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High-Curie-temperature $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ obtained by resistance-monitored annealing

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We show that by annealing $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films at temperatures significantly lower than in previous studies, and monitoring the resistivity during growth, an unprecedented high Curie temperature T_C and conductivity can be obtained. T_C is unambiguously determined to be 118 K for Mn concentration $x=0.05$, 140 K for $x=0.06$, and 120 K for $x=0.08$. We also identify a clear correlation between T_C and the room temperature conductivity. The results indicate that Curie temperatures significantly in excess of the current values are achievable with improvements in growth and post-growth annealing conditions. © 2002 American Institute of Physics.
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The p -type dilute magnetic semiconductor $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ is potentially of great importance for magnetoelectronic applications. However, the realization of this will require a substantial increase in the ferromagnetic transition temperature T_C . The current record value of ≈ 110 K (Ref. 1) was obtained soon after the first discovery of ferromagnetism in this system.² More recently, postgrowth annealing was identified as a technique for increasing T_C . Hayashi *et al.*³ found that for short annealing times (15 min), the largest T_C values were obtained for annealing temperatures slightly in excess of the growth temperature, while elsewhere^{4,5} a 90 min anneal at the growth temperature was reported to optimize T_C . Longer annealing times and higher temperatures resulted in a reduction of T_C .^{3–6} Yu *et al.*⁷ showed strong evidence that the increase of T_C was related to the removal of Mn interstitial atoms that occur during the nonequilibrium growth of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, and act as double donors, compensating the itinerant holes and thus reducing the carrier mediated ferromagnetism. In all cases, the improved T_C is accompanied by an increased hole density and conductivity, consistent with the removal of compensating defects. However, in spite of a claim that the annealing procedure employed in Ref. 5 is optimized, the T_C values obtained do not exceed 110 K. This is in contrast to mean field predictions of room temperature ferromagnetism in $\text{Ga}_{0.9}\text{Mn}_{0.1}\text{As}$,⁸ leading to suggestions that T_C in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ is fundamentally limited to 110 K.⁷

Here we show that, by carefully controlling the growth and annealing conditions, Curie temperatures significantly in excess of 110 K can be obtained. In contrast to the earlier studies, much longer annealing times and lower temperatures are employed. Furthermore, the effect of the anneal is monitored *in situ* by measurement of the resistivity. The resistivity is shown to give a good measure of the effect of annealing on T_C .

The 45 nm thick $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples with $0.015 \leq x \leq 0.08$ were prepared on GaAs(001) substrates by low-temperature molecular beam epitaxy using As_2 . The samples

were grown at the highest temperatures possible while maintaining two-dimensional growth; the growth temperature T_g for the samples discussed is shown in Table I. However, we note that the quantitative value of T_g cannot be measured with a high degree of accuracy, and therefore cannot be directly compared with the postgrowth annealing temperature. The use of As_2 in preference to As_4 has been shown to lower the concentration of As antisite defects, so that the Mn interstitial is likely to be the most important compensating defect.⁹ Therefore, we expect low-temperature annealing to have a pronounced effect on these films. The as-grown samples showed metallic conduction at low temperatures across the whole doping range. The growth, structure, and magnetotransport of these samples is discussed in detail elsewhere.^{9,10} The samples were photolithographically fabricated into Hall bars, and the surface was capped with PMMA to prevent oxidation and As desorption during the anneal. Annealing was performed in an oven at a temperature of $(175 \pm 5)^\circ\text{C}$, while monitoring the resistance of the Hall bars using an ac resistance bridge. The effect of annealing on T_C is expected to be most pronounced at high Mn concentrations, as reported elsewhere.⁵ Therefore, we focus our study on samples with $x=0.05$ – 0.08 .

Figure 1 shows the resistivity ρ of samples with $x=0.05$ and $x=0.06$, monitored *in situ* while annealing, as a function of the annealing time. We established that the sample comes into equilibrium at the anneal temperature in less than 1 h. For both samples, ρ falls monotonically throughout the anneal, with a rate that decreases with increasing time. This is in contrast to Ref. 4, where for significantly higher annealing temperatures the resistivity (measured at room temperature after annealing) was found to fall initially, before increasing for annealing times exceeding 2 h, with a similar trend observed for T_C .

The increased resistance observed previously for long annealing times suggests the presence of two competing thermally activated processes, giving, respectively, an increase and a decrease in the conductivity and T_C . The first mechanism was originally ascribed to the diffusion of As antisite defects;⁴ however, recent evidence has shown that the

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TABLE I. Mn concentration x , growth temperature T_g , Curie temperature T_C , conductivity at room temperature $\sigma_{300\text{ K}}$ and at 4.2 K $\sigma_{4.2\text{ K}}$, for as-grown and annealed $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films.

x	T_g (°C)	As-grown			Annealed		
		T_C (K)	$\sigma_{300\text{ K}}$ ($\Omega^{-1}\text{ cm}^{-1}$)	$\sigma_{4.2\text{ K}}$ ($\Omega^{-1}\text{ cm}^{-1}$)	T_C (K)	$\sigma_{300\text{ K}}$ ($\Omega^{-1}\text{ cm}^{-1}$)	$\sigma_{4.2\text{ K}}$ ($\Omega^{-1}\text{ cm}^{-1}$)
0.05	210	76	294	345	118	478	671
0.06	200	76	270	286	140	531	757
0.08	185	56	135	32	120	313	349

annealing-enhanced T_C is related to the removal of highly mobile Mn interstitial atoms, for which the activation energy is relatively low.⁷ The reduction of T_C at longer annealing times may be due to the removal of Mn from the electrically active Ga sites, for which the activation energy will be much higher. Therefore, the much lower annealing temperature employed in the present study compared with elsewhere [175 °C compared with 250 (Ref. 4) or 282 °C (Ref. 7)] leads to an almost complete suppression of the latter mechanism while still allowing for the precipitation of Mn interstitials (albeit on a longer timescale).

The low temperature annealing has a pronounced effect on T_C and the conductivity, as shown in Fig. 2. Figure 2(a) shows ρ versus temperature T for the sample with $x=0.06$, as-grown and after a 200 hour anneal. Both curves show typical behavior for metallic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$,¹ with ρ showing an initial increase on cooling from room temperature, followed by a peak corresponding approximately to T_C and a sharp decrease, and finally increasing again for temperatures below around 4 K. The reduction of ρ due to annealing becomes larger with decreasing temperature. Also, the peak in the ρ vs T curve moves from around 80 K in the as-grown sample to 165 K in the annealed sample, signifying an increase in T_C .

The peak in the ρ vs T curve gives a reasonable estimate of T_C for relatively low values ($T_C < 100$ K), within the errors associated with the broadness of the peak, but is found to overestimate T_C for higher values. A more accurate method of obtaining T_C is by using the anomalous Hall effect. This is large in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, dominating the normal Hall effect even at temperatures much higher than T_C ,^{1,6} and is proportional to the perpendicular component of the sample magnetization. The Hall resistance R_{xy} of the annealed 6% sample is shown in Fig. 2(b), for an external magnetic field B

applied perpendicular to the sample surface, at sample temperatures 110, 130, and 140 K.

A complication with determining the temperature dependence of the magnetization $M(T)$ from these measurements is that the anomalous Hall resistance is also an uncertain function of ρ , with skew and side-jump scattering models predicting either a linear or quadratic dependence.¹ However, T_C can be determined with a high degree of accuracy using Arrott plots.^{1,10} Here, M^2 is plotted as a function of B/M at a given temperature, where M is the magnetization given by R_{xy}/ρ^n , with $n=1$ or 2 depending on the scattering mechanism. The linear part of the graph at high fields is extrapolated to $B/M=0$, and the intercept of this at the y axis is proportional to the square of the saturation magnetization.

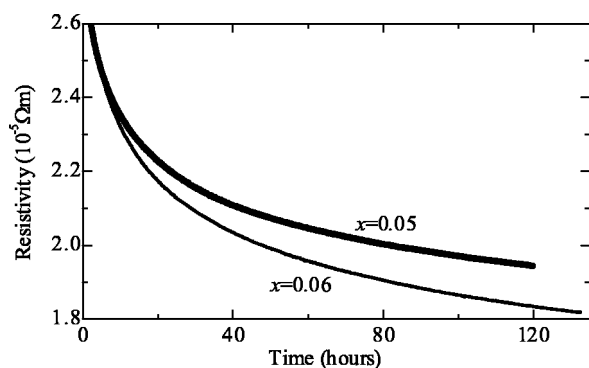


FIG. 1. *In situ* monitored resistivity vs annealing time at 175 °C, for GaMnAs thin films with 5% (thick line) and 6% (thin line) Mn concentrations.

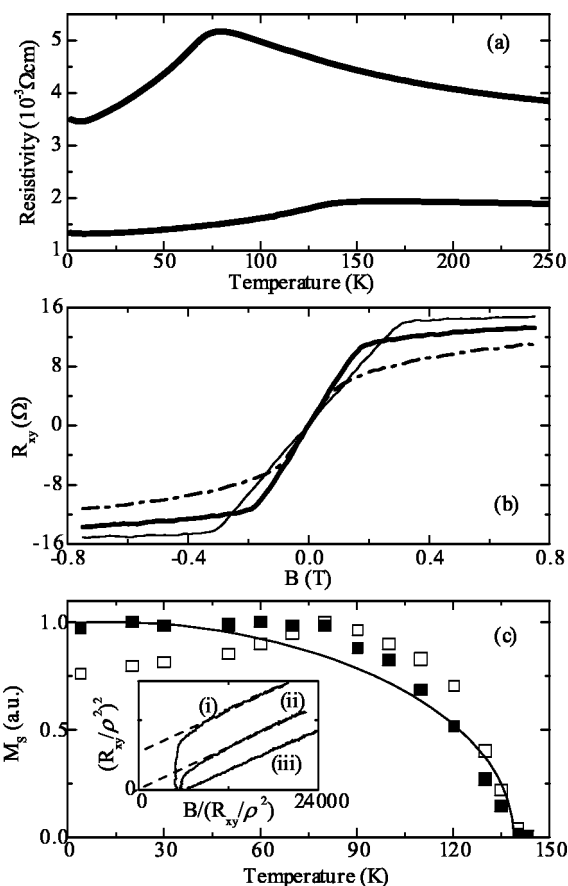


FIG. 2. (a) Resistivity vs temperature for as-grown and annealed $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}$; (b) Hall resistance vs external magnetic field for annealed $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}$ at 110 K (thin line), 130 K (thick line), and 140 K (broken line); (c) saturation magnetization vs temperature obtained from Arrott plots for annealed $\text{Ga}_{0.94}\text{Mn}_{0.06}\text{As}$ assuming linear (open squares) and quadratic (closed squares) dependence of anomalous Hall resistance on ρ , and Brillouin function for $T_C = 140$ K (line); inset of (c) Arrott plots at (i) 135 K, (ii) 140 K, (iii) 143 K.

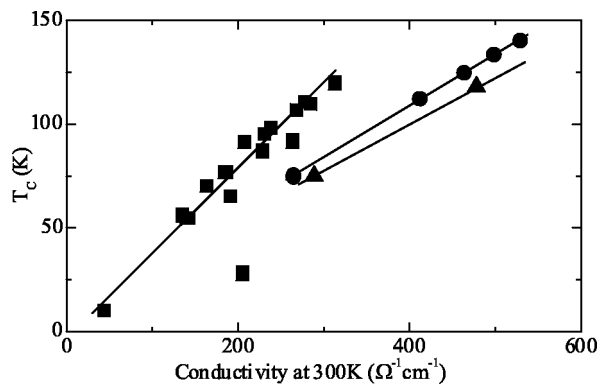


FIG. 3. Curie temperature vs room temperature conductivity for GaMnAs films with $x=0.08$ (squares), $x=0.06$ (circles), $x=0.05$ (triangles). Straight lines are to guide the eye.

Some Arrott plots for temperatures close to T_C for the annealed $x=0.06$ sample are shown in the inset of Fig. 2(c). These plots are for $n=2$; however, using $n=1$ gives the same value for T_C within an error of ± 1 K, so T_C can be determined unambiguously by this method.

The as-grown values of T_C and the conductivity, and the highest values obtained by annealing, are shown in Table I for the different Mn concentrations. The Zener model of ferromagnetism, which has been successful in describing many of the properties of dilute magnetic semiconductor systems,^{8,11,12} predicts a T_C that scales approximately as $x p^{1/3}$, where p is the density of holes. Therefore, T_C should be largest when compensation is weak and $p \approx x$, giving $T_C \sim x^{4/3}$. Using this relationship and the parameters given in Ref. 8, we obtain theoretical maximum values of $T_C \approx 150$, 190, and 280 K for $x=0.05$, 0.06, and 0.08, respectively. Thus, although the observed Curie temperatures represent a significant improvement over all previously reported values, they still fall short of these ideal values by a sizable margin. Although it has been predicted that for low compensation the mean field model breaks down and the carrier-induced ferromagnetism is suppressed due to the increasing importance of antiferromagnetic RKKY oscillations,¹³ this is not borne out by experiment.¹⁰

The reduction in T_C observed experimentally going from $x=0.06$ to $x=0.08$ may be related to a higher defect density in the latter sample. The growth temperature is decreased with increasing Mn concentration. Therefore, the lower growth temperature for $x=0.08$ is likely to result in the incorporation of higher numbers of compensating As antisite defects, which are stable at the low annealing temperatures employed in the present study.⁷ However, it may be possible to obtain a further increase in T_C with longer anneals or different annealing temperatures.

Figure 3 shows the Curie temperature for a series of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ samples, as-grown and annealed, as a function of the conductivity $\sigma_{300\text{ K}}$ measured at room temperature and under zero magnetic field. For all the samples, T_C increases with increasing $\sigma_{300\text{ K}}$, with a gradient that increases with increasing Mn concentration. The data points in Fig. 3 correspond to samples annealed at different temperatures and

times, and also in the case of $x=0.08$ to samples taken from different wafers. In spite of this, a clear trend can be observed, indicating that the high-temperature resistivity is a good measure of T_C . Jungwirth *et al.* calculated zero temperature conductivities in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ within the Boltzmann relaxation time approximation, including scattering from the random Mn ion distribution as well as from Mn interstitials and As antisites.¹² For weakly compensated samples with Mn concentration $x=0.06$, theoretical conductivities in excess of $5000\ \Omega^{-1}\text{cm}^{-1}$ were obtained. The highest conductivity obtained in the present study is considerably less than this prediction. If we assume, as in Ref. 12, that the large difference is due to additional defects occurring during growth, which are not removed by the low-temperature annealing process and are not accounted for by the theoretical model, then this implies that there is still considerable scope for increasing the conductivity, with increased control of the growth conditions and postgrowth treatment. Therefore, if the trend shown in Fig. 3 continues to higher conductivities, this will be accompanied by a considerable increase in T_C , bringing this closer to the mean-field-predicted values and opening up the possibility of room temperature ferromagnetism. In summary, by careful control of growth conditions and resistance-monitored low-temperature annealing of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, we have obtained ferromagnetic transition temperatures up to 140 K. This conclusively demonstrates that T_C is not fundamentally limited to 110 K. We have no reason to think that our growth and annealing procedures are optimum. These results indicate that further increases are to be expected and that we are not close to some fundamentally limited T_C in this system.

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