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Crystallization of GeSn thin films deposited on Ge(100) substrate by magnetron sputtering

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ABSTRACT

The influence of growth temperature and Sn content on crystallization of GeSn on Ge substrate prepared by magnetron sputtering was investigated. Single crystal GeSn thin films with Sn content of 1–3.4% were achieved with rapid thermal annealing at 600 °C for the initial sputtered amorphous GeSn at relatively lower deposition temperature(180–350 °C), while polycrystalline GeSn thin films were formed for the GeSn having been crystallized during deposition process at higher deposition temperature(≧450 °C). It was demonstrated that the sputtered amorphous GeSn could be solid phase crystallized on Ge substrate at high annealing temperature. In contrast, insufficient atom migration at low annealing temperature or multi-nucleation during sputtering process at higher growth temperature rendered the polycrystalline GeSn films. The crystallization temperature of GeSn thin film decreases with increase of Sn/Ge ratio in the sputtered GeSn films, while the Sn composition in the crystallized GeSn alloys is dominated by annealing temperature due to severe tin segregation.

1. Introduction

In recent years, GeSn alloys have received extensive attention due to their variable band gap. It is possible to adjust the bandgap from 0.66 to 0 eV by changing Sn composition in the GeSn alloys. The GeSn alloys direct-transition behavior can be predicted when the Sn content is greater than 0.09.[1–9] This feature of GeSn alloy makes it a promising material for optoelectronic devices.[10–18] However, the following difficulties are encountered in the preparation of GeSn thin films. First, the low solid solubility of Sn in Ge less than 1% that hinders the formation of high Sn content GeSn thin films. Second, the high Sn content produces a lager lattice mismatch between GeSn and Ge, which increases the difficulty of growing high quality GeSn layers. Third, during the preparation of the GeSn thin film, Sn has a low melting point and lower surface energy relative to Ge that can cause severe Sn segregation.[9]

The above problems can be solved by the non-equilibrium growth method and controlling the growth temperature and the Sn content.[19–22] High quality single crystalline GeSn thin films have been epitaxially grown on Si and Ge substrate by molecular beam epitaxy (MBE) or ultra high vacuum chemical vapor deposition(UHV-CVD), and successfully applied in Si-based laser, photodetectors and MOSFETs.[23–31] Sputtering is another low-cost method to be widely used for preparing amorphous and crystal semiconductor films. Zheng et al.[8] demonstrated that crystalline GeSn and GeSiSn thin films could be well grown by sputter epitaxy. Tsukamoto et al.[9] also reported that crystalline GeSn alloys were grown by sputter expitaxy. The target of most of the works was to directly grow single crystalline GeSn alloys epitaxially by carefully controlling the growth conditions.[32–39] Sputtering + RTA is just another method to obtain crystal GeSn films, the formation of crystalline GeSn alloys by thermal annealing of an amorphous GeSn layer should be more favorable due to its low cost and the relaxation of the rigor growth conditions.[40–43] The transformation of amorphous GeSn thin films to crystalline GeSn alloys needs further investigation to get high crystal quality GeSn alloys for optoelectronic device applications. Compared with CVD and MBE, sputtering appears to offer greater potential for the cost-effective mass manufacturing of $Ge_{1-x}Sn_x$ alloys.

In this work, we study the effect of annealing temperature on the crystallization of GeSn films with various Sn contents grown at various temperatures. The transition from amorphous GeSn thin film to single crystal is realized by solid phase epitaxial growth under relatively simple growth conditions.

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2. Experiment

The n-type Ge(100) wafers with a phosphorus doping concentration of 2×10^{16} cm^{-3} were cleaned twice by acetone and ethanol organic ultrasonic, respectively and then successively immersed in a 1:4 solution of $HCl + H_2O$ and 1:20 solution of $HF + H_2O$ to remove the native germanium oxide. Finally, wafers were rinsed in deionized water and spin-dried. Putting the cleaned germanium substrate in the sputtering chamber with the base pressure for 2×10^{-5} Pa, the wafers were heated to 450 °C to deoxidize for 30 min. A Ge buffer layer of about 50 nm in thickness was deposited by a dc magnetron sputtering of the germanium target with a purity of 99.999% at 450 °C. The base vacuum pressure of the sputtering system is 2.0×10^{-5} Pa. The deposition pressure was maintained at 0.4 Pa in the argon atmosphere, and the dc power was kept at 50 W. The Ge-coated substrates were cooled separately to 180 °C, 200 °C, 220 °C, 350 °C, and 450 °C, and then 500 nm thick GeSn thin film was deposited by sputtering Ge and Sn targets arranged in a confocal sputter-up configuration. During the deposition, the sputtering pressure was kept at 0.4 Pa. Various thin films with different Sn content were achieved by adjusting power ratio of the Ge target and the Sn target from 7 to 60. The detailed growth conditions are listed in Table 1. The experiment of group I is to study the effect of Sn content on the crystallization of GeSn thin films. The experiment of group I is to study the effect of Sn content on the crystallization of GeSn thin films. The experiment of group II is to study the effect of growth temperature on the crystallization of GeSn thin films. All samples were subjected to rapid thermal annealing at 400 °C, 500 °C, 600 °C for 30 s. The crystallization process of the GeSn thin films was researched by Raman spectroscopy, atomic-force microscopy, X-ray diffraction(XRD) and Transmission Electron Microscope(TEM).

3. Results and discussion

Fig. 1 shows the Raman spectra of GeSn thin film with Sn content of 3%, 14% and 25% prepared at 200 °C and suffered from rapid thermal annealing at 400 °C, 500 °C, and 600 °C for 30 s, respectively. The peak near 300 cm^{-1} is Ge-Ge mode from crystalline GeSn alloys. All of the as-grown samples are amorphous GeSn thin films with a broad weak Raman peak. There are several factors affecting the crystallization of GeSn thin films, such as Sn content, growth rate and growth temperature. The as-grown GeSn is amorphous due to the relatively low growth temperature and high growth rate. It is shown that the samples with Sn content of 14% and 25% begin to crystallize at annealing temperature of 400 °C, and the sample with Sn content of 3% begins to be crystallized at 500 °C. The full width at half maximum (FWHM) of Ge-Ge peak from GeSn films decreases with increase of annealing temperature or with increase of initial tin content in the amorphous GeSn films. This result shows that the higher Sn content GeSn thin films are more easily crystallized with improved crystal quality at the same annealing temperature. the Sn composition for various growth temperature at different anneal temperature is listed in Table 2. The Sn composition of crystallized GeSn was mainly determined by thermal annealing temperature.

Table 1
Growth conditions of the GeSn thin film.

Group I	Sample ID	Sn and Ge power ratio	Growth temperature	Thickness	Sn Content
	Sample 1	1:60	200 °C	500 nm	3%
	Sample 2	1:10	200 °C	500 nm	14%
	Sample 3	1:7	200 °C	500 nm	25%
Group II	Sample ID	Sn and Ge power ratio	Growth temperature	Thickness	Sn Content
	Sample 1	1:10	180 °C	500 nm	14%
	Sample 2	1:10	200 °C	500 nm	14%
	Sample 3	1:10	220 °C	500 nm	14%
	Sample 4	1:10	350 °C	500 nm	14%
	Sample 5	1:10	450 °C	500 nm	14%

Fig. 2(a)-(d) shows the Raman spectra of GeSn thin films with 14% Sn content prepared at 180–450 °C before and after thermal annealing. As shown in Fig. 2(a), broad weak Raman peaks from Ge-Ge mode are observed for the samples grown at 180–350 °C, and a narrower peak for the sample grown at 450 °C, indicating that GeSn thin films begin to crystallize during growth process at 450 °C or above. The asymmetric peak is due to the incomplete crystalline of GeSn films grown at 450 °C. In order to improve the crystal quality of GeSn thin films, the GeSn thin films grown at various temperatures were treated by rapid thermal annealing at 400 °C, 500 °C, and 600 °C for 30 s, respectively. As shown in Fig. 2(b), all of the samples with GeSn thin films have been crystallized after rapid thermal annealing at 400 °C. The peak position of Ge-Ge mode shifts to high energy for the samples prepared at 200 °C to 350 °C, compared with that of the samples grown at 180 °C and 450 °C. The FWHM of Ge-Ge mode from samples grown at 180 °C is much broader than other samples. It is suggested that the amorphous GeSn grown at 180 °C is not completely crystallized. In this range of growth temperature, Sn concentration in the as- deposited GeSn samples is almost the same. when the growth temperature is close to GeSn eutectic point, initial nucleation occurs during the growth process and the crystalline is subsequently improved by annealing. When growth temperature is much lower than GeSn eutectic point, few crystal nucleuses can be formed during growth process, which slows down the crystallization process of GeSn during thermal annealing at 400 °C. This results in the incomplete crystallization of GeSn grown at 180 °C. The value of FWHM at different growth temperatures is shown in Fig. 2(e). The partial amorphous phase in the GeSn thin films renders the Raman scattering peak to low energy. For the sample grown at 450 °C, thermal annealing at 400 °C has little effect on its crystallization and no obvious shift of Raman peak is observed compared to the sample before annealing. As shown in Fig. 2(b)-(d), the Raman scattering peak position of Ge-Ge mode shifts to high energy with increase of annealing temperature and the peak position at 500 °C or 600 °C keeps a constant for all of the samples regardless of their growth temperature. This result suggests that Sn segregation occurs and the substitute Sn composition is mainly determined by the annealing temperature.

Two sets of AFM images of the samples with GeSn thin films grown at 180 °C and 450 °C were selected to observe the changes of the surface morphology with annealing temperature, as shown in Fig. 3. The surface roughness of the GeSn thin films sputtered at 180 °C is much smoother than that prepared at 450 °C. Crystallization of GeSn thin films sputtered at 450 °C should be responsible for the rough surface. For both sets of the samples, the surface roughness increases gradually with increase of annealing temperature and becomes very rough at 600 °C. The changes in the growth feature of GeSn from solid-phase to liquid-phase during RTA at 600 °C should be the main reason for the increase of surface roughness. Additionally, the segregation of Sn during RTA further increases the roughness.[46] The surface morphology of the samples after thermal annealing at 600 °C is very different. The integrity of GeSn film deposited at 180 °C is more perfect than that grown at 450 °C after annealing at 600 °C, which consists of many independent islands. The morphology might be related to the crystalline properties of GeSn thin films. X-ray diffraction (XRD) measurements were carried out to characterize the crystalline of GeSn thin films.

Fig. 4(a)-(d) show the XRD 2θ-scans of GeSn thin films with 14% Sn content prepared at 180–450 °C before and after thermal annealing. Our XRD test instrument is the Rigaku Ultima system. The x-ray is a Cu-kα source with a wavelength of 1.5406 Å. Only the (111) diffraction peak from GeSn thin films are detected for the as-grown samples prepared at 450 °C, as shown in Fig. 4(a). The appearance of (111) peak indicates that polycrystalline GeSn alloys are formed during growth process at 450 °C. After thermal annealing at 400 °C and 500 °C, all of the samples grown at various temperature are crystallized and crystal quality becomes better with elevation of annealing temperature, which is