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Achieving high Curie temperature in (Ga,Mn)As

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We study the effects of growth temperature, Ga:As ratio, and postgrowth annealing procedure on the Curie temperature T_C of (Ga,Mn)As layers grown by molecular beam epitaxy. We achieve the highest T_C values for growth temperatures very close to the two-dimensional–three-dimensional phase boundary. The increase in T_C, due to the removal of interstitial Mn by postgrowth annealing, is counteracted by a second process, which reduces T_C and which is more effective at higher annealing temperatures. Our results show that it is necessary to optimize the growth parameters and postgrowth annealing procedure to obtain the highest T_C. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2992200]

(Ga,Mn)As is one of the most widely studied dilute magnetic semiconductor systems exhibiting carrier mediated ferromagnetism. For this material to be useful in device applications, it will be necessary to increase the Curie temperature (T_C) above room temperature. Theory predicts that T_C is proportional to the magnetic moment density, which depends upon the density of substitutional Mn ions x_S.[1,2] This trend has been confirmed experimentally for samples with x_S $<6.8\%$ grown by molecular beam epitaxy (MBE) with T_C reaching 173 K.[2] $x_S \approx 6.8\%$ is achieved for total Mn concentration $x_{\mathrm{total}} \approx 9\%$ with the additional $\approx 2.2\%$ incorporated as interstitial Mn ($\mathrm{Mn_I}$), which can be removed by postgrowth annealing.[3] Recent attempts to grow (Ga,Mn)As with larger x_{total} have failed to achieve T_C in excess of the previous record[2] and have produced conflicting results with T_C decreasing,[4] saturating,[5] or increasing[6] with increasing x_{total}. In Ref. 5, it was found that T_C saturated at 165 K for x_{total} $>10\%$, leading the authors to suggest that the Zener model may not be applicable in the heavily alloyed regime. However, in another study, Olejnik *et al.*[7] reported $T_C = 180$ K for $x_{\mathrm{total}} = 11\%$, obtained by etching and annealing the sample. These studies used superconducting quantum interference device (SQUID) magnetometry[5,7] or anomalous Hall[4,6] effect to determine T_C. Both methods are established techniques for determining T_C. The range of different results obtained by different groups for $x_{\mathrm{total}} > 10\%$ indicates that more research is required to understand how growth parameters and postgrowth annealing procedures affect the achievable T_C when $x_{\mathrm{total}} > 10\%$. Here we present a detailed study of the epitaxial growth of (Ga,Mn)As layers with $x_{\mathrm{total}} \approx 12\%$ and T_C up to 185 K. We show that the T_C depends sensitively on the growth temperature and the postgrowth annealing procedures.

25 nm (Ga,Mn)As layers were grown by low temperature (~ 200 °C) MBE on low temperature grown GaAs buffer layers on semi-insulating GaAs (001) substrates, using a Veeco Mod Gen III MBE system. The As flux was provided by a Veeco Mk5 valved cracker, set to produce As_2. On a separate test sample, the growth rate was calibrated using reflected high energy electron diffraction (RHEED) oscillations[8] and the valve setting for As stoichiometry at 580 °C was found. The stoichiometric point was found by observing the transition from the As-rich 2×4 to the Ga-rich 4×2 surface reconstruction.[9] The re-evaporation rate of As is higher at 580 °C than at ~ 200 °C, which was found to correspond to $\sim 10\%$ higher As incorporation, allowing a low temperature stoichiometric point to be calculated. Relative adjustments were then made by varying the beam equivalent pressure (BEP).

Excess As or Ga has been shown to lead to the formation of $\mathrm{As_{Ga}}$ antisites or three-dimensional (3D) growth of GaAs, respectively.[10] In agreement with previous studies, we find that T_C is highly sensitive to the Ga:As ratio.[5,10] We obtain the highest T_C for a (Ga+Mn):As ratio of 1:1.1 (determined using the method described above) and find that a small deviation from this value leads to a pronounced reduction in the maximum obtainable T_C.

Measurement of the substrate temperature T_g was performed using a band edge spectrometer (Bandit from K-Space) under reflection geometry. Typical measurements of T_g during growth are shown in Fig. 1(b) for a series of films with $x_{\mathrm{total}} = 12\%$. The growth temperatures were maintained within ± 1 °C of the nominal value during the growth of the 25 nm (Ga,Mn)As layers (4.5 min) by using a low temperature buffer layer and suitable power ramps. Typically T_g remained constant or increased at $\leq 0.5°/\mathrm{min}$ while two-dimensional (2D) growth was maintained and then decreased at a similar rate after the 2D-3D phase boundary was crossed, presumably due to a change in surface emissivity.

Each wafer was cut into samples with dimensions 5×4 mm^2, which were then annealed at temperatures below the growth temperature (see below). This is an established method[3] for the removal of $\mathrm{Mn_I}$, which are detrimental to the ferromagnetism.[11] T_C was determined from measurements of the remnant magnetization in a Quantum Design magnetic property measurement system (MPMS) SQUID magnetometer. Each sample was cooled in a field of 0.1 T before measuring remnance as a function of increasing temperature in zero applied field.

Figure 1(a) shows T_C for fully annealed samples taken at different distances from the center of three wafers, with T_g at the start of (Ga,Mn)As growth of 204 °C (wafer 1), 202 °C

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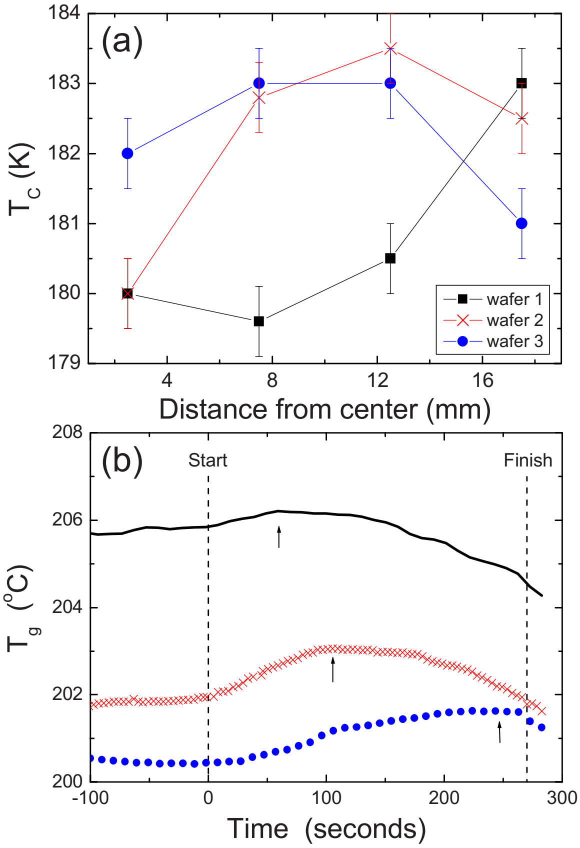

FIG. 1. (Color online) (a) Curie temperature as a function of the distance from the center of the wafer for wafers 1 (black squares) and 2 (red crosses) annealed at 180 °C for 48 h and wafer 3 (blue circles) annealed at 170 °C for 116 h. (b) Temperature at the center of wafers 2 (red crosses), 3 (blue circles), and a wafer (black line) grown at a slightly higher temperature than wafer 1 measured by band edge spectrometry as a function of time during the growth of the (Ga,Mn)As layers. The start and end points of the growth of the (Ga,Mn)As layers are indicated by vertical lines. The arrows indicate the approximate point where the 2D-3D RHEED transition occurs.

(wafer 2), and 200 °C (wafer 3). The distance at which the maximum T_C is obtained moves from the edge of the wafer toward the center as the growth temperature is decreased. Monitoring the RHEED pattern at different points across the wafer indicates that the temperature across the wafer during growth decreases by approximately 2 °C from the center to the edge. These results show that the maximum T_C is very sensitive to the growth temperature and that the optimum conditions lie very close to the 2D-3D phase boundary, which moves closer to the center of each wafer as the measured substrate temperature is decreased. It is therefore crucial to maintain temperature stability to the accuracy illustrated in Fig. 1(b) in order to obtain the highest possible T_C.

Figure 2 shows T_C measured for a series of samples taken from wafer 2 and annealed at temperatures in the range 160–220 °C. The anneal time t_a is obtained using the model described in Ref. 3 such that Dt_a is the same as for a sample annealed at 180 °C for 48 h, where $D=D_0e^{-Q/kT}$ is the diffusivity of Mn_I and $Q=1.4$ eV is the activation energy. We found that these anneal times allowed T_C to reach a saturation value and further annealing did not significantly increase or decrease T_C. It is clear that annealing at higher temperature results in a lower T_C, suggesting that there is a second process, detrimental to ferromagnetism, which is dependent on temperature. As shown in the inset to Fig. 2, annealing a

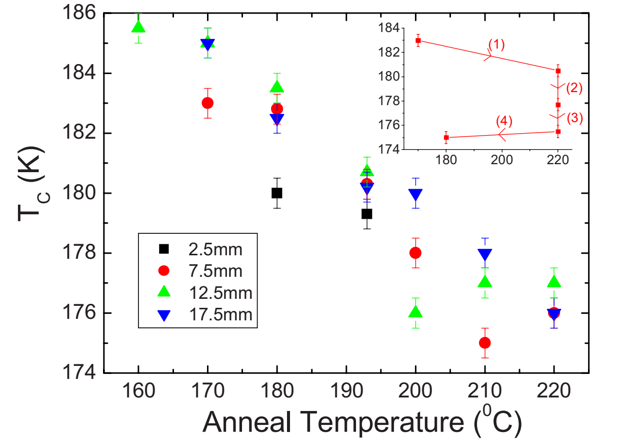

FIG. 2. (Color online) Curie temperature after annealing for 2.6 h (220 °C), 5.2 h (210 °C), 13 h (200 °C), 18 h (193 °C), 48 h (180 °C), 116 h (170 °C), and 280 h (160 °C) for a series of samples taken from wafer 2. Samples were taken from four different distances from the center of the wafer. Inset: T_C for a sample taken 7.5 mm from the center annealed at 170 °C for 116 h then at 220 °C for (1) 1 h, (2) 2 h, and (3) 2 h intervals, then at 180 °C for 48 h (4).

sample at 220 °C after initially annealing at 170 °C results in a decrease of T_C to a value similar to samples annealed at 220 °C initially. Subsequent annealing at 180 °C does not result in an increase of T_C indicating that the second process is not reversible. Further characterization of the samples will be required to elucidate the mechanism responsible for the decrease of T_C at higher annealing temperatures. Possible mechanisms might involve the loss of substitutional Mn to form MnAs precipitates or to interstitial sites. Other mechanisms might involve the formation of native defects such as As_{Ga} and Ga_{As} antisites, which would compensate carriers.

In addition to the wafers described above, we have grown wafers with $x_{total}=10\%$ and 11%. In the absence of moment compensation, T_C should increase roughly linearly with ferromagnetic Mn moment density.[2] Figure 3 shows Curie temperature versus the moment density measured at 2 K in zero applied field, for annealed samples showing the high-

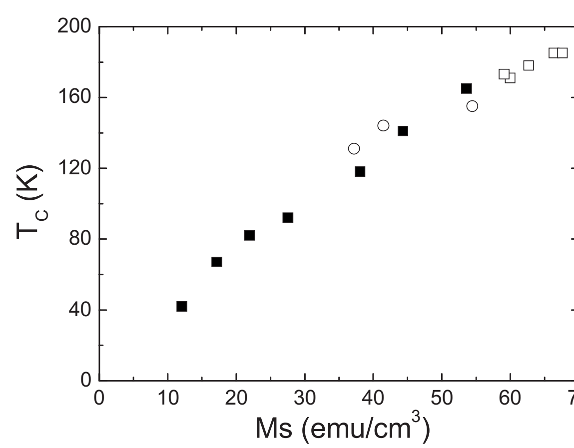

FIG. 3. Curie temperature vs the spontaneous magnetization measured at 2 K for annealed samples showing the highest T_C for a given x_{total}. Open squares correspond to the samples with $x_{total} \geqslant 10\%$ discussed in this paper while closed squares correspond to our previously reported results for $x_{total} < 10\%$ (Ref. 2), which were grown on a different MBE system (Mod Gen II). For comparison, open circles correspond to samples grown on the Mod Gen III for $x_{total} < 10\%$ showing that we can achieve similar results on either MBE system.

est T_C for a given x_{total} in this and our previous study.[2] For $x_{total} \geqslant 10\%$, the T_C continues to increase, but with a slightly sublinear trend. However, we should point out that we consistently achieve higher T_C than previous reports for $x_{total} \geqslant 10\%$, and it is clear from Fig. 2 that the annealing procedure has not yet been fully optimized for these samples since T_C shows no sign of saturating as the anneal temperature is reduced.

With increasing x_{total}, the growth temperature must be reduced in order to maintain 2D growth, but this increases the probability of forming As_{Ga} antisites and other compensating defects. Hence, precise control over the growth parameters becomes more important for incorporating Mn onto the substitutional sites and for achieving the corresponding increase in T_C. We have shown that T_C is extremely sensitive to the growth temperature and (Ga+Mn):As ratio for MBE grown (Ga,Mn)As layers with $x_{total} \geqslant 10\%$. Additionally, we have found that the postgrowth annealing temperature determines the maximum achievable T_C due to a temperature dependent mechanism in addition to the out diffusion of Mn_I. These sensitivities may explain why some previous efforts to improve T_C in material with $x_{total} \geqslant 10\%$ have not been successful.

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