

Preparation and Characterization of Micro-Crystalline Hydrogenated Silicon Carbide p-Layers

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Abstract. We present initial results of a study whose goal is to develop a process leading to SiC p-layers compatible with a superstrate p-i-n cell structure, deposited in an RF PECVD system. Experimental variables were dopant gas, CH₄ and H₂ gas flows normalized to the sum of SiH₄ and CH₄ flows, and the power. Compared to B₂H₆, doping with B(CH₃)₃ lowered the conductivity by a factor of 40 and reduced the fraction of crystallinity from 87% to 53%. The c-Si fraction decreased strongly with increasing CH₄ flow. No evidence of Si-C bonding was identified in the Raman spectra of these samples. Finally, it has been demonstrated that high conductivity p-layers (>1 S/cm) having high c-Si volume fraction (~85%) can be deposited on glass at low power density (84 mW/cm²) which is compatible with deposition on TCO substrates for device fabrication.

INTRODUCTION

The p-layer is critical to a-Si solar cell performance since the p-i junction is the dominant junction in the p-i-n solar cell (1). One of the most significant developments in a-Si solar cell technology was the incorporation of C in the a-Si p-layer by the group at Osaka University in the early 1980's (2). The a-Si:C p-layer leads to increased quantum efficiency (QE) at short wavelengths due to its higher transmission and to increased open circuit voltage (V_{oc}) due to increased built-in voltage (V_B). Considerable effort has been made in the past 15 years to improve the a-Si:C p-layer properties (3).

Alternatively, there has been considerable effort focused on changing the structure of the p-layer from amorphous to "microcrystalline" (μc). These μc layers are typically inhomogeneous with a mix of a-Si or a-Si:C with c-Si crystallites of several tens of nanometers. The grain size, fraction crystallinity, and conductivity depend strongly on extrinsic variables such as the thickness and substrate (4,5). Independent of deposition method or substrate, it is found that increased hydrogen dilution ($H_2/SiH_4 \sim 100-200$) and RF power are required to produce μc films.

Microcrystalline p-layers have been incorporated into superstrate (6) and substrate (7) type of solar cells without substantially improving device performance. The problem

lies first on the two phase nature of these p-layers resulting in devices having two p-i junctions in parallel. In addition, c-Si has lower bandgap than what one would like to see in a window layer. The challenge regarding μc p-layers is to develop a process that results in single phase SiC films of high conductivity which is compatible with deposition on transparent conductive oxides (TCO).

Several groups have attempted to deposit μc -SiC using conditions based on those giving μc -Si p-layers. Growth of SiC films by standard RF PECVD(8,9), photo-CVD (10) and ECR CVD (11, 12) has been investigated. With the exception of reference 12 where a mixture of c-Si and c-SiC was obtained, all other groups report that their films consist of c-Si crystallites surrounded by a-Si:C material; i.e., they found no evidence of SiC structure.

In this paper, we present initial results of a study whose goal is to develop a process leading to SiC p-layers compatible with a superstrate p-i-n cell structure, deposited in an RF PECVD system.

EXPERIMENTAL PROCEDURE

Films were deposited in an RF(13.56 MHz) PECVD system having an electrode area of 119 cm^2 , on 7059 glass substrates from mixtures of SiH_4 , CH_4 , H_2 with B_2H_6 and $\text{B}(\text{CH}_3)_3$ (TMB) as dopant gases. Total pressure and substrate temperatures were kept constant at 1 Torr and 175°C respectively. Experimental variables were dopant gas, CH_4 and H_2 gas flows normalized to the sum of SiH_4 and CH_4 flows, and the power.

Co-planar conductivity vs. temperature, optical spectrophotometry and micro-Raman spectroscopy were used to determine optoelectronic properties and the structure of the films. Structurally, the films were characterized by their crystalline volume fraction, X_c , computed by the formula (13, 14),

$$X_c = I_{c\text{-Si}} / (I_{c\text{-Si}} + 0.9 \times I_{a\text{-Si}})$$

where the intensities are the integrated intensities of the TO bands obtained from the baseline corrected deconvolution of the Raman spectrum as illustrated in Figure 1 for a film consisting of a-Si and c-Si phases.

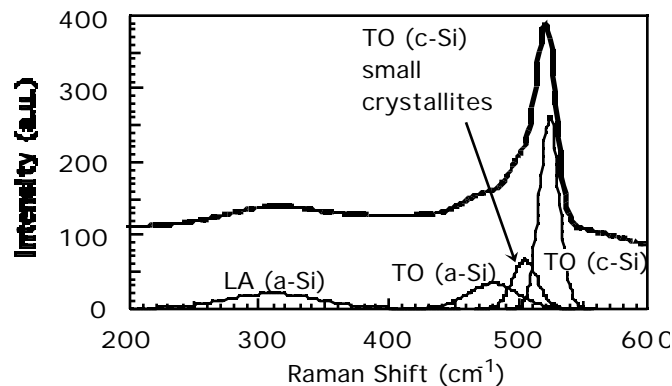


Figure 1. Raman spectrum of a typical a-Si/c-Si films deconvoluted to its gaussian components.

RESULTS

Comparing Effects of B_2H_6 and $B(CH_3)_3$

The p-layers were deposited under conditions previously determined to yield high conductivity μ -Si n-layers. These layers were deposited without any CH_4 to compare the doping effectiveness of B_2H_6 and $B(CH_3)_3$. Table 1 gives the conditions and critical material parameters where E_a is the activation energy and σ_d the dark conductivity. Since B_2H_6 has twice as many B atoms per unit volume compared to $B(CH_3)_3$, the normalized flow values listed under B_2H_6 are twice the actual flow. This way normalized flow values, in either case, represent B atom delivery into the reaction zone.

TABLE 1. Deposition conditions and characteristics of μ -Si films with different doping gases.

Normalized Flow			Power (W)	Thickness (μ m)	E_a (eV)	σ_d (S/cm)	X_c (%)
B_2H_6	TMB	H_2					
0		100	50	0.11	0.38	5×10^{-6}	85
0.02		100	50	0.20	0.04	1.2	87
0.03		100	50	0.24	0.03	1.3	52
	0.01	100	50	0.17	0.11	0.02	71
	0.02	100	50	0.18	0.07	0.03	53

Compared to B_2H_6 , doping with $B(CH_3)_3$ lowered the conductivity by a factor of 40, increased the activation energy by 0.03 eV, and reduced the fraction of crystallinity from 87% to 53%. The much greater amorphous component for the film doped with $B(CH_3)_3$ may be due to C containing species in the gas phase suppressing nucleation as is reported for CH_4 (8). We note that only one group reports high conductivity μ -Si layers with $B(CH_3)_3$ dopant (5). All other groups use either B_2H_6 or BF_3 . In view of the fact that TMB suppresses crystallinity more than B_2H_6 , for the rest of the present investigation only B_2H_6 was used as the dopant source.

Effect of CH_4 on Crystallinity

In order to determine the effect of CH_4 on the crystallinity of the films a series of undoped films were deposited at different normalized CH_4 flow keeping all other parameters constant, including SiH_4 partial pressure P_s . Again, these deposition parameters are the ones that yielded high crystalline fraction for non-carbon containing films. Table 2 gives the deposition conditions and critical material parameters of the films. The data indicates the steep decline of the c-Si fraction with the increasing amount of CH_4 in the gas phase.

TABLE 2. Deposition conditions and characteristics of films with different normalized CH_4 flows.

Normalized Flow		Power (W)	P_s (mT)	Thickness (μ m)	E_a (eV)	σ_d (S/cm)	X_c (%)
CH_4	H_2						
0	100	50	9.9	0.11	0.38	5×10^{-6}	85
0.33	100	50	9.9	0.33	0.67	3×10^{-10}	38
0.43	100	50	9.8	0.34	0.75	2.5×10^{-12}	0
0.5	100	50	9.8	0.36	0.82	2.1×10^{-13}	3

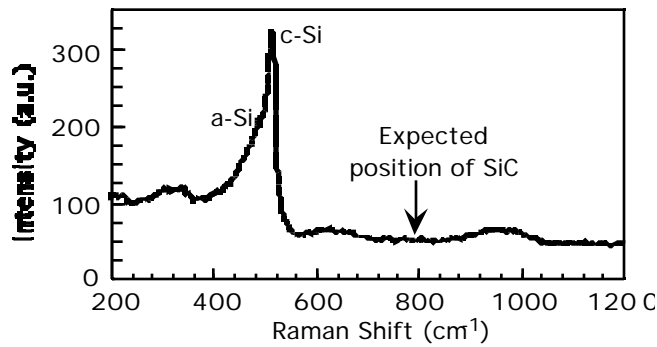


Figure 2. Raman spectrum of a μ c-Si film deposited with CH_4 normalized flow of 0.33.

Raman spectra of these films showed only the presence of c-Si and a-Si phases, as can be seen in a typical spectrum in Figure 2. No carbon containing species, such as SiC, were identified in these samples. This observation leads us to conclude that all the carbon in the film is located within the amorphous phase.

Effect of Hydrogen Dilution

The effect of H_2 dilution on the properties of the B-doped C containing films were investigated in a series of runs where normalized H_2 flow was progressively increased. During these runs normalized flows of CH_4 , B_2H_6 and power were kept constant at 0.33, 0.02 and 50 W levels. Analysis of the Raman spectra of the films showed, as before, the presence of c-Si and a-Si phases only. The change of c-Si volume fraction in the films as a function normalized H_2 flow is plotted in Figure 3 along with the variation of the SiH_4 partial pressure. The crystalline fraction increases strongly with H_2 dilution while SiH_4 partial pressure decreases, as would be expected. At the present time it was not possible to decouple H_2 dilution and SiH_4 partial pressure in our reactor. Therefore, even though a large increase in the c-Si volume fraction accompanies increases in the H_2 dilution, this variation cannot uniquely ascribe to H_2 dilution alone because of the significant variation in the SiH_4 partial pressure.

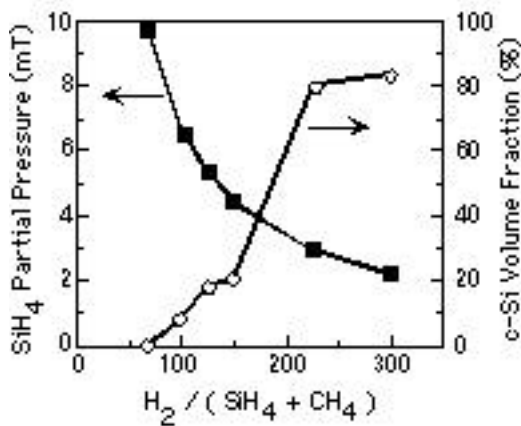


Figure 3. Variation of c-Si fraction and SiH_4 partial pressure with H_2 dilution.

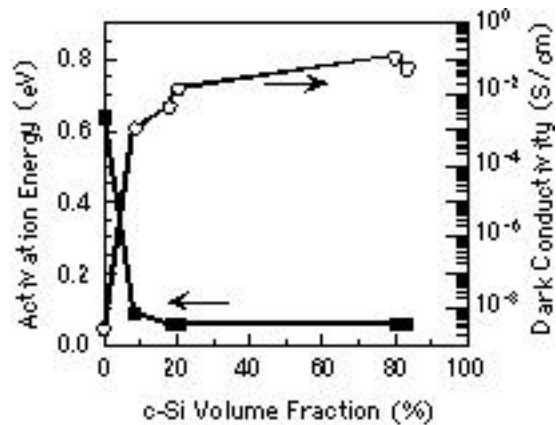


Figure 4. Conductivity and activation energy as a function of c-Si fraction.

Room temperature in-plane conductivity and the activation energy of the films as a function of the c-Si volume fraction are shown in Figure 4. The data indicates that c-Si regions begin to form a connected network at a volume fraction less than 10% and control in-plane electrical transport thereafter.

Effect of RF Power

The effect of RF power was investigated in the range of 10 to 50W, corresponding to power density range from 84 to 420 mW/cm². For this set of experiments normalized flows of H₂, CH₄, B₂H₆ and SiH₄ partial pressure were kept constant at 300, 0.33, 0.02 and 2.2 mT levels. Raman spectra showed that, as before, only c-Si and a-Si phases are present in the films. The activation energies were measured to be around 0.05 eV for all the films, which indicates that in-plane c-Si phase controls in-plane electrical transport.

Figure 5, where room temperature dark conductivity and the c-Si volume fraction is plotted against discharge power, shows that for SiH₄ partial pressure of 2.2 mT, crystallinity is independent of power while conductivity decreases with increasing power. This decrease in conductivity cannot be explained with the available data.

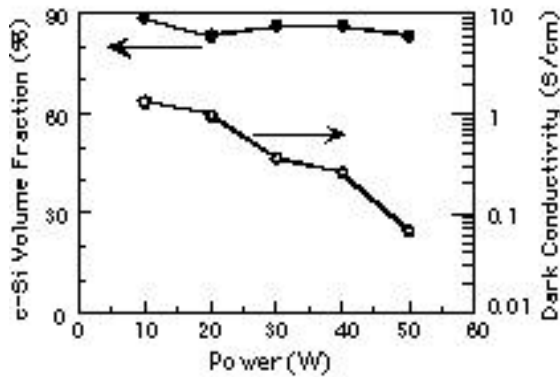


Figure 5. c-Si volume fraction and dark conductivity as a function of discharge power.

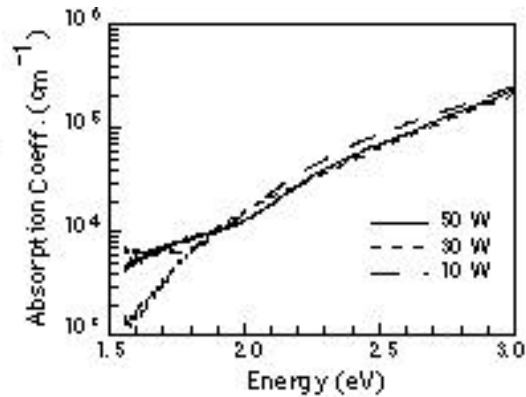


Figure 6. Absorption coefficient as a function of energy at three different discharge power levels.

Optical analysis of the films are displayed in Figure 6 in the form of absorption coefficient vs. energy. Within experimental errors absorption at high energies is independent of power, suggesting that the amount of carbon in the amorphous phase is also independent of the discharge power.

CONCLUSIONS

It has been demonstrated that high conductivity p-layers having high c-Si volume fraction (>85%) can be deposited on glass at low power density (84 mW/cm²) which is compatible with deposition on TCO substrates for device fabrication.

Proper and quantitative interpretation of H₂ dilution experiments requires depositions under constant SiH₄ partial pressure.

For normalized CH₄ flow of 0.5 microcrystalline films consist of c-Si and carbon containing a-Si phases.

It has been shown also that at low SiH₄ partial pressures c-Si volume fraction and optical absorption are independent of discharge power.

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