The Effects of Codoping of Be and Mg on Incorporation of Mn in GaAs

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Abstract Samples of GaMnAs, GaMnAs codoped with Be, and GaMnAs simultaneously codoped with Be and Mg were grown via low-temperature molecular beam epitaxy (LT-MBE). Be codoping is shown to take the Ga sites into the lattice efficiently and to increase the conductivity of GaMnAs. Additionally, it shifts the semiconducting behavior of GaMnAs to metallic while the Mn concentration in the GaMnAs solid solution is reduced. However, with simultaneous codoping of GaMnAs with Be and Mg, the Mn concentration increases dramatically several times over that in a GaMnAs sample alone. Mg and Be are shown to eject Mn from the Ga sites to form MnAs and MnGa precipitates.

Key words GaMnAs, Be codoping, Mg codoping, MBE, Magnetic semiconductor PACS: 75.50Pp, 75.70Ak, 81.15.Hi

1. Introduction

GaMnAs as a dilute magnetic semiconductor has been intensively studied, being one of the most promising candidates for spintronic materials.¹⁻⁴⁾ While the Curie temperature (T_c) of homogenous GaMnAs has been limited to 110 K,²⁾ trials were carried out to enhance T_c by reducing the defects of Mn interstitial and As antisites in increasing the carrier concentration. Low temperature post-annealing is one favorable method being used by many groups of scientists to remove these defects,⁵⁻⁸⁾ and they are able to obtain GaMnAs samples with T_c of around 150 K. Two dimensional hole gas (2DHG) created by Mn δ -doping in GaAs followed by low temperature post-annealing can further enhance T_c to 250 K.^{9,10)} It is also reported that the T_c of p-type GaAs:C can go as high as 280 K¹¹⁾ when ion implanted with Mn.

As it is difficult to further increase the Mn concentration in homogenous GaMnAs, several groups have tried to increase the hole concentration to enhance T_c by codoping of acceptor Be.¹²⁻¹⁴⁾ Codoping of Be increases hole concentration; on the other hand, it also increases Mn interstitial defects.¹²⁾ Mg is also known to be an acceptor and is well used as a dopant in semiconductor materials, such as GaAs¹⁵⁾ and GaMnN.^{16,17)} The ionic

radius of Mg is not only larger than Be but also larger than Ga. It is possible to compensate for lattice distortion caused by smaller ionic radius of Be than Ga, which, in turn, can affect the structural, electric and magnetic properties of GaMnAs. Therefore, studying the effect of simultaneous codoping of Be and Mg on GaMnAs becomes a very interesting subject of further research.

2. Experimental procedure

Samples were grown at $T_s = 300^\circ\text{C}$ via LT-MBE^{18,19)} on semi-insulating GaAs (001) substrate which was degreased in trichloroethane, acetone, and methanol, followed by etching in sulfuric acid solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 8 : 1 : 1$). The LT-MBE system was homemade and equipped with solid sources of Ga, As, Mn, Mg and Be. A closed-cycle water chiller cooled the cells, and a liquid nitrogen shroud surrounded the sample holder. The background pressure with flowing liquid nitrogen was in the low 10^{-10} Torr range. A reflection high-energy electron diffraction (RHEED) gun was provided for *in-situ* monitoring of the surface reconstruction during the growth. The substrate temperature was calibrated by deoxidation of the GaAs substrate, which is known to occur at $\sim 580^\circ\text{C}$. The substrates were first deoxidized at $\sim 610^\circ\text{C}$ for 30 minutes; then, a ~ 250 -nm-thick buffer GaAs layer was grown at $T_s = 580^\circ\text{C}$ at a growth rate of $0.5 \mu\text{m/h}$. The layers were grown at an As_4 pressure of

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$\sim 2.5 \times 10^{-6}$ Torr, where the highest specular beam RHEED intensity was observed during growth for the smoothest growth front. RHEED was also a useful tool to observe the MnAs precipitation during growth *in situ*. The substrate temperature was then lowered under the arsenic flux for the growth of GaMnAs, GaMnAs codoped with Be and GaMnAs simultaneously codoped with Be and Mg. For the LT-growth, the Ga flux was adjusted to a growth rate of $0.25 \mu\text{m/h}$ at an As_4 pressure of $\sim 1.4 \times 10^{-6}$ Torr.

The Mn cell temperature was fixed at $T_{\text{Mn}} = 910^\circ\text{C}$ for all samples, which is the maximum Mn flux for getting homogenous GaMnAs. The fixed Mn flux in each sample is very convenient to adapt in studying the effects of codoping. Be flux was set at $T_{\text{Be}} = 1175^\circ\text{C}$; at this temperature, metallic GaAs:Be could take place. Mg fluxes were assigned at $T_{\text{Mg}} = 360^\circ\text{C}$ and 380°C , with $T_{\text{Mg}} = 360^\circ\text{C}$ being the maximum flux needed to obtain homogenous GaAs:Mg. The GaMnAs film grown without codoping will be called sample “M”, and the GaMnAs:Be film will be called ‘BM’ sample. The GaMnAs:(Be,Mg) samples with Mg fluxes of $T_{\text{Mg}} = 360^\circ\text{C}$ and 380°C will be called as “MBM1” and “MBM2”, respectively.

The Mn concentration was measured by using an electron probe x-ray microanalysis (EPMA) and secondary ion mass spectrometry (SIMS). The structural properties of the grown layers were investigated by using q -2 q X-Ray diffraction (XRD). The electrical and the magnetic properties were investigated using Hall-effect measurements in van der Pauw geometry and a superconducting quantum interference device (SQUID).

3. Results And Discussion

The XRD measurement for all samples is shown in Fig. 1. From the XRD pattern, no obvious peak can be observed in samples M and BM except for GaAs (002) and GaAs (004) peaks which are located about 31° and 66° , respectively. Homogenous morphology of sample M is already determined via RHEED pattern during growth, while inhomogeneous morphology of sample BM with very slight precipitation is also confirmed even if no peaks related to precipitations are observable in XRD pattern. This indicates that the in-situ monitoring tool of RHEED is a more sensitive one than XRD in detecting precipitation. The peaks emerging clearly in MBM1

Fig. 1. θ -2 θ XRD patterns for sample M, BM, MBM1 and MBM2. A possible phase identification of the precipitations is made.

sample and MBM2 sample at positions 27° , 42° and 45° are from the MnAs and MnGa (and maybe Mn) precipitations as will be further proven. Compared with sample M and sample BM, the emergence of these components corresponding to XRD peaks in sample MBM1 and sample MBM2 should be attributed to the codoping of Mg. This will be discussed in detail, but we have to mention that the ring patterns of RHEED during the growth of MBM samples indicate polycrystalline nature of the films due to excess precipitates.

Mn atomic fraction is determined by EPMA and SIMS measurement, as indicated in Fig. 2; (a) is the result derived from EPMA, while the SIMS results in (b) qualitatively confirm the changing tendency of Mn concentration in each sample indicated in (a). From Fig. 2(a), we can see that compared with the reference sample M, Mn concentration in sample BM is slightly decreased due to the codoping of Be. With additional doping with Mg in sample MBM1, however, Mn concentration interestingly rather increased. A further higher Mg codoping then decreased the Mn concentration.

The decrease of Mn concentration in sample BM is not large but is detectable as confirmed by the SIMS results in Fig. 2 (b). The slight change can be attributed to the competition between Be and Mn atoms during growth to seat on Ga ions' sites in the lattice. However, it can be seen with several evidences that Be is much more efficient than Mn in taking the Ga sites. Firstly, as revealed by the resistivity measurement in Fig. 3, the Be codoping changed the film conductivity by more than two orders of magnitude and from semiconducting to metallic. This dramatic change occurred because Be

Fig. 2. Mn concentrations in the samples characterized with (a) EPMA measurement and (b) SIMS measurement.

preferentially takes the Ga sites as well as its smaller acceptor binding energy than Mn.²⁰⁾ Be, being an effective acceptor, not only contributes to high conductivity, but also renders a metallic characteristic. Secondly, the RHEED showed reconstruction patterns pertaining to MnAs precipitation during the growth. The observation indicates that Mn that competes with Be for incorporation does not substitute Ga, but rather forms separated phase of MnAs. This will be further confirmed later in the magnetization measurements.

In conclusion, Mn substitutes Ga in GaMnAs solid solution. However, when Mn and Be are simultaneously doped in GaAs, Be preferably substitutes Ga sites and Mn atoms are expelled out of the sites to form MnAs and other precipitates. It is interesting to observe that the Be concentrations are still kept constant with additional Mg codoping in MBM samples as revealed by the SIMS measurement result in Fig. 4. Therefore, Be preferably occupy the Ga sites through the competition with Mn and Mg that, as a consequence, is to be expelled out of the substitutional sites.

Fig. 3. Temperature dependence resistivity measured for sample M, BM, MBM1 and MBM2.

Fig. 4. Relative Be concentrations of sample BM, MBM1 and MBM2 measured by SIMS.

The most interesting phenomenon takes place in samples MBM1 and MBM2. With simultaneous codoping of Be and Mg, total Mn concentration has increased several times of that in the reference sample M and sample BM (Fig. 2(a)). It is interesting because the increase of Mn content occurred in more competitive condition for incorporation. The overall resistivity of the films are still governed mostly by the Be dopants as shown in Fig. 3, where the conductance is only slightly improved. The conductance improvement can be attributed mainly to the increase of the metallic precipitates and some additional Mg substitution of the Ga sites. Note again that all the Mn atoms dramatically increased in the samples were consumed by the ferromagnetic precipitates so that the amount of precipitates a lot increased. This can be confirmed by the magnetization measurements in Fig. 5. In the figure, the rise of magnetization at low temperature in sample M is attributed to the ferromagnetic GaMnAs solid solution. However,

Fig. 5. Temperature dependence of saturation magnetization for sample M, BM, MBM1 and MBM2.

the magnetization in samples BM, MBM1 and MBM2 is of MnAs (and MnGa) precipitates, not of a GaMnAs solid solution. The flat magnetization at low temperatures in MBM samples supports that they do not contain GaMnAs solid solution. Namely MBM samples are made of matrix mostly of GaAs:Be and MnAs (and MnGa) precipitates. In other words, in the MBM samples, the metallic conductance is mainly promoted by a highly Be doped matrix and the magnetization is promoted by the ferromagnetic precipitates.

Now the question is how simultaneous codoping of Mg and Be enhance Mn incorporation, and consequently, the precipitation in the lattice. In the meantime, recall that codoping with Be alone slightly reduced the Mn incorporation. We also observed that there is competition between Mn and Mg for incorporation when Mg alone is codoped as illustrated by the inset in Fig. 2(a). Namely, codoping of Mg or Be alone reduces the Mn incorporation, but simultaneous codoping of Mg and Be enhances the Mn incorporation. This may be explained as the following. The atomic radii of Ga, Mn, Be and Mg are 0.139, 0.130, 0.113 and 0.160 nm, respectively,²¹⁾ and they may be taken as the relative size of the atoms in the lattice. Because of the differences in the ionic size of the dopants, the development of lattice distortion in the matrix is inevitable. A lattice shrinkage occurs in the sample with Be doping due to the smaller ionic radius of Be as compared to Ga; conversely, a lattice expansion takes place in the case of Mg codoping.²²⁾ The expansion or shrinkage of the lattice might reduce the space volume at the interstitial sites. In the meantime, the codoping of Mg and Be can compensate the ionic size effect in the lattice so that the interstitial sites with increased space

Fig. 6. Hall loops for sample MBM1 at the temperature of 150 K, 200 K, 300 K and 325 K measured via Hall-effect measurement.

volume can introduce more Mn atoms and lead to more MnAs and MnGa precipitations.

However, in sample MBM2, with further increase in Mg flux, Mn incorporation even to interstitial sites decreases via competition. Recall that the Ga sites are primarily occupied by Be atoms as shown by the SIMS measurement denoted in Fig. 4; the Be concentration is almost the same in samples BM, MBM1 and MBM2. Therefore, Mn competes with Mg for the interstitial sites as well as for the Ga sites in the matrix. In sample MBM2 grown under higher Mg flux, the excess Mg atoms would enter into the interstitial sites and kick out Mn ions. As a result, smaller amount of metallic MnAs and MnGa precipitates were formed in MBM2, and this resulted in higher resistivity (Fig. 3) and lower magnetization (Fig. 5) than sample MBM1.

The temperature dependence magnetization measured via SQUID is shown in Fig. 5. A rapid drop in magnetization in sample M took place at temperature below 70 K indicating a low Curie temperature (T_c) with the GaMnAs component. The small and rather flat magnetization of sample BM originates from the small amount of MnAs precipitation, which has T_c of 313 K.²³⁾ As far as samples MBM1 and MBM2 are concerned, the greatly enhanced magnetization comes from the high Mn concentration brought about by the participation of Mg, as analyzed above. The first formation contributing to the ferromagnetism in samples MBM1 and MBM2 is determined as ferromagnetic MnAs, which is indicated by the quick drop in magnetization at T_c of MnAs.

The Hall-resistivity measured on sample MBM1 with varying temperature is summarized in Fig. 6. They showed

hysteresis loops and anomalous Hall components at all temperatures examined. Note that the magnetism at 325 K should originate from material other than MnAs precipitates, and it is most probably MnGa precipitation due to the XRD measurement in Fig. 1. Therefore the anomalous Hall components at other lower temperatures owe to the sum of MnAs and MnGa precipitations. Note that the Hall resistivity increased with temperature up to 300 K and then decreased at 325 K. This decrease can be due to the vanishing magnetization of MnAs. In conclusion, the clear Hall loop observed at 325 K is due to the high T_c of MnGa (more than 400 K).²⁴⁾ Note also that, in samples MBM1 and MBM2, there is no observable drop in magnetization at temperatures below 100 K, indicating that there is no observable GaMnAs composition in both samples. This again proves that the participation of Mg in Be codoped GaMnAs drives Mn ions out of Ga ions' sites and inhibits the formation of GaMnAs composition.

4. Conclusions

The effect of the simultaneous codoping of Be and Mg on the incorporation of Mn in the GaAs matrix is investigated. Be was shown to be the element that primarily occupy the Ga sites and render GaAs matrix the metallic conductance. As a consequence, Mn atoms are kicked out of the Ga sites and form precipitates in the forms of MnAs (and MnGa). Similar result was observed with Mg codoping, and can be explained by the competition between the impinging elements during the thin film growth with distorted interstitial sites. When Mg and Be are simultaneously codoped, however, a dramatic increase of Mn content was observed. This interesting phenomenon was explained by the relatively enlarged interstitial sites due to the compensation of the lattice distortion caused by Be and Mg. The precipitates were proved to be MnAs and MnGa through anomalous Hall effect measurement up to 325 K.

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