

Mössbauer Study of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$

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The rutile polycrystal $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ prepared with ^{57}Fe enriched iron have been studied by Mössbauer spectroscopy, X-ray diffraction and VSM. The Mössbauer spectrum of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ consists of a ferromagnetic and a paramagnetic phase over all temperature ranging from 4 to 300 K. Isomer shifts indicate Fe^{2+} for the ferromagnetic phase, but Fe^{3+} for the paramagnetic phase of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ sample. It is noted that the magnetic hyperfine field of ferromagnetic phase had the value about 1.48 times as large as that of $\alpha\text{-Fe}$. The XRD data for $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ showed a pure rutile phase with tetragonal structures without any segregation of Fe into particulates within the instrumental resolution limit. The magnetic hysteresis (M - H) curve at room temperature showed an obvious ferromagnetic behavior and the magnetic moment per Fe atom under the applied field of 1 T was estimated to be about $0.71\mu_B$, suggesting a low spin configuration of Fe ions.

Key words : magnetic semiconductors, rutile, ferromagnetism

I. Introduction

Diluted magnetic semiconductors (DMS) have been studied extensively in the last decade, because of their potential usage of both charge and spin degrees of freedom of carriers in the electronic devices, namely, the spintronics. However, the origin of ferromagnetism in semiconductor remains an issue of discussions [1, 2]. Recently, cobalt-doped anatase titanium dioxide, $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$, thin films were reported to be ferromagnetic even above 400 K [1] with a $0.32 \mu_B/\text{Co}$ 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 $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$. It was reported that the moment is as high as $1.25 \mu_B/\text{Co}$, and claimed that the ferromagnetism strongly depends on the oxygen deficiency [4, 5]. These results seem to show that the ferromagnetism in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ 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]. For those reasons, it is important to clarify the origin of ferromagnetism in the oxide-based high T_c DMS. 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 for DMS, TiO_2 rutile has been the subject of many experimental and theoretical investigations.

The purpose of this study is to carry out Mössbauer spectroscopy, X-ray diffraction and magnetic-susceptibility measurements on rutile $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ to examine magnetic properties and separated contribution of the ferromagnetic and paramagnetic phases to the magnetization.

II. Experiment

Synthesis of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ sample was accomplished by the following direct-composition method. The starting materials were Fe_2O_3 and TiO_2 powders of 99.995 and 99.999 % 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 $10^\circ\text{C}/\text{h}$. 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 recorded using a conventional Mössbauer spectrometer of the electromechanical type with $30 \text{ mCi } ^{57}\text{Co}(\text{Rh})$ source. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder and

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clamped between two thin boron nitride plates. Magnetic susceptibility measurements were performed with the vibrating sample magnetometer (VSM).

III. Results and Discussion

Fig. 1 shows an X-ray diffraction patterns for $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ at room temperature. X-ray diffraction patterns of $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ were obtained with Cu $K\alpha$ radiation. A slow scanning speed of 0.25° advance in $2\theta/\text{min}$ was used in order to optimize resolution of the closely spaced reflections. The XRD data for $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ showed a pure rutile phase with tetragonal structures, without any segregation of Fe into particulates within the instrumental resolution limit. It is noteworthy that the trace of metallic Fe phase was not observed from XRD patterns for rutile $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$. This result is consistent with that of the

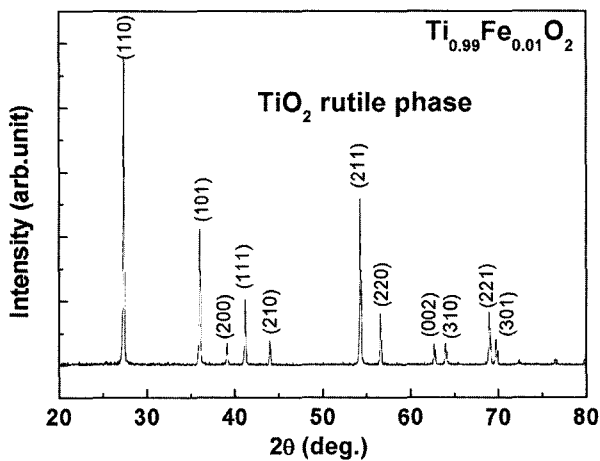


Fig. 1. XRD patterns of $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ powder sample after annealing at 900°C for 24 h.

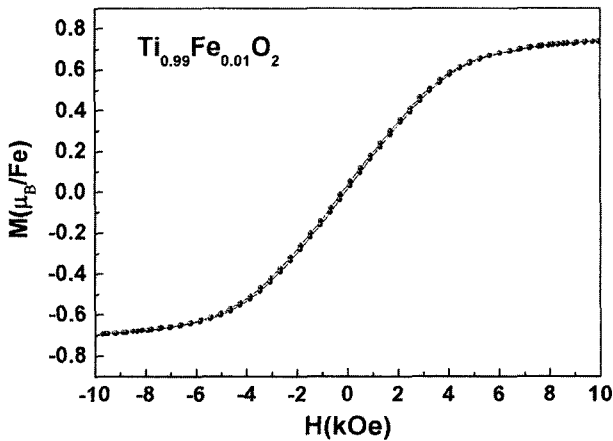


Fig. 2. Hysteresis curve of the $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ powder sample measured at room temperature.

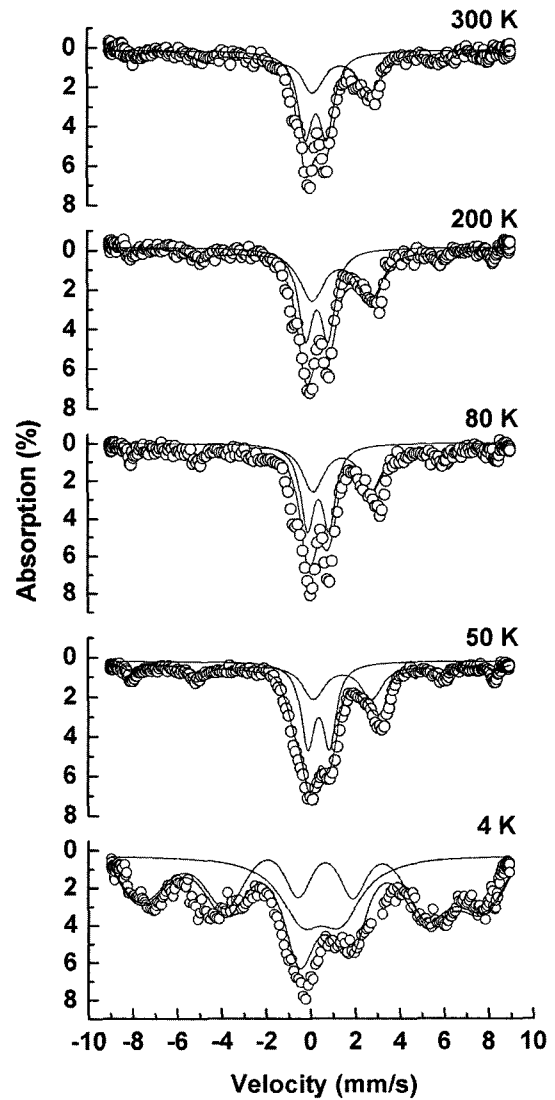


Fig. 3. Mössbauer spectra of $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ at various temperatures ranging from 4 to 300 K.

XRD for the rutile phase $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ ($0.01 \leq x \leq 0.12$) films fabricated by Park *et al.* [8]. A typical hysteresis (M - H) curve measured at room temperature for the rutile $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ is shown in Fig. 2. The magnetic hysteresis curve at room temperature showed an obvious ferromagnetic behavior and the magnetic moment per Fe atom under the applied field of 1 T was estimated to be about $0.71 \mu_B$, proved by Mössbauer experiment. The observed magnetic moment of the rutile $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ seems to suggest a low spin configuration of Fe ions [8]. The coercive field is estimated to be about 40 Oe for the rutile $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$.

It seems to be that the coercive field results from the magnetic correlation between iron particles instead of that of iron clusters. Fig. 3 shows some of the Mössbauer spectra of $\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_2$ at various absorber temperatures

ranging from 4 to 300 K. The Mössbauer spectrum of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ consists of a ferromagnetic (six-Lorentzian) and a paramagnetic phase (doublet) over all temperature ranges. Using the least-squares computer program [9], the separation of the ferromagnetic phase (six-Lorentzian) and the paramagnetic phase (doublet) of the $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ Mössbauer spectrum was achieved. The line 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 Curie temperature was determined to be 1,150 K. The Curie temperature of the system is expected to be different from that of Fe metal ($T_C=1,043$ K). The magnetic hyperfine field of the ferromagnetic phase in the $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ is found to be 500 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 $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ had the value about 1.48 times as large as that of α -Fe. The isomer shift at room temperature for the ferromagnetic phase of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ are found to be 0.93 mm/s relative to the Fe, which is consistent with the low spin Fe^{2+} charge state [11]. However, the isomer shift for the paramagnetic phase of $\text{Ti}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ indicates Fe^{3+} . Those results indicate that the Fe impurities substituted into Ti atoms instead of the formation of iron clusters.

Acknowledgements

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