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Structural and optical study of GaMnAs/GaAs

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GaMnAs/GaAs was obtained with mass-analyzed low energy dual ion beam depostion technique with Mn ion energy of 1000 eV and a dose of 1.5×10^{18} Mn^+/cm^2 at the substrate temperature of 400°C and was annealed at 840°C. X-ray diffraction spectra showed that $Ga_{5.2}Mn$, Ga_5Mn_8, α-Mn and Mn_3Ga were obtained in the as-grown sample. After annealing Mn_3Ga and α-Mn disappeared, Ga_5Mn_8 tended to disappear, $Ga_{5.2}Mn$ crystallized better and new phase of Mn_2As was generated. The photoluminescence spectra of the as-grown sample showed that the 1.5042 eV GaAs exciton peak, 1.4875 eV peak involving a carbon acceptor and a broad band near 1.35 eV. After annealing at 840°C, the 1.5042 eV peak and 1.4875 eV shifted to 1.5065 and 1.4894 eV, respectively, and the photoluminescence intensity of the 1.35 eV band increased greatly. © *2004 Kluwer Academic Publishers*

1. Introduction

As an important semiconductor, GaAs has been extensively and deeply studied. Recently the GaAs-based diluted magnetic semiconductor and magnet-GaAs hybrid structures are attracting more and more attention. Among these, the materials containing the magnetic transition metal Mn are the best studied (such as GaMnAs [1] and MnAs/GaAs [2]). But these research mainly focus on crystal structure, magnetism and magnetic transport. Only few references discuss the optical property of this kind of materials [3].

In GaAs, Mn atom can replace Ga or As to form the alloy GaMnAs. While Mn in GaAs achieve a high concentration, the new phase Ga-Mn and/or Mn-As can be seperated out. Mn at a Ga site(Mn_{Ga}) in GaAs form a deep acceptor center with the binding energy of ~0.11 eV [4–6].

In this paper, we refered to GaAs deposited with Mn ions as GaMnAs. We report the X-ray spectra and observation of photoluminescence (PL) spectra of Ion-Beam-deposition grown GaMnAs/GaAs. $Ga_{5.2}Mn$, Ga_5Mn_8, α-Mn and Mn_3Ga were seperated out in the as-grown sample. After annealing Mn_3Ga and α-Mn disappeared and Mn_2As was generated. The bound exciton line, carbon-induced recombination peak and a deeper broad band near 1.35 eV were observed by PL measurment.

2. Material preparation

The samples were prepared by mass-analyzed low energy dual ion beam deposition system. Mn ions were uniformly deposited on semi-insulating GaAs(001) substrate with Mn ion energy of 1000 eV and a dose of 1.5×10^{18} Mn^+/cm^2 at the substrate temperature of 400°C. This type of ion-beam depostion system consists of ion beam systems and vacuum systems. The depostion ions can be purified by its magnetic analyzer, thus can make the growth sample very pure. All GaAs substrate were etched and cleaned before sample growth. Purity of Mn used in the experiment was 99.98%. Mn need not to be etched and cleaned because of purifying function of growing apparatus itself. In order to clean the absorbed impurities on the surface of GaAs substrate, the substrate was bombarded by Argon ion for 10 min during the sample growth. It took 60 min to grow each sample.

Some of the sample was annealed for 70 min at the atmosphere of flowing N_2 at 840°C and the flowing rate of N_2 is 0.5 L/min. During the annealing process, the sample surface was attached to a polished GaAs wafer

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so as to prevent Mn and As from evaporating the sample surface.

3. Measurement and analyses

X-ray diffraction (XRD) and Auger electron spectroscopy (AES) were employed for structural and compositional analyses of the sample. PL measurement was employed for optical study of the sample.

3.1. AES spectra and XRD spectra

In order to investigate the composition of sample surface, Auger electron spectroscopy were employed. The Auger electron spectroscopy system used in this experiment is PHI-610/SAM. Fig. 1 is the AES spectrum of the as-grown sample surface, from which it can be seen that there is manganese, gallium, arsenic, carbon, sulfur and oxygen at sample surface. The reason for the carbon and sulfur is that the sample surface was contaminated after the sample was taken out from growth chamber. The element oxygen was introduced mainly by oxidation of manganese after the sample was taken out from growth chamber.

In order to investigate the structure, XRD patterns of the sample were obtained with 2θ-θ scan using Cu K_α radiation. Fig. 2 is the XRD spectrum of the as-grown sample, from which it can be seen that there

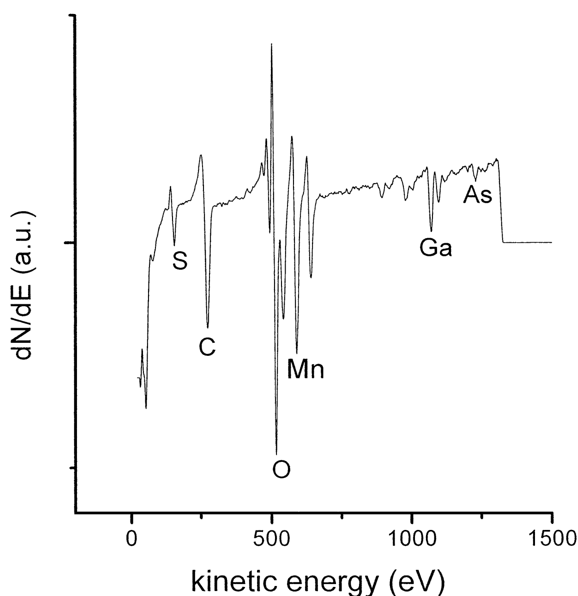

Figure 1 AES spectra of the as-grown sample surface.

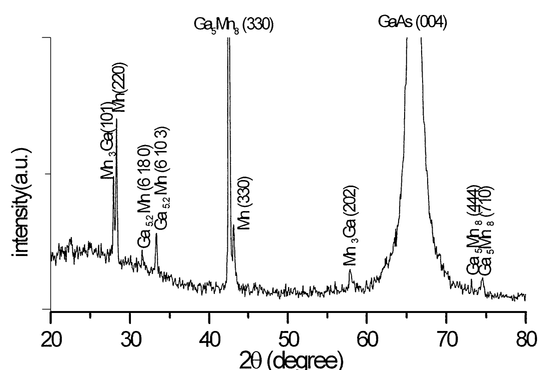

Figure 2 X-ray diffraction spectra of the as-grown sample.

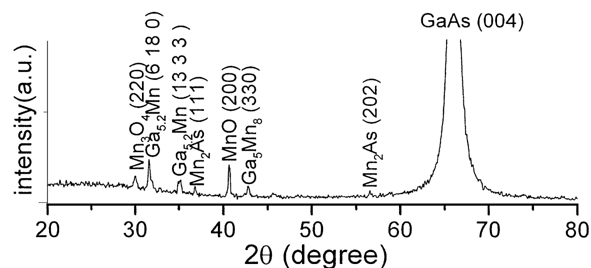

Figure 3 X-ray diffraction spectra of the sample after annealing.

are four phases $Ga_{5.2}Mn$, Ga_5Mn_8, α-Mn and Mn_3Ga. The crystal structure of α-Mn is fcc with lattice constant $a = 0.8912$ nm. The structure system of Ga_5Mn_8 is cubic system with the lattice constant $a = 0.8992$ nm. The stucture system of Mn_3Ga is hexagonal system with the lattice constants $a = 0.5404$ nm and $c = 0.4357$ nm. In the Fig. 2 the highest peak is from the diffraction of GaAs (004). At the left of GaAs (004) peak, there are seven diffraction peaks which are in sequence from the diffraction of Mn_3Ga (101), α-Mn (220), $Ga_{5.2}Mn$ (6 18 0), $Ga_{5.2}Mn$ (6 10 3), Ga_5Mn_8 (330), α-Mn (330) and Mn_3Ga (202). At the right of GaAs (004) peak, there are diffraction peaks of Ga_5Mn_8 (444) and Ga_5Mn_8 (710). The peak of Ga_5Mn_8 (330) in the sample is very strong and narrow, indicating that the growth conditions of the sample are quite suited to the nucleation and growth of Ga_5Mn_8.

Fig. 3 is the XRD spectrum of the sample after annealing, from which it can be seen that there are five phases excepting GaAs, $Ga_{5.2}Mn$, Ga_5Mn_8, Mn_2As, Mn_3O_4 and MnO. The crystal system of Mn_2As is tetragonal system with the lattice constants $a = 0.3767$ nm and $c = 0.6277$ nm. In the Fig. 3, the highest peak is from the diffraction of GaAs (004). At the left of GaAs (004) peak, there are eight diffraction peaks which are in sequence from the diffraction of Mn_3O_4 (220), $Ga_{5.2}Mn$ (6 18 0), $Ga_{5.2}Mn$ (13 3 3), Mn_2As (111), MnO (200), Ga_5Mn_8 (330) and Mn_2As (202). After annealing at 840°C Mn_3O_4, MnO and Mn_2As appeared, whereas Mn_3Ga and α-Mn disappeared. Mn_3O_4 and MnO are the products of oxidation of Mn due to the intake of oxygen into annealing atmosphere during anealing and crystallize well under high annealing temperature. The appearance of Mn_2As shows that Mn_2As can nucleate and growth at the high temperature of 840°C. The disappearance of α-Mn resulted partially from the diffusion and combination of Mn with elements Ga and As, and partially resulted from the oxidation of Mn at the high temperature of 840°C. The disappearance of Mn_3Ga suggests that Mn_3Ga is not stable at 840°C. At the same time the intensity of peak of Ga_5Mn_8 markedly decreased, indicating that Ga_5Mn_8 is also unstable at 840°C. After annealing the diffraction peaks of $Ga_{5.2}Mn$ become slightly stronger and sharper, indicating that $Ga_{5.2}Mn$ crystallized better during annealing. The annealing was beneficial to the growth of $Ga_{5.2}Mn$ and Mn_2As.

3.2. PL spectra

In order to study the optical properties of the sample, the Argon ion laser was used as PL excitation light

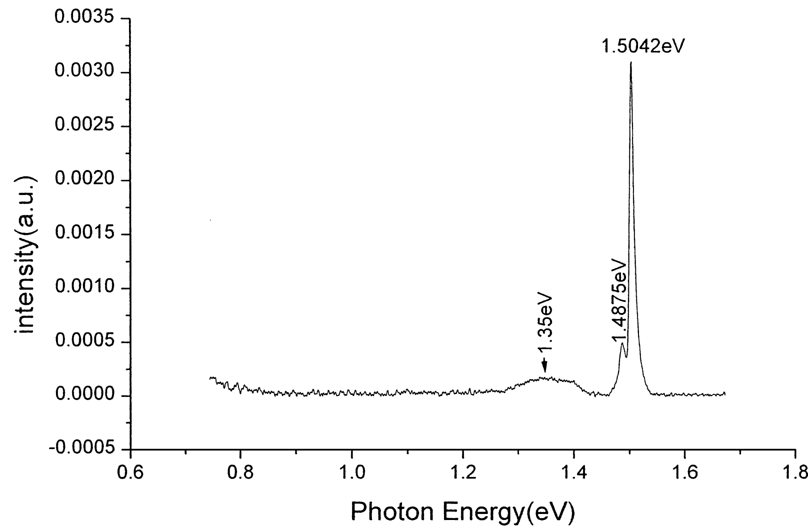

Figure 4 15 K PL spectra of the sample before annealing.

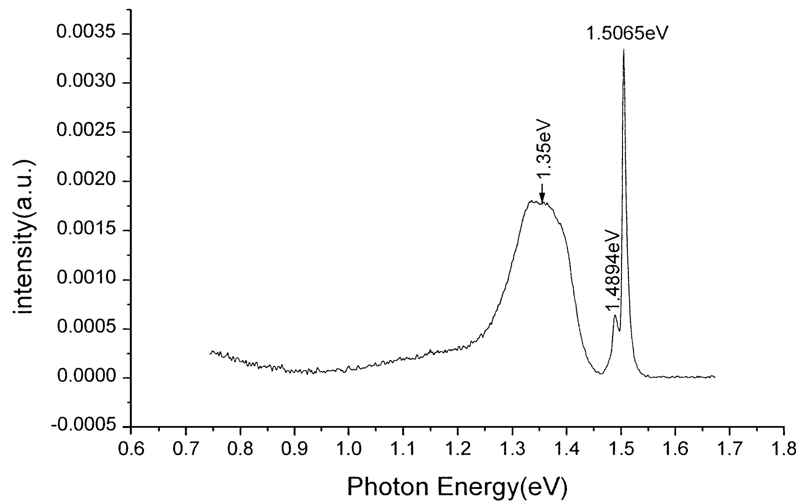

Figure 5 15 K PL spectra of the sample after annealing.

with the wavelength of 514.5 nm and excitation power of 200 mW.

Fig. 4 is the PL spectrum of the as-grown sample at 15 K. Three luminescence regions were obtained, namely, the bound exciton line at 1.5042 eV, impurity-induced recombination peak at 1.4875 eV and a deeper broad band near 1.35 eV.

The emission band near 1.35 eV is broad and weak, which may result from the GaAs substrate lattice damage due to Mn ion bombardment during the sample growth. Therefore, in order to recover GaAs lattice, the sample was annealed at 840°C. Fig. 5 is the PL spectrum of the sample after annealing at 15 K. The structure of the annealed PL spectum is similar to the as-grown PL spectrum, but there are two differences between the two PL spectra.

One of the difference is that the 1.5042 and 1.4875 eV peak shifted to 1.5065 and 1.4894 eV respectively. It is probably caused by the deformation in the sample surface film due to the introduction of Mn ion, which lead to the decrease of the bandgap compared with the perfect crystal GaAs. As a result, the photon energy of interband transition decreases with the decrease of the bandgap. After annealing, the bandgap returns to the original value due to the elimination of the deformation by releasing the strain in the lattice. Accordingly, the photon energy of interband transition increases with the restoration of bandgap. The other striking difference is that the PL intensity of 1.35 eV emission increased greatly after annealing.

In the following, we will simply discuss the physical origins of the three emision bands.

3.2.1. 1.5065 eV and 1.4894 eV peak

Because the intensity and shape of 1.5065 eV peak and 1.4894 eV peak are almost unchanged compared with that of the peak 1.5042 and 1.4875 eV respectively, the origin of the first two peaks should be the same as that of the peak 1.5042 eV and 1.4875 eV respectively.

According to the location and sharpness of peak, the 1.5065 eV peak should be attributed to the GaAs bound exciton radiative transition.

The 1.4984 eV is in good agreement with the donor-acceptor pair (DAP) transition involving the carbon at a As site (C_{AS}) [7]. Although the photon energy of some

other impurity-induced radiative recombination (such as Zn [4]) is also close to the 1.4894 eV, the peak should be assigned as C(As)-related DAP radiative recombination, because AES spectra of this kind of sample show no other shallow acceptor impurities, excepting carbon, in the sample.

3.2.2. 1.35 eV broad emission band

As to the origin of the emission band near 1.35 eV, there are several possibilities listed below.

(1) During the sample growth, a number of defects may be generated due to the bombardment and introduction of Mn ion. Under this condition, a series of quasi-continuous defect levels may appear in the bandgap, which can be responsible for the 1.35 eV emission band due to the photoluminescence overlapping.

(2) After annealing, the new phase Mn_2As appeared in the sample, at the same time the PL intensity of $\sim$1.35 eV emission band increased. There may be some internal relation between the two significant changes. That is to say, the 1.35 eV emission band may be attributed to semiconducting Mn_2As. Although X-ray diffraction did not detect Mn_2As in the as-grown sample, the existence of Mn_2As can not be ruled out. Maybe the content of Mn_2As is too small to be detected and it is the small quantity of Mn_2As that lead to the weak PL intensity of the as-grown sample.

(3) Mn on Ga site forms an acceptor state. A emission from the free or donor bound electrons to the Mn acceptor is located at about 1.35 eV, which has been reported already in other papers [3–6]. So it is possible that the $\sim$1.35 eV emission band obtained in our samples is attributed to the Mn acceptor related radiative recombination. And before annealing the number of optical active Mn ions on Ga sites is few, which corresponds to low relevant PL intensity. After annealing the number of optical active Mn ions on Ga sites is enhanced greatly, so relevant PL intensity greatly increased.

(4) In GaAs, Mn ion can replace Ga or As to form the alloy GaMnAs. In comparison with GaAs, the bandgap of GaMnAs will be changed with the concentration of Mn. When Mn in GaAs achieve a certain concentration, the alloy GaMnAs-related radiative recombination may be responsible for the 1.35 eV band.

Altogether, 1.35 eV emission band may results from one or several of the above possibilities.

4. Summary

In conclusion, the XRD and PL measurment were employed for structural and optical study of ion-beam deposition grown GaMnAs/GaAs. The XRD result showed that $Ga_{5.2}Mn$, Ga_5Mn_8, Mn_3Ga and α-Mn were obtained in the sample grown at the substrate temperature of 400°C. The strong and sharp Ga_5Mn_8 peak indicated that the growth conditions were quite suited to the nucleation and growth of Ga_5Mn_8. After annealing at 840°C, Mn_3Ga and α-Mn disappeared, Ga_5Mn_8 tended to disappear, $Ga_{5.2}Mn$ crystallized better and new phase of Mn_2As was generated, which showed that the annealing was beneficial to the growth of $Ga_{5.2}Mn$ and Mn_2As. The PL result showed that the excition peak, carbon-induced recombination peak and a broad emission band near 1.35 eV were observed in both the as-grown PL spectra and the annealed PL spectra. The exciton and carbon induced peaks shift to the higher energy after annealing at 840°C. This blue shift may arise as a result of the restoration of the bandgap of GaAs compared with the decreased bandgap of the as-grown sample. The PL intensity of the 1.35 eV emission increases greatly after annealing. The physical origin of the 1.35 eV emission is an open question, it may be attributed to one or several of the following: defect level, semiconducting Mn2As, Mn on a Ga site, and the alloy GaMnAs.

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