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Above-room-temperature ferromagnetism in GaSb/Mn digital alloys

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Digital alloys of GaSb/Mn have been fabricated by molecular-beam epitaxy. Transmission electron micrographs showed good crystal quality with individual Mn-containing layers well resolved, no evidence of three-dimensional MnSb precipitates was seen in as-grown samples. All samples studied exhibited ferromagnetism with temperature-dependent hysteresis loops in the magnetization accompanied by metallic *p*-type conductivity with a strong anomalous Hall effect (AHE) up to 400 K (limited by the experimental setup). The anomalous Hall effect shows hysteresis loops at low temperatures and above room temperature very similar to those seen in the magnetization. The strong AHE with hysteresis indicates that the holes interact with the Mn spins above room temperature. All samples are metallic, which is important for spintronics applications. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1481184]

Ferromagnetic III–Mn–V semiconductors, such as GaMnAs, InMnAs random alloys, and heterostructures based on them, have revealed many interesting physical properties and spintronic device possibilities.[1,2] The InAs/GaSb-based heterostructure system has, due to the unique band alignment, the additional advantage of spatially separating electrons and holes, which permits optical and electrical tuning of ferromagnetism.[3,4] Furthermore, these materials and heterostructures are strong candidates for active components of spintronic devices due to the high mobility of InAs and the extensive applications of the heterostructure systems as infrared sources and detectors. However, while GaMnAs and InMnAs exhibit well-defined hysteresis loops in the ferromagnetic phase in GaMnSb, the reported T_C is low (25 K) and the hysteresis loops are very small.[5]

The highest T_C observed in the III–V materials so far is 110 K in GaMnAs.[6,7] Theoretical calculations based on the Zener model with free holes mediating the exchange interaction have shown that the spin–orbit interaction and the density of states at the Fermi energy are important parameters in determining T_C.[8] These calculations, which focused on conventional alloys containing randomly distributed Mn in the host materials, predict room temperature ferromagnetism in GaMnN and ZnMnO. These materials have been investigated experimentally, and ferromagnetism at high temperatures in crystalline ZnCoO and in GaMnN has been reported.[9,10] However, epitaxial growth of both ZnO- and GaN-based ferromagnetic materials and their integration with commonly used III–Vs remain problematic. Room temperature ferromagnetism has been recently observed in TiO_2 containing Co.[11]

One approach to increasing T_C and the quality of III–V ferromagnetic semiconductors is to incorporate Mn into the host materials in the form of digital alloys, this approach has been explored recently in the GaAs/Mn system.[12,13] This approach would lead to submonolayers of MnAs in GaAs or InAs, or MnSb in GaSb. Because only 1/2 ML of Mn can be deposited with this technique,[12,13] lateral two-dimensional (2D) islands of MnAs or MnSb (depending on the host material) can be expected in addition to randomly distributed Mn ions within the Mn-containing layers. Some migration of Mn into adjacent layers of the host lattice is also expected. The advantage of such structures is that the carriers in a digital alloy can interact with both the magnetic and the semiconducting components of the structures. This contrasts with the case of 3D precipitates embedded in III–V structures, for which there appears to be no carrier interaction with ferromagnetism.[14]

The mechanism(s) of ferromagnetism for GaAs/Mn digital alloys remain unclear,[15,16] partly because of the large range of hole concentrations and the observation of both metallic and activated electrical transport with similar T_Cs,[12,13] and also the complexity of Mn/carrier interactions in general.[17,18] The absence of established theories and the likelihood of lateral 2D MnAs or MnSb islands in the digital alloys under investigation suggests that a comparison of T_C for bulk MnAs and MnSb (in the NiAs structure) might be useful as a rough guide to understanding the qualitative behavior and suggesting fruitful avenues to explore in the search for higher T_C. The Curie temperature for MnAs is 310 K, while that for MnSb is 580 K. This suggests that GaSb/Mn might be an interesting candidate for increased T_C.[19]

Recently, random alloys of GaMnSb have been grown by molecular beam epitaxy and their structural, magnetic, and electrical properties characterized.[5,14] Two types of samples were studied: high-temperature-grown (T_{growth}

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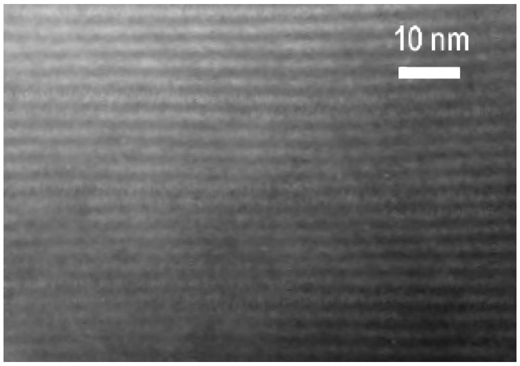

FIG. 1. TEM image of a digital alloy with a repeat unit of Mn (0.5 ML)/GaSb (12 ML). The dark lines correspond to Mn-containing layers.

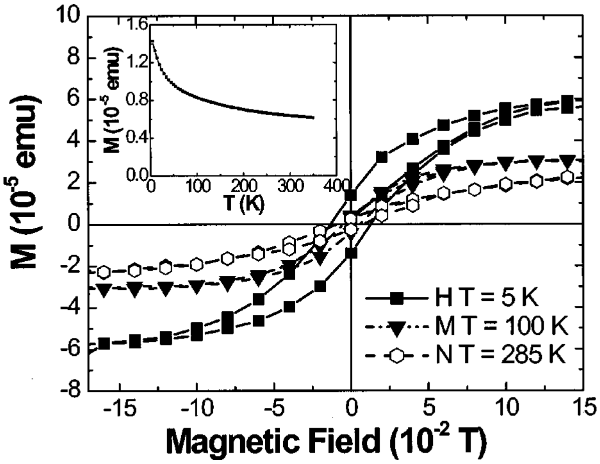

FIG. 2. Hysteresis loops of the sample shown in Fig. 1, observed with a SQUID magnetometer and temperature dependence of the remanent magnetization (inset).

$>550\,°C$) GaMnSb samples that contain 3D MnSb precipitates, and low-temperature (LT)-grown GaMnSb samples that do not show precipitates. As is the case for GaMnAs, LT growth is necessary to avoid MnSb precipitation. Samples grown at high temperatures with 3D MnSb precipitates are characterized by nearly temperature independent hysteresis loops between liquid helium temperature and room temperature.[14] There is no observable anomalous Hall effect (AHE) in the same temperature range, indicating no measurable interaction between the carriers and the ferromagnetic precipitates. In contrast, in the GaMnSb samples grown at LT without precipitates, a strong AHE was observed below 25 K with a negative AHE coefficient;[5] this was taken to be evidence of ferromagnetism, similar to the case for LT-grown GaMnAs. The highest T_C reported for GaMnSb random alloys (from magnetotransport data) is approximately 25 K, much lower than that for GaMnAs.[5]

In this work we examine GaSb/Mn digital alloys grown by MBE on (100) GaAs substrates. Because of the large lattice mismatch between GaSb and GaAs (7.5%), the digital alloys were grown on GaSb buffer layers (nominally 500 nm). The growth was monitored with reflection high-energy electron diffraction (RHEED). The GaSb/Mn digital alloys consist of 50 periods of 0.5 ML Mn layers separated by GaSb layers of various thicknesses. For electrical measurements, p^+ contacts were made in a van der Pauw configuration by Au metallization and subsequent diffusion at 250 °C.

We characterized the samples with superconducting quantum interference device (SQUID) magnetometry, transmission electron microscopy (TEM), magnetic force microscopy, and magnetotransport measurements in the van der Pauw and Hall bar configurations. This combination of measurements allowed us to elucidate the magnetic and the structural properties, as well as the interaction between the Mn spins and the itinerant carriers. A TEM image of one of the digital alloys, consisting of 0.5 ML of Mn and 12 ML of GaSb as the repeat unit, is shown in Fig. 1. The image clearly shows the well-resolved 2D Mn-containing layers (dark) and the GaSb spacer layers (light), and indicates good structural quality. We note that the thickness of Mn-containing layers cannot be estimated from the micrograph, because TEM is sensitive to the strain distribution, rather than the chemical composition. Importantly, there is no indication of 3D MnSb precipitates at this resolution and we have seen no evidence at higher resolution.[20]

All samples showed ferromagnetism above room temperature, as indicated by hysteresis loops in the magnetization (all samples studied showed qualitatively similar magnetic behavior). The ferromagnetism is observed at temperatures up to 400 K, the upper limit of our magnetometer, and thus we can only state that $T_C > 400$ K. The hysteresis loops show clear temperature dependence over the entire range of temperatures studied, as can be seen in Fig. 2. Ferromagnetic behavior at room temperature is also seen in GaMnSb, when there are 3D MnSb precipitates, with temperature-independent hysteresis loops in which the room temperature coercive field is nearly identical to that at 5 K. One can thus conclude from the SQUID measurements that the observed ferromagnetism in the present samples is not due to 3D MnSb precipitates.

Our magnetotransport measurements allow us to examine the interactions between charge carriers and magnetic ions, as has been done in previous studies of magnetic semiconductors.[5,6,14] All samples exhibit metallic behavior, rather than the thermally activated behavior observed in our studies of GaAs/Mn digital alloys.[13] The zero-field resistance is only weakly dependent on temperature. As discussed earlier, one of the most important properties of ferromagnetic semiconductors is the interaction between itinerant carriers and localized electron spins in Mn ions. At low applied fields, the AHE provides information about the Mn-generated internal field experienced by itinerant carriers. The AHE first decreases with temperature but remains strong up to 400 K (data are shown in Fig. 3 for 4 and 400 K for simplicity)—the slope of the Hall resistance near zero field is a measure of the magnetization, as well as strength of its coupling with the carriers. The sign of the AHE is related to the band structure of the itinerant carriers and the spin–orbit interaction.[21] We note that other possibilities, such as two carrier (electrons and holes) conduction, can also lead to behavior like that of Fig. 3. The hysteretic behavior (demonstrated by the open loops in the inset to Fig. 3 at 4 and 400 K) is an unambiguous signature of both ferromagnetism for the magnetic component and its interaction with itinerant carriers (holes).

As mentioned above, previous work on GaMnSb samples containing 3D MnSb precipitates showed no clear AHE even at liquid helium temperature.[14] The AHE ob-

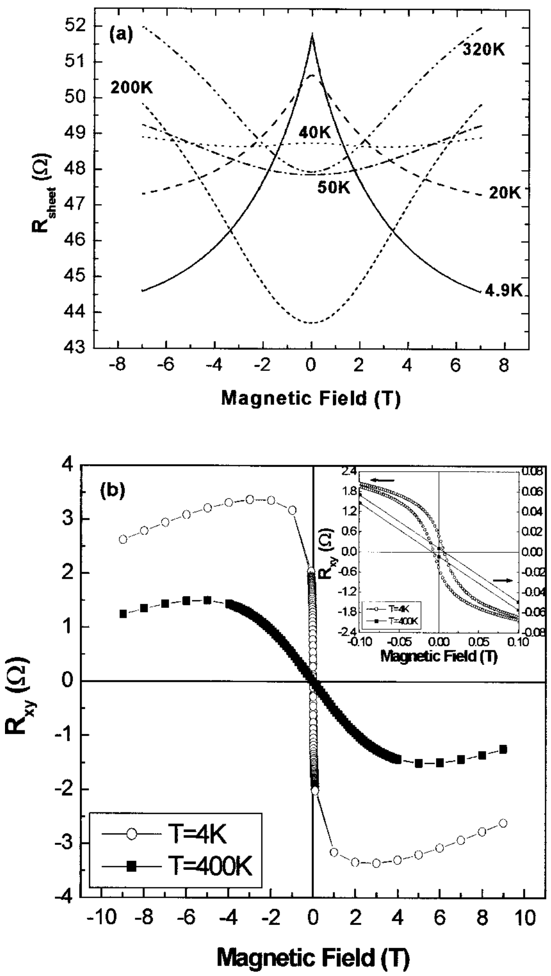

FIG. 3. (a) The temperature dependence of the magnetoresistance and (b) the anomalous Hall effect of the sample shown in Fig. 1. The insert in (b) is the expanded plot for the low field region.

served in LT-grown GaMnSb random alloys with no MnSb precipitates decreased rapidly above T_C (25 K), vanishing completely above 50 K. This behavior is clearly related to ferromagnetism in the random alloys.[5] The AHE coefficient is negative for the GaSb/Mn digital alloys at all temperatures, as for GaMnSb random alloys.[5] This is presently not understood. The AHE itself, even in "conventional" ferromagnetic metals, is not fully understood.[21,22]

Temperature dependent magnetization and magnetotransport data both reveal additional complexity in the ferromagnetism associated with the as-grown samples. There is an initial rapid drop of the remanent magnetization with temperature at low temperatures, which changes to a much slower decrease at higher temperatures. This change occurs between 30 and 50 K, as shown in Fig. 2. The behavior does not correspond to any of the typical power-law behaviors of magnetization seen in other thin films of ferromagnetic materials,[23] very recent work in a magnetic polaron picture exhibits a concave behavior of the remanent magnetization below T_C.[17] The rapid decrease at low temperature followed by a very slow (in some samples nearly constant) decrease with temperature at high temperatures suggests possible coexistence of two material phases, both ferromagnetic. The magnetoresistance shown in Fig. 3(a) also changes from negative to positive with increasing temperature between 40 and 50 K. The behavior below 40 K is qualitatively the same as that for previously studied LT-grown GaMnSb random alloys, the positive magnetoresistance above 40 K is dramatically different.[5] In the case of LT-grown GaMnSb random alloys, the negative magnetoresistance decreases quickly once the temperature is raised above T_C (25 K) and the sheet resistance becomes independent of magnetic field above 50 K.

Based on the present results we suggest the following picture. The Mn-containing layers consist of quasi-2D GaSb/Mn random alloys (similar to 3D GaMnSb random alloys with randomly distributed Mn ions) and quasi-2D islands of zinc-blende MnSb. The isolated Mn portion (2D GaMnSb random alloy) is ferromagnetic below 30–50 K, depending on the sample. This is responsible for some similarities between the GaSb/Mn digital alloys and GaMnSb random alloys at low temperatures. The observed ferromagnetism at higher temperatures is associated with the 2D MnSb islands, which may be related to the high T_c in bulk MnSb (580 K). A detailed theoretical study is needed to fully understand the mechanisms involved.

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