Room temperature spin polarized magnetic semiconductor

Soack Dae Yoon, Carmine Vittoria, and Vincent G. Harris

Center for Microwave Magnetic Materials and Integrated Circuits, Department of Electrical and Computer Engineering, Northeastern University, Boston, MA 02115 USA

Alan Widom

Department of Physics, Northeastern University, Boston, MA 02115 USA

Alternating layers of granular Iron (Fe) and Titanium dioxide (TiO$_2$-$\delta$) were deposited on (100) Lanthanum aluminate (LaAlO$_3$) substrates in low oxygen chamber pressure using a controlled pulsed laser ablation deposition technique. The total thickness of the film was about 200 nm. The films show ferromagnetic behavior for temperatures ranging from 4 to 400 K. The layered film structure was characterized as p-type magnetic semiconductor at 300 K with a carrier density of the order of $10^{20}$/cm$^3$. The undoped pure TiO$_2$-$\delta$ film was characterized as an n-type magnetic semiconductor. The hole carriers were excited at the interface between the granular Fe and TiO$_2$-$\delta$ layers similar to holes excited in the metal/n-type semiconductor interface commonly observed in Metal-Oxide-Semiconductor (MOS) devices. The holes at the interface were polarized in an applied magnetic field raising the possibility that these granular MOS structures can be utilized for practical spintronic device applications.

PACS numbers: 75.50.Pp, 71.30.+h, 72.20.-i, 71.70.Gm, 72.25.-b, 73.40.Qv

INTRODUCTION

The search for semiconductors exhibiting magnetism at room temperature has been long and unyielding. However, recently much progress has been made toward this goal [1, 2, 3, 4, 5, 6, 7, 8]. By doping a host semiconductor material with transition metal ferromagnetic atoms, dilute ferromagnetic semiconductors have been produced with Curie temperatures ($T_c$) as high as 160 K [9]. Hall effect measurements below $T_c$ showed evidence for carriers being spin polarized raising hopes for spintronics applications. Specifically, metallic Manganese (Mn) was doped into Gallium arsenide (GaAs) whereby approximately 100% of the carriers were spin polarized [10].

We have reported the magnetic and transport properties of magnetic semiconductor films of TiO$_2$-$\delta$, where $\delta$ indicates the degree of oxygen deficiency or defects in the film [9, 10]. The Curie temperature, $T_c \approx 880^\circ K$, was well above room temperature with a saturation magnetization of $M_s \approx 32$ Gauss. Titanium dioxide, TiO$_2$, is a well known wideband gap oxide semiconductor, belonging to the group IV-VI semiconductors, described in terms of an ionic model of Ti$^{4+}$ and O$^{2-}$ [11, 12, 13, 14, 15]. Its intriguing dielectric properties allow its use as gate insulator materials in the Field-Effect-Transistor (FET) [10]. Also, TiO$_2$ is characterized to be an n-type semiconductor with an energy gap varying in the range 3 volt $< \Delta / e < 9$ volt depending on sample preparation [11, 12, 13, 14, 15]. Films of TiO$_2$-$\delta$ on substrates of (100) Lanthanum aluminate (i.e. LaAlO$_3$) were deposited by a pulsed Laser-Ablation-Deposition (LAD) technique at various oxygen chamber pressures ranging from 0.3 to 400 mtorr. The origin of the presence of Ti$^{2+}$ and Ti$^{3+}$ (as well as Ti$^{4+}$) ions was postulated as a result of the low oxygen chamber pressure during the films growth [9]. Oxygen defects gave rise to valence states of Ti$^{2+}$ and Ti$^{3+}$ (in background of Ti$^{4+}$) whereby double exchange between these sites dominated. The same carriers involved in double exchange also gave rise to impurity donor levels accounting for the transport properties of the film. The dilute number of carriers were spin polarized, yet the magnetic moment was still rather small [10]. For example, normal Hall resistivity was measured to be much bigger than any anomalous Hall resistivity [10]. In order to increase the anomalous contribution to the Hall effect and thereby increase the number of spin polarized carriers, we have fabricated a layered structure of TiO$_2$-$\delta$/metallic Iron (Fe). The intent was to introduce a substantial magnetization component internally to semiconductor TiO$_2$-$\delta$.

The basic difference between our layered composite and the previously reported magnetic semiconductors by others is that in our films the Fe layers co-exist in a metallic state, whereas magnetic semiconductors prepared by others the transition metal co-exists as metal oxides and often oxide clusters [4, 5, 6, 7, 17, 18]. This major difference is important in terms of the magnetic and transport properties of the magnetic semiconductor presently produced by us and that of others [4, 5, 6, 7, 17, 18]. For example, metallic Fe contains a significant higher moment and Curie temperature than any other transition metal oxides. Also, the presence of metallic Fe allows for the creation of a reservoir of conduction electrons in the conduction band and, therefore, holes in TiO$_2$-$\delta$ layers. As electrons from the conduction band of TiO$_2$-$\delta$ are thermally “dumped ” into the metallic Fe conduction band,
hires are created in TiO$_{2-\delta}$ much like in junctions of metal/semiconductor interfaces or in Metal Oxides Semiconductor (MOS) devices. Conduction of holes occurs in TiO$_{2-\delta}$ layers. This mechanism gives rise to lower resistivity at high temperature in contrast to pure TiO$_{2-\delta}$ reported earlier\cite{9}, where the carriers were only electrons. No such mechanism is possible in magnetic semiconductors doped with transition metal oxides. We refer here that in our layered semiconductor of Fe/TiO$_{2-\delta}$ the magnetization, $M_s \approx 250$, at room temperature, $T_c$ above 800$^\circ$K, nearly 100% of the carriers are spin polarized and the room temperature resistivity is lowered by as factor of $\sim 10^{-3}$ relative to films of the undoped TiO$_{2-\delta}$ semiconductors previously produced\cite{9}.

**EXPERIMENTAL PROCESS**

Thin films consisting of alternating layers of granular iron (Fe) and Titanium dioxide (TiO$_2$-) were deposited by a pulsed laser ablation deposition (LAD) technique from binary targets of TiO$_2$ and metallic Iron (Fe) on (100) Lanthanum aluminate (LaAlO$_3$) substrates. We refer to this technique as the Alternating Targets LAD (or ALT-LAD)\cite{20, 21}. Alternate layers of granular Fe and TiO$_{2-\delta}$ were deposited sequentially to produce films whose crystal structure was aimed to be similar to that of pure TiO$_2$. Targets of TiO$_2$ and Fe were mounted on a target rotator driven by a servomotor and synchronized with the trigger of the pulsed excimer laser, $\lambda$ = 248 nm. In each deposition cycle, the ratio of laser pulses incident upon the TiO$_2$ target to those upon the Fe target was 6:1. The substrate temperature, laser energy density, and pulse repetition rate were maintained at 700$^\circ$C, $\approx 8.9$J/cm$^2$, and 1 Hz, respectively. The deposition was carried out in a pure oxygen background of around 10 torr in order to induce defects in the TiO$_2$ host. There were a total of 4200 laser pulses (3600 pulses on TiO$_2$ target and 600 pulses on Fe target) for each film resulting in a thickness of approximately 200 nm as measured by a Dek-Tek 3 step profilometer. Crystal and surface structure measurements were performed by x-ray diffractometer (XRD) and Scanning-Electron-Microscopy (SEM). In order to measure the ratio of Ti to Fe, method of Energy Dispersion X-Ray Spectroscopy (EDS) within the SEM column was employed. Magnetic hysteresis loops and dc-electrical and magneto-resistivity of the resulting films were measured using a Quantum Design Physical Property Measurement System (PPMS) in the temperature range between 4$^\circ$K and 400$^\circ$K.

**RESULTS AND DISCUSSIONS**

Crystallographic properties of the AT-LAD films were measured using x-ray diffractometry (XRD). Results indicate multiple phases of TiO$_2$, metallic Fe, and iron oxide (Fe$_2$O$_3$). FIG.1 shows a representative XRD spectrum of the film. The diffraction peaks at 2$\theta$ = 37.76$^\circ$ and 80.714$^\circ$ were indexed to the (004) and (008) planes, respectively, of the Anatase TiO$_{2-\delta}$TiO$_{2-\delta}$. The metallic Fe phase was identified by the diffraction peaks appearing at 2$\theta$ = 44.643$^\circ$ and 98.929$^\circ$ which are indexed to the (110) and (220) planes\cite{24}, respectively. Fe$_2$O$_3$ peaks were also observed in the spectrum implying that the embedded granular Fe was possibly partially oxidized.

For steady currents and with the magnetic intensity $H$ aligned normal to the film plane, the resistance matrix $R$ in the plane of the film may be written as\cite{23}

$$R = \begin{pmatrix} R_{xx} & R_{xy} \\ R_{yx} & R_{yy} \end{pmatrix} = \frac{1}{t} \begin{pmatrix} \rho & -\rho_H \\ \rho_H & \rho \end{pmatrix}$$ \hspace{1cm} (1)

FIG. 1: X-ray diffraction spectrum for a representative layered film of granular Fe in TiO$_{2-\delta}$.

FIG. 2: Resistivity, $\rho$ as a function of temperature, $T$, for the layered granular Fe in TiO$_{2-\delta}$ film (dashed line) and the pure TiO$_{2-\delta}$ (solid line) from the reference\cite{9}.
wherein ρ and ρ_H represent, respectively, the normal-resistivity and the Hall resistivity. A ρ as a function of temperature for the layered film was measured in an applied field of H = 0 Oe and shown in FIG.2. We note that the value of ρ(T) was quite small at high temperature. The ρ(T) behavior for pure TiO_{2−δ} film 10 (solid line) is also shown in FIG.2 exhibiting a typical metal-insulator transition in the temperature range of 4°K and 300°K. In contrast to the ρ for pure TiO_{2−δ}, ρ for the layered film is a factor of 1000 lower and is constant for temperatures between 225°K and 400°K. The ρ value at 300°K was measured to be 183 μΩcm, and is about a factor of 20 larger than the resistivity of pure Fe[20].

We have modeled the mechanism for transport in this layered film in a sketch shown in inset of FIG.3[13, 27, 28]. A common chemical potential energy or Fermi energy in the layered film implies that the conduction band of TiO_{2−δ} layers is degenerate with the metallic Fe conduction band. Electrons hopping between Ti^{2+} and Ti^{3+} sites would find a conduit into the metallic conduction band whereby holes are created in the TiO_{2−δ} layers and therefore a small potential barrier at the interface. This is illustrated schematically in FIG.3. Since, the Fe metallic particles are isolated or disconnected, conduction in the TiO_{2−δ} layers is via hole conduction. At very low temperatures, where thermal kinetic energy is not sufficient to raise conduction electrons into the conduction band of the Fe particles, conduction is mostly due to electron carriers in TiO_{2−δ} layers. In FIG.3 Hall resistivity is plotted as a function of temperature. Indeed, at high temperature carriers are holes and electrons for T < 50°K. Furthermore, the number of carriers relative to pure TiO_{2−δ} has increased by factor 1000 and the mass of holes is approximately about 10 times larger than the electron mass. Effectively, the Hall resistivity in the composite layered structure is decreased by a factor of 1000 relative to pure TiO_{2−δ}. The experimental data at 300°K shows ρ_H = 34.00 mΩ cm for pure TiO_{2−δ} and ρ_H = 53.81 μΩ cm for layered granular Fe TiO_{2−δ} (or approximately a factor of 630 smaller).

The spontaneous magnetization was measured to be nearly constant as a function of temperature as shown in FIG.4. The measurement was performed with an external dc-magnetic field of 10 kOe applied normal to the film plane (out-of-plane measurement). The out-of-plane magnetic hysteresis loop behavior at 305°K is shown in the inset of FIG.4. The film can be fully saturated with a field of 10 kOe, since the coercive field was measured to be 2 kOe. Field cooled (FC) and zero-field-cooled (ZFC) M(H, T) data in FIG.4 shows no difference which implies that no spin glass effects are present in the films. The magnetization (M_s) of pure TiO_{2−δ} was measured to be about T.M_s ≈ 32 Gauss at 300°K which is considerably smaller than that measured for the Fe/TiO_{2−δ} films. Clearly, the measured magnetization of the layered films must be due to the presence of metallic Fe.

Finally, we have measured an anomalous Hall effect in magnetic field sweeps between -90 and 90 kOe as shown in FIG.5. The film exhibited strong polarization and hysteresis behavior as a function of applied field at 300°K. Since, the anomalous Hall effects may be observed in the presence of a spontaneous magnetization[24, 50] we infer that about 10^{20} cm^{-3} hole carriers are spin polarized. This polarized carrier density value is a factor of 1.2 larger than the carrier density estimated from normal Hall measurement, where carrier density was estimated with only applied H, at 30°K. This indicates that nearly all of the carriers were spin polarized by the spontaneous magnetization. FIG.5 indicates that the carrier polarization is not affected by external field up
FIG. 5: Hall resistivity, $\rho_H$, versus $H$ at 300°K. Carrier polarization density is of the order of $10^{20}/cm^3$ with a Hall resistivity value of 0.8 $\mu\Omega$ cm.

to 3kOe, which can be an advantage for memory device applications [31, 32].

CONCLUSIONS

Magnetic and magneto-transport data for layered films of metallic iron (Fe) and oxygen defected titanium oxide (TiO$_{2-\delta}$) are reported in this letter. The essence of this paper showed that conduction carriers of the films were strongly coupled to residual magnetic moments of metallic iron (Fe) layers in the layered structure. The dramatic reduction of normal resistivity ($\rho(T)$) of the films is a consequence of two factors: (1) oxygen defects in the TiO$_{2-\delta}$ layers induced electron hopping; (2) electrons from the TiO$_{2-\delta}$ were “dumped” into the conduction band of Fe layers to create holes in TiO$_{2-\delta}$ similar to a Metal Oxide Semiconductor (MOS) structure. As a result the number of carriers increased, and at room temperature, the majority carriers were holes with a density of $5 \times 10^{20}/cm^3$ as measured by normal Hall measurements. The holes in TiO$_{2-\delta}$ were polarized due to the presence of ferromagnetic metallic Fe, where the spin polarized density was measured to be $6 \times 10^{20}/cm^3$. Therefore, spintronics and spin dependent memory applications can be based upon the results presented here.

* Corresponding author e-mail: syoon@ece.neu.edu

1 Electronic address: vittoria@lepton.neu.edu
2 Electronic address: harris@ece.neu.edu
3 Electronic address: widom@neu.edu

[1] H. Ohno, Science 281, 951 (1998).
[2] K. Ueda, H. Tahata, and T. Kawai, Appl. Phys. Lett. 79, 988 (2001).
[3] Y. Masumoto et al., Science 291, 854 (2001).
[4] S.J. Pearton et al., Mat. Sci. and Engr. R40, 137 (2003).
[5] S.A. Chambers and R.F.C. Farrow, MRS Bulletin 28, 729 (2003).
[6] I. Žutić, J. Fabian, and D. Sarma, Rev. Mod. Phys. 76, 32 (2004).
[7] J.M.D. Coey, M. Venkatesan, and C.B. Fitzgerald, Nat. Maters. 4, 173 (2005).
[8] M.A. García et al., Phs. Rev. Lett. 94, 217206 (2005).
[9] S.D. Yoon et al., J. Phys.; Condens. Matter. 18, L355 (2006).
[10] S.D. Yoon et al., e-print cond-mat/0704.2211 (2007).
[11] M. Earle, Phys. Rev. 61, 56 (1942).
[12] R.G. Breckenridge and W.R. Hosler, Phys. Rev. 91, 793 (1953).
[13] N. Daude, C. Gout, and C. Jouanin, Phys. Rev. B 15, 3220 (1977).
[14] J. Pascual, J. Camassel, and H. Mathieu, Phys. Rev. B 18, 5606 (1978).
[15] H. Tang et al., Solid State Comm. 87, 847 (1993).
[16] S.A. Campbell et al., IBM J. Res. Develop. 43, 383 (1999).
[17] S.R. Shinde et al., Phys. Rev. B 67, 115211 (2003).
[18] Z.K. Wang et al., J. Appl. Phys. 93, 7870 (2003).
[19] B.G. Streetman, “Solid State Electronic Devices,” ch. 8, 301, Prentice Hall, Inc., Englewood Cliffs, New Jersey (1990).
[20] X. Zuo et al., Appl. Phys. Lett. 87, 152505 (2005).
[21] S.D. Yoon et al., J. Appl. Phys. 99, 08M109 (2006).
[22] Natl. Bur. Stand. (U.S.) Monogr. 25, 82 (1969).
[23] C.J. Howard, T.M. Sabine, and F. Dickson, Acta Crystallographica, B: Structural Science B47, 462 (1991).
[24] H.E. Swanson, J.C. Doukan, and G.M. Ugrinic, Natl. Bur. Stand. (U.S.), Circ. 5, 539 (1955).
[25] L.D. Landau and E.M. Lifshitz, “Electrodynamics of continuous media,” 1982 ch. 4, Elsevier Butterworth-Heinemann, Oxford (1982).
[26] R.C. Weast and M.J. Astle, “CRC Handbook of chemistry and physics,” section E, 81, CRC press, Inc. Boca Raton, Florida, 63rd edition (1982).
[27] M.L. Knotek and P.J. Feibelman, Phys. Rev. Lett. 40, 964 (1978).
[28] Z. Zhang, S.P. Jeng, and V. Henrich, Phys. Rev. B 43, 12004 (1991).
[29] C.L. Chien and C.R. Westgate, “The Hall effect and its applications,” Plenum Press, New York and London (1980).
[30] R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954).
[31] G. Prinz, Science 282, 1660 (1998).
[32] S.A. Wolf et al., Science 294, 1488 (2001).