Ferromagnetic $Ga_{1-x}Mn_xAs$ produced by ion implantation and pulsed-laser melting

M. A. Scarpulla[a] and O. D. Dubon[b]
Department of Materials Science & Engineering, University of California at Berkeley, Berkeley, California 94720 and Lawrence Berkeley National Laboratory, Berkeley, California 94720

K. M. Yu and O. Monteiro
Lawrence Berkeley National Laboratory, Berkeley, California 94720

M. R. Pillai and M. J. Aziz
Division of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

M. C. Ridgway
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australia

(Received 26 September 2002; accepted 3 January 2003)

We demonstrate the formation of ferromagnetic $Ga_{1-x}Mn_xAs$ films by Mn ion implantation into GaAs followed by pulsed-laser melting. Irradiation with a single excimer laser pulse results in the epitaxial regrowth of the implanted layer with Mn substitutional fraction up to 80% and effective Curie temperature up to 29 K for samples with a maximum Mn concentration of $x \approx 0.03$. A remanent magnetization persisting above 85 K has been observed for samples with $x \approx 0.10$, in which 40% of the Mn resides on substitutional lattice sites. We find that the ferromagnetism in $Ga_{1-x}Mn_xAs$ is rather robust to the presence of structural defects. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555260]

The integration of diluted magnetic semiconductors (DMSs) into quantum structures may enable such innovative technologies as spin-based optoelectronics and even quantum computing.[1–3] The addition of a few atomic percent Mn to GaAs results in the formation of ferromagnetic $Ga_{1-x}Mn_xAs$, the most widely studied III–V DMS. In general, only limited success has been achieved in the preparation of potentially useful DMSs because of the low solubility of magnetic species in semiconductor hosts. In the case of $Ga_{1-x}Mn_xAs$, the range of Mn compositions required to achieve this phase (typically $x \leqslant 0.09$) is some 2–3 orders of magnitude greater than the equilibrium solubility limit; therefore, synthesis must be carried out far from equilibrium. Mn ion implantation followed by rapid thermal annealing (RTA) has been reported to lead to the formation of MnAs or Ga_xMn_y precipitates,[4–7] although one group has reported magnetic circular dichroism signals consistent with $Ga_{1-x}Mn_xAs$ after RTA at 300 °C.[8] Until now, ferromagnetic $Ga_{1-x}Mn_xAs$ has been produced exclusively by low-temperature molecular-beam epitaxy (LT-MBE), in which case the formation of Mn-containing second phases is kinetically suppressed.

Here, we present an alternative, highly versatile method for the formation of ferromagnetic $Ga_{1-x}Mn_xAs$ using Mn^+ implantation into GaAs followed by pulsed-laser melting (PLM). The rapid melting and recrystallization associated with laser processing leads to a high level of Mn incorporation in the regrown layer, while suppressing the formation of second phases. Compared to MBE, our synthesis approach has fewer restrictions on the choice of host semiconductor and alloying species. Thus, it enables the investigation of a wide range of materials systems. The incorporation of conventional dopant species into semiconductors using PLM has been studied extensively,[9] but alloying with magnetic impurities at the atomic percent level has not been explored.

Semi-insulating GaAs (001) wafers were implanted at room temperature with Mn^+ ions to 0.34×10^{16} cm^{-2} at 150 keV and to 1.1×10^{16} cm^{-2} at 300 keV. This combination of ion doses and energies resulted in an amorphized layer of about 2500 Å with a relatively uniform Mn concentration in the range of 1–1.5 at. %. Each sample was irradiated in air with a single pulse from a $XeCl^+$ excimer laser [$\lambda = 308$ nm, full width at half maximum (FWHM) = 30 ns]. A multiprism homogenizer was used to produce a uniform fluence ranging between 0.40 and 0.61 J/cm^2 over the sample area of approximately 5 mm × 5 mm. The 488-nm line of an argon-ion laser was used to monitor the time-resolved reflectivity of the samples during the laser irradiation. The melt duration (τ_{melt}) ranged between 250 and 400 ns for this range of fluence, as determined by a constant reflectivity signal consistent with a layer of molten GaAs. The threshold fluences at which crystalline and amorphous GaAs melt were determined to be 0.22 and 0.08 J/cm^2, respectively.

The structure of the $Ga_{1-x}Mn_xAs$ layers was studied by channeling Rutherford backscattering spectrometry (c-RBS) using a 2-MeV He^+ beam and by x-ray diffractometry (XRD). Particle-induced x-ray emission (PIXE) experiments were also carried out during the c-RBS, and this combination of data was used to determine the lattice location of Mn. A dc superconducting quantum interference device magnetometer was used to measure the in-plane magnetic behavior of the

[a]Electronic mail: mascarpulla@lbl.gov
[b]Electronic mail: oddubon@socrates.berkeley.edu

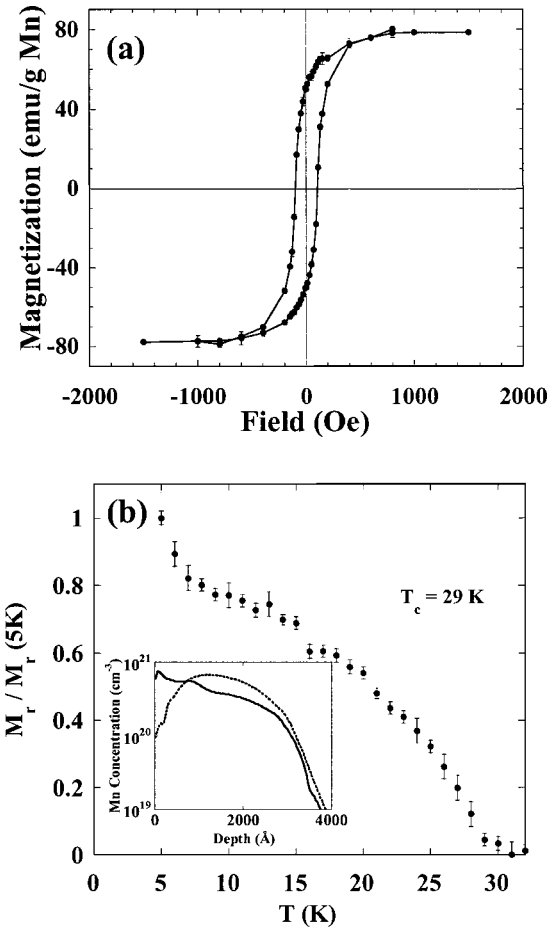

FIG. 1. (a) Magnetization (M) vs magnetic field (H) measured at 5 K for a sample implanted at 150 and 300 keV and irradiated at 0.41 J/cm^2. The saturation magnetization and coercivity are, respectively, 78 emu/g Mn and ~100 Oe. A diamagnetic background due to the substrate has been removed. (b) Remanent magnetization (normalized to remanent magnetization at 5 K) vs temperature for the same sample; the inset shows Mn concentration vs depth before (dashed) and after (solid) laser melting for the same sample.

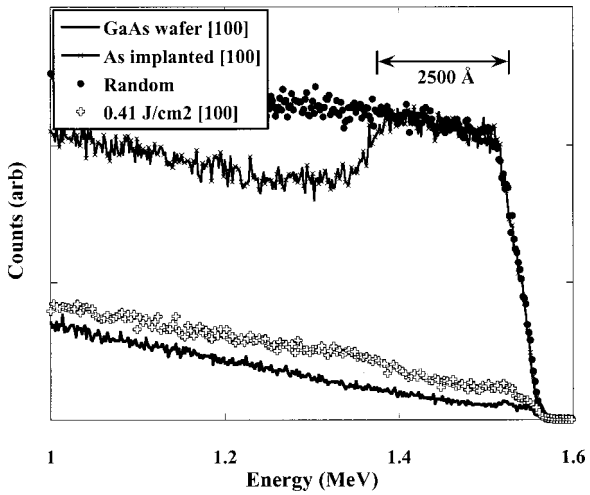

FIG. 2. [001] c-RBS spectra from a sample implanted at 150 and 300 keV and irradiated at 0.41 J/cm^2. The channeled spectrum before irradiation coincides with the random spectrum to a depth of ~2500 Å, indicating full amorphization to this depth during ion implantation. The spectrum from an unimplanted GaAs wafer is presented for reference.

films along the [001] direction. Mn depth profiles with an estimated resolution of 50 Å were obtained by secondary ion mass spectrometry (SIMS) using a 5.5 keV Cs^+ primary ion beam. Electrochemical capacitance–voltage profiling was used to obtain the net concentration of electrically active acceptors (presumed to be substitutional Mn) as a function of depth. For each of the samples examined, the net acceptor concentration was found to range between 10^{20} and 10^{21} cm^{-2} over the depth of the layer, and to closely follow (within the ~15% combined experimental uncertainty) the Mn profile determined by SIMS.

Figure 1(a) presents the film magnetization (M) versus applied field (H) measured at 5 K for a sample irradiated at 0.41 J/cm^2. Open, nearly square hysteresis loops were observed at 5 K for all of the samples, with lower coercivity (H_c) and saturation (M_{sat}) being observed for those samples irradiated at higher fluences. The main panel of Fig. 1(b) presents the remanent magnetization (M_r) versus temperature for this sample. An effective Curie temperature (T_C) of 29 K was determined by extrapolating the data with negative curvature down to zero magnetization. It is apparent from the inset of Fig. 1(b), which depicts the Mn concentration profiles determined by SIMS before and after laser irradiation, that significant Mn redistribution toward the surface occurs during the PLM and rapid liquid-phase epitaxy process. Thus, as the Curie temperature of $Ga_{1-x}Mn_xAs$ has been shown to depend on Mn concentration,[2] the temperature dependence of film magnetization represents a superposition of contributions arising from regions throughout the Mn depth distribution.

Figure 2 presents [001] c-RBS data from a sample before (as-implanted) and after laser irradiation at 0.41 J/cm^2. c-RBS from the as-implanted sample reveals a ~2500-Å layer of amorphous GaAs (with yields similar to the spectrum measured at random incidence). After PLM, the channeled yield of this surface 2500-Å layer drops dramatically, reflecting the epitaxial regrowth of the implanted region. While the yield from the regrown layer is slightly higher than that of the virgin wafer—indicating the presence of structural defects—a single crystal layer has been achieved.

θ–2θ XRD yielded only GaAs substrate peaks. The absence of additional peaks discounts the presence of polycrystallinity. High-resolution scans showed a shoulder on the (004) peak at lower diffraction angles (larger lattice parameter), consistent with a layer of $Ga_{1-x}Mn_xAs$ of varying Mn composition.

The fact that the films exhibit ferromagnetic behavior that disappears well below room temperature indicates that magnetic contributions from ferromagnetic second phases such as MnAs (T_C=318 K)[5] and Ga_xMn_y (T_C=450–800 K)[4,6] compounds are not responsible for the observed ferromagnetic behavior. However, their presence in small amounts or as superparamagnetic precipitates below our XRD detection limit cannot be completely ruled out based upon this current work. A transmission electron microscopy study is underway to help clarify this issue.

Simultaneous c-RBS and PIXE spectra were collected from the sample irradiated at 0.41 J/cm^2 in both the [001] and [011] channeling directions. From these data, the substitutional fraction of Mn was determined to be 80% in both of the axial directions. Because the substitutional fractions determined in the two directions were identical within the experimental uncertainty of <5%, we postulate that nonsubsti-

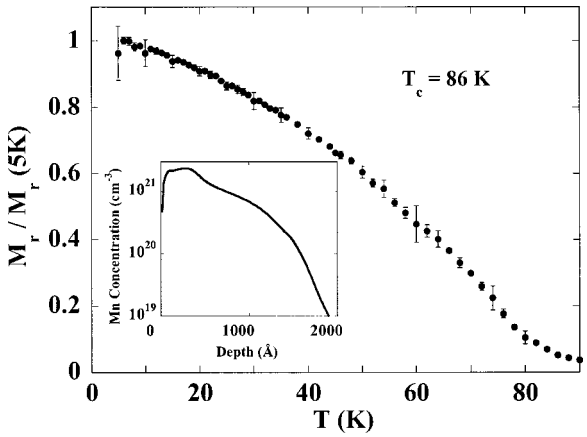

FIG. 3. Remanent magnetization vs temperature for a sample implanted using MEVVA and irradiated with a KrF^+ excimer laser at 0.3 J/cm^2; the inset shows Mn concentration vs depth after laser melting.

tutional Mn exists as clusters or precipitates too small to be detected by XRD and not as interstitials in tetrahedral or hexagonal sites.[10] This is quite different from as-grown LT-MBE samples, in which a large fraction of Mn atoms occupy these interstitial sites.[10] The presence of Mn in other types of interstitial sites cannot be ruled out based on the present channeling measurements.

In order to determine whether Curie temperatures near the 110 K reported for MBE-grown films with $x \approx 0.05$[2,3] could be achieved using our synthesis approach, another set of samples was prepared. An identical GaAs wafer was implanted with Mn ions to a dose of 1.5×10^{16} cm^2 using the metal-vapor vacuum arc (MEVVA) technique[11] at an accelerating voltage of 35 kV and roughly equal fractions of Mn^{1+} and Mn^{2+}. These samples were laser melted at a fluence of 0.30 J/cm^2 using a KrF^+ laser ($\lambda = 248$ nm, FWHM$=38$ ns). The lower ion energies used in MEVVA result in shallower implanted layers, which can be regrown with higher crystalline quality.

The remanent magnetization as a function of temperature for a sample from this set is presented in Fig. 3. The inset shows the Mn depth profile for the irradiated sample. The maximum Mn concentration of 4×10^{21} cm^{-3}, or $x \approx 0.10$, is in excess of the concentration ($x \approx 0.05$) required to achieve a T_C of 110 K if all Mn atoms reside on Ga sublattice. However, c-RBS and PIXE reveal that only 40% of Mn atoms are substitutional, corresponding to a substitutional Mn content of $x \approx 0.04$, which is consistent with the observed effective T_C of 86 K. This sample exhibits a greater coercivity ($\sim$150 Oe) and saturation magnetization ($\sim$110 emu/g Mn) at 5 K than observed in samples of lower Mn concentration.

In conclusion, we have demonstrated the formation of ferromagnetic films of $Ga_{1-x}Mn_xAs$ using ion implantation followed by pulsed-laser melting. The films are epitaxial and single-crystalline. Without significant process optimization, we have achieved Curie temperatures above liquid nitrogen temperature. The observation of ferromagnetism in our $Ga_{1-x}Mn_xAs$ layers, which contain both structural defects and Mn composition gradients, suggests that the magnetic coupling between Mn in this system is rather robust to both of these factors. This versatile synthesis approach opens exciting opportunities for the study of a wide range of diluted magnetic semiconductor materials, including quaternary alloys and multi-dopant systems. Moreover, this process can also be exploited to create all-planar spin-injection devices and circuits.

The work at the Lawrence Berkeley National Laboratory was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The work at Harvard was supported by NASA Grant No. NAG8-1680. We thank A. Stacy and E. Carleton for the use of facilities. Thanks also to Y. Gao and W. Walukiewicz for helpful discussions. One of the authors (M.A.S.) acknowledges support from an NSF Graduate Research Fellowship.

[1] G. A. Prinz, Science **282**, 1660 (1998).
[2] H. Ohno, Science **281**, 951 (1998).
[3] H. Ohno, J. Magn. Magn. Mater. **200**, 110 (1999), and references therein.
[4] J. Shi, J. M. Kikkawa, R. Proksch, T. Schaeffer, D. D. Awschalom, G. Medeiros-Ribeiro, and P. M. Petroff, Nature (London) **377**, 707 (1995).
[5] P. J. Wellmann, M. Garcia, J.-L. Feng, and P. M. Petroff, Appl. Phys. Lett. **71**, 2532 (1997).
[6] J. Shi, J. M. Kikkawa, D. D. Awschalom, G. Medeiros-Ribeiro, P. M. Petroff, and K. Babcock, J. Appl. Phys. **79**, 5296 (1996).
[7] J. De Boeck, R. Oesterholt, A. Van Esch, H. Bender, C. Bruynseraede, C. Van Hoof, and G. Borghs, Appl. Phys. Lett. **68**, 2744 (1996).
[8] K. Ando, A. Chiba, H. Tanoue, F. Kirino, and M. Tanaka, IEEE Trans. Magn. **35**, 3463 (1999).
[9] See, for example, *Laser Annealing of Semiconductors*, edited by J. M. Poate and J. W. Mayer (Academic, New York, 1982).
[10] K. M. Yu, W. Walukiewicz, T. Wojtowicz, I. Kuryliszyn, X. Liu, Y. Sasaki, and J. K. Furdyna, Phys. Rev. B **65**, 201303(R) (2002).
[11] I. G. Brown, Rev. Sci. Instrum. **65**, 3061 (1994).