Electronic transport in oxygen deficient ferromagnetic semiconducting $TiO_{2-\delta}$

2007 J. Phys.: Condens. Matter 19 326202

(http://iopscience.iop.org/0953-8984/19/32/326202)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 326202 (7pp) doi:10.1088/0953-8984/19/32/326202

Electronic transport in oxygen deficient ferromagnetic semiconducting $TiO_{2-\delta}$

Soack Dae Yoon[1,3], **Vincent G Harris**[1], **Carmine Vittoria**[1] **and Allan Widom**[2]

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

E-mail: syoon@ece.neu.edu, harris@ece.neu.edu, vittoria@neu.edu and allan.widom@gmail.com

Received 18 April 2007, in final form 8 June 2007
Published 13 July 2007
Online at stacks.iop.org/JPhysCM/19/326202

Abstract

$TiO_{2-\delta}$ films were deposited on (100) lanthanum aluminate, $LaAlO_3$, substrates at a low oxygen chamber pressure, $P \approx 0.3$ mTorr, employing a pulsed laser ablation deposition technique. In previous work, it was established that the oxygen deficiency in these films induced ferromagnetism. In this work it is demonstrated that this same oxygen deficiency also gives rise to semiconductor titanium ion impurity donor energy levels. Measurements of the transport resistivity of thin films of $TiO_{2-\delta}$ are presented, as a function of temperature and magnetic field. The magnetoresistivity and Hall resistivity are explained in terms of electronic excitations from the titanium ion donor levels into the conduction band.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Today, materials research is focused toward a technology base whereby miniature devices operating at high speed, over a wide range of frequencies, and exhibiting multifunctional properties can be developed routinely and efficiently [1–6]. Titanium dioxide, TiO_2, is a well known wide band gap oxide semiconductor belonging to the group IV–VI semiconductors. It is described in terms of a model structure of Ti^{4+} and O^{2-} ions. It has large dielectric constant and dielectric anisotropy, and various crystal structures [7–9]. TiO_2 is known to be an n-type semiconductor with a large energy gap in the range $3\ \text{V} < \Delta/e < 9\ \text{V}$ depending on the sample preparation [10–14]. Previously [15], thin $TiO_{2-\delta}$ films of thickness in the range $200\ \text{nm} < t < 400\ \text{nm}$ were deposited on (100) substrates of lanthanum aluminate, $LaAlO_3$. Bulk TiO_2 does not order magnetically at room temperature. However, spontaneous

[3] Author to whom any correspondence should be addressed.

magnetization in $TiO_{2-\delta}$ films [15] occurred in the temperature range 4 K $< T <$ 880 K. The spontaneous magnetization was attributed to the oxygen deficiency induced during the growth of the films. It was argued that oxygen deficiency caused an imbalance in the ionic charge neutrality of the film, thereby creating electron donor impurity ions of Ti^{2+} and Ti^{3+} in addition to the usual Ti^{4+} ions. Ferromagnetism, i.e. net magnetic moments in the Ti^{2+} and Ti^{3+} ions, was a result of superexchange interactions between these ions via the oxygen ions. Calculations indicate that of all possible superexchange permutations, double exchange may be the most dominant interaction in view of the filled electron bands of the oxygen ions [16]. It is well known [17, 18] that such double exchange favours ferromagnetism.

Our purpose is to argue that the *same* magnetic ions and oxygen deficiency as gave rise to magnetism in $TiO_{2-\delta}$ films also play a vital role in the electronic *transport properties*. Specifically, the existence of donor Ti^{2+} and Ti^{3+} ions in our films allows for electronic excitations into conduction bands. The number of carriers in the conduction band varies only mildly with magnetic field and more strongly with temperature. Indeed, the measurements reported here for the Hall resistivity are approximately linear in the magnetic field and the magnetoresistivity is only very mildly field dependent. The magnetoresistivity and Hall resistivity have very similar temperature dependences, reflecting the variation of the number of mobile electron transport carriers with temperature. Measurements of transport properties of TiO_2 films as well as the theoretical analysis are discussed in section 2. The films were deposited employing a pulsed laser ablation deposition (PLD) technique at an oxygen pressure of $P \approx 0.3$ mTorr. Final arguments are presented in section 3.

2. Magnetotransport measurements

Pulsed laser ablation deposition (PLD) techniques were employed with a weakly paramagnetic magnetic TiO_2 target. Thin films of oxygen deficient $TiO_{2-\delta}$ were produced on (100) lanthanum aluminate, $LaAlO_3$, substrates. During the PLD process, the substrate temperature was fixed at $T = 700\,^{\circ}C$ while varying the oxygen pressure in the range 0.3 mTorr $< P <$ 400 mTorr. Films deposited at $P \approx 0.3$ mTorr exhibited spontaneous magnetization and were therefore selected for measurements of magnetotransport film properties. Conventional square four-wire distribution and collinear four-wire measurement techniques were employed for the Hall and normal resistivity measurements, respectively. Square shapes of the $TiO_{2-\delta}$ films, $a \times b = 5 \times 5$ mm^2 in size, were selected for the measurements. The thicknesses of the films were in the range 200 nm $< t <$ 400 nm. The details of the magnetic and crystallographic characterization as well as other impurities and contaminants in the films were previously reported [15]. The films were measured as having an anatase TiO_2 structure with $(00l)$ plane orientation. The c-axis lattice parameter, determined by peak profile fitting of $(00l)$ peaks, was 0.950 ± 0.0017 nm, which compares favourably with 0.952 nm for the bulk anatase structure of TiO_2. X-ray photoemission spectroscopy (XPS) measurements were performed and confirmed that no other magnetic impurities contaminated the $TiO_{2-\delta}$ films [19].

For steady currents and with the magnetic intensity **H** directed normal to the film, the resistance matrix R for in the plane of the film may be written as [20]

$$\mathsf{R} = \begin{pmatrix} R_{xx} & R_{xy} \\ R_{yx} & R_{yy} \end{pmatrix} = \frac{1}{t} \begin{pmatrix} \rho & -\rho_{\mathrm{H}} \\ \rho_{\mathrm{H}} & \rho \end{pmatrix} \tag{1}$$

wherein ρ and ρ_{H} represent, respectively, the magnetoresistivity and the Hall resistivity. The resistance matrix R of the $TiO_{2-\delta}$ films was measured by a conventional four-terminal technique using a gold-plated resistance sample puck from the Quantum Design physical property measurement system (PPMS). As the ferromagnetic moment per unit volume is small

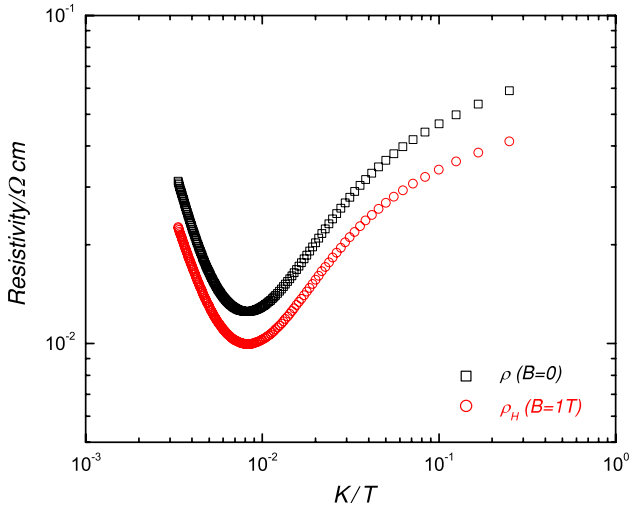

Figure 1. Plotted on logarithmic scales are the magnetoresistivity ρ at zero magnetic field intensity and the Hall resistivity $\rho_{\rm H}$ at $B = 1$ T versus inverse temperature. The temperature variations are quite similar, i.e. the Hall angle $\theta_{\rm H} = \arctan(\rho_{\rm H}/\rho)$ is fairly uniform in temperature.

on the scale of applied magnetic intensities, $|\mathbf{M}| \ll |\mathbf{H}|$, the magnetic field intensity may be identified with the magnetic induction $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$, i.e. $\mathbf{B} \approx \mu_0\mathbf{H}$. As a consequence of such a weak magnetization $\mathbf{M}$, the anomalous Hall resistivity is negligible, where the saturation magnetization of the film was measured to be $4\pi\mathbf{M_s} \approx 4 \times 10^{-2}$ T in the temperature range between 4 and 300 K. The original Hall expression for $\rho_{\rm H}$ is sufficiently accurate. The magnetoresistivity is here described by the Drude model. Altogether, we may analyse the data in terms of the simple conventional expressions

$$\rho_{\rm H} = \frac{B}{ne} \qquad \text{and} \qquad \rho = \frac{m}{ne^2\tau}, \tag{2}$$

wherein n is the density per unit volume of carriers in the conduction band.

In figure 1 are shown measurements of ρ at zero magnetic intensity, and $\rho_{\rm H}$ at $\mu_0 H = 1.0$ T is plotted as a function of temperature T. One notes that the temperature variations of ρ and $\rho_{\rm H}$ are quite similar, as they are for other semiconductors [21, 22]. The Hall angle $\theta_{\rm H}$, as defined by

$$\tan\theta_{\rm H} = \frac{\rho_{\rm H}}{\rho} \equiv \frac{eB\tau}{m} \equiv \omega_c\tau, \tag{3}$$

is experimentally fairly uniform in temperature. The electronic properties of single-crystal bulk rutile $TiO_{2-\delta}$ and anatase TiO_2 were previously measured in the references [23, 24]. The δ values for the bulk rutile and the anatase $TiO_{2-\delta}$ were quite small as reported: $\delta = 0.0004$ or smaller, whereas the δ values for our films were large, $\delta \approx 0.2$. In general, $\omega_c\tau$ expressed in equation (3) can be expected to be very large for pure materials (with $\delta = 0$), where the scattering is mainly due to phonons. We measured $\omega_c\tau \approx 0.7$ at $\mu_0 H = 1.0$ T, and have not observed magnetic quantum oscillations (Shubnikov–de Haas effect) in films of $TiO_{2-\delta}$ reported here. In the films of $TiO_{2-\delta}$, the mobility can be larger than the one reported by [23, 24]. This is an experimental fact. We interpreted this increase in mobility as due to our semiconductor films being heavily doped ($\delta = 0.2$). The donor electrons in heavily doped semiconductors can be exceedingly mobile within the conduction band [25]. There is

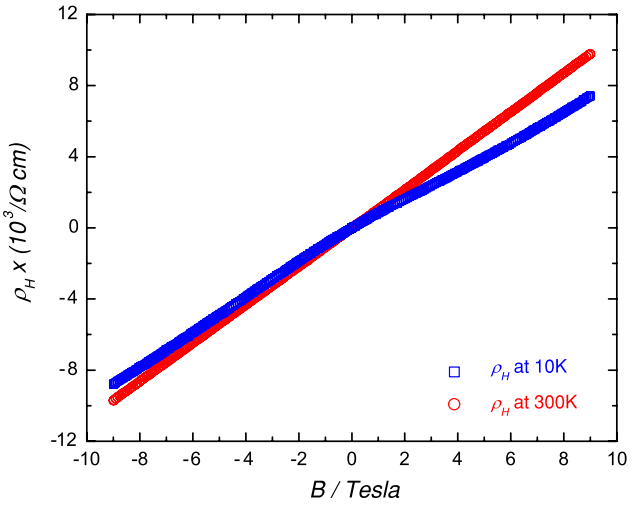

Figure 2. Shown are plots for a film deposited at 0.3 mTorr of the Hall resistivity ρ_{H} for two temperatures, $T = 10$ and 300 K. In the high temperature regime, the linear behaviour in magnetic field $\rho_{\mathrm{H}} = (B/ne)$ is accurately obeyed. In the low temperature regime there are experimental deviations from linear behaviour.

no energy band gap between the donor band and the conduction band, where the donor energy band overlaps into the conduction band in the heavily doped semiconductor. In [23, 24], the data given imply an energy gap below the conduction band due to the small $\delta = 0.0004$ or lightly doped semiconductors, which suppressed the high mobility [25].

The Hall resistivities ρ_{H} as a function of magnetic field were measured at fixed temperature with applied field sweeps in the range $-9\ \mathrm{T} < \mu_0 H < +9\ \mathrm{T}$. The data for a high and low temperature are plotted in figure 2. For high temperatures, the experimental data are in excellent agreement with the linear magnetic field behaviour for ρ_{H} in equation (2). For low temperatures, the agreement with the linear behaviour in the magnetic field is only fair. Nevertheless, it is experimentally clear that the carriers are n-type and the carrier densities may be determined by

$$n = \frac{B}{e\rho_{\mathrm{H}}}, \tag{4}$$

quite accurately for high temperatures and somewhat less accurately for low temperatures. The resulting variation of the density of carriers n with temperature T is shown in figure 3. The two striking features of the resulting inferred density of carriers are as follows. (i) The density of carriers does not appear to vanish in the low temperature limit $T \to 0$. In fact, there appears to be a low density of carriers in the ground state $TiO_{2-\delta}$ system of approximately

$$n_0 \approx \frac{8.1 \times 10^{16}}{\mathrm{cm}^3} \tag{5}$$

at liquid helium temperatures. This suggests that the electron chemical potential is placed very slightly in the conduction band by the Ti^{2+} donors. The double-exchange mechanism lowers that part of the conduction band containing electrons with spins parallel to those localized spins producing the magnetization [26]. These effects allow for the low density of ground state carriers. (ii) The density of carriers as a function of temperature exhibits a clear maximum. We attribute this maximum in the number of carriers to the decrease of the magnetization M to values below the saturation value M_{s} as the temperature is raised. Theoretically, one finds

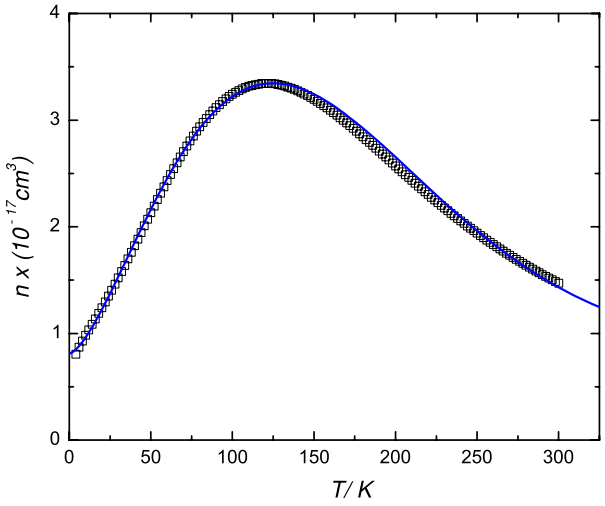

Figure 3. Shown is the inferred density of carriers n as a function of temperature taken from Hall resistivity data in a fixed magnetic field of $B = 1$ T. Also shown (solid curve) is the fit to equations (5) and (6) with $\xi = 0.0065$ and $\theta = 125$ K.

from spin wave theory that $\lim_{T\to 0}[1-(M(T)/M_s)]/T^{3/2} = A_0$. For the temperature range of experimental interest here, we find that $M(T) \approx M_s[1 - A_1 T^{5/2}]$. If the rise in the carrier band lowest energy state is proportional to the deviation of the magnetization from saturation [27], i.e. if $\Delta E \propto (M_s - M)$, then a reasonable phenomenological expression for the density of carriers, both in the ground state and in the thermally excited states, is

$$n(T) = n_0 + \frac{\xi}{\lambda_T^3} \exp\left[-\left(\frac{T}{\theta}\right)^{3/2}\right], \tag{6}$$

wherein the electron thermal wavelength

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}, \tag{7}$$

ξ is a dimensionless constant and θ is derived from the Boltzmann factor $\exp(-\Delta E/k_B T)$ on the right-hand side of equation (6). That the density of carriers is the sum of ground state and thermally activated terms is at the heart of our phenomenology. As can be seen from the data in figure 3, the model gives rise to a good fit to the experimental data.

Finally in figure 4, the magnetoresistivity is plotted as a function of magnetic field in both the high and low temperature regimes. One may view the fractional change in magnetoresistivity,

$$f(B,T) = \frac{\rho(B,T) - \rho(0,T)}{\rho(0,T)}, \tag{8}$$

as a measure of how strongly the carrier density n and the carrier lifetime τ vary with magnetic field. In the high temperature regime, the fractional change in the magnetoresistivity is quite small $|f_{\text{high}}| < 0.003$. In the low temperature regime the fractional change in magnetoresistivity is again fairly small $|f_{\text{low}}| < 0.022$. Altogether, the magnetic field variations of the magnetoresistivity obey $|f| < 2.2\%$ in all regimes. That the deviations are small provides experimental support for the Hall–Drude model of electronic transport in equation (2) for the oxygen deficient $TiO_{2-\delta}$ ferromagnetic semiconductor.

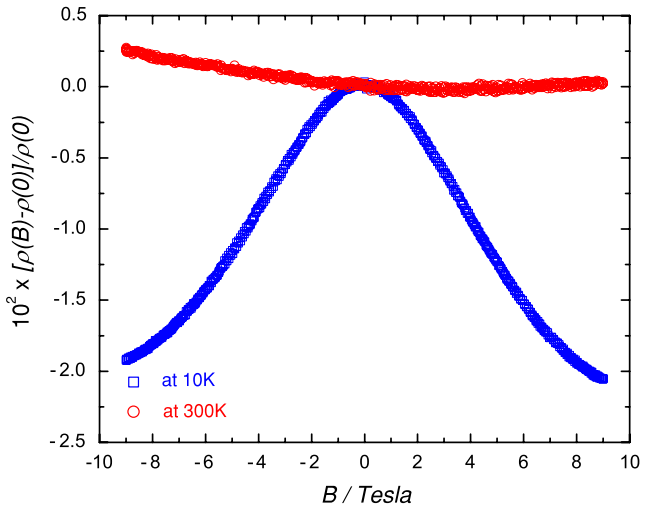

Figure 4. The fractional change f of the magnetoresistance in equation (8) is plotted as a function of the magnetic field. The squares and circles represent, respectively, the measurements taken at temperatures $T = 10$ and 300 K.

3. Conclusion

The magnetoresistivity and Hall resistivity of oxygen deficient $TiO_{2-\delta}$ magnetic semiconductor films have been measured. The data can be understood on the basis of the Hall–Drude model of resistivity from mobile carriers. The anomalous magnetic moment contribution to the Hall resistivity is small in most regimes since the ferromagnetic moment resides mainly on the dilutely distributed ions Ti^{2+} and Ti^{3+} and the magnitude is small, $|\mathbf{M}| \ll |\mathbf{H}|$. The distributions of Ti^{2+} and Ti^{3+} at oxygen defect sites introduce an impurity wide donor band which overlaps the conduction band of $TiO_{2-\delta}$ and, therefore, enhances the mobility of the $TiO_{2-\delta}$ films. Mobilities as high as 0.7 $m^2\ V^{-1}\ s^{-1}$ were measured for our films ($\delta = 0.2$); these are much higher than for single-crystal $TiO_{2-\delta}$, with small δ, where the impurity donor levels do not overlap the conduction band. The Drude relation time τ is only weakly dependent upon the magnetic field $\mathbf{B}$ and the temperature T, so the Hall resistivity ρ_H and the normal resistivity ρ vary similarly with temperature. The experimental data can thereby be described in terms of a temperature dependent mobile carrier density $n(T)$. Apart from an expected Zeeman internal magnetic field splitting of the conduction band wherein the carrier spins align themselves parallel to the spins of the local ionic ferromagnetic moments, there also appears to be a small but finite mobile carrier density that persists even in the $T \to 0$ limit. The theory of such quantum ground state carriers in double-ferromagnetic-exchange semiconductors is worthy of further investigation.

References

[1] Ohno H 1998 *Science* **281** 951
[2] Prinz G 1998 *Science* **282** 1660
[3] Wolf S A *et al* 2001 *Science* **294** 1488
[4] Pearton S J *et al* 2003 *Mater. Sci. Eng.* R **40** 137
[5] Zutic I, Fabian J and Das Sarma S 2004 *Rev. Mod. Phys.* **76** 323
[6] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nat. Mater.* **4** 173

[7] Masumoto Y *et al* 2001 *Science* **291** 854
[8] Toyosaki H *et al* 2003 *Preprint* cond-mat/0307760
[9] Higgins J S *et al* 2004 *Phys. Rev.* B **69** 073201
[10] Earle M 1942 *Phys. Rev.* **61** 56
[11] Breckenridge R G and Hosler W R 1953 *Phys. Rev.* **91** 793
[12] Daude N, Gout C and Jouanin C 1977 *Phys. Rev.* B **15** 3229
[13] Pascual J, Camassel J and Mathieu H 1978 *Phys. Rev.* B **18** 5606
[14] Tang H *et al* 1993 *Solid State Commun.* **87** 847
[15] Yoon S D *et al* 2006 *J. Phys.: Condens. Matter* **18** L355
[16] Yoon S D *et al* 2007 *J. Magn. Magn. Mater.* **309** 171
[17] Zener C 1951 *Phys. Rev.* **82** 403
[18] De Gennes P-G 1960 *Phys. Rev.* **118** 141
[19] Yoon S D *et al* 2007 *J. Magn. Magn. Mater.* at press
[20] Landau L D and Lifshitz E M 1984 *Electrodynamics of Continuous Media* (Oxford: Butterworth-Heinemann) chapter 3, p 90
[21] Debye P P and Conwell E M 1954 *Phys. Rev.* **93** 693
[22] Von Molnar S 1970 *IBM J. Res. Dev.* **14** 269
[23] Yagi E, Hasiguiti R R and Aono M 1996 *Phys. Rev.* B **54** 7945
[24] Forro L *et al* 1994 *J. Appl. Phys.* **75** 633
[25] Bonch-Bruyenvich V L 1966 *The Electronic Theory of Heavily Doped Semiconductors* (New York: Elsevier) chapter 2, pp 5–9
[26] Jungwirth J *et al* 2006 *Rev. Mod. Phys.* **78** 809
[27] Kubo K 1974 *J. Phys. Soc. Japan* **36** 32