Magnetic Tunnel Junctions With $Co:TiO_2$ Magnetic Semiconductor Electrodes

Y. J. Lee, A. Kumar, I. J. Vera Marún, M. P. de Jong, and R. Jansen

MESA$^+$ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

Spin-polarized tunneling is investigated in magnetic tunnel junctions containing an ultrathin interfacial layer of $Co:TiO_2$ magnetic semiconductor. The $Co:TiO_2$ layers (0 to 1 nm thick) are inserted at the $SrTiO_3/Co$ interface in $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Co$ tunnel junctions. For all junctions we find a negative tunnel magnetoresistance, which decreases upon the insertion of $Co:TiO_2$, while the junction resistance increases strongly. This suggests that the ultrathin $Co:TiO_2$ is a paramagnetic insulator that acts as an additional tunnel barrier, in contrast to thick (180 nm) layers grown under comparable conditions, which exhibit metallic impurity band conduction and room-temperature ferromagnetism.

Index Terms—**Cobalt-doped TiO_2, $La_{0.67}Sr_{0.33}MnO_3$, magnetic semiconductor, magnetic tunnel junction, spintronics.**

I. Introduction

THE reported ferromagnetism in wide band gap oxides and nitrides has been of interest in the quest for a room-temperature dilute magnetic semiconductor (DMS), which is desired for the realization of practical spintronic devices. However, the origin of the reported room-temperature ferromagnetism in transition metal doped oxide semiconductors is still quite controversial. The initial theoretical prediction [1] concerns p-type material, with the sp-d exchange interaction as a key ingredient for magnetism mediated by mobile charge carriers. However, the doped oxides exhibiting ferromagnetism contain oxygen vacancies and are n-type semiconductors. It seems unlikely that the originally proposed theory is applicable to such systems. Other proposed models include ferromagnetic exchange interaction between magnetic ions via a donor impurity band [2], and hybridization between the conduction band and the magnetic ions [3]. There are also many reports claiming that the observed magnetism in these oxides is not charge carrier mediated, but of extrinsic origin [4]. In order to address this issue, cobalt-doped titanium dioxide $(Co:TiO_2)$ is a good material to investigate in detail since it has been shown to exhibit room-temperature ferromagnetism [5], anomalous Hall effect (AHE) [6], [7], optical magnetic circular dichroism [8], and impurity band conduction [9].

One of the consequences of carrier-mediated ferromagnetism is that the carriers should be spin polarized. Here, we aim to investigate the spin polarization of the charge carriers in anatase $Co:TiO_2$ via spin-polarized tunneling in a magnetic tunnel junction (MTJ). Ultrathin $Co:TiO_2$ layers (Co concentration 1.4%) are inserted between the $SrTiO_3$ (STO) tunnel barrier and the Co metal electrode of $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Co$ magnetic tunnel junctions. The epitaxial $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) bottom electrode in combination with the STO barrier functions as a spin analyzer with a given positive tunnel spin polarization (TSP), allowing one to probe the TSP of the interface on the opposite side of the STO barrier containing the $Co:TiO_2$. This provides insight into the origin of magnetism in $Co:TiO_2$ and the possible role of the carriers [10]. The $Co:TiO_2$ thin films were grown in anatase phase under conditions for which room-temperature ferromagnetism, AHE, and metallic impurity band conduction were previously observed [7], [9]. We investigate how the sign of the tunnel magnetoresistance (TMR) and its bias dependence change upon insertion of the $Co:TiO_2$ layers, and compare the results with $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Co$ junctions without the $Co:TiO_2$ studied previously [11].

II. Experiment

We have grown LSMO (8.5 nm)/STO (3.1 nm)/Co (11 nm)/Au (5 nm) heterostructures onto STO(001) single crystal substrates by pulsed laser deposition using a stoichiometric ceramic target for LSMO and a single crystalline target for STO. The substrates were chemically treated and annealed at 950°C to obtain a TiO_2 termination [12]. Perovskites were grown at 750°C and 1 Hz laser repetition rate under O_2 pressures of 0.35 mbar and 0.30 mbar, respectively, for LSMO and STO. After deposition of the STO barrier, the O_2 pressure was increased to 1 bar and kept at this value during cooling to room temperature, in order to obtain proper O content. Metal Co counter electrodes and Au capping layers were deposited at room temperature without O_2 gas present. Junctions fabricated according to this process are referred to as "standard junctions."

To study the tunnel spin polarization of $STO/Co:TiO_2$ interfaces, a series of MTJ structures was fabricated with ultrathin $Co:TiO_2$ films deposited onto the STO tunnel barriers. Since the growth conditions for ferromagnetic $Co:TiO_2$ (i.e., 9×10^{-5} mbar O_2 and substrate temperature of 550°C) are radically different from the conditions used to grow the LSMO and STO perovskites, we adopted the following procedure. After growth of the STO tunnel barrier, the samples were cooled to room temperature in 1 bar O_2 as described above. Then, the layer stack was heated again to 550°C in 9×10^{-5} mbar O_2 for the $Co:TiO_2$ deposition, followed by cooling to room temperature in the same 9×10^{-5} mbar O_2 pressure, and deposition of the Co and Au metals at room temperature. These conditions avoid having a high oxygen content in the $Co:TiO_2$ layer, which

Manuscript received October 30, 2009; revised January 15, 2010; accepted March 07, 2010. Current version published May 19, 2010. Corresponding author: R. Jansen (e-mail: ron.jansen@el.utwente.nl).

Digital Object Identifier 10.1109/TMAG.2010.2046019

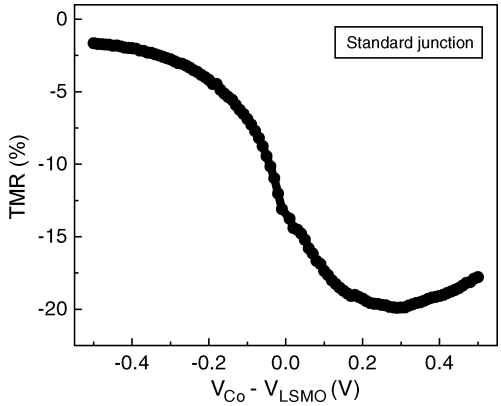

Fig. 1. TMR versus bias voltage for a standard LSMO/STO/Co magnetic tunnel junction at 10 K. Positive bias corresponds to electrons tunneling from the LSMO into the Co.

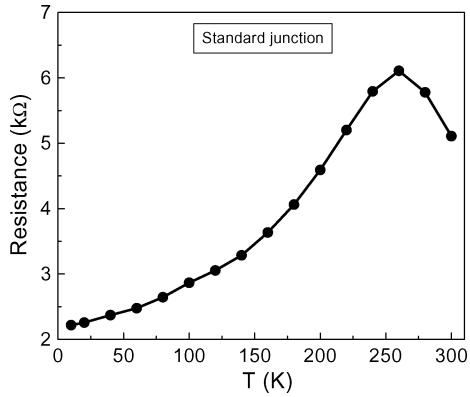

Fig. 2. Tunnel resistance versus temperature T for a standard LSMO/STO/Co magnetic tunnel junction with parallel magnetization configuration and +100 mV bias.

would lead to insulating behavior and loss of room-temperature ferromagnetism [9]. However, the process may lead to oxygen deficiency in the STO barrier (and in the underlying LSMO), which is known to affect the TMR of the structures [11]. Therefore, we also fabricated reference LSMO/STO/Co MTJs without the insertion of Co:TiO_2, but going through the same process as for the junction with Co:TiO_2. That is, these junctions were heated to 550°C at 9×10^{-5} mbar O_2 for the exact same time as is required for Co:TiO_2 deposition, but without depositing any Co:TiO_2. Such samples will be referred to as "reference junctions" and are expected to have the same oxygen content in the STO barrier as junctions with the Co:TiO_2.

Standard lithographic techniques are used to define junctions with circular active areas of 100 μm, as previously described [11]. DC current-voltage measurements were carried out in a four-point cross geometry. The TMR ratio is defined as $(R_{ap} - R_p)/R_p$, where R_{ap} and R_p are the resistances for antiparallel and parallel magnetization of the two electrodes, respectively. For all results presented here, the condition is satisfied that the junction resistance is at least 10 times the electrode square resistance [13].

III. Results and Discussion

Fig. 1 shows the variation of the TMR in the standard junction with bias voltage. The TMR is negative and asymmetric with respect to bias polarity, with a maximum TMR (absolute value) of about 20% at +300 mV, and vanishing TMR for high negative bias. These results are similar to that described in previous reports [11], [14]. The negative TMR is indicative of a negative tunneling spin polarization at the STO/Co interface [11], [14]. Fig. 2 shows the dependence of the resistance R_p of the standard junction on temperature (T). The resistance has a maximum at about 260 K and decreases at low temperature. Such temperature dependence was also observed in similar structures [11], [15], and is usually attributed to a reduced effective ordering temperature of the LSMO, accompanied by a metal-insulator transition, at the LSMO/STO interface [16].

Next, we studied the effect of Co:TiO_2 insertion on the MTJ characteristics, for junctions with, respectively, 0.5 and 1 nm

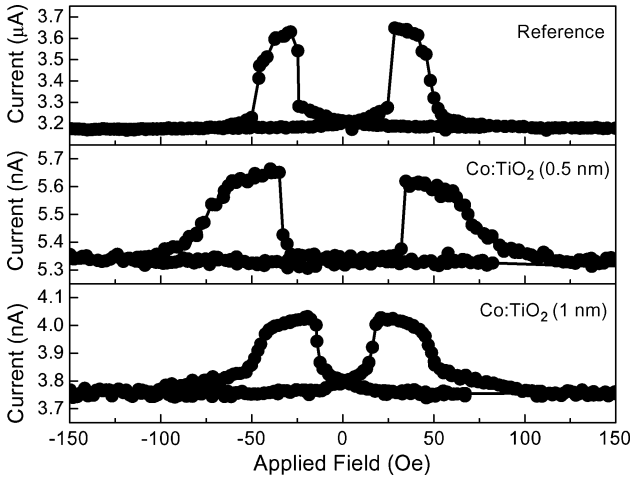

Fig. 3. Tunnel current versus applied magnetic field for the LSMO/STO/Co reference junction (top panel), a LSMO/STO/Co MTJ with 0.5 nm of Co:TiO_2 inserted at the STO/Co interface (middle panel), and a LSMO/STO/Co junction with 1.0 nm of Co:TiO_2 inserted at the STO/Co interface (bottom panel). All data taken at 10 K and for +100 mV bias.

Co:TiO_2 added between STO and Co. As shown in Fig. 3, a sizeable and negative TMR is observed for MTJs with 0.5 nm and 1 nm Co:TiO_2 inserted, and also for the reference junction (Co:TiO_2 deposition conditions mimicked but no Co:TiO_2 deposited). The TMR with 1 nm of Co:TiO_2 is slightly higher than with 0.5 nm, but the difference is only small and within the junction-to-junction variation of the TMR that is always present. Fig. 4 shows the bias dependence of the TMR. All junctions show an asymmetric bias dependence as for the standard junction, but with different TMR maxima: at +50 mV (+40 mV) for MTJs with 0.5 nm (1 nm) Co:TiO_2 inserted, and at +150 mV for the reference MTJ. Moreover, the TMR decreases rapidly with bias beyond the maximum, which is similar to that of LSMO/STO/Co junctions with oxygen deficient barriers [11]. In contrast, standard LSMO/STO/Co MTJs feature a broad maximum at +300 mV, with a slow decay of the TMR as the bias voltage is increased to higher positive values (see Fig. 1). For the junctions with Co:TiO_2, the magnitude of the TMR is significantly smaller as compared to that of the reference junction, and the TMR maximum becomes more narrow and shifts toward

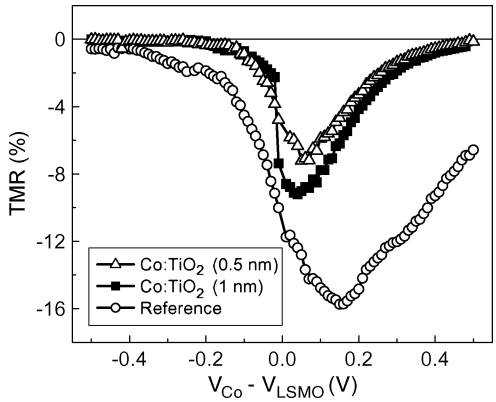

Fig. 4. TMR versus bias for the reference junction (circles), an MTJ with 0.5 nm of Co:TiO_2 inserted (triangles), and an MTJ with 1 nm of Co:TiO_2 inserted (squares). All data taken at 10 K.

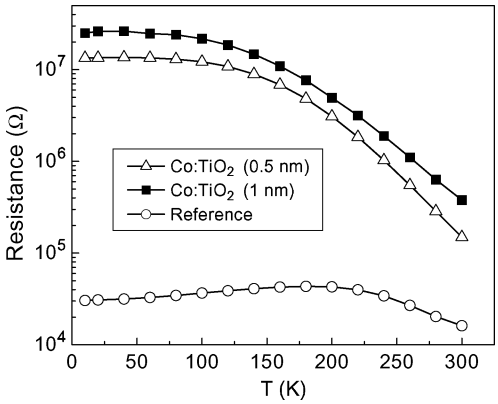

Fig. 5. Tunnel resistance versus temperature T with parallel magnetization configuration and +100 mV bias for the reference junction (circles), an MTJ with 0.5 nm of Co:TiO_2 inserted (triangles), and an MTJ with 1 nm of Co:TiO_2 inserted (squares).

zero bias. In addition, the junction resistance increases significantly upon insertion of the Co:TiO_2 by about 3 orders of magnitude at 10 K (see Fig. 5). We can exclude that this is due to the loss of oxygen in the tunnel barrier, as this should also be present for the reference junction. Comparing Fig. 2 and Fig. 5, we observe that the reference junction has an order of magnitude higher junction resistance in comparison with the standard MTJ. This difference is attributed to the change in oxygen content of the STO barrier due to heating of the structure to 550°C under oxygen poor conditions (9×10^{-5} mbar).

The strong increase of the junction resistance upon insertion of the Co:TiO_2, accompanied by a decrease of the TMR, provides some clues about the electronic and magnetic properties of the ultrathin Co:TiO_2 films. The higher junction resistance suggests an increased effective barrier thickness, which in turn points to insulating behavior of the inserted Co:TiO_2 layers. This is somewhat surprising since thicker films of Co:TiO_2 (180 nm), grown under comparable conditions (550°C at 7×10^{-5} mbar O_2) on STO substrates, exhibit impurity band conduction and are (semi-)conducting with a carrier density of 5×10^{18} cm^{-3} and mobility of about 20 cm^2/Vs at room temperature, and resistivity of the order of 0.1 Ωcm in the range between 10 and 300 K [9]. Hence, it was expected that the inserted Co:TiO_2 would become part of the electrode, rather than act as a tunnel barrier. An ultrathin film of only a nm thick (the unit cell of anatase Co:TiO_2 along the c-axis growth direction is 0.95 nm) may have different electronic properties and behave as a 2-D system which does not exhibit impurity band formation under these growth conditions. Alternatively, the film properties may be affected by the contact with the metal Co electrode on top of it. For instance, this may lead to carrier depletion in the Co:TiO_2, leaving it insulating.

If the Co:TiO_2 is indeed insulating and acts as an additional tunnel barrier, the tunneling electrons, and the associated negative TMR, originate from the Co metal at the interface with the Co:TiO_2. Since thick, more resistive Co:TiO_2 films grown under oxygen rich conditions are found to be paramagnetic at room temperature [9], the reduced TMR is also readily explained. For, the spin-polarized tunneling electrons originating from the Co would then experience spin-flip scattering by paramagnetic Co ions present in the Co:TiO_2 part of the tunnel barrier, which is known [17], [18] to reduce the TMR. Note that in previous work [11], the introduction of a pure TiO_2 layer (without Co doping) was found not to change the TMR, which indicates that the reduction of the TMR observed here is not due to changes in the Co metal electrode or its interface with the oxides, but due to the Co doping in the TiO_2.

IV. Conclusion

It is found that the TMR and junction resistance of epitaxial LSMO/STO/Co magnetic tunnel junctions changes significantly upon the insertion of ultrathin layers of Co:TiO_2 magnetic semiconductor at the STO/Co interface. The magnitude of the TMR decreases but remains negative, while the junction resistance increases strongly. This is consistent with an effectively insulating and paramagnetic Co:TiO_2 adding to the tunnel barrier, with the tunneling electrons originating mostly from the Co:TiO_2/Co interface, and experiencing spin-flip scattering by paramagnetic Co in the Co:TiO_2. Because the properties of the ultrathin Co:TiO_2 in contact with a metal Co electrode appear different from thicker films grown under similar conditions, the experiments unfortunately do not confirm or rule out a finite spin polarization of carriers in thicker Co:TiO_2 films.

Acknowledgment

This work was financially supported by the Netherlands Nanotechnology Network NANONED (supported by the Ministry of Economic Affairs).

References

[1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, "Zener model description of ferromagnetism in zinc-blende magnetic semiconductors," *Science*, vol. 287, p. 1019, 2000.

[2] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, "Donor impurity band exchange in dilute ferromagnetic oxides," *Nature. Mater.*, vol. 4, p. 173, 2005.

[3] J. W. Quilty, A. Shibata, J.-Y. Son, K. Takubo, T. Mizokawa, H. Toyosaki, T. Fukumura, and M. Kawasaki, "Signature of carrier-induced ferromagnetism in $Ti_{1-x}Co_xO_{2-\delta}$: Exchange interaction between high-spin Co^{2+} and the Ti 3d conduction band," *Phys. Rev. Lett.*, vol. 96, p. 027202, 2006.

[4] S. A. Chambers, "Ferromagnetism in doped thin-film oxide and nitride semiconductors and dielectrics," *Surf. Sci. Rep.*, vol. 61, p. 345, 2006.
[5] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, "Room-temperature ferromagnetism in transparent transition metal-doped titanium dioxide," *Science*, vol. 291, p. 854, 2001.
[6] H. Toyosaki, T. Fukumura, Y. Yamada, K. Nakajima, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, "Anomalous Hall effect governed by electron doping in a room-temperature transparent ferromagnetic semiconductor," *Nature. Mater.*, vol. 3, p. 221, 2004.
[7] R. Ramaneti, J. C. Lodder, and R. Jansen, "Anomalous Hall effect in anatase Co:TiO_2 ferromagnetic semiconductor," *Appl. Phys. Lett.*, vol. 91, p. 012502, 2007.
[8] Y. Hirose, T. Hitosugi, Y. Furubayashi, G. Kinoda, K. Inaba, T. Shimada, and T. Hasegawa, "Intrinsic Faraday spectra of ferromagnetic rutile $Ti_{1-x}Co_xO_{2-\delta}$," *Appl. Phys. Lett.*, vol. 88, p. 252508, 2006.
[9] R. Ramaneti, J. C. Lodder, and R. Jansen, "Kondo effect and impurity band conduction in Co:TiO_2 magnetic semiconductor," *Phys. Rev. B*, vol. 76, p. 195207, 2007.
[10] H. Toyosaki, T. Fukumura, K. Ueno, M. Nakano, and M. Kawasaki, "A ferromagnetic oxide semiconductor as spin injection electrode in magnetic tunnel junction," *Jpn. J. Appl. Phys.*, vol. 44, pt. 2, p. L896, 2005.
[11] I. J. Vera Marún, F. M. Postma, J. C. Lodder, and R. Jansen, "Tunneling magnetoresistance with positive and negative sign in $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/Co$ junctions," *Phys. Rev. B*, vol. 76, p. 064426, 2007.
[12] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank, and H. Rogalla, "Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide," *Appl. Phys. Lett.*, vol. 73, p. 2920, 1998.
[13] J. S. Moodera, L. R. Kinder, J. Nowak, P. LeClair, and R. Meservey, "Geometrically enhanced magnetoresistance in ferromagnet-insulator-ferromagnet tunnel junctions," *Appl. Phys. Lett.*, vol. 69, p. 708, 1996.
[14] J. M. De Teresa, A. Barthelemy, A. Fert, J. P. Contour, R. Lyonnet, F. Montaigne, P. Seneor, and A. Vaures, "Inverse tunnel magnetoresistance in $Co/SrTiO_3/La_{0,7}Sr_{0,3}MnO_3$: New ideas on spin-polarized tunneling," *Phys. Rev. Lett.*, vol. 82, p. 4288, 1999.
[15] J. Z. Sun, K. P. Roche, and S. S. P. Parkin, "Interface stability in hybrid metal-oxide magnetic trilayer junctions," *Phys. Rev. B*, vol. 61, p. 11244, 2000.
[16] M. Viret, M. Drouet, J. Nassar, J. P. Contour, C. Fermon, and A. Fert, "Low-field colossal magnetoresistance in manganite tunnel spin valves," *Europhys. Lett.*, vol. 39, p. 545, 1997.
[17] R. Jansen and J. S. Moodera, "Influence of barrier impurities on the magnetoresistance in ferromagnetic tunnel junctions," *J. Appl. Phys.*, vol. 83, p. 6682, 1998.
[18] R. Jansen and J. S. Moodera, "Magnetoresistance in doped magnetic tunnel junctions: Effect of spin scattering and impurity-assisted transport," *Phys. Rev. B*, vol. 61, p. 9047, 2000.