Effect of low temperature annealing on the crystallinity of III-V based diluted magnetic semiconductors

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Abstract

Low-temperature annealing after molecular-beam epitaxial growth of III-V based diluted magnetic semiconductors, (Ga,Mn)As and (In,Mn)As has been found to improve the crystallinity of the films. That is, the Curie temperature and the conductivity are greatly enhanced. This effect is probably due to the removal of excess As atoms which passivate doped Mn acceptors. The present method provides a way for reproducible systematic studies of these materials.

1. Introduction

The problem of low solubility of magnetic ions in zinc-blende III-V semiconductors was partially overcome by low-temperature molecular-beam epitaxy (LT-MBE) and successful synthesis of (In,Mn)As[1] and (Ga,Mn)As[2] was reported[3]. These materials are now attracting much attention because: 1) they are statically ferromagnetic; 2) the ferromagnetism can be controlled by external parameters, e.g. light illumination[4] or application of gate voltage[5], via the concentration of holes.

However the growth technique has a serious problem, which is the sensitivity of crystallinity to the growth conditions. For example, a slight change in the growth temperature results in huge difference in the low-temperature resistivity of the films despite no change is observed in the growth mode monitored with reflection high energy electron diffraction (RHEED)[6]. In (In, Mn)As, the growth temperature even switches the sign of majority carriers[1].

In this article, we report annealing of (Ga, Mn)As[7] and (In, Mn)As at comparatively low temperatures (slightly above the growth temperature) after growth largely enhances the conductivity and the ferromagnetic transition temperature ($T_{\rm C}$) of the grown films. In a wide range of annealing parameters (annealing time and temperature ($T_{\rm a}$)), the physical properties of resultant films are uniform and a function of Mn content x. This means the hybridized method of synthesis is stable for the growth conditions and provides a way of systematic studies of these materials.

2. Experiment

Films of (Ga, Mn)As and (In, Mn)As were grown by low-temperature (LT) molecular beam epitaxy (MBE). The growth temperatures were 225˚C and 300˚C respectively for (Ga,Mn)As and (In,Mn)As. (Ga,Mn)As films were grown on (001) GaAs buffer layers grown at 600˚C. At the beginning of growth of (Ga,Mn)As, the pattern of RHEED changed from c(4×4) to 1×1 and 1×2 superstructure appeared after about 50nm deposition. Long-lived specular-spot oscillation was observed. The patterns were streaky throughout the growths. (In, Mn)As films were also directly grown on GaAs buffer layers or thin (few nm) InAs buffer layers. During the first 20nm deposition of (In,Mn)As, the RHEED patterns were slightly spotty, then gradually changed to streaky 1×1. The parameters of wafers used in the present study are listed in Tab.1.

sample	thickness (nm)	Mn (%)	$p_{\rm as-grown}$ (cm^{-3})
(Ga,Mn)As	200	5	3.4×10^{19}
(In,Mn)As	600	2	2.1×10^{18}
(In,Mn)As	200	1	1.0×10^{19}
(In,Mn)As	1000	0.3	2.0×10^{19}
(In,Mn)As	1000	0.2	1.8×10^{19}

Table 1: Film thickness, Mn concentration and hole concentration of as-grown sample are listed for the films used in the present study.

Mn content x were obtained from the shift of (004) X-ray diffraction peak for (Ga,Mn)As. This method cannot be applied to (In, Mn)As because the shift of diffraction peak is so small and the peak is significantly broadened. Hence in order to estimate Mn concentration in (In, Mn)As, we calibrate the Mn flux from the results in (Ga, Mn)As and the In flux from the specular-spot oscillation in RHEED.

After the growth, the substrates were cleaved into 4mm×4mm squares. The annealing after the growth were performed in N_2 gas flow. The annealing time was fixed at 15 minutes. The ferromagnetic transition temperature ($T_{\rm C}$) were determined from magnetization measurement with a superconducting quantum interference device (SQUID) for (Ga,Mn)As and by measurement of anomalous Hall effect for (In,Mn)As. Hole concentration was estimated from room temperature Hall coefficient. The resistivity (ρ) was measured by van der Pauw method with a conventional

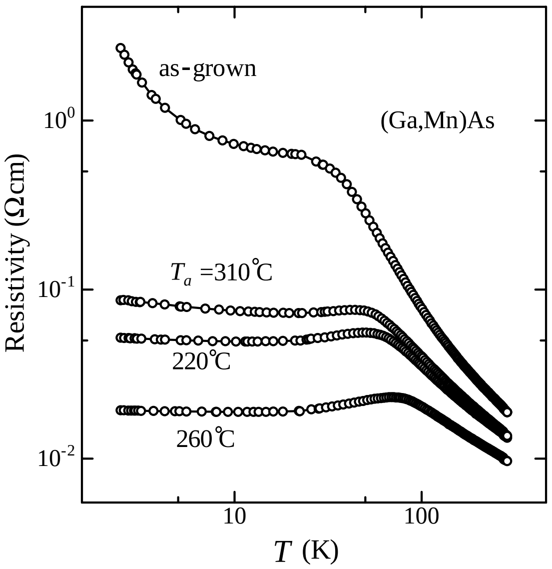

Figure 1: Temperature dependences of resistivity for the as-grown sample of (Ga,Mn)As with Mn content 0.05 and for those annealed at 220, 260 and 310 ˚C.

four-wire AC resistance bridge.

3. Results and discussion

As for (Ga, Mn)As, we mainly investigated the wafer with Mn content 0.05. Figure 1 shows temperature dependence of ρ. The as-grown sample shows typical insulating behavior besides a hump structure around 40K. This structure is known to appear approximately at $T_{\rm C}$. As $T_{\rm a}$ increased, ρ decreased and the temperature dependence changed from insulating to metallic. The hump structure shifted to higher temperature indicating that $T_{\rm C}$ also increased with the annealing. We confirmed this surmise by magnetization measurement.

The effect of the low-temperature annealing on $\rm Ga_{0.95}Mn_{0.05}As$ is summarized in Fig.2. The hole concentration p and $T_{\rm C}$ have maxima at around 260˚C while ρ at 8K takes minimum at the same temperature and the lattice constant a monotonically decreases with the increase of $T_{\rm a}$.

The decrease in ρ and the enhancement of $T_{\rm C}$ are surprising results because it was reported that ρ increase and the decrease of $T_{\rm C}$ were caused by annealing at fairly low temperatures[8]. This result precedent to ours is presumably due to some precipitation of MnAs clusters. Actually $T_{\rm C}$ decreases and ρ starts to increase as $T_{\rm a}$ increases beyond 260˚C. On the other hand, $T_{\rm C}$ and ρ remain almost at constants if we keep $T_{\rm a}$ below 260˚C and the annealing time shorter than an hour. This tells that it is crucial to keep $T_{\rm a}$ below some critical temperature to improve the transport and magnetism in the films.

An important feature is that ρ, p, and $T_{\rm C}$ have their saturation values, which are insensitive to the annealing condition as long as $T_{\rm a}$ is kept below the critical temperature. The saturation values are also comparatively insensitive to the MBE growth parameters and can be expressed as a function of Mn content. Another remarkable point in Fig.3 is that the optimized $T_{\rm C}$ reaches almost 100K, which is highest so far reported for (Ga, Mn)As directly grown on GaAs buffers[9]. The ferromagnetism in III-V based diluted magnetic semiconductors (DMSs) is considered to be mediated by itinerant holes and it is natural that $T_{\rm C}$ is enhanced with the increase in p. Hence “LT-MBE plus LT-annealing” provides a stable method to synthesize (Ga, Mn)As with highest quality.

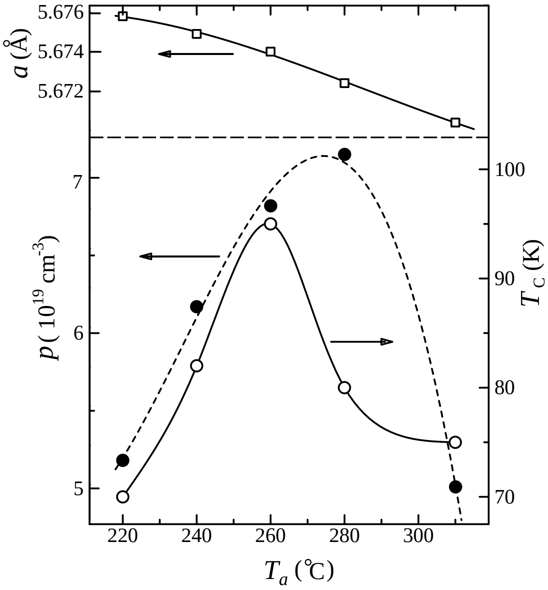

Figure 2: Variation of lattice constant (a), hole concentration (p), and ferromagnetic transition temperature ($T_{\rm C}$) versus annealing temperature $T_{\rm a}$ in (Ga,Mn)As.

We applied the same method to (In, Mn)As. Figure 3 shows temperature dependence of the resistivity for the sample with x =0.02. The decrease in ρ is much larger than those in (Ga,Mn)As, manifesting that this method is also applicable and effective to (In, Mn)As, though it is not clear that conduction in the sample with lowest ρ is metallic or not. We summarize the effect of annealing for (In, Mn)As with various Mn concentration in Fig.4. The increase in p is much stronger in (In, Mn)As and persists to about 400˚C. For x =0.01, the maximum value of p ($7{\times}10^{19}{\rm cm}^{-3}$) is recorded, which is a few times higher than the highest value so far reported for (In, Mn)As[10]. The ratio of active Mn acceptors to the doped Mn atoms is about 50% at the maximum. This result can hardly be explained by MnAs precipitation because such cluster formation should cause *decrease* in the hole concentration. The full width at half maximum (FWHM) of X-ray diffraction peak decreases with the annealing, which support improvement of the crystallinity.

Another characteristic feature in Fig.4 is that the enhancement in p is strongly dependent on the Mn concentration. Annealing has no effect on p for samples with low Mn concentration. The hole concentration p in the as-grown

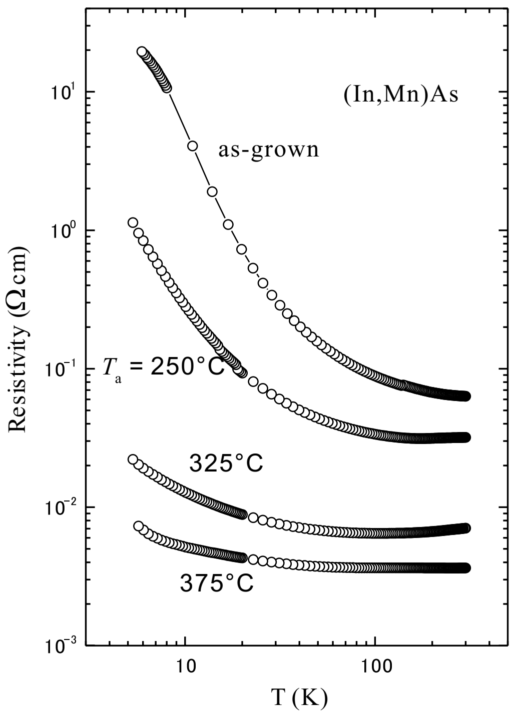

Figure 3: Temperature dependence of resistivity for the sample of (In, Mn)As with Mn content 0.02 and for those annealed at up to 375°C.

sample takes maximum at about x =0.003 in accordance with a previous report[10]. The annealing is effective only for the samples with the Mn concentration higher than that for the maximum of p in the as-grown sample (x_m). This indicates that the ratio of passive Mn atoms begins to increase at x_m and the annealing deforms lattice structure around the Mn atoms and activates such passive atoms. Similar tendency is also observed in (Ga, Mn)As, for which a systematic study is now under way.

In spite of the large enhancement in p, the rise in $T_{\rm C}$ is only 2K. On the other hand, $T_{\rm C}$ as high as 30K is reported for two-dimensional hole system at (In, Mn)As/GaSb hetero-interface. Thus, low $T_{\rm C}$ in the present experiment is not due to the intrinsic limit of the material. On the contrary, $T_{\rm C}$ as high as room temperature is expected from an optical conductivity measurement[11]. Further study is needed to clarify the cause of low $T_{\rm C}$ in (In, Mn)As.

Now we discuss the origin of the effect of low-temperature annealing. The most probable origin is the evaporation of excess As atoms, which are incorporated into the films during LT-MBE[12]. Some of such As atoms should passivate Mn acceptors and decrease p, forming Mn-As complexes. The situation is similar to the passivation of Mg acceptors by excess H atoms in GaN, which is removed by high-temperature annealing[13]. This scenario explains small decrease in the lattice constant by the annealing because LT-MBE grown GaAs have lattice constants larger than that of bulk GaAs due to excess As atoms. Single As interstitials are also expected to work as deep donors, which compensate the holes emitted from Mn acceptors. However this dose not explain the strong dependence of the effect of annealing on the Mn concentration.

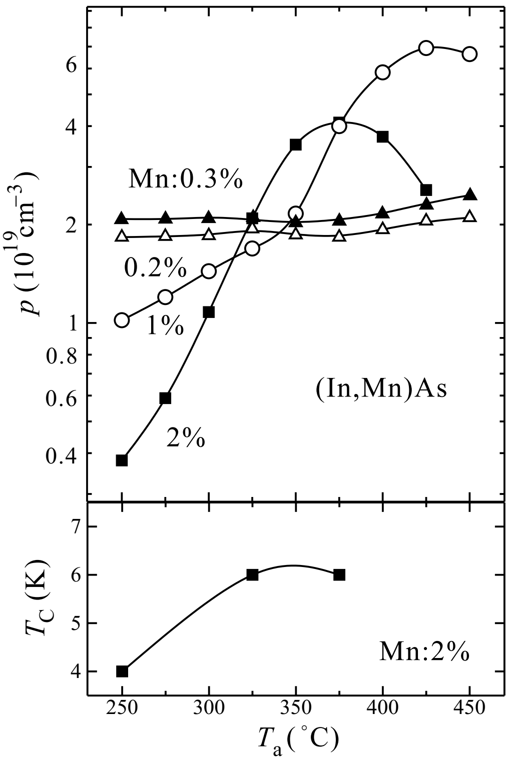

Figure 4: Variation of hole concentration (p), and ferromagentic transition temperature ($T_{\rm C}$) versus annealing temperature $T_{\rm a}$ in (In, Mn)As with various Mn concentration.

We would like to stress that the present method is useful for a systematic study of III-V based DMSs. One can discuss the material properties without troubled with extrinsic effects due to the sensitivities for growth conditions. Also, the annealing effect itself can be utilized to adjust material parameters. For example, by adjusting the annealing time, one can continuously change the hole concentration in a single specimen. This brings insulator-to-metal transition (MIT) in the specimen and can be used for the study of the MIT itself[14]. In summary, we report that annealing after LT-MBE growth at comparatively low temperature improves the crystallinity of III-V based DMSs. This effect is probably due to the removal of excess As atoms which passivate doped Mn acceptors.

Acknowledgements

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References

[1] H. Munekata, H. Ohno, S. von Molnar, A. Segmuller, L.L. Chang and L. Esaki, Phys. Rev. Lett. 63, 1849 (1989).

[2] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).

[3] A. Shen, H. Ohno, F. Matsukura, Y. Sugawara, N. Akiba, T. Kuroiwa, A. Oiwa, A. Endo, S. Katsumoto and Y. Iye, J. Cryst. Growth **175/176**, 1069 (1997).

[4] S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi and H. Munekata, Phys. Rev. Lett. **78**, 4617 (1997).

[5] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno and K. Ohtani, Nature **408**, 944 (2001).

[6] H. Shimizu, T. Hayashi, T. Nishinaga and M. Tanaka, Appl. Phys. Lett. **74**, 398 (1999).

[7] T. Hayashi, Y. Hashimoto, S. Katsumoto and Y. Iye, Appl. Phys. Lett. **78**, 1691 (2001).

[8] A. Van Esch, L. Van Bockstal, J. De Boeck, G. Verbanck, A. S. van Steenbergen, P. J. Wellmann, G. Grietens, R. Bogaerts, F. Herlack and G. Borghs, Phys. Rev. **B56**, 13103 (1997).

[9] A. Oiwa, S. Katsumoto, A. Endo, M. Hirasawa, Y. Iye, H. Ohno, F. Matsukura, A. Shen and Y. Sugawara, Solid State Commun. **103**, 209 (1997).

[10] A. Oiwa, A. Endo, S. Katsumoto, Y. Iye, H. Ohno and H. Munekata, Phys. Rev. **B59**, 5826 (1999).

[11] K. Hirakawa, S. Katsumoto, T. Hayashi, Y. Hashimoto and Y. Iye, submitted to Phys. Rev. B.

[12] S. O'Hagan and M. Missous, J. Appl. Phys. **75**,7835 (1994).

[13] S. Nakamura, Semicond. Sci. Technol. **14**, R27 (1999).

[14] T. Hayashi, Y. Hashimoto, S. Kasumoto and Y. Iye, to be published in Proc. 20th Int. Conf. Phys. Semicond.