Ferromagnetism in (In,Mn)As Diluted Magnetic Semiconductor Thin Films Grown by Metalorganic Vapor Phase Epitaxy

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In$_{1-x}$Mn$_x$As diluted magnetic semiconductor (DMS) thin films have been grown using metalorganic vapor phase epitaxy (MOVPE). Tricarbonyl(methylcyclopentadienyl)manganese was used as the Mn source. Nominally single-phase, epitaxial films were achieved with Mn content as high as $x = 0.14$ using growth temperatures $T_g \geq 475 \, ^\circ$C. For lower growth temperatures and higher Mn concentrations, nanometer scale MnAs precipitates were detected within the In$_{1-x}$Mn$_x$As matrix. Magnetic properties of the films were investigated using a superconducting quantum interference device (SQUID) magnetometer. Room-temperature ferromagnetic order was observed in a sample with $x = 0.1$. Magnetization measurements indicated a Curie temperature of 333 K and a room-temperature saturation magnetization of 49 emu/cm$^3$. The remnant magnetization and the coercive field were small, with values of 10 emu/cm$^3$ and 400 Oe, respectively. A mechanism for this high-temperature ferromagnetism is discussed in light of the recent theory based on the formation of small clusters of a few magnetic atoms.

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I. INTRODUCTION

An approach to spin-sensitive devices for electronic applications, that may exhibit improved spin injection, is the use of III-V diluted magnetic semiconductors (DMSs). These alloys, which incorporate a small percentage of magnetic atoms into the semiconductor host, have been shown to exhibit ferromagnetic behavior up to 110 K. However, for these materials to find widespread applications, the ferromagnetism should be stable at room temperature. Consequently, much of the current experimental work is directed towards increasing their ferromagnetic transition temperature, $T_c$. Since theory predicts that the transition temperature increases with the magnetic-ion concentration, efforts have centered on increasing such concentration. The solubility of magnetic ions, however, is often quite low.

III-V DMS have been grown using low-temperature molecular beam epitaxy (LT-MBE) at temperatures lower than 300 °C to prevent phase separation. Nevertheless, recently we have demonstrated the growth of single-phase, ferromagnetic In$_{1-x}$Mn$_x$As, with $x \leq 0.14$, using metalorganic vapor phase epitaxy (MOVPE) at temperatures as high as 520 °C. In this report, we present the results of our investigation of the magnetic properties of these films. We have observed room-temperature ferromagnetic behavior in a nominally single-phase $p$-type In$_{0.9}$Mn$_{0.1}$As film. In contrast, a comparable high $T_c$ has not been observed in single-phase (In,Mn)As grown using LT-MBE. A possible mechanism for the observed high-temperature ferromagnetism, based on transition metal clustering at the atomic level, will be discussed.

II. EPITAXY OF (In,Mn)As

(In,Mn)As films were prepared using atmospheric pressure MOVPE, as described earlier. Films were grown at temperatures between 475–520 °C on semi-insulating GaAs(001) substrates. The precursors used were trimethylindium (TMIn), tricarbonyl(methylcyclopentadienyl)manganese (TCMn) and 0.3% arsine (AsH$_3$) in hydrogen. Phase composition was determined using double-crystal x-ray diffraction (XRD) using Cu K$_\alpha_1$ radiation. Energy dispersive x-ray spectroscopy (EDS) was used to determine the Mn concentration in the films.

Figure shows the 0-2θ x-ray diffraction pattern with the zinc-blende (004) and (002) reflections for a 300 nm thick In$_{0.9}$Mn$_{0.1}$As film grown at 520 °C. No other peaks were observed, indicating that the alloy was phase pure to within 0.1 volume percent. The rocking-curve FWHM for this film was 0.25°. Azimuthal ($\phi$) scans for the (202) reflections of the film and substrate were recorded to confirm epitaxy. Figure shows the four-fold-symmetric diffraction pattern for the (202) reflections of the (In,Mn)As film compared with that of the GaAs substrate. Excellent epitaxial alignment is observed despite the ~7% lattice mismatch between the film and the substrate.

MnAs was observed in films grown at temperatures lower than 475 °C and for Mn concentrations greater than $x = 0.14$. Growth at temperatures higher than ~530 °C resulted in very little deposition presumably due to increased indium and manganese desorption from the surface.
III. MAGNETIC PROPERTIES

A. Magnetic field dependence

The magnetic properties of the (In,Mn)As thin films were measured using a SQUID magnetometer. The magnetic field was applied perpendicular to the plane of the film along the easy axis of magnetization for (In,Mn)As. The substrate diamagnetic contribution was subtracted from the total magnetization signal. The remaining data consisted of the paramagnetic and ferromagnetic contributions from the film. The total magnetization is given by:

\[ M_{tot}(T, H) = M_F(T, H) + [\chi_p(T) + \chi_d(GaAs)]H \]  

where \( M_F(T, H) \) is the ferromagnetic component of the film, \( \chi_p \) is the paramagnetic susceptibility of the film, \( \chi_d \) is the substrate diamagnetic susceptibility, \( T \) is the temperature, and \( H \) is the applied magnetic field. The magnetic response of a nominally single-phase In_{0.9}Mn_{0.1}As film is shown in Figure 3 for applied magnetic fields up to 20 kOe and temperatures of 5, 150 and 300 K. The inset of Figure 3 shows the complete hysteresis loop for this sample at 5 K. At this temperature the measured saturation magnetization normalized to the film volume was 62 emu/cm\(^3\) with a remanence of 10 emu/cm\(^3\) and a coercive field of 400 Oe. When the temperature was increased to 300 K, the saturation magnetization decreased only to 49 emu/cm\(^3\).

![FIG. 2: Azimuthal, \(\phi\), x-ray diffraction scans for the \{202\} reflections of In_{0.9}Mn_{0.1}As and GaAs indicating the degree of epitaxy with the GaAs substrate. The angle of the \{202\} diffracting planes with respect to the sample surface is \(\chi = 45^\circ\).](image)

The magnetization as a function of temperature was measured for the single-phase In_{0.9}Mn_{0.1}As sample discussed above. The sample was zero-field cooled and then subjected to a 10 kOe applied magnetic field perpendicular to the plane of the film. After subtraction of the diamagnetic substrate contribution, the resulting magnetization is shown in Figure 4.

![FIG. 4: Azimuthal, \(\phi\), x-ray diffraction scans for the \{202\} reflections of In_{0.9}Mn_{0.1}As and GaAs indicating the degree of epitaxy with the GaAs substrate. The angle of the \{202\} diffracting planes with respect to the sample surface is \(\chi = 45^\circ\).](image)

![FIG. 1: \(\theta-2\theta\) x-ray diffraction scan of In_{0.9}Mn_{0.1}As/GaAs(001) showing the respective \{002\} and \{004\} reflections. No evidence of MnAs second phase was observed.](image)

B. Temperature dependence

The Curie temperature of 335 K was measured for this sample. Such a high Curie temperature for a III-V dilute magnetic semiconductor has been previously attributed to the presence of MnAs, which has a Curie temperature of 318 K. However, the presence of MnAs was not observed by x-ray diffraction in this sample as shown in Figure 4. If a second phase were present, the measured magnetization of 62 emu/cm\(^3\) would correspond to a MnAs volume fraction of approximately 10%. This should certainly be observable by x-ray diffraction. If on the other hand the MnAs was present as nanoprecipitates, the magnetization would be considerably smaller as observed in (Ga,Mn)As films. Thus the magnetization data is consistent with the alloy film being a single-phase. Currently, we are investigating precipitate formation further through transmission electron microscopic analysis.

The value of the saturation magnetization of (In,Mn)As is given by \( M_s = N_{Mn}g\mu_B J_{Mn} \), where \( N_{Mn} \) is the nominal concentration of Mn ions, \( g \) is the Landé
factor and is equal to 2 for Mn, $\mu_B$ is the Bohr magneton, and $J_{\text{Mn}}$ is the spin of Mn. The measured $M_s$ using $x = 0.1$, corresponding to $N_{\text{Mn}} = 1.8 \times 10^{21} \text{ cm}^{-3}$, gives a value of $\mu = 3.6 \mu_B$. This corresponds to a value of $J_{\text{Mn}}$ between 4/2 and 3/2. This is interpreted as an indication of the presence of valence states other than $\text{Mn}^{2+}$.

The temperature dependence of the magnetization was compared to the Brillouin function for different values of the total angular momentum, $J$. The lack of agreement between the Brillouin function and the measured data above 150 K indicates that the transition to the ferromagnetic state may not be second order, in which the change in magnetization value is continuous with increasing temperature. It may be first order.

Magnetic disordering as a first order phase transformation has previously been reported and a model to describe this behavior was developed by Bean and Rodbell. The model predicts that if the exchange interaction is a strong function of the inter-atomic spacing and the lattice is compressible, then the ferromagnetic to paramagnetic transition will be first-order. By introducing a strain energy term into the free energy formulation and minimizing with respect to the reduced magnetization, it was shown that the temperature dependence of the magnetization for $J = 1/2$ is given by

$$T/T_o = (\sigma \tanh^{-1} \sigma)(1 + \eta \sigma^2/3 - PK\beta)$$

where $\eta \equiv 3/2NK\beta$, $\sigma$ is the reduced magnetization (normalized to the saturation magnetization), $N$ is the number of magnetic dipoles per unit volume, $k$ is the Boltzmann constant, $K$ is the compressibility, $\beta$ is the slope of the dependence of $T_c$ on volume, and $T_o$ is the Curie temperature if the lattice were not compressible. $P$ and $T$ are the pressure and temperature respectively.

For $\eta < 1$, the transition is second order, and Equation 2 reduces to the Brillouin function for $\eta = 0$. For $\eta > 1$, the transition is first order and the magnetization exhibits a discontinuity at the transition temperature. The measured magnetization was compared with the model of Bean and Rodbell for different values of $\eta$ as shown in Figure 3. As can be seen, the best fit occurred for $\eta = 1$. This indicates that the phase transformation for the alloy has an intermediate character between first and second order.

A deviation between theory and experiment at temperatures above the Curie temperature was also observed. This was addressed in the initial work by Bean and Rodbell and is a consequence of the long-range interaction implicit in the model. Molecular field theory which was used in the model, indicates no order above the Curie temperature for a normal ferromagnet. Experimentally, however, significant short-range order can be observed.

For comparison, the ferromagnetic to paramagnetic phase transition of MnAs has been shown to be first-order with a value of $\eta = 2$. We have measured the temperature dependence of the magnetization for an (In,Mn)As sample which exhibited MnAs phase forma-
C. Origin of Ferromagnetism

The ferromagnetism observed in III-V DMS films has been previously explained within the framework of sp-d exchange interactions between the Fermi sea and the localized magnetic moments. 

Similar to RKKY theory, this hole-mediated ferromagnetism theory predicts that the Curie temperature is dependent upon both magnetic ion concentration and hole concentration. Using this model Dietl et al. predicted that the transition temperature for (In,Mn)As with a Mn concentration of 5% should be 35 K, which is much lower than that observed in the present study. One possible explanation for the difference is that Mn in the alloy is not randomly distributed on In sites but is present as atomic clusters. This is supported by the recent calculations of van Schilfgaarde and Mryasov based on local density functional theory.

These calculations predict that due to the strong attractive coupling between the Mn ions and the semiconductor cation nuclei, there is a large driving force for the formation of Mn clusters consisting of two or more Mn atoms located at nearest-neighbor cation sites. These atomic clusters in turn can stabilize the ferromagnetic state; according to this model, the presence of free carriers is not required. Although the model does not consider kinetic effects, which may determine whether Mn clustering occurs, the growth temperature used for our films is likely sufficient to overcome any kinetic barrier to cluster formation. Indeed clustering of the transition-metal ion has been observed in other III-V DMSs grown at high temperatures and may also occur in other materials that have been shown to exhibit ferromagnetic behavior while having $n$-type conductivity. Presently, we are pursuing extended x-ray absorption fine structure (EXAFS) measurements of these films to determine the local environment of Mn.

IV. CONCLUSIONS

In conclusion, epitaxial, single-phase In$_{0.9}$Mn$_{0.1}$As films have been grown using metalorganic vapor phase epitaxy at temperatures as high as 520 °C. Temperature and field-dependent magnetization measurements indicated a single-phase film (as measured by x-ray diffraction) to be ferromagnetic with a Curie temperature of 333 K. Modelling of the magnetization data indicated that the ferromagnetic-to-paramagnetic phase transition was intermediate between first and second order. The origin of the observed ferromagnetism was discussed in the light of a new theory based on the formation of transition-metal clusters.

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19 Mn substitutes on the In sublattice forming clusters containing 2 or 3 Mn atoms. For magnetic “dimers”, the Mn atoms are located at nearest-neighbor cation sites as in Ref. [13].