AIP Applied Physics Letters

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Citation: Appl. Phys. Lett. **82**, 2302 (2003); doi: 10.1063/1.1564285
View online: http://dx.doi.org/10.1063/1.1564285
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v82/i14
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Highly enhanced Curie temperature in low-temperature annealed [Ga,Mn]As epilayers

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(Received 18 October 2002; accepted 3 February 2003)

We report Curie temperatures up to 150 K in annealed $Ga_{1-x}Mn_xAs$ epilayers grown with a relatively low As:Ga beam equivalent pressure ratio. A variety of measurements (magnetization, Hall effect, magnetic circular dichroism and Raman scattering) suggest that the higher Curie temperature results from an enhanced free hole density. The data also indicate that, in addition to the carrier concentration, the sample thickness limits the maximum attainable Curie temperature in this material, suggesting that the free surface of $Ga_{1-x}Mn_xAs$ epilayers may be important in determining their physical properties. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1564285]

The ferromagnetic semiconductor $Ga_{1-x}Mn_xAs$—first developed using low temperature molecular beam epitaxy (MBE) in 1996[1]—continues to elicit substantial interest for semiconductor spintronics.[2] While a detailed understanding of ferromagnetism in this material remains the subject of active discussion, theoretical studies suggest that the Curie temperature (T_C) could in principle reach values above 300 K.[3–5] Hole compensation by defects has thus far limited T_C to a maximum value of $\sim$110 K in as-grown epilayers ($x \sim 0.05$)[6] as well as in postgrowth annealed[7] samples ($0.05 \lesssim x \lesssim 0.083$).[8,9] Such observations prompted the suggestion that $T_C \sim 110$ K could be limited by fundamental constraints on the maximum attainable free hole concentration in low temperature grown $Ga_{1-x}Mn_xAs$.[10] Recent work, however, has revived the promise of higher temperature ferromagnetism by the postgrowth annealing of a variety of $Ga_{1-x}Mn_xAs$ samples.[11–13]

Here we demonstrate an alternative combination of growth and annealing parameters that consistently yields $Ga_{1-x}Mn_xAs$ epilayers with $110\ \mathrm{K} \lesssim T_C \lesssim 150\ \mathrm{K}$. These results are reproduced in two different MBE systems using either As_2 or As_4. We find that both the hole density (p) and the epilayer thickness (t) influence the maximum attainable T_C, which has strong implications for heterostructure design. Furthermore, measurements of T_C vs p over an order of magnitude in hole density elucidate the prospects for achieving room temperature ferromagnetism in $Ga_{1-x}Mn_xAs$.

To establish the general applicability of the growth protocol described here, the $Ga_{1-x}Mn_xAs$ samples are grown in two different MBE systems (EPI 930 and Varian GenII), that use uncracked As_4 and cracked As_2 ($T_{\mathrm{cracker}} \sim 690\,°\mathrm{C}$), respectively for the arsenic source. In the EPI chamber, the substrate temperature is measured using standard thermocouple techniques and in the GenII chamber using band edge thermometry.[14] In this letter, we focus on samples grown in the former system, with samples grown in the latter confirming the principal results. All samples are grown on (001) semi-insulating, epiready GaAs substrates using growth conditions that are similar to those described elsewhere[8] except for a lower As:Ga beam equivalent pressure ratio (15:1 as compared with the 20:1 ratio typically used in earlier work). $Ga_{1-x}Mn_xAs$ epilayers with thickness (t) in the range $10 < t < 100$ nm are deposited on a buffer structure that consists of a high temperature GaAs epilayer grown under standard conditions, followed by a low temperature GaAs epilayer grown at 250 °C. A clear (1×2) reconstruction is observed in the reflection high energy electron diffraction during growth, and x-ray diffraction and room temperature magnetization studies show no indication of large MnAs precipitates, as in other high quality $Ga_{1-x}Mn_xAs$ samples. The as-grown wafers are subjected to postgrowth annealing for 90 min at 250 °C in a nitrogen atmosphere. Both as-grown and annealed samples are characterized using a battery of techniques whose full details are provided elsewhere:[8,15,16] these include electron microprobe analysis, Raman scattering, superconducting quantum interference device (SQUID) magnetometry, magnetoresistance, Hall effect and magnetic circular dichroism (MCD).

Figure 1(a) shows SQUID magnetization data as a function of temperature for two samples of $Ga_{0.915}Mn_{0.085}As$ with $t = 15$ and 50 nm, both as grown and after annealing. The data demonstrate that T_C is increased above 110 K after annealing in both samples, reaching a maximum value of $T_C \sim 150$ K for the 15-nm-thick sample. Figure 1(b) shows the thickness dependence of T_C (discussed in detail below), with all other growth parameters kept nominally identical. Figures 2(a) and 2(b) demonstrate the enhanced T_C in these samples through hysteresis loops and Hall effect measurements, and

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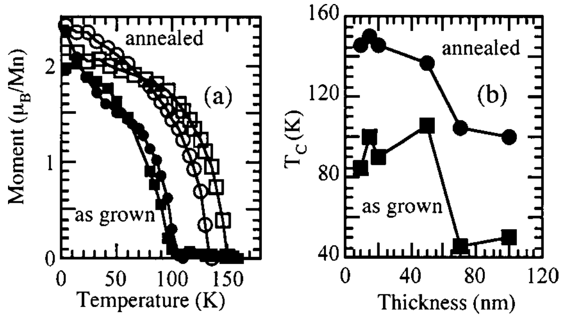

FIG. 1. (a) Magnetization (in units of Bohr magnetons/Mn) vs temperature for $Ga_{1-x}Mn_xAs$ ($x \sim 0.085$) epilayers with $t = 15$ nm (squares) and 50 nm (circles), as grown and after annealing (field in plane). (b) Curie temperature for $Ga_{1-x}Mn_xAs$ ($x \sim 0.085$) epilayers of varying thickness.

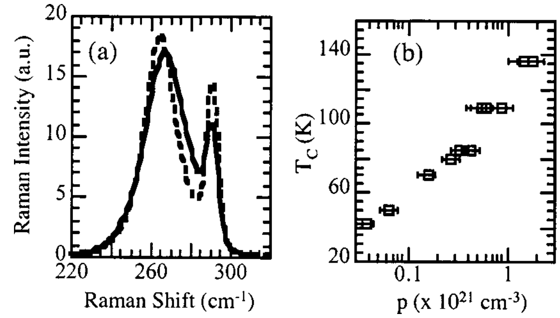

FIG. 3. (a) Raman spectra at 300 K of a 50-nm-thick $Ga_{1-x}Mn_xAs$ ($x = 0.085$) epilayer before (solid line) and after (dashed line) annealing. The spectra are measured with 457 nm excitation in the $z(Y,Y)z$ configuration. (b) Curie temperature (from magnetization) vs hole density (from Raman scattering) for a wide range of postgrowth annealed $Ga_{1-x}Mn_xAs$ samples of different Mn content. The samples with $T_C \leqslant 110$ K have thickness $t = 123$ nm, while the two samples shown with $T_C \sim 140$ K have $t = 50$ nm.

also show that the properties of these samples are qualitatively similar to those reported previously for $Ga_{1-x}Mn_xAs$. The coercive fields ($H_C < 20$ Oe even at temperatures down to 5 K) are consistent with the typical values found in the most metallic random alloy $Ga_{1-x}Mn_xAs$ samples in earlier studies.[17] The temperature dependence of the spectrally resolved MCD signal also confirms the ordering temperature obtained from magnetization data [Fig. 2(c)]. However, while the amplitude of the MCD varies with the magnetization as a function of both temperature and field,[16,18] the spectrum does not reveal an absorption edge between 600 and 900 nm. This is consistent with the smearing of band-edge features in the MCD spectra in high carrier density $Ga_{1-x}Mn_xAs$ samples.[16] The values of T_C obtained using the anomalous Hall effect, SQUID magnetization, and MCD all agree to within experimental uncertainty, indicating that the

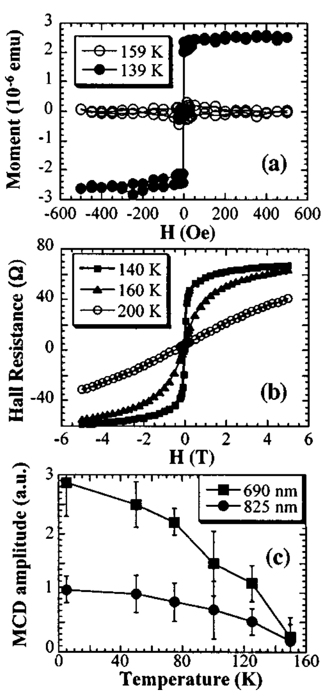

FIG. 2. (a) Magnetization hysteresis loops (field in plane) shown at different temperatures for the 15-nm-thick sample in Fig. 1 ($T_C \sim 150$ K). (b) Hall resistance vs magnetic field at different temperatures for the 15 nm sample in Fig. 1 ($T_C \sim 150$ K). (c) Temperature dependence of the amplitude of the MCD signal measured at 825 nm and 690 nm. The data are taken in transmission geometry using a 50 nm $Ga_{1-x}Mn_xAs$ (x~0.085) epilayer grown on a stop etch layer of $Ga_{0.55}Al_{0.45}As$.

ferromagnetism in these higher T_C $Ga_{1-x}Mn_xAs$ samples originates from band holes interacting with local Mn moments.

The hole density p is measured through a Raman scattering technique wherein the Raman line shape is deconvoluted into the coupled plasmon-longitudinal optical phonon mode and the unscreened longitudinal optical phonon mode components.[15] Representative data from such a measurement in a 50 nm $Ga_{1-x}Mn_xAs$ sample are shown in Fig. 3(a). Analysis of such data shows that annealing increases the hole density of as-grown samples [e.g., in Fig. 3(a), annealing increases the carrier density from $p \sim 0.18 \times 10^{21}$ cm^{-3} to $p \sim 1.5 \times 10^{21}$ cm^{-3}]. We can place these results within a larger context by examining the variation of T_C with hole density p for a wide range of annealed samples [Fig. 3(b)] from our previous studies.[9] An empirical fit shows that $T_C \sim p^{1/3}$ and an extrapolation of this trend indicates that—using present growth conditions—enhancing the T_C of $Ga_{1-x}Mn_xAs$ to 300 K would require an additional order of magnitude increase in p.

It is clear from this work and previous studies that postgrowth annealing enhances the carrier concentration and can be used to maximize the T_C of $Ga_{1-x}Mn_xAs$. While the precise effects of annealing are still unclear, recent ion channeling studies[10] have given some insights to the problem. These experiments show that a significant fraction of Mn ions in $Ga_{1-x}Mn_xAs$ occupies nonsubstitutional, interstitial sites (Mn_I), and that annealing decreases the concentration of Mn_I. Since Mn_I acts as a donor and hence compensates holes, optimal annealing increases p and correspondingly enhances T_C. The enhanced hole density in our annealed samples is consistent with such a scenario, although the relatively small increase in the ferromagnetic moment in some of our samples implies that a large fraction of Mn ions are still not contributing to the ferromagnetic state even after annealing.[9]

In addition to the effects of annealing, an important clue to the limitations on T_C in $Ga_{1-x}Mn_xAs$ comes from the thickness dependence of T_C in our samples, shown in Fig. 1(b) for a consistent set of $Ga_{0.915}Mn_{0.085}As$ samples wherein all the other growth parameters are nominally identical. The data indicate that—for the present set of growth and annealing conditions—the highest T_C in both as-grown and annealed samples occurs for 10 nm$\lesssim t \lesssim$50 nm and that T_C is suppressed for larger t. The increase in T_C in thinner samples appears to be a general phenomenon,[19] and we have not succeeded in achieving $T_C > 110$ K for annealed samples with $t > 50$ nm. Preliminary experiments carried out in the Varian system (wherein the substrate temperature is directly controlled during growth using an optical monitoring technique)[14] suggest that the thickness effect is unrelated to changes in substrate temperature during growth. While it is difficult to speculate in detail without additional microscopic information, it seems that the thickness dependence of T_C may be associated with the proximity of a free surface. Indeed, a recent theoretical calculation suggests that the Mn defect sites have rather different energetics near a free surface.[20] Furthermore, we find that $Ga_{1-x}Mn_xAs$ epilayers capped with a thin epilayer (~10–50 nm) of GaAs typically show a decrease in T_C upon annealing, rather than an increase, indicating that the nature of the surface of the $Ga_{1-x}Mn_xAs$ directly affects the properties of the entire epilayer.

In summary, we have shown that $Ga_{1-x}Mn_xAs$ epilayers can be prepared with Curie temperatures as high as 150 K, and that—for the current set of growth and annealing conditions—the thickness of the epilayers plays a crucial role in determining the maximum obtainable T_C. The values of T_C also seem to scale well with the carrier concentration over a wide range of samples. While further increases in T_C certainly seem possible, extrapolation of our results implies that room temperature ferromagnetism in $Ga_{1-x}Mn_xAs$ would need almost an order of magnitude increase in the free hole density.

This research has been supported by ONR No. N00014-99-1-0071, ONR No. N00014-99-1-0077, ONR No. N00014-99-1-0716, DARPA/ONR No. N00014-99-1093, DARPA/ONR No. N00014-99-1096, DARPA No. N00014-00-1-0951, and NSF DMR No. 01-01318.

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