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The role of hydrogen in hydrogenated microcrystalline silicon film and in deposition process with VHF-PECVD technique*

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The role of hydrogen in hydrogenated microcrystalline silicon (μc-Si:H) thin films in deposition processes with very high frequency plasma-enhanced chemical vapour deposition (VHF-PECVD) technique have been investigated in this paper. With *in situ* optical emission spectroscopy (OES) diagnosis during the fabrication of μc-Si:H thin films under different plasma excitation frequency ν_e (60MHz–90MHz), the characteristic peak intensities (I_{SiH^*}, $I_{H\alpha^*}$ and $I_{H\beta^*}$) in SiH_4+H_2 plasma and the ratio of ($I_{H\alpha^*}$ + $I_{H\beta^*}$) to I_{SiH^*} were measured; all the characteristic peak intensities and the ratio ($I_{H\alpha^*}$ + $I_{H\beta^*}$)/I_{SiH^*} are increased with plasma excitation frequency. It is identified that high plasma excitation frequency is favourable to promote the decomposition of SiH_4+H_2 to produce atomic hydrogen and SiH_x radicals. The influences of atomic hydrogen on structural properties and that of SiH_x radicals on deposition rate of μc-Si:H thin films have been studied through Raman spectra and thickness measurements, respectively. It can be concluded that both the crystalline volume fraction and deposition rate are enhanced with the increase of plasma excitation frequency, which is in good accord with the OES results. By means of FTIR measurements, hydrogen contents of μc-Si:H thin films deposited at different plasma excitation frequency have been evaluated from the integrated intensity of wagging mode near 640 cm^{-1}. The hydrogen contents vary from 4% to 5%, which are much lower than those of μc-Si:H films deposited with RF-PECVD technique. This implies that μc-Si:H thin films deposited with VHF-PECVD technique usually have good stability under light-soaking.

Keywords: VHF-PECVD technique, hydrogenated microcrystalline silicon, role of hydrogen, optical emission spectroscopy

PACC: 8115H, 7280N, 7360F

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) thin film has played an important role in the application to stable high-efficiency solar cells for its good stability during light irradiation.[1−3] Usually, μc-Si:H thin film is prepared from highly H_2-diluted SiH_4 with radio frequency (RF) plasma-enhanced chemical vapour deposition (PECVD) at a very low-deposition rate, resulting in the severe limitation of applications of μc-Si:H thin films in low-cost solar cells. In order to increase the deposition rate to grow μc-Si:H thin film, deposition techniques such as hot wire CVD, electron cyclotron resonance CVD and very high frequency plasma-enhanced chemical vapour deposition (VHF-PECVD) have been successfully adopted.[4−6] Comparatively, VHF-PECVD is more compatible to well-established RF-PECVD technique than the other ones, then it has been paid more and more attention in the last decade.[7−12] Recently, we have made also some progress in the study of μc-Si:H films deposited using the VHF-PECVD technique.[13−19]

However, owing to more complicated energy supply than the RF-PECVD technique, the VHF-PECVD system has some shortcomings such as poor stability and reproducibility, so it is necessary to study the dynamical process of material growth during VHF-PECVD. As is well known, hydrogen is a key

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radical in the fabrication of μc-Si:H thin film, thus it is important to investigate the behaviour of hydrogen in the deposition process and in the deposited μc-Si:H thin film. We even think that it should be helpful for researchers to know more about the growth mechanism of μc-Si:H thin film grown with VHF-PECVD technique. Here, with *in situ* optical emission spectroscopy (OES) diagnosis during the deposition of μc-Si:H thin films and FTIR absorption spectra experiments on μc-Si:H thin films, the role of hydrogen in the deposition process and in μc-Si:H thin films have been studied, respectively. Moreover, with measurements of Raman spectra and thickness of the sample, the influence of plasma excitation frequency on structural properties and deposition rates of μc-Si:H films have been discussed also.

2. Experimental details

All μc-Si:H thin films studied here were prepared in a capacitive-coupled three-chamber VHF-PECVD system under different plasma excitation frequency (ν_e). The base vacuum of reaction chamber was approximately 1×10^{-4}Pa; a pair of rectangle electrodes of a size of 4×6 cm^2 and with electrode gap of 2.0 cm were used. Two types of substrates. Corning 7059 glass and optically polished single crystalline silicon wafers, have been used for different characterizations. For each μc-Si:H thin film deposition, the corresponding plasma excitation frequencies were 60, 70, 80 and 90MHz, and the other deposition conditions were kept the same as the following: silane concentration (S_c) 4%, total gas flow rate (F_r) 75 sccm, working gas pressure (P_g) 120 Pa, substrate temperature (T_s) 200 °C and plasma power 24 W.

During the deposition of μc-Si:H thin films under different plasma excitation frequency, a PR650 spectrometer, working in the wavelength range of 380 to 780 nm, was used to perform the *in situ* OES diagnosis of VHF plasma. The experimental setup for OES measurement has been described in detail elsewhere.[15] Raman scattering spectra were measured with Micro-Raman scope MKI2000 (Renishaw), which worked at 632.8nm, 5 mW and with a resolution less than 1cm^{-1}. The thickness of μc-Si:H thin film was obtained from the optical transmission and reflection (T&R) spectra measured by optical multichannel analysis-OMA (EG&G). Then the deposition rate was calculated through the thickness divided by the corresponding deposition time. FTIR absorption spectra were measured by a Fourier transform absorption spectroscopy Nicolet Megna-560E.S.P, working in transmission mode within the wave number range of 400–4000 cm^{-1} with resolution 0.9 cm^{-1} and 200 scans.

3. Results and discussion

3.1. *In situ* OES diagnosis

The OES spectra of VHF-generated SiH_4+H_2 plasma with different plasma excitation frequency are shown in Fig.1, from which, several peaks are easily observed. For μc-Si:H thin film deposited using PECVD technique, the characteristic peak intensities corresponding to key radicals such as SiH* (~412 nm) and atomic hydrogen (H_{α^*} ~656 nm, H_{β^*} ~486 nm) should be found,[17] and these peak intensities and the ratio of $I_{H^*}/I_{SiH^*}((I_{H\alpha^*}+I_{H\beta^*})/I_{SiH^*})$ are plotted in Fig.2. As can be seen in Fig.2, all the peak intensities SiH*, H_{α^*}, H_{β^*} and I_{H^*}/I_{SiH^*} are increased significantly with plasma excitation frequency in almost the same way. These results indicate that high plasma excitation frequency can effectively promote the decomposition of SiH_4+H_2 to produce atomic hydrogen and SiH radicals. However, the increases of all intensities slow down within the range of higher excitation frequency. We think it is mainly caused by the fixed amount of the reactive gas source SiH_4 and H_2.[14]

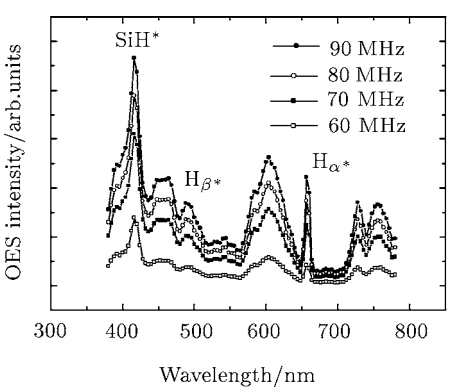


Fig.1. OES spectra of VHF-generated SiH_4+H_2 plasma.

Torres *et al* have reported that the value $I_{H\alpha}{}^*/I^*_{SiH}$ above 1 was found to be an indicator for the transition from amorphous to microcrystalline films.[20] However, as characterized with Raman spectra in the following section, μc-Si:H thin films can be obtained for all the values of I_{H^*}/I_{SiH^*} below 1 according to our results. Such a difference implies that the threshold value I_{H^*}/I_{SiH^*} or $I_{H\alpha^*}/I^*_{SiH}$ for amorphous

to microcrystalline transition is also strongly dependent on other deposition conditions, in other words, there are many factors co-existing in a particular deposition system.

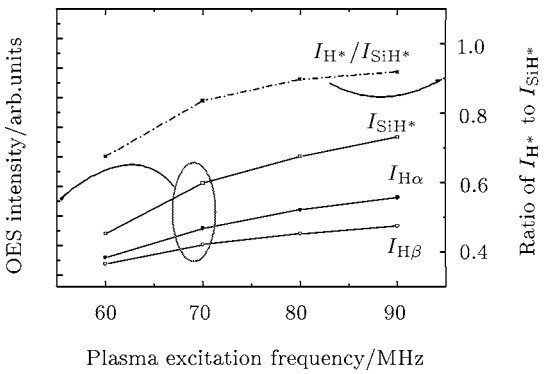


Fig.2. OES intensities versus plasma excitation frequency gas source SiH_4 and H_2.[14]

3.2. Raman spectra and thicknesses

Figure 3 shows the Raman spectra of μc-Si:H thin films deposited on Corning 7059 glass under different plasma excitation frequencies. From Fig.3, the crystalline volume fraction X_c and the average grain size d can be obtained empirically,[21−23] the corresponding results of X_c and d are shown in Fig.4. As can be seen from Fig.4, X_c seems to be more sensitive to plasma excitation frequency than d. For all μc-Si:H thin films the average grain sizes are about 8.4 nm, with excitation frequency increasing from 60 to 90 MHz, the crystalline volume fraction X_c increases first and reaches a maximum at 80 MHz (~65%), then decreases appreciably between 80 and 90 MHz.

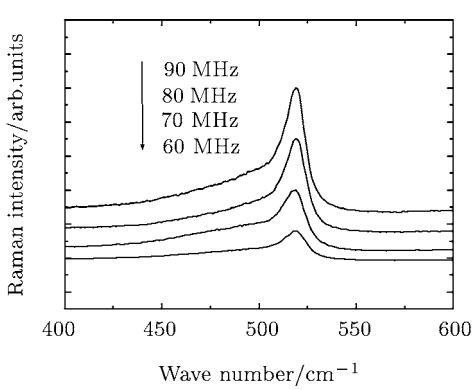


Fig.3. Raman spectra of μc-Si:H deposited under different plasma excitation frequencies.

The optical transmission and reflection (T&R) spectra have also been measured on the μc-Si:H thin films deposited on Corning 7059 glass. From fitting the interference fringes in the optical T & R spectra, the sample thickness and refractive index can be obtained.[24] Here we mainly focus on the former, the refractive index will be reported elsewhere. According to the measurements of sample thickness and the corresponding deposition time, deposition rate can be obtained. As shown in Fig.5, the deposition rate increases from 0.74 to 1.3 nm/s when plasma excitation frequency increases from 60 to 90 MHz.

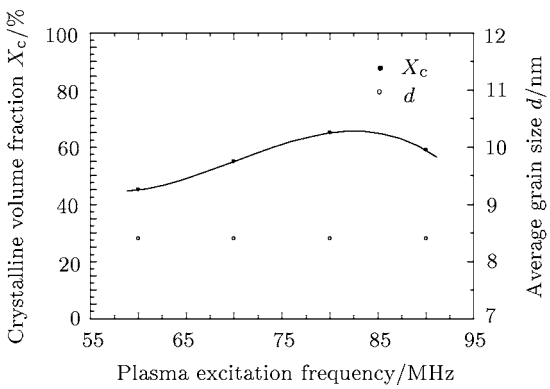


Fig.4. Crystalline volume fraction X_c and average grain size d with excitation frequency.

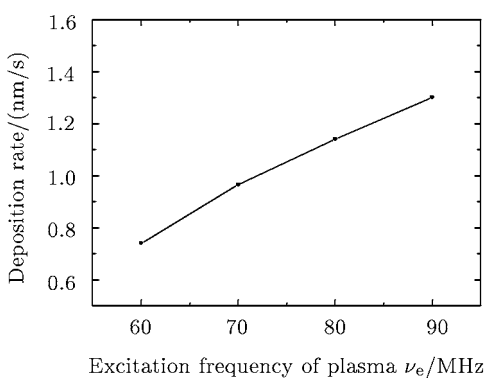


Fig.5. Deposition rate with excitation frequency.

Both the crystalline volume fraction and deposition rate are in good accord with the above OES results. Although quantitative relations need further study, a qualitative explanation can be given here. In general, radicals corresponding to atomic hydrogen mainly concern with the crystallization of μc-Si:H film and the deposition rate is mainly determine by SiH_x ($x = 1, 2, 3$) radicals. Compared to conventional RF deposition at 13.56 MHz, VHF plasma leads to lower electron temperature and higher electron density. Hence, higher plasma excitation frequency is favourable to produce higher density of atomic hydrogen, higher etching rate to remove the disordered

material, higher hydrogen coverage of the growing surface to promote surface diffusion of precursors,[11] and thus it is easy to realize the crystallization of deposited silicon films. However, too high excitation frequency would lead to the decrease of crystalline volume fraction of μc-Si:H film, which could be caused by lower etching energy of H under higher excitation frequency.[25] Furthermore, decomposition of SiH_4 can also be enhanced by higher excitation frequency to produce more SiH_x $(x = 1, 2, 3)$ radicals, providing more sources of favourable gas phase reactive species, then the deposition rate can be increased.

3.3. FTIR spectra

FTIR spectra measurements were carried out on μc-Si:H thin films deposited on the optically polished single crystalline silicon wafers. A typical FTIR spectrum is shown in Fig.6. As can be seen from Fig.6, the wagging mode of Si-H in μc-Si:H thin film is the strongest of all and shifted to 613 cm^{-1}, which is different from 640 cm^{-1} of that in a-Si:H thin film. In a-Si:H thin film, the hydrogen content can be conveniently determined from the absorption modes near 640 and 2000 cm^{-1}, and in μc-Si:H thin film, the integrated intensity near 640 $cm^{-1}$and a proportionality constant of $2.1\times10^{19}cm^{-2}$ are commonly adopted.[26,27]

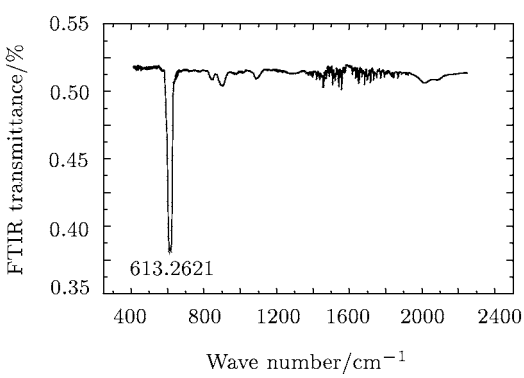


Fig.6. Typical FTIR spectrum of μc-SiH: film.

Figure 7 shows the hydrogen contents of μc-Si:H thin films deposited under different plasma excitation frequencies. From Fig.7, it can be seen that the hydrogen contents in μc-Si:H thin films are decreased with the increase of plasma excitation frequency, and for all the VHF-PECVD deposited μc-Si:H samples, low hydrogen contents (about 4% to 5%) can be observed. These values are much less than those of μc-Si:H films deposited by means of RF-PECVD technique. It has been confirmed that hydrogen is usually a leading factor to cause Staebler–Wronski effect[28] in a-Si:H thin film, and consequently hydrogen has strong influence on the stability of μc-Si:H thin films. Thus it is easy to understand why μc-Si:H thin films deposited by VHF-PECVD technique usually have good stability under light irradiation, which is confirmed by comparative light-soaking experiments on two typical μc-Si:H thin films deposited by means of VHF-PECVD and RF-PECVD.

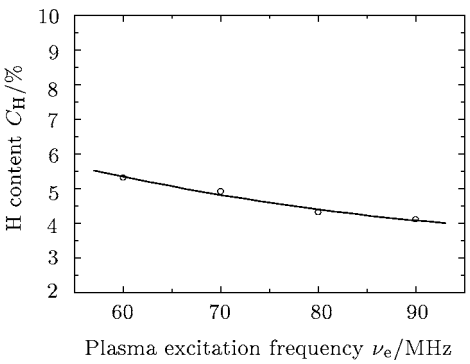


Fig.7. Hydrogen content versus excitation frequency.

4. Summary

In conclusion, in terms of FTIR spectra characterization and *in situ* OES diagnosis, the role of hydrogen in μc-Si:H thin film and in deposition process under VHF-PECVD have been investigated. It is identified that the introduction of very high frequency is not only helpful to decompose the hydrogen-diluted silane to produce atomic hydrogen and SiH_x, but also make the hydrogen content in μc-Si:H thin films greatly decreased. This is why the μc-Si:H thin films deposited by VHF-PECVD technique usually have better stability under light-soaking than those prepared by RF-PECVD. Moreover, through Raman spectra and thickness measurements, the essential influence of atomic hydrogen on crystalline volume fraction and that of SiH_x radicals on deposition rate of μc-Si:H thin films have also been investigated. Both crystalline volume fraction and deposition rate are enhanced with the increase of plasma excitation frequency, which is in good accord with the OES results.

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