Mössbauer Study of $Ti_{1-x-y}Co_xFe_yO_2$

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Mössbauer spectra of $Ti_{1-x-y}Co_xFe_yO_2$ ($0.01\leq x$, $y\leq 0.05$) prepared with ^{57}Fe enriched iron have been taken at various temperatures ranging from 80 to 300 K. The Mössbauer spectrum of $Ti0.94Co_{0.03}Fe_{0.03}O_2$ consists of a ferromagnetic (six-Lorentzian), a paramagnetic phase (doublet) and armorphous phase over all temperature ranges. Isomer shifts indicate Fe^{3+} for the ferromagnetic phase and the paramagneic phase of $Ti_{1-x-y}Co_xFe_yO_2$ samples. It is noted that the magnetic hyperfine field of ferromagnetic phase had the value about 1.5 times as large as that of α-Fe. The XRD data for $Ti_{1-x-y}Co_xFe_yO_2$ showed mainly rutile phase with tetragonal structures without any segregation of Co and Fe into particulates within the instrumental resolution limit. The magnetic moment per (Co+Fe) atom in $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ under the applied field of 1 T was estimated to be about $0.332\mu_B$ which is ten times as large as that of $Ti_{0.97}Co_{0.03}O_2$, $0.024\mu_B$ per Co atom, suggesting a high spin configuration of Co and Fe ions.

Key words : magnetic semiconductors, rutile, low spin

I. Introduction

There has been much attention paid to diluted magnetic semiconductors (DMS) in the last decade, but the origin of ferromagnetism in semiconductor remains an issue of discussions [1, 2]. Recently, cobalt-doped anatase titanium dioxide, $Ti_{1-x}Co_xO_2$, thin films were reported to be ferromagnetic even above 400 K [1] with a 0.32/Co magnetic moment, and the magnetic ordering was explained in terms of the carrier-induced ferromagnetism [3] as in the III-V based DMS.

Chambers *et al.* [4, 5] reproduced the ferromagnetism of $Ti_{1-x}Co_xO_2$. It was reported that the moment is as high as 1.25/Co, and claimed that the ferromagnetism strongly depends on the oxygen deficiency [4, 5]. These results seem to show that the ferromagnetism in $Ti_{1-x}Co_xO_2$ is originated from the ordered low spin Co^{2+} state due to the charge carriers induced by oxygen defects. However, considering the fact that the ferromagnetism strongly depends on the growth condition [5], the possibility of the Co segregation cannot be excluded in this system [6]. Furthermore, it was reported that the anatase TiO_2 is a crystalline defected easily [7]. Rutile is known to be the most stable phase. Due to its scientific and practical importance, TiO_2 rutile has been the subject of many experimental and theoretical investigations.

The purpose of this study is to carry out Mössbauer, X-ray and magnetic-susceptibility measurements on rutile $Ti_{1-x-y}Co_xFe_yO_2$ ($0.01\leq x$, $y\leq 0.05$) to examine magnetic properties and separated contribution of the ferromagnetic and paramagnetic phases to the magnetization.

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II. Experiment

Synthesis of $Ti_{1-x-y}Co_xFe_yO_2$ sample was accomplished by the following direct-composition method. The starting materials were TiO_2, CoO, and Fe_2O_3 powders of 99.999, 99.999, and 99.9 % purities, respectively. Mixtures of the proper proportions of the elements sealed in evacuated quartz ampoule were heated at 900 °C for one day and then slowly cooled down to room temperature at a rate of 10 °C/h. In order to obtain single phase material, it was necessary to grind the sample after the first firing and to press the powders into pellets before annealing them for a second time in evacuated and sealed quartz ampoule. Mössbauer spectra were achieved using a conventional Mössbauer spectrometer of the electromechanical type with 50 mC_i $^{57}Co(Rh)$ source. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder and clamped between two thin boron nitride plates. Magnetic susceptibility measurements were performed with the vibrating sample magnetometer (VSM).

III. Results and Discussion

Figure 1 shows an X-ray diffraction patterns for $Ti_{1-x-y}Co_xFe_yO_2$ (x, y=0.03, 0.05) at room temperature. X-

ray-diffraction patterns of $Ti_{0.99}{}^{57}Fe_{0.01}O_2$ were obtained with Cu *Ka* radiation. The XRD data for $Ti_{1-x-y}Co_xFe_yO_2$ showed mainly rutile phase with tetragonal structures, $CoTiO_3$ and Fe_2TiO_5 second phase without any segregation of Co and Fe into particulates within the instrumental resolution limit. It is noteworthy that the trace of metallic Co or Fe phase was not observed from XRD patterns for rutile $Ti_{1-x-y}Co_xFe_yO_2$. This result is consistent with that of the XRD for the rutile phase $Ti_{1-x}Co_xO_2$ ($0.01 \le x \le 0.12$) films fabricated by Park *et al.* [8].

When the same concentration of Co and Fe was co-doped into TiO_2, $CoTiO_3$ second phase showed more obvious peaks than those of Fe_2TiO_5. It seems that in TiO_2 structure Co ions easily combined into $CoTiO_3$ because the free combining energy of Co ion is lower than that of Fe ions.

Hysteresis (*M-H*) curves measured at room temperature for the rutile $Ti_{0.97}Co_{0.03}O_2$, $Ti_{0.97}Fe_{0.03}O_2$, and $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ are shown in Fig. 2. Magnetization was highly enhanced when TiO_2 was co-doped by the same concentration of Co and Fe in comparison to the substitution of Co or Fe only into TiO_2. The magnetic hysteresis curves showed an obvious ferromagnetic behaviour. And the magnetic moment per (Co+Fe) atom in $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ under the applied field of 1 T was estimated to be about $0.332\mu_B$ which is ten times as large as that of $Ti_{0.97}Co_{0.03}O_2$, $0.024\mu_B$ per Co atom. The observed magnetic moment of the rutile $Ti_{1-x-y}Co_xFe_yO_2$ seems to suggest a high spin configuration of Co and Fe ions [8].

Figure 3 shows some of the Mössbauer spectra of

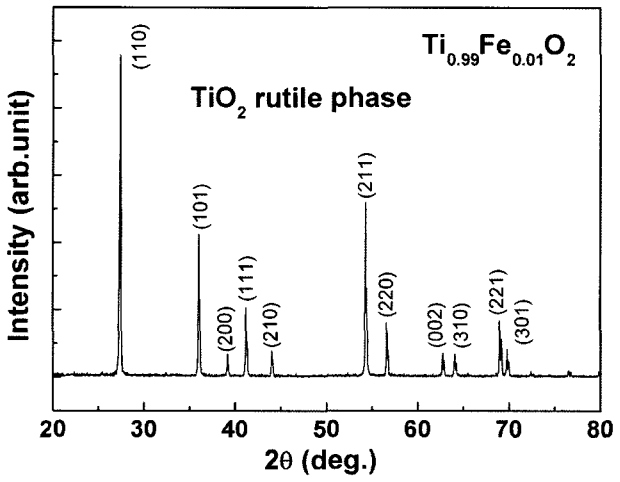

Fig. 1. XRD patterns of $Ti_{1-x-y}Co_xFe_yO_2$ (x, y=0.03,0.05) powder sample after annealing at 900 °C for 24 h.

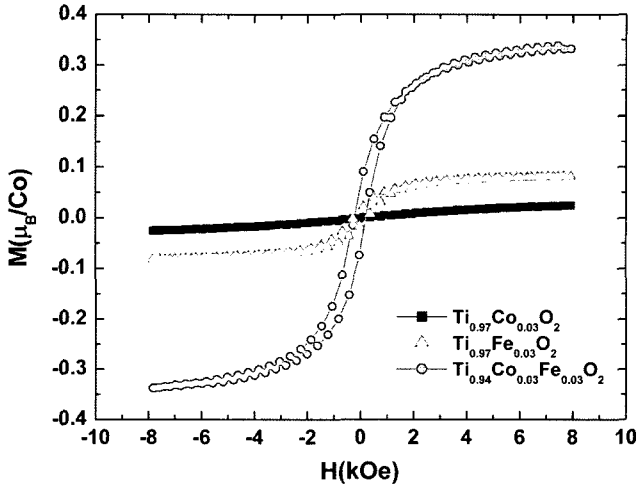

Fig. 2. Hysteresis curves of $Ti_{0.97}Co_{0.03}O_2$, $Ti_{0.97}Fe_{0.03}O_2$, and $Ti_{0.96}Co_{0.03}Fe_{0.03}O_2$ powder sample measured at room temperature.

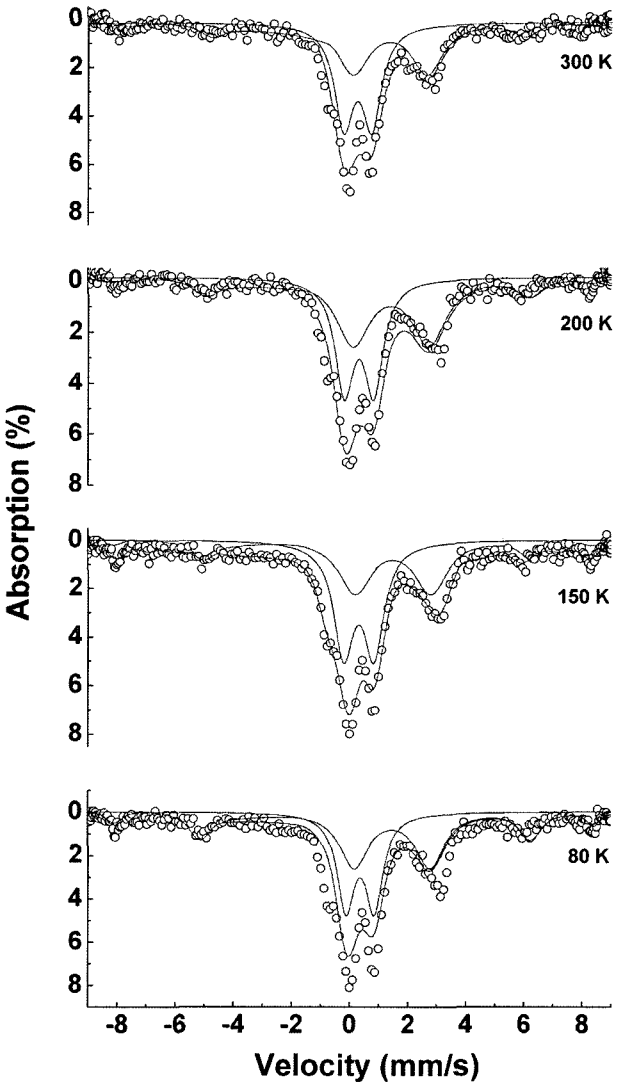

Fig. 3. Mössbauer spectra of $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ at various temperatures ranging from 80 to 300 K.

$Ti0.94Co_{0.03}Fe_{0.03}O_2$ at various absorber temperatures ranging from 80 to 300 K.

The Mössbauer spectrum of $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ consists of a ferromagnetic (six-Lorentzian), a paramagnetic (doublet) and armorphous phase (Fe_2TiO_5) over all temperature ranges. Using a least-squares computer program [9], the separation of the ferromagnetic phase (six-Lorentzian) and the paramagnetic phase (doublet) of the $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ Mössbauer spectrum was achieved. The widths that are assumed to be the same in respective subspectra and over all absorption areas of the spectra are independently varied as free parameters.

The magnetic hyperfine field of the ferromagnetic phase in the $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ is found to be 491 kOe, whereas that of α-Fe be 330 kOe at room temperature [10]. It is noted that the magnetic hyperfine fields of the ferromagnetic phase in the $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ had the value about 1.5 times as large as that of α-Fe. The isomer shift at room temperature for the ferromagnetic phase of $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ are found to be 0.22 mm/s relative to the Fe, which is consistent with the high spin Fe^{2+} charge state [11]. The isomer shift for the paramagnetic phase of $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ indicates Fe^{3+}. Those results indicate that the Fe impurities substituted into Ti atoms instead of the formation of iron clusters.

IV. Conclusions

We investigated the ferromagnetism observed in rutile phase $Ti_{1-x-y}Co_xFe_yO_2$ ($0.01 \le x$, $y \le 0.05$) using X-ray, VSM and Mössbauer spectroscopy. The XRD data for $Ti_{1-x-y}Co_xFe_yO_2$ showed mainly rutile phase with tetragonal structures, $CoTiO_3$ and Fe_2TiO_5 second phase without any segregation of Co and Fe into particulates within the instrumental resolution limit. The magnetic hysteresis curves showed an obvious ferromagnetic behaviour. And the magnetic moment per (Co+Fe) atom in $Ti_{0.94}Co_{0.03}Fe_{0.03}O_2$ under the applied field of 1 T was estimated to be about $0.332\mu_B$ which is ten times as large as that of $Ti_{0.97}Co_{0.03}O_2$, $0.024\mu_B$ per Co atom, suggesting a high spin configuration of Co and Fe ions.

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References

[1] Y. Matsumoto, M. Murakami, T. Shono, T. Hasagawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854(2001).
[2] Y. L. Soo *et al.*, Appl. Phys. Lett. **81**, 655(2002).
[3] J. König, H.-H. Lin, and A. H. MacDonald, Phys. Rev. Lett. **84**, 5628(2000).
[4] S. A. Chambers, S. Thevuthasan, R. F. C. Farrow. R. F. Marks, J. U.Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycki, D. L. Ederer, and U. Diebold, Appl. Phy. Lett. **79**, 3467(2001).
[5] S. A. Chambers, Materials Today April, 34(2002).
[6] S. R Shinde *et al.*, cond-mat/0203576.
[7] G. S. Herman, M. R. Sievers, and Y. Gao, Phys. Rev. Lett. **84**, 3354(2000); T. Uustare, J. Aarik, and M. Elango, Appl. Phys. Lett. **65**, 2551(1994).
[8] W. K. Park, R. J. Ortega-Hertogs, J. S. Moodera, A. Punnoose, and M. S. Seehra, J. Appl. Phys. **91**, 8093(2002).
[9] K. S. Baek, E. J. Hahn, and H. N. Ok, Phys. Rev. B **36**, 763(1987).
[10] H. M. Lee, S. J. Kim, I. B. Shim, and C. S. Kim, IEEE Tans. Magn. **39**, 2788(2003).
[11] J. M. Sullivan and S. C. Erwin, Phy. Rev. B **67**, 144415 (2003).