Effects of Li intercalation on magnetic properties of Co-doped rutile TiO_2

2004 J. Phys.: Condens. Matter 16 S5697

(http://iopscience.iop.org/0953-8984/16/48/030)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S5697–S5700 PII: S0953-8984(04)79440-0

Effects of Li intercalation on magnetic properties of Co-doped rutile TiO_2

Min Sik Park[1] **and B I Min**

Department of Physics and Electron Spin Science Center, Pohang University of Science and Technology, Pohang 790-784, Korea

E-mail: mspark@physics.postech.ac.kr

Received 15 April 2004
Published 19 November 2004
Online at stacks.iop.org/JPhysCM/16/S5697
doi:10.1088/0953-8984/16/48/030

Abstract

We have investigated the electronic structures and magnetic properties of Li-intercalated Co-doped rutile TiO_2. For non-intercalated $Ti_{0.9375}Co_{0.0625}O_2$, the half-metallic and low-spin ($\sim 0.94\ \mu_B$/Co) ground state is obtained. By Li intercalation, $Ti_{0.9375}Co_{0.0625}O_2$ becomes a paramagnetic insulator at the concentration of $Li/Ti = 0.067$. At the higher concentration of $Li/Ti = 0.133$, it becomes a paramagnetic metal. Hence, as in the transition metal doped anatase TiO_2 case, we expect that the magnetic and transport properties of Co-doped rutile TiO_2 can be controlled by an electric field.

1. Introduction

It has been reported that Co-doped anatase TiO_2 film ($Ti_{1-x}Co_xO_2$) shows ferromagnetism even above room temperature [1, 2]. Also, for Co-doped rutile TiO_2 thin films, room temperature ferromagnetism has been reported [3–5]. For the rutile case, the magnetic moment per Co atom was estimated to be about 0.31–1 μ_B, which suggests a low-spin ground state of Co atoms. However, still controversial is the issue of whether or not the ferromagnetism in these systems is an intrinsic diluted magnetic semiconductor (DMS) property [6]. As in the anatase TiO_2 phase, depending on the film growth conditions (mainly oxygen condition), the rutile TiO_2 sample becomes Co-substitutional or interstitial or of metal cluster form, which results in different magnetic properties.

Independently of the DMS project, Li intercalation in the anatase TiO_2 has been studied extensively. For anatase TiO_2, Li intercalation proceeds very efficiently at room temperature, but the anatase TiO_2 ages quickly at elevated temperature. On the contrary, for rutile TiO_2, only a small amount of Li can be accommodated at room temperature. But, at elevated temperature, the performance improves dramatically [7].

---

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

It is essential that the ferromagnetic property of the DMS can be controlled by an electric field or light. We have previously proposed a spintronic and electrochromic device made of Li-intercalated transition-metal-doped anatase TiO_2 which can be controlled by an electric field [8]. Since the rutile TiO_2 phase is more stable, it would be much better if one could fabricate a device based on the rutile TiO_2 phase. The rutile TiO_2 is a large band gap (∼3 eV) transparent semiconductor which attracts considerable technological interest, for applications such as catalysis, electrochromism and sensors. In particular, transparent ferromagnetic semiconductors have potential to serve as the integration of the electronic circuits and magnetic storage devices with display units [9].

We have investigated the Li intercalation effects on the electronic structure and magnetism in Co-doped rutile TiO_2. We also discuss the possibility for spintronic and electrochromic device application.

2. Computational method

To obtain the electronic band structure, we have used the linearized muffin-tin orbital (LMTO) band method in the local-spin-density approximation (LSDA). We have considered a supercell containing 16 fu in the primitive unit cell ($a = b = 9.1874, c = 5.9238$ Å). The explored configurations are $Ti_{0.9375}Co_{0.0625}O_2$ with intercalated Li concentrations of $Li/Ti = 0.067$ and 0.133. We considered the case that one Ti is substituted by one Co such that $Ti_{15}Co_1O_{32}$. A total of 64 empty spheres are employed at the interstitial sites to enhance the packing ratio in the LMTO band calculation. We have chosen the Li intercalation position among high symmetry empty spheres.

3. Results and discussion

We have first calculated the electronic structure of rutile TiO_2 without Co-doping and Li intercalation. The overall band structure of the present LMTO result is consistent with existing results [10], except that the energy gap is estimated to be a bit larger, ∼3.4 eV. The overestimated energy gap is due to the open structure of rutile TiO_2 and the minimal basis of the LMTO band method. The valence band top and the conduction band bottom correspond to mainly O 2p and Ti 3d states, respectively.

Next, we have studied the electronic structure of Co-doped rutile TiO_2 without Li intercalation. According to existing band results [11], the ferromagnetic state is the most stable phase for the substitutional case. Hence, in the present work, we considered only the ferromagnetic ground state. As shown in figure 1(A), we have obtained the half-metallic ground state for $Ti_{0.9375}Co_{0.0625}O_2$. The Fermi energy cuts the Co t_{2g} spin-down states[2]. The total spin magnetic moment is 1 μ_B, which comes mostly from Co ions, 0.94 μ_B. The calculated magnetic moment indicates the low-spin (LS) state of Co, which is consistent with experimental results [3, 4]. The characters of localized d states are mainly t_{2g}^3 spin-up and t_{2g}^2 spin-down states, seemingly corresponding to the nominal ionic valence of Co^{4+}.

Now, we have performed band calculations for the Li-intercalated cases. Similar to the case of the anatase phase [12], we have obtained the paramagnetic insulating ground state for $Li/Ti = 0.067$ (upper panels of figure 1(B)). Note that the Li intercalation plays a role in the n-type carrier doping. The insulating ground state results from the exact filling up of Co t_{2g}^2

[2] This result is different from the insulating ground state of [11]. This may be due to the different band structure method they used (pseudopotential method in the GGA approximation).

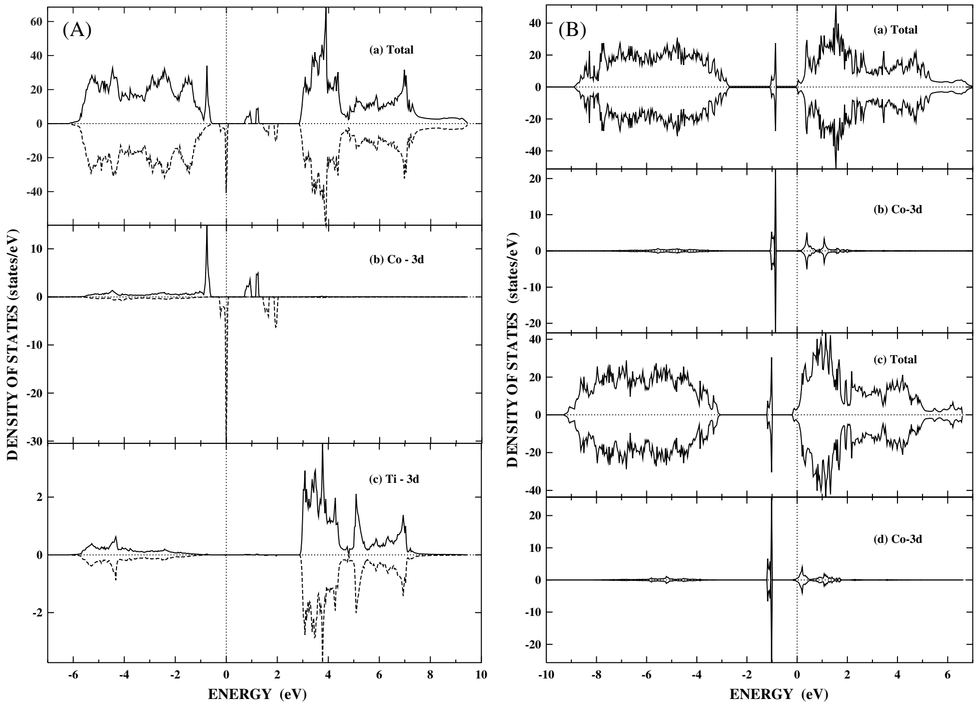

Figure 1. Total and projected local density of states of (A) $Ti_{0.9375}Co_{0.0625}O_2$, (B) Li-intercalated $Ti_{0.9375}Co_{0.0625}O_2$ ((a),(b): Li/Ti = 0.067, (c),(d): Li/Ti = 0.133).

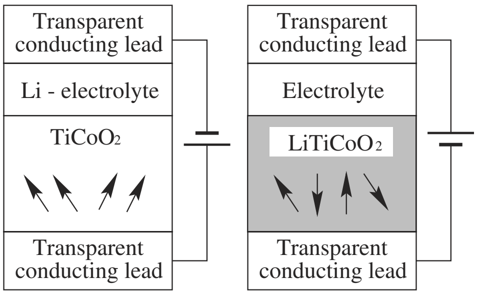

Figure 2. Schematic diagrams for an electric-field controlled non-volatile ferromagnetic and electrochromic multifunctional device. Left: Co-doped rutile TiO_2 which is ferromagnetic. Right: Li-intercalated Co-doped rutile TiO_2 which becomes non-magnetic.

spin-down states by Li intercalation. It is seen that the unoccupied Co e_g bands are shifted upward to be hybridized with the Ti 3d conduction band.

For higher Li concentration of $Li/Ti = 0.133$, a paramagnetic and metallic ground state is obtained, as shown in the lower panels of figure 1(B). Now the Co t_{2g} states are fully occupied, and the Fermi level cuts the Co e_g and Ti 3d states so that the conduction carriers consist of hybridized Co 3d and Ti 3d states. It thus reflects that the simple rigid band concept does not work, as in Li-intercalated Mn-doped anatase TiO_2 [13], that is, the extra carriers provided by the intercalated Li fill not only the empty Co 3d states but also the empty Ti 3d states.

This study suggests that the magnetic and transport properties of Co-doped rutile TiO_2 can be controlled by varying the Li-intercalation ratio. The Li intercalation can be controlled by an electric field. Hence we expect that the spintronic and electrochromic multifunctional device can be fabricated based on the Li-intercalated Co-doped rutile TiO_2, as shown in figure 2 [8]. However, to make a useful display device one needs to have a reasonable switching time. The current limit on the colouring process in the conventional Li-intercalated TiO_2 system is below 1 s. Since the drift velocity is proportional to inverse square root mass, a hundred times thinner film system is needed for Li-intercalated spintronic devices for them to have the same response time as electronic devices.

In conclusion, we have studied the electronic and magnetic properties of Li-intercalated Co-doped rutile TiO_2 and found that magnetic properties can be controlled by varying the Li-intercalation ratio.

Acknowledgments

This work was supported by the eSSC at POSTECH and in part by the KRF (KRF-2002-070-C00038).

References

[1] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
[2] Chambers S A *et al* 2001 *Appl. Phys. Lett.* **79** 3467
[3] Matsumoto Y, Takahashi R, Murakami M, Koida T, Fan X, Hasegawa T, Fukumura T, Kawasaki M, Koshihara S and Koinuma H 2001 *Japan. J. Appl. Phys.* **40** L1204
[4] Park W K, Ortega-Hertogs R J, Moodera J S, Punnoose A and Seehra M S 2002 *J. Appl. Phys.* **91** 8093
[5] Hong N H, Sakai J, Prellier W and Hassini A 2003 *Appl. Phys. Lett.* **83** 3129
[6] Kim J Y *et al* 2003 *Phys. Rev. Lett.* **90** 017401
[7] Koudriachova M V, Harrison N M and de Leeuw S W 2002 *Comput. Mater. Sci.* **24** 235
[8] Park M S and Min B I 2003 *Phys. Rev.* B **68** 033202
[9] Ohno H 2001 *Science* **291** 840
[10] Poumellec B, Durham P J and Guo G Y 1991 *J. Phys.: Condens. Matter* **3** 8195
[11] Geng W T and Kim K S 2003 *Phys. Rev.* B **68** 125203
[12] Park M S, Kwon S K and Min B I 2003 *Physica* B **328** 120
[13] Park M S, Yu U and Min B I 2004 *J. Magn. Magn. Mater.* **272–76** e1487