Vol 17 No 4, April 2008
1674-1056/2008/17(04)/1394-06

Chinese Physics B

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Effects of deposition pressure and plasma power on the growth and properties of boron-doped microcrystalline silicon films*

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(Received 17 October 2007; revised manuscript received 21 November 2007)

Using diborane as doping gas, p-doped μc-Si:H layers are deposited by using the plasma enhanced chemical vapour deposition (PECVD) technology. The effects of deposition pressure and plasma power on the growth and the properties of μc-Si:H layers are investigated. The results show that the deposition rate, the electrical and the structural properties are all strongly dependent on deposition pressure and plasma power. Boron-doped μc-Si:H films with a dark conductivity as high as $1.42\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$ and a crystallinity of above 50% are obtained. With this p-layer, μc-Si:H solar cells are fabricated. In addition, the mechanism for the effects of deposition pressure and plasma power on the growth and the properties of boron-doped μc-Si:H layers is discussed.

Keywords: boron-doped μc-Si:H films, thin film solar cells, Raman crystallinity, dark conductivity
PACC: 7280N, 7830G, 8115H

1. Introduction

P-doped layers are very important to the performance of silicon thin film solar cells.[1,2] In order to achieve a perfect solar cell performance, high optical transmittance and high conductivity for p-layers are required. A p-doped μc-Si:H layer can be considered to be "good", if its Raman crystallinity is ≥ 0.5 (on ZnO) and the corresponding dark conductivity (σ_{d}) at room temperature (on glass) is above $1\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$ for a thickness of about 20–30 nm. In practice, even thinner μc-Si:H p-doped window layers are used in solar cells, due to the requirement for high transparency. Studies have indicated that boron-doped μc-Si:H films are an attractive alternative in the sense of their high doping efficiency, high electrical conductivity, and low optical absorption. This type of material has now been used in solar cells to improve the photovoltaic performance.[1,3] The effects of hydrogen dilution, diborane (B_2H_6) concentration and substrate temperature on the properties of films have been widely studied.[4−7] However, there is little information about the influence of the deposition pressure and plasma power on the properties of p-doped μc-Si:H layers. We believe that the deposition pressure and the plasma power are also critical parameters in determining the growth and the properties of p-doped μc-Si:H layers, and they are worthy to be studied thoroughly.

In this paper, we present the structural and the electrical properties of boron-doped p-type μc-Si:H films deposited at different deposition pressures and plasma powers. The doped mechanism is also discussed.

2. Experimental details

Boron-doped microcrystalline layers were grown on quartz glass substrates by using the conventional RF PECVD technique (13.56MHz) in a separated chamber of the same cluster tool system using diborane (diluted to 0.1% in H_2) as dopant gas to prepare p-type materials. The silane and the diborane concen-

*Project supported by the State Key Development Program for Basic Research of China (Grant No 2006CB202601), and Basic Research Project of Henan province, China (Grant No 072300410140).
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trations are defined as $C_{Si} = F_{SiH_4}/(F_{SiH_4}+F_{H_2})$ and $C_B = F_{B_2H_6}/F_{SiH_4}$, respectively, where F_{SiH_4}, F_{H_2}, and $F_{B_2H_6}$ represent the flow rates of SiH_4, H_2 and B_2H_6 correspondingly . The thicknesses of the p-doped μc-Si:H films were measured by using a profilometer, and the deposition rate (R_d) was determined by the thickness divided by the deposition time. The p-i-n single junction microcrystalline silicon solar cells were grown on glass substrates coated with SnO_2/ZnO films, and Al layers were evaporated as back contacts. The p-i-n structures were comprised of a 30 nm thick microcrystalline p-layer, a 1μm-thick microcrystalline i-layer, and a 50 nm thick amorphous n-layer. The doped layers were prepared by rf excitation using phosphine (diluted to 0.1% in H_2) as dopant gas, and the intrinsic layer was prepared by using the VHF technique at 75 MHz.The detailed deposition parameters are listed in Table 1.

The dark conductivity (σ_d) was measured at room temperature by using coplanar Al contacts. To study the crystallinity of the films, Raman spectra were measured in a back-scattering configuration by using a Raman spectrometer with a He–Ne laser exciting source. 5.0 mW output power and 632.8 nm wavelength were used in measurement. The crystalline ratio, R_c, was obtained to be[8]

$$R_c = (I_{520} + I_{510})/(I_{520} + I_{510} + I_{480}),$$

where I_{520} and I_{510} are the intensities of crystalline-like peaks whereas I_{480} is the intensity of amorphous-like peak of the transverse optic Si–Si vibrations in the Raman spectra.[9,10] An x-ray diffractometery (XRD) with a Cu$K\alpha$ radiation source was employed to determine the orientations of the crystallites. Scan electron microscopy (SEM) was used to investigate the surface morphology of boron-doped microcrystalline layers. The solar cells were characterized by measuring the current–voltage characteristic under AM 1.5 illumination and the spectral response.

Table 1. The deposition parameters of boron-doped μc-Si:H films and solar cells (p_c, i_c and n_c). T_{sub} is the substrate temperature, P_W is the plasma power, p_d is the deposition pressure, d_{ele} is the electrodes distance and C_P is the PH_3 concentration.

Film style	C_{SiH_4}/%	Total flow/sccm	d_{ele}/cm	T_{sub}/°C	P_W/W	p_d/Pa	C_B/%	C_P/%
p	1	200	2	150	20–130	133	0.5	–
					50	79.8–332.5		
p_c	1	200	2	150	50	239.4	0.5	–
i_c	4	250	1.5	200	140	305.9	–	–
n_c	1	200	2	170	50	133	–	0.8

3. Results and discussion

3.1. The effect of plasma power

Figure 1 shows the dependences of Raman crystallinity and dark conductivity on plasma power. R_c increases with the increase of plasma power at first. The maximum crystallinity is about 82% at P_W =90 W. With P_W increasing further, the crystallinity begins to decrease. However, in general, σ_d decreases with P_W increasing. An interesting phenomenon is that σ_d increases suddenly at P_W =90 W. It may be caused by the increasing of Raman crystallinity. It is known that the dark conductivity is determined by carrier concentration and drift mobility. Increasing crystallinity would result in an increase in drift mobility. The detailed analysis is given later.

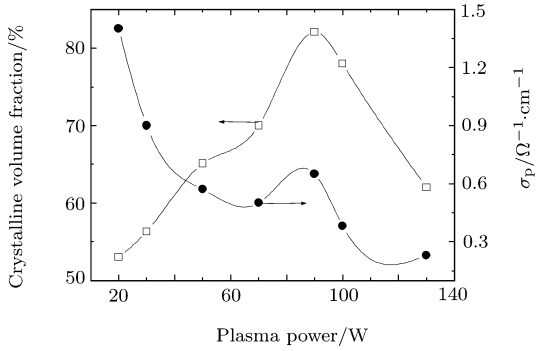


Fig.1. Variation of crystalline volume fraction and dark conductivity with plasma power.

Shown in Fig.2 are the x-ray diffraction spectra of samples prepared at different plasma powers. Three diffraction peaks corresponding to (111), (220) and (311) are observed in all spectra which have a preferential orientation of (111). With P_W increasing, the intensities of these peaks increase first and then decrease, indicating the change of crystallinity in films. The film deposited at P_W=90 W shows the largest intensities and the smallest full width at half-maximum (FWHM) of the diffraction peaks, suggesting that this sample has the highest volume fraction and the largest grain size in the deposited films. Figure 3 shows the SEM surface morphologies of films deposited at different plasma powers. The grain size increases with P_W at first, and the largest grain size is obtained at P_W =90 W. With P_W increasing further, the grain size begins to decrease. The result accords with those from the x-ray spectra and the Raman crystallinity.

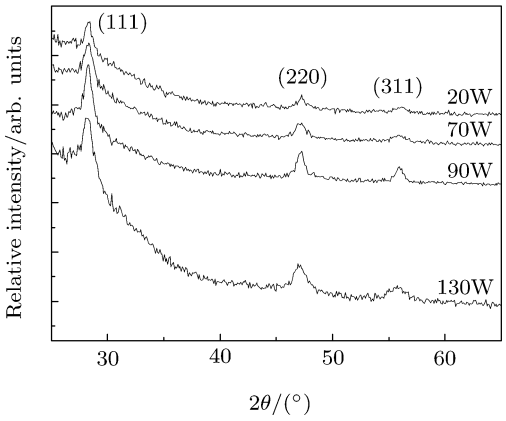


Fig.2. XRD spectra of boron-doped μc-Si:H films at different plasma powers.

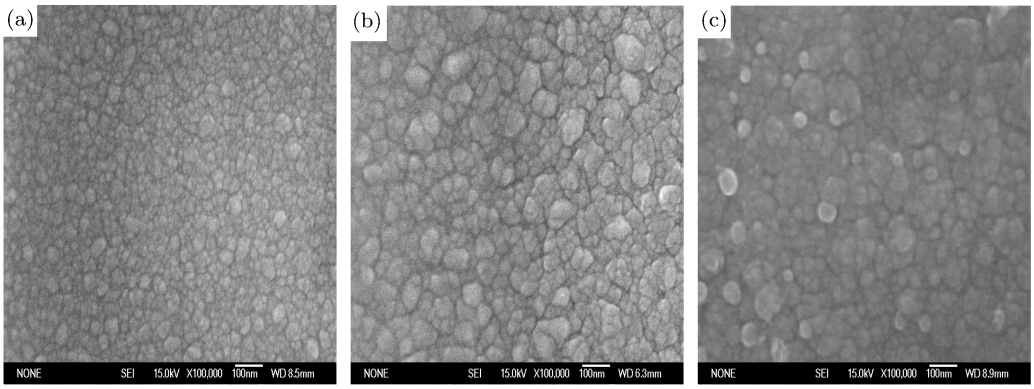


Fig.3. SEM images of thin films at different plasma powers: 20 (a), 90 (b), and 130W (c).

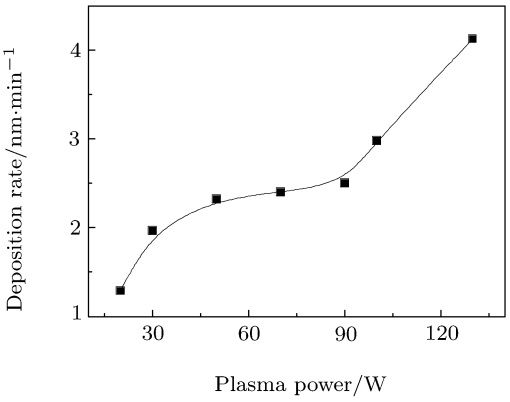


Fig.4. Variation in deposition rate with plasma power.

The dependence of deposition rate on plasma power is shown in Fig.4. R_d increases slightly with P_W at first. However, with P_W increasing up to above 90W, R_d increases rapidly. The increasing of R_d is related to the density of film precursors (such as SiH_3 radicals) and the density of surface dangling bonds that increases with P_W.

3.2. The effect of deposition pressure

Figure 5 shows the variations in crystalline volume fraction and dark conductivity with deposition pressure. With p_d increasing, R_c and σ_d each increase gradually and reach a maximum. As p_d increasing further, R_c and σ_d decrease. An interesting phenomenon is that the variation in R_c with pressure is not fully

consistent with that in σ_d. A maximum σ_d of $1.42\,\Omega^{-1}\cdot cm^{-1}$ is obtained, with p_d being about 2.4×10^2 Pa, while the highest crystalline volume fraction of 65% is obtained at $p_d = 1.3\times10^2$Pa. This result suggests that the electrical properties are determined not only by R_c. Using a p-layer, which was deposited under parameters corresponding to this maximum, σ_d, as a window layer, we fabricated p-i-n single junction microcrystalline silicon solar cells, and obtain a primary efficiency of 5.24 %. The current–voltage characteristic is shown in Fig.6.

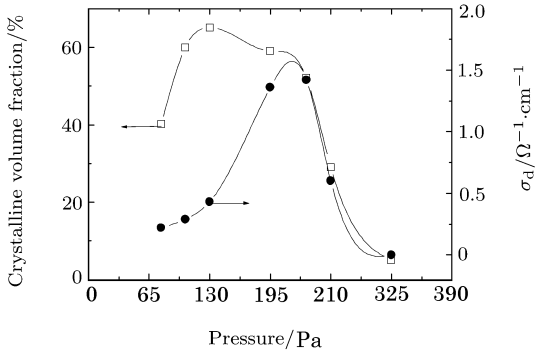


Fig.5. Variations in crystalline volume fraction and dark conductivity of thin films with pressure.

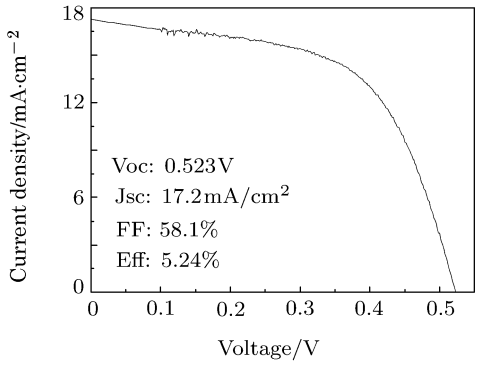


Fig.6. The current–voltage characteristic of single junction microcrystalline silicon solar cells.

Figure 7 shows the x-ray diffraction spectra of boron-doped μc-Si:H films deposited under different pressures. With p_d increasing, the intensities of three peaks increase first and then decrease. The film deposited at $p_d = 1.3\times10^2$Pa shows the largest intensities and the smallest FWHM, indicating that it has the highest crystallinity and the largest grain size in the deposited films. The result accords with that from the Raman spectra. The dependence of deposition rate on pressure is shown in Fig.8. With p_d increasing, the values of R_d increase and reach saturation levels at higher pressures.

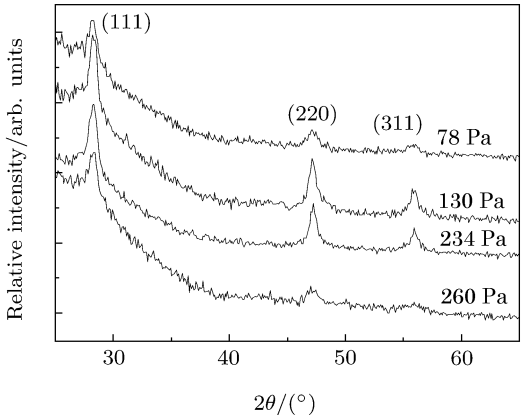


Fig.7. XRD spectra of boron-doped μc-Si:H thin films at different deposition pressures.

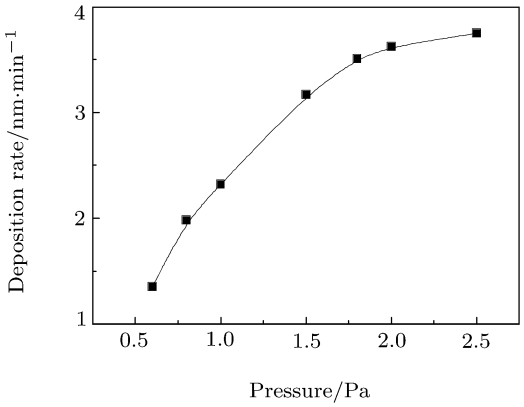


Fig.8. Variation in deposition rate with pressure.

3.3. Discussion

Our experimental results show that the growth rate, the electrical and the structural properties of boron-doped μc-Si:H films are all strongly dependent on P_W and p_d. We propose that the influences of P_W and P_d on the properties result from their influences on the growth process. The growth precursors of μc-Si:H films are generally believed to be SiH_3 radicals,[11−14] which come from the dissociation of the source gas SiH_4 and the abstraction reaction between SiH_4 and H atom in plasma, and the deposition process is influenced by the dangling bonds on the growing surface and the density of SiH_3 radicals that can effectively react with the sites of dangling bonds.

In doping process, boron atoms react with Si grains to form B–Si bonds. Also, B atoms can react with H atoms to form B–H–Si and B–H complexes, in

which boron is passivated by hydrogen, leading to be electrically inactive.[15−18]

At low plasma powers, lots of H atoms produced by electrons impact dissociation are annihilated by SiH_4 molecules.[23] So, the H/SiH_3 ratio in plasma is low, and the surface H-coverage is lower. The SiH_3 radicals coming from the plasma react directly with dangling-bonds, in which there is diffusion so that disordered Si–Si bonds are formed, leading to lower Raman crystallinity. However, the lower H-coverage enhances the formation of B–Si bonds, leading to a higher carrier concentration. Thus, the σ_d is high in film. With P_W increasing, the SiH_3 density, especially the number of H radicals in the plasma increase.[20] So, the surface H-coverage increases, leading to a higher crystallinity and a larger grain size of the material, which in turn enhance the carrier mobility. With surface H-coverage increasing, the surface density of B–H–Si bonds increases, giving rise to a reduction in carrier concentration. So, the enhancement of carrier mobility and the decrease of carrier concentration make σ_d decrease first and then increase with P_W. However, with P_W increasing further, when P_W exceeds 90 W, ions energy increases with P_W, which is detrimental to the quality of μc-Si:H, causing defect formation and deterioration in crystallinity. On the other hand, the increasing of B–H–Si bonds can decrease the Raman crystallinity and the grain size due to the interruption of orderly growth by inserting H atoms. So, R_c, grain size and σ_d decrease. In addition, the deposition rate increases with P_W due to the continuous increasing of SiH_3 density in plasma.

With the increase of P_d, the mean free path for ions decreases due to the increasing of ion collision rate, leading to the decrease in ion energy. So, the film properties are enhanced due to the decrease of ion bombardment on growing surface. R_c and σ_d increase with P_d first. With P_d increasing further, the atomic hydrogen concentration decreases[21,22] So, the ratio of atomic hydrogen flux to the SiH_3 radical flux decreases with the increase of pressure. As a result, the crystalline volume fraction decreases with P_d increasing. On the other hand, the number of surface dangling bonds increases with H/SiH_3 ratio decreasing. Thus, the density of B–Si bonds increases, giving rise to an increase in carrier concentration. σ_d increases continually with P_d. However, when P_d >234Pa, the decrease of atomic hydrogen concentration becomes significant. The surface dangling bond density rapidly increases and SiH_3 radicals coming from plasma react directly with these dangling-bonds, in which there is no diffusion, thereby leading to the sharp decreasing of Raman crystallinity. So, R_c and σ_d decrease together. At a constant level of RF power, a balance between the increase in dissociation rate due to increased silane partial pressure and the decrease of dissociation due to reduced electron temperature is obtained at higher pressures, which restricts the maximum of SiH_3 density. Based on this, saturation in deposition rate is expected to occur at higher pressures.

4. Conclusions

The effects of plasma power and deposition pressure on the growth and the properties of boron-doped μc-Si:H are investigated. The obtained results suggest that the growth rate, the structural and the electrical properties of the samples are all strongly dependent on P_W and P_d. In order to deposit boron-doped μc-Si:H films with higher values of R_c and σ_d, it is very important to decrease ion energy, maintain higher H/SiH_3 ratio in plasma and appropriate H-coverage on surface. Boron-doped μc-Si:H films with a dark conductivity as high as $1.42\,\Omega^{-1}\mathrm{cm}^{-1}$ and a crystallinity of above 50% are deposited in experiment. Using this p-layer, the μc-Si:H solar cells with a primary efficiency of 5.24% are obtained.

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