Effect of Al-doping on crystallization and optical properties of SiGe NP: SiO_2 thin films

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SiGe nanoparticles (NPs): SiO_2 thin films with and without Al-doping were prepared by ions implantation methods. The effect of Al-doping on the microstructure and photoluminescence (PL) properties of specimen under different annealing temperature (T_a) has been investigated. PL, X-ray diffraction (XRD) and High resolution transmission electron microscope (HRTEM) examination were carried out. The specimen exhibited a red light emission under 325 nm excitation wavelength at room temperature.The origin of PL emission was ascribed to quantum confinement effect. The introduce of Al element led to the decrease of the lowest crystallization temperature from 800 to 500 ℃. Furthermore, the reaction of Al-induced phase separation process was discussed based on the principles of thermodynamic reaction and the Gibbs free energy.

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1. Introduction

SiGe NPs was a promising alloying material for quantum devices, infrared detectors and modulation-doped field effect transistors [1]. Low-temperature formation of SiGe thin films on insulating substrates has been expected to realize advanced system in-display, three-dimensional ultra-large-scale integrated circuits and solar cell [2]. Many studies have been performed for Si NPs, and the PL were reported in the visible and near-infrared regions [3]. As for SiGe alloy NPs, the band gap energy could be controlled not only by the size of NPs but also by the Ge ratio. Much work on synthesizing SiGe NPs has already been done, but most of which failed to control the band gap energy [4, 5]. During high temperature annealing process, the diffusion of Si and Ge atom was an obstacle to the formation of SiGe NPs. In addition, high temperature annealing was harmful to the semiconductor technology.

To overcome these problems, metal induced crystallization has been investigated intensively [6-9]. The general driving force in crystallization was the difference of the free energy between the amorphous and the crystalline phases [6]. Dimova et al. firstly demonstrated that the SiGe thin films could be obtained by Al-induced crystallization at temperatures as low as 500 ℃[7]. Peng et al. found an enhancement in the crystallization of SiGe thin films at the T_a from 300 ℃to 500 ℃[8]. In this paper, the metal induced crystallization was realized by Al-doping into the SiGe: SiO_2 thin films instead of common methods such as heating the metal/SiGe: SiO_2 thin films. The effect of Al-doping on the crystallization and the PL emission properties from specimen at different T_a were reported.

2. Experiments

300-nm-thick SiO_2 layers were thermally grown at 1100 ℃ by dry oxidation of n-type Si substrates. Si ions were implanted into SiO_2 films at 36 keV with a dose of 1.8×10^{16} cm^{-2}. Subsequently, Ge ions were implanted using a dose of 1.2×10^{16} cm^{-2} at a energy of 70 keV. Then the as-implanted samples were divided into two serials. One serial were annealed in the range of 400-800 ℃ in N_2 ambient for 1 hr (labled as A1, A2, A3, A4 and A5). The second serial were doped with Al element at a dose of 4×10^{14} cm^{-2} and then were annealed under the same conditions (labled as B1, B2, B3, B4 and B5). According to the SRIM code simulations, the mean projected range of doping ions (Si, Ge and Al) in SiO_2 was calculated to be about 50 nm.

X-ray diffraction (XRD, X Pert PRO) measurement were carried out with a diffractometer (Cu Kα X-ray, λ=0.15406 nm). High resolution transmission electron microscope (HRTEM, JEM-2010) was used to determine the microstructure characterizations of nc-SiGe. The compositional analysis of the specimen were carried out by the energy dispersive X-ray spectrometer (EDS) in HRTEM. PL spectra were measured at room temperature using a He-Cd laser with a wavelength of 325 nm, and detected by a CCD detector.

3. Results and discussions

Fig. 1 show the XRD patterns of A (Fig. 1a) and B (Fig. 1b) serial specimens. The broad band around 2θ=25° is attributed to the amorphous SiO_2 matrix. The absence of

characteristic peak of SiGe phase indicates that the structure of SiGe was mostly amorphous at a low T_a. When the T_a = 800 ℃ for A serial (T_a = 500 ℃ for B serial), Bragg reflection peak at 28.1° becomes clearly visible. This peak correspondes to the characteristic peak of the SiGe(111), which indicates the formation of SiGe NPs. From the comparative experimental results, it is easy to find the effect of Al-induced crystallization processing.

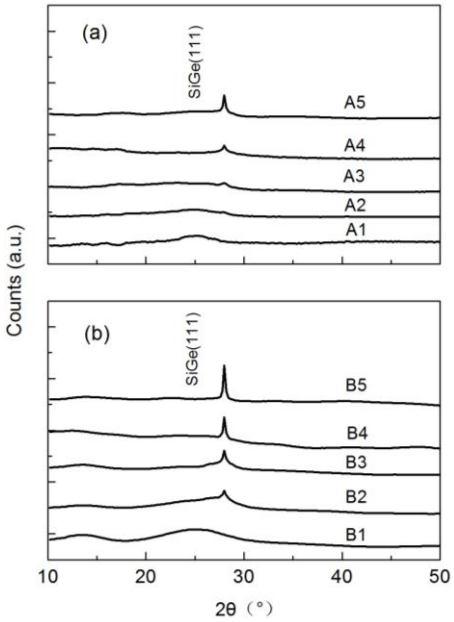

Fig. 1. XRD diffraction spectra of specimen A (a) and B (b) serial.

The formation of SiGe NPs is also verified by the HR-TEM observation. Fig. 2 presents the HR-TEM images of sample B2 (annealed at 500 ℃). Some spherical NPs are identified in the matrix. The size of the SiGe NPs is determined as ~3-4 nm. Furthermore, the compositions of sample A2 and B2 are detected by the EDS examination (as shown in Fig. 3), O, Si, Ge and Al peaks are visible in the EDS spectra for sample B2 and Al peak is absence for sample A2. The results show the Al element is doped into the SiO_2 matrix.

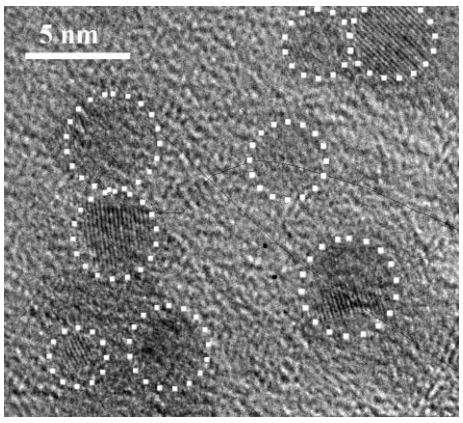

Fig. 2. HR-TEM image of sample B2 (Al-doping at a dose of 4×10^{14} cm^{-2} and annealed at 500 ℃).

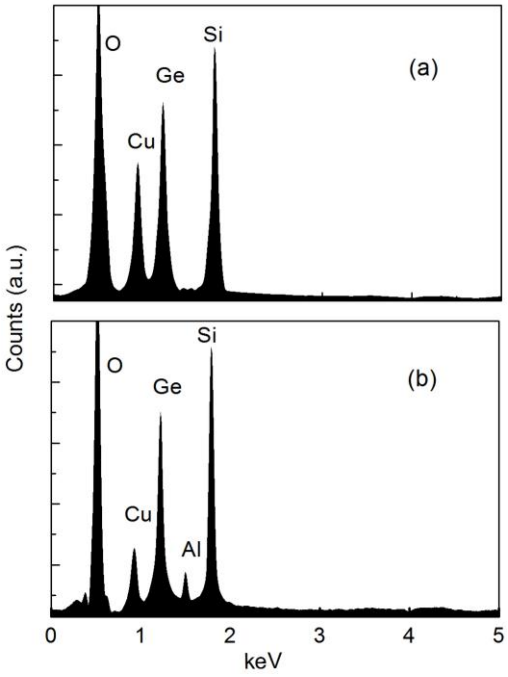

Fig. 3. EDS spectra of sample A2 (a) and B2 (b).

The temperature dependence of PL spectra from A serial specimen are shown in Fig. 4. Specimen exhibit a PL peak centered around ~700 nm (1.87 eV). With the increase of T_a, the intensity of PL peak are enhanced gradually. At the same time, the PL peak red shiftes gently as T_a increases. The Fig. 5 shows the PL spectra from B serial specimen. Speimen exhibites a PL peak located at ~650 nm. The results shows that higher T_a is benifical the PL emission intensity (According to research aim, PL from the samples with T_a >is not given). Different from the PL peak of A serial, the position of PL peak of B serial pecimen is independent with T_a.

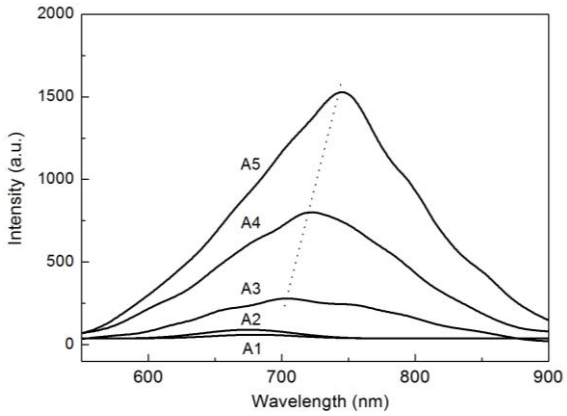

Fig. 4. PL spectra of A serial specimen (without Al-doping and annealed at 400-800 ℃).

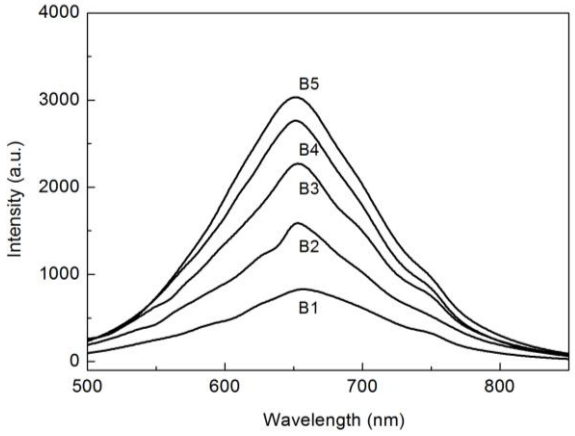

Fig. 5. PL spectra of B serial specimen (with Al-doping and annealed at 400-800 ℃).

Commonly, the PL peaks of SiGe NPs: SiO_2 system origin from defect center or quantum confinement effect. From the experimental result, the quantum confinement is considered as a possible mechanism for the PL emission. According to Brus's model [10]: $E=E_g + (\pi^2\hbar^2/2\mu D^2)$. where the E (and E_g) is the bandgap of the NPs (and bulk), $\hbar$ is the planck constant, μ is the reduced mass of exciton, D is the diameter of the NPs. As for Si, we used E_g = 1.1 eV and μ = 0.13 m_0 (m_0 being the electron rest mass). As for Ge, we used E_g = 0.67 eV and μ = 0.028 m_0. When the average size of Si or Ge NPs were ~3.3 nm, the band gaps of Si NPs was about 1.87 eV (662 nm) and that of Ge NPs was about 1.93 eV (642 nm). Considering the NPs were composed of Si and Ge elements, the band gap was in the range of 1.87-1.93 eV. The theoretical values were in agreement with the experimental results (~650 nm) approximately. Therefore, the quantum confinement effect of alloy SiGe NPs was responsible for the PL emission from this thin films [11]. As for sample A2, the density of SiGe NPs was too lower to be detected by the XRD diffraction spectrum. According to PL spectrum and Brus's model, the diameter (D^*) of SiGe NPs was about ~3.8 nm.

To probe the mechanism of metal induced crystallization of Si NPs, many studies were carried out. Tu et al. suggested that, when the metal Ni or Pt atoms diffuse into the interstitial site of Silicon lattice, the Si-Si covalent bond would transit into metal bond due to the inducing of the metal atoms [12]. The weakening of Si-Si bond promoted the crystallization of Si NPs at lower T_a. According to this model, Huhman et al. explained the induced crystallization of nc-Si embedded in a-Si/Au thin films [13]. However, Konno et al. have not found the metastable state metal Silicide suggested by Huhman et al., which indicated this theory was controversial [14]. In this work, When the SiO_2 thin films were doped with Si and Ge, this thin films turned into $SiGeO_x$ thin films (omitting the ratio of Si/Ge). During annealing treatment process, two steps of phase separation would happen as following:

$$Si + GeO_x \rightarrow Ge + SiO_x \quad (1)$$

$$SiO_x \rightarrow (1\text{-}x/2)Si + (x/2)SiO_2 \quad (2)$$

According formula (1) and (2), we draw a conclusion:

$$SiGeO_x \rightarrow Ge + (1\text{-}x/2)Si + (x/2)SiO_2 \quad (3)$$

The variation of Gibbs free energy in process (3) was:

$$\Delta G_1 = G(Ge) + (1\text{-}x/2)G(Si) + (x/2)G(SiO_2) - G(SiGeO_x) \quad (4)$$

After Al ions were doped into the $SiGeO_x$ thin films, the reaction would take place:

$$y\text{Al} + SiGeO_x \rightarrow (1\text{-}x/2+3y/4)Si + Ge + yAlO_{3/2} + +(x/2\text{-}3y/4)SiO_2 \quad (5)$$

The variation of Gibbs free energy in this process (5) was:

$$\Delta G_2 = G(Ge) + (1\text{-}x/2+3y/4)G(Si) + yG(AlO_{3/2}) + +(x/2\text{-}3y/4)G(SiO_2)\text{-}yG(Al)\text{-}G(SiGeO_x) \quad (6)$$

According to process (4) and (6):

$$\Delta G_2 - \Delta G_1 = [(3y/4)G(Si) + yG(AlO_{3/2})] - -[(3y/4)G(SiO_2) + yG(Al)] \quad (7)$$

The process of $[(3y/4)G(SiO_2) + yG(Al)]$ was an exothermal reaction and the Gibbs free energy decreased[15]. So the reaction (5) would automatically head for the direction of $[(3y/4)G(Si) + yG(AlO_{3/2})]$. L. Bi et al. have enhaced the phase separation and Si NPs growth in SiO_x films by adding a nickel interlayer [16]. The value of (ΔG_2 - ΔG_1) was easy to be solved according to L. Bi's derivation: $\Delta G_2 - \Delta G_1 = 3kT\ln(D^*/D)$. In this paper, the value of D^*/D was estimated to be 1.15, so $\Delta G_2 - \Delta G_1$ = 3 kJ mol^{-1}. Thermodynamic and kinetic analysis indicated a reduction of 3 kJ mol^{-1} in the SiGe NPs nucleation activation free energy by adding the Al element. Hence it reduced the nucleation temperature of SiGe NPs from 800 ℃ to 500 ℃. The Al-doping was beneficial to the formation of SiGe NPs.

4. Conclusion

In this paper, the microstructure and PL of SiGe NPs: SiO_2 thin films with and without Al-doping were investigated. Specimen exhibited a red light emission under 325 nm excitation wavelength at room temperature. XRD diffraction results indicated that Al-induced crystallization processing enhanced the nucleation of SiGe NPs and led to the decrease of the lowest crystallization temperature from 800 ℃ to 500 ℃. Furthermore, the reaction of Al-induced phase separation process was discussed based on the principles of thermodynamic reaction and the Gibbs free energy. It indicated that Al-doping has a potential use in controlling the crystallization of SiGe NPs: SiO_2 thin films.

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