Influence of ignition condition on the growth of silicon thin films using plasma enhanced chemical vapour deposition*

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The influences of the plasma ignition condition in plasma enhanced chemical vapour deposition (PECVD) on the interfaces and the microstructures of hydrogenated microcrystalline Si (μc-Si:H) thin films are investigated. The plasma ignition condition is modified by varying the ratio of SiH_4 to H_2 (R_H). For plasma ignited with a constant gas ratio, the time-resolved optical emission spectroscopy presents a low value of the emission intensity ratio of Hα to SiH* ($I_{H\alpha}/I_{SiH^*}$) at the initial stage, which leads to a thick amorphous incubation layer. For the ignition condition with a profiling R_H, the higher $I_{H\alpha}/I_{SiH^*}$ values are realized. By optimizing the R_H modulation, a uniform crystallinity along the growth direction and a denser μc-Si:H film can be obtained. However, an excessively high $I_{H\alpha}/I_{SiH^*}$ may damage the interface properties, which is indicated by capacitance–voltage (C–V) measurements. Well controlling the ignition condition is critically important for the applications of Si thin films.

Keywords: plasma enhanced chemical vapour deposition, microcrystalline silicon, ignition condition

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1. Introduction

Plasma enhanced chemical vapour deposition is a conventional technique for the preparation of the low-cost μc-Si:H thin film solar cells.[1] However, a high-quality μc-Si:H thin film with a dense and homogeneous structure along the growth direction is seldom achieved with constant deposition parameters, especially for high rate deposition.[1,2]

Various modulation techniques[3−8] have been adopted at the initial growth stage to improve the film quality. It is well known that a high H dilution of SiH_4 at the initial growth stage of the film is beneficial to the increase of the nucleation density, the improvement of the vertical uniformity of crystallinity, and the delay of the formation of a mound structure.[3−7] As a result, the mass density, the optoelectronic properties of the films, and the performances of the solar cells can be improved. The reported results indicate that the growth condition at the initial stage has an important influence on the evolution of the thin film microstructure.

However, the essential role of the modulation technique is not well understood due to the instability and the complexity of the plasma in the initial ignition stage. Moreover, in different application scopes, for example, thin film solar cells and Si heterojunction solar cells, the function of the modulation technique needs to be further explored.

In this study, the flow rate of silane is varied in the initial growth stage to modify the ignition condition of the plasma. The function of the H dilution modulation technique is demonstrated by analysing the influence of the ignition condition on the plasma optical emission spectrum, the crystallinity uniformity along the growth direction, and the hydride stretching modes in the thin film. For different application scopes of the film deposition, the influence of the H dilution modulation on the interfacial property of Si film/c-Si heterojunction is also investigated. The role of the modulation techniques is analysed for achieving high-performance Si based solar cells.

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2. Experiment

Silicon thin films were grown on Eagle 2000 Corning glass and polished CZ silicon wafer substrates by capacitive coupled radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) with a mixture of silane and hydrogen. The deposition pressure, the substrate temperature, and the RF power were fixed at 500 Pa, 200 °C, and 0.46 W/cm^2, respectively. The hydrogen flow rate was fixed at 200 sccm. The ignition condition was changed by controlling the silane flow rate, i.e., the hydrogen dilution ratio.

Figure 1 shows the variation of the setting SiH_4 flow rate with time in three different ignition conditions. For condition S35, SiH_4 with a steady flow rate of 3 sccm was well mixed with H_2 (200 sccm) before the plasma ignition, i.e., a flow rate ratio of SiH_4 to H_2 (R_H) was kept at 0.015 in the whole deposition process. For condition S34, pure H_2 (200 sccm) was introduced into the chamber before the ignition. The silane was introduced with a feed rate lineally increasing from 0 sccm to 3 sccm in 2 min, and the plasma was ignited when the silane started to feed into the deposition chamber. For condition S33, silane of 3 sccm was set to feed into the chamber exactly in the time of the plasma ignition. And then the SiH_4 flow rate of 3 sccm and R_H were fixed during the deposition. It should be pointed out that the actual gas flows feeding into the chamber may have a few seconds delay compared with those shown in Fig. 1 for conditions S34 and S33 because of the distance between the mass flowmeters and the chamber for the mixture process.

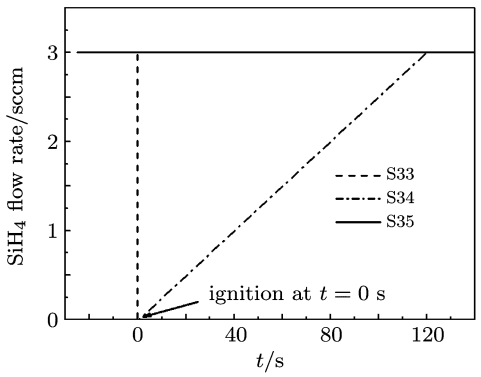


Fig. 1. Variations of silane flow rate with time in different ignition conditions.

Raman scattering spectra of the Si thin films on glass substrates were measured (HORIBA JobinYvon HR800, excitation wavelength of 514 nm). The crystalline volume fraction of μc-Si:H was estimated by using formula $X_C = (I_{500}+I_{520})/(0.88I_{480}+I_{500}+I_{520})$, where I_{480}, I_{500}, and I_{520} represent the integral intensities of the amorphous phase, the small grain or grain boundary, and the crystal phase, respectively. The constant 0.88 is the Raman scattering cross section ratio of the amorphous phase to the crystal phase. Infrared absorption spectra were recorded by using a Fourier-transform infrared spectrometer (Nicolet Avatar 360FT-IR). The influence of the ignition condition on the interfacial properties of the Si thin layer on c-Si was characterized by the high frequency capacitance–voltage (C–V) measurement (HP model P4280A meter, 1 MHz). The structure of Al/μc-Si:H/p-c-Si/Al was used for the C–V measurement. The plasma optical emission spectra were recorded by using a Synerjyvon spectrometer during the deposition of the silicon thin film.

3. Results and discussion

3.1. Time dependences of plasma emission intensities under different ignition conditions

Time dependences of the emission intensities of H_α and SiH^* were recorded for 5 min starting from the plasma ignition. The H_α emission (656.2 nm) corresponding to the transition of 3s→2p of the excited atomic H originates from the electron impact dissociations of H_2 and SiH_4 and the excitation of atom H, which is usually considered to reflect the atomic H concentration in the plasma. The SiH^* emission (414 nm) corresponds to transition $A^2\Delta$–$X^2\Pi$ of the excited SiH^* produced by the collision between electron and SiH_4.[9] In the silane/hydrogen plasma system, usually the emission intensity ratio of H_α to SiH^* ($I_{H\alpha}/I_{SiH^*}$) is used to predict the crystallization of the silicon films.[10]

Figure 2 presents the time dependences of I_{SiH^*}, $I_{H\alpha}$, and $I_{H\alpha}/I_{SiH^*}$ under the three ignition conditions. For the constant gas ratio condition (S35), I_{SiH^*} and $I_{H\alpha}$ decrease rapidly with time and then level off after 90 s, which is consistent with the observation of Hrunski *et al.*[3] and Nunomura *et al.*[11] The rapid reduction of I_{SiH^*} and $I_{H\alpha}$ is due to the decomposition and the transient depletion of the initial SiH_4. As the processes proceed, the diffusion and the supply of silane are balanced, the emission intensity becomes steady. As depicted in Fig. 2(c), ratio $I_{H\alpha}/I_{SiH^*}$ under ignition condition S35 is low in the initial growth stage and then increases to a saturation value. The

low value of $I_{H\alpha}/I_{SiH^*}$ in the initial stage indicates a low atomic H concentration. In this case, the nucleation at the initial stage is difficult, a thick amorphous incubation layer is inevitable, and the structural uniformity along the growth direction is blemished.

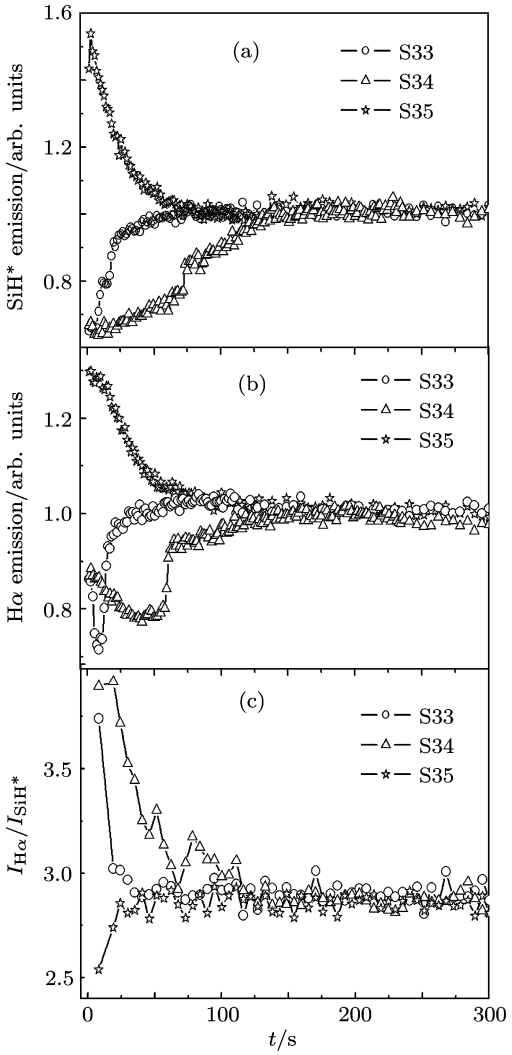


Fig. 2. Time dependences of (a) $I_{H\alpha}$, (b) I_{SiH^*}, and (c) $I_{H\alpha}/I_{SiH^*}$ under three different ignition conditions.

For ignition conditions S33 and S34, the processes start from the H_2 plasma. Afterwards, SiH_4 is fed into the deposition chamber with different flow rate profiles. At $t = 0^+$, no SiH_4 is fed in, but a weak signal of SiH^* is observed in both conditions, which is due to the reaction of the plasma with the electrodes and the chamber wall covered with silicon. At $t > 0$, the values of I_{SiH^*} and $I_{H\alpha}$ for S33 and S34 show similar trends due to the same ignition condition, and are much smaller than those for the S35 condition. With the feeding of SiH_4 in different rates, the SiH^* intensities increase in different slopes and finally reach a balanced value in 70 s and 150 s for S33 and S34, respectively. The longer saturation time for S34 is due to the low feeding rate of silane.

For the time dependence of H_α, the emission intensities of H_α for S33 and S34 show similar trends with a valley shape. Both of them first decrease and then increase to the balance value. The decrease in the H_α intensity at the initial stage is caused by the annihilation of the atomic H due to reaction $SiH_4+H \rightarrow SiH_3+H_2$ when a small amount of silane is added into the hydrogen plasma. With enough silane added, H_α can be produced from the SiH_4 decomposition ($e+SiH_4 \rightarrow SiH_{4-n} + nH$), which compensates the annihilation reaction and finally reaches a higher steady value. The minima of $I_{H\alpha}$ appear at 10 s and 50 s for S33 and S34, respectively, because of the different feeding rates of SiH_4.

The ratios of $I_{H\alpha}/I_{SiH^*}$ exhibit high values for both S33 and S34 at $t > 0^+$ because of the high R_H. With SiH_4 fed into the hydrogen plasma, i.e., R_H is reduced, the values of $I_{H\alpha}/I_{SiH^*}$ decrease and then saturate at ∼20 s for S33 and ∼100 s for S34. The balance time depends on the feeding rate of SiH_4. The high value of $I_{H\alpha}/I_{SiH^*}$ indicates a high atomic H concentration in the reaction region at the initial growth stage. Therefore, although the later R_H values are the same for the three ignition conditions, a higher nucleation density and a thinner amorphous incubation layer are expected for each of the S33 and the S34 ignition conditions than those for the S35 ignition condition. The Raman scattering results described below confirm the above prediction.

3.2. Influence of ignition condition on the microstructure of Si thin films

Raman scattering measurement was carried out to investigate the influence of the ignition condition on the microstructure of the thin film. The thicknesses of the samples are the same (about 800 nm). The values of volume fraction of crystalline (X_c) of the films for the three ignition conditions are similar (∼55%), indicated by the conventional Raman scattering measurements with the excitation laser wavelength of 514 nm incident from the top surface of the film.

The laser is incident from the back side. Raman scattering spectra of S33, S34, and S35 films show their different phase structures. An amorphous phase is observed from the film deposited under the S35 condition. A small peak appears at 520 cm^{-1} in the Raman spectrum for S33, and the calculated X_c is 28%. The X_c of 36% is obtained under the S34 condition.

This result indicates that the ignition condition does not affect the crystallization of the upper part of the film, however it affects the nucleation of the initial-growth layer significantly. A high $R_{\rm H}$ provides a high value of the initial $I_{{\rm H}\alpha}/I_{{\rm SiH}^*}$, as shown in Fig. 2(c), which indicates a high concentration of H atoms at the initial growth stage. As a result, the thickness of the incubation layer is reduced and the vertical uniformity of crystallinity is improved, which are consistent with the results in our previous report.[6] However, the crystallinity near the substrate is not as high as that in the upper part of the film due to the limited modulation process. According to our previous results, an appropriate $R_{\rm H}$ modulation is required to enhance the crystallization in the initial growth layer and to achieve a better uniformity of crystallinity.

The FT-IR absorption spectra were measured for the Si thin films deposited on polished Si substrates under different ignition conditions. Figure 3 shows the FT-IR absorption spectra in the range of 1900–2200 cm^{-1} for the three samples. In the range of 1850–2200 cm^{-1}, several Si–H$_X$ stretching modes (SMs) of bulk hydrides are included, which are extreme low wave-number SMs (ELSM, 1895–1960 cm^{-1}), low wave-number SMs (LSM, 1980–2010 cm^{-1}), middle wave-number SMs (MSM, ∼2040 cm^{-1}), high wave-number SMs (HSM, 2070–2100 cm^{-1}), etc.[4,12] The ELSM, the LSM, the MSM, and the HSM deduced from the multi-peak Gaussian fittings are depicted in Fig. 3. The percentages of the integrated absorption intensities of these SMs are given in Table 1.

In the IR spectra of the μc-Si:H thin film with a high crystallinity, narrow HSMs (NHSM, 2080–2140 cm^{-1}) are usually observed.[4,12,13] The NHSMs correspond to mono-, di-, and tri-hydrides at the crystalline surfaces, which are related to the existence of plenty of micro-voids in the material and usually are accompanied with the post deposition oxidation.[4,12] The μc-Si:H thin films prepared under the three ignition conditions do not show the NHSMs (absent in Table 1), which implies that relatively high-quality μc-Si:H films appear in the transition region from the amorphous to the microcrystalline phase ($X_{\rm c}$ ∼55%). It is confirmed that neither Si–O–Si SMs (950–1200 cm^{-1}) nor O$_x$Si–H$_y$ (2250 cm^{-1}) mode is detected from the IR spectra of these μc-Si:H films measured even 3 months after the deposition.

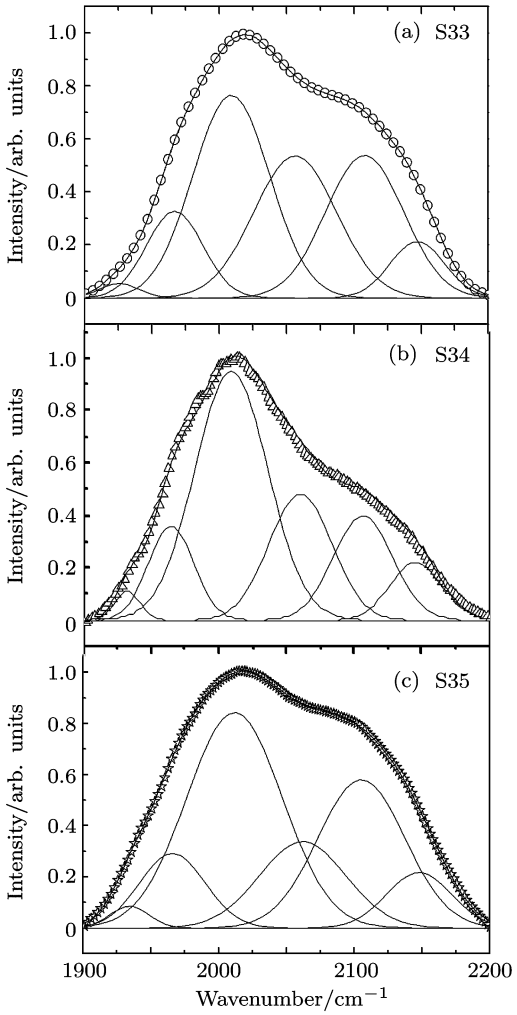


Fig. 3. IR absorption spectra of microcrystalline Si thin films under ignition conditions (a) S33, (b) S34, and (c) S35.

Moreover, all the Fourier transform infrared (FTIR) spectra of the three samples exhibit the ELSMs with the similar integrated intensities, as shown in Table 1. The ELSMs are usually observed in μc-Si:H with ⟨220⟩ preferred orientation and are related to the hydrogenated vacancies in grains. So a small number of ELSMs in Table 1 indicates that the μc-Si:H film has an expected ⟨220⟩ preferred orientation.

Table 1. Integrated absorption intensities of SMs under different ignition conditions.

Condition	ELSM /%		LSM/%	MSM/%	HSM/%	
	1925–1934 cm^{-1}	∼ 1965 cm^{-1}	2007–2011 cm^{-1}	2060–2063 cm^{-1}	2095–2107 cm^{-1}	2137–2147 cm^{-1}
S33	1.2	10.4	33.1	25	23.7	6.6
S34	1.8	10.6	45.5	19.6	15.2	7.3
S35	1.7	9.7	40.7	14.9	25.7	7.2

Besides the NHSMs, the percentage of the HSMs in the total SMs is usually of concern. The HSMs are related to the Si–H_X bonds in the inner surface of the micro-voids, which reflect the mass density of the μc-Si:H film. The LSM and the MSH are assigned to the hydrogen in vacancies within the bulk of the a-Si:H tissue. For condition S34, the fraction of the integrated intensity of HSMs is the lowest and the total integrated area under the ELSMs, the LSMs, and the MSMs is the highest, which imply the denser bulk tissue and the better passivation of the grain boundaries for condition S34 than those for conditions S33 and S35.[4,12] During the initial 100 s, $I_{H\alpha}/I_{SiH^*}$ is much higher for condition S34 than those for conditions S35 and S33, as shown in Fig. 2(c). The rich atomic H in the plasma breaks the weak Si–Si bonds and increases the nucleation density remarkably in the initial stage as observed in our previous research. The high density of the nuclei and the etching effect of H weaken the shadowing effect and hinder the formation of large clusters.[7] Therefore, the compact tissue with small clusters is formed, and the micro-voids are reduced.

The FTIR spectrum indicates that a suitable silane-profile ignition condition is beneficial to the realization of better hydrogen passivation of the grain boundaries and a denser bulk matrix with less microcavities and cracks as well.

4. Influence of ignition condition on interface between Si film and c-Si

In the Si thin film/c-Si heterojunction solar cells, a high-quality ultrathin intrinsic Si buffer layer and the interface between the Si thin film and the c-Si are crucial to achieve a high open voltage and a high efficiency. The initial transient stage of the plasma will seriously affect the quality of the thin film layer and the density of the interface states.[11] The C–V measurements at 1 MHz were carried out to investigate the interface properties of the μc-Si:H/p c-Si prepared under the different ignition conditions.

Figure 4 shows the variations of square of the depletion region width W^2 with bias voltage V deduced from the C–V measurements for the μc-Si:H prepared under the above three ignition conditions. The slope of W^2–V is related to the effective density of the interface defects between μc-Si:H and c-Si.[14] The μc-Si:H prepared under the S35 condition seems to present the best passivation of the c-Si surface.

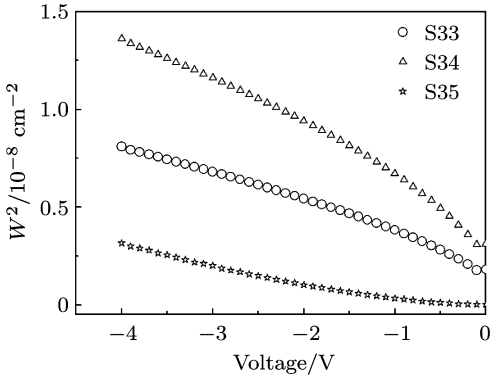


Fig. 4. Variations of W^2 with V for samples prepared under different ignition conditions.

The above phenomenon is comprehensible. Generally, an appropriate atomic H surface treatment of the c-Si surface is beneficial to the surface passivation.[15] However, an excessive H treatment may deteriorate the interface because of the excessive etching effect by H, especially in the PECVD process. From Fig. 2(c), it can be seen that the S34 condition shows a high value of $I_{H\alpha}/I_{SiH^*}$ in the initial 100 s compared with that under conditions S33 and S35, which may lead to a serious H etching at the c-Si surface.

Another issue to be addressed is that a high concentration of H atoms may cause the partial epitaxial growth of silicon film on the c-Si surface. The partial epitaxial growth may lead to a high defect density in the interface. For condition S34, the partial epitaxial structure is likely to form on the c-Si substrate, thereby producing a high density of interface defects. However, condition S35 under which a thicker amorphous incubation layer is produced may provide a good passivation of the c-Si surface, and then a low density of interface defects is obtained. This is coincident with the requirement for complete amorphous phase Si film serving as a buffer layer in high-efficiency heterojunction Si solar cells.

5. Conclusion

The influences of plasma ignition conditions on the growth of Si film deposited on glass and c-Si substrates are investigated by using the Raman, the FTIR, and the C–V measurements combined with the time-resolved optical emission spectroscopy in the initial growth stage.

For the silane/hydrogen plasma ignited with a constant gas ratio, the emission intensities of SiH^* and H_α decrease with time, and $I_{H\alpha}/I_{SiH^*}$ presents a low value at the initial growth stage. Such an ignition condition leads to not only a thick amorphous incubation layer, but also a high HSM intensity in the FTIR spectrum, which means less dense bulk matrix of the μc-Si:H film.

For the ignition conditions with SiH_4 profiling i.e., R_H modulation, high $I_{H\alpha}/I_{SiH^*}$ values are realized at the initial stage compared with that with a constant gas ratio. The proper modulation technique is benefit to forming more uniform crystallinity along the growth direction and providing a better hydrogen passivation of the grain boundaries, which realizes a denser material with less micro-voids.

However, the C–V measurements indicate that excessive high $I_{H\alpha}/I_{SiH^*}$ may damage the interface properties for films growing on c-Si due to the overetching of H or the partial epitaxial growth. The above investigation indicates that well controlling the ignition condition is critical to the applications of the Si film. Different ignition conditions need to be considered for preparing thin film solar cells and heterojunction solar cells.

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