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Optical properties of Mn^+ doped GaAs

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Photoluminescence is one of the most useful techniques to obtain information about optoelectronic properties and defect structures of materials. In this work, Mn-doped GaAs structure materials were prepared by Mn^+ ion implantation at room temperature into GaAs. The implanted samples were subsequently annealed at various temperatures under N_2 atmosphere to recrystallize the samples and remove implant damage. The room temperature and low temperature photoluminescence of Mn-doped GaAs were investigated, respectively. A strong peak was found for the sample annealed at 950℃ for 5 s. Transitions near 0.989 eV (1254 nm), 1.155 eV (1074 nm) and 1.329 eV (933nm) were identified and formation of these emissions was analyzed for all prepared samples. This structure material could have myriad applications, including information storage, magneto-optical properties and energy level engineering.

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1. Introduction

Recently, semiconductors doped with active impurities have attracted great interest in both basic research and commercial applications because of their electronic, optical, magnetic, or biological characteristics [1-3]. Furthermore, impurity ions doped into these structures can influence the electronic structure and transition probabilities [4]. In particular, when doped with magnetic ions (e.g. Mn^{2+}), these materials can produce unique magnetic and magneto-optical properties and provide unparalleled opportunities for the new field of spintronics [5].

As a technologically important direct-band-gap semiconductor, GaAs has attracted much interest because of its compatibility with conventional microelectronics, so it is considered as a promising host material. Transitional metal ions (e.g. Mn^+ and In^+) have been doped into GaAs by ion implantation [6], sputtering [7], molecular beam epitaxy [1], liquid phase epitaxy [3], etc. These doped GaAs semiconductor materials have a wide range of applications in laser, magnetic-opto devices, and light emitting display. Accordingly, special attention has been paid to their luminescence properties. However, the luminescence properties are still controversial. In GaAs:Mn, a peak near 1.41 eV has been well documented [8], which is attributed to transition from the conduct band of GaAs to Mn acceptor. In addition, some peaks centered at 1.49 and 1.36 eV were observed by Y.Kim [9]. Recently, P.B. Parchinskiy et al. reported an emission peak around 1.32 eV in GaMnAs embedded into MnAs cluster and assigned it to the defects level generated in the phase separation process [10]. Here, effects of the annealing temperature of Mn-doped GaAs on its photoluminescence were investigated and the origin of the photoluminescence was also discussed.

2. Experimental

A semiconductor sample was grown a 500 nm buffer layer at 590℃ (i.e., under normal GaAs growth conditions) by molecular beam epitaxy on a n-type GaAs (001) substrate. The sample was implanted normally into Mn^+ ions with energy of 80 keV and a dose of $1*10^{15}$ Mn^+ ions cm^{-2} at room temperature. Subsequently, samples were annealed followed by pulsed laser melting under N_2 atmosphere, at various temperatures with the sample sitting face down on a fresh GaAs wafer. The surface topography was investigated by atomic force microscopy (AFM) in atmosphere in the contact mode with a Solver P47 (Russia) scanning probe microscope. Room temperature photoluminescence (RT-PL) and low temperature photoluminescence (LT-PL) spectra were performed using InGaAs diode using standard lock-in techniques and Ar laser (514 nm) as the excitation source.

3. Results and discussion

Morphology of the as-prepared and annealed samples was examined by AFM observation. A representative AFM image is presented in Fig. 1. After annealed at 715℃, some quasi-spherical nanoparticles with an average size of about 35 nm appear. More and more nanoparticles are observed after annealed at 950℃ for 5 s.

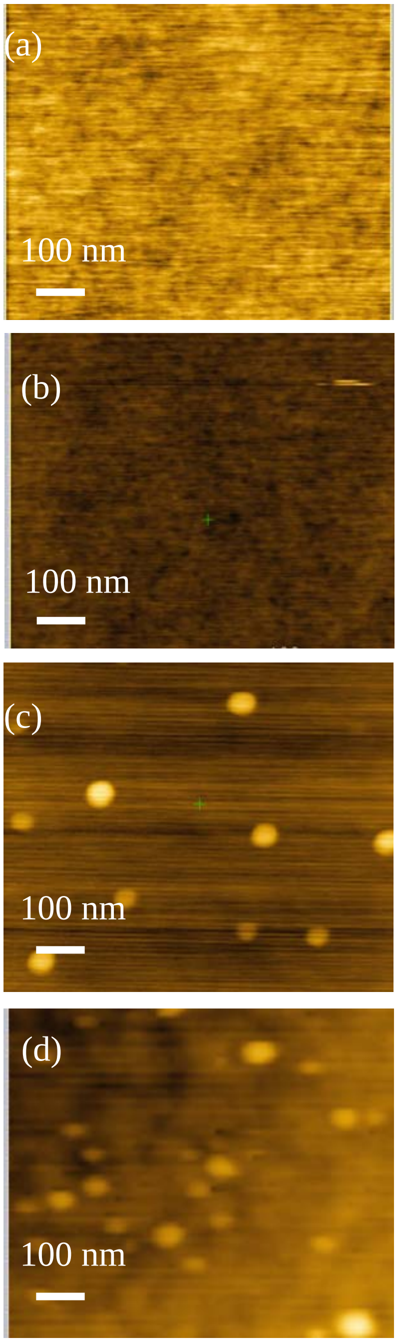

Fig. 1. AFM images of these as-prepared Mn+ doped GaAs samples after annealed at (a) 630 ºC for 15 s, (b) 650 ºC for 5 s, (c) 715 ºC for 5 s and (d) 950 ºC for 5 s.

PL is a highly sensitive and nondestructive tool for the detection of residual impurities in doped semiconductor materials. In order to learn electronic structure and defect information of all the as-prepared and annealed samples, we performed PL measurements at low temperature and room temperature for all as-prepared and annealed samples. Fig. 2 shows the PL emission spectra at room temperature of these samples. As shown in Fig. 2, all these sample show only a broad peak, which are centered at 0.970 eV (1278 nm). In addition, it was found that the peak centered at 0.970 eV (1278 nm) shows little change with the variation of the annealing temperature.

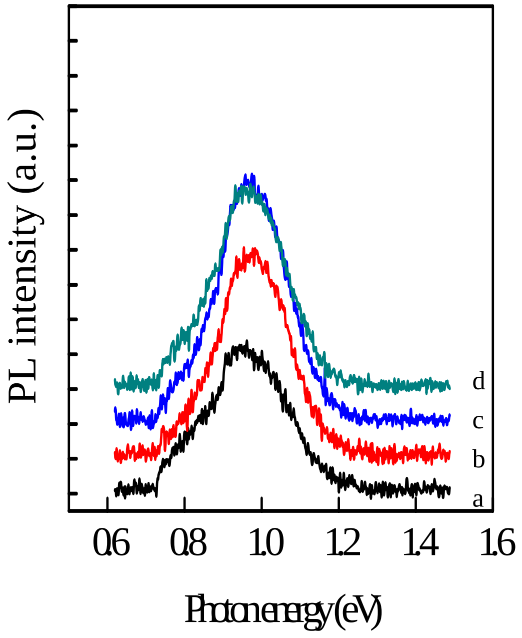

Fig. 2. RT-PL spectra of these as-prepared Mn+ doped GaAs samples after annealed at (a) 630 ºC for 15 s, (b) 650 ºC for 5 s, (c) 715 ºC for 5 s and (d) 950 ºC for 5 s.

Fig. 3 shows the LT (15 K)-PL emission spectra for the as-prepared and annealed samples. The LT- PL spectra of the Mn-doped GaAs sample annealed at 630 ℃ are broad and asymmetric and can be deconvoluted into three weak peaks, which are centered at 0.989 eV (1254 nm), 1.155 eV (1074 nm) and 1.329 eV (933 nm), respectively. In addition, the peak at 1.155 eV is blue-shifted lightly and the luminescence intensity is diminished with the increase of anneal temperature. While the peak at 1.329 eV shifts towards lower energy with increasing annealing temperature, while the relative intensity of the peak near 1.329 eV (933 nm) is greatly enhanced.

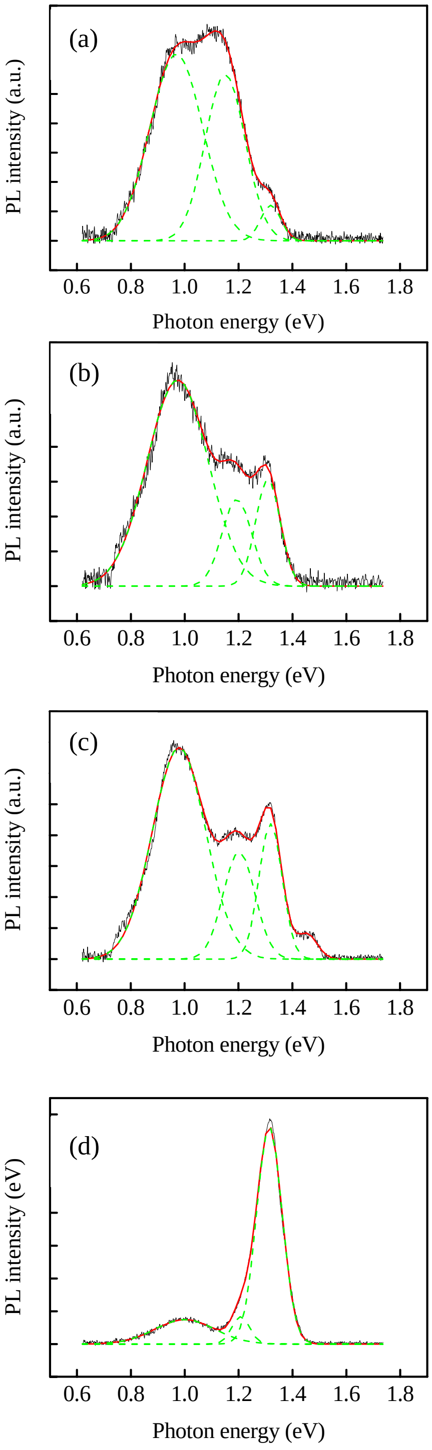

Fig. 3. LT (15K) PL spectra of these as-prepared Mn+ doped GaAs samples after annealed at (a) 630 ºC for 15 s, (b) 650 ºC for 5 s, (c) 715 ºC for 5 s and (d) 950 ºC for 5 s. The experimental data are shown in solid circles. The dashed lines are the individual components by Gaussian fitting, and the solid lines are the sum of individual fitting lines.

The broad peak near 0.970 eV shifts to higher energy (0.989 eV) with decreasing measurement temperature. Since the temperature dependence of the peak positions might be, in general, explained by the increasing of the band gap energy (Eg) with decreasing measurement temperature [11]. In addition, it was found that the emission peak position is insensitive to the anneal temperature. Moreover, the undoped sample also shows such a broad peak. So, it is suggested that in our case, the peak centered at 0.970 eV or 0.989 eV should result from native defect states of GaAs, but not from impurity states related with Mn dopants. When Mn^+ ions are doped into GaAs, more defect states (Ga vacancy, As antisites, As vacancy) will be introduced. The PL peak at 1.155 eV has been known as deep level due to the recombination between the Ga-vacancy-related donor and the valence band [12]. As shown in Fig.4, the peak intensity at 1.155 eV is diminished and the emission relative intensity near 1.329 eV is greatly enhanced with the increase of anneal temperature, which indicates that high temperature annealing reduced the number of Ga vacancy greatly. With the increase of anneal temperature, the peak at 1.155 eV systematically shifted to higher energy, which indicated that the level of Ga vacancy is farther from the valence band. For the emission peak near 1.329 eV, different origins were proposed. Y. Kim [9] attributed the emission peak near 1.32 eV to the transition between the conduction band of GaAs and the Mn acceptor in the GaAs band gap. While T. Yoon et al. [13] observed that shallow Mn acceptors level not only depends on structural characteristics of this material but also Mn concentration and measurement temperature. P.B. Parchinskiy et al. [10] proposed the emission near 1.32 eV is related with some defects generated in the phase separation process. However, when transition from Ga vacancy to valence band is diminished, the emission relative intensity centered at 1.329 eV is enhanced. By AFM measurements, the crystallinity of GaAs is improved and some nanoparticles are formed after higher temperature annealing. So, it is suggested that the peak centered at 1.329 eV (933 nm) should not result from defects level in the phase separation but can be interpreted as the transition from the conduction band to the Mn acceptor level.

4. Conclusions

The LT- PL spectra of the as-prepared and annealed Mn-doped GaAs samples are broad and asymmetric and can be deconvoluted into three Gaussian peaks. Of these, the peak centered at 0.989 eV is related with native defects of GaAs. The PL peak at 1.155 eV originates from deep level due to the recombination between the Ga-vacancy-related donor and the valence band. The peak centered at 1.329 eV can be due to Mn-related emission.

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