Transactions of the Materials Research Society of Japan 32[4] 1215-1218 (2007)

Magnetization of Transition Metal Doped ZnO by Mechanical Milling

Yoshihide Kimishima, Kensuke Irie, Masahiro Matsuo, Masatomo Uehara and Koki Homma

Department of Physics, Faculty of Engineering, Graduate School of Yokohama National University,
Tokiwadai 79-5, Hodogaya, Yokohama 240-8501, Japan
Fax: +81-45-339-4182, e-mail: kimi@ynu.ac.jp

Possibilities of V and Fe doping into ZnO by mechanical milling of the mixed powders of ZnO and V_2O_5 or γ-Fe_2O_3 were suggested from the results of x-ray powder diffraction measurements. Milled powders of nominal $V_{0.05}Zn_{0.95}O$ did not show the ferromagnetism, but nominal $Fe_{0.1}Zn_{0.9}O$ powders showed room temperature ferromagnetism, suggesting that this system is the diluted magnetic semiconductor.
Key Words : Dilute magnetic semiconductor, Oxide, Mechanical alloying, Ferromagnetism, Magnetization

1. INTRODUCTION

Transition metal (TM) doped diluted magnetic semiconductor (DMS) $(TM)_xZn_{1-x}O$ has been studied by many authors to realize the new room temperature ferromagnetic materials for the spintronics devises [1]. The II-VI semiconductor of ZnO has a wide band gap of about 3.4 eV and a stable wurtzite crystal structure. It is transparent in visible region and becomes a good conductor by doping of metallic elements. Therefore transition metal-doped ZnO has been expected as the multifunctional material with magnetic, conductive and optical properties.

The *ab initio* calculations for the properties of ZnO, doped with the 3*d* transition metals, were performed by Korringa-Kohn-Rostoker (KKR) Green function method [2], and it was concluded that the V, Cr, Fe, Co and Ni in ZnO stabilized the ferromagnetic state with extremely high Curie temperature T_c by the carrier mediated double exchange mechanism.

In the present study, TM-dopings into ZnO were tried by mechanical milling using planetary ball mill from oxide precursors of TM and Zn.

2. SAMPLE PREPARATION AND EXPERIMENTAL

Commercial TM oxides (V_2O_5, VO_2, Cr_2O_3, CrO_2, Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3, CoO, Co_3O_4, and NiO) and Wurtzite-ZnO, were used as the precursor for $(TM)_xZn_{1-x}O$ 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^3, 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_α x-ray powder diffraction (XRD). 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 ZnO powder milled by WC vial and balls 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 [3]. By mechanical milling, 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.

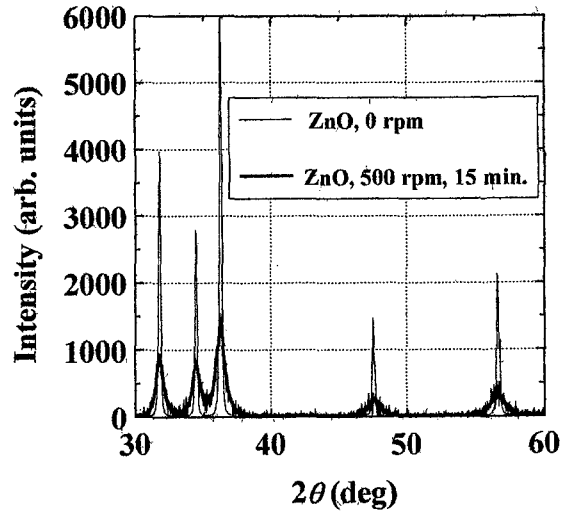

Fig. 1 XRD patterns of wurtzeit ZnO powder before and after milling at 500 rpm for 15 minutes.

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 about 45 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 ZnO nano-particles or

partially amorphous ZnO. Unchanged crystal symmetry of wurtzite type showed the possibility of transition metal doping into ZnO by the mechanical milling method.

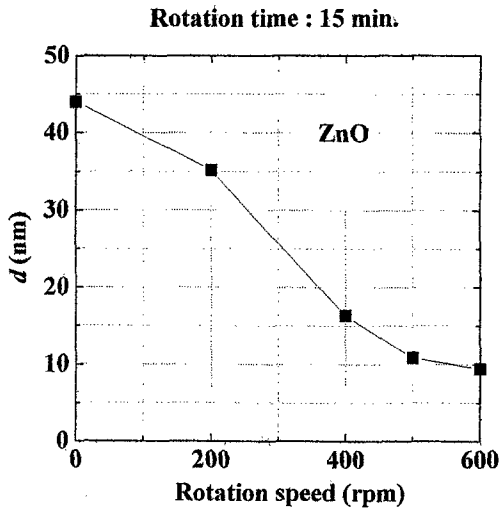

Fig. 2 Rotation speed-dependence of particle diameter of ZnO powder milled for 15 minutes.

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 ZnO by mechanical milling. Therefore, here we introduce the experimental results of V and Fe doped ZnO.

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

The XRD results for nominal $V_{0.05}Zn_{0.95}O$, which means the mixed and milled powder of $0.025V_2O_5$ + 0.95ZnO, are shown in Fig. 3. The asterisks show diffraction peaks of orthorhombic V_2O_5, which has the lattice parameters of a = 0.4383 nm, b = 0.3571 nm and c = 1.1544 nm [4]. 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 pure ZnO with d of 9-10 nm and no diffraction peak of V_2O_5.

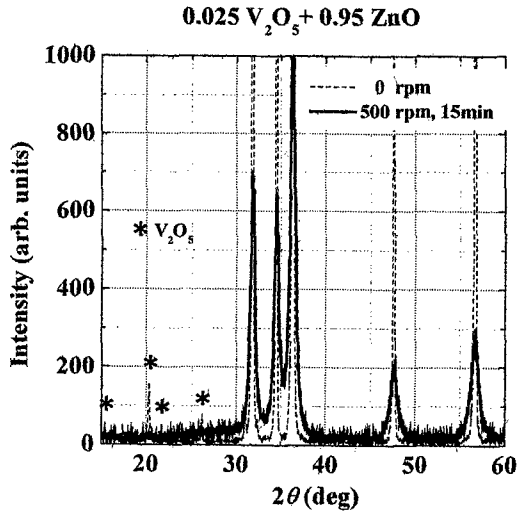

Fig. 3 XRD patterns of nominal $V_{0.05}Zn_{0.95}O$ before and after milling at 500 rpm for 15 minutes.

The XRD patterns of V_2O_5 before and after milling at 500 rpm for 15 minutes are shown in Fig. 4. Since the milled powder of V_2O_5 shows XRD pattern of pure V_2O_5 with d of about 20 nm, it is confirmed that amorphous phase of V_2O_5 is not produced by mechanical milling of pure V_2O_5. For the mixed and milled powder of $0.025V_2O_5 + 0.95ZnO$, the XRD peak of V_2O_5 completely disappeared, as shown in Fig. 3. It is hard to consider that XRD pattern of V_2O_5 can not be seen due to the production of amorphous V_2O_5 phase by mixing and milling together with ZnO powder. Therefore we assume that the V-doping into ZnO may be realized by the mechanical milling at 500 rpm for 15 min.

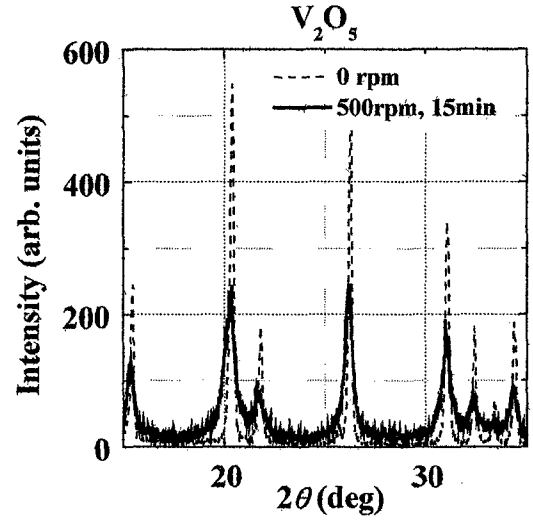

Fig. 4 XRD patterns of V_2O_5 before and after milling at 500 rpm for 15 minutes.

Though the room temperature ferromagnetism was reported for the conductive thin films of V-doped ZnO [5-7], our milled powder of nominal $V_{0.05}Zn_{0.95}O$ was insulating and showed no response to strong magnetic field. If ferromagnetism of $V_xZn_{1-x}O$ thin films is mediated by carriers, there is also a potential for our milled powder of $V_{0.05}Zn_{0.95}O$ to show ferromagnetism by carrier doping.

3.3 Nominal system of $Fe_{0.1}Zn_{0.9}O$

The XRD results for nominal $Fe_{0.1}Zn_{0.9}O$, which means the mixed and milled powder of $0.05(\gamma\text{-}Fe_2O_3) + 0.9ZnO$, are shown in Fig. 5. Comparing the profile of the sample before milling (0 rpm), the milled samples show only broadened diffraction peaks of pure ZnO with the size of 9-10 nm. After milling at 500 rpm for 15 min., the diffraction peaks of cubic $\gamma\text{-}Fe_2O_3$, which has the lattice

parameters of $a = 0.83539$ nm [8], disappeared.

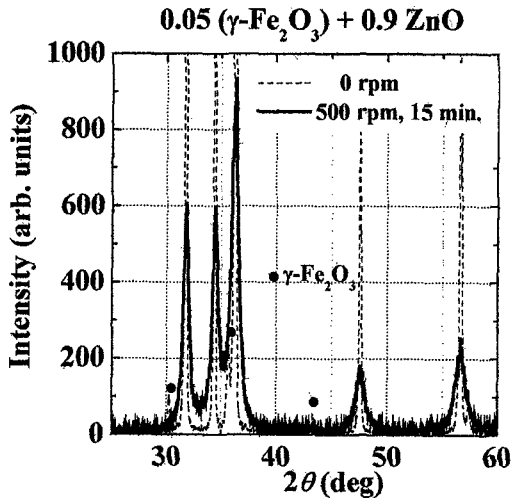

Fig. 5 XRD patterns of nominal $Fe_{0.1}Zn_{0.9}O$ before and after milling at 500 rpm for 15 minutes.

The XRD patterns of pure γ -Fe_2O_3 before and after milling at 500 rpm for 15 minutes are shown in Fig. 6. Milled powder of pure γ -Fe_2O_3 shows the broadened XRD pattern of γ -Fe_2O_3 with d of about 15 nm and α -Fe_2O_3 [9] with d of about 10 nm. For the mixed and milled powder of $0.05(\gamma$ -$Fe_2O_3)$ + 0.9ZnO, the XRD peak of γ -Fe_2O_3 completely disappeared and no α -Fe_2O_3 phase appeared. It cannot be considered that XRD pattern of γ -Fe_2O_3 disappeared due to the production of amorphous γ -Fe_2O_3 phase by mixing and milling with ZnO powder. Therefore we expected that the Fe-doping into ZnO may be also realized by the mechanical milling.

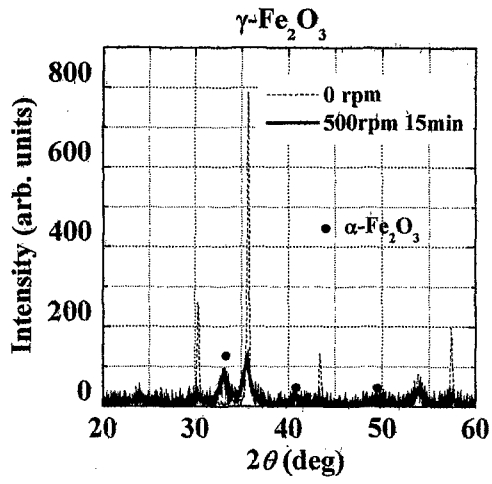

Fig. 6 XRD patterns of γ -Fe_2O_3 before and after milling at 500 rpm for 15 minutes.

3.4 Magnetic property of $Fe_{0.1}Zn_{0.9}O$

Field and temperature dependent magnetizations of milled powders of $Fe_{0.1}Zn_{0.9}O$ and pure γ -Fe_2O_3 are shown in Figs. 7, 8 and 9, where the magnetization values were taken per unit weight of γ -Fe_2O_3. The saturation magnetization M_s of milled $Fe_{0.1}Zn_{0.9}O$ are about 15 and 30 emu/g at 300 K and 5 K, respectively. Meanwhile M_s of milled γ -Fe_2O_3 are about 7 and 8 emu/g at 300 K and 5 K, respectively.

Room temperature ferromagnetism were reported for pure $Fe_xZn_{1-x}O$ thin film [10,11] and bulk [12-14]. However room temperature ferromagnetism by secondary phase such as γ -Fe_2O_3 [15], α -Fe [16], Fe_2O [17] were also reported for thin film and bulk system.

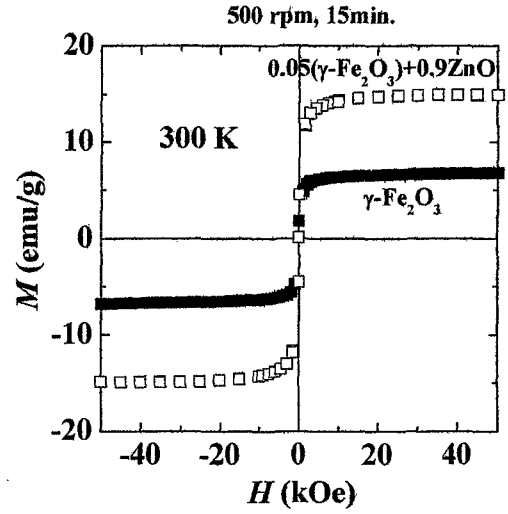

Fig. 7 Magnetization curves of milled powders of $Fe_{0.1}Zn_{0.9}O$ and γ -Fe_2O_3 at 300 K.

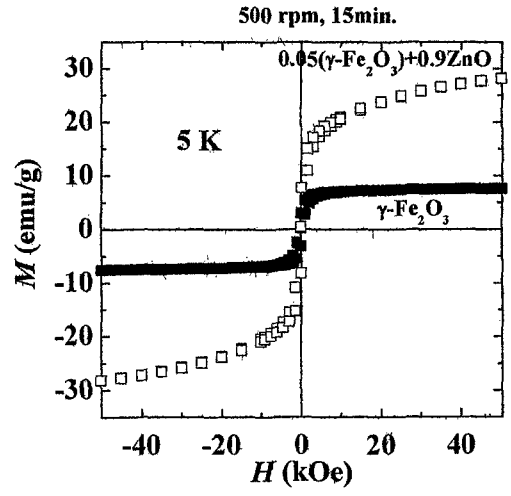

Fig. 8 Magnetization curves of milled powders of $Fe_{0.1}Zn_{0.9}O$ and γ -Fe_2O_3 at 5 K.

As for the present results of magnetization of nominal $Fe_{0.1}Zn_{0.9}O$, we suggest some possibilities. More gradual magnetization process of milled $Fe_{0.1}Zn_{0.9}O$ than that of milled γ -Fe_2O_3 in Fig. 8 shows that $Fe_{0.1}Zn_{0.9}O$ includes super-paramagnetic nano-particles, which is also

confirmed by the Curie-Weiss like part of *M-T* curve in Fig. 9, especially below 100 K. However, If we subtract the super-paramagnetic contribution M_{sp} from the *M-H* and *M-T* curves, residual magnetizations, $\Delta M = M - M_{sp}$, of about 15 emu/g exist between 5 and 300K. The ΔM of nominal $Fe_{0.1}Zn_{0.9}O$ is two times larger than the M_s~8 emu /g of milled γ -Fe_2O_3. Therefore we can assume that the Fe-doping into ZnO realized and large ΔM was induced from the doped Fe. The mechanically milled $Fe_{0.1}Zn_{0.9}O$ powder is expected to be one of the candidates of diluted magnetic semiconductors.

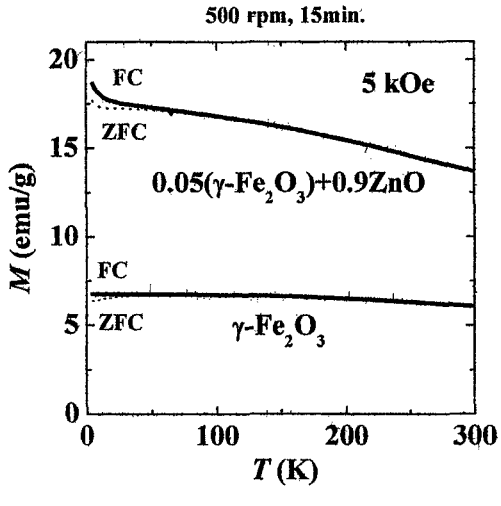

Fig. 9 Thermo-magnetic curves of milled powders of $Fe_{0.1}Zn_{0.9}O$ and γ -Fe_2O_3 between 5 and 300 K under 5 kOe.

CONCLUSION

Doping of V and Fe into ZnO can be expected for the mechanically milling of the mixed powders of ZnO and V_2O_5 or γ -Fe_2O_3. Milled powders of nominal $V_{0.05}Zn_{0.95}O$ did not show the ferromagnetism, but nominal $Fe_{0.1}Zn_{0.9}O$ powders showed room temperature ferromagnetism, which suggested the possibility of diluted magnetic semiconductor in the system of $Fe_{0.1}Zn_{0.9}O$. It is a problem to identify the contributions of super-paramagnetic nano-γ -Fe_2O_3 particles and doped Fe into ZnO by transmitted electron microscopy (TEM) and energy dispersive x-ray analysis (EDX). These experimental results shall be reported in the near furure.

ACKNOWLEDGEMENT

The present work was supported by the "Strong Correlation Technology Project" in Venture Business Laboratory of Yokohama National University.

REFERENCES

[1] R. Janish, P. Gopal and N.A. Spaldin, *J. Phys.: Condens. Matter*, **17**, R657-R689 (2005).
[2] K. Sato and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* **39**, L555-58 (2000).
[3] H. Schulz and K.H. Thiemann, *Solid. State Commun.*, **32**, 783-85 (1979).
[4] V. Shklover, T. Haibach, F. Ried, R. Nesper and P. Novák, *J. Solid State Chem.*, **123**, 317-23 (1996).
[5] H. Saeki, H. Tabata and T. Kawai, *Solid. State Commun.*, **120**, 439-443 (2001).
[6] N.H. Hong, J. Sakai and A. Hassini, *J. Appl. Phys.*, **97**, 10D312-1-3 (2005).
[7] N.H. Hong, J. Sakai and A. Hassini, *J. Phys. : Condens. Matter*, **17**, 199-204 (2005).
[8] S.N. Inamdar and S.K. Haram, *J. Nanosci. Nanotech.*, **6**, 2155-2158 (2006).
[9] D. A. Sadykov, L.A. Isupova, S.V. Tsybulya, S.V. Cherepanova, G.S. Kitvak, E.B. Burgina, G.N. Kustova, V.N. Kolomiichuk, V.P. Ivanov, E.A. Paukshtis, A.V. Golovin and E.G. Avvakumov, *J. Solid State Chem.*, **123**, 191-202 (1996).
[10] M. Venkatesan, C.B. Fitzgerald, J.G. Lunney and J.M.D. Coey, *Phys. Rev. Lett.*, **93**, 177206-1-4 (2004).
[11] N.H. Hong, *J. Magn. Magn. Mater.*, **303**, 338-343 (2006).
[12] A.Y. Polyakov, A.V. Govorkov, N.B. Smirnov, N.V. Pashkova, S.J. Pearton, K. Ip, R.M. Frazier, C.R. Abernathy, D.P. Norton, J.M. Zabada and R.G. Wilson, *Mater. Sci. Semicon. Process.*, **7**, 77-81 (2004).
[13] G.Y. Ahn, S-I. Park, S.J. Kim and C.S. Kim, *J. Magn. Magn. Mater.*, **304**, e498-e500 (2006).
[14] S.K. Mandal, A.K. Das, and T.K. Nath, *Appl. Phys. Lett.*, **89**, 144105-1-3 (2006).
[15] S.D. Yoon and Y. Chen, *J. Appl. Phys.*, **99**, 08M109-1-3 (2004).
[16] K. Potzger, S. Zhou, H. Reuther, A. mücklich, F. Eichhorn, N. Schell, W. Skorupa, M. Helm and J. Fassbender, *Appl. Phys. Lett.*, **88**, 052508-1-3 (2006).
[17] S. Kolesnik, B. Dabrowski and J. Mais, *J. Appl. Phys.*, **95**, 2582-2586 (2004).

(Received December 10, 2006;Accepted March 5, 2007)