

# Ferromagnetism of V and Fe Doped TiO<sub>2</sub> by Mechanical Milling

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Vanadium and iron doped rutile-type TiO<sub>2</sub> were prepared by mechanical milling (MM) at 500 rpm for 15 minutes from the powder mixtures of  $(x/2)V_2O_5 (V_2O_3) + (1-x)TiO_2$  and  $(x/2)\gamma-Fe_2O_3 + (1-x)TiO_2$ . XRD results showed the particle diameter  $d$  was about 10 nm for host TiO<sub>2</sub> powder by MM, and MM for the mixtures of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and  $\gamma-Fe_2O_3$ /TiO<sub>2</sub> realizes the V and Fe doped TiO<sub>2</sub> nano powders. Magnetization measurement showed that  $M$  at 300 K and 5 kOe was  $0.002(x=0.1)-0.004(x=0.05) \mu_B/V$ -ion for V<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>,  $0.024(x=0.05)-0.035(x=0.1) \mu_B/Fe$ -ion for Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>. Thus the diluted ferro-magnetic semiconductor powder of (V,Fe)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> with  $T_C$  higher than room temperature were successfully prepared by MM. But all of them were insulators, and not half metallic.

Key Words : Rutile TiO<sub>2</sub>, Dilute magnetic semiconductor, Mechanical alloying, Ferromagnetism, Magnetization

## 1. INTRODUCTION

Transition metal (TM) doped diluted magnetic semiconductor (DMS) (TM)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> has been studied to realize the new room temperature ferromagnetic materials for the spintronics devices [1]. The II-VI semiconductor of TiO<sub>2</sub> has a wide band gap of about 3.4 eV and a stable rutile-type crystal structure. It is transparent in visible region and becomes a good conductor by doping of metallic elements. Therefore transition metal-doped TiO<sub>2</sub> has been expected as the multifunctional material with magnetic, conductive and optical properties.

The *ab initio* calculations for the (TM)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> (TM= Mn, Fe, Co, Ni and Cu) were performed [2], and it was concluded that magnetic moments appeared for Mn, Fe and Co, but not for Ni and Cu. For example, the magnetic moment of Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> ( $x=0.06-0.25$ ) were  $1.7-2.7 \mu_B/Fe$ , which depended on the oxygen vacancies and not on  $x$ .

For the V-doped rutile TiO<sub>2</sub>, magnetism and electronic structure were theoretically investigated [3], and stable ferromagnetic state was found. The electronic structure was half-metallic by local density approximation (LDA), but it was semiconductive by LDA+Hubbard coefficient. The calculated V magnetic moment were 0.79 and 0.92  $\mu_B$  for LDA- and LDA+H-result, respectively.

In the present study, TM-dopings into TiO<sub>2</sub> were tried by mechanical milling (MM) using planetary ball mill from oxide precursors of TM and TiO<sub>2</sub>.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL

Commercial TM oxides (V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>,  $\alpha-Fe_2O_3$ ,  $\gamma-Fe_2O_3$ , CoO, Co<sub>3</sub>O<sub>4</sub>, and NiO) and rutile-TiO<sub>2</sub>, were used as the precursor for (TM)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> samples. The powder mixtures of TM-oxide and ZnO with the value of  $x$  between 0.05 and 0.20 were milled by the planetary ball mill (Fritch Pulverisette-7, Germany) with WC vials. The inner diameter and volume of each vial were 40 mm and 45 cm<sup>3</sup>, respectively, and the WC

balls with 15 mm diameter were used as the grinding media. About 2 g of powder mixture was the starting material. The volume ratio of balls and powder was about 50 : 1. Rotation speed and rotating time were kept at 500 rpm and 15 min, respectively.

The composition of milled powders were characterized by the CuK  $\alpha$  X-ray powder diffraction (XRD). The superconducting quantum interference device (SQUID) were used for the magnetization measurements.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Mechanical milling effect for TiO<sub>2</sub> powder

XRD patterns of TiO<sub>2</sub> powder milled by WC vial and balls showed that of rutile TiO<sub>2</sub> with the lattice parameters of  $a = 0.4594$  nm and  $c = 0.29589$  nm [3]. The partial phase of anatase in the TiO<sub>2</sub> precursor disappeared after MM. By MM, diffraction peak intensity decreased as the rotation speed increased between 100 rpm and 500 rpm. At 600 rpm, XRD patterns were same as that of 500 rpm.

From the half width of each diffraction peak, the mean crystallographic correlation length  $d$  of TiO<sub>2</sub> powder was estimated by Sherrer's formula. The rpm-dependence of TiO<sub>2</sub> particle diameter is shown in Fig. 1. The  $d$  of commercial TiO<sub>2</sub> powder was about 50 nm, and it monotonously decreased as the rotation speed of ball mill increased. At 500 rpm,  $d$  decreased to about 10 nm. Above 500 rpm,  $d$  was nearly constant at 10 nm.

From the above results, it could be assumed that the mechanical milling produced TiO<sub>2</sub> nano-particles or partially amorphous TiO<sub>2</sub>. Unchanged crystal symmetry of rutile type showed the possibility of transition metal doping into TiO<sub>2</sub> by the mechanical milling method.

Since the above results were reproducible for the samples with different milling time above 15 minutes, we adopted the shortest milling time of 15 minutes in the following sample preparations. Increasing temperature of milling vial and balls was evident for the rotation speed

higher than 400 rpm. Therefore we could not neglect the heating effect for the following experimental results.

We tried to dope V, Cr, Fe, Co and Ni, but only V and Fe showed the possibility of doping into TiO<sub>2</sub> by mechanical milling. Therefore, here we introduce the experimental results of V and Fe doped TiO<sub>2</sub>.

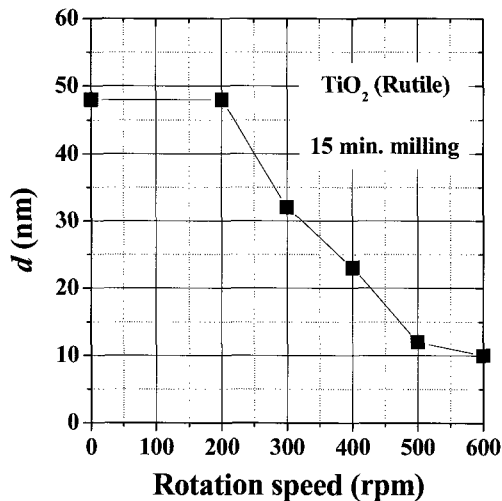


Fig. 1 Rotation speed-dependence of particle diameter of rutile-TiO<sub>2</sub> powder milled for 15 minutes.

### 3.2 V doping into rutile TiO<sub>2</sub>

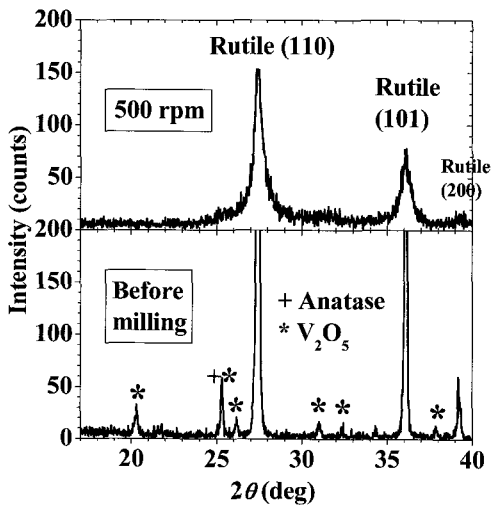


Fig. 2 XRD patterns of (0.025V<sub>2</sub>O<sub>5</sub> + 0.95TiO<sub>2</sub>) before and after milling at 500 rpm for 15 minutes.

The XRD results for V<sub>0.05</sub>Ti<sub>0.95</sub>O<sub>2</sub>, which means the mixed and milled powder of 0.025V<sub>2</sub>O<sub>5</sub> + 0.95TiO<sub>2</sub>, are shown in Fig. 2. Miller indices are shown only for rutile TiO<sub>2</sub> [4]. The asterisks show diffraction peaks of orthorhombic V<sub>2</sub>O<sub>5</sub>, which has the lattice parameters of  $a = 0.4383$  nm,  $b = 0.3571$  nm and  $c = 1.1544$  nm [5]. A peak with cross-mark shows that of anatase TiO<sub>2</sub> [6]. Comparing the profile of the sample before milling (0 rpm), the milled samples at 500 rpm for 15 minutes only show the broadened diffraction peaks of rutile TiO<sub>2</sub> with

$d$  of 9-10 nm and no diffraction peak of V<sub>2</sub>O<sub>5</sub> and anatase TiO<sub>2</sub>. Therefore we assume that the V-doping into TiO<sub>2</sub> is realized by MM at 500 rpm for 15 min.

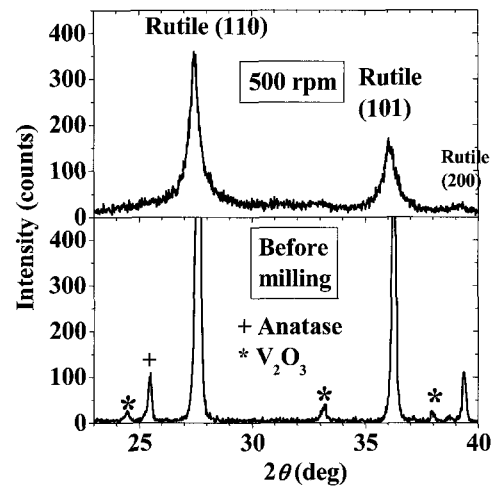


Fig. 3 XRD patterns of (0.05V<sub>2</sub>O<sub>3</sub> + 0.9TiO<sub>2</sub>) before and after milling at 500 rpm for 15 minutes.

The XRD results for the mixed and milled powder of 0.025V<sub>2</sub>O<sub>3</sub> + 0.95TiO<sub>2</sub>, are shown in Fig. 3. Miller indices are shown only for rutile TiO<sub>2</sub>, and the asterisks show diffraction peaks of V<sub>2</sub>O<sub>3</sub>, which has the lattice parameters of  $a = 0.49515$  nm and  $c = 1.4003$  nm [7]. A peak with cross-mark shows that of anatase TiO<sub>2</sub>. Since the milled samples at 500 rpm for 15 minutes only show the broadened diffraction peaks of rutile TiO<sub>2</sub>, the V-doping into TiO<sub>2</sub> can be also assumed for this system.

### 3.3 Fe doping into rutileTiO<sub>2</sub>

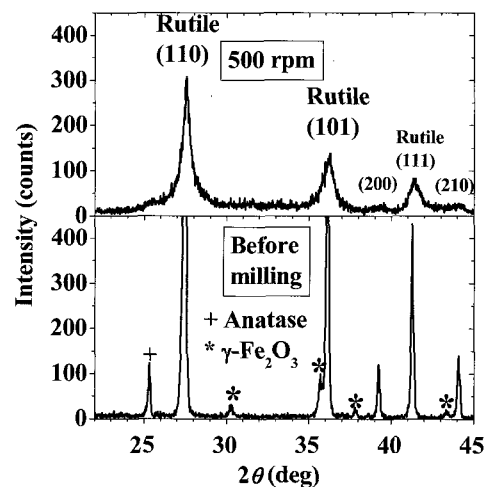


Fig. 4 XRD patterns of 0.025(γ-Fe<sub>2</sub>O<sub>3</sub>)+0.95TiO<sub>2</sub> before and after milling at 500 rpm for 15 minutes.

The XRD results for nominal Fe<sub>0.05</sub>Ti<sub>0.95</sub>O<sub>2</sub>, which means the mixed and milled powder of 0.025(γ-Fe<sub>2</sub>O<sub>3</sub>) + 0.95TiO<sub>2</sub>, are shown in Fig. 4. Comparing the profile of the sample before milling (0 rpm), the milled samples

show only broadened diffraction peaks of pure  $\text{TiO}_2$  with the size of 9-10 nm. After milling at 500 rpm for 15 min., the diffraction peaks of cubic  $\gamma\text{-Fe}_2\text{O}_3$ , which has the lattice parameters of  $a = 0.83539$  nm [8], and that of anatase  $\text{TiO}_2$  disappeared

### 3.4 Magnetic property of V-doped rutile $\text{TiO}_2$

Temperature dependences of magnetization were shown in Fig. 5 for  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ . The  $x = 0.05$  and 0.1 sample from  $[(x/2)\text{V}_2\text{O}_5 + (1-x)\text{TiO}_2]$  show weakly ferromagnetic behavior with Curie temperature  $T_c$  far above 300 K, but paramagnetic behaviors appeared below 100 K. Meanwhile the  $x = 0.1$  sample from  $[0.05\text{V}_2\text{O}_3 + 0.9\text{TiO}_2]$  shows a paramagnetic behavior below 300 K.

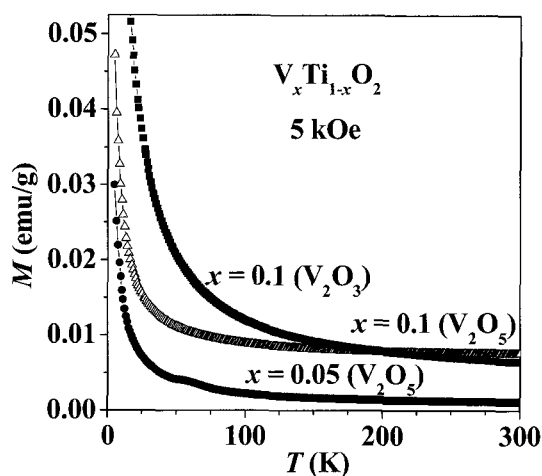


Fig. 5 Thermo-magnetic curves of  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$  between 5 and 300 K under 5 kOe.

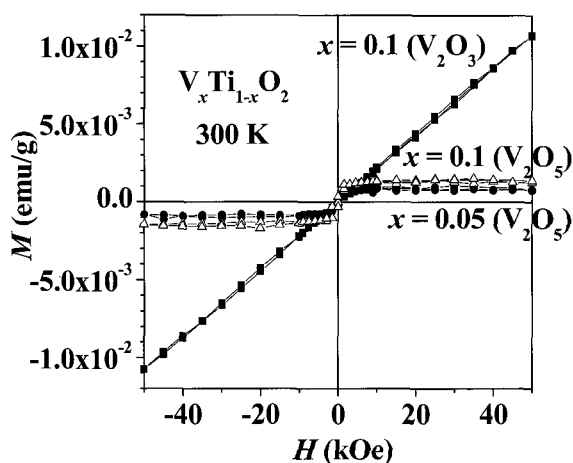


Fig. 6 Magnetization curves of  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$  at 300 K.

Field dependent magnetizations of  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$  are shown in Fig. 6, where the magnetization values were taken per unit weight of each sample. The saturation magnetization  $M_s$  of milled  $[(x/2)\text{V}_2\text{O}_5 + (1-x)\text{TiO}_2]$  at 300 K are about  $0.86 \times 10^{-3}$  and  $1.4 \times 10^{-3}$  emu/g for  $x=0.05$  and 0.1 sample, respectively. They correspond to  $0.0041 \mu_B/\text{V-ion}$  for  $x=0.05$  and  $0.0021 \mu_B/\text{V-ion}$  for

$x=0.1$ . Meanwhile  $M$  of milled  $[0.05\text{V}_2\text{O}_3 + 0.9\text{TiO}_2]$  is completely paramagnetic at 300 K.

In the previous work, room temperature ferromagnetism of  $\text{V}_{0.05}\text{Ti}_{0.95}\text{O}_2$  was only observed for anatase  $\text{TiO}_2$  thin films [9], where the  $M_s$  was  $3\text{-}5 \mu_B/\text{V-ion}$  at 300 K. Extremely small  $M_s$  in the present  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$  system might be due to the coexistence of amorphous V-clusters with paramagnetic property as shown in Fig. 5.

### 3.5 Magnetic property of Fe doped rutile $\text{TiO}_2$

Temperature dependences of magnetization were shown in Fig. 7 for  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ . The  $x = 0.05$  and 0.1 samples also show the ferromagnetic behaviors with Curie temperature  $T_c$  far above 300 K. Paramagnetic behaviors due to impurities appeared below about 50 K.

Field dependent magnetizations of  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$  are shown in Fig. 8. The saturation magnetization  $M_s$  are about 0.084 and 0.24 emu/g for  $x=0.05$  and 0.1 sample, respectively. They correspond to  $0.024 \mu_B/\text{Fe-ion}$  for  $x=0.05$  and  $0.035 \mu_B/\text{Fe-ion}$  for  $x=0.1$ .

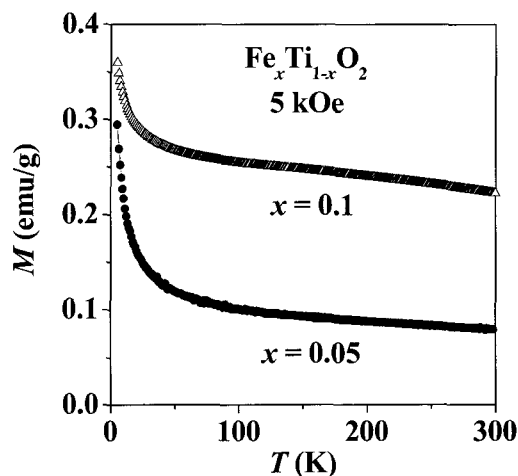


Fig. 7 Thermo-magnetic curves of  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$  between 5 and 300 K under 5 kOe.

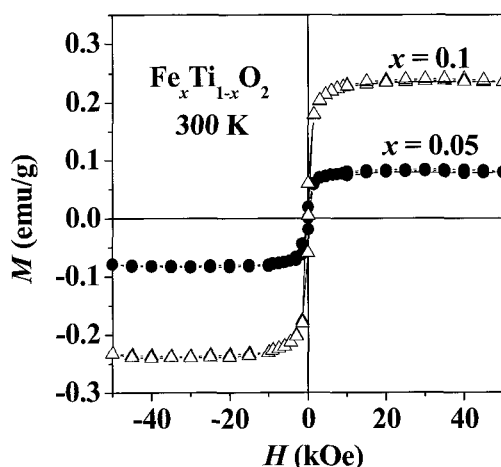


Fig. 8 Magnetization curves of  $\text{V}_x\text{Ti}_{1-x}\text{O}_2$  at 300 K.

Room temperature ferromagnetism were reported for Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> thin film [10,11] and bulk [12, 13]. However room temperature ferromagnetism by secondary phase such as Fe<sub>3</sub>O<sub>4</sub> [14],  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [15] or absence of ferromagnetism [16] were also reported for thin film and bulk system.

In the Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2-y</sub> ( $x=0.02, 0.06$  and  $0.08$ ) reduced thin films [10], the saturation magnetization per Fe ion were 2.3-2.4  $\mu_B$  and independent of  $x$ . In the Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> thin film of  $x=0.126$ , small  $M_s$  of 0.051  $\mu_B/Fe$  was detected [11]. In the bulk Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> system, the  $M_s$  of 0.4-0.7  $\mu_B/Fe$  were observed [12, 13].

Relatively small  $M_s$  in our Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> system may be due to the distortion or deficiency in the crystal lattice under instantly high pressure and high temperature by mechanical milling process.

#### CONCLUSION

V and Fe could be doped into rutile-TiO<sub>2</sub> by the mechanical milling of the mixed powders of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>5</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Milled V<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> powders prepared from  $[(x/2)V_2O_5+(1-x)TiO_2]$  ( $x=0.05$  and  $0.1$ ) showed the weak ferromagnetism at 300 K, but the V<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>2</sub> prepared from  $[0.5V_2O_5+0.9TiO_2]$  was completely paramagnetic below 300 K. The Fe<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> powders from  $[(x/2)\gamma-Fe_2O_3+(1-x)TiO_2]$  ( $x = 0.05$  and  $0.1$ ) showed visible room temperature ferromagnetism.

Thus the diluted ferro-magnetic semiconductor powder of (V,Fe)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> with  $T_c$  higher than room temperature were successfully prepared by mechanical milling. But all of them were insulators, and not half metallic. It is a problem to identify the V- and Fe-doping into ZnO by transmitted electron microscopy (TEM) and energy dispersive x-ray analysis (EDX). These experimental results shall be reported in the near future.

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