AIP Applied Physics Letters

Preparation of ferromagnetic (In,Mn)As with a high Curie temperature of 90 K

T. Schallenberg and H. Munekata

Citation: Appl. Phys. Lett. **89**, 042507 (2006); doi: 10.1063/1.2236210
View online: http://dx.doi.org/10.1063/1.2236210
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v89/i4
Published by the American Institute of Physics.

Preparation of ferromagnetic (In,Mn)As with a high Curie temperature of 90 K

T. Schallenberg[a] and H. Munekata
Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, 4259-G2-13 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

(Received 15 May 2006; accepted 7 June 2006; published online 27 July 2006)

The authors found high Curie temperatures of up to 90 K in annealed (In,Mn)As epilayers grown by molecular beam epitaxy using a relatively high V/III beam flux ratio. Magnetization data suggest that increasing the As beam flux results in an increase in the effective Mn content, and the carrier transport data indicate an increase in the hole concentration from a 10^{19} to 10^{20} cm^{-3} range with low-temperature annealing after growth. The highest Curie temperature was obtained in lattice matched (In,Mn)As/Al(As,Sb) samples. Both Hall effect and magneto-optical polar Kerr rotation measurements confirm that the high Curie temperature is due to hole-mediated ferromagnetism.
 [DOI: 10.1063/1.2236210]

Hole-mediated ferromagnetism in (III,Mn)V semiconductors is one of the outstanding advantages to pursue spintronics in semiconductors, since it is controllable by optical[1] and electrical[2] means. From the application point of view, it is important to find new ways to increase the Curie temperature T_C of (III,Mn)V. Low-temperature (LT) molecular beam epitaxy (MBE) has made it possible to increase the solubility limit of magnetic ions in the III-V matrix.[3] However, the LT growth has also been found to result in high numbers of Mn interstitial (Mn_i) and As antisite (As_{III}) defects, which electrically compensate substitutional Mn acceptors (Mn_{III}) and reduce the hole concentration p. Of these two kinds of defects, only Mn_i defects could be removed by postgrowth annealing without causing thermal degradation.[4,5] On the basis of the p-d Zener model ($T_C \propto p^{1/3}$),[6] it is widely believed that samples having a high T_C should be grown under a low As flux to suppress the number of As_{III} defects.[7–9]

In this letter, we discuss a different approach for increasing the T_C of a (III,Mn)V semiconductor. Our method, which was developed while investigating (In,Mn)As epitaxial films, consists of (a) LT growth with excess As_4 flux to increase the amount of substitutional Mn ions and (b) postgrowth LT annealing to recover a high hole concentration. Lattice matching to an Al(As,Sb) buffer layer also plays an important role in achieving a high T_C of 90 K.

(In,Mn)As thin films were grown by MBE on Al(As,Sb)/GaAs substrates. First, a highly resistive $AlAs_ySb_{1-y}$ buffer layer (500–800 nm thick) was deposited on a semi-insulating GaAs(001) substrate at a substrate temperature T_s of 560 °C. This was followed by LT-MBE of a 20-nm-thick (In,Mn)As epitaxial layer at T_s=200 °C. In, Mn, and As_4 fluxes were impinged simultaneously to initiate the growth. The In beam flux was fixed at 7.5×10^{14} at. s^{-1} cm^{-2}, which yielded a high growth rate of 1.5 μm/h at T_s=200 °C. We define the ratio of r=1 as the minimum V/III flux ratio r required to realize LT growth with an arsenic stabilized surface.[10] The total Mn content x =[Mn]/([In]+[Mn])=0.10 in a 2.8-μm-thick (In,Mn)As reference sample was determined by secondary ion mass spectroscopy and electron probe microanalysis. Referring to this reference value, the Mn content in thin (In,Mn)As films was varied by controlling the Mn/In flux ratio. Postgrowth annealing was carried out at 190 °C in the air atmosphere for 4 h.

The growth of InMnAs films was monitored by reflection high-energy electron diffraction (RHEED). Under conventional InMnAs growth conditions with $r<3$,[11,12] a spotty RHEED pattern was observed during the initial stage of growth, but this changed to a streaky (2×1) pattern as growth proceeded, as shown in the inset A in Fig. 1(a). In contrast, the RHEED patterns remained spotty throughout the growth with $r>3$ (see inset B). For all the samples studied in this work, no second phase was observed by RHEED.

The hole concentration and the mobility were extracted from room-temperature Hall effect data obtained by the van der Pauw method with a magnetic field H of ±4.6 kOe. The magnetization M of InMnAs films was measured by using a superconducting quantum interference device magnetometer. The Curie temperature was determined as the temperature at which the hole-mediated ferromagnetic component disappears in the M-T curves. The curves were measured under

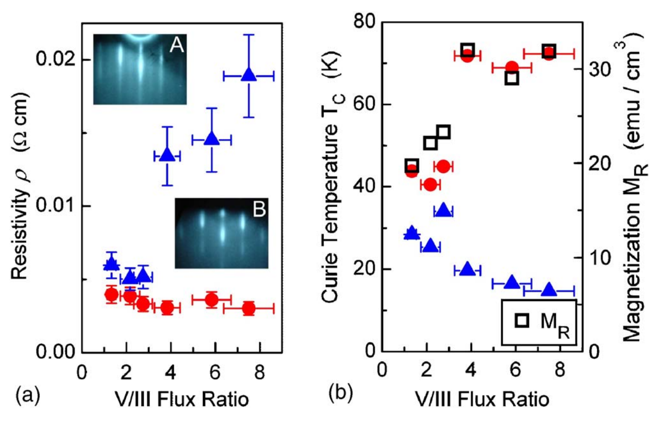

FIG. 1. (Color online) (a) Resistivity ρ at 300 K and (b) Curie temperature T_C of six (In,Mn)As(x=0.10)/AlSb samples grown using various V/III beam flux ratios r. Insets A and B in (a) show the RHEED patterns acquired after the growth of (In,Mn)As with r=1.3 and r=3.8, respectively. Triangles and circles in both (a) and (b) represent as-grown and annealed samples, respectively. Remanent magnetization M_R at 4 K is also shown in (b) by open squares.

[a]FAX: +81-45-924-5179; electronic mail: timo@isl.titech.ac.jp

$H=10$ Oe after magnetizing the sample at 4 K with $H \geqslant 3$ kOe. Double crystal x-ray diffraction θ-2θ scans were measured around the [004] reflection.

In the following, we first describe the results of the Hall and the magnetization measurements for a series of six (In,Mn)As ($x=0.10$)/AlSb samples that were grown with different V/III ratios of $r=1.3$, 2.2, 2.8, 3.8, 5.8, and 7.5. We then extend our discussion to (In,Mn)As/$AlAs_ySb_{1-y}$ samples ($r>3$) to investigate the dependence of T_C on Mn content ($0.01<x<0.16$) and lattice mismatch.

The resistivities ρ of the as-grown and the annealed (In,Mn)As($x=0.10$)/AlSb samples are plotted in Fig. 1(a) as a function of the V/III ratio r. For the as-grown samples [represented by triangles in Fig. 1(a)] ρ increases as r increases; $\rho=0.005-0.006\ \Omega$ cm for $r<3$, whereas $\rho=0.019\ \Omega$ cm for $r=7.5$. The hole concentrations at room temperature (RT) are $p=(1.2-1.3)\times 10^{20}$ and $(4.6-4.8)\times 10^{19}$ cm^{-3} for $r<3$ and $r>3$, respectively. The mobilities are $\mu=7-10$ cm^2/V s for both cases. The p values suggest that a large As_4 flux promotes the incorporation of excess As and results in strongly compensated films, as has been discussed by other workers.[13,14]

For annealed samples, resistivities ρ [represented by circles in Fig. 1(a)] are less than those of the nonannealed samples and do not show a strong dependence on r; $\rho=0.003-0.004\ \Omega$ cm and tends to decrease with increasing r. The hole concentration at RT is consistently higher for the annealed samples, $p=(1.6-1.9)\times 10^{20}$ cm^{-3}. The mobilities μ are in the range of 8–13 cm^2/V s. High-field transport measurements (-15 T$\leqslant H \leqslant 15$ T) at 1.8 K revealed that $p=2.0\times 10^{20}$ cm^{-3} and $\mu=9.4$ cm^2/V s for the sample with $r=2.8$. The good agreement between the p values obtained from the two different experiments indicates that characterization by the RT, low-field van der Pauw method is practical in (In,Mn)As.

Plots of the Curie temperature T_C and remanent magnetization M_R as a function of r are shown in Fig. 1(b). As-grown samples [represented by filled triangles in Fig. 1(b)] have $T_C=29\pm 4$ and 17 ± 3 K for $r<3$ and $r>3$, respectively. The low T_C for $r>3$ can be understood in terms of the reduced hole concentration. As represented by the filled circles in Fig. 1(b), T_C increased in all samples on annealing. In the low r regime ($r<3$), T_C increased up to 40–50 K, which was previously the upper limit of T_C in the literature.[11,12] To our surprise, samples in the high r regime ($r>3$) exhibited a T_C of up to 72 K, which is the highest value reported so far for (In,Mn)As. The strong dependence of T_C on r is obviously not related to the hole concentration p.

Remanent magnetization M_R measured at 4 K for the annealed (In,Mn)As/AlSb films shows a similar trend as that observed for T_C. As represented by the open squares in Fig. 1(b), $M_R=22\pm 2$ emu/cm^3 for $r<3$, whereas $M_R=31\pm 2$ emu/cm^3 for $r>3$. Since these films have well-defined square hysteresis loops (not shown), the M_R values can give us a rough estimate of the amount of Mn ions which participate in the formation of ferromagnetic ordering. Assuming a moment $S=4/2$ ($S=5/2$), the effective Mn contents $x_{\rm eff}$ are 0.033 (0.026) and 0.047 (0.037) for $r<3$ and $r>3$, respectively. These analyses suggest that $x_{\rm eff}$ can be enhanced by growing (In,Mn)As films in an As-rich condition. That As-rich condition assists the formation of substitutional Mn acceptors has also been pointed out in a recent theoretical work.[15] It should be noted that growth with a high As flux results in a high T_C only when postgrowth annealing gives rise to a high hole concentration.

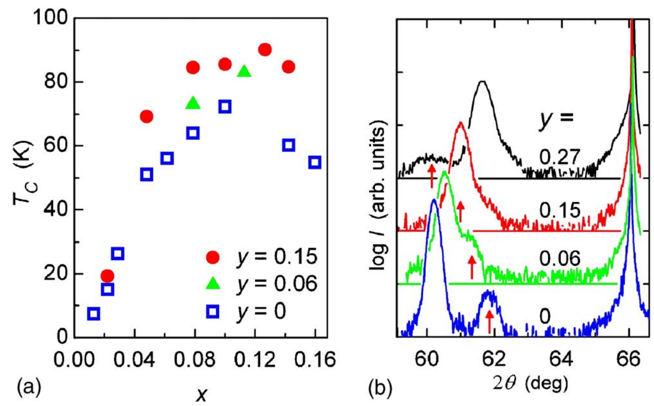

FIG. 2. (Color online) (a) A plot of Curie temperature T_C vs overall Mn content x for annealed (In,Mn)As layers that were grown using relatively high V/III flux ratios of $r=4-12$. Open squares, filled triangles, and filled circles represent samples with various arsenic contents y in Al(As,Sb) buffer layers. (b) θ-2θ data of x-ray diffraction of the (004) reflection for (In,Mn)As/$AlAs_ySb_{1-y}$/GaAs samples with $y=0$, 0.06, 0.15, and 0.27.

Figure 2(a) shows T_C of InMnAs/AlAsSb samples as a function of Mn content x. We first discuss samples with AlSb buffers ($y=0$). The open squares in Fig. 2(a) show that T_C initially increases as x increases, reaching $T_C=72$ K when $x=0.10$, and then decreases as x increases further. Magnetization measurements done on samples with $x=0.10$ indicate the presence of a ferromagnetic second phase with $T_C \approx 300$ K and a saturation magnetization of ~ 2 emu/cm^3, which corresponds to a MnAs volume fraction of $x_{\rm MnAs} \approx 0.004$. For very high x values, the amount of the second phase is strongly enhanced at the expense of the InMnAs phase ($T_C=55$ K at $x=0.16$).

Figure 2(b) shows θ-2θ scans of InMnAs/$AlAs_ySb_{1-y}$ samples relative to the GaAs (004) peak at $2\theta=66.0°$. The data for $y=0$ exhibit two peaks at $2\theta=60.2°$ and $2\theta=61.8°$ for $AlAs_ySb_{1-y}$ and InMnAs (indicated by small arrows), respectively. With increasing y, the peaks shift in the direction opposite each other. For $y=0.15$, the lattice mismatch is minimized, below (beyond) which InMnAs layers undergo tensile (compressive) strain.

In Fig. 2(a), the filled triangles and circles represent the T_C values for InMnAs/$AlAs_ySb_{1-y}$ samples with $y=0.06$ and $y=0.15$, respectively. The T_C values are higher in the samples with reduced lattice mismatch relative to InMnAs/AlSb samples ($y=0$).

At present, the highest Curie temperature of 90 K was achieved in (In,Mn)As ($x=0.127$; $r=12$) layers grown on a lattice matched $AlAs_ySb_{1-y}$ ($y=0.15$) surface. The hole concentration p was 1.6×10^{19} cm^{-3} for the as-grown sample ($T_C=20$ K), whereas it increased to $p=2.4\times 10^{20}$ cm^{-3} after annealing. Reducing the lattice mismatch and using the method described in this study, we were able to achieve a Curie temperature that exceeds the value expected from the chemical trend in the p-d Zener model.[6]

Behaviors which are characteristic of hole-mediated ferromagnetism are observed in all samples including the one with $T_C=90$ K. An increase in resistance due to spin-disorder scattering is observed at around 90 K in the resistivity data, as shown by the solid curve in Fig. 3(a). Spectra of the polar

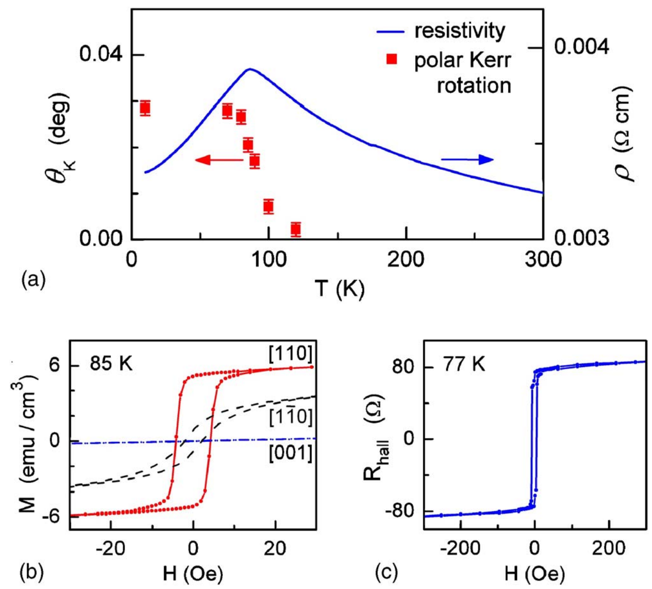

FIG. 3. (Color online) (a) Temperature dependence of resistivity ρ (solid line) and polar Kerr rotation θ_K (closed squares) of the T_C=90 K sample (x=0.127, y=0.15). Polar Kerr rotation was measured at a photon energy of 2.75 eV with a perpendicular magnetic field of 2 kOe. (b) M-H curves of the T_C=90 K sample along three different crystal axes. The direction of an external magnetic field is parallel to the corresponding crystal axis. (c) Hall resistance hysteresis curve for the T_C=83 K sample (x=0.115, y=0.06) obtained in a liquid nitrogen bath. H is applied perpendicular to the sample plane.

Kerr rotation θ_K show enhanced signals around the E_1 critical point of InAs (E_1=2.6 eV, not shown), and the temperature dependence of θ_K ($h\nu$=2.75 eV and $H_\perp$=2 kOe) shows a steep reduction around the Curie temperature [see the filled squares in Fig. 3(a)].

The magnetic anisotropy of our samples depends on the hole concentration and the buffer-induced strain. As far as the annealed samples are concerned, all the InMnAs films grown on $AlAs_ySb_{1-y}$ with $y<0.08$ exhibit perpendicular anisotropy. This is exemplified by the Hall resistance hysteresis curve shown in Fig. 3(c) (T_C=83 K with x=0.115 and y=0.06). By contrast, the three M-H curves measured along different crystal axes of a lattice matched (In,Mn)As/Al(As,Sb) sample (T_C=90 K with x=0.127 and y=0.15) show in-plane magnetization with uniaxial anisotropy along the [110] direction [see Fig. 3(b)]. These results confirm the earlier report on strain engineering in (In,Mn)As/(In,Al)As heterostructure.[12]

In contrast to the annealed samples, most of the as-grown samples favor in-plane magnetization. Even InMnAs/AlSb samples having a large tensile strain exhibit in-plane magnetization when the hole concentration is low ($r>3$). Obviously, annealing changes the magnetic anisotropy by changing the hole concentration in the InMnAs film, which is qualitatively in accordance with theoretical consideration for (Ga,Mn)As.[16]

Finally, let us briefly compare our results with that of other studies which report room-temperature ferromagnetism in InMnAs films grown by metal organic vapor phase epitaxy (MOVPE).[17–19] Those samples show a hole-mediated ferromagnetic InMnAs phase ($T_C<30$ K) and a ferromagnetic second phase (T_C=330 K) which is believed to originate from ordered Mn atoms. They are highly resistive ($\rho>0.05\ \Omega$ cm) and exhibit very weak magneto-optical effects. Therefore, our T_C=90 K sample is not related to the second phase found in the MOVPE (In,Mn)As films.

In summary, our method in part goes against the current trend of suppressing defect formation to realize high T_C in III-V-based ferromagnetic semiconductors. It involves low-temperature molecular beam epitaxy with excess As beam flux, followed by postgrowth low-temperature annealing. High As beam flux during the MBE growth seems to increase the amount of Mn ions which participate in the ferromagnetic ordering. Low-temperature annealing is effective in that it restores a high hole concentration of about 2×10^{20} cm^{-3}. The combination of both steps results in high Curie temperatures up to 90 K, which has never been anticipated for (In,Mn)As.

The authors thank Dr. T. Akazaki of the NTT Basic Research Laboratory for the collaboration in the study of high-field carrier transport measurements. This work is supported in part by the NSF-IT program (DMR-0325474) and by the Priority Area Scientific Research "Semiconductor Nanospintronics" from MEXT (No. 14076210).

[1] S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi, and H. Munekata, Phys. Rev. Lett. **78**, 4617 (1997).
[2] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, Nature (London) **408**, 944 (2000).
[3] H. Munekata, H. Ohno, S. von Molnar, Armin Segmüller, L. L. Chang, and L. Esaki, Phys. Rev. Lett. **63**, 1849 (1989).
[4] K. M. Yu, W. Walukiewicz, T. Wojtowicz, I. Kuryliszyn, X. Liu, Y. Sasaki, and J. K. Furdyna, Phys. Rev. B **65**, 201303 (2002).
[5] D. E. Bliss, W. Walukiewicz, J. W. Ager III, E. E. Haller, K. T. Chan, and S. Tanigawa, J. Appl. Phys. **71**, 1699 (1992).
[6] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[7] K. C. Ku, S. J. Potashnik, R. F. Wang, S. H. Chun, P. Schiffer, N. Samarth, M. J. Seong, A. Mascarenhas, E. Johnston-Halperin, R. C. Myers, A. C. Gossard, and D. D. Awschalom, Appl. Phys. Lett. **82**, 2302 (2003).
[8] V. Avrutin, D. Humienik, S. Frank, A. Koeder, W. Schoch, W. Limmer, R. Sauer, and A. Waag, J. Appl. Phys. **98**, 23909 (2005).
[9] T. Jungwirth, K. Y. Wang, J. Mašek, K. W. Edmonds, Jürgen König, Jairo Sinova, M. Polini, N. A. Goncharuk, A. H. MacDonald, M. Sawicki, A. W. Rushforth, R. P. Campion, L. X. Zhao, C. T. Foxon, and B. L. Gallagher, Phys. Rev. B **72**, 165204 (2005).
[10] W. J. Schaffer, M. D. Lind, S. P. Kowalczyk, and R. W. Grand, J. Vac. Sci. Technol. B **1**, 688 (1983).
[11] T. Slupinski, A. Oiwa, S. Yanagi, and H. Munekata, J. Cryst. Growth **237–239**, 1326 (2002).
[12] X. Liu, W. L. Lim, Z. Ge, S. Shen, M. Dobrowolska, J. K. Furdyna, T. Wojtowicz, K. M. Yu, and W. Walukiewicz, Appl. Phys. Lett. **86**, 112512 (2005).
[13] M. Kaminska, Z. Liliental-Weber, E. R. Weber, T. George, J. B. Kortright, F. W. Smith, B.-Y. Tsaur, and A. R. Calawa, Appl. Phys. Lett. **54**, 1881 (1989).
[14] M. Missous and S. O'Hagan, J. Appl. Phys. **75**, 3396 (1994).
[15] P. Mahadevan and A. Zunger, Phys. Rev. B **68**, 075202 (2003).
[16] T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B **63**, 195205 (2001).
[17] A. J. Blattner and B. W. Wessels, Appl. Surf. Sci. **221**, 155 (2004).
[18] P. T. Chiu, S. J. May, and B. W. Wessels, Appl. Phys. Lett. **85**, 780 (2004).
[19] S. J. May, A. J. Blattner, and B. W. Wessels, Phys. Rev. B **70**, 73303 (2004).