



# Growth and properties of hydrogenated microcrystalline silicon thin films prepared by magnetron sputtering with different substrate temperatures

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**Abstract** Hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) thin films were deposited by an radio frequency (RF) (13.56 MHz) magnetron sputtering at different substrate temperatures (100–300 °C), and the influences of substrate temperature on the growth and properties of  $\mu\text{-Si:H}$  thin films were investigated. Surface roughness and crystallinity of the thin films increase as substrate temperature increases. And all thin films are at the transition region ( $X_c = 49.2\% \sim 61.0\%$ ). The  $\mu\text{-Si:H}$  thin films deposited at lower substrate temperature ( $\leq 200$  °C) represent a weak (220) preferred orientation, while the thin films deposited at higher substrate temperature ( $\geq 250$  °C) exhibit a weak (111) preferred orientation. The  $\mu\text{-Si:H}$  thin films have a dense structure, and the structural compactness of the thin films slightly increases with substrate temperature increasing. The Fourier transform infrared spectroscopy (FT-IR) results indicate that the  $\mu\text{-Si:H}$  thin films have a low hydrogen content (3.9 at%–5.6 at%), which is in favor of reducing light-induced degradation effect.

**Keywords**  $\mu\text{-Si:H}$  thin films; Magnetron sputtering; Substrate temperature; Hydrogen content

## 1 Introduction

Hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) thin films gain much attention as a material for thin-film solar cells, thin-film transistors and image sensors due to their excellent optical and electrical properties [1–3]. There are a variety of deposition techniques used to prepare  $\mu\text{-Si:H}$  thin films, such as hot-wire chemical vapor deposition (HWCVD) [4, 5], plasma-enhanced chemical vapor deposition (PECVD) [1, 6] and magnetron sputtering [7–9]. The magnetron sputtering process is a good alternative because it has a capability for large area deposition and process controllability, and, especially, it is a safe process not using toxic and explosive gases [9, 10]. Previous studies showed that  $\mu\text{-Si:H}$  thin films can be obtained by frequency (RF) magnetron sputtering with a silicon target when the sputtering discharge is operated with the  $\text{H}_2/\text{Ar}$  gas mixture [7–9, 11]. And it was found that the growth and properties of  $\mu\text{-Si:H}$  thin films would be influenced by deposition conditions such as substrate temperature, RF power, total pressure and partial hydrogen and argon dilution [7–9, 11–14]. The substrate temperature is a crucial deposition condition for optimization of growth and properties of  $\mu\text{-Si:H}$  thin films [14, 15]. The lowering of substrate temperature for  $\mu\text{-Si:H}$  thin films deposited on glass substrate ( $< 400$  °C) or even on flexible plastic substrate ( $< 200$  °C) is an attractive goal for extension of application areas and reduction in fabrication cost [14]. Thus, it makes sense to investigate the effect of substrate temperature on growth and properties of  $\mu\text{-Si:H}$  thin films. The aim of the present work is to investigate how substrate temperature affects the growth and properties of  $\mu\text{-Si:H}$  thin films deposited by magnetron sputtering.

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## 2 Experimental

The  $\mu\text{-Si:H}$  thin films were prepared using an RF (13.56 MHz) magnetron sputtering system with a 78.74 cm-diameter-silicon wafer as the target. The glass and double-sided polished silicon wafer were used as the substrates for different measurements. The thin films on glass substrates were used for atomic force microscopy (AFM), Raman, spectroscopic ellipsometry (SE) and X-ray diffraction (XRD) measurements, and the thin films on double-sided polished silicon substrates were used for Fourier transform infrared spectroscopy (FT-IR) measurements. In all case, the gas was directly introduced near the target surface to improve its utilization. In addition, the base pressure, RF power, gas pressure and hydrogen dilution ratio ( $\text{H}_2/(\text{Ar} + \text{H}_2) \times 100\%$ ) were fixed at  $\sim 1 \times 10^{-5}$  Pa, 200 W,  $\sim 0.2$  Pa and 60 %, respectively. The substrate temperature varied in the range of 100–300 °C. The thickness of thin films is  $\sim 200$  nm as determined by SE.

The surface morphology and surface roughness of  $\mu\text{-Si:H}$  thin films were measured using AFM (CSPM 5500) in contact mode. The crystal structure of  $\mu\text{-Si:H}$  thin films was analyzed using XRD (Burker AXS D8) with grazing angle mode (Cu  $K\alpha$  radiation, 40 kV, 40 mA). The crystallinity of thin films was characterized by a confocal micro-Raman spectroscopy (Renishaw inVia-reflex) using a 488-nm Ar + laser for excitation; laser power density was fixed at  $1.2 \text{ mW}\cdot\text{mm}^{-2}$  to avoid induced crystallization. The approximate crystalline volume fraction ( $X_C$ ) of  $\mu\text{-Si:H}$  thin films was estimated as:

$$X_C = (I_{505} + I_{520}) / (I_{480} + I_{505} + I_{520}) \quad (1)$$

where  $I_{480}$ ,  $I_{505}$  and  $I_{520}$  are the integrated intensities of scattering peaks at  $\sim 480 \text{ cm}^{-1}$  (amorphous phase),  $\sim 505 \text{ cm}^{-1}$  (defective part of the crystalline phase) and  $\sim 520 \text{ cm}^{-1}$  (crystalline phase), respectively [11, 16]. The hydrogen bonding configuration and total bonded hydrogen content ( $c_H$ ) of thin films were determined by FT-IR (Thermo Nicolet 6700) in the wave number range of 4000–400  $\text{cm}^{-1}$ . The  $c_H$  of  $\text{Si:H}$  thin films is proportional to the area of the absorption band ( $A_{640}$ ) at  $640 \text{ cm}^{-1}$ , as calculated using the equation:

$$c_H = \frac{A_{640}}{N} \int \frac{\alpha(\omega)}{\omega} d\omega \quad (2)$$

where  $A_{640} = 2.1 \times 10^{19} \text{ cm}^{-2}$ ,  $N = 5.0 \times 10^{22} \text{ cm}^{-3}$ ,  $\alpha(\omega)$  is the absorption coefficient at wavenumber ( $\omega$ ) [14, 17].

## 3 Results and discussion

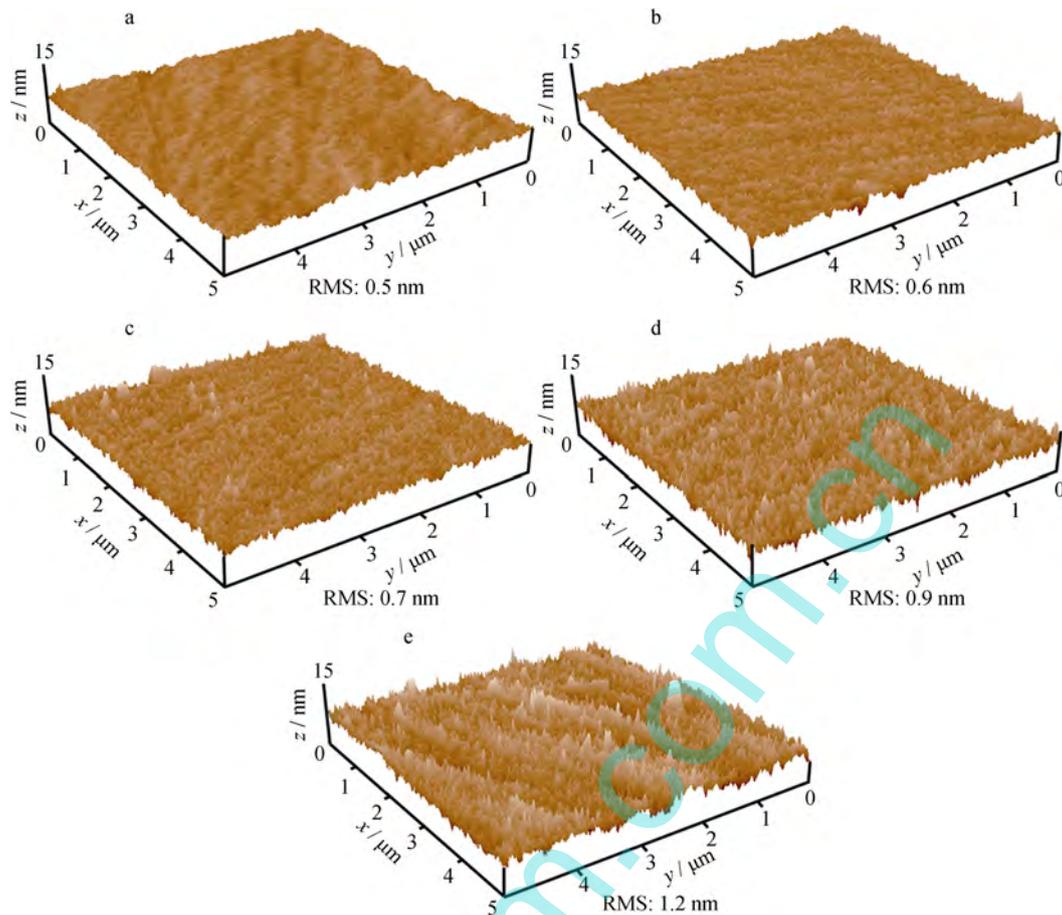
Figure 1 shows the AFM images of  $\mu\text{-Si:H}$  thin films deposited at different substrate temperatures. It can be seen

that surface of deposited thin films become more and more rough with substrate temperature increasing. The surface roughness of thin films increases from  $\sim 0.5$  to  $\sim 1.2$  nm with the substrate temperature increasing from 100 to 300 °C. It may be due to the fact that increasing substrate temperature enhances the surface migration of deposition precursors and leads to the changes in the crystallization behavior and microstructure of  $\mu\text{-Si:H}$  thin films [18, 19].

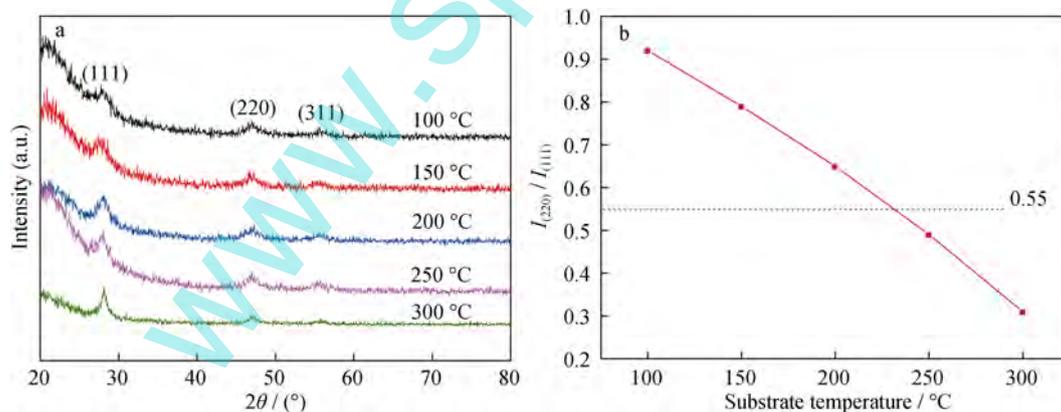
Figure 2a shows the XRD patterns of  $\mu\text{-Si:H}$  thin films deposited at different substrate temperatures. The XRD patterns of all thin films have three small diffraction peaks at about  $2\theta = 28.4^\circ$ ,  $47.3^\circ$  and  $56.1^\circ$ , corresponding to the Si (111), (220) and (311) diffraction peaks, respectively, which indicates that Si crystallites form under such conditions [16, 20]. And the XRD signal turns intensive with substrate temperature increasing, indicating that the crystallinity is enhanced [16, 20]. During the growth of  $\mu\text{-Si:H}$  thin films, the atomic hydrogen density and the surface diffusion coefficient of deposition precursors would increase as substrate temperature increases. The increased atomic hydrogen density and surface diffusion coefficient occurring on the surface would enhance the surface diffusion length of deposition precursors. Thus, deposition precursors adsorbed on the surface can find energetically favorable sites, leading to an enhancement of crystallinity [21, 22].

Moreover, the variation trend of the ratio of the intensity of (220) peak to that of (111) peak ( $I_{(220)}/I_{(111)}$ ) as function of the substrate temperature was investigated. As shown in Fig. 2b,  $I_{(220)}/I_{(111)}$  decreases from  $\sim 0.9$  to  $\sim 0.3$  as substrate temperature increases from 100 to 300 °C.  $I_{(220)}/I_{(111)}$  is higher than 0.55 at lower substrate temperature ( $\leq 200$  °C), while lower than 0.55 at higher substrate temperature ( $\geq 250$  °C). 0.55 is a critical value to determine the preferred orientation of the  $\mu\text{-Si:H}$  due to the fact that the value of  $I_{(220)}/I_{(111)}$  of Si powder is 0.55 [20]. Any deviation from 0.55 is considered as the signal of preferential growth in the  $\mu\text{-Si:H}$  [20]. Therefore, the  $\mu\text{-Si:H}$  thin films deposited at lower substrate temperature ( $\leq 200$  °C) represent a weak (220) preferred orientation, while those deposited at higher substrate temperature ( $\geq 250$  °C) exhibit a weak (111) preferred orientation.

Figure 3a shows the Raman spectra of  $\mu\text{-Si:H}$  thin films deposited at different substrate temperatures. The Raman spectra of all  $\mu\text{-Si:H}$  thin films have a narrow and predominant peak located at  $\sim 518 \text{ cm}^{-1}$ , indicating that the thin films contain a crystalline Si structure [11, 16]. The peak width becomes narrower as substrate temperature increases, implying that the crystallinity of thin films increases as substrate temperature increases [11, 16]. The Raman results are in good agreement with the XRD results. In addition,  $X_C$  of thin films as a function of substrate temperature is shown in Fig. 3b. As substrate



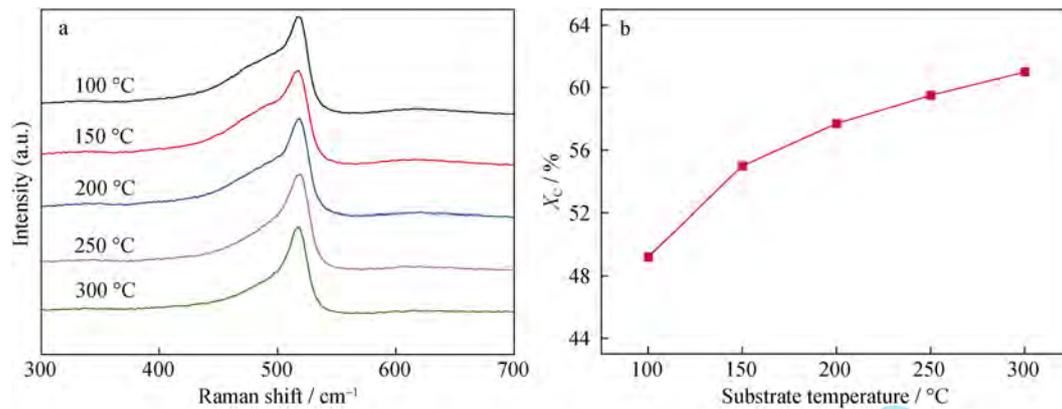
**Fig. 1** AFM images of  $\mu\text{-Si:H}$  thin films deposited at different substrate temperatures: **a** 100 °C, **b** 150 °C, **c** 200 °C, **d** 250 °C and **e** 300 °C. (RMS: average of roughness of a surface)



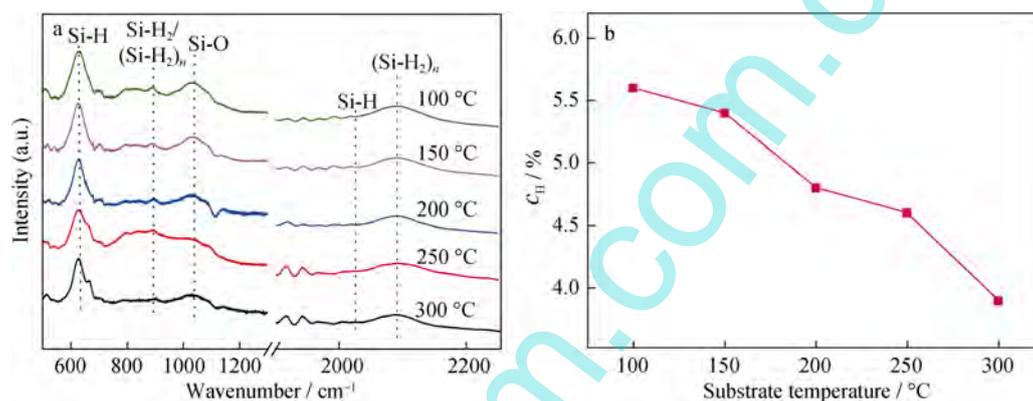
**Fig. 2** XRD patterns of  $\mu\text{-Si:H}$  thin films deposited at different substrate temperatures **a** and integrated XRD intensity ratio of (220) to (111) peaks (designated as  $I_{(220)}/I_{(111)}$ ) as a function of substrate temperature **b**. Dotted line referring to  $I_{(220)}/I_{(111)}$  value of standard silicon powder pattern

temperature increases from 100 to 300 °C,  $X_C$  increases from  $\sim 49.2\%$  to  $\sim 61.0\%$ . It was reported that  $\mu\text{-Si:H}$  thin-film solar cells with intrinsic absorber layer at the transition region usually exhibit an optimal performance,

and the crystalline fraction of  $\mu\text{-Si:H}$  thin films deposited by PECVD at transition condition often falls in the range of 40%–60% [6, 23]. It can be said, therefore, that all  $\mu\text{-Si:H}$  thin films obtained here have a suitable crystallinity.



**Fig. 3** Raman spectra of  $\mu\text{c-Si:H}$  thin films deposited at different substrate temperatures **a** and crystal volume fraction ( $X_c$ ) of  $\mu\text{c-Si:H}$  thin films as a function of substrate temperature **b**



**Fig. 4** FT-IR absorption spectra of  $\mu\text{c-Si:H}$  thin films deposited at different substrate temperatures **a** and total bonded hydrogen content ( $c_H$ ) of  $\mu\text{c-Si:H}$  thin films as a function of substrate temperature **b**

Figure 4a shows FT-IR absorption spectra of  $\mu\text{c-Si:H}$  thin films deposited at different substrate temperatures. The FT-IR absorption spectra of all thin films manifest some major absorption bands at  $500\text{--}700\text{ cm}^{-1}$ ,  $840\text{--}900\text{ cm}^{-1}$ ,  $1000\text{--}1100\text{ cm}^{-1}$ , and  $1900\text{--}2200\text{ cm}^{-1}$ . The FT-IR absorption spectra of Si:H thin films were extensively investigated, and assignment of the absorption bands to a particular Si-H bond configuration was well established [14, 17]. The absorption bands at  $500\text{--}700\text{ cm}^{-1}$ ,  $840\text{--}900\text{ cm}^{-1}$ ,  $1000\text{--}1100\text{ cm}^{-1}$  and  $1900\text{--}2200\text{ cm}^{-1}$  are attributed to Si-H wagging/rocking mode,  $\text{Si-H}_2/(\text{Si-H}_2)_n$  stretching/bending mode, Si-O stretching mode and  $\text{Si-H}/(\text{Si-H}_2)_n$  stretching mode, respectively [14, 17, 24]. In this case, the peak related to the wagging/rocking mode locates at  $\sim 630\text{ cm}^{-1}$ , indicating the presence of a crystalline phase in these samples [12, 13, 24]. The peak related to stretching absorption band locates at  $\sim 2090\text{ cm}^{-1}$ , and no absorption peak can be found at  $\sim 2010\text{ cm}^{-1}$ , which suggests that the hydrogen is predominately bonded to Si as  $\text{Si-H}_2$  and  $(\text{Si-H}_2)_n$  complexes [17, 24]. The

stretching/bending mode (assigned to  $\text{Si-H}_2/(\text{Si-H}_2)_n$  complexes) at  $\sim 840\text{ cm}^{-1}$  can also be observed for all thin films. And the intensity of all absorption bands decreases with substrate temperature increasing. This indicates that  $c_H$  decreases with substrate temperature increasing.  $c_H$  estimated from the integrated intensity of the wagging/rocking mode. And the variation of  $c_H$  as a function of substrate temperature is shown in Fig. 4b. It can be seen that  $c_H$  decreases from  $\sim 5.6\text{ at}\%$  to  $\sim 3.9\text{ at}\%$  with the substrate temperature increasing from 100 to  $300\text{ }^\circ\text{C}$ . This variation may be attributed to the decrease in amorphous fraction or grain boundary in the thin films or a the decreasing saturation of dangling bonds by hydrogen as substrate temperature increases, because hydrogen is mainly bonded with amorphous matrix and grain boundaries in  $\mu\text{c-Si:H}$  thin films [16, 17]. An interesting phenomenon is that  $c_H$  values of all  $\mu\text{c-Si:H}$  thin films are mostly lower than 5 at%. It was reported that the degradation of Si thin-film solar cell can be suppressed by reducing  $c_H$  in the intrinsic Si thin films [16]. Thus, the low  $c_H$  in these  $\mu\text{c-Si:H}$  thin films should

be more beneficial for Si thin-film solar cell because it could be more stable under prolonged luminescence. Moreover, the peak related to Si–O stretching mode is also shown in Fig. 4a. It is considered as an indication of the less dense material that is prone to suffer post-oxidation [20, 25]. The intensity of these peaks is very weak for all thin films here, and the intensity decreases with substrate temperature increasing. This indicates that  $\mu\text{-Si:H}$  thin films have a dense structure, and thin films deposited at higher substrate temperature are denser.

#### 4 Conclusion

In this work, it was systematically investigated the growth and properties of  $\mu\text{-Si:H}$  thin films deposited by an RF (13.56 MHz) magnetron sputtering with different substrate temperatures (100–300 °C). As substrate temperature increases, the surface roughness and crystallinity of the  $\mu\text{-Si:H}$  thin films increase. This may be attributed to the enhanced surface migration of deposition precursors due to the increase in substrate temperature. The  $\mu\text{-Si:H}$  thin films deposited at lower substrate temperature ( $\leq 200$  °C) represent a weak (220) preferred orientation, while the thin films deposited at higher substrate temperature ( $\geq 250$  °C) exhibit a weak (111) preferred orientation. The FT-IR results indicate that  $\mu\text{-Si:H}$  thin films have a dense structure, and the structural compactness of thin films slightly increases with substrate temperature increasing. An interesting phenomenon is that hydrogen contents of all  $\mu\text{-Si:H}$  thin films are mostly lower than 5 at%, which is in favor of reducing light-induced degradation effect.

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