Effect of low-temperature annealing on transport and magnetism of diluted magnetic semiconductor (Ga,Mn)As

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We report improvements in the crystallinity of a III-V-based diluted magnetic semiconductor (Ga,Mn)As by heat treatment (annealing) after growth at comparatively low temperatures. This method can be used to raise the Curie temperature to 100K without the need for severe optimization of growth conditions, as well as to adjust the material parameters to desired values.

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High ferromagnetic transition temperature $T_{\rm C}$ ($\sim$ 100K) and metallic conduction in the diluted magnetic semiconductor (DMS) (Ga,Mn)As[1, 2, 3] make this material promising for application to magnetooptics and spin electronics. The mechanism of the ferromagnetic ordering is one of the most important issues in the physics of these III-V-based DMSs. It is now well established that the holes provided by the Mn acceptors mediate the interaction between the localized magnetic moments of the Mn ions that are randomly distributed with an average spacing of a few lattice constants[2, 4]. The Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is the first candidate examined experimentally[5]. The double exchange (DE) model is another candidate, and a band-structure calculation in (In,Mn)As[6], which is a similar system to (Ga,Mn)As[7], supports the DE model. This calculation also predicts a relationship between the stability of ferromagnetism and the degree of compensation by As antisites[6]. Hence a systematic study of the relation between the excess As and $T_{\rm C}$ would provide a touchstone for this model.

In the synthesis of (Ga,Mn)As, metastability of the zincblende phase requires highly nonequilibrium growth methods, e.g., low-temperature molecular beam epitaxy (LTMBE)[8]. Therefore the quality of films thus grown is very sensitive to the growth conditions. For example, a 10-degree difference in the substrate temperature during the growth can lead to a considerable difference in the transport property as well as in magnetism even though there is no difference in the growth mode as observed by electron diffraction[9]. The knowledge of growth gained to date suggests that the excess As atoms at the growth surface strongly degrade the crystallinity, and that nearly stoichiometric growth is required to obtain high-$T_{\rm C}$ and metallic conduction. This is a rather delicate situation for epitaxial growth.

In this Letter, we report an experiment on the effect of heat treatment (annealing) at comparatively low temperatures (around the growth temperatures) on the magnetic and transport properties of (Ga,Mn)As. It is known that annealing at high temperatures ($\sim$ 600°C) causes phase separation of MnAs (NiAs-type crystalline structure) and GaAs (zinc blende), and the resultant composite material becomes an insulator[10]. In contrast to this, we unexpectedly found that low-temperature annealing leads to higher $T_{\rm C}$ and more metallic transport. A conceivable cause of this improvement is evaporation of the excess As atoms. This method could have important consequences in basic science and in applications.

The initial (Ga,Mn)As film was grown in a standard manner as follows[1]. On a 500nm-thick GaAs buffer layer, which was grown on a (001) semi-insulating GaAs substrate at 580°C, a 200nm-thick film of (Ga,Mn)As with a nominal Mn content of 5% was grown by ordinal LTMBE at 210°C. The V/III (As_4/Ga) ratio was about 3.

After this growth, the substrate was cleaved into 4mm$\times$4mm squares. The hole concentration p was estimated from the room-temperature Hall coefficient obtained by the van der Pauw method for each sample. The distribution of p (Δp) was 10% at approximately the average value of 3.5$\times$ 10^{19} cm^{-3}. This Δp is negligible compared with the variation due to the annealing. Annealing after growth was performed in N_2 gas flow. The annealing time was fixed at 15 minutes. Resistivity was measured with a conventional AC bridge, and magnetization with a commercial superconducting-quantum-interference-device (SQUID) susceptometer. The lattice constant a vertical to the growth plane was measured based on (004) X-ray diffraction peak.

Figure 1 shows the temperature dependence of the resistivity for the as-grown sample and for the samples annealed at temperatures T_a ranging from 220°C to 310°C. As the temperature decreases, the resistivity of the as-grown sample exhibits a hump at approximately 40K, followed by an increase with activation energy at lower temperatures. The origin of the hump structure is still open to argument[11] although it is experimentally established that the maximum always appears at approximately $T_{\rm C}$. With increasing T_a to 260°C, the resistivity markedly decreases and the activation-type temperature dependence changes to a slow increase with a decrease in temperature, in a manner characteristic of "dirty metals". At the same time, the temperature of the resistivity hump increases indicating that $T_{\rm C}$ increases after annealing; this feature is confirmed by magnetization measurement. When T_a exceeds 260°C, the resistivity starts to increase again and the

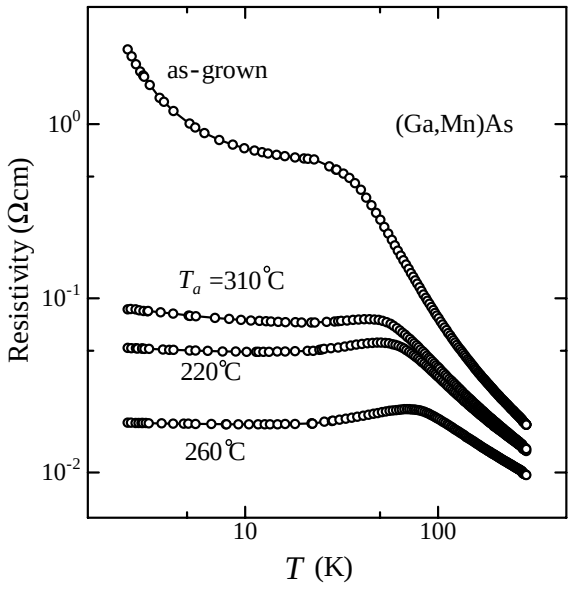

Figure 1: Temperature dependences of resistivity for the as-grown sample and for those annealed at 220, 260 and 310˚C.

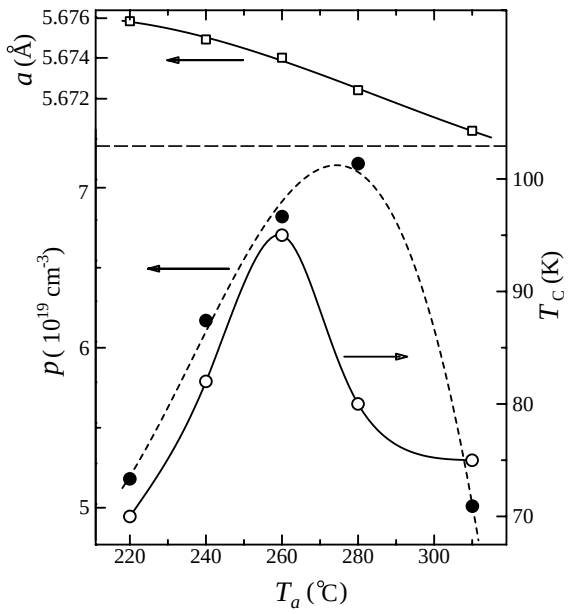

Figure 2: Variation of lattice constant (a), hole concentration (p), and ferromagnetic transition temperature ($T_{\rm C}$) versus annealing temperature T_a.

decrease of $T_{\rm C}$ follows.

Figure 2 summarizes the effect of low-temperature annealing on $T_{\rm C}$, as determined by magnetization measurement, a and p. $T_{\rm C}$ and p show maxima at approximately 260˚C while a decreases monotonically with T_a. The decrease in a is steeper for higher T_a. During this decrease in a, it is difficult to conceive that Mn atoms evaporated from the substrate, considering the inherent vapor pressure. There was no increase in the full-width at half-maximum of the X-ray diffraction peak, which indicates that the annealing caused no significant inhomogeneity in the films.

The above results are rather surprising considering the reports of the decrease of the ferromagnetic transition temperature with annealing, even at temperatures slightly above the growth temperature[12]. The main difference in the experiments of Van Esch et al.[12] from ours could be the annealing temperature. The lowest annealing temperature in ref.12 caused a 1% change in Mn concentration based on Vegard's law, while only changes of $0.1-0.5$ % were observed when T_a was below 260˚C in the present results. We note that Vegard's law no longer holds in the present system, as discussed below.

It may appear that MnAs clusters precipitate during annealing resulting in decrease of the Mn concentration in the (Ga,Mn)As phase of the composite system, leading to the decrease of a. Indeed Van Esch et al.[12] attributed the decrease of a to the decrease of the Mn concentration. Since the Mn content of 5% is slightly higher than the optimal density for $T_{\rm C}$[2], a decrease of the Mn content from 5% means an increase of $T_{\rm C}$. This is, however, not the case, at least when T_a is below 260˚C. An effect similar to that of low-temperature annealing arises when the grown film is kept at a temperature slightly higher than the growth temperature immediately after the growth in the MBE chamber with no As beam. No trace of the precipitation of MnAs clusters at the surface was detected in the reflective high-energy electron diffraction (RHEED) pattern up to the substrate temperature of 260˚C. Another clue is shown in Fig.3, in which $T_{\rm C}$ of the present work and those of a series of as-grown samples reported by Oiwa et al.[2] are plotted against a. The two curves are apparently different, which indicates that the decrease of the Mn content in (Ga,Mn)As, if it does occur, cannot explain the increase of $T_{\rm C}$.

Based on the above results, one can infer that low-temperature annealing causes the evaporation of excess As atoms in the film. The as-grown sample contains a considerable amount of interstitial As atoms which act as deep donors. This makes the lattice constant larger; in fact, GaAs films grown by LTMBE usually have lattice constants larger than that of ordinary high-quality GaAs[13]. According to the first-principle calculation of the band structure, As interstitials compensate holes generated by Mn and act against the stability of ferromagnetism[6].

Although the above scenario explains the present results qualitatively, it should be noted that further experiments suggest some modifications. For example, we observed that when the nominal Mn concentration was lowered from 5%, the increase of p due to annealing was strongly reduced. This suggests that perhaps Mn-As complexes, rather than simple As interstitials, cause the initial reduction of p.

The results presented in Figs. 1 to 3 are indicative of some qualitative changes occurring at approximately T_a=280˚C. This could be a sign of the precipitation of MnAs, which escapes detection in magnetization measurements due to the small volume of MnAs. Longer annealing time ($\sim$ 30 min-

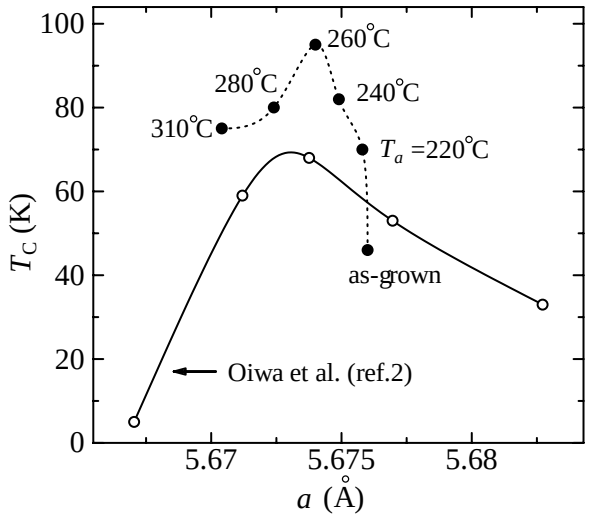

Figure 3: Ferromagnetic transition temperature $T_{\rm C}$ as a function of lattice constant a. Open circles correspond to data reported in ref.[2].

utes) at 260˚C slightly increases $T_{\rm C}$ though very long annealing times ($\sim$ 80 hours) clearly causes sample degradation. This means that 260˚C is the critical temperature at which very slow MnAs precipitation starts.

It is noteworthy that $T_{\rm C}$ rises to as high as 96K, a value close to the highest $T_{\rm C}$ reported for (Ga,Mn)As (110K) [5]. This means that one can obtain films of the highest quality without the need for complicated optimization of growth conditions[9]. It should also be noted that the highest $T_{\rm C}$ obtained after the treatment is determined mostly by the Mn content. On the other hand, samples with various $T_{\rm C}$ can be obtained from a single as-grown film by adjusting T_a and annealing time.

These features can be utilized to investigate the nature of ferromagnetism and transport in (Ga,Mn)As. For example, $T_{\rm C}$ can be varied without changing the Mn concentration. Thus this variation of $T_{\rm C}$ is due to that of the interaction between Mn spins; the variations of physical quantities should be closely related to the nature of the interaction. The present results are in qualitative agreement with the prediction obtained using the band calculation, although more detailed measurements and theoretical calculations are needed to arrive at definitive conclusion. Infrared absorption spectra of these specimens would provide some hints on the mechanism of ferromagnetic coupling[11]. A sample can be prepared so as to be in the critical region of the metal-insulator transition, by adjusting the annealing parameters, and utilized to investigate the critical behavior[14].

In summary, we found that the heat treatment of (Ga,Mn)As at comparatively low temperatures greatly improves the crystallinity. This is probably due to the evaporation of excess As atoms which form complexes with Mn dopants. This procedure can benefit basic science and lead to practical applications.

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