Magnetization of V Doped ZnO and TiO$_2$ by Mechanical Milling

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V doped ZnO and TiO$_2$ were obtained by mechanical milling by planetary ball mill from oxide precursor of V$_2$O$_5$. Both of V$_{0.05}$Zn$_{0.95}$O and V$_{0.2}$Ti$_{0.8}$O$_2$ milled powders showed room temperature ferromagnetism with high Curie temperature, which suggested the possibility of diluted magnetic semiconductor in this system.
Key Words : Dilute magnetic semiconductor, Oxide, Mechanical alloying, Ferromagnetism, Magnetization

1. INTRODUCTION

Diluted magnetic semiconductor (DMS) [1] has been paid much attention by many authors because of the room temperature ferromagnetism by a few or a few tenth % of magnetic ions of transition metal or rare earth metal. Therefore DMS is one of the candidates for the basic material of spintronics devise such as magnetic random access memory (MRAM) *etc.*

The origin of ferromagnetism in DMS has been considered to be due to the carrier-induced Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction or double exchange interaction [1]. However the *ab initio* calculations [2] suggested for ferromagnetism of ZnO-based DMS that 3*d* transition metal atoms showed the ferromagnetic order without carrier doping. In the Al co-doped ZnO:Co DMS bulk films prepared by plasma-enhanced metal-organic chemical vapor deposition (MOCVD), the Curie temperature higher than room temperature was observed [3]. However, in Co$_{0.25}$Zn$_{0.75}$O films by pulsed laser deposition (PLD) [4], Co clusters led to room temperature ferromagnetism in inhomogeneous films. Meanwhile, the PLD *films* of V$_x$Zn$_{1-x}$O (*x* = 0.05 - 0.15) also showed ferromagnetism at room temperature [5]. Though there were V-clusters in that system, the V-clusters could not show ferromagnetism like as the Co-clusters. Therefore the room temperature ferromagnetism of DMS is more reliable for V$_x$Zn$_{1-x}$O than for Co$_x$Zn$_{1-x}$O system.

In the present study, the production method of V$_x$Zn$_{1-x}$O and V$_x$Ti$_{1-x}$O$_2$ *powders* was investigated by mechanical milling using planetary ball mill, since the rutile-TiO$_2$ is another candidate of basic material of ferromagnetic DMS [6].

2. SAMPLE PREPARATION AND EXPERIMENTAL

Commercial Wurtzite-ZnO, Rutile-TiO$_2$ and V$_2$O$_5$ were used as the precursor for V$_x$Zn$_{1-x}$O or V$_x$Ti$_{1-x}$O$_2$ samples. The powder mixtures of V$_2$O$_5$ and ZnO or TiO$_2$ were milled by the planetary ball mill (Fritch Pulverisette-7, Germany) with Cr-steel vials. The inner diameter and volume of each vial were 40 mm and 45 cm^3, respectively, and the Cr-steel balls with 15 mm diameter were used as the grinding media. About 2 g of powder mixture was the starting material which contained 0.11 g and 0.44 g of V$_2$O$_5$-dopant for the case

of V$_{0.05}$Zn$_{0.95}$O and V$_{0.2}$Ti$_{0.8}$O$_2$, respectively. The volume ratio of balls and powder was about 30 : 1. Rotation speed was varied from 100 rpm to 700 rpm, and rotating time was kept as 30 min.

The composition of milled powders were characterized by the Cu*K* α x-ray powder diffraction (XRD). Vibrating sample magnetometer (VSM) and the superconducting quantum interference devise (SQUID) were used for the magnetization measurements.

3. EXPERIMENTAL RESULTS AND DISCUSSION
3.1 Mechanical milling effect for ZnO powder

XRD patterns of milled ZnO powder are shown in Fig. 1. Each pattern showed that of hexagonal wurtzeit ZnO with the lattice parameters of *a* = 0.3253 nm and *c* = 0.5213 nm [7]. By mechanical milling, diffraction peak intensity decreased as the rotational speed increased between 100 rpm and 500 rpm. Above 500 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 ZnO powder was estimated by Sherrer's formula. The rpm-dependence of ZnO particle diameter is shown in Fig. 2. The *d* of commercial ZnO powder was above 100 nm, and it rapidly decreased by mechanical milling. Between 100
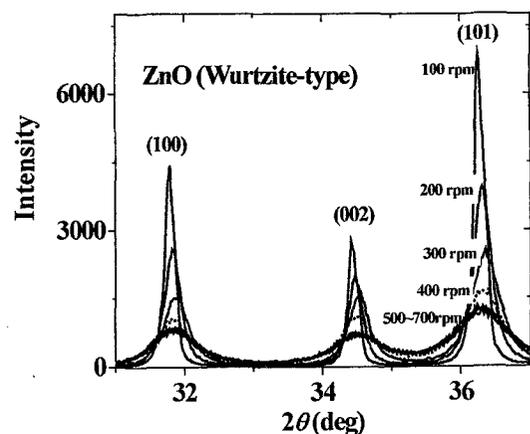
Fig. 1 XRD patterns of wurtzeit ZnO powder milled by 100 ~ 700 rpm.
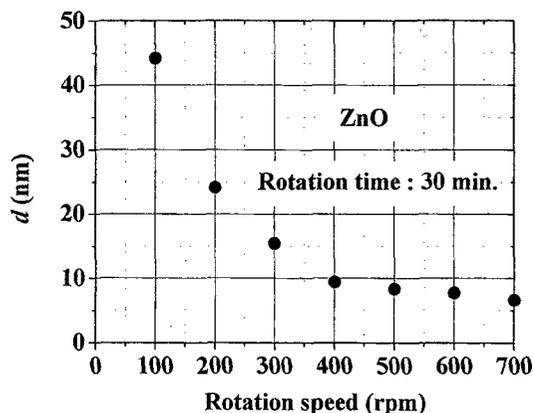
Fig. 2 Rpm-dependence of particle diameter milled ZnO powder.

rpm and 400 rpm, d changed from 45 nm to 10 nm. Above 500 rpm, d was nearly constant at 6 ~ 8 nm.

From the above results, it could be assumed that the mechanical milling produced nano-particles or partially amorphous phase of ZnO. Unchanged crystal structure of wurtzite type showed the possibility of transition metal doping into ZnO by the mechanical milling method.

Since the above results were reproducible for the samples with different milling time above 30 minutes, we adopted the shortest milling time of 30 minutes in the following sample preparations. Rising temperature of milling vial was evident for the rotation speed higher than 400 rpm. Therefore we could not neglect the heating effect for the following experimental results. For the precursor wetted by ethanol, the milling effect became significantly weak. Therefore we used dried powder of precursors in all sample preparations, though the moisture effect was not estimated quantitatively.

3.2 Doped system of $V_{0.05}Zn_{0.95}O$

The XRD results for $V_{0.05}Zn_{0.95}O$ are shown in Fig. 3. Comparing the profile of the sample without milling (0 rpm), the milled samples show the broadening of diffraction peaks as same as those of ZnO. Even at 300 rpm, the diffraction peaks of orthorhombic V_2O_5, which
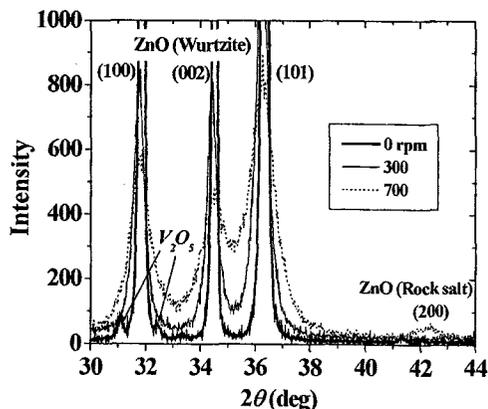
Fig. 3 XRD patterns of $V_{0.05}Zn_{0.95}O$.

has the lattice parameters of $a = 0.4383$ nm, $b = 0.3571$ nm and $c = 1.1544$ nm [8], disappeared and the wurtzite pattern scarcely shifted to lower diffraction angle of 2θ.

Since the ion radius of V^{2+} is larger than that of Zn^{2+} when the coordination number is six, we think that the V-doping into ZnO can be realized by the mechanical milling even at 300 rpm.

As shown in Fig. 3, a very broadened diffraction peak of rock salt type ZnO was observed only for the 700 rpm sample. Since the rock salt type ZnO is known as the high temperature and high pressure phase with the lattice parameter of $a = 0.4278$ nm [9], it was probably due to the pressure and heating up by collision and friction among balls and vial wall in the ball mill for 700 rpm.

Magnetization curves of $V_{0.05}Zn_{0.95}O$ at 300 K are shown in Figs. 4 and 5. Here it should be noted that the left vertical axis is for the 700 rpm sample, and the right vertical axis is for the 300 rpm sample. The saturation magnetization M_s is very large as about 8 emu/g for the 700 rpm sample. Meanwhile the $M(H)$ of 300 rpm sample
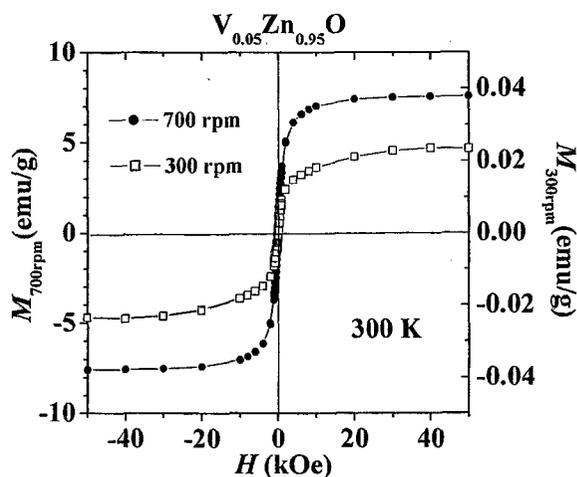
Fig. 4 Magnetization curves of $V_{0.05}Zn_{0.95}O$ at 300 K.
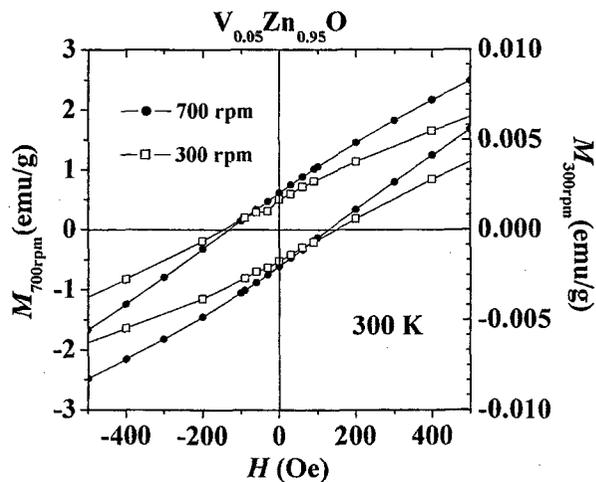
Fig. 5 Magnetization curves of $V_{0.05}Zn_{0.95}O$ at 300 K in low field region.

shows weakly ferromagnetic behavior. The difference in M_s of 300 rpm and 700 rpm sample may be due to larger doping rate of V^{2+} in the 700 rpm sample than that in 300 rpm sample.

However the $M(H)$-curve of 300 rpm sample shows nearly same coercive force H_c of about 150 Oe as for the 700 rpm sample. Therefore, from the point of view about magnetic anisotropy, 300 rpm sample has a magnetically equivalent property to that of 700 rpm sample. As for the contamination effect by magnetic impurities from the milling vial and balls, it was elucidated that the contribution to the M_s of $V_{0.05}Zn_{0.95}O$ was less than a few %.
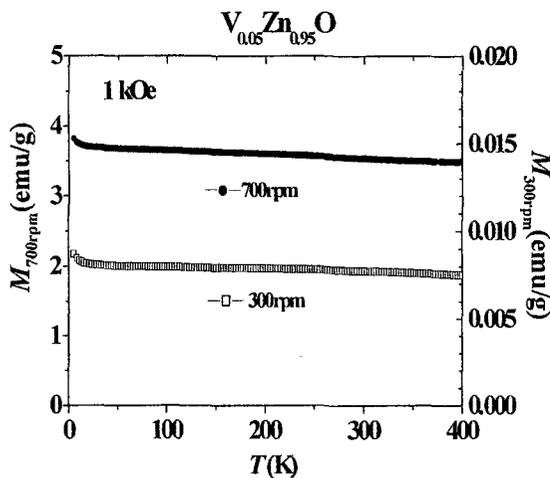
Fig. 6 Temperature dependent magnetization of $V_{0.05}Zn_{0.95}O$ between 77 K and 400 K under magnetic field of 1 kOe.

In Fig. 6, temperature dependence of magnetization are shown for $V_{0.05}Zn_{0.95}O$. Both of 300 rpm and 700 rpm sample have nearly constant magnetization under the field of 1 kOe between 5 K and 400 K. This result means that the present $V_{0.05}Zn_{0.95}O$ system is a room temperature ferromagnet with very high Curie temperature T_c which is far larger than 400 K.

3.3 Doped system of $V_{0.2}Ti_{0.8}O_2$

The XRD results for $V_{0.2}Ti_{0.8}O_2$ are shown in Fig. 7. Comparing the profile of the sample without milling (0 rpm), the milled samples show the broadening of diffraction peaks of rutile TiO_2 with the lattice parameters of $a = 0.4594$ nm and $c = 0.29589$nm [10]. At 700 rpm, the diffraction peaks of V_2O_5 [8] disappeared and the diffraction pattern of rutile TiO_2 scarcely shifted to higher diffraction angle of 2θ. If V^{4+} is successfully doped, the shortening of lattice parameter should occur due to the smaller ion radius of V^{4+} than that of Ti^{4+} for the coordination number of six. Therefore we think that the V-doping into TiO_2 is also realized by the mechanical milling at 700 rpm. We prepared only a 700 rpm sample because of the the maximum M_s of 700 rpm sample in $V_{0.05}Zn_{0.95}$ O.

Magnetization curves of $V_{0.2}Ti_{0.8}O_2$ at 300 K are shown in Figs. 8 and 9. The saturation magnetization M_s
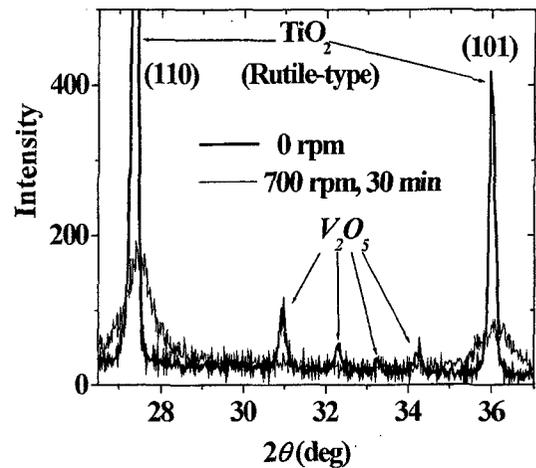
Fig. 7 XRD patterns of mechanically milled $V_{0.2}Ti_{0.8}O_2$ powder.
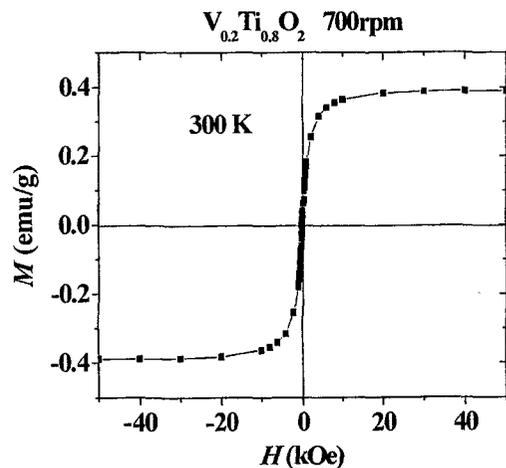
Fig. 8 Magnetization curve of mechanically milled $V_{0.2}Ti_{0.8}O_2$ at 300 K.
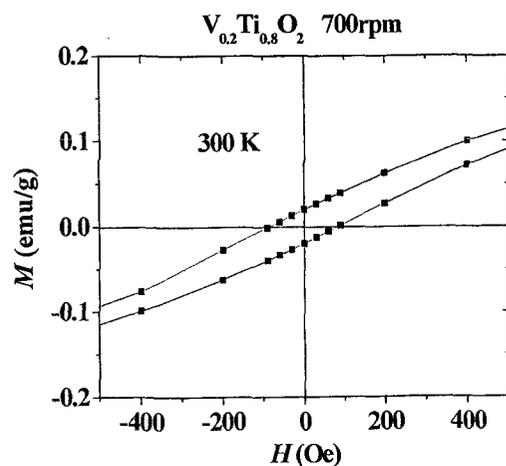
Fig. 9 Magnetization curve of $V_{0.2}Ti_{0.8}O_2$ at 300 K in low field region.

is about 0.4 emu/g and the coercive force H_c is about 100 Oe for the 700 rpm sample. Both of M_s- and H_c-value are smaller than those of 700 rpm sample of $V_{0.05}Zn_{0.95}O$. It may be due to the smaller spin polarization of $3d$ electrons in $V_{0.2}Ti_{0.8}O_2$ than that in $V_{0.05}Zn_{0.95}O$.

In Fig. 10, temperature dependence of magnetization is shown for $V_{0.2}Ti_{0.8}O_2$. The 700 rpm sample has nearly constant magnetization under the field of 1 kOe between 5 K and 400 K. Relatively steep change of M below 20 K may be due to the magnetic impurity from the precursor of TiO_2 and V_2O_5, or Cr-steel vial and balls. This result also means that the present $V_{0.2}Ti_{0.8}O_2$ system is a room temperature ferromagnet with very high Curie temperature T_c which is far larger than 400 K as same as $V_{0.05}Zn_{0.95}O$ system.

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Fig. 10 Temperature dependence of magnetization of $V_{0.2}Ti_{0.8}O_2$ between 77 K and 400 K under magnetic field of 1 kOe.

CONCLUSION

The V^{2+} doped ZnO and V^{4+} doped TiO₂ were obtained by mechanical milling by planetary ball mill from oxide precursor of V_2O_5. Both of the $V_{0.05}Zn_{0.95}O$ and $V_{0.2}Ti_{0.8}O_2$ milled powders were elucidated as the room temperature ferromagnet with Curie temperature higher than 400 K. These results show the possibility of ferromagnetic DMS in these system. Saturation magnetization M_s was very large in 700 rpm sample of $V_{0.05}Zn_{0.95}O$. This result shows that the optimum doping of V^{2+} is realized in this system, being expected as a candidate of application to spintronics device.

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