Optical absorption enhancement of μc-SiGe:H films deposited via high pressure and high power*

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Hydrogenated microcrystalline silicon-germanium (μc-SiGe:H) films are fabricated by radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD). The optical absorption coefficient and the photosensitivity of the μc-SiGe:H films increase dramatically by increasing the plasma power and deposition pressure simultaneously. Additionally, the microstructural properties of the μc-SiGe:H films are also studied. By combining Raman, Fourier transform infrared (FTIR) and X-ray fluoroscopy (XRF) measurements, it is shown that the Ge-bonding configuration and compactability of the μc-SiGe:H thin films play a crucial role in enhancing the optical absorption and optimizing the quality of the films via a significant reduction in the defect density.

Hydrogenated microcrystalline silicon-germanium alloy (μc-$Si_{1-x}Ge_x$:H), a variable narrow-bandgap material, has become increasingly attractive in recent years due to its potential application in multi-junction solar cells. μc-$Si_{1-x}Ge_x$:H has a higher absorption coefficient than μc-Si:H within the solar spectrum[1-7]. However, the mechanism of the effects on the optical absorption properties of the μc-$Si_{1-x}Ge_x$:H materials, such as deposition conditions and structural characteristics, is unclear.

In recent years, high-pressure depletion[8-10] has been widely used in preparing μc-Si:H films. It has been shown that using a high deposition pressure is an efficient way to reduce the ion damage and provide sufficient silane molecules in the reaction zone[8,9,11,12]. Moreover, high plasma power is beneficial for facilitating the crystallinity of the films deposited by PECVD. In this study, we report an investigation of the influence of the reaction pressure and power on the optical absorption properties of μc-$Si_{1-x}Ge_x$:H films and correlate the microscopic structures with the optical absorption.

The μc-SiGe:H films were deposited by RF-PECVD using an SiH_4–GeH_4–H_2 gas mixture on Corning Eagle 2000 glass at 200 ℃. The deposition pressure (p_g) varied from 266.6 Pa to 666.5 Pa, and the plasma power (P_W) varied from 40 W to 100 W. The crystalline volume fraction of the samples, $X_c=(I_c+I_i)/(I_c+I_i+I_a)$, was calculated by Raman spectroscopy, where I_a, I_i and I_c correspond to the integrated intensities of the Raman peaks near 480 cm^{-1}, 500 cm^{-1} and 520 cm^{-1}, respectively[13]. Raman spectra were measured using an He–Ne laser (λ=6328 Å) light source (LabRAM HR800). Fourier transform infrared (FTIR) spectroscopy with reference to an undeposited c-Si wafer was applied to determine the molecular bonding in the μc-SiGe:H films. To obtain the optical absorption coefficient spectra, the transmission and reflection spectra were recorded. The Ge concentrations of μc-SiGe:H thin films were characterized by X-ray fluoroscopy (XRF, NanoScope IV).

First, the optical absorption properties as well as the dark and photo-conductivities of μc-SiGe:H films as a function of the power are shown in Fig.1. As P_W increases from 40 W to 60 W, the optical absorption of the samples increases dramatically in the energy (E) region from 1.0 eV to 1.8 eV, and the conductivities indicate a phase transition from a-SiGe:H to μc-SiGe:H. This finding is attributed to the increased crystallinity of the samples under higher-power conditions. A higher X_c can facilitate the optical absorption of μc-SiGe:H films when 1.0 eV<E<1.8 eV. However, both the optical absorption and the photosensitivity of the samples decrease as the power further increases up to 100 W, which is mainly due to the increased defect density and the reduced qual-

ity of the μc-SiGe:H films with excessively high crystallinity as shown in Fig.1(b) .

(a)

(b)
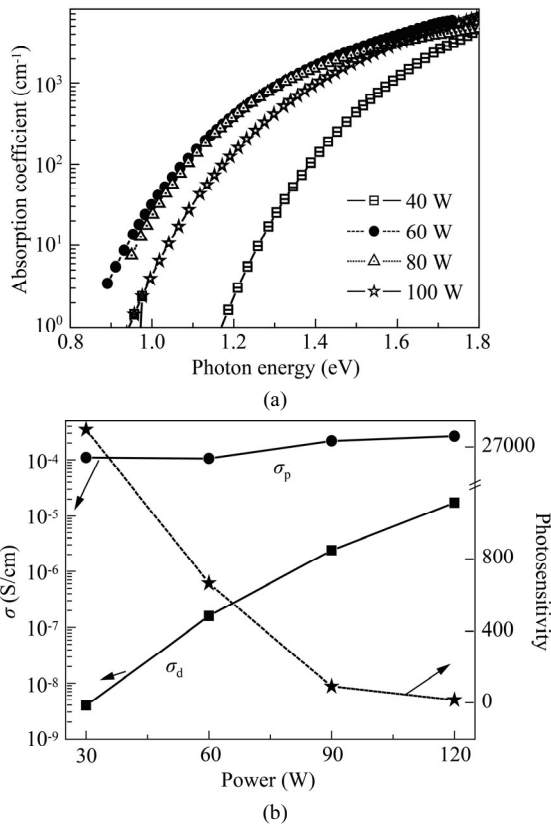
Fig.1 (a) The absorption coefficient and (b) dark and photo-conductivities of the μc-Si$_{1-x}$Ge$_x$:H films as a function of power

The deposition power is fixed at 60 W and the reaction pressure is varied from 266.6 Pa to 666.5 Pa. The optical absorption properties and the dark and photo-conductivities of the samples as a function of the pressure are illustrated in Fig.2, where both the optical absorption and the photosensitivity increase initially and then decrease as p_g increases, and neither extremely high nor extremely low p_g produces the films with good optical absorption and photosensitivity.

It has been generally accepted that a relatively high p_g increases electron density and decreases electron energy in the reaction zone. Many research groups have found that high pressure shifts the ionic energy to a lower distribution and increases the ionic flux to the growing surface[11,12,14]. However, the polymerization of silane molecules occurs under an extremely high p_g, which causes the formation of the powder during deposition and deteriorates the performance of the μc-SiGe:H films[9,11,12].

Based on the above analyses, the optical absorption and photosensitivity of the samples increase under P_W = 60 W and p_g = 399.9 Pa. As mentioned above, both P_W and p_g are crucial parameters in determining the photoelectric properties of μc-SiGe:H films. Combining the

advantages of both the high-power and high-pressure conditions, we further investigate the performance of films by increasing P_W and p_g simultaneously. We vary P_W and p_g at the same time but keep the P_W/p_g (60 W/399.9 Pa) ratio constant, i.e., (40 W, 266.6 Pa)—(100 W, 666.5 Pa).


(a)

(b)
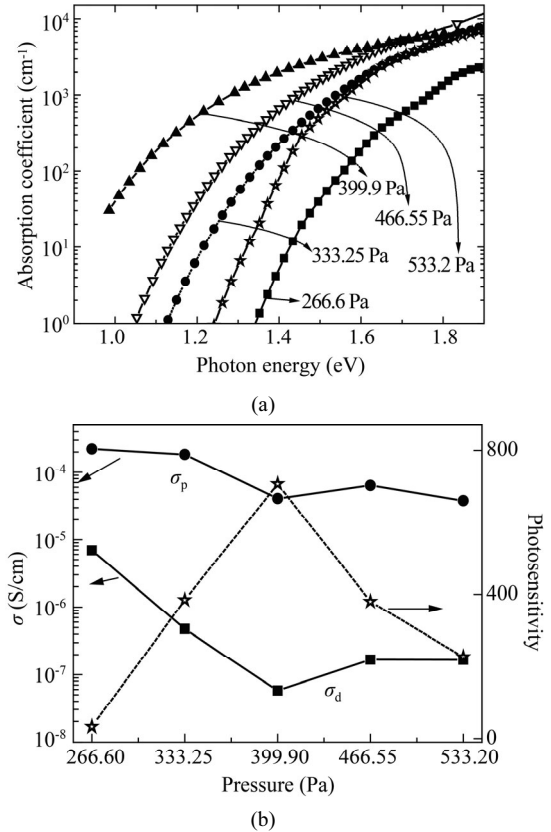
**Fig.2 (a) The absorption coefficient and (b) dark and photo-conductivities of the μc-Si$_{1-x}$Ge$_x$:H films as a function of pressure**

Fig.3 shows the absorption coefficients of the μc-Si$_{1-x}$Ge$_x$:H films under different P_W and p_g conditions, where the absorption coefficient decreases from (40 W, 266.6 Pa) to (60 W, 399.9 Pa). However, a systematic lower-energy shift is identified associated with P_W and p_g from (60 W, 399.9 Pa) to (100 W, 666.5 Pa). Fig.4 shows the dark and photo-conductivities of the same samples shown in Fig.3. It is clear that the photo-conductivity is almost constant, while the dark conductivity decreases by nearly one order of magnitude as P_W and p_g increase from (40 W, 266.6 Pa) to (100 W, 666.5 Pa). This indicates that the defect density decreases and the quality of the μc-SiGe:H film is optimized by the high-power and high-pressure condition. We correlate optical and electronic properties of the μc-SiGe:H film with the structural evolution and chemical bonding configurations, and analyze the main factor affecting the optical absorption and electronic properties.

The bandgap and compactability of the μc-SiGe:H film are two important parameters related to its optical

absorption properties[15,16]. X_c and the Ge content of the μc-Si$_{1-x}$Ge$_x$:H films are closely related to the bandgap of the films. Thus, we firstly investigate the variations of Ge content and X_c with the increase of P_W and p_g as shown in Fig.5 and Fig.6. The Ge content in the samples presents a decreasing tendency, which contributes to the increase of the decomposition of silane under high P_W and p_g condition. Because the lower Ge content can expand the bandgap of μc-SiGe:H films, the change in the Ge content is not the factor responsible for the optical absorption improvement under this condition.
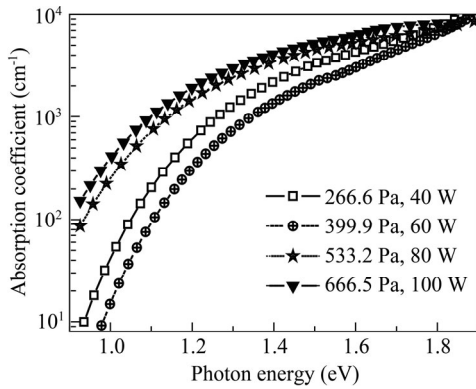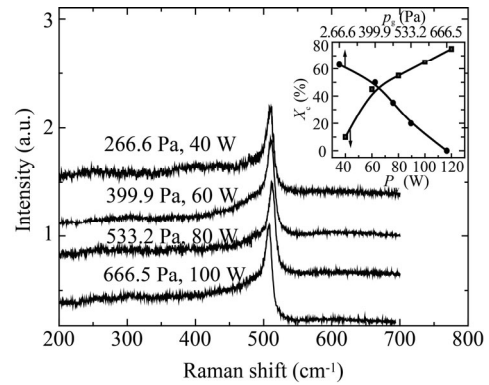

Fig.3 Absorption coefficients of the films under different P_W and p_g conditions
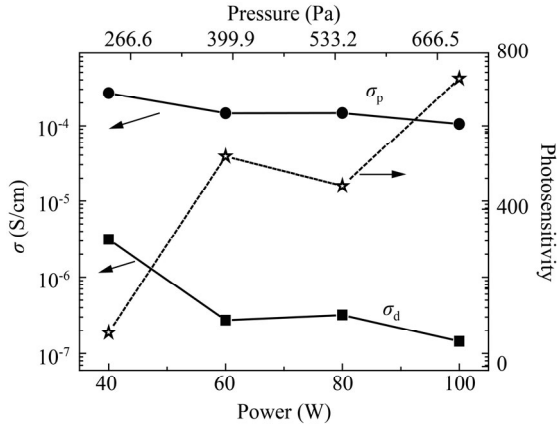
Fig.4 Dark and photo-conductivities and photosensitivities under different P_W and p_g conditions
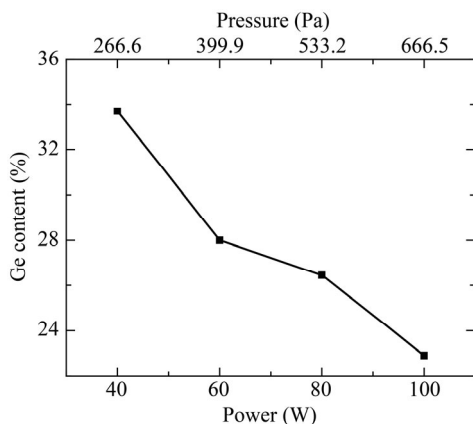
Fig.5 Ge contents for different P_W and p_g
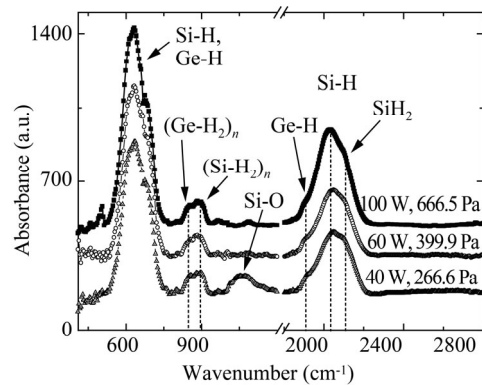

Fig.6 Raman spectra for different P_W and p_g

The Raman scattering spectra of the samples show slight differences in X_c from (40 W, 266.6 Pa) to (100 W, 666.5 Pa) (Fig.6). X_c of the samples as a function of P_W or p_g is shown in the inset (Fig.6) as well, where X_c increases with the power but decreases with the reaction pressure. Therefore, the similar values of X_c in the films are a consequence of the interaction between power and pressure from (40 W, 266.6 Pa) to (100 W, 666.5 Pa).

Therefore, the increase in the optical absorption is not due to the change in the X_c or Ge content of the μc-Si$_{1-x}$Ge$_x$:H films under high P_W and p_g, which can thus be mainly attributed to the change in the bonding configuration and compactability of the films.

FTIR spectroscopy is used to investigate the silicon/germanium hydrogen bonding configuration in the μc-Si$_{1-x}$Ge$_x$:H films as shown in Fig.7, where the Si–O–Si stretching modes in 1000–1100 cm^{-1} decrease dramatically as P_W and p_g increase. This indicates a decrease in the void volume fraction of the films and a denser microstructure at relatively high P_W and p_g.
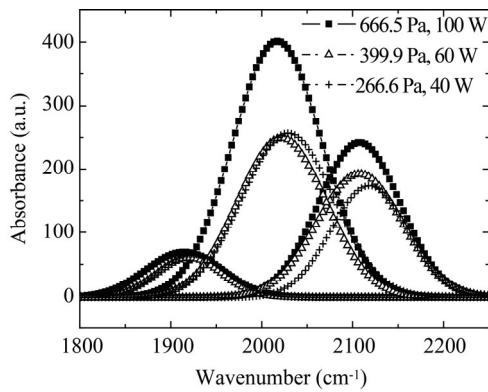

Fig.7 FTIR spectra for different P_W and p_g conditions

The fitting spectra of the region 1850–2300 cm^{-1} of μc-Si$_{1-x}$Ge$_x$:H films deposited in different P_W and p_g conditions are illustrated in Fig.8. The peaks of the stretching modes of Ge–H, Si–H and Si-H$_2$ are located at 1890 cm^{-1}, 2000 cm^{-1} and 2090 cm^{-1}, respectively[17]. According to Eqs.(1) and (2), we define a parameter called Ge–H preference ($P_{Ge–H}$) to describe the hydrogen distribution in the films. Specifically, $P_{Ge–H}<1$ indicates the

under-termination of Ge atoms by hydrogen as well as extra Ge dangling bonds[18], while the μc-Si$_{1-x}$Ge$_x$:H films have fewer Ge dangling bonds when P_{Ge-H} is close to 1. The microstructure factor (R) is calculated to estimate the compactability of thin μc-Si$_{1-x}$Ge$_x$:H films. Tab.1 presents P_{Ge-H} and R of the same samples shown in Fig.8, where P_{Ge-H} is the highest and R is the lowest under high P_W and p_g, corresponding to fewer Ge dangling bonds and the improved compactability of μc-Si$_{1-x}$Ge$_x$:H films.

$$R = \frac{I_{2090}}{I_{2090} + I_{2000}} \quad . \tag{1}$$

$$P_{Ge-H} = (\frac{I_{1890}}{I_{2000}}) / (\frac{Y}{1-Y}) \quad . \tag{2}$$

Fig.8 Spectral fitting for the region of 1850–2300 cm^{-1} under different P_W and p_g conditions

Tab.1 Ge–H preference (P_{Ge-H}) and microstructure factor (R) of the μc-Si$_{1-x}$Ge$_x$:H films under different P_W and p_g

	666.5 Pa, 100 W	399.9 Pa, 60 W	266.6 Pa, 40 W
R	0.38	0.44	0.40
P_{Ge-H}	0.8	0.72	0.63

Based on the above analyses, we attribute the increase of the absorption coefficient to several different reasons. On the one hand, the bonding configuration of Ge in the thin films plays an important role in determining the absorption coefficient of the films; specifically, fewer Ge dangling bonds decrease the defect density and consequently enhance the optical absorption. On the other hand, increasing power and pressure simultaneously can facilitate the film compactness, which improves the quality of the films and consequently increases the absorption coefficient.

In conclusion, the variation mechanisms of the absorption coefficient, microstructure and quality of the μc-Si$_{1-x}$Ge$_x$:H films are strongly affected by the power and pressure. As P_W and p_g increase simultaneously, the optical absorption coefficient of the μc-Si$_{1-x}$Ge$_x$:H films

increases, X_c remains nearly constant and the Ge content decreases slightly, while X_c and Ge content are not the factors responsible for the optical absorption enhancement. Associated with the increased structural compactability and fewer Ge dangling bonds of the μc-Si$_{1-x}$Ge$_x$:H films deposited under high P_W and p_g condition, the defect density reduction and quality improvement are crucial for increasing the absorption coefficient.

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