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The influence of H_2/Ar ratio on Ge content of the μc-SiGe:H films deposited by PECVD

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A B S T R A C T

An alternative approach of adjusting the Ge content in μc-SiGe:H films is explored by changing the H_2/Ar flow rate ratio. The results reveal that the Ge content and film deposition rate both decrease with the increasing flow rate ratio of H_2/Ar. Optical constants of the films are obtained by simulating the optical transmission spectrum using a modified envelope method. The dark conductivity and activation energy are investigated by measuring the temperature-dependent conductivity. The dependence of Ge content, deposition rate and optoelectronic properties on flow rate ratio of H_2/Ar is discussed.

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1. Introduction

In recent decades, the photovoltaic (PV) industry is undergoing rapid growth and it will maintain rapid growth in the foreseeable future. In order to improve the conversion efficiency, researchers propose a multi-band gap solar cell, which utilizes material whose band gap can be tailored to absorb different parts of the solar spectrum. Because of narrow and variable band gap, hydrogenated silicon germanium (SiGe:H) thin film has been used as a middle or bottom cell active layer material in multi-band gap thin film solar cell [1–4].

At present, the plasma enhanced chemical vapor deposition (PECVD) remains the major technique for fabrication of SiGe films at low temperature. The Ge content of the SiGe films is adjusted by changing the flow rate ratio of silane (SiH_4) and germane (GeH_4) [5]. Furthermore, the crystallinity deteriorates rapidly when Ge is incorporated by addition of GeH_4 to the plasma used to prepare microcrystalline silicon [6]. The authors have reported that the addition of Ar to the plasma can efficiently increase the crystallinity of μc-Si:H films [7]. This study motivates us to prepare μc-SiGe:H using H_2 and Ar as diluted gases.

In this work, the authors explore an alternative approach of adjusting the Ge content in μc-SiGe:H films by changing the ratio of H_2/Ar. In addition, the influence of H_2/Ar flow rate ratio on microstructure and optoelectronic properties of μc-SiGe:H films are investigated in detail.

2. Experimental details

The μc-$Si_{1-x}Ge_x$:H films were deposited in a standard RF (13.56 MHz) capacitively coupled PECVD system from a mixture of SiH_4 and GeH_4 diluted in H_2 and Ar. The substrate temperature, total pressure and RF power density were kept constant at 250 °C, 130 Pa and 0.34 W/cm^2, respectively. The gas flow rate was 1.5 sccm of SiH_4, 1.0 sccm of GeH_4 and the total flow rate of H_2 and Ar was kept at 100 sccm. The flow rate ratio of H_2/Ar was varied from 40:60 to 70:30.

The Ge content in the films was examined using x-ray photoelectron spectroscopy (XPS), which performed on a PerkinElmer PHI-5702 multi-functional X-ray photoelectron spectroscopy equipped with a monochromatic Al Kα X-ray source. The grain size and bond structure were investigated by X-ray diffraction (XRD) and Raman scattering spectrum. The XRD measurement was performed on a Rigaku D/Max-IIIC X-ray diffractometer in a standard θ–2θ configuration using Cu Kα radiation (0.15406 nm). Raman spectrum was measured using a Jobin-Yvon HR800 spectrometer with an excitation wavelength of 532 nm. The optical transmission spectra were performed over a wavelength range of 400–2500 nm using a double-beam ultraviolet–visible–near infrared spectrophotometer (Shimadzu UV3600). The film thickness and optical properties were obtained through simulating the optical transmission spectra. The temperature-dependent (300–423 K) dark conductivity was measured using a Keithley 6517A electrometer with coplanar configuration by vacuum evaporation of Al electrodes on films. The activation energy (E_a) was deduced from the Arrhenius plot.

3. Results and discussion

3.1. Ge content

The Ge content in the films examined by means of XPS is listed in Table 1. It can be seen that the Ge content decreases with increasing flow rate ratio of H_2/Ar. It is well known that the atomic hydrogen plays a considerable role in the formation process of Si-based films [8,9]. As the flow rate ratio of H_2/Ar increases, the increased atomic H flux in the plasma results in the increase of surface coverage by

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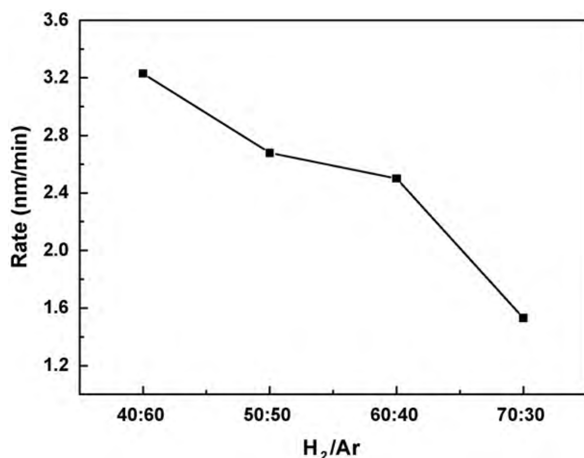

Fig. 1. The deposition rate as a function of H_2/Ar ratio.

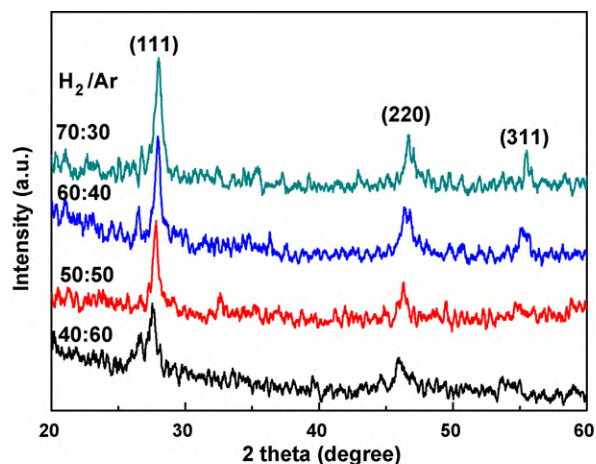

Fig. 2. The XRD patterns of μc-SiGe:H films deposited at different H_2/Ar ratio.

bonded hydrogen. The film precursors (SiH_3, GeH_3, etc.) reach the film growing surface and then start to diffuse on the surface. Bonding of precursors to the growing surface needs dangling bonds and the removal of hydrogen from the surface is a necessary step in the deposition of films. Considering the fact that the bond formation energy for Si–H is larger than that for Ge–H, the hydrogen atoms can preferentially bond with Ge precursors and leave a dangling bond on the surface, another precursors diffuse toward the dangling bond site leading to growth [10,11]. Meanwhile, atomic H reaching the film growing surface preferentially breaks the Ge–Ge bonds due to the bond formation energy for Ge–Ge is smaller than that for Si–Si, the site is replaced with a new precursor, SiH_3, which forms a strong Si–Si bond [12]. In short, we think the increase of surface coverage and etching effect of H atomic lead to the decrease of Ge content in the films.

The deposited rate is estimated from dividing the thickness of the film by deposition time (plotted in Fig. 1). It is shown that the deposition rate decreases as increasing flow rate ratio of H_2/Ar. We think there are two reasons results in the decrease of deposition rate. First, the plasma density decreases as the decreasing Ar flow rate, which leads to the decrease of dissociation efficiency of source gases, the film precursors reaching the growing surface reduce [13]. Second, the H atomic etching effect increases with the increasing H_2/Ar ratio, which results in the decrease of deposition rate [14].

The XRD spectra of the μc-$Si_{1-x}Ge_x$: H films are shown in Fig. 2. Peaks corresponding to the (1 1 1), (2 2 0) and (3 1 1) planes are indication of diamond crystal structure. All the films show preferential orientation of (1 1 1) plane. A shift of peak position towards the larger 2θ value is observed, which is attributed to the decrease of lattice constant with the decreasing Ge content [15]. The average grain size of the samples listed in Table 1 are obtained through the calculation from the full width at half maximum (FWHM) of the (1 1 1) diffraction peak by Scherrer formula. It can be seen that the grain size maintain at a larger value, which reveals that the films have good crystallinity.

Table 1
The results of μc-SiGe:H films deposited at different H_2/Ar flow rate ratio. Ge content is examined by means of XPS. $d_{(111)}$ is the grain size calculated from XRD (1 1 1) peaks. The absorption coefficient α_0 (at 2 eV) and refractive index n_0 (at 1.6 μm) are obtained by simulating the optical transmission spectra.

H_2:Ar	Ge content	$d_{(111)}$ (nm)	α_0 (cm^{-1})	n_0
40:60	0.53	19.0	17839	3.63
50:50	0.49	23.3	15329	3.55
60:40	0.28	24.9	9405	3.25
70:30	0.17	21.9	5607	3.23

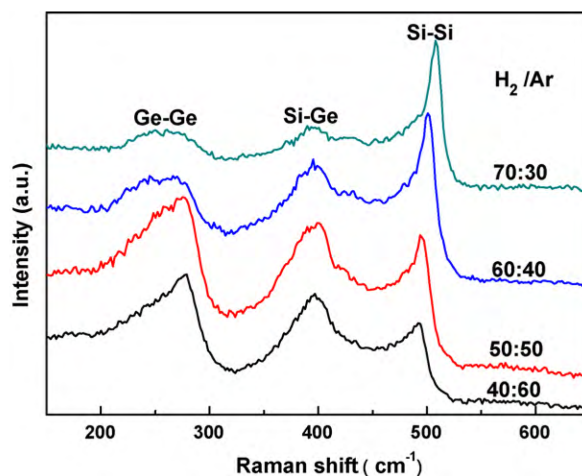

Fig. 3. Raman spectra of μc-SiGe:H films deposited at different H_2/Ar ratio.

Fig. 3 shows the Raman scattering spectra of μc-SiGe:H films prepared at different H_2/Ar flow rate ratio. Peaks centered at ~500, ~400 and ~280 cm^{-1} are attributed to Si–Si, Si–Ge and Ge–Ge transverse optic (TO) vibrations modes, respectively. The peak position of Ge–Ge, Si–Ge and Si–Si vibrations are sensitive to Ge content and a monotonic shift of these peaks with Ge content has been reported [16]. The Si–Si peak strongly red-shifts while Ge–Ge peak strongly blue-shifts with increasing Ge content. It is because that the Si–Si and Ge–Ge bonds receive the tensile and compressive stress due to the difference of bond length between Si and Ge [1].

3.2. Optical properties

It is well known that the refractive index and absorption coefficient of semiconductor film are key factor for an optoelectronic device. Manifacier et al. [17] introduce an envelop method, which modified by Swanepoel [18], to obtain the refractive index and absorption coefficient by simulating the transmission spectrum. In this paper, the authors utilize the envelop method to investigate the refractive index and absorption coefficients of the μc-SiGe:H samples. According to Ref. [19], considering the absorption of the transparent glass substrate, the transmission $T(\lambda)$ can be calculated using the following equations:

$$T(\lambda) = \frac{A(1-L)\exp(-\alpha t)}{B + C\ \exp(-\alpha t) + D\ \exp(-2\alpha t)}, \quad (1)$$

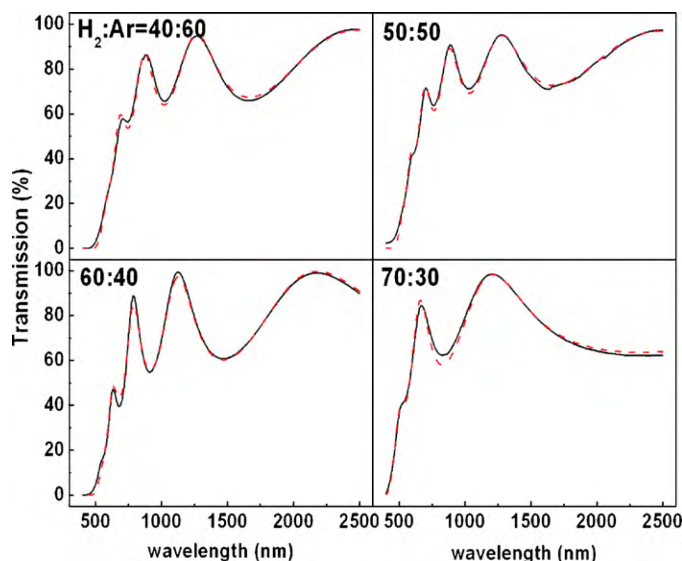

Fig. 4. Experimental (solid) and simulated (dotted) transmission spectra of μc-SiGe:H films.

where α is the absorption coefficient, t is the film thickness, L is the light scattering or reflection loss at the film surface. Other parameters are the same as in Ref. [19]. Wavelength-dependent refractive index $n(\lambda)$ and absorption coefficient $\alpha(\lambda)$ of the thin films are calculated by following equations:

$$n(\lambda) = n_{\infty} + \frac{A_n}{\lambda^2} \tag{2}$$

$$\alpha(\lambda) = A_{\alpha} \ \exp\left(\frac{h\nu}{\Gamma_{\alpha}}\right). \tag{3}$$

The optical band gap E_g are obtained from the experimental transmission spectra by Tauc plot using the following equations:

$$T = W \ \exp(-\alpha t) \tag{4}$$

$$\alpha = \frac{B_a}{h\nu}(h\nu - E_g)^2, \tag{5}$$

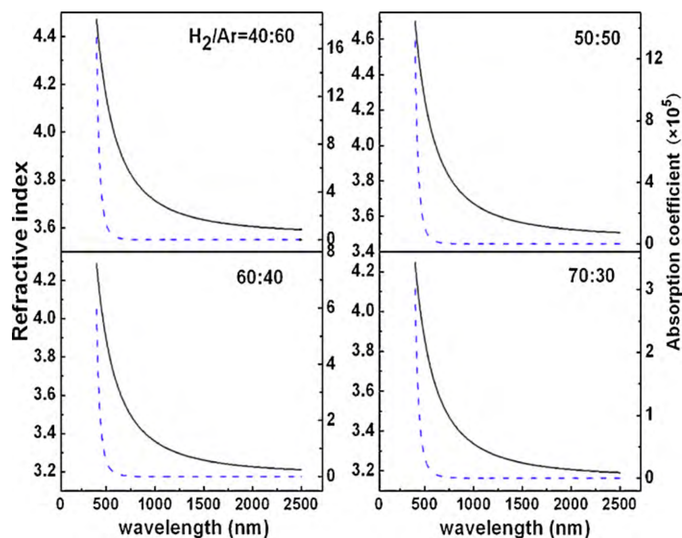

Fig. 5. The refractive indices (solid) and absorption coefficient (dotted) as a function of wavelength for μc-SiGe:H films.

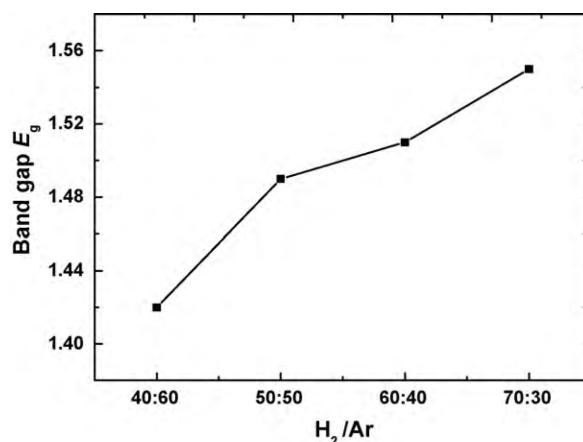

Fig. 6. Optical band gap as a function of H_2/Ar ratio.

Combining Eq. (4) and Eq. (5), we obtain the following equation:

$$\left(\frac{-h\nu \ln T}{t}\right)^{1/2} \propto (h\nu - E_g). \tag{6}$$

The simulated transmission spectra of μc-SiGe:H agree with the experimental ones very well (in Fig. 4). The calculated wavelength-dependent refractive index and absorption coefficient are shown in Fig. 5 and the values at certainty wave are listed in Table 1. The refractive indices of the μc-SiGe:H decrease with the increase of H_2/Ar flow rate ratio. The reason is that the decrease of Ge content, which results in the decrease of density [20]. Meanwhile, the absorption coefficients of μc-SiGe:H films also decrease with the decrease of Ge content [21]. The optical band gap of the films is plotted in Fig. 6 as a function of H_2/Ar flow rate ratio. It can be found that the optical band gap increases from 1.42 eV to 1.55 eV as the increasing H_2/Ar ratio. The above results reveal that the Ge content can be adjust by changing the H_2/Ar ratio.

3.3. Transport properties

The results on dark conductivity measurement are plotted in Fig. 7. The dark conductivity decreases from $1.19 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$ to $1.39 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ when Ge content decreases from 0.53 to 0.28. The trend is consistent with other literature [22,23]. What needs to pay attention is that the dark conductivity increases from 1.39×10^{-4} to $5.01 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ as the Ge content decreases

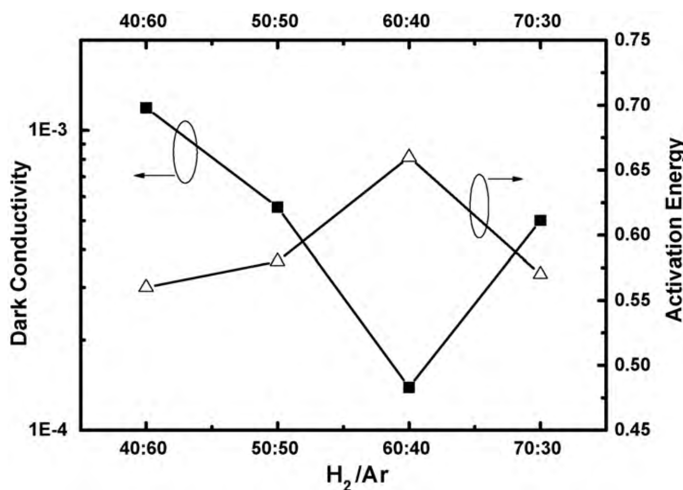

Fig. 7. The dark conductivity (■) and activation energy (△) as a function of H_2/Ar ratio.

from 0.28 to 0.17. The reason may be that the effect of hydrogen passivation increases while H_2 flow rate increases in the diluted gas, which results in the decrease of defect density [24,25]. The dark conductivity activation energy is also plotted in Fig. 7. The value first increases from 0.56 to 0.66 when Ge content decreases from 0.53 to 0.28, which is attributed to the increase of energy band gap. However, the activation energy decreases to 0.57 eV when Ge content further increases to 0.17. It is because that the decrease of defect density as the increase of hydrogen passivation effect, which results in the Fermi level shifts to conduction band.

4. Conclusion

In summary, the authors deposited μc-SiGe:H films by PECVD with different H_2/Ar flow rate ratio. The results revealed that the Ge content in the films can be adjusted by changing the flow rate ratio of H_2/Ar. The deposition rate decreased as the increase of H_2/Ar flow rate ratio, which due to the decrease of plasma density. The XRD and Raman results revealed that the films had good microcrystalline structure. The optical constants were obtained by simulating the optical transmission spectra. The results showed that the refractive index and absorption coefficient decreased with the increasing H_2/Ar flow rate ratio. The dark conductivity and activation energy were investigated by measuring the temperature-dependent conductivity. It was found that the μc-SiGe:H films could be deposited by PECVD using H_2 and Ar as diluted gas. Meanwhile, the Ge content in the films could be adjusted by changing the H_2/Ar ratio.

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