Photoluminescence from SiGe NPs: SiO$_2$ Thin Films Co-doped with Al

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Different doses of Al atoms were implanted into SiGe-rich SiO$_2$ thin films, and the impacts of the doping dose and the annealing temperature on the photoluminescence (PL) from these thin films were investigated. Al-doping promoted the nucleation of SiGe nanoparticles (NPs). The addition of Al enhanced the PL intensity owing to an increase in the number of nucleation sites. However, the Al impurity generated a deep recombination level in the band gap of the SiGe NPs. When the Al-doping dose was 6×10^{14} cm^{-2}, the intensity of the PL reached a maximum.

I. INTRODUCTION

Much study has been performed for Si or Ge NPs due to the potential utilization for infrared detectors, ultra-large-scale integrated circuits, advanced system in-displays and modulation-doped field effect transistors [1–3]. The band gap energy of SiGe alloy NPs can be controlled not only by the size of the NPs but also by the ratio of Si to Ge. Much work on the preparation of SiGe NPs has been carried out, most of which failed [4, 5]. Forming the SiGe NPs was difficult because of the diffusion of Si and Ge atoms during the process of high-temperature annealing. At the same time, the emitted intensity of luminescence needed to be enhanced for practical applications. Better emission efficiency and an increase in NP concentration were necessary. For this, metal-induced crystallization has been investigated intensively. He *et al.* reported that the introduction of a Ni interlayer promoted phase separation, leading to a larger number of smaller Si NPs and an increase in luminescence [6,7].

The general driving force in crystallization was the difference in the free energy between the amorphous and the crystalline phases [8]. Malinovska *et al* investigated the possibility of preparing SiGe films by using Al-induced crystallization and showed that SiGe films can be formed by crystallization at a temperature of 500 °C [9]. Peng *et al.* reported the Al-induced crystallization of amorphous

SiGe thin films by annealing at 300 - 500 °C and verified an enhancement of crystallization [10].

In our previous work, Al-induced crystallization processing was shown to enhance the nucleation of SiGe NPs and to result in a decrease in crystallization for temperatures from 800 to 500 °C [11]. In this paper, we report the effect of Al-doping dose on the PL emission of SiGe NPs: SiO$_2$ thin films.

II. EXPERIMENTS AND DISCUSSIONS

SiO$_2$ layers, 300-nm-thick, were thermally grown at 1100 °C by using dry oxidation of n-type Si substrates (2 - 5 Ω·cm). Si ions, 1.8×10^{16} cm^{-2}, were implanted into the SiO$_2$ layers at an energy of 36 keV by using a metal vapor vacuum arc (MEVVA) implanter. Subsequently, Ge ions, 1.2×10^{16} cm^{-2}, were implanted at an energy of 70 keV. Then the as-implanted samples were divided into three series. One series was doped with elemental Al at a dose of 4×10^{14} cm^{-2} and was then annealed at 400 - 1100 °C (labeled as A1, A2,..., A6). The second series were doped with Al at dose of 0, 2, 4, 6, 8, 10 $\times 10^{14}$ cm^{-2} and was then annealed at 500 °C (labeled as B1, B2,..., B6). According to the TRIM code simulations, the mean projected range (R$_P$) of the doping ions in SiO$_2$ was calculated to be about 50 nm without consideration of the sputtering effect.

Raman spectroscopy was used to analyze the composition of the NPs. The spectra were acquired using a

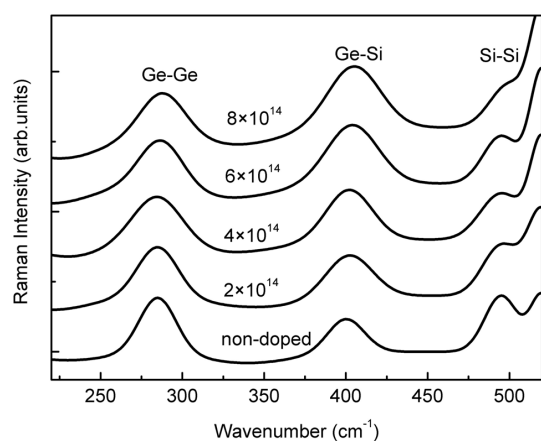*E-mail: zsxiao@buaa.edu.cn; Tel/Fax: +8610-82317579

Fig. 1. Raman spectrum of sample B annealed at 500 °C with various Al-doping doses.
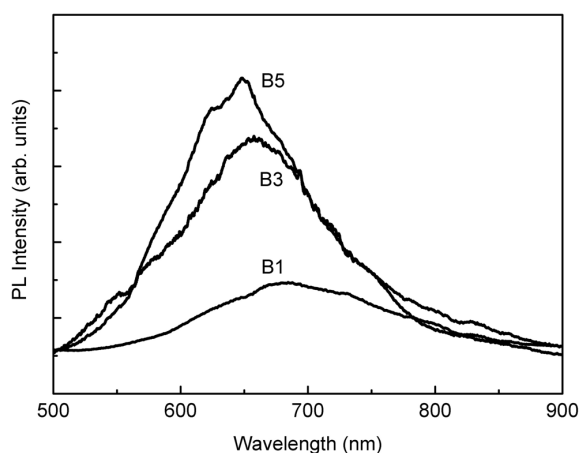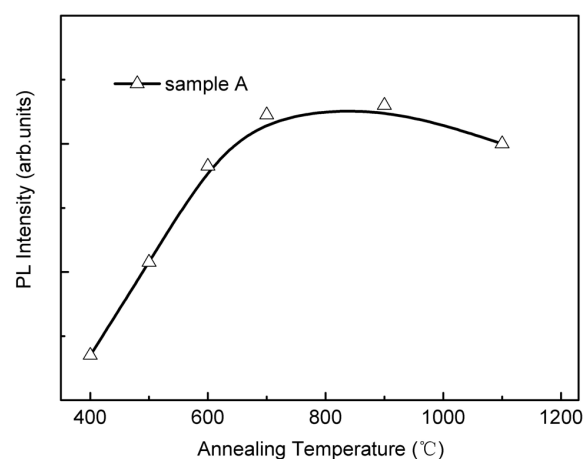

Fig. 2. PL spectra of samples B1, B3, and B5.

Fig. 3. Dependency of the PL intensity of the sample A series on the annealing temperature.

Fig. 4. Dependencing of the PL peak position and intensity of the sample B series on the Al-doping dose.

JY-T64000 spectrometer operating in backscattering geometry at an excitation wavelength of 325 nm. PL spectra were measured at room temperature using a He-Cd laser with a wavelength of 325 nm and a CCD detector.

Figure 1 shows Raman spectra of the sample B series annealed at 500 °C with different Al-doping doses. The samples exhibit three Raman peaks related to Ge-Ge (275 - 300 cm^{-1}), Si-Ge (380 - 415 cm^{-1}) and Si-Si ($\sim$480 cm^{-1}) bond vibrations, respectively, the three Raman peaks of the SiGe NPs: SiO$_2$ thin films were broadening with increasing Al-doping dose, which indicates a decrease in the diameter of the SiGe NPs [12]. However, it was hard to calculate an accurate size for the SiGe NPs because the stresses and the compositional change could also have contributed to the shifts of Raman peaks. In addition, the integral intensity of the Si-Ge Raman peak increased gradually.

The PL spectra of samples B1, B3, and B5 are shown in Fig. 2. With increasing Al-doping dose, the PL peaks of those samples were blue shifted from 680 nm to 650 nm (1.82 - 1.90 eV), and the intensities of the integrated PL were enhanced by the Al doping. The dependency

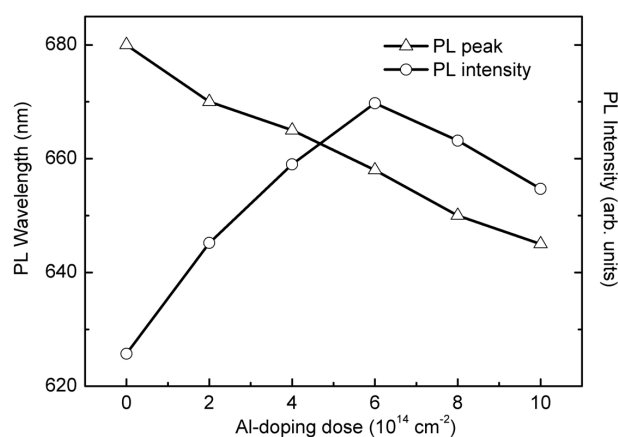of the PL intensity of the sample A series on annealing temperature is shown in Fig. 3. The PL intensity increased rapidly in the range of 400 - 700 °C and then remained relatively stable at 700 - 900 °C. When the annealing temperature was above 900 °C the PL intensity decreased slightly.

Figure 4 shows the dependencies of the wavelength center and the intensity of the PL peak on the Al-doping dose (annealed at 500 °C). With increasing Al-doping dose, the center position of the PL peaks ranged from 680 nm to 647 nm. The intensity of the PL peak reached a maximum when the Al-doping dose was 6×10^{14} cm^{-2}.

SiGe NPs could form at an annealing temperature of 500 °C spherical crystals with a size of $\sim$3 - 4 nm were observed in the matrix [11]. When the annealing temperature was above 300 °C the following reaction can be triggered [10]: Al + SiO$_x$ $\rightarrow$ Si + AlO$_x$. Due to the bond energy of Ge-O being less than that of Si-O, the reaction of the GeO$_x$ compound with Al atoms is more easier. The doping of Al atoms promoted phase separation and was beneficial to the formation of SiGe NPs

[13]. The diffusions of Si and Ge atoms were obstacles to preparing the SiGe NPs. In order to investigate the formation of SiGe NPs at different Al-doping doses, we performed Raman examinations. From Fig. 1, the broadening of the Raman spectra indicate that the size of the SiGe NPs shrank with increasing Al-doping dose. At the same time, the integral intensity of the Si-Ge Raman peak increased gradually, which revealed that the addition of Al atoms promoted the formation of SiGe NPs during the lower-temperature annealing process.

The quantum confinement of an electron-hole pair in the SiGe NPs was considered as a possible mechanism for the visible PL. According to Brus's model [14],

$$E = E_g + (\pi^2 \hbar^2 / 2\mu R^2), \qquad (1)$$

where the E (and E_g) is the bandgap of the NPs (and bulk), h is the planck constant, μ is the reduced mass of exciton, R is the diameter of the NPs. Because the bandgap of SiGe NPs was controlled by the Si/Ge ratio, firstly we can calculate the bandgap of pure Si and pure Ge NPs. In this work, as for Si, we used $E_g = 1.1$ eV and $\mu = 0.13\ m_0$ (m_0 being the electron rest mass). As for Ge, we used $E_g = 0.67$ eV and $\mu = 0.028\ m_0$. When the Si or Ge NPs were $\sim$3.3 nm in diameter, 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 PL peaks of SiGe NPs centered around $\sim$680 - 650 nm, corresponding to bandgap of 1.82 - 1.90 eV. The theoretical values were in approximate agreement with the experimental results. Therefore, we propose that quantum confinement effect of SiGe NPs is responsible for the 658 nm PL emission.

In Fig. 3, the increase in the PL intensity of the A series in the initial stage was due to the formation of the NPs and indicated that Al-induced crystallization processing enhanced the nucleation of SiGe NPs in the films. During the high-temperature annealing process, the diffusions of Si and Ge in the NPs cause more P_b centers ($\cdot$Si $\equiv$ Si, which is known to be a major source of charge trapping at the Si or the Ge/SiO$_2$ interface), and the P_b centers can annihilate the PL emission and decrease the PL intensity of the samples [15]. The variation in the PL intensity of the A series can be explained by the competition between SiGe NPs and P_b centers.

Since Al atoms play the role of extra nucleation centers [7], an increase in the Al-doping dose will lead to an increase in the nucleation density. As a result, the size of the SiGe NPs decreases, which has been verified by the broadening in the Raman spectra (as shown in Fig. 1). A blue-shift PL peak from 680 nm to 645 nm was found and was ascribed to a decrease in the size of the NPs. From Fig. 2 and Fig. 4, it was easy to find that the Al doping enhanced the PL intensity at first and then deteriorated it, On the one hand, the addition of elemental Al could enhance the PL intensity owing to an increase in the nucleation sites. On the other hand, the Al impurity will generate an efficient deep recombination level in the band gap of the NPs, so the luminescence from SiGe NPs will be quenched by a further addition of elemental Al [16].

III. CONCLUSION

In this research, the effects of Al-doping dose and annealing temperature on the microstructure composition and PL were investigated. The addition of elemental Al enhanced the PL intensity compared to the undoped samples. However, when the Al-doping dose was above 6×10^{14} cm^{-2}, the PL deteriorated because the Al impurity generated a deep trap level in the band gap of the NPs. The above results imply that Al doping has a potential use in controlling the crystallization of nc-SiGe films in improving their PL performance.

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