Vol 18 No 8, August 2009
1674-1056/2009/18(08)/3563-05

Chinese Physics B

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Influence of the total gas flow rate on high rate growth microcrystalline silicon films and solar cells*

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(Received 22 August 2008; revised manuscript received 5 November 2008)

This paper reports that high-rate-deposition of microcrystalline silicon solar cells was performed by very-high-frequency plasma-enhanced chemical vapor deposition. These solar cells, whose intrinsic μc-Si:H layers were prepared by using a different total gas flow rate ($F_{\rm total}$), behave much differently in performance, although their intrinsic layers have similar crystalline volume fraction, opto-electronic properties and a deposition rate of ~ 1.0 nm/s. The influence of $F_{\rm total}$ on the micro-structural properties was analyzed by Raman and Fourier transformed infrared measurements. The results showed that the vertical uniformity and the compact degree of μc-Si:H thin films were improved with increasing $F_{\rm total}$. The variation of the microstructure was regarded as the main reason for the difference of the J–V parameters. Combined with optical emission spectroscopy, we found that the gas temperature plays an important role in determining the microstructure of thin films. With $F_{\rm total}$ of 300 sccm, a conversion efficiency of 8.11% has been obtained for the intrinsic layer deposited at 8.5 Å/s (1 Å=0.1 nm).

Keywords: microcrystalline silicon, high rate, solar cell, total gas flow rate
PACC: 8115H, 8630J, 7360F

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) produced by plasma-enhanced chemical vapor deposition (PECVD) is extensively employed as a stable and narrow-gap photovoltaic material in both single-junction and multi-junction structures.[1−5] However, μc-Si:H solar cells require a thick intrinsic layer ($>$ 1 μm) to absorb a sufficient amount of sunlight, because of its indirect optical transition. Hence, the high rate growth of μc-Si:H is a crucial issue for the low-cost industrialization of solar cells.[6] For this purpose, high power, high pressure and very high plasma excitation frequency have been used.[7−10] However, a high-rate growth of the device-quality for μc-Si:H has been generally difficult because of such problems as ion bombardment and powder formation that are often encountered during the high-rate growth process.[7] In addition, many results also show that not all μc-Si:H films with low defect density and good optoelectronic properties always lead to high efficiency solar cells.[8]

In this study, we also find this inconsistent phenomenon between i-layer properties and cell performance. Additionally, we found that increasing the total gas flow rate ($F_{\rm total}$) was an effective method to eliminate this inconsistent phenomenon. Then, in order to investigate this phenomenon, the influences of $F_{\rm total}$ on the deposition process and micro-structural properties were studied in detail. At last, conversion efficiency of 8.11% has been obtained at 8.5 Å/s with $F_{\rm total}$ of 300 sccm.

2. Experiment

The p, i, and n layers of the μc-Si:H solar cells were deposited in individual chambers of a cluster-tool deposition system[11] by PECVD to form p–i–n single-junction diodes. Figure 1 shows a schematic picture of the deposition chamber. The electrode configuration

*Project supported by the National Basic Research Program of China (Grant Nos 2006CB202602 and 2006CB202603), the Tianjin Assistant Foundation for the National Basic Research Program of China (Grant No 07QTPTJC29500), and the Natural Science Foundation of Tianjin (Grant No 07JCYBJC04000).
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consists of a 12.5×12.5 cm^2 powered electrode and a 12×12 cm^2 substrate carrier in a carrier support as the grounded electrode. Substrate size is 10×10 cm^2. The films were deposited on Eagle 2000 glasses that were etched in HF acid (5%) for 5 minutes.[12] For Fourier transformed infrared (FTIR) studies samples were deposited on a crystalline silicon wafer. Solar cells were deposited on textured SnO_2/ZnO or texture-etched ZnO-coated glass substrates. The solar cell structure was a glass / TCO / p-μc-Si:H / i-μc-Si:H / n-a-Si:H/ back reflector with an active area of 0.253 cm^2.

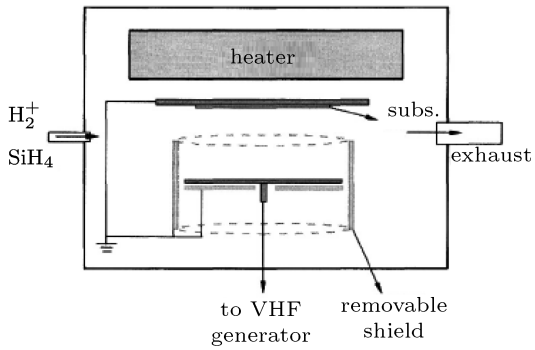


Fig.1. A schematic diagram of the PECVD deposition chamber.

Raman spectra were measured by Renishaw RM2000, which used a 514 nm Ar^+ excitation source. The ratio of the integrated intensities of Gaussian peaks fitted to the Raman signal attributed to crystalline grains (at 500 cm^{-1} and 520 cm^{-1}) and disordered regions (480 cm^{-1}), $X_c = (I_{520} + I_{500})/(I_{520} + I_{500} + I_{480})$ is used as a semi-quantitative value of the crystalline volume fraction.[13]

The optical emission spectrum (OES) measurement was carried out by a PR650 spectrometer at a position near the substrate surface. The FTIR spectral studies were conducted by using Magna-560E.S.P in the range of 4000–400 cm^{-1}.

3. Results and discussion

3.1. Solar cell performance

Firstly, a series of μc-Si:H films were deposited at different F_{total}, while the SC (SC= $[SiH_4]/([SiH_4]+[H_2])$) were simultaneously adjusted to yield almost similar structural and opto-electronic properties. The corresponding parameters of these μc-Si:H films are given in Table 1.

Table 1. The properties of μc-Si:H films obtained at various F_{total}.

F_{total}/sccm	Rd/(Å/s)	σ_d/(s/cm)	σ_p/σ_d	$\alpha_{(0.8\,eV)}/cm^{-1}$	X_c/%
100	8.0	2.9×10^{-7}	480	2.5	59.5
200	8.5	1.9×10^{-7}	500	3.2	60.0
300	9.0	2.0×10^{-7}	510	2.9	59.7
400	8.6	3.0×10^{-7}	490	3.0	60.6
500	8.5	3.3×10^{-7}	480	3.3	61.5

The J–V parameters of solar cells, which consists of the above μc-Si:H as absorbent layers, is summarized in Table 2. The solar cells were all deposited on textured SnO_2/ZnO coated glass substrates and provided with only Al back reflectors. From Table 2, it can be found that all solar cell parameters, i.e. J_{sc}, V_{oc}, FF and η are strongly dependent on the F_{total}. All the J–V parameters firstly increase then come to an saturation when F_{total} increases from 100 to 500 sccm. In particular, the J–V parameters show a drastic increase when F_{total} was increased from 200 to 300 sccm. According to the lower gas utilization at higher F_{total} and good performance, the proper F_{total} was 300 sccm in this experiment.

Table 2. The illuminated J–V parameters of μc-Si:H p–i–n solar cells for i layers deposited at different F_{total}.

sample	F_{total}/sccm	$J_{sc}/(mA/cm^2)$	V_{oc}/mV	FF/%	η/%
1	100	16.5	410	49	3.31
2	200	16.8	430	53	3.83
3	300	18.32	490	63	5.66
4	400	18.4	480	62	5.48
5	500	18.6	485	61	5.50

A further increase of solar cell efficiency has been made by using texture-etched ZnO-coated glass substrates and a ZnO/Al back reflector, as well as an improvement of p/i interfaces. As a result, a conversion efficiency of 8.11% has been obtained at 8.5 Å/s with F_{total} of 300 sccm (Fig.2).

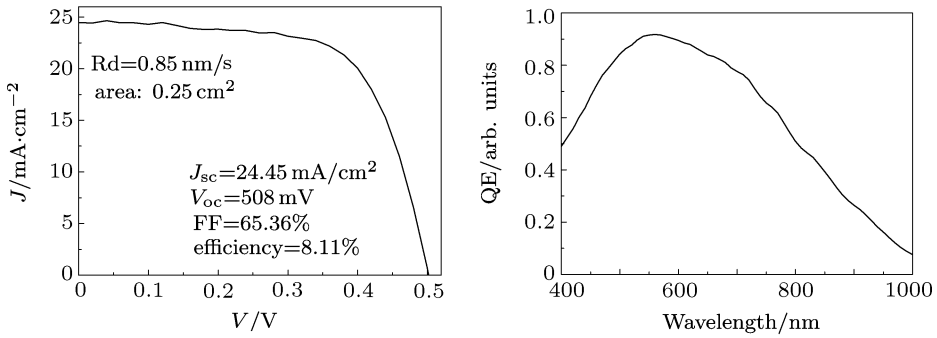


Fig.2. The illuminated J–V characteristics and QE spectrum of a 8.11% efficient μc-Si:H solar cell deposited at 8.5 Å/s (i-layer deposition F_{total}: 300 sccm).

From the above results, the microstructure of the μc-Si:H thin films was studied to find the reason for the variation of the J–V parameters with F_{total}.

3.2. The variation of vertical uniformity of the μc-Si:H thin films with the F_{total}

The X_{c} varied with the thickness of μc-Si:H films at different F_{total} is shown in Fig.3. It shows that the X_{c} increases with thickness for each F_{total}. The increase within the 1000 nm thickness is distinctively more pronounced for the low F_{total}. This indicates that the variation degree of X_{c} with thickness decreases with the increase of F_{total}, i.e. the uniformity of the microstructure is improved.

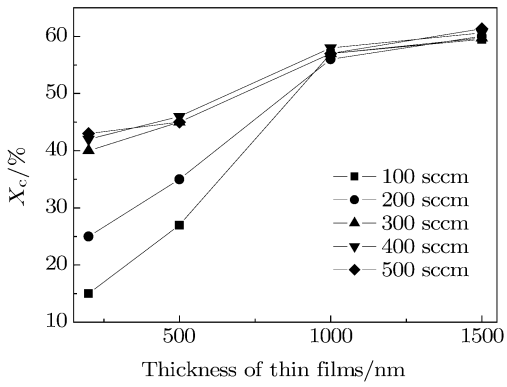


Fig.3. The variation of X_{c} with the thickness of μc-Si:H films at different F_{total}.

3.3. Fourier transforms infrared spectroscopy

The FTIR spectra of Si:H films have major infrared transmission bands near 640 cm^{-1} and 2000 cm^{-1} associated with the wagging and stretching modes of vibration of the Si-H bond. The stretching mode peak can be deconvoluted into two Gaussian peaks around 2000 cm^{-1} and 2100 cm^{-1}, which depend on the surroundings of the hydrogen atom. The absorption peak will be formed in 2000 cm^{-1} when the hydrogen atom exists in a compact network and in 2100 cm^{-1} when the hydrogen atom exists in a hollow or crystal boundary. So the microstructure factor, defined as $R = I_{2100}/(I_{2000} + I_{2100})$, can be used to scale the compact degree of Si:H films. It also can be used as an easy-to-use tool to optimize μc-Si:H properties at high deposition rates, without the necessity for integrating every film in a solar cell device during the film optimization process.[14]

Figure 4 shows how the FTIR spectra and the microstructure factor R varies with F_{total}. It obviously shows that the peak around 2000 cm^{-1} increases while the peak around 2100 cm^{-1} decreases with increasing F_{total}. The microstructure factor R decreases from 68% to 48% as F_{total} increases from 100 sccm to 300 sccm and then almost keeps constant as F_{total} increases to 500 sccm. It indicates that the properties of μc-Si:H increase as F_{total} increases from 100 sccm to 300 sccm and then are nearly invariable, which have a similar behavioural tendency with the variation of

the J–V parameters.

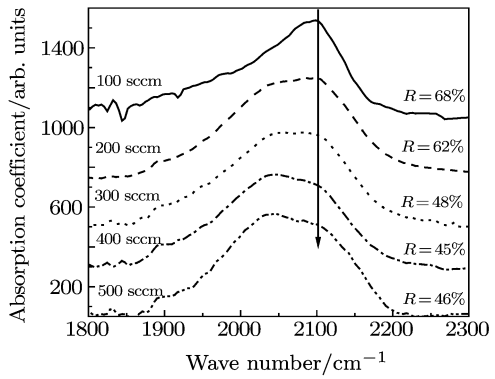


Fig.4. The variation of FTIR spectra and the microstructure factor R with $F_{\rm total}$.

3.4. Optical emission spectrum (OES)

The properties of μc-Si:H films are also strongly related to the plasma characteristics during deposition. The OES can provide valuable information about plasma states occurring in the reactive gas.[15,16] The OES detected by PR650 was used to get the precursory information such as SiH* (414 nm), H^*_β (486 nm), H^*_α (656 nm) and H* (612 nm).

Figure 5 shows that the SiH*/H^*_β ratio varies with deposition time at different $F_{\rm total}$. The SiH*/H^*_β ratio decreases during deposition for each $F_{\rm total}$. The drop within the first few seconds is distinctively more pronounced for the low $F_{\rm total}$. With the increase of $F_{\rm total}$, the drop becomes gentle. Since the SiH*/H^*_β ratio is reported to correlate with film crystallinity,[17–19] thus the structure development is stronger for the low $F_{\rm total}$, which is consistent with the Raman's results.

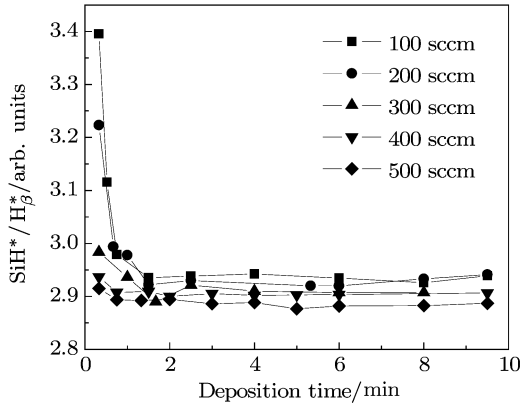


Fig.5. Variation of the SiH*/H^*_β ratio with deposition time at different $F_{\rm total}$.

In order to analyse the variation of vertical structures and properties of μc-Si:H films with $F_{\rm total}$, we show the variation of the H^*_β/H^*_α ratio with deposition time at different $F_{\rm total}$ in Fig.6. The H^*_β/H^*_α ratio has been reported to correlate with the hydrogen plasmas electron temperature ($T_{\rm e}$).[20] It can be seen that the H^*_β/H^*_α ratio increases during the deposition for each $F_{\rm total}$. The increase within the first several seconds is distinctively more pronounced for the low $F_{\rm total}$. This is similar to the variation of the SiH*/H^*_β ratio. It means that the variation of vertical structures is related to the variation of $T_{\rm e}$. The H^*_β/H^*_α ratio which was detected at 180 s first decreases then keeps constant with the increase of $F_{\rm total}$.

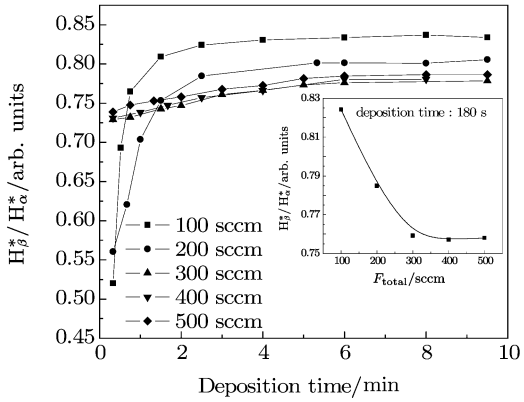


Fig.6. Variation of the ratio H^*_β/H^*_α with deposition time at different $F_{\rm total}$ (the inset demonstrates the variation of H^*_β/H^*_α ratio at 180 s with $F_{\rm total}$).

From Figs.3, 4 and 6, it can be seen that the vertical uniformity and the compact degree of μc-Si:H thin films were improved when the ratio H^*_β/H^*_α detected at 180 seconds decreases. It is known that if the $T_{\rm e}$ increases, SiH_2 radical production is promoted in the plasma because it needs higher electron energy in comparison with the film precursor SiH_3, and then the formation rate of the higher silane molecule is enhanced.[21] It means that the degree of suppressed crystal and the defect density increases with the increase of $T_{\rm e}$. This could be the reason for the variation of the properties with $F_{\rm total}$.

The variation of $T_{\rm e}$ with $F_{\rm total}$ may be correlated with the gas temperature. The gas temperature quickly increases as soon as the plasma is ignited followed by a slow increase of substrate temperature.[22] With the increase of $F_{\rm total}$, the thermal plasma can be let off faster. This can prevent $T_{\rm e}$ from increasing further, which not only decreases the $T_{\rm e}$ but also decreases the variation degree of $T_{\rm e}$ during deposition. It can be seen that the properties of the μc-Si:H thin films all first increase then are nearly invariable with

the increase of F_{total}. According to the lower gas utilization at higher F_{total}, the choice of proper F_{total} was essential under the given conditions. In this experiment, the 300 sccm was proper.

4. Conclusions

In this paper, the effects of F_{total} on the high rate growth microcrystalline silicon thin films and solar cells were studied. From the measurements of the Raman spectrum and FTIR, it showed that the vertical uniformity and the compact degree of μc-Si:H thin films improved with the increase of the total gas flow rate. From the results of OES, it showed that variation of the ratio SiH^*/H^*_β was consistent with the Raman's results and the variation of the ratio H^*_β/H^*_α ratio correlated to the microstructure of μc-Si:H thin films. By detailed analysis, we found that the gas temperature further increased at low F_{total}, which increased the T_{e}, and decreased the performances of μc-Si:H thin films.

From the above results, we also found that the performances of μc-Si:H thin films first increased then came to saturation with F_{total} increasing to 300 sccm. As a result, an 8.11% efficient μc-Si:H solar cell deposited at 8.5 Å/s has been obtained at 300 sccm.

Acknowledgments

The authors thank Dr. F. Finger at IPV, FZ Jülich for supplying the ZnO:Al thin films.

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