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Low temperature growth of highly conductive boron-doped germanium thin films by electron cyclotron resonance chemical vapor deposition

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A B S T R A C T

The effect of the doping ratio (B_2H_6/GeH_4) on the structural and electrical properties of boron doped hydrogenated germanium films deposited by the electron cyclotron resonance chemical vapor deposition process has been investigated. By increasing the flow rate of B_2H_6/GeH_4 from 0.025 to 0.125, more boron related radicals are available to desorb hydrogen atoms from the growing surface. This leads to degradation of the structure of the amorphous phase identified by Raman and X-ray diffraction spectroscopy. The incorporation of boron enhances the carrier concentration from 1.65×10^{19} cm^{-3} to 2.25×10^{20} cm^{-3} and reduces the resistivity from 0.131 Ω·cm to 0.018 Ω·cm as measured by Hall measurement. These highly conductive boron-doped hydrogenated Ge films can be useful as low resistance doped layer in devices to achieve better performance. Moreover, we are able to deposit highly conductive boron-doped Ge films at a low growth temperature (180 °C) and low hydrogen dilution ratio ($H_2/GeH_4 = 33$), in this study. Such a low temperature process can overcome some problems with high temperature deposition process that limit application in devices. Furthermore, the low hydrogen dilution ratio can minimize an ion bombardment effect on the films.

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1. Introduction

Germanium (Ge) thin films have recently been attracting much attention. The lower optical bandgap can absorb the near infrared light to generate a photo current and the high mobility of it can transport the carriers easily. Such a material has been used to develop the bottom cell of multi-junction solar cells [1,2], thermo-photovoltaics [3–5], and photo-detectors [6]. In these devices, the deposition of the doping layer is important and has a significant influence on the performance of the device. Highly conductive doping layers can reduce the resistance of the devices to achieve better performance.

Heavily boron-doped Ge thin films can be prepared by the co-sputtering method, where the electrical properties can be improved by increasing the substrate temperature [7], optimizing the power level applied to boron target [8], or using rapid thermal annealing [8]. However, the high temperature process (255–500 °C) will limit its application in devices. In order to prevent this problem and to avoid the high temperature process, the hot-wire chemical vapor deposition method (HW-CVD) is used to deposit highly conductive p-type Ge thin films at low temperature (200 °C) [9], but the high flow of hydrogen gas may result in an ion bombardment effect from the severe etching effect of H atoms that will reduce the device performance. The electron cyclotron resonance chemical vapor deposition (ECR-CVD) process offers a number of advantages, including improved control of the deposition process, less ion damage to the growing film, high plasma densities and the possibility of high deposition rates. In a previous study, we obtained the amorphous to microcrystalline silicon phase transition at a lower hydrogen dilution ratio ($H_2/SiH_4 = 0.71$) compared with conventional plasma enhanced chemical vapor deposition, demonstrating the high dissociation of ECR-CVD [10]. Furthermore, the uniformity of ECR plasma was ±6.3% over 160 mm and ±12.5% over 200 mm as reported by Kawai et al. [11]. This indicates that ECR-CVD could be another choice for the fabrication large area of solar cells for industrial use in the future.

In this investigation, boron-doped hydrogenated Ge (B-doped Ge:H) thin films are deposited on glass substrates at a low growth temperature (180 °C) using ECR-CVD. The effect of the B_2H_6 doping ratio (B_2H_6/GeH_4) on the structural and electrical properties of the B-doped Ge:H films is studied. The results show that B-doped Ge:H films with high crystallinity can be obtained at a lower hydrogen dilution ratio ($H_2/GeH_4 = 33$) than with HW-CVD due to the high plasma density of ECR-CVD, which has the further advantage of minimizing the ion bombardment effect during film growth. The resistivity of B-doped Ge:H films can be reduced by the addition of B_2H_6 during deposition and the increase in the carrier concentration results in low resistivity (0.018 Ω·cm). Moreover, this low temperature process can overcome some problems with the high temperature process that limit its application in devices.

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2. Experimental details

B-doped Ge:H films were prepared at a growth temperature of 180 °C by the ECR-CVD method. The films were deposited on glass and c-Si substrates for the different characteristics measured. The deposition time was adjusted for each sample to keep at the same thickness of 150 nm. The source gasses were comprised of a mixture of hydrogen (H_2), 10% germane (GeH_4) diluted in helium, and 0.5% diborane (B_2H_6) diluted in H_2. The hydrogen dilution ratio (H_2/GeH_4) was kept at 33. In this investigation, we kept the microwave power and working pressure at 600 W and 4 Pa, respectively. The effects of varying the B_2H_6 doping ratio, B_2H_6/GeH_4 from 0.025 to 0.125 on the film properties were studied. The structural and electrical properties of the films were characterized using X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and Hall measurements.

3. Results and discussion

3.1. Deposition rates

The B-doped Ge:H films grown on glass substrates are kept at the same thickness of 150 nm. The deposition rates calculated by using the thickness measurements are shown in Fig. 1. It is shown that the deposition rate decreased from 0.28 to 0.144 nm/s when the B_2H_6/GeH_4 ratio was increased from 0.025 to 0.125.

3.2. Structural properties

3.2.1. XRD patterns

The low angle XRD patterns in Fig. 2 show the evolution of the structure of B-doped Ge:H films deposited on glass substrates with various B_2H_6/GeH_4 ratios. The XRD patterns of a Ge film that exhibits the crystalline phase usually has three distinct peaks at 2θ: ~27.3°, 47.5°, and 53.7°, corresponding to the (111), (220), and (311) crystal orientations, respectively. Our XRD patterns of B-doped Ge:H films are shown in Fig. 2, and Fig. 3 shows the crystallite sizes for different crystalline Ge orientations ($d_{(111)}$, $d_{(220)}$, $d_{(311)}$) as estimated using Scherrer's formula [12]:

$$d_{X\text{-ray}} = 0.9\lambda / B\cos(\theta), \qquad (1)$$

where λ is the wavelength of the X-ray, θ is the diffraction angle, B is the full width at half maximum (FWHM) in radians of the peaks. The larger crystallite size of Ge for the (220) peak indicates a preferential crystalline orientation. There is a decrease in the crystallite size shown for three crystalline orientations with the increase of B_2H_6/GeH_4 ratios. This implies that increasing the B_2H_6/GeH_4 ratio will suppress the formation of the crystalline germanium phase, favoring the growth of amorphous germanium during deposition. When the B_2H_6/GeH_4 is 0.083, the (311) crystal orientation cannot be distinguished. The B-doped Ge:H film becomes amorphous when the B_2H_6/GeH_4 ratio is increased up to 0.125.

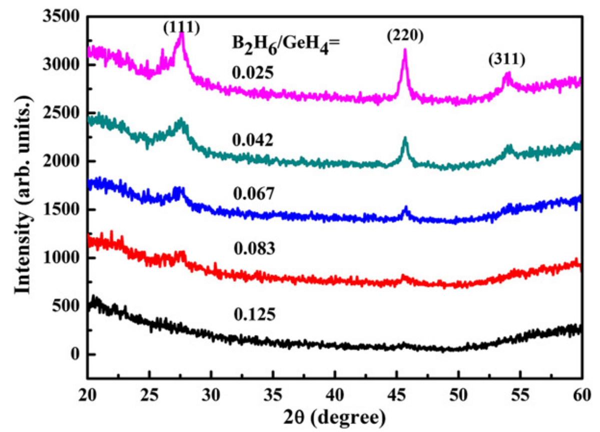

Fig. 2. XRD patterns obtained using different B_2H_6/GeH_4 ratios measured by X-ray diffraction.

3.2.2. Raman spectra

Fig. 4 shows the Raman spectra of B-doped Ge:H films deposited on glass substrates with different B_2H_6 doping ratios. In Raman spectra of Ge, a peak at ~300 cm^{-1} indicates the characteristic TO phonon mode in the crystalline phase of Ge ideally. On the other hand, a broad peak centered around 280 cm^{-1} indicates the amorphous phase of Ge. Our spectra contain a very broad peak which has contribution from both these (crystalline and amorphous) peaks in different proportions. We decompose the Raman spectra with two Gaussian peaks at 280 cm^{-1} and 300 cm^{-1} in the region of 240–320 cm^{-1} by a least-squares fitting method to obtain the peak position and FWHM of the TO phonon mode in the crystalline Ge phase, as shown in Fig. 5. The lower value of FWHM for the TO phonon mode and the peak position near to 300 cm^{-1} which is ideal crystalline Ge TO peak indicate better structure of crystalline Ge for low doping ratios. It is obvious that with the increase in the B_2H_6 doping ratio, the structure of B-doped Ge:H film becomes more amorphous. This result is consistent with the XRD patterns shown in Fig. 2.

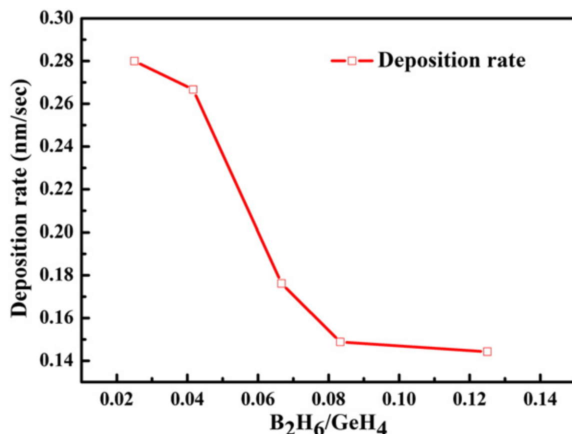

Fig. 1. Deposition rate with various B_2H_6/GeH_4 ratios modulated from 0.025 to 0.125. The incorporation of B_2H_6 will decrease the deposition rate.

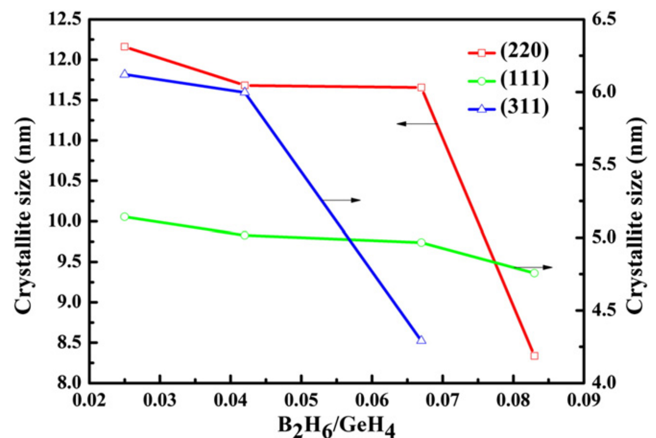

Fig. 3. The crystallite size for three crystalline orientation estimated by Scherrer's formula. The increasing of the B_2H_6/GeH_4 ratio will degrade the structure from crystalline to amorphous Ge.

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