# Intrinsic ferromagnetic properties of $Ti_{0.94}Fe_{0.06}O_2/Ti_{0.94}Mn_{0.06}O_2$ superlattice films for dilute magnetic semiconductor applications

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Superlattice films have been proposed to get dilute magnetic semiconductor (DMS) with an intrinsic room-temperature ferromagnetism. For a $TiO_2$-based DMS superlattice structure, each layer was alternately doped by two different transition metals (Fe and Mn) and deposited to a thickness of approximately 2.7 Å on $r$-$Al_2O_3(1102)$ substrates by pulsed laser deposition. Samples of $Ti_{0.94}Fe_{0.06}O_2$ (TiFeO), $Ti_{0.94}Mn_{0.06}O_2$ (TiMnO), and $Ti_{0.94}(Fe_{0.03}Mn_{0.03})O_2$ show a low remanent magnetization and coercive field, as well as superparamagnetic features at room temperature. On the other hand, superlattice films (TiFeO/TiMnO) show a high remanent magnetization and coercive field, resulting in intrinsic ferromagnetic properties. The superlattice films composed of alternating layers of $Ti_{0.94}Fe_{0.06}O_2$ and $Ti_{0.94}Mn_{0.06}O_2$ exhibit intrinsic ferromagnetic properties for dilute magnetic semiconductor applications. © *2006 American Institute of Physics*.
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Spintronics has attracted considerable interest because of recent developments in the physics of spin-dependent phenomena. Dilute magnetic semiconductors (DMSs) are being considered for use as one of the components in spintronic devices.[1] Numerous investigators have studied DMS, in which transition metal atoms are introduced into a crystal, thus inserting local magnetic moments into the lattice. $TiO_2$-based DMS doped by cobalt,[2–6] iron,[7] and manganese[8] was recently reported to show ferromagnetic properties, even at temperatures above 300 K, and the magnetic ordering was explained in terms of carrier-induced ferromagnetism, as observed for a III-V based DMS. An anomalous Hall effect in reduced Co-doped rutile $TiO_{2-\delta}$ films[9,10] and the co-occurrence of superparamagnetism in highly reduced Co-doped rutile $TiO_{2-\delta}$ films[9] have also been reported. The suppression in cobalt metal segregation in the reduced Co-doped rutile $TiO_{2-\delta}$ films was also reported to result from the Sb doping of $TiCoO_{2-\delta}$ films.[11,12] Cobalt metal segregation still remains as a significant hurdle to intrinsic DMS properties. An extraordinary Hall effect and ferromagnetic properties in Fe-doped reduced rutile have also been reported.[7] However, ferromagnetic properties at room temperature in these films arose from $Fe_2O_3$ clusters that were present in the films. Manganese-doped reduced rutile films exhibit superparamagnetic properties at room temperature. The clusters present in the films act as important drawbacks in a DMS. Unfortunately, it appears that the formation of clusters in $TiO_2$-based DMS prepared by a normal deposition technique cannot be eliminated. The intrinsic requirements for DMS are the absence of clusters in films and an intrinsic ferromagnetic property at room temperature.

To realize these two requirements for DMS, we propose a concept of superlattice structure for $TiO_2$-based DMS and report here on the characterization of the structural and ferromagnetic properties of superlattice films at room temperature. The superlattice films were composed of alternating layers of $Ti_{0.94}Fe_{0.06}O_2$ and $Ti_{0.94}Mn_{0.06}O_2$, and thicknesses of each layer are approximately 2.7 Å. They were deposited on $r$-$Al_2O_3(1102)$ substrates at a deposition temperature of 500 °C and at a deposition pressure of $6.5 \times 10^{-4}$ Pa by pulsed laser deposition using a KrF excimer laser ($\lambda = 248$ nm). As a counterpart of the superlattice films, alloy films were normally grown using a single $Ti_{0.94}(Fe_{0.03}Mn_{0.03})O_2$ target using the same deposition conditions. The total thickness of the superlattice and of the matching alloy films is approximately 200 nm in each case. In this letter, an intrinsic ferromagnetic property and evidence for the lack of clusters in the superlattice films are demonstrated through various measurements and compared with the alloy films.

X-ray diffraction (Rigaku D/MAX-RC) experiments using Cu $K_\alpha$ radiation and a Ni filter were carried out to determine the crystal structure and preferred orientation of the films. The surface morphologies were examined by atomic force microscopy (AutoProbe CP). The compositional distri-

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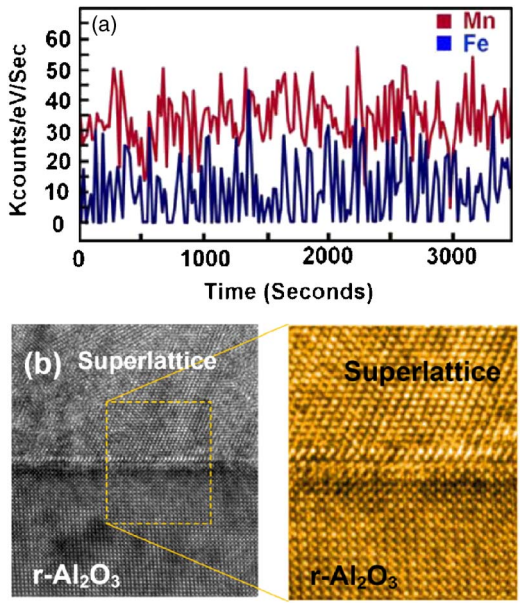


FIG. 1. (Color online) (a) Compositional distribution of elemental Fe and Mn in superlattice films by scanning Auger spectroscopy (the alternating layer thicknesses of $Ti_{0.94}Fe_{0.06}O_2$ and $Ti_{0.94}Mn_{0.06}O_2$ in superlattice films are about 2.7 Å). (b) High-resolution transmission electron microscopy (HRTEM) images of the superlattice films (interface between the superlattice and substrate was focused in order to investigate the presence of clusters).

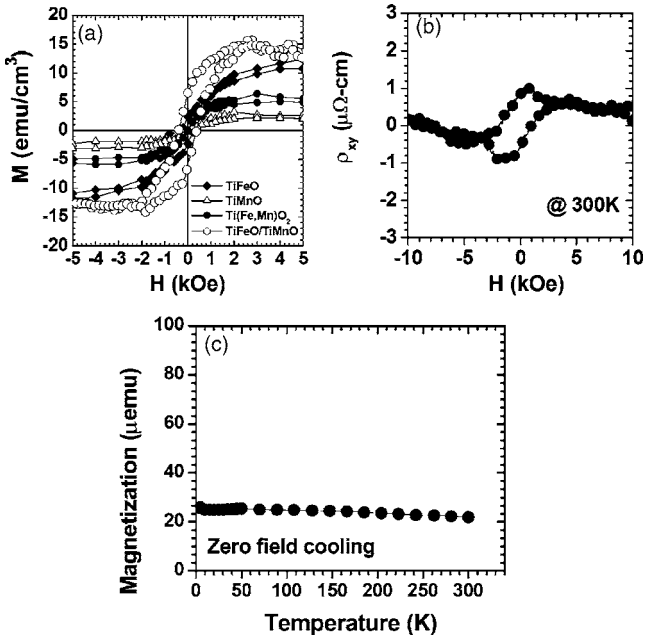


FIG. 2. (a) Magnetic hysteresis curves of various materials taken at room temperature. (b) Hall resistivity of the superlattice films with a 2.7 Å thickness as a function of applied magnetic field at 300 K. (c) Zero-field cooled (ZFC) magnetization-temperature curve of the superlattice films deposited at 500 °C.

bution of elemental Fe and Mn in the alternating layers of the films was determined by scanning Auger microscopy (VG Scientific Microlab 350). The composition in the alloy films and superlattice films was confirmed by Rutherford backscattering spectroscopy. Metal clusters in the superlattice films could be clearly observed by high-resolution transmission electron microscopy (HRTEM). The resistivity of the films was measured with an electrometer (CMT-SR 1000) using a four-point probe method, and the Hall effect for the films was measured in a van der Pauw configuration using a physical property measurement system (Quantum Design). Magnetic measurements were performed in a dc superconducting quantum interference device magnetometer and a vibrating sample magnetometer. Images of both the domains and domain switching in the superlattice films were investigated using magnetic force microscopy (MFM).

200 nm thick $Ti_{0.94}(Fe_{0.03}Mn_{0.03})O_2$ alloy films and superlattice films show an epitaxial growth of the rutile (101) plane on *r*-$Al_2O_3$(1102) substrates, and the superlattice films had crystallinity higher than that of $Ti_{0.96}(Fe_{0.03}Mn_{0.03})O_2$ alloy films. Figure 1(a) shows an Auger electron spectroscopy (AES) depth profile which confirms the presence of 2.7 Å thick alternating layers in superlattice films deposited at 500 °C. The depth profile shows a distribution of elemental Fe and Mn along the film thickness. The distribution of elemental Fe and Mn in the alternating layers is not regular because the depth resolution of AES decreases with distance from the surface of the films. However, the presence of alternating layers was clearly confirmed by the AES depth profile. HRTEM images of the superlattice films are shown in Fig. 1(b). The TEM observations indicate that the superlattice films are epitaxially grown and that the lattice planes of the films and substrate are clearly observable and their orientations are well defined. In order to confirm cluster formation at an interface, the interface layer was magnified as shown in the image on the right side of Fig. 1(b). The TEM observations focused on the interface layer clearly indicate no sign of segregation of an impurity phase in the superlattice films.

Figure 2(a) shows the magnetic hysteresis curves for various materials taken at room temperature. The samples of $Ti_{0.94}Fe_{0.06}O_2$ (TiFeO), $Ti_{0.94}Mn_{0.06}O_2$ (TiMnO), and $Ti_{0.94}(Fe_{0.03}Mn_{0.03})O_2$ [Ti(Fe,Mn)O] show a low remanent magnetization and coercive field, followed by superparamagnetic properties at room temperature. On the other hand, the superlattice films (TiFeO/TiMnO) show a high remanent magnetization and coercive field, resulting in intrinsic ferromagnetic properties. Remanent magnetization and coercive field of the superlattice films are approximately 7.2 emu/$cm^3$ and 390 Oe, respectively. The anomalous Hall effect which is controlled by charge carriers in a room-temperature ferromagnetic semiconductor can provide direct evidence for intrinsic ferromagnetism. The Hall resistivity of the superlattice measured at 300 K as a function of applied magnetic field is shown in Fig. 2(b). An anomalous Hall effect exhibits hysteresis loops with coercivities corresponding to those in the ferromagnetic hysteresis loops. An anomalous Hall effect in the TiFeO films deposited at 500 °C was not observed because they show a high resistivity. On the other hand, TiMnO films and TiMnFeO alloy films show hysteresis loops without coercivities, corresponding to those having superparamagnetic properties. Our data suggest that the superlattice films indeed show ferromagnetic semiconductor characteristics. Figure 2(c) shows the variation in a zero-field cooled (ZFC) magnetization-temperature curve at an applied magnetic field of 1000 Oe in superlattice films deposited at 500 °C. The ZFC curve in the magnetization-temperature relationship constitutes additional evidence as to whether the films contain a segregated impurity phase. If the films contain a segregated impurity, the magnetization in the ZFC curve would show a hump at the blocking temperature and

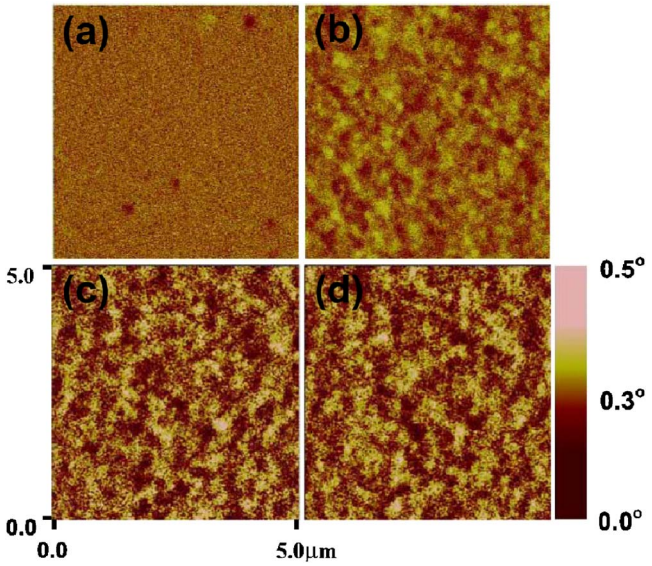


FIG. 3. (Color online) Phase images by MFM in (a) alloy films and (b) superlattice films with alternating layer thicknesses of 2.7 Å. Domain images measured at (c) up and (d) down magnetization directions of the superlattice films using a cantilever. A magnetic field of 300 G was applied at the cantilever.

then decrease with decreasing temperature below the blocking temperature.[10] As shown in Fig. 2(c), no hump with decreasing temperature is present in the ZFC curve and the magnetization of the superlattice films maintains a constant value with increasing temperature from 0 to 300 K. This result, together with the TEM analysis, clearly verifies that the superlattice films do not contain a segregated impurity phase.

Additional evidence for an intrinsic ferromagnetic property in the superlattice films is the observation of both domain and domain switching by MFM. Figures 3(a) and 3(b) show MFM images of $Ti(Fe,Mn)O_2$ alloy films and superlattice films with a 2.7 Å alternating layer thickness, respectively. The domains in the ferromagnetic films were observed using the phase images obtained by MFM. No domains were observed in the alloy films shown in Fig. 3(a), which corresponds to superparamagnetic properties in $Ti(Fe,Mn)O_2$ alloy films. On the other hand, superlattice films [see Fig. 3(b)] with an alternating layer thickness of 2.7 Å show clear evidence of magnetic domains in $5\times5$ $\mu m^2$ images. Figures 3(c) and 3(d) show the domain images measured in the up and down magnetization directions, respectively, using a cantilever with an applied field of about 300 G. In MFM images of superlattice films as shown in Figs. 3(c) and 3(d), the contrast was completely reversed at the same direction. This means that the domains were switched in the direction of the applied magnetic field, indicating an intrinsic ferromagnetic property as shown in the *M-H* curves for the superlattice films in Fig. 2(a). From the above experimental results, superlattice films composed of $Ti_{0.94}Fe_{0.06}O_2$ and $Ti_{0.94}Mn_{0.06}O_2$ alternating layers with thicknesses of approximately 2.7 Å exhibit intrinsic ferromagnetic properties for dilute magnetic semiconductor applications.

In summary, superlattice films composed of alternating layer of $Ti_{0.94}Fe_{0.06}O_2$ and $Ti_{0.94}Mn_{0.06}O_2$ with layer thicknesses of approximately 2.7 Å were prepared on *r*-$Al_2O_3$(1102) substrates at 500 °C by pulsed laser deposition. The superlattice films exhibit higher remanent magnetization and a greater coercive field than TiFeO, TiMnO, and Ti(Fe,Mn)O films. An anomalous Hall effect in superlattice films exhibits hysteresis loops with coercivities corresponding to those in the ferromagnetic hysteresis loops. Superlattice films do not contain a segregated impurity phase and exhibit a clear switching of domains by an applied magnetic field.

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