in the order of decreasing substrate

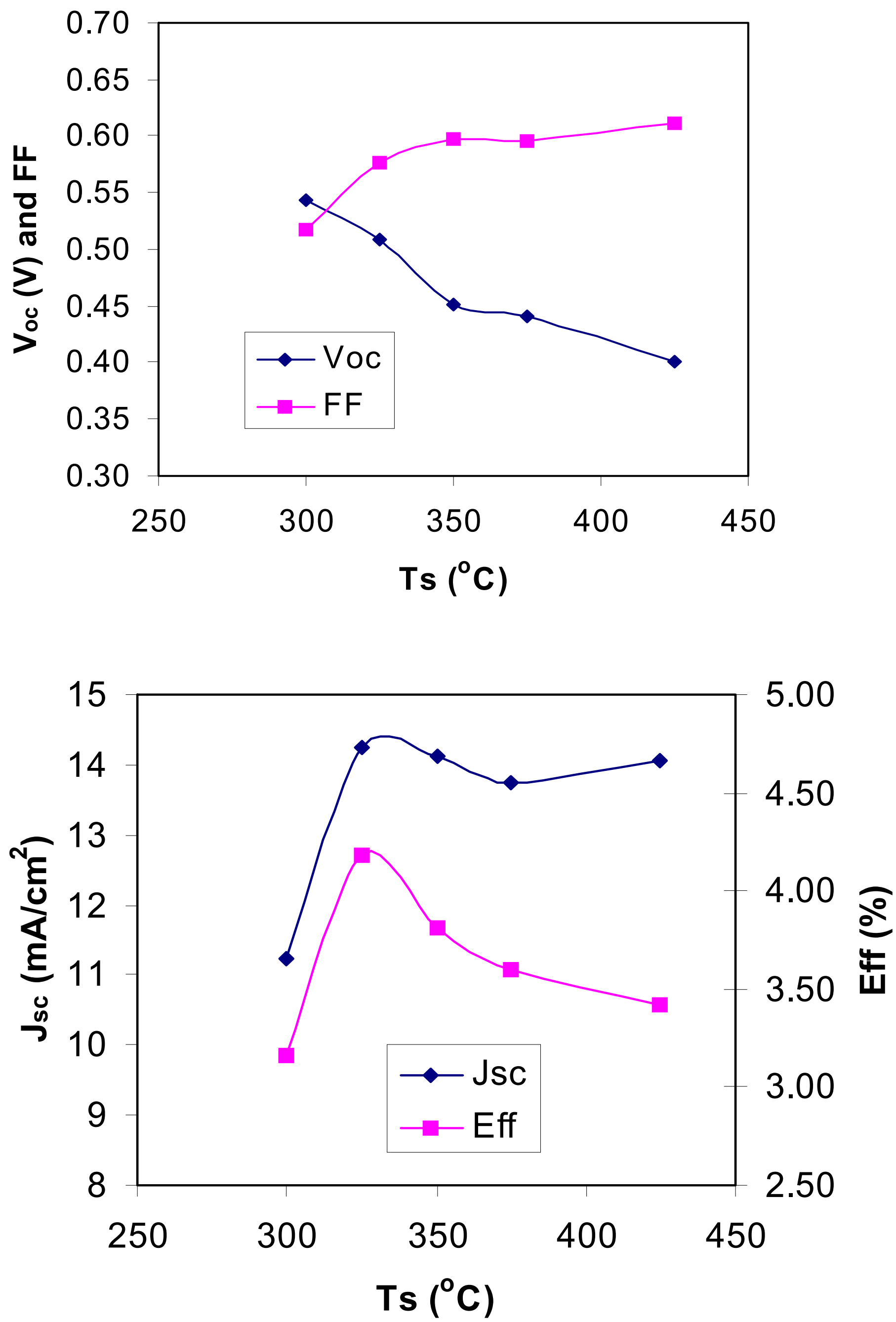

Figure 3. μc-Si:H solar cell performance as a function of substrate temperature.

temperature. At temperatures above 320 °C, the solar cells show microcrystalline characteristics even without hydrogen dilution. With decreasing substrate temperatures, the open circuit voltage (V_{oc}) increases, indicating an increase of amorphous component. Here, we need to be cautious since V_{oc} is not a very reliable measure of microcrystallinity. The material quality, such as defect density, also plays an important role in determining V_{oc}. At lower temperatures, either a high microwave power or a high hydrogen dilution is needed to keep the material in the microcrystalline region.

Table III. Deposition conditions and cell characteristics of μc-Si:H single-junction solar cells made using microwave glow discharge at high deposition rates.

Run #	T (°C)	Power (W)	Press (mTorr)	H_2 (sccm)	SiH_4 (sccm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF
7833	410	700	25	0	50	17.3	0.379	0.520
7826	390	700	21	0	50	15.7	0.404	0.484
7810	350	700	20	0	50	16.2	0.421	0.449
7850	320	700	22	0	50	13.6	0.432.	0.499
7851	320	725	24	0	50	16.8	0.403	0.501
7857	320	725	30	50	50	16.8	0.342	0.488
7858	320	725	35	75	50	14.4	0.349	0.460
7874	300	725	35	75	50	12.9	0.403	0.491
7875	275	725	35	75	50	11.7	0.443	0.449
7876	275	725	35	100	50	12.0	0.345	0.502
7877	250	725	35	100	50	12.9	0.571	0.461
7878	250	725	35	125	50	11.2	0.449	0.475
7879	250	725	35	150	50	11.9	0.420	0.455
7880	250	725	35	175	50	11.5	0.534	0.438
7881	250	725	35	200	50	10.4	0.641	0.539

3. Effects of microwave power on μc-Si:H solar cells

In order to sustain the plasma, a certain level of microwave power is required. Table IV lists a set of J-V characteristics of μc-Si:H solar cells made with the same conditions except for different microwave powers. It is noted that V_{oc} decreases significantly with the increase of microwave power, which may be due to an increase of crystalline volume fraction. However, J_{sc} does not increase as much as we expected. In addition, FF decreases with the increase of microwave power, which implies that the quality of the material becomes poorer with higher microwave power. Although the crystalline volume fraction may be high with high power, the defect density may be high too. In this case, the J_{sc} does not increase due to recombination through defects, and at the same time, low FF appears. However, when the power is too low, the J_{sc} is also low, which means that there are not enough crystallites to absorb the long wavelength photons. Overall, 650 W of microwave power produces the best solar cell under these conditions. One should keep in mind that the material properties and solar cell performance depend on many other parameters. Different combinations of plasma parameters may need different power to produce the best solar cell.

Table IV. J-V characteristics of μc-Si:H solar cells made with different microwave power.

Sample #	Power (W)	Eff (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF
7040	850	2.96	15.16	0.359	0.544
7042	750	3.18	14.14	0.437	0.515
7041	650	4.83	15.77	0.494	0.620
7045	550	4.77	12.50	0.609	0.627

4. Effects of Chamber Pressure and Ion Bombardment on μc-Si:H Solar Cells

We also systematically studied the effects of chamber pressure on solar cell performance. In general, we find that it is easier to reach the amorphous/microcrystalline transition under a lower pressure than under a higher one. It is well know that the ion bombardment is high under a low pressure. The ion bombardment might promote the microcrystalline formation, but the continued growth of crystallites may be disturbed. In addition, a high microwave power might also cause a high defect density and a low cell performance. We explored the possibility of making μc-Si:H under high pressure with high H_2 dilution. First, we made solar cells under 80 mTorr with various hydrogen dilutions. Figure 4 plots the J-V characteristics of solar cells made under 80 mTorr with various SiH_4 flow rates but a fixed H_2 flow rate. The deposition time was adjusted to produce similar intrinsic layer thicknesses. With SiH_4 flow rates larger than 30 sccm, V_{oc} is around 0.9 V and does not change with H_2 dilution ratio within experimental errors, indicating the materials are amorphous. When the SiH_4 flow rates are in the range of 14 to 30 sccm, the cells show a mixed-phase nature; and finally, the microcrystalline phase is achieved with SiH_4 flow rate lower than 14 sccm, as evidenced by low V_{oc} and high J_{sc}.

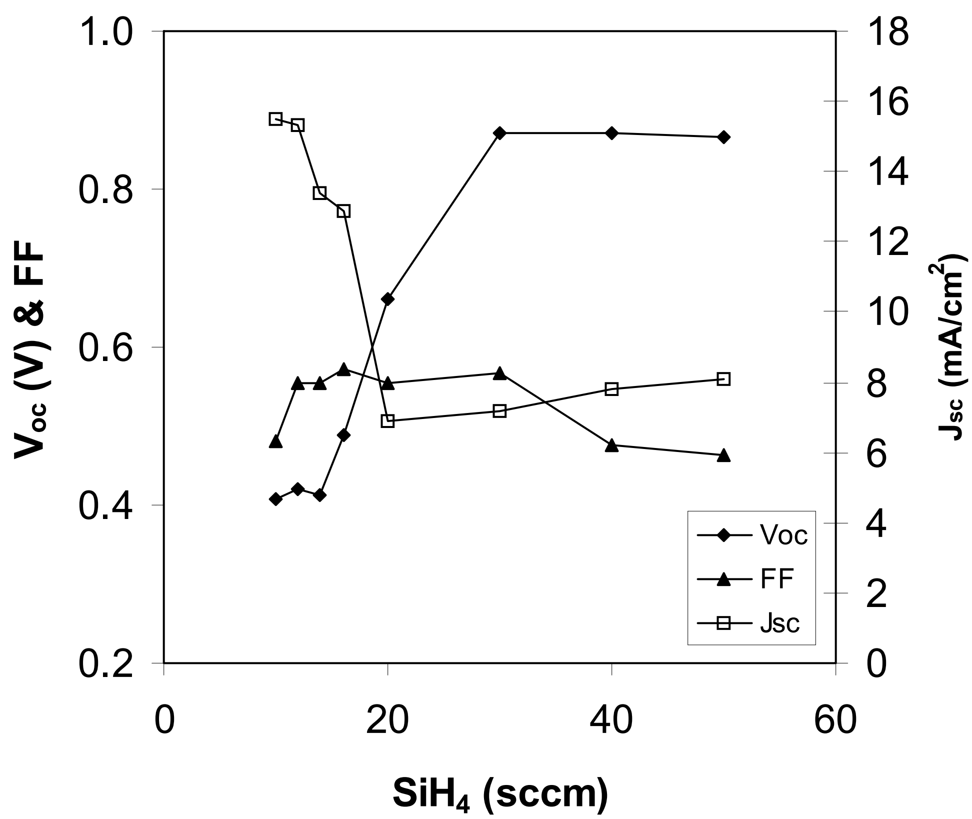

Figure 4. J-V characteristics of solar cells made using microwave plasma under 80 mTorr with a fixed H_2 flow rate but various SiH_4 flow rates.

Unfortunately, the μc-Si:H solar cells made under high pressure show significant ambient degradation similar to those unoptimized μc-Si:H solar cells deposited using MVHF [6]. The J_{sc} degrades without intentional light soaking.

Next we tried even higher pressures and found that under high pressures around 1.0 Torr the plasma glow appears to only surround the gas inlet (most of the chamber space is in the dark) and consequently the deposition rate is very low. We could only obtain reasonably high deposition rate under pressures lower than 200 mTorr. However, under 200 mTorr, most of the deposited materials are amorphous. Table V lists the J-V characteristics for a set of solar cells made under 200 mTorr. Since under high pressure, the plasma is easy to sustain, we started with low power. It appears that all the cells show high V_{oc} for the H_2 dilution range. From previous experience, we know that under a given pressure, high microwave power and high substrate temperature promote microcrystalline formation. The next experiment was to investigate whether we can deposit μc-Si:H under 200 mTorr with high microwave power. Table VI summaries the performance of solar cells made with different microwave powers but with the same gas flow rates. It shows that high power is needed to make the amorphous/microcrystalline transition. However, at our current stage, we have not obtained promising results to the high-pressure regime.

Table V. J-V characteristics of a series of μc-Si:H solar cells made under 200 mTorr with 300 W of microwave power and various H_2 and SiH_4 flow rates.

Sample #	H_2 (sccm)	SiH_4 (sccm)	Eff (%)	J_{sc} (mW/cm^2)	V_{oc} (V)	FF
7751	150	50	1.4	4.2	0.707	0.465
7752	150	30	2.4	5.3	0.840	0.535
7753	150	20	2.6	5.7	0.860	0.521
7813	160	15	3.6	5.8	0.911	0.668

Table VI. J-V characteristics of a series of μc-Si:H solar cells made under 200 mTorr with different microwave powers. The gas flow rates were 160 sccm of H_2 and 15 sccm of SiH_4.

Sample #	Power (W)	Eff (%)	J_{sc} (mW/cm^2)	V_{oc} (V)	FF
7818	700	4.0	11.0	0.773	0.470
7752	800	3.6	10.8	0.681	0.489
7753	900	2.9	10.6	0.519	0.533
7813	1000	3.1	11.1	0.527	0.524

5. Effects of SiF_4 on μc-Si:H solar cells

Hydrogen dilution ratio is a very important parameter to control the amorphous to microcrystalline transition. However, many mechanisms are involved in microcrystalline formation when high hydrogen dilution is used [7-9]; among them, one explanation is the etching effect. Atomic hydrogen etches the weakly bonded amorphous structures away and leaves the strongly bonded crystalline structures on the growing surface. It is well known that fluorine-containing gases have a stronger etching effect than atomic hydrogen. In addition, fluorine forms stronger chemical bonds with silicon than hydrogen with silicon. The strong Si-F bonds may have a positive effect on grain boundary passivation. Based on this analysis, we tried to introduce SiF_4 in the microwave plasma for μc-Si:H solar cell deposition. Table VII lists a series of μc-Si:H solar cells made under various conditions with different SiF_4 flow rates. From sample 7951 to sample 7955, we found that the materials with SiF_4 become amorphous as indicated by the increased V_{oc} and reduced J_{sc}. This result is very surprising to us because we thought that fluorine would help in forming microcrystalline due to its strong etching effect. We tried to start from a baseline with more microcrystalline volume fraction by increasing the substrate temperature to 350 ºC (sample 7865). We added small amounts of SiF_4 between 0.5 to 5 sccm. One can see that even a small amount of SiF_4 (0.5 sccm) has reduced J_{sc} significantly. We also investigated different deposition conditions and found that a small amount of SiF_4 always deteriorates the μc-Si:H solar cell performance significantly by reducing J_{sc}. The reason for the negative effect of SiF_4 in μc-Si:H solar cells is not clear at this moment. Further studies on the material properties will help to understand this mystery.

Table VII. J-V characteristics of μc-Si:H single-junction solar cells made using microwave glow discharge with mixtures of SiH_4, SiF_4, and H_2 under various conditions. The bolded data are for the cells without SiF_4.

Sample No	Eff (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	$H_2/SiH_4/SiF_4$ (sccm)	Ts (°C)	Press (mTorr)	Time (min)
7951	**2.3**	**15.6**	**0.400**	**0.366**	**50/50/0**	**300**	**22**	**5**
7953	1.3	6.4	0.772	0.271	50/50/5	300	22	5
7954	1.5	6.4	0.770	0.294	50/50/10	300	22	5
7955	2.1	6.3	0.877	0.382	50/50/15	300	22	5
7956	**2.6**	**15.1**	**0.379**	**0.450**	**50/50/0**	**350**	**22**	**5**
7962	0.5	2.8	0.539	0.339	50/50/5	350	22	5
7970	0.5	4.0	0.394	0.318	50/50/0.5	350	22	5
7971	0.3	1.4	0.520	0.384	50/50/1	350	22	5
7972	**2.0**	**14.8**	**0.363**	**0.364**	**50/50/0**	**350**	**22**	**5**
7968	0.3	1.4	0.518	0.427	50/50/5	350	12	5
7975	**2.9**	**14.4**	**0.364**	**0.561**	**50/50/0**	**350**	**12**	**5**
7969	0.2	0.9	0.556	0.419	50/50/5	350	15	5
7976	**2.9**	**15.1**	**0.354**	**0.539**	**50/50/0**	**350**	**15**	**5**

6. Optimization of the cell structure

The solar cell performance not only depends on the material quality, but also on the device structure, especially at the interface. It is well known that crystal grows starting from an amorphous incubation layer. In an *nip* solar cell, the incubation layer is on top of the *n* layer. If the incubation layer is too thick, it will affect the carrier transport. Since the deposition rate is very high for microwave glow discharge, the transition from an amorphous incubation layer to a fully microcrystalline phase could not be very sharp. In this case, the cell performance is strongly limited by the interface. Experimentally, we found that if the intrinsic μc-Si:H layer is directly deposited onto an a-Si:H *n* layer, the cell shows a crossover between the dark *J-V* and the light *J-V* curves as shown in Fig. 5(a). We then developed a recipe for an *n* type μc-Si:H layer. Fig. 5(b) shows the *J-V* characteristics of a μc-Si:H solar cell deposited using the same *i* and *p* layers as the cell shown in Fig. 5(a) except for a μc-Si:H *n* layer. The *J-V* curves do not crossover, and the FF is significantly improved. The μc-Si:H *n* layer can be considered as a seed layer for intrinsic μc-Si:H growth, which leads to a good interface between the *n* and *i* layers. We also found that a slow rate intrinsic μc-Si:H buffer layer deposited using RF glow discharge has the same effect as a seed layer and can improve the FF significantly.

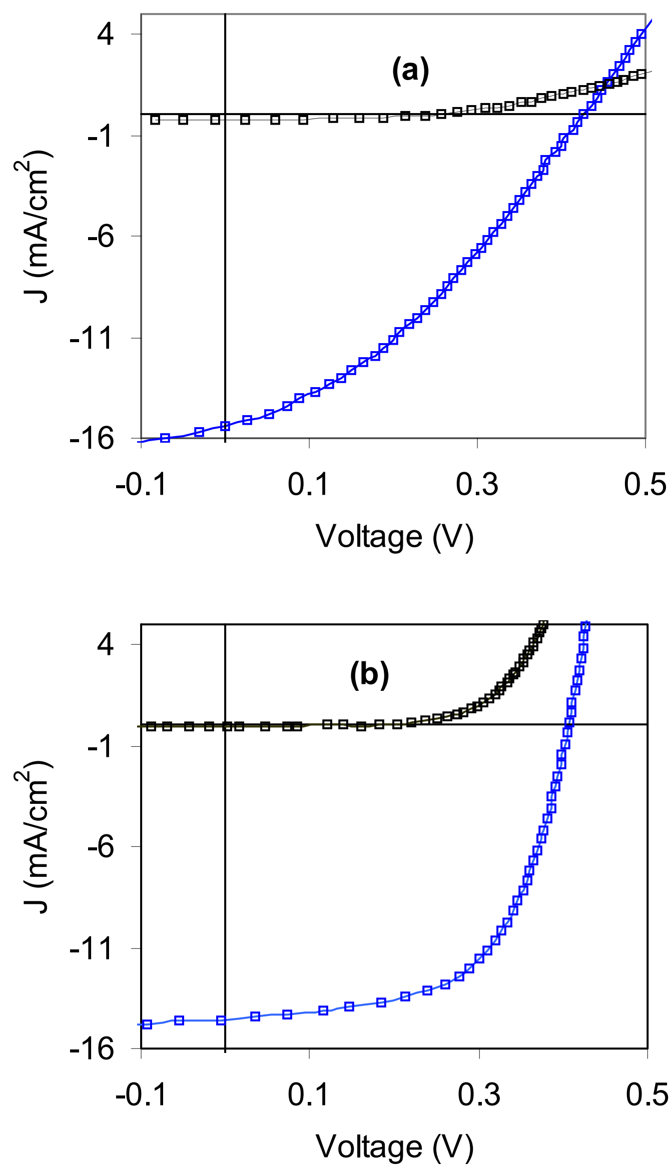

Figure 5. *J-V* characteristics of μc-Si:H solar cells with (a) an a-Si:H *n* layer and with (b) a μc-Si:H *n* layer. The *i* and *p* layers were deposited using the same conditions for the two cells.

7. Material characterization

Introduction

Compared to low rate μc-Si:H solar cells deposited using RF and MVHF glow discharge, high rate μc-Si:H solar cells made using microwave glow discharge show low J_{sc} as shown in the previous sections. In order to get a better understanding of the material quality, we measured a few samples using XRD, Raman and SAXS to study the crystal structure and microvoid density. One possibility for the poor performance of the high rate microwave deposited μc-Si:H solar cell could be the impurity diffusion after deposition, especially during the ITO deposition.

Microcrystal Structure

A 0.9 μm thick μc-Si:H film was deposited on Al foil using microwave glow discharge using the conditions for making the intrinsic layer of a μc-Si:H solar cell. The sample was sent to Colorado School of Mines for XRD and SAXS measurements. As a comparison, one RF low-rate sample and one MVHF medium rate sample were also measured. Figure 6 shows the XRD spectra for the three samples. The strong peaks at 38° and 44-45° are due to the Al foil substrate and the stainless-steel sample holder. A relatively low intensity of the microcrystal peaks, especially the (220) peak, from the microwave deposited film indicates a low microcrystal volume fraction. Table VIII lists the relative peak intensities (normalized to the (111) peak) and grain size estimated from the width of the peaks by the Scherrer equation. The $I_s/I(111)$ is the relative intensity of the shoulder at 27°. Compared to the RF low rate and the MVHF medium rate samples, the microwave high rate μc-Si:H has preferential orientation along (111), where the RF low rate sample was along (220). The MVHF medium rate sample appears to be close to a random distribution. The grain sizes estimated from different peaks on the XRD spectrum are similar for the microwave deposited sample, but significantly increase in the (220) and (311) directions in the RF and MVHF deposited samples. The low J_{sc} in the microwave deposited μc-Si:H solar cells could be due to the smaller grain size and lower microcrystal volume fraction. Significant differences in preferential orientation also appear for the samples deposited using different techniques, but the effect on solar cell performance is not clear at this moment.

Table VIII. Relative peak densities and grain sizes estimated from XRD spectra of the RF, MVHF and microwave deposited μc-Si:H films. A random orientation gives I(220)/I(111)=0.6 and I(311)/I(111)=0.35.

Sample	I_{220}/I_{111}	I_{311}/I_{111}	I_s/I_{111}	L(111) (nm)	L(220) (nm)	L(311) (nm)
μ-wave	**0.28**	**0.21**	**0.12**	**6.0**	**6.1**	**5.4**
MVHF	0.83	0.41	0.10	8.1	10.4	7.7
RF	1.64	0.21	0.35	8.6	25.3	13.2

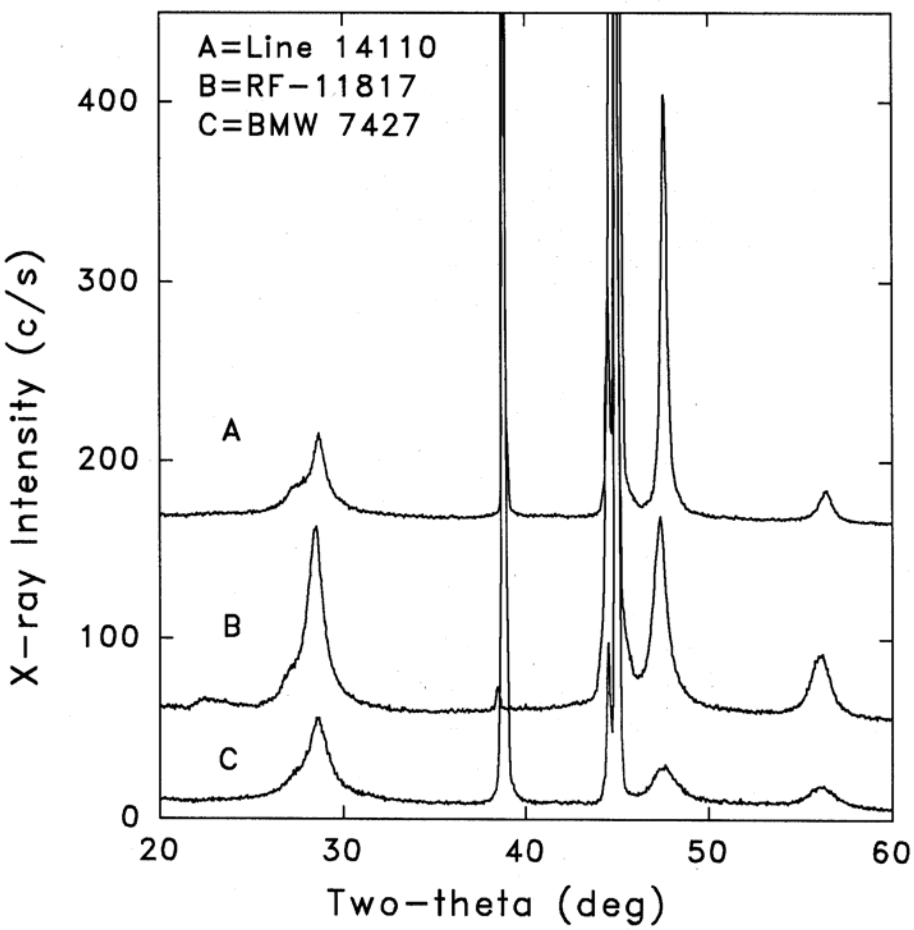

Figure 6. XRD patterns from a RF low rate (A), an MVHF medium rate (B) and a microwave high rate μc-Si:H films.

Microvoid Density

Figure 7 shows the SAXS data from the three films as discussed in the previous section. The intensities from all three samples are higher than those normally obtained from a-Si:H films. The curves show slightly different shapes, indicating different size distributions of scattering objects. Distributions of spheres were used to fit the data and this yields the solid lines through each data set shown in Fig. 7. Each sample was tilted at 45 degrees relative to the X-ray beam and the resulting SAXS is compared to the non-tilted data. Quantitative results are summarized in Table IX. It appears that the SAXS intensity in the high rate microwave deposited sample is higher than the RF and MVHF deposited samples. If the scattering objects are microvoids, the microvoid density is much higher in the microwave deposited μc-Si:H than in those samples deposited using RF and MVHF. A large Q_0/Q_{45} for the RF low rate sample may correlate to the strong (220) orientation observed by XRD spectra as shown in Fig. 6. This result may imply that the microvoids (or other scattering objects) are associated with the grain boundaries. If that is the case, the lower SAXS intensity in the RF low rate μc-Si:H film than in the microwave high rate μc-Si:H film means a better grain boundary in the RF low rate sample. In addition, the microwave high rate μc-Si:H film has the lowest flotation density as shown in Table IX, which is associated with the highest hydrogen contents as shown in Table X.

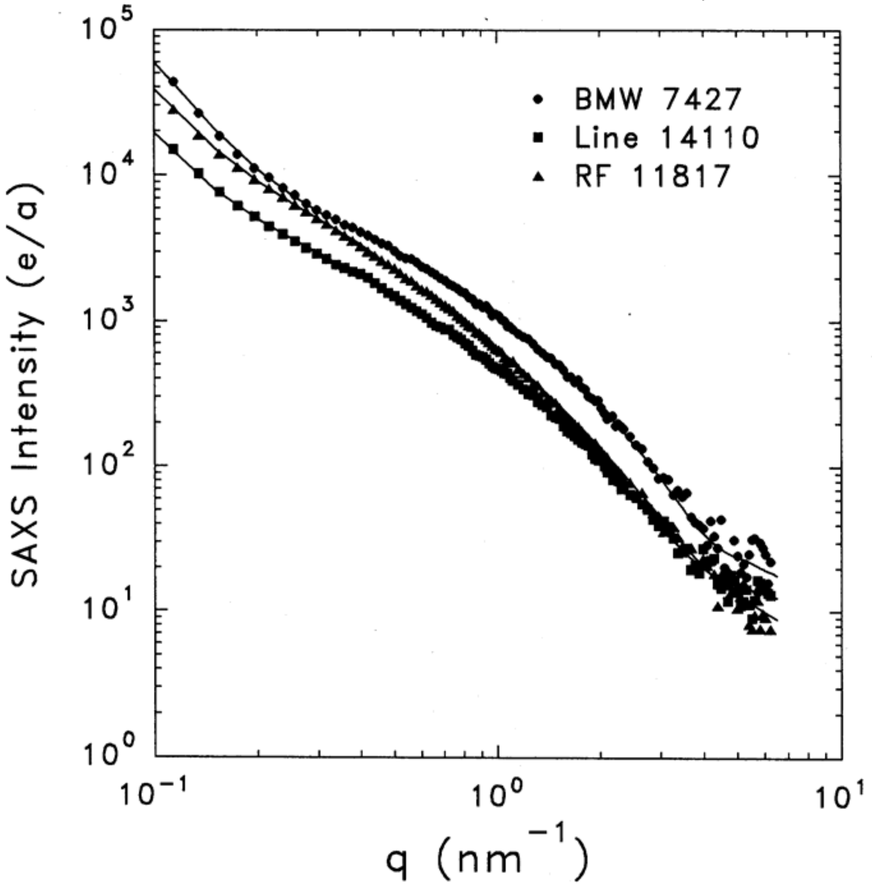

Figure 7. SAXS spectra of a high rate microwave deposited μc-Si:H film (BMW7427), a medium rate MVHF deposited μc-Si:H film (RF11817), and a low rate RF deposited μc-Si:H film (LINE14110).

Table IX. Parameters for fitting the SAXS spectra in Fig. 7, where t is the thickness, Q_T the total integrated SAXS intensity, A_p the Porod slope at low q, I_{diff} the angle-independent scattering intensity, <D> the average sphere diameter, Q_0/Q_{45} the ratio of total integrated intensities with sample in non-tilted and 45^o-tilted orientations relative to x-ray beam, f_{max} the maximum void fraction, and ρ_{flot} the flotation density of film removed from Al-foil substrate.

Sample	t (μm)	Q_T (10^{24} eu/cm^3)	A_p (eu/nm^3)	I_{diff} (eu)	<D> (nm)	Q_0/Q_{45}	f_{max} (vol.%)	ρ_{flot} (g/cm^3)
μ-wave	0.9	7.54	55	12	3.1	1.7	3.1	2.227
MVHF	1.8	4.89	33	7	4.1	3.2	1.2	2.250
RF	1.2	3.19	16	10	3.8	3.7	0.7	2.235

Table X. Hydrogen contents in a-Si:H layers deposited by different techniques at various rate. The data were obtained by SIMS analysis.

Sample	H in a-Si:H (atoms/cm^3)	H in μc-Si:H (atoms/cm^3)		
		high	low	average
μ-wave	**5.1×10^{21}**	**4.8×10^{21}**	**4.0×10^{21}**	**4.4×10^{21}**
MVHF	6.2×10^{21}	3.6×10^{21}	2.2×10^{21}	2.9×10^{21}
RF	7.7×10^{21}	3.4×10^{21}	2.8×10^{21}	3.1×10^{21}

8. Optimized μc-Si:H single-junction and a-Si:H/μc-Si:H double-junction solar cells made with microwave glow discharge at high rates

μc-Si:H single-junction solar cell

We have concentrated on the optimization of microwave glow discharge parameters to search for the best conditions for μc-Si:H solar cell deposition. To date, we have achieved an active-area efficiency of 4.9% at a deposition rate of over 30 Å/s. The J-V characteristics and quantum efficiency are shown in Fig. 8. Compared to the MVHF deposited μc-Si:H solar cells, the microwave μc-Si:H solar cells have low J_{sc}. We have tried to increase the thickness of the intrinsic layer, but did not obtain higher J_{sc}. We speculate that the crystal volume fraction in the microwave deposited material is too low to achieve high J_{sc}. X-ray diffraction measurements confirmed this speculation. When we increase the microcrystalline volume fraction, the material becomes porous and suffers post-oxidization.

a-Si:H/μc-Si:H double-junction solar cells

We have used the optimized μc-Si:H single-junction cell in an a-Si:H/μc-Si:H double-junction structure. The a-Si:H top cell was deposited using RF glow discharge at a low rate and the μc-Si:H bottom cell was deposited using microwave at a high deposition rate ~ 30 Å/s. The solar cell performance was measured under AM1.5 illumination at 25 ºC. Figure 9 shows the J-V characteristics of the best a-Si:H/μc-Si:H double-junction solar cell made up to date, which has an initial active-area efficiency of 7.2%. Compared to RF low rate and MVHF medium rate cells, the microwave high rate a-Si:H/μc-Si:H double-junction solar cell showed poorer performance. All three characteristic parameters (J_{sc}, V_{oc} and FF) need to be improved. Although the current is strongly top-cell limited, the FF is still low, which could be due to the low FF of the μc-Si:H bottom cell.

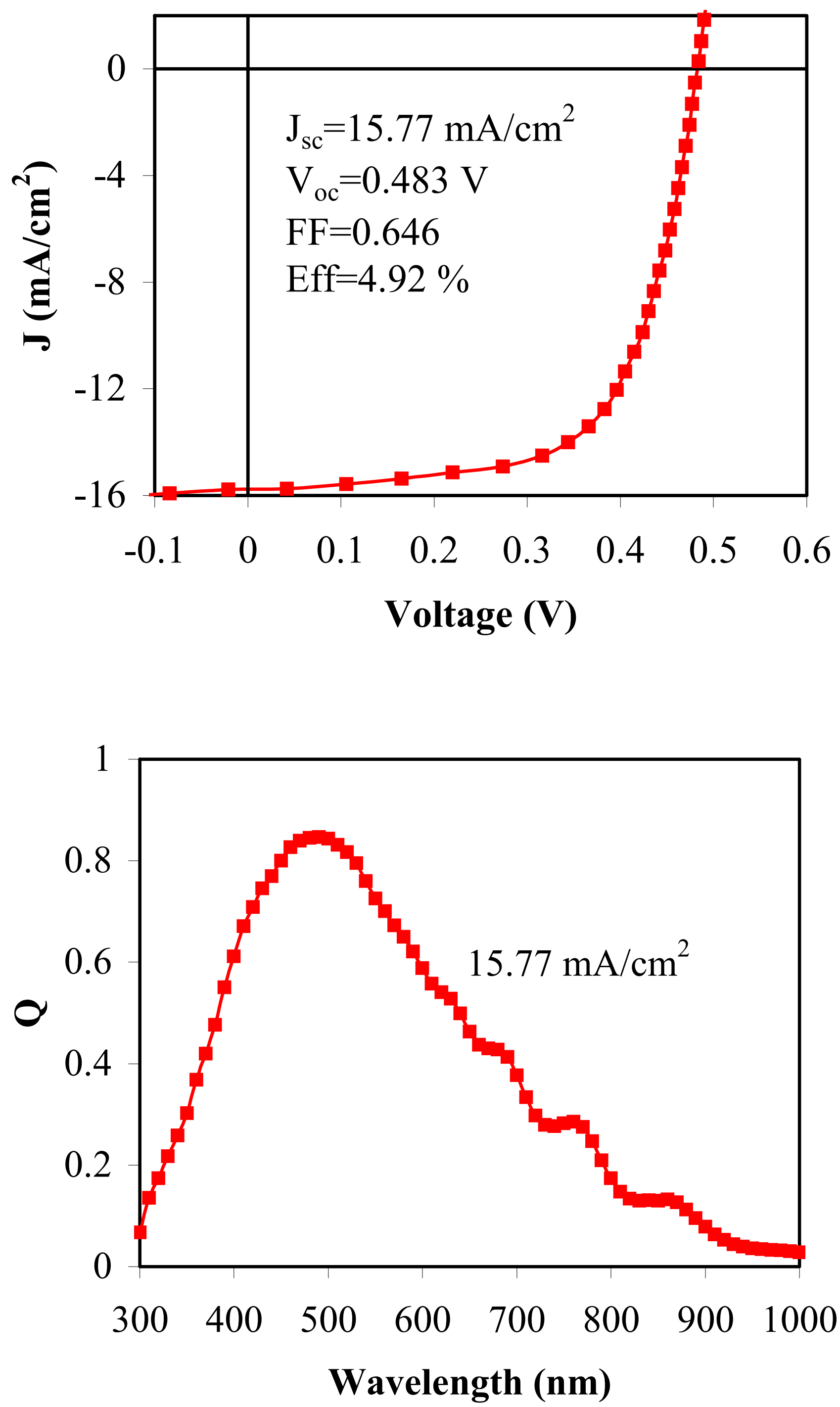

Figure 8. J-V characteristics and quantum efficiency of a microwave glow discharge deposited μc-Si:H solar cell.

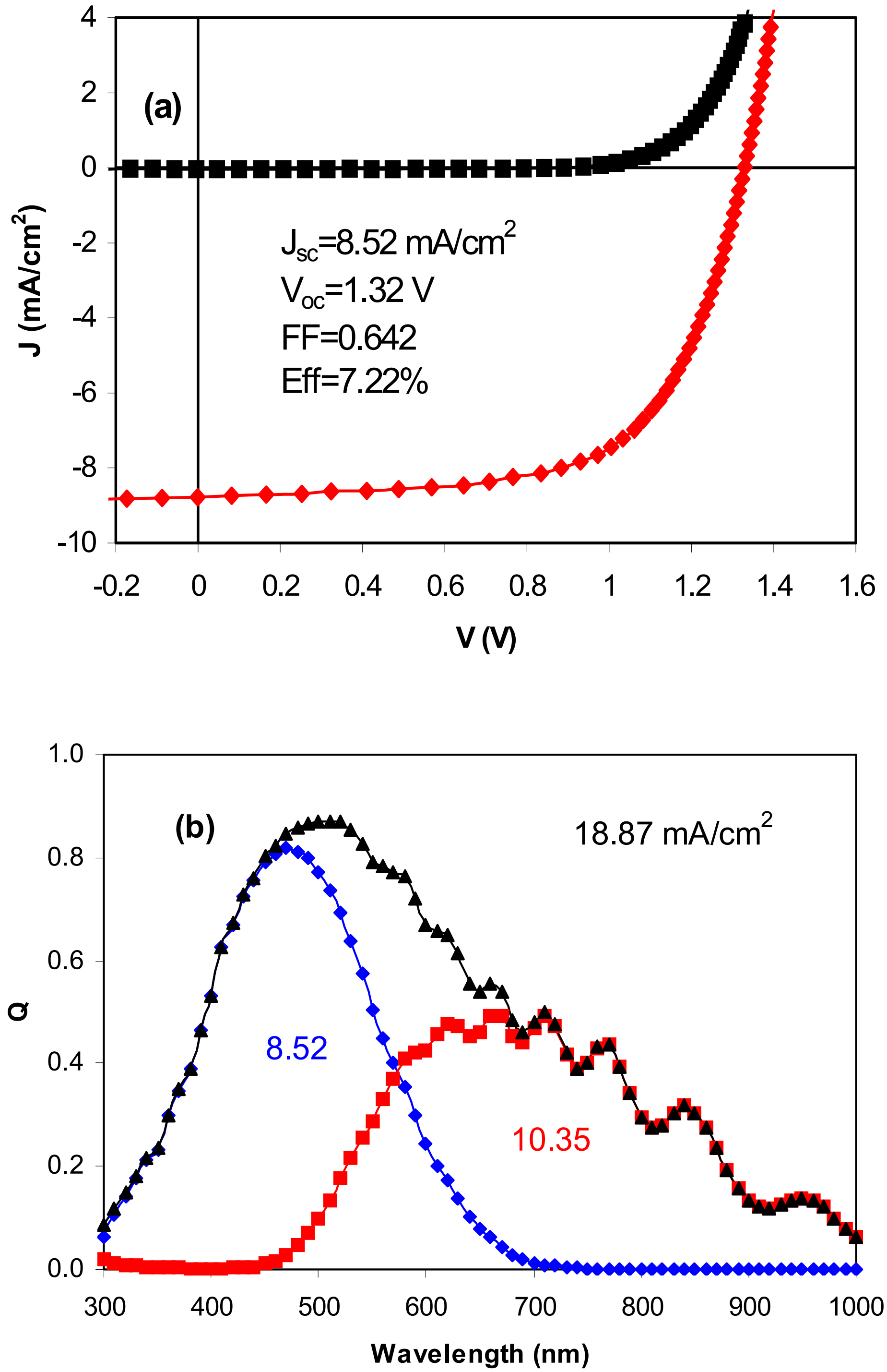

Figure 9. J-V characteristics and quantum efficiency of an a-Si:H/μc-Si:H double-junction solar cell, where the μc-Si:H bottom cell was made using microwave glow discharge for 210 seconds.

9. Summary

We have used a microwave glow discharge system to deposit μc-Si:H solar cells at high deposition rates. We searched for the optimized condition for μc-Si:H solar cell efficiency. The parameters explored include H_2, Ar and Ne dilution, pressure, substrate temperature, and microwave power. We used SiF_4 for additional etching to promote microcrystalline formation. We also optimized the cell structure and controlled the interface between the doped layers and the intrinsic layer.

The material properties were studied using X-Ray diffraction, Raman, and small angle X-ray scattering. We compared the results to the μc-Si:H films deposited using RF and MVHF and found that the microwave deposited μc-Si:H has a preferential growth direction along (111), which is different from the (220) preferential direction of RF and MVHF deposited μc-Si:H films. We believe that the high-energy ion bombardment resulted in discontinuous growth of grains and suppressed the (220) preferential orientation. SAXS measurements find that the microwave deposited μc-Si:H film has a high microvoid density up to 3% in volume, which is significantly higher than those in the RF and MVHF deposited μc-Si films (around 0.5% in volume).

We have achieved a μc-Si single-junction cell having an initial active-area efficiency of 4.92%, where the intrinsic μc-Si:H layer was deposited in 210 seconds corresponding to about 30 Å/sec. Using this recipe in the bottom cell of an a-Si/μc-Si double-junction structure, we have obtained an initial active-area efficiency of 7.2% with J_{sc}=8.52 mA/cm^2, V_{oc}=1.32 V, and FF=0.642.

We conclude that microwave plasma can deposit μc-Si:H solar cells at very high rates ~20-30 Å/s. The material quality and solar cell performance are not as good as those deposited using RF and MVHF glow discharge techniques. The main differences between the microwave plasma deposited μc-Si:H and those deposited with RF and MVHF are (111) orientation instead of (220) orientation based on XRD and high microvoid density based on SAXS measurements.

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. **REPORT DATE** *(DD-MM-YYYY)*	2. **REPORT TYPE**	3. **DATES COVERED** *(From - To)*
August 2005	Subcontract Report	1 July 2001–31 August 2004

4. TITLE AND SUBTITLE
Microcrystalline Silicon Solar Cells: Final Technical Progress Report, 1 July 2001 – 31 August 2004

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S. Guha and J. Yang

5d. PROJECT NUMBER
NREL/SR-520-38355

5e. TASK NUMBER
PVA52201

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
United Solar Ovonic Corporation
Troy, Michigan

8. PERFORMING ORGANIZATION REPORT NUMBER
NCQ-1-30619-04

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/SR-520-38355

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES
NREL Technical Monitor: R. Matson

14. ABSTRACT *(Maximum 200 Words)*
The objective of the research under this subcontract is to explore, identify, evaluate, and develop non-conventional photovoltaic technologies capable of making a breakthrough in the production of low-cost electricity from sunlight. The specific objectives are to 1) develop microwave glow-discharge parameters for the deposition of high-quality microcrystalline silicon (μc-Si:H) thin films at high rate, 2) characterize this microcrystalline material, and 3) fabricate high-efficiency microcrystalline *nip* solar cells.

15. SUBJECT TERMS
PV; microcrystalline silicon; solar cells; low-cost electricity; microwave glow-discharge parameters; thin film; high efficiency; hydrogen dilution

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
Unclassified	Unclassified	Unclassified	UL		19b. TELEPONE NUMBER (*Include area code*)

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

F1146-E(05/2004)