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High-density microwave plasma of SiH₄/H₂ for high rate growth of highly crystallized microcrystalline silicon films

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Abstract

The plasma parameter for the fast deposition of highly crystallized microcrystalline silicon ($\mu\text{c-Si}$) films with low defect density is presented using the high-density and low-temperature microwave plasma of a SiH₄-H₂ mixture. A very high deposition rate of $\sim 65 \text{ \AA/s}$ has been achieved at SiH₄ concentration of 67% diluted in H₂ with high Raman crystallinity $I_c/I_a > 3$ and low defect density of $1\text{--}2 \times 10^{16} \text{ cm}^{-3}$ by adjusting the plasma condition. Contrary to the conventional rf and VHF plasma CVDs, the defect density of the $\mu\text{c-Si}$ films strongly depend on substrate temperature T_s and it increased with increasing T_s despite at T_s below 300°C , suggesting that the real surface temperature at the growth surface was higher than the monitored value. Sufficient supply of deposition precursors such as SiH₃ at the growth surface under an appropriate ion bombardment was effective for the fast deposition of highly crystallized $\mu\text{c-Si}$ films as well as the suppression of the incubation and transition layers at the initial growth stage.

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1. Introduction

Recently, the potential application of microcrystalline silicon ($\mu\text{c-Si}$) film for optoelectronic devices such as thin film solar cells has been demonstrated (highlighted) because of its enhanced carrier mobility and stability against photo-induced degradation in contrast to the amorphous Si (a-Si) films counterpart. Solar cells with $\mu\text{c-Si}$ film as intrinsic absorber layer has been fabricated with high conversion efficiency ($>9\%$) and long-term stability against light soaking [1]. However, as a matter of fact, to realize sufficient sunlight absorption, a thickness of the $\mu\text{c-Si}$ film over $2\ \mu\text{m}$ is required due to its indirect optical transition property. In this regard, for mass product of high performance, low-cost photovoltaics, uniform and fast deposition of highly crystallized $\mu\text{c-Si}$ films with low defect density is a crucial issue. To overcome the difficulty, several high-density plasma sources have been developed, such as very high frequency (VHF) plasma, inductive coupling plasma (ICP) and surface wave plasma (SWP)[2-6]. To date, we have studied the high-density and low-temperature microwave plasma utilizing a spoke antenna and applied it for the fast deposition of $\mu\text{c-Si}$ films to the Si thin film solar cells [7-9]. This microwave plasma shows a high-density of $10^{11-12}\ \text{cm}^{-3}$ and low-temperature of 1-2 eV in Ar, which maintained uniform and stable states up to 30 Torr.

In this paper, the effect of a SiH_4 supply method on the film deposition rate, film crystallinity, homogeneity and defect density is presented for the fast deposition of highly crystallized $\mu\text{c-Si}$ films with low defect density. In addition, the contribution of the ion bombardment during the film growth is a primary subject in this work.

2. Experimental

A high-density and low-temperature microwave plasma used in this study was composed of a conventional microwave generator (2.45 GHz, $<1.5\ \text{kW}$), spoke antenna and Al_2O_3 dielectric window. The details of the apparatus are described elsewhere [7]. The film deposition was performed at the distance between the Al_2O_3 dielectric window and substrate holder of 6 cm, where highly crystallized Si film was fabricated in our previous work [8]. The microwave power and the working pressure were 700 W and 80 mTorr, respectively. In this study, SiH_4 was introduced using the shower head established at the 2 cm just above the substrate holder under the steady flow of the H_2 plasma. The deposition parameters were the SiH_4

concentration $R = \text{Fr}(\text{SiH}_4) / [\text{Fr}(\text{SiH}_4) + \text{Fr}(\text{H}_2)]$ (Fr: flow rate), substrate temperature T_s , and the substrate dc bias V_{sub} . The R was varied in the range from 5 to 67% by increasing $\text{Fr}(\text{SiH}_4)$ from 3 to 30 sccm with $\text{Fr}(\text{H}_2)$ of 15 sccm. The plasma diagnostics were also performed using optical emission spectroscopy (OES) as a function of R . The OES emission intensity SiH (414 nm) and the OES intensity ratio of H_α (656 nm) to SiH, $\text{H}_\alpha/\text{SiH}$, were monitored to study the correlation with the film deposition rate and film crystallinity, respectively. Resulting $\mu\text{-Si}$ films were characterized using Raman spectroscopy, x-ray diffraction (XRD), electron spin resonance (ESR) to evaluate the film crystallinity I_c/I_a , deposition rate R_d and ESR spin density N_s . In addition, the spectroscopic ellipsometry (SE) study was employed to discriminate the microstructure of corresponding $\mu\text{-Si}$ films.

3. Results

3.1 Fast deposition of highly crystallized $\mu\text{-Si}$ films

Figure 1 shows the film deposition rate and Raman crystallinity I_c/I_a plotted as a function of R . Here, the I_c/I_a was defined as the ratio of integrated intensity of Raman peak centered at 520 cm^{-1} from crystalline phase to peak centered at 480 cm^{-1} from amorphous phase. The inset also shows the residence time of SiH_4 determined from $\tau = pV/Q$, assuming the same pumping speed S , pressure p , flow rate of SiH_4 Q , and for the effective chamber volume V , respectively. A monotonic increase in the deposition rate with R at constant 80 mTorr implies that the SiH_4 is almost completely decomposed in the plasma and the deposition rate is limited by the amount of SiH_4 introduced into the chamber. The R_d increased with R and a high deposition rate of 65 \AA/s has been achieved while maintaining high Raman crystallinity I_c/I_a above 3.5 despite a high R condition of 65%.

The OES plasma diagnostics were also performed simultaneously in the $\text{SiH}_4\text{-H}_2$ plasma as a function of R . The R dependence of SiH emission intensity and OES intensity ratio $\text{H}_\alpha/\text{SiH}$ are summarized in Figs. 1(a) and (b), respectively. Both SiH emission intensity and film deposition rate also simultaneously increased with increasing R . This result suggests that SiH emission intensity is a possible monitor for the film deposition rate. In addition, a good correlation between the OES intensity ratio $\text{H}_\alpha/\text{SiH}$ and the Raman crystallinity I_c/I_a were observed as shown in Fig. 1(b). The $\mu\text{-Si}$ film deposition was confirmed when the ratio $\text{H}_\alpha/\text{SiH}$ was over ~ 5 in this plasma.

Figure 2 shows the Raman crystallinity I_c/I_a for the $\mu\text{-Si}$ films included

in Fig. 1 plotted as a function of H_a/SiH normalized by the film deposition rate $[H_a/SiH]/R_d$, this value being thought to indicate the relative flux of H radicals to the flux of film precursors during the mono layer growth. The dotted line also corresponds to that from RF ICP plasma CVD [4]. Notably, the Raman crystallinity I_c/I_a in the high-density microwave plasma was larger markedly than the rf ICP CVD even in the small $[H_a/SiH]/R_d$ value and it almost pass through zero. These results suggest that μc -Si film formation occurs in the wide deposition conditions due to the high generation efficiency of atomic hydrogen.

3.2 Microstructure of μc -Si films monitored by SE

The imaginary part of dielectric function $\langle \epsilon_2 \rangle$ spectra of μc -Si films are shown in Fig. 3 fabricated at different Rs. One can clearly distinguish the appearance of the fine structures at 3.4 eV and 4.2 eV, attributing to the E_1 and E_2 optical band transitions, respectively, being observed a signature of the presence of crystalline phase. This confirmed the formation of μc -Si films even under high SiH_4 concentration conditions. The amplitude of the ϵ_2 spectrum depends on the crystalline volume fraction, the crystallite size, the surface roughness and the film porosity. The magnitude of $\langle \epsilon_2 \rangle$ increased markedly with increasing the film deposition rate, which can be interpreted in terms of less degrees of bulk homogeneity and surface roughness. To better understand the film microstructure, $\langle \epsilon_2 \rangle$ spectra were analyzed using a fitting procedure with Bruggeman effective medium approximation (BEMA) [10].

$$\sum_i f_i \frac{\langle \epsilon_i \rangle - \langle \epsilon \rangle}{\langle \epsilon_i \rangle + 2\langle \epsilon \rangle} = 0, \sum f_i = 1$$

Where, $\langle \epsilon_i \rangle$ and f_i indicate the pseudodielectric function and the volume fraction of the i th component, respectively. A four-layer model was used for the spectra analysis composed of 1) the a-Si incubation layer; 2) the nucleation and transition layer from a-Si incubation layer to μc -Si; 3) the μc -Si bulk layer and 4) a surface roughness layer. The fitting procedure was performed with thickness d_i ($i=1-4$), volume fraction of c-Si, a-Si, voids and SiO_2 , f_{c-Si} , f_{a-Si} , f_{void} , f_{SiO_2} , as free parameters. The contribution of f_{c-Si} was analyzed using a reference ϵ_2 spectrum of poly-Si given by Jellison [11]. A probable structure was determined by minimizing the mean square error χ^2 between the measured and calculated ellipsometric error parameters by a linear regression method [12].

$$x^2 = \frac{1}{2N-M} \sum_{i=1}^N \left[\left(\tan \Psi_i^c - \tan \Psi_i^m \right)^2 - \left(\cos \Delta_i^c - \cos \Delta_i^m \right)^2 \right]$$

Where, the superscripts c and m represent the calculated and measured values, and N and M are the numbers of the measured and calculated wavelength, respectively. For all the spectra analyzed here, the χ^2 was confined within 5. The best fitted volume fraction of c-Si in the bulk, f_{c-Si} , and void in the bulk and surface layers, f_{void} , are summarized in Fig. 4 for corresponding μ c-Si samples in Fig. 4. No marked decrease of f_{c-Si} in the bulk layer was observed with R up to 67%, which was in the range of 65-75%. The d_1 and d_2 corresponding to the amorphous incubation layer and the transition layer, respectively, also tend to increase with increasing R, suggesting that they were determined mostly by the film deposition rate. The f_{void} in the bulk and surface over layer decreased markedly when R was over 40%.

3.3 Reduction of defect density in the μ c-Si films

Figure 5 shows the ESR spin density for the corresponding μ c-Si films plotted against the deposition rate fabricated using different SiH_4 gas supply methods at T_s of 150 and 250°C. One is the supply of a $\text{SiH}_4\text{-H}_2$ mixture from the shower ring set just beneath the Al_2O_3 window plate. The other is the supply of SiH_4 independently using the shower head established at the 2 cm above the substrate holder under the steady flow of H_2 plasma. Here, the film deposition was performed by varying $\text{Fr}(\text{SiH}_4)$ from 3 to 30 sccm under $\text{Fr}(\text{H}_2)=15$ sccm and total pressure of 80 mTorr. It is notable that the N_s decreased by about one order of magnitude when the shower head was used at both T_s conditions compared with those from a $\text{SiH}_4\text{-H}_2$ mixture using the shower ring despite the same deposition condition. However, the N_s was almost independent of $\text{Fr}(\text{SiH}_4)$ of order of $3\text{-}4 \times 10^{16} \text{ cm}^{-3}$, which was still one order of magnitude larger than that of high quality μ c-Si film reported [13]. The inset shows the T_s dependence of ESR spin density for the μ c-Si films prepared at $\text{Fr}(\text{SiH}_4)/\text{Fr}(\text{H}_2)=5/15$ sccm. The N_s depend on T_s and it increased monotonically with T_s , contrary to the result of the conventional rf plasma. This suggests that the real temperature of the growing surface is higher than the monitored value because of the plasma heating, which resulted in the promotion of the abstraction of H and the creation of dangling bond despite T_s below 300°C. Thus, sufficient supply of SiH_3 and atomic H are effective to suppress the creation of dangling bond. Lower T_s is also one of probable conditions for further reducing the

N_s . As a consequent, the low T_s of 150°C reduced N_s as low as $1-2 \times 10^{16} \text{ cm}^{-3}$, although the film Raman crystallinity was slightly deteriorated, $I_c/I_a \sim 2$ while maintaining the high deposition rate of 65 Å/s. The dark- and photo-conductivities under white light 100 mW/cm² exposure conditions were of order of 10^{-7} S/cm and $>5 \times 10^{-6} \text{ S/cm}$, respectively in the corresponding $\mu\text{c-Si}$ films. The activation energy of conductivity was 0.6-0.65 eV, implying an intrinsic behavior.

3.4 Effects of substrate dc bias on the growth of $\mu\text{c-Si}$ films

To understand the effect of the ion bombardment during the film growth at high R_d conditions, the deposition study was performed under different V_{sub} conditions at a high deposition rate of $\sim 60 \text{ Å/s}$ on the Al coated glass substrate at 80 mTorr and T_s of 250°C. Figure 6 shows R_d , Raman crystallinity I_c/I_a and ESR spin density N_s for $\mu\text{c-Si}$ films plotted as a function of V_{sub} . Notably, the Raman crystallinity was improved markedly under V_{sub} of -20~-40V condition with a slight reduction of N_s while maintaining a high deposition rate, although the R_d was almost independent of V_{sub} . These results suggest that the appropriate ion bombardment during the film growth is effective to improve the crystallinity and homogeneity of $\mu\text{c-Si}$ films.

The microstructure of corresponding $\mu\text{c-Si}$ films was also studied using SE. Figure 7(a) shows the $\langle \varepsilon_2 \rangle$ spectra for corresponding $\mu\text{c-Si}$ films in Fig. 8. The magnitude of $\langle \varepsilon_2 \rangle$ implying the degree of the homogeneity in the bulk and surface over layer, was larger and the fine structures E_1 (3.4 eV) and E_2 (4.2 eV) also tended to be fine for $\mu\text{c-Si}$ films fabricated under the V_{sub} of -20~-30V conditions, suggesting that the homogeneity being improved in the bulk and surface. The $\langle \varepsilon_2 \rangle$ spectra were also analyzed using the same fitting procedure with a four-layer model described above. The result is summarized in Fig. 7(b). It is notable that the thicknesses of the initial incubation layer d_1 and the transition layer d_2 are relatively thinner with less volume fraction of void f_{void} under the negative V_{sub} conditions. These results imply that the crystalline Si phase appear from the early stage of the film growth.

4. Discussion

In this study, SiH_4 was supplied independently under the steady flow of H_2 plasma using the shower head established at the 2 cm above the substrate holder. Compared with our previous results from a $\text{SiH}_4\text{-H}_2$ mixture using the gas supply ring set just beneath the Al_2O_3 plate, the R_d is

promoted markedly with enhancing Raman crystallinity (Figs, 2 and 3). As a result, the fast deposition of highly crystallized $\mu\text{-Si}$ films of 65 Å/s has been achieved with Raman crystallinity I_c/I_a of 3.5 despite high R of 67%. This result is quite different with the conventional rf and VHF PE-CVD, in which the $\mu\text{-Si}$ films can be formed only when R was less than 10%. This is attributed to the efficient dissociation of H_2 due to high electron-density plasma, providing the sufficient atomic hydrogen. In fact, the relative concentration of atomic H per one mono-layer deposition $[H_a/\text{SiH}]/R_d$ is higher than that of rf ICP plasma as shown in Fig. 2, which results in the preferential growth of $\mu\text{-Si}$ films [4]. In addition, the result implies that there no exists a threshold value of relative flux ratio of H to film precursor for the $\mu\text{-Si}$ formation and the crystallization takes place in any R conditions, because I_c/I_a value approaches to zero with decreasing R.

On the other hand, the generation rate of film deposition precursors such as SiH_3 is determined by the product of electron density and number density of SiH_4 . However, even if large number density of SiH_3 is generated in the high-density plasma, the film deposition rate depends on the position of the substrate holder, because it is determined by both the generation rate and the diffusion loss of SiH_3 during transporting to the growth surface. Therefore, the supply of SiH_4 from near the substrate holder under the intense H_2 plasma is effective to suppress the diffusion loss of SiH_3 and to promote the deposition rate. In fact, both SiH emission intensity and intensity ratio H_a/SiH were larger than those from the gas supply from a ring set just beneath the Al_2O_3 window plate. The good correlation between the film deposition rate and the SiH emission intensity was observed. In addition, the OES emission intensity ratio H_a/SiH correlated well to the Raman crystallinity. Notably, the $\mu\text{-Si}$ film growth was confirmed at 80 mTorr when the ratio H_a/SiH was over 5.

The degrees of the film homogeneity and surface roughness depend on the deposition rate R_d and they are improved with increasing R as shown in Fig. 4. The incubation layer thickness d_1 was thinner, although f_{void} was relatively larger in the bulk and at the surface at low R below 40%. The d_1 and d_2 (interface layer thickness) tend to increase markedly along with the reduction of f_{void} , when R was over 40%. These originated from the less $f_{\text{c-Si}}$ by increasing $f_{\text{a-Si}}$ with R. The d_1 and d_2 were mostly determined by the film deposition rate. Thus, for the application to solar cells, further reduction of d_1 and d_2 are required, because the transport property of photo excited carrier is deteriorated as a series resistance. To this aim, the appropriate ion bombardment is effective to promote the crystallization from the early stage of the growth as shown in Fig. 7. However, the $f_{\text{c-Si}}$ was maintained to be 65% despite high R of 67%, which was due to the high generation

efficiency of atomic hydrogen in this plasma.

The N_s in the $\mu\text{-Si}$ films is one of the most important structural properties, particularly for solar cell applications, because dangling bonds form deeply localized electronic states in the band gap and act as recombination centers for photo excited carriers. However, as shown in the inset of Fig. 5, the N_s increased with T_s even at T_s below 300°C due to the plasma heating, which inferred that the thermal abstraction of the H at the growth surface was promoted in all T_s region. These caused the generation of dangling bond on the growing surface. According to the surface diffusion model of SiH_3 , these steady state surface dangling bonds can be incorporated into the bulk layer, causing an increase in the number density of dangling bond in resulting films. In this high-density microwave plasma, the plasma heating will also enhances the abstraction of bonded H at the growth surface, accelerating the production rate of steady state dangling bond. Therefore, they provide high density growing sites (dangling bonds). The steady state dangling bond density on the growing surface is determined by the balance between the generation and saturation rate of dangling bond. Therefore, it is expected that N_d can be reduced and R_d will be promoted by going to a higher SiH_3 growth flux (precursor-assisted defect suppression) and atomic hydrogen [14]. On the one hand, the generation rate of dangling bond will be accelerated by the plasma heating, providing sufficient growth site (dangling bond) for the attachment of successive SiH_3 to form Si-Si bond contributing to film growth. Thus, large number density of SiH_3 on the surface saturates the DB rather effectively, resulting in the dramatically enhanced deposition rate and markedly reduced defect density in the films by supplying SiH_4 from near the growth surface using a shower head. As a consequence, the N_s decreased by one order of magnitude to be $3\text{-}4 \times 10^{16} \text{ cm}^{-3}$ while maintaining a high deposition rate of 65 \AA/s . However, it was almost independent of R , which was still one order of magnitude larger than the value of a high quality $\mu\text{-Si}$ film reported [13]. This is caused by the enhanced H abstraction due to the plasma heating. The use of a high H_2 dilution and/or lower T_s is a possible condition to overcome this difficulty. Lowering T_s and wall temperature also tend to decrease the electron temperature T_e . As a consequent, the N_s reduced to be $1\text{-}2 \times 10^{16} \text{ cm}^{-3}$ while maintaining the high deposition rate T_s of 150°C by suppressing the thermal abstraction of surface terminated H.

As shown in Figs. 6 and 7, an appropriate ion bombardment during the film growth was effective to promote the film crystallinity with a slight reduction of defect density while maintaining a high deposition rate. Moreover, SE analysis indicated that the thickness of the initial incubation and subsequent interface layers was reduced under the substrate bias V_{sub} of

-20~-30V condition. These results are in a good agreement with our previous result of the film deposition by mixing a small amount of He and Ar in the SiH₄-H₂ mixture plasma [15]. Thus, the XRD diffraction peak intensity ratio of the (220) to (111) $I_{(220)}/I_{(111)}$ was enhanced preferentially when the OES emission intensity ratio $I_{\text{He}}/I_{\text{ArI}}$ was 0.8-1.1. Here, the threshold energies of 575 nm and 750.4 nm emissions of 585 nm He and 750.4 nm ArI correspond to 23.07 eV and 13.5 eV, respectively, corresponding to the *hot electron population* in the SiH₄-H₂ plasma. No marked changes in the SiH₄-H₂ plasma emission was observed except the emissions of He and Ar, as far as the OES measurement was concerned. Here, if the low electron-temperature T_e plasma is crucial for fabricating highly crystallized $\mu\text{c-Si}$ films, the $I_{(220)}/I_{(111)}$ value should be still higher even in the $I_{\text{He}}/I_{\text{ArI}}$ value below 3-4. This imply that moderate *hot electron population* i.e., an appropriate ion bombardment during the film growth is effective for the preferential growth of the (220) orientation, which is suitable for the Si thin film solar cells. In addition, the appropriate ion energy provides a sufficient energy to accelerate the relaxation of Si network at the growing surface and they promote the crystallite nucleation. In fact, *in situ* SE study of the $\mu\text{c-Si}$ film growth using the MWP revealed that the relaxation of the Si network during the film growth showed a long time constant at a high deposition rate condition of over 20 Å/s. The optical constant, phase angle Δ value increased during several tens milliseconds even after turning off the plasma [16]. On the other hand, no significant changes of optical constants phase shift ψ and phase angle Δ with time were observed after turning off the plasma in the low R_d condition of 2-3 Å/s. Thus, the relaxation of Si network is promoted within several mono layers near the growth surface at a high deposition rate condition. The deposition study of $\mu\text{c-Si}$ films using the deuterium D₂ dilution in place of mono hydrogen H₂ also suggest the effectiveness of an appropriate ion bombardment for promoting the crystallization [17]. These results indicate that higher flux of SiH₄ under the moderate ion bombardment is effective to promote the growth of rigid $\mu\text{c-Si}$ network at a high deposition rate condition.

5. Conclusion

We have demonstrated the plasma parameters for the fast deposition of $\mu\text{c-Si}$ films with low defect density using the high-density and low-temperature microwave plasma. Fast deposition was performed at very high deposition rate of ~65 Å/s for $\mu\text{c-Si}$ film growth at T_s of 150°C with high Raman crystallinity $I_c/I_a > 2$ and low defect density of $1-2 \times 10^{16} \text{ cm}^{-3}$.

The OES measurement revealed that SiH emission intensity and intensity ratio of H_α /SiH were good monitors for film deposition rate and film crystallinity, respectively. Contrary to the conventional rf plasma, the N_s increased with increasing T_s even at T_s below 300°C, suggesting that the real surface temperature at the growth surface was higher than the monitored value and the abstraction of hydrogen was accelerated. To overcome this difficulty, the combination of the supply of sufficient supply of SiH₃ and atomic hydrogen under an appropriate ion bombardment condition is very effective for fast deposition of highly crystallized μ c-Si films without creating additional defects as well as to improve the film homogeneity and surface smoothness.

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Figure captions

FIG. 1 (a) Film deposition rate and SiH(414 nm) emission intensity plotted as a function of SiH₄ concentration R. Inset shows the residence time of SiH₄ as a function of R. (b) Raman crystallinity I_c/I_a and H_α/SiH intensity ratio plotted against R. The Fr(H₂) and working pressure were constant at 15 sccm and 80 mTorr, respectively.

FIG. 2 Raman crystallinity I_c/I_a plotted as a function of OES emission intensity ratio H_α/SiH normalized by the film deposition rate R_d.

FIG. 3 Imaginary part of pseudodielectric function $\langle \epsilon_2 \rangle$ spectra for resulting μ c-Si films fabricated at different R conditions at 80 mTorr.

FIG. 4 Changes of the f_{c-Si} and f_{void} in the bulk layer, as well as the incubation layer and coalescence layer thicknesses, d_1 and d_2 , with SiH₄ concentration R for corresponding μ c-Si films in Fig. 3.

FIG. 5 ESR spin density N_s for corresponding μ c-Si films in Figs. 3 and 4 as well as those for samples prepared at T_s=150°C plotted as a function of film deposition rate R.

FIG. 6 (a) Film deposition rate and Raman crystallinity I_c/I_a plotted as a function of substrate dc bias V_{sub}. (b) ESR spin density N_s for μ c-Si films plotted against V_{sub}. The μ c-Si films were fabricated on Al coated glass from a SiH₄-H₂ mixture of R=67% at Fr(H₂) =15 sccm, working pressure of 80 mTorr and T_s of 250°C, respectively.

FIG. 7 (a) Imaginary part of pseudodielectric function $\langle \epsilon_2 \rangle$ spectra of μ c-Si films grown under different substrate dc bias V_{sub} conditions. (b) Substrate dc bias V_{sub} dependence of f_{c-Si} and f_{void} in the bulk and surface over layer as

well as the incubation layer and the interface layer thicknesses, d_1 and d_2 , respectively.