

Magnetic Properties of Fe-Doped Rutile

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Ball-milling method was applied to dissolve Fe into titanium dioxide (TiO₂). X-ray diffraction indicated the starting anatase changed to a rutile-type structure with oxygen deficiency after ball milling. Transmission electron microscopy and X-ray absorption experiments were conducted to examine the possible existence of magnetic impurities in the ball-milled powders after they were leached in HCl solutions. Temperature dependence of the resistivity shows semiconducting behavior and the magnetic hysteresis loops at 5 and 300 K exhibit ferromagnetic characteristics. Fe-doped TiO₂ films were also prepared by pulsed laser deposition. The magnetic properties of the films are discussed.

KEY WORDS: magnetic semiconductor; rutile, TiO₂; ball milling; pulsed laser deposition.

Magnetic semiconductors have received considerable attention because of their combined magnetic and transport properties. The spin degree of freedom provides an added dimension to semiconductor-based electronic transport. These materials will play an important role in the technology and applications of spin-electronics [1]. However, the Curie temperature T_c of most of the magnetic semiconductors reported so far is much lower than room temperature. For example, the Mn-doped GaAs, a very interesting and carefully studied magnetic semiconductor, has the $T_c \sim 110$ K [2]. Raising T_c to room temperature or above is very important for any practical applications.

Recently, it has been reported that room temperature magnetic semiconductors were found by doping Co into anatase TiO₂ [3] or ZnO [4] films, and incorporating Mn by solid-state reaction into CdGeP₂ [5].

Here, we report doping Fe into rutile by ball milling and pulsed laser deposition. The magnetic and transport properties of Fe-doped rutile are discussed.

The solubility of Fe in rutile is small, ranging from 3% at 1623 K to 1% at 1073 K [6]. To enhance the solubility of Fe in rutile, ball-milling method was applied to diffuse more Fe into the titanium dioxide. The mixture of pure titanium dioxide (anatase) and Fe powder with 95:5 ratio (weight) was sealed in hardened steel chamber and ball milled in a SPEX 8000 Mixer/Mill for 25 h. To remove possible Fe or its oxide particles in the ball-milled powders, 1 g of ball-milled powders were put into 80 mL of 7% HCl solution and stirred 12 h continuously. TiO₂ does not react with HCl, while Fe and its oxides dissolve in the acid. The acid leach was carried out four times and with higher HCl concentrations. The powders were finally cleaned by distilled water and dried in a glove box. The structure characterization was carried out using a Philips Analytical X-ray diffraction system (XRD), JEOL 2010 transmission electron microscope (TEM) with EDAX X-ray energy dispersive spectrum (EDS), and JSM 5410 scanning electron microscope (SEM) with EDS. X-ray absorption investigation was conducted at the Canadian Light Source. The transport and magnetic properties of the samples were measured with a physical property measurement system (PPMS) and superconducting quantum interference device (SQUID).

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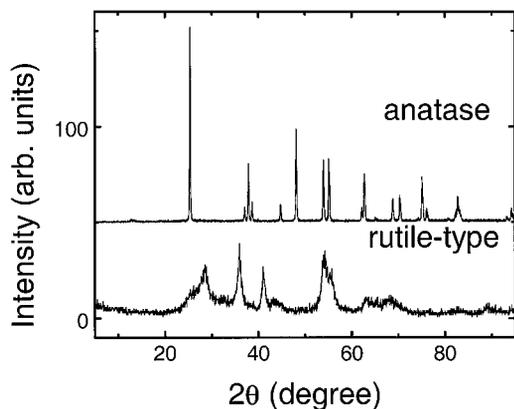


Fig. 1. X-ray diffraction patterns for the original and ball-milled samples. The positions of the XRD peaks for the milled sample fit the expected spectrum of a rutile-type structure.

Figure 1 is the X-ray diffraction spectra for the original and milled samples. The positions of the XRD peaks for the milled sample fit the expected spectrum of a rutile-type structure with oxygen deficiency. This means that there is a phase transformation from anatase to rutile during ball milling. This is reasonable for rutile is the most stable structure among the three types of titanium dioxide, rutile, anatase, and brookite. From the XRD patterns, one cannot see any peak from iron, iron oxide, or any known Ti—Fe—O compound. The peaks become broad for the milled sample compared to the original powders. This means that after milling the size of the particles decreases rapidly.

The particles are of irregular shape and their size is between 20 and 100 nm. This kind of wide size distribution is often observed in powders prepared by ball-milling method. To determine the composition of the particles, EDS analysis was carried out to analyze a large number of particles. The diameter of the electron beam in our TEM can reach 2.5 nm, so we can determine the composition of each individual particle. All particles analyzed contain three elements (Fe, Ti, and O), and the Fe content is in the range of 5–13 wt.%. No systematic variation of the Fe concentration with particle size was found. The accuracy of the Fe concentration was also hindered by the instrument limitation of TEM. It should be pointed out that no pure Fe particle, its oxide, or iron-rich Ti—Fe—O that may be magnetic has been observed with TEM and EDS. The SEM with EDS was used to determine the average content of Fe and it was about 10.5 wt.%. This means that in addition to the Fe powders introduced at the beginning of the milling, some Fe was

transferred from the hardened steel vial/ball and diffused into TiO₂.

Preliminary analysis of the X-ray absorption data suggests the local structure of the Fe is of an ordered structure. The valence of Fe is very similar to that of Fe in FeTiO₃ reference compound, as compared by the absorption edge energies, although the local structures of the two are different. There is no immediately obvious evidence of existence of bcc iron or any other form of metallic iron content in the sample. A pre-edge feature near the metallic iron absorption edge in both spectra of FeTiO₃ reference and the sample complicates the quantitative negative conclusion. However, the data suggest an upper limit of any possible metallic iron at <5% of the total iron content in the sample.

The resistivity of the ball-milled sample increases exponentially with the decrease of temperature, exhibiting the characteristics of a semiconductor. The original TiO₂ powder is insulating. Figure 2 shows the magnetic hysteresis loops at 5 and 300 K for the ball-milled sample. Both loops show ferromagnetic characteristics and the coercivities are 490 and 50 Oe, respectively. There is a rapid increase of magnetization with increasing field at first. However, after the applied field is greater than 1 T, the increase of magnetization is very slow at 300 K while there is still a steady increase of magnetization at 5 K. The magnetization is 5.8 and 14.8 emu/g at 300 and 5 K, respectively, and there is no evidence of saturation of magnetization at 5 K even in a field of 9 T. The difference in magnetization curves between 300 and 5 K suggests there is a distribution of the Curie temperature. Some of the Fe-doped sample orders ferromagnetically at temperatures lower than room temperature because of the

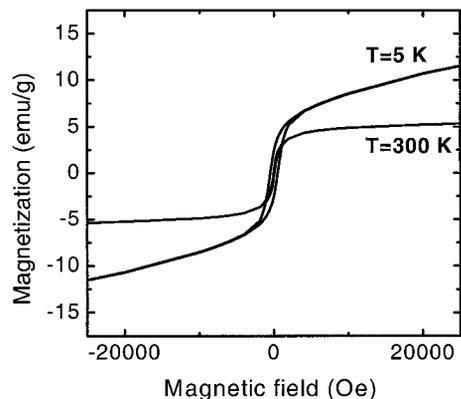


Fig. 2. Magnetization versus field of ball-milled Fe-doped TiO₂.

variation in the doping level. At room temperature, only a portion of the sample contributes to the magnetization, which has a relatively low saturation value. At low temperature, more particles become magnetically ordered and the saturation magnetization increases.

There are two possible origins of the observed ferromagnetism in our ball-milled sample that should be considered. The first possibility is the existence of impurities like pure Fe particle, ferromagnetic iron oxide such as Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, or Fe-rich Fe—Ti—O. The second origin is Fe-doped rutile. We discount the first possible origin: firstly, any iron and its ferromagnetic oxide particles should have, in principle, been dissolved in HCl solution according to their chemistry; secondly, the X-ray diffraction indicated there was no such suspected impurities in the sample; thirdly, EDS analysis of a large number of particles did not find pure iron, its oxides, or Fe-rich Fe—Ti—O. The X-ray absorption results also suggest that there is not enough metallic iron impurities that could give rise to the observed magnetization. We think that the Fe doping in rutile is the plausible cause for the observed ferromagnetism in our sample.

Fe-doped rutile TiO_2 films were also prepared by pulsed laser deposition. The nominal composition of the targets was $\text{Fe}_{0.06}\text{Ti}_{0.94}\text{O}_2$. Depositions were done in a variety of atmospheres including vacuum and flowing Ar, O_2 , and H_2 . Postdeposition annealing was also carried out at different temperatures and atmosphere. A sample deposited at 300°C and subsequently annealed shows the best ferromagnetic properties at room temperature. The magnetization is shown as a function of applied field in Fig. 3.

In conclusion, we report the magnetic properties of Fe-doped rutile-type TiO_2 prepared by ball milling as well as by pulsed laser deposition. The magnetic characteristics suggest it is possible that these systems exhibit ferromagnetism at room temperature.

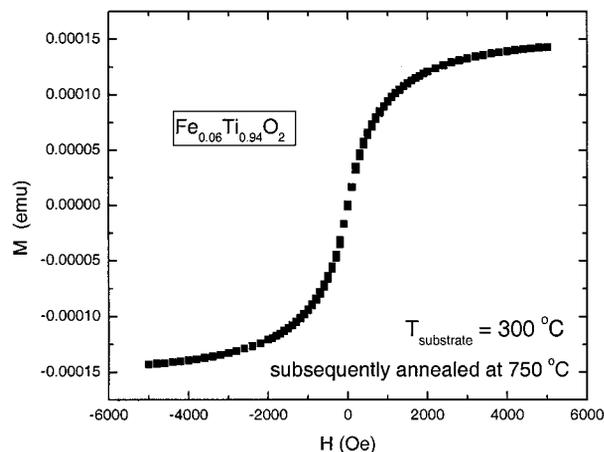


Fig. 3. Magnetization versus applied field of a PLD film $\text{Fe}_{0.06}\text{Ti}_{0.94}\text{O}_2$ measured at room temperature.

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