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Authors
Scarpulla, M.A.
Dubon, O.D.
Yu, K.M.
et al.

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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
Lawrence Berkeley National Laboratory, Berkeley, CA 94720

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

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

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

ABSTRACT

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.

[a] Email: mascarpulla@lbl.gov, [b] Email: oddubon@socrates.berkeley.edu

The integration of diluted magnetic semiconductors (DMSs) into quantum structures may enable new technologies such 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 DMSs. 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 $x \leq 0.09$) 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 approach to the formation of ferromagnetic $Ga_{1-x}Mn_xAs$ using Mn^+ implantation into GaAs followed by pulsed laser melting. The extremely short time scales associated with laser processing lead to a high level of Mn incorporation in the regrown layer while suppressing the formation of second phases. The incorporation of conventional dopant species into semiconductors using pulsed laser melting has been studied extensively [9], but alloying with magnetic impurities at the atomic percent level has not been pursued.

Semi-insulating GaAs (001) wafers were implanted at room temperature with Mn^+ ions to 0.34 x 10^{16} cm^{-2} at 150 keV and 1.1 x 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 (λ = 308 nm, 30 ns FWHM). A multi-prism 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 x 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. 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-SQUID magnetometer was used to measure the in-plane magnetic behavior of the 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 (ECV) 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} – 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 Figure 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 Figure 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 pulsed laser melting 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 pulsed laser melting, 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 X-ray diffractometry 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) that is consistent with a layer of $Ga_{1-x}Mn_xAs$ of varying 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 X-ray diffraction 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 non-substitutional Mn exists as clusters or precipitates too small to be detected by X-ray diffractometry and not as interstitials in tetrahedral or hexagonal sites [10]. This is quite different from as-grown LT-MBE samples, where a large fraction of Mn atoms occupy these interstitial sites [10]. It should be mentioned that 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 x 10^{16} cm^{-2} using the metal vapor vacuum arc (MEVVA) technique [11] at an accelerating voltage of 35 keV 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 (λ= 248 nm, FWHM = 38 ns).

The remanent magnetization as a function of temperature for a sample from this set is presented in Figure 3. The inset shows the Mn depth profile for the irradiated sample. The maximum Mn concentration of 4x10^{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 sub-lattice. However, channeling PIXE reveals 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 (~150 Oe) and saturation magnetization (~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 with the underlying GaAs substrate and are characterized by a non-uniform Mn concentration profile due to redistribution during regrowth. Curie temperatures above liquid nitrogen temperature have been achieved. This versatile approach for the synthesis of diluted magnetic semiconductors opens exciting opportunities for the study of a wide range of materials systems and the realization of spin-injection devices using relatively simple fabrication methods.

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Figure Captions:

Figure 1 – (a) Magnetization (M) vs. magnetic field (H) measured at 5K 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.

Figure 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.

Figure 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.

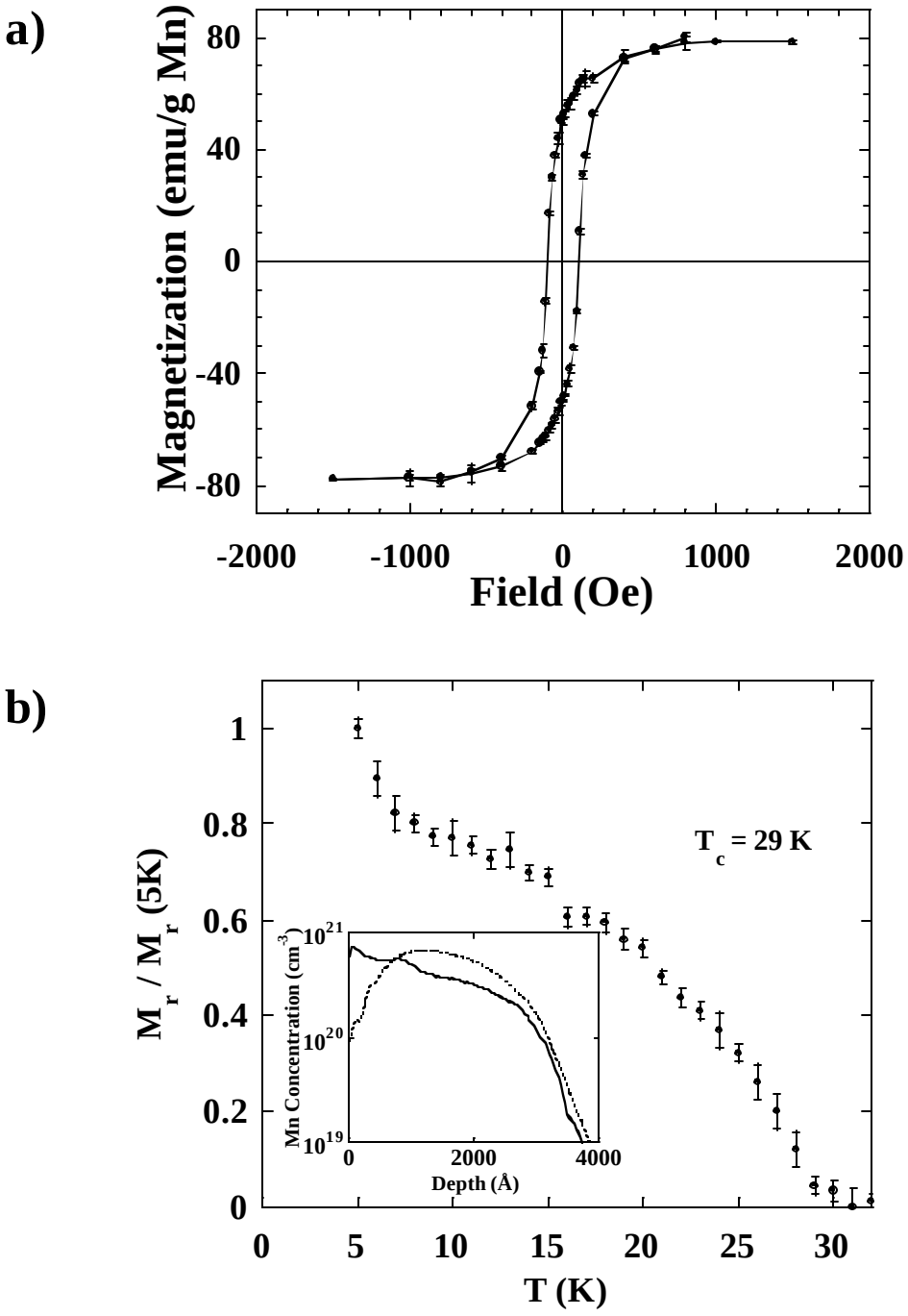

Figure 1 – M.A Scarpulla, et al.

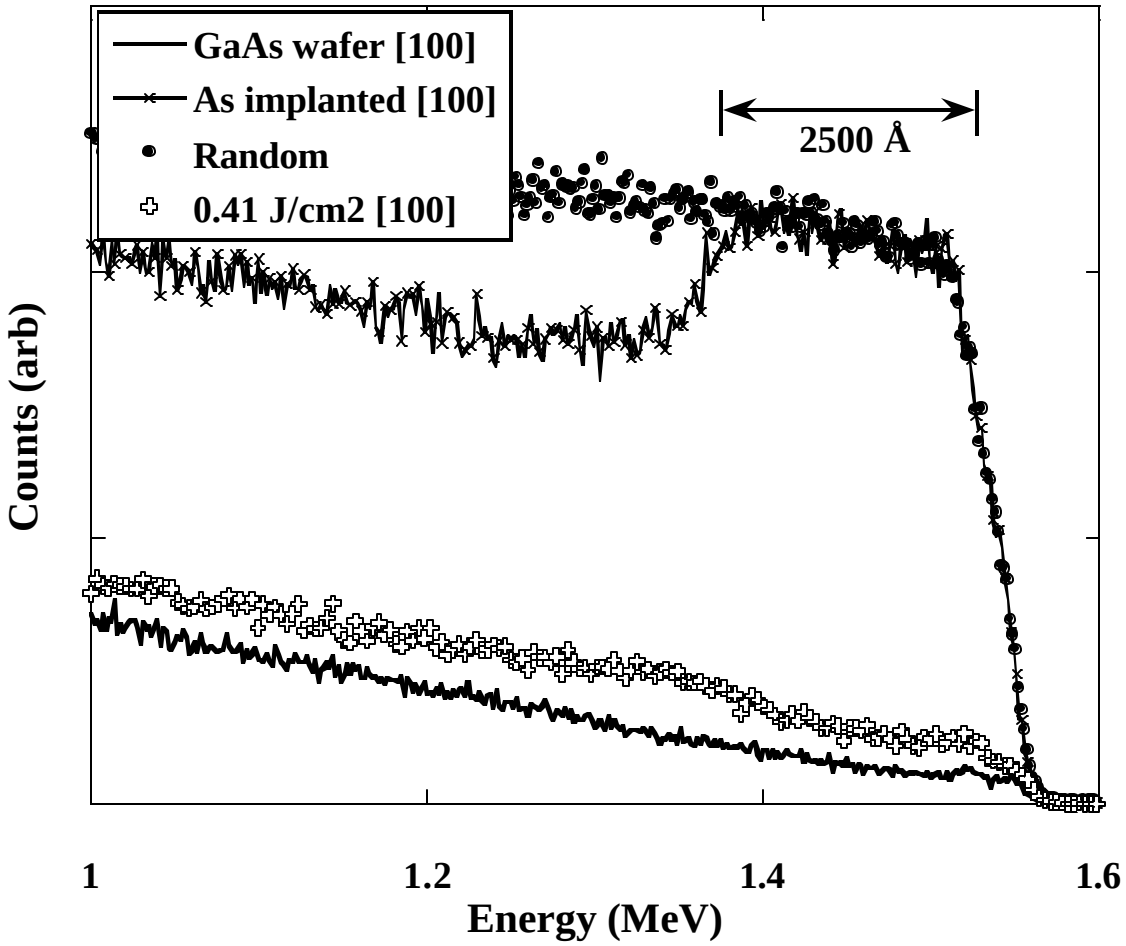

Figure 2 – M.A Scarpulla, et al.

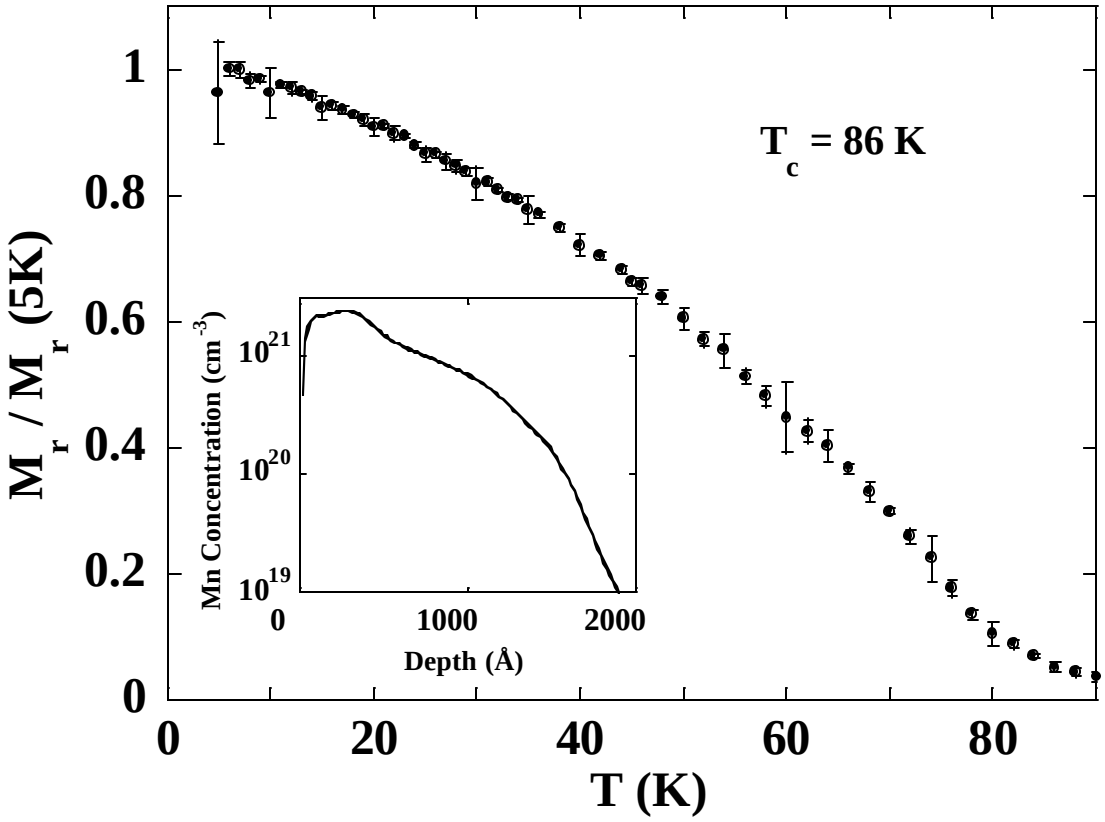

Figure 3 – M.A Scarpulla, et al.