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Influence of reaction gas flows on the properties of SiGe:H thin film prepared by plasma assisted reactive thermal chemical vapour deposition*

Zhang Li-Ping(张丽平)†, Zhang Jian-Jun(张建军), Shang Ze-Ren(尚泽仁), Hu Zeng-Xin(胡增鑫), Geng Xin-Hua(耿新华), and Zhao Ying(赵 颖)

Institute of Photo-Electronics Thin Film Devices and Technique, Nankai University, Tianjin Key Laboratory of Photo-Electronic Thin Film Devices and Technology Laboratory of Opto-electronic Information Science and Technology (Nankai University, Tianjin University), Chinese Ministry of Education, Tianjin 300071, *China*

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A new preparing technology, very high frequency plasma assisted reactive thermal chemical vapour deposition (VHFPA-RTCVD), is introduced to prepare SiGe:H thin films on substrate kept at a lower temperature. In the previous work, reactive thermal chemical vapour deposition (RTCVD) technology was successfully used to prepare SiGe:H thin films, but the temperature of the substrate needed to exceed 400°C. In this work, very high frequency plasma method is used to assist RTCVD technology in reducing the temperature of substrate by largely enhancing the temperature of reacting gases on the surface of the substrate. The growth rate, structural properties, surface morphology, photoconductivity and dark-conductivity of SiGe:H thin films prepared by this new technology are investigated for films with different germanium concentrations, and the experimental results are discussed.

Keywords: SiGe:H thin film, plasma assisted RTCVD, growth rates, optoelectronics property
PACC: 7280, 7830, 7300

1. Introduction

Hydrogenated amorphous or microcrystalline silicon–germanium alloys have been widely investigated since these materials can be utilized as middle or bottom cell active layer materials in multi-band gap thin film solar cells.[1−3] The main reason is that the optical bandgap of silicon–germanium alloys can be widened from 1.7 eV to 1.0 eV by increasing germanium concentration (abbreviated GC) in the alloys, which can extend the spectral range to longer wavelengths and consequently achieve higher collection efficiency.[4]

At present, plasma enhanced chemical vapour deposition (PECVD[5,6]) remains the major technique for the fabrication of SiGe:H films.[7−9] Some alternative methods, such as electron–cyclotron resonance (ECR) plasma deposition[10] and hot wire (HW) deposition,[11] have also produced promising results. But the growth rates of the films prepared by these methods are always low and plenty of dangling bonds are formed with increasing GC. Zhang *et al*[12] made a TFT device by using reactive thermal chemical vapour deposition (RTCVD) which exhibited a good promise to solving these problems. However, a high substrate temperature exceeding 400°C is needed for this technology, which limits the use of many flexible or low cost substrates.

In this work, very high frequency plasma method is used to assist the RTCVD technology. The main advantage of this method is that it can greatly enhance the temperature of reacting gases on the surface of the substrate so as to reduce the need of high substrate temperature. Some properties of SiGe:H thin films prepared by VHFPA-RTCVD technology under varying reaction gas flows were investigated. The growth rate of thin films was measured using optical multicentre analyser. The crystallization and phase transi-

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†Corresponding author. E-mail: zlp_wan@yahoo.com.cn

tion of thin films were observed using Raman spectrum and atomic force microscopy (AFM), respectively. Photo- and dark-conductivities were investigated employing the coplanar contact configuration. At the end of this paper, the experimental results are discussed and some conclusions are drawn.

2. Experimental details

SiGe:H thin films are prepared by VHFPA-RTCVD on the Corning Eagle2k glass. The temperature of the substrate is 200°C. The feedstock gases are H_2, Si_2H_6 and GeF_4. The plasma excitation frequency is 60 MHz. The electrode size is 50 cm^2. The pressure and power are 100 Pa, 20 W and 66.66 Pa, 10 W, respectively.

In the total gas flow, the concentration of silicon germanium in the reaction gas flow varies from 1%–5%, which is denoted by (S + G)C

$$= ([Si_2H_6]\times 2+[GeF_4])/([H_2]+[Si_2H_6]\times 2 + [GeF_4]).$$

The increase of (S + G)C means H_2 dilution decreases. Germanium concentration in the reaction gas flow varies from 2%–40%, which is denoted by GC = $[GeF_4]/([Si_2H_6]\times 2+[GeF_4])$.

The thickness of the films is in the range of 400 and 600 nm, which is measured by optical multi-centre analyzer. The structural properties of the SiGe:H films are characterized by Raman spectra using an incident Ar laser beam at 514.5 nm. The surface morphology is observed by atomic force microscopy (AFM, NanoScope IV), and the photo-conductivity (using AM1.5) and dark-conductivity measurements employ the coplanar contact configuration.

3. Results

3.1. Growth rate

It is meaningful to investigate the growth rate of thin films because it reflects the density of growth precursors in the plasma. Here, growth rates of the SiGe:H thin films are investigated under different (S + G)Cs and GCs. Figure 1 shows the change of growth rates of SiGe:H deposited with different (S + G)Cs at GC of 10.5% and 15.0%, respectively. The growth rates show a strong increasing trend with the increase of (S + G)C, and which are similar to GCs of 10.5% and 15.0%.

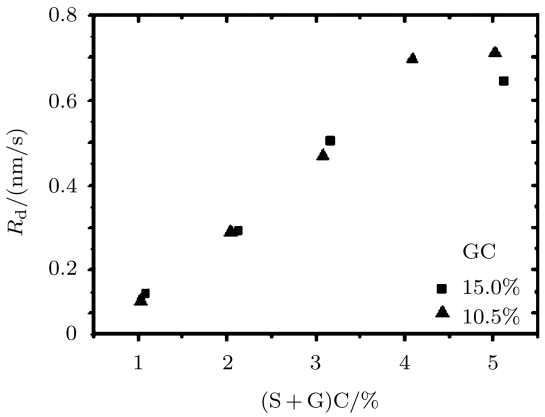


Fig.1. Growth rates of SiGe:H deposited at GC of 10.5% and 15.0% and different (S + G)Cs.

Figure 2 shows the relationship between GCs and growth rates of SiGe:H deposited at (S + G)C of 2% and 5%. Under (S + G)C = 2% (high H_2 dilution), the growth rates of SiGe:H thin films are nearly the same at different pressures and powers (100 Pa and 20 W is denoted by solid squares, and 66.66 Pa and 10 W is denoted by solid stars). While under (S + G)C = 5% (low H_2 dilution) the growth rates decrease with the increase of GC.

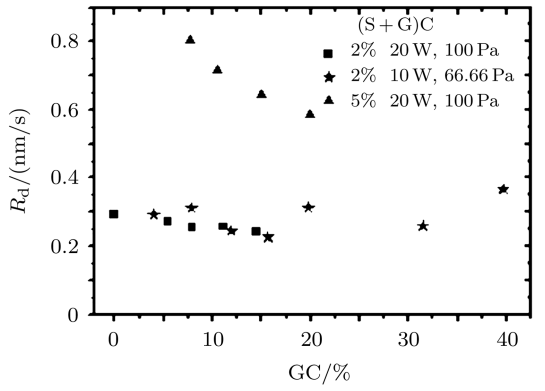


Fig.2. Growth rates of SiGe:H deposited at (S + G)C of 2% with different GCs.

As illustrated in Fig.1, the deposition rate shows a strong dependence on the concentration of total reaction gases (S + G)C, namely the H_2 dilution. But in Fig.2, the deposition rate shows a weak dependence on the GC in the reaction gas flow under the high H_2 dilution but a strong dependence on the GC under the low H_2 dilution.

3.2. Structural properties

As we know, different growth rates may lead to different structures of SiGe:H thin films. Raman spectra is used to investigate the influence of (S + G)C and GC on the structure of SiGe:H alloys. μc-SiGe:H alloys have three characteristic spectra[13] and their relatively features are: the feature at $\sim 290\,\mathrm{cm}^{-1}$ is due to Ge–Ge vibrations; the feature at $\sim 403\,\mathrm{cm}^{-1}$ is due to Si–Ge vibrations; and the $\sim 510\,\mathrm{cm}^{-1}$ feature is due to Si–Si vibrations.

Figure 3 shows the Raman spectra of SiGe:H deposited at GC of 10.5% and different (S + G)Cs. With the increase of (S + G)C, the crystal volume fraction deceases. Similar results are found for the structure of the series prepared with GC = 10.5% and 7.5%. For each series the Raman spectrum shows a transition region between microcrystalline and amorphous growth,

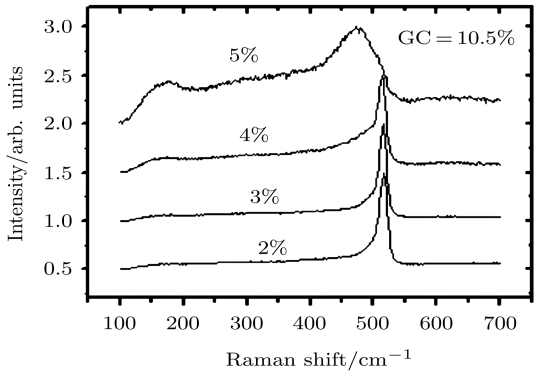


Fig.3. Raman spectra of SiGe:H deposited at GC of 10.5% and different (S + G)C of 2–5%.

(S + G)C varies from 5.5% for GC = 15.0% to 4.5% and 3.5% for GC = 10.5% and 7.5%, respectively. Figure 4 shows the Raman spectra of SiGe:H films deposited at (S + G)C = 5% at different GCs. The three relative Raman shifts at located at $\sim 290\,\mathrm{cm}^{-1}$, $\sim 400\,\mathrm{cm}^{-1}$ and $\sim 480/508/512\,\mathrm{cm}^{-1}$, are due to the Ge–Ge, Si–Ge and Si–Si bond vibrations, respectively. With the decrease of GC the line width of the peak of Si–Si bond vibration is broadened, which reflects the gradual increase of amorphous fraction in SiGe:H thin films. And when GC equals to 10.5%, SiGe:H has transited to amorphous phase.

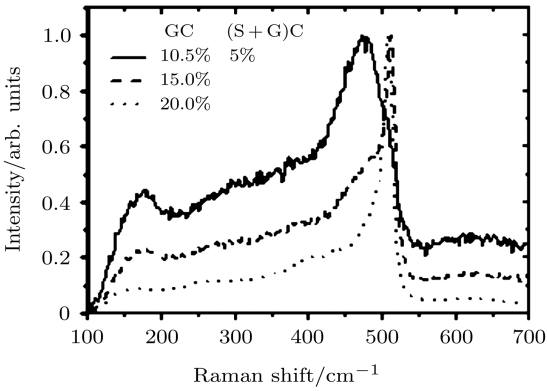


Fig.4. Raman spectra of SiGe:H films deposited at (S + G)C of 5% for GC = 10.5, 15.0 and 20.0%.

As illustrated in Fig.4, when (S + G)C = 5%, the crystal volume fraction of SiGe:H thin films increase with GC. It means that the phase transition from microcrystalline to amorphous growth in SiGe:H thin films happens easily at a lower GC.

3.3. Surface morphology

Thin film alloys are always supposed to have a higher volume fraction when germanium fraction is enhanced. Atomic force microscopy (AFM) is used to investigate the microstructures of thin films with different germanium fractions. Figures 5(a) and 5(b) show the atom force microscope images of SiGe:H alloys deposited at (S + G) of 3% for GC = 15.0% and 20.0%, respectively. On the surface of the two alloys,

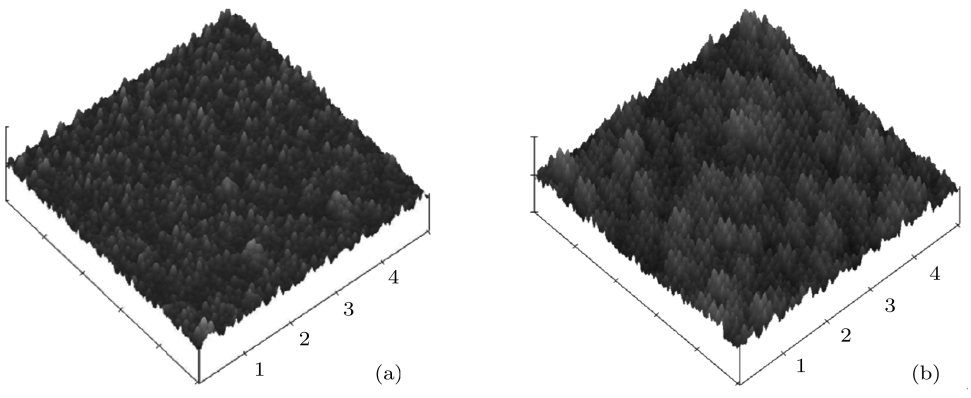


Fig.5. AFM of SiGe:H films deposited at (S + G) of 3% for GC = 15.0% (a) and 20.0% (b).

crystal grains assemble slightly at GC = 15.0% but are stacked up distinctly at 20.0%. It indicates that plenty of clusters, holes and cracks are formed in the thin film with the increase of germanium fraction.

3.4. Photo- and dark-conductivity

Figure 6 shows the photo- and dark-conductivities and photosensitivity of SiGe:H films deposited at GC of 10.5% with varying (S + G)Cs. In the figure, the solid squares denote the photoconductivity, the solid

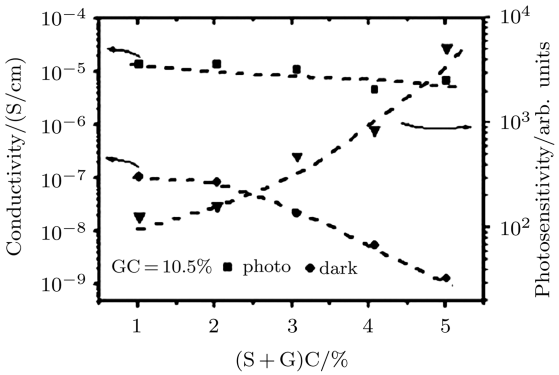


Fig.6. Photo- and dark-conductivities and photosensitivity of SiGe:H films deposited at GC of 10.5% for (S + G)C = 1–5%.

circles denote the dark-conductivity, and the solid triangles denote the photosensitivity. With the increase of (S + G)C, photo-conductivity and dark-conductivity show a similar decreasing trend. Correspondingly, the photosensitivity increases all along, and when (S + G)C = 5% the photo-sensitivity increases steeply to 10^4 due to the phase transition of SiGe:H thin film from microcrystalline to amorphous phase, as shown in Fig.3. Figure 7 shows the changes of photo- and dark-conductivities and photosensitivity of SiGe:H films deposited at (S + G)C of 2% with

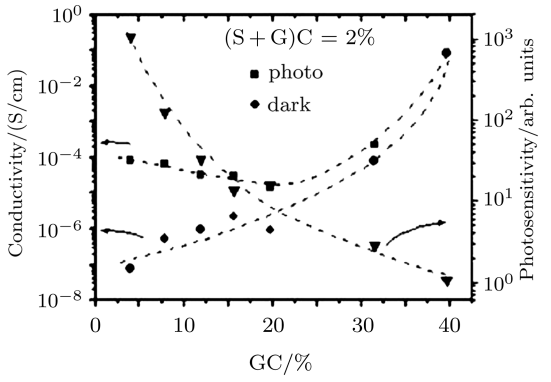


Fig.7. Photo- and dark-conductivities and photosensitivity of SiGe:H films deposited at (S + G)C of 2% and different GCs.

varying GCs. With the increase of GC, the photoconductivity decreases slowly and then increases when GC exceeds 20%. The dark-conductivity shows a gradual rise up to 10^{-1} S/cm. As a result, the photosensitivity decreases all along until up to 10^0.

4. Discussion

We see from Figs.1 and 2 that the average growth rates of SiGe:H thin films are mainly determined by (S + G)C and subordinately influenced by GC. Under high hydrogen dilution ((S + G)C< 3%), the change of GC in the reaction gas flow only has a little influence on the growth rates even when GC increases up to 40%. It is because that the SiGe:H thin films under a high hydrogen dilution are almost completely crystallized, and the proportions of SiH^* or GeH^* to H^* in the plasma of different GCs are nearly identical. Correspondingly, the growth rates of SiGe:H thin films under a high hydrogen dilution are nearly identical. On the contrary, under a low hydrogen dilution ((S + G)C> 4%), the growth rates are strongly influenced by the change of GC in the reaction gas flow, as for (S + G)C = 5% shown in Fig.2. It can be seen from Fig.4 that the amorphous phase fraction in thin films varies greatly with different GCs and decreases with the increasing GC under a low hydrogen condition. As a result, the growth rates have a decrease for higher GC. Namely, growth rates are correlated with the growth precursors in the plasma.

Raman spectra of different GC series under constant (S + G)C indicate that under a high hydrogen dilution the increasing of GC has a little influence on crystal volume fraction. But as shown in Fig.4, under a small hydrogen dilution the incorporation of more GC can obviously enhance the crystal volume fraction. This is because the incorporation of germanium promotes the formation of crystal grains in the films.[12] As shown in Fig.5, the surface morphology varies with different GCs, which is relevant to the growth of alloys. It is due to that the growth precursors of germanium have higher generation rate and surface reactivity than those of silicon.[3] Moreover, the alloys show a strong crystallizing ability when GC is 20%. It indicates that, thin films of high GC will prefer to crystallization, and thin films of low GC are easier to promote the phase transition from microcrystalline to amorphous growth than that of high GC under low hydrogen dilution. This is just contrary to Krause's

experimental result,[8] and it may be due to the difference in the reaction gases. As we know, the bond dissociation energy of GeF_4 is larger than that of GeH_4 used in Krause's. So, under the same power density Ge– bond of GeF_4 is less likely to dissociate than that of GeH_4, and this may lead to more passivated Ge-bond in our plasma. In a word, GeF_4 can promote the crystalline growth in the growth stage.

With the increase of GC, optoelectronic properties present both favourable and unfavourable aspects to active material of solar cells. When GC increases, the mobility edge shifts to lower energies due to the shrinking of the bandgap, which can extend the spectra response. However, when GC increases, the photosensitivity decreases due to a significant increase of defect states. As shown in Fig.7, the photoconductivity decreases when GC is lower than 20%, and the possible reason is that plenty of photo-carriers are lost when abundant Ge is incorporated into the alloys. At the same time, dark-conductivities keep an increasing tendency with the increase of GC and there may be two reasons: one is that a great deal of deficiency states are produced due to redundant GeF_4; the other is that plenty of clusters (show in Fig.5(b)) emerge and a significant number of holes and cracks are formed in the film, which may lead to the formation of O^{2-} vacancies. When GC is larger than 20.0%, the Ge fractions in thin films have a soaring, and consequently, the photo-conductivity has a steep rise for a higher absorption of germanium.[14] But further increase of dark conductivity results in the deterioration of photosensitivity right down to 10°.

5. Conclusions

In this work, very high frequency plasma assisted reactive thermal chemical vapour deposition (VHFPA-RTCVD) is used to prepare SiGe:H thin films on substrates at a temperature as low as 200°C. We have observed that the growth rates of SiGe:H thin films depend both on (S + G)C and GC under a low hydrogen dilution, but depend mainly on (S + G)C under a high hydrogen dilution. We have observed that the phase transition in SiGe:H alloys from microcrystalline to amorphous growth happens easier for the lower GC than the higher GC. And we have also observed both of photo- and dark-conductivities are influenced by the rising in defect states with the increase of germanium incorporation. From this work, we conclude that very high frequency plasma assisted method is a useful way to reduce the need of high temperature substrate. We also conclude that GeF_4 can promote the crystalline growth in the growth stage.

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