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Effects of hydrogen dilution ratio on properties of Boron-doped germanium films by hot-wire chemical vapor deposition

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Boron-doped (B-doped) hydrogenated micro-crystallized Ge films (μc-Ge:H) with different hydrogen dilution ratio (D_H) were prepared by hot-wire chemical vapor deposition (HWCVD) at a substrate temperature of 200 ℃ to investigate the impact of D_H on properties of the films. Properties of the samples were studied with XRD, Raman spectroscopy, Fourier transform infrared spectrometer, Hall effects with Van der Pauw method and reflection spectroscopy. It is found that the increase of D_H improves the structural properties of B-doped μc-Ge:H films, reduces residual stress and enhances the preferential growth of Ge(220). D_H has a great effect on B-doping efficiency and reflectivity in near infrared waveband of the films. The lower D_H, the higher B-doping efficiency and reflectivity are.

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1. Introduction

Germanium (Ge) is widely used in infrared detectors, complementary metal oxide semiconductor (CMOS) [1], et al. Because of narrow bandgap and high carrier mobility in it, Ge is also an excellent material for tandem solar cells [2,3]. In recent years, many low dimensional Ge structures, such as nano-Ge dots, porous Ge, Ge nanoclusters [4-6], have been studied.

Hot-wire chemical vapor deposition (HWCVD) is an excellent low-substrate-temperature technique to deposit films. Comparing with plasma-enhanced chemical vapor deposition (PECVD), it has many advantages, such as higher deposition rate, no ion bombardment to the substrate, long-term stability of properties of films, et al [7-10]. Some works [11,12] have shown us that Ge films can be prepared by HWCVD. But there are still fewer works on effects of preparation parameters on properties of the Ge films by HWCVD.

In this paper, we report our work on preparing Boron-doped (B-doped) hydrogenated micro-crystallized Germanium (μc-Ge:H) films with different hydrogen dilution ratio (D_H) on glass substrate by HWCVD at low substrate temperature. The effects of hydrogen dilution ratio on the properties of B-doped Ge:H films will be presented.

2. Experimental details

Two parallel straight tungsten filaments with a diameter of 0.5 millimeter were set 1 centimeter apart from each other and 4 centimeters above the substrate. The filament and substrate temperature were fixed at about 1800 ℃ and 200 ℃, respectively. Hydrogen (H_2) diluted germane (GeH_4) and diborane (B_2H_6) were used as gas sources. The doped films were deposited at a constant diborane - gas – to - germane ratio, R_B=6% ($R_B = F_{Bt}/F_{GeH4}$×100%, where the F's are gas flow rates) and deposition pressure, $P_{deposition}$=2.0 Pa. The thicknesses of all the samples were kept at 140~170 nanometers (nm). The impact of D_H (D_H=F_{H2} /(F_{GeH4} +F_{H2} +F_B)×100%) on properties of B-doped μc-Ge:H films prepared by HWCVD were studied.

X-ray Diffraction (XRD, D8 ADVACE Bruker) with a Cu $K\alpha$= 1.54 Å was employed to study the crystal structure of the films. A JY-T6400 Raman spectrometer was applied to estimate structure property of the films with Raman spectra measured at room temperature in the back-scattering geometry using the 514.5 nm excitation laser light. Fourier transform infrared spectrometer (FTIR, Nicolet Nexus 670FT-IR) was used to measure the infrared absorption of the prepared films. Van der Pauw method was used to test electrical properties of the films, including conductivity, Hall mobility and effective doping concentration. And a Cary 5000 spectrophotometer was used to detect reflection spectra in near infrared waveband.

3. Results and discussion

Fig. 1 shows the XRD results of the samples with different D_H and $\sigma_{(220)}$, $R_{I(220)/I(311)}$ and grain sizes as a function of D_H , in which $\sigma_{(220)}$ is the internal stress in the

(220) direction and $R_{I(220)/I(311)}$ is the intensity ratio of the peaks (220) and (311). $\sigma_{(220)}$ is given as [13]:

$$\sigma_{(220)}=-(E/v)(d_n-d_0)/d_0$$

in which d_0=0.56575 nm is the lattice spacing for standard Ge powder sample and d_n is experimentally observed value for the samples for XRD, E is Young's modulus, which is taken as 100 GPa and v is the Poisson's ratio taken as 0.26 [14].

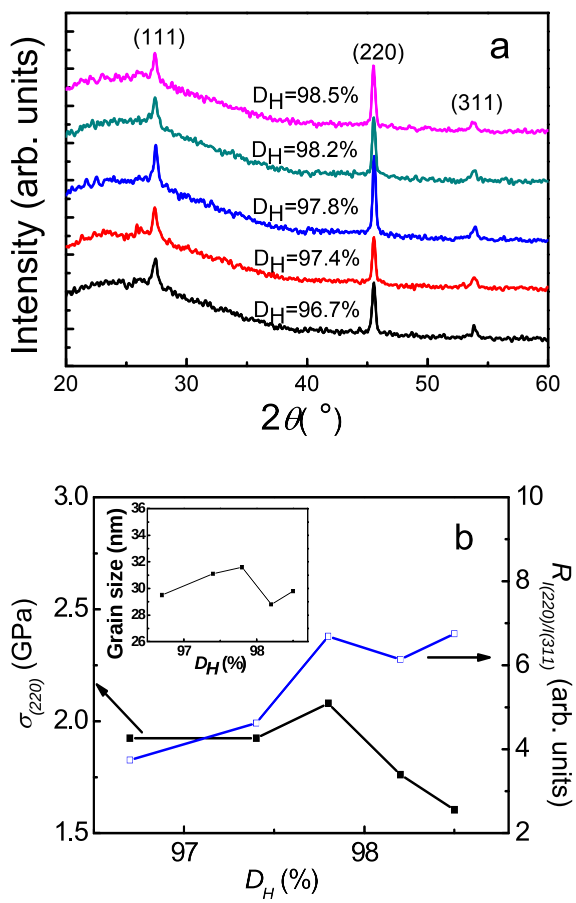

Fig. 1. a, XRD for samples with different D_H ; b, $\sigma_{(220)}$ and $R_{I(220)/I(311)}$ as a function of R_{dopant}. The insert is the calculated grain sizes of samples with different D_H according to Scherrer formula.

It is obvious that $\sigma_{(220)}$ in all the samples is tensile stress and in the range of a few GPa. It is found that D_H has obvious effects on preferential growth and residual stress of the films. With the increase of D_H, $R_{I(220)/I(311)}$ increases while $\sigma_{(220)}$ decreases, except for the one with D_H=97.8%. So the increase of D_H enhances preferential orientation of Ge(220) and reduces residual stress in the films. In Fig.1, the sample with D_H=97.8% has strange values from the others, and we suspected there might be something wrong during the preparation process. When D_H increases, the films has lower depositing rate and concentration of hydrogen atoms in the chamber is higher. Maybe this is the reason for effects of D_H on $\sigma_{(220)}$ and $R_{I(220)/I(311)}$. Some work has suggested that internal stress has effect on process of crystallization of films [15]. So the increase of $R_{I(220)/I(311)}$ may be due to the decrease of $\sigma_{(220)}$. According to Scherrer formula, the average grain sizes of samples are all about 30 nm as shown in the inset of Fig.1.b. So the films are micro-crystallized and they have no distinct differences on grain sizes.

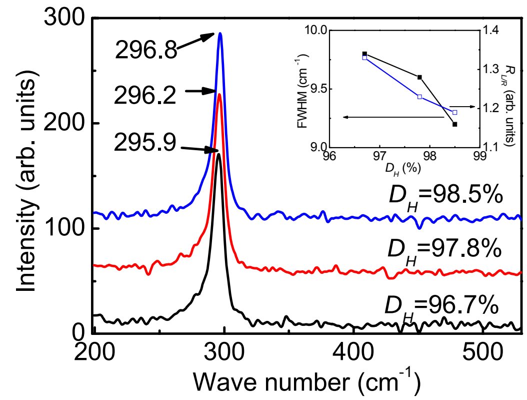

Fig. 2. Raman spectra of samples with D_H=96.7%, 97.8% and 98.5%. The insert is the FWHM and $R_{L/R}$ as a function of D_H.

Raman spectroscopy results are shown in Fig. 2. There is an asymmetric peak at about 296 cm^{-1}. The full width at half maximum (FWHM) and the ratio of left half width and right width ($R_{L/R}$) show us the crystallization quality of the films. The lower the parameters, the better crystallization the film is. As shown in the insert in Fig.2, FWHM and $R_{L/R}$ both decrease with the increase of D_H. So the crystallization quality becomes better as D_H increases. The position of the peak becomes close to the position of bulk c-Ge peak at 300 cm^{-1} with D_H increasing, which means that the residual stress in the films becomes weaker as D_H increases [16]. And this is consistent with the XRD results.

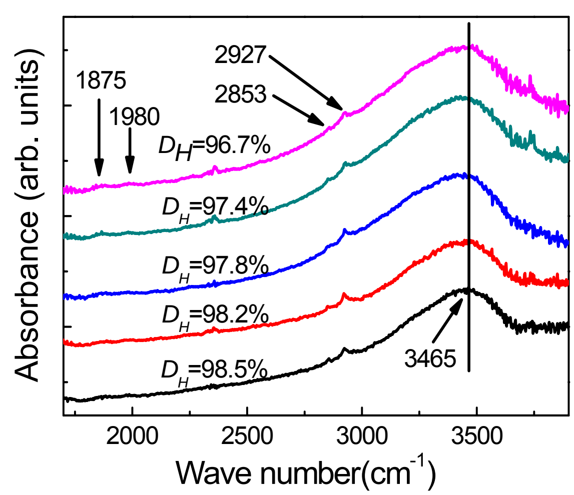

Fig. 3. FTIR of samples with different D_H

As shown in Fig. 3, all the samples have quite weak peaks at about 1875 cm^{-1} and 1980 cm^{-1}, which means that there are few Ge-H and Ge-H_2 in the films [17]. The broad band peak at about 3465 cm^{-1} is attributed to intersubband transitions in the Ge quantum dots [18]. Comparing the IR spectra in Fig. 3, It is found that the broad peak at about 3465 cm^{-1} has a slightly blue-shift with increase of D_H. The carrier concentration also decreases with increase of D_H as shown in Fig.4. And the decrease of carrier concentration makes the bandgap broadening [19]. We consider that this phenomenon induces a blue-shift in the absorption spectra of the samples with the increase of D_H. The double-peak at about 2853 cm^{-1} and 2927 cm^{-1} is attributed to the crystallization orientation of films, especially to the preferential orientation of Ge(220), which we have discussed in another paper [20]. The polarization angle of incident light is fixed in the FTIR testing process, the intensity of Ge(220) is slightly changed in Fig. 1. a, so there is no obvious change of the relative intensity of the double-peak at about 2853 cm^{-1} and 2927 cm^{-1}.

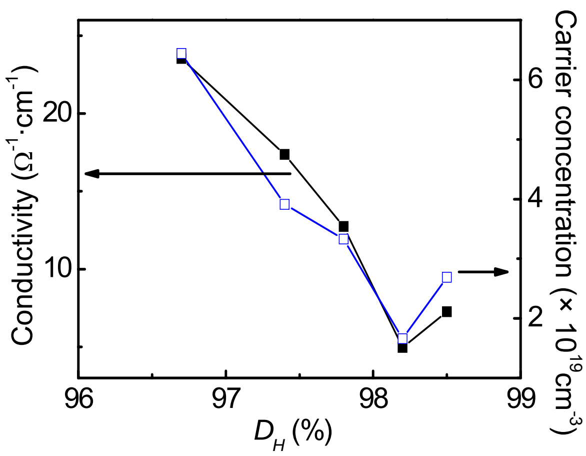

Fig. 4. Conductivity and carrier concentration as a function of D_H

Hall effect measurement with Van der Pauw method was applied to analyze conductivity, effective-doping concentration and Hall mobility of the B-doping films. The results are shown in Fig. 4. It is observed that D_H has great effects on electrical properties of the μc-Ge:H films. The maximum conductivity is 23.5 $\Omega^{-1}\cdot cm^{-1}$ at D_H =96.7% and the lowest value is 5.0 $\Omega^{-1}\cdot cm^{-1}$ at D_H =98.2% in these samples. It is obvious that the carrier concentration and conductivity have almost the same relationship with the increase of D_H. The decrease of them at high D_H may be due to the formation of B-H complexes [21]. Comparing with Fig. 1 and Fig. 2, we deduced that the electrical properties have direct relation with the structural properties. Increasing of doping efficiency leads to the decline of the structural properties of the films.

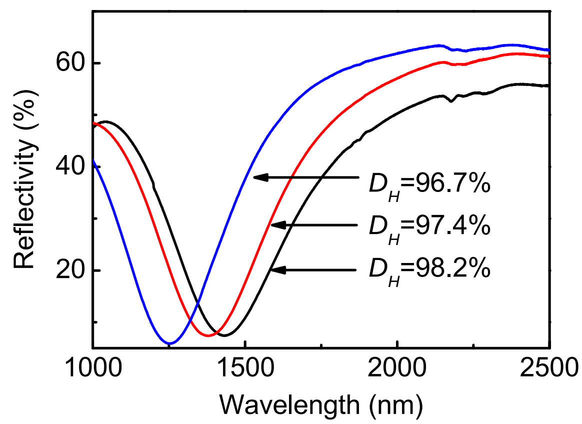

Fig. 5. Reflectivity of samples with different D_H

Reflection spectra in near infrared waveband were also tested for some samples as shown in Fig. 5. The relationship of reflectivity and conductivity is shown in the formula below [22]:

$$R = \left(\frac{(n_r - 1)^2 + \kappa^2}{(n_r + 1)^2 + \kappa^2} \right)$$

in which, $n_r = n_\infty \left[1 - \frac{f}{4} \frac{\omega_0 \delta\omega}{(\delta\omega)^2 + \Gamma^2/4} \right]$ and $\kappa = n_\infty \frac{f}{4} \frac{\omega_0 \Gamma/2}{(\delta\omega)^2 + \Gamma^2/4}$. R means reflectivity and δ is conductivity. It was also reported that the reflectivity in the infrared reflection is proportional to the conductivity of the films in the case of high conductivity and relatively high thickness [23]. So the reduction of conductivity of the films should be the reason for the decrease of reflectivity at wavelength >1500 nm with the increase of D_H.

4. Conclusion

B-doped μc-Ge:H films with different D_H were prepared by HWCVD at a substrate temperature of 200 ℃. According to the Raman spectra and XRD of the samples, it is found that the increase of D_H is beneficial to the structural properties of B-doped μc-Ge:H films. Furthermore, the increase of D_H reduces residual stress and enhances the preferential growth of Ge(220). D_H has a great effect on B-doping efficiency of the films. The maximum of conductivity about 23.5 $\Omega^{-1}\cdot cm^{-1}$ at D_H =96.7% was gained with Van der Pauw method. The lower

D_H is, the higher B-doping efficiency is. The increase of D_H also reduces reflectivity in near infrared waveband of the samples.

Acknowledgments

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