Ferromagnetism in SnO₂ by Mechanical Milling

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Room temperature ferromagnetism was observed in the rutile-type SnO₂ by mechanical milling (MM). XRD results showed that the particle diameter d of SnO₂ powder was 22-32 nm after MM. Magnetization measurement showed that saturated magnetization M_s at 300K was 7.8×10^{-2} , 4.6×10^{-1} and 6.0×10^{-1} emu/mol for the milled samples at 100, 200 and 300 rpm, respectively. The oxygen vacancies may be produced on the surface of SnO₂ nano-particles by the MM above 100 rpm for 15 minutes.

Key Words : SnO₂, Mechanical milling, Ferromagnetism, Magnetization

1. INTRODUCTION

Transition metal-doped rutile-SnO₂ has been expected as the multifunctional material with magnetic, conductive and optical properties. The *ab initio* calculations for the (TM)_xSn_{1-x}O₂ (TM= V, Mn, Fe and Co) were performed [1-3], and it was concluded that ferromagnetic moments appeared for Fe, Co, but not for V and Mn. In the study by our group [4], the TM oxides (V₂O₅, VO₂, Cr₂O₃, CrO₂, Fe₃O₄, α -Fe₂O₃, γ -Fe₂O₃, CoO, Co₃O₄, NiO or CuO) and SnO₂, were used as the precursor for the (TM)_xSn_{1-x}O₂ samples. The TM of V, Fe, Ni and Cu could be doped into rutile-SnO₂ by the mechanical milling of the above mixtures. Milled TM_{0.1}Sn_{0.9}O₂ (TM=Fe, Ni and Cu) powders showed the ferromagnetism at 300 K, but the V_{0.1}Sn_{0.9}O₂ was nonmagnetic.

Except for the TM-doped SnO₂, the room temperature ferromagnetism, induced by the oxygen vacancies, has been reported for SnO₂ thin films, nano-particles and nano-wires [5-8]. As for the SnO₂ nano-particles [6], the sample preparations were performed by chemical reaction between organic solvent and metal nitrate. However the observed magnetization was nearly paramagnetic with very small hysteresis in Ref. 6.

In the present study, SnO₂ nano-particles were prepared by the mechanical milling (MM) method using planetary ball mill, and the production of vacancy was expected on the surface of SnO₂ nano-particle. The observation of clear magnetic hysteresis at room temperature is reported for the present system.

2. SAMPLE PREPARATION AND EXPERIMENTAL

The commercial rutile-SnO₂ powder was used as the precursor. The SnO₂ powder was 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 cm³, respectively, and the WC balls with 15 mm diameter were used as the grinding media. About 2 g of SnO₂ powder was the starting material. The volume ratio of balls and powder was about 50 : 1. Rotation speed and rotating time were kept at 100-300 rpm and 15 min, respectively.

The 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 SnO₂ powder

XRD patterns of SnO₂ powder milled by WC vial and balls showed that rutile-SnO₂ structure [9] was kept even after the milling. By MM, the diffraction peak intensity decreased and broadened as the rotation speed increased, as shown in Fig.1.

Fig. 1 XRD patterns of SnO₂ before and after milling at rotation speed of 300 rpm for 15 minutes.

From the half widths of each diffraction peak, the mean crystallographic correlation length d of SnO₂ particle was estimated by Sherrer's formula. The rpm-dependence of SnO₂ particle diameter is shown in Fig. 2. The d of commercial SnO₂ powder was about 35 nm, and it monotonously decreased as the rotation speed of ball mill increased. At 300 rpm, d decreased to about 22 nm.

Fig. 2 Rotation speed-dependence of particle diameter of SnO_2 powder milled for 15 minutes.

The lattice-parameters a and c are plotted in Fig.3 for the rotation speeds of ball mill. The a and c increased at 100 rpm, and they scarcely decreased between 100 and 300 rpm. The abrupt changes of lattice parameters at 100 rpm may show the production of vacancies at the d of about 30 nm by mechanical milling. 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 present sample preparations.

Fig. 3 Rotation speed-dependence of lattice-parameters a and c of SnO_2 powder milled for 15 minutes.

3.2 Magnetic properties

Temperature and field dependences of ΔM are shown in Fig.4(a) and (b) for milled samples at 100, 200 and 300

rpm, respectively. The ΔM was defined as following,

$$\Delta M = M_{\text{meas}} - M(0\text{rpm}) \quad (1).$$

Here M_{meas} is the measured magnetization of milled samples, and $M(0\text{rpm})$ is the magnetization of non-milled sample.

In Fig.4(a), the changes in ΔM 's for the milled samples are relatively small between 100 and 300K, which show the ferromagnetic Curie temperature T_c to be far above 300 K. The Curie-Weiss like behaviors below 50 K may be due to some magnetic impurities. The ferromagnetic behaviors were more clearly observed in Fig.4(b) which show the hysteretic magnetization at 300 K.

Fig. 4 Thermo-magnetic curves at 5 kOe (a), and magnetization curves at 300 K (b) of milled SnO_2 samples.

The saturation magnetization M_s , remanent magnetization M_r and cohesive field H_c are shown in Fig. 5, where the M_s , M_r and H_c increase with increasing rpm between 0 and 200. The ferromagnetism, induced by the vacancies on the surface of SnO_2 nano-particles [6, 7], are expected from these experimental results.

The M_s at 300 K were 7.8×10^{-2} , 4.6×10^{-1} and 6.0×10^{-1} emu/mol for the milled samples at 100, 200 and 300 rpm, respectively. The cohesive fields H_c were 59, 300 and 252 Oe for the milled samples at 100, 200 and 300 rpm, respectively. The change in the M_s -values may be due to the concentration of vacancies on the surface of nano-particles in each sample.

Fig. 5 Saturation magnetization M_s , remanent magnetization M_r and cohesive field H_c of SnO_2 powder milled for 15 minutes.

In Fig. 6, the ΔM of milled sample annealed in air at 300 K for 1 hour and 60 days, respectively. The ΔM of 60 days annealed sample is smaller than that of 1 hour annealed one at 300 K. The decreasing of magnetization shows the possibility of decreasing oxygen vacancy due to oxidation through the room temperature annealing. So the presence of oxygen vacancies may be qualitatively examined.

Room temperature ferromagnetism were reported for $\text{M}_{0.1}\text{Sn}_{0.9}\text{O}_2$ [4], where $M = \text{Fe}, \text{Ni}$ and Cu . In the $\text{Fe}_{0.1}\text{Sn}_{0.9}\text{O}_2$, large M_s of 2.9 emu/mol was observed for the sample including Fe^{2+} ions, but M_s of the sample without Fe^{2+} ions was small M_s of about 2×10^{-3} emu/mol. The M_s 's were also small as about 2×10^{-3} emu/mol in $\text{Ni}_{0.1}\text{Sn}_{0.9}\text{O}_2$ and $\text{Cu}_{0.1}\text{Sn}_{0.9}\text{O}_2$. The coercive fields of H_c were 400-1000 Oe for all of the cases.

As for the SnO_2 with oxygen vacancies, Sandaresan *et al.* [6] reported a ferromagnetic behavior, where the magnetization M was 2.6×10^{-1} emu/mol at 2 kOe with no cohesive field. The present magnetic results of mechanically milled SnO_2 show that a large magnetic moment can be obtained in the nano-powder prepared by mechanical method, not by chemical method.

Recently, the surface induced ferromagnetism was

theoretically estimated [10], where the lowest energy levels of structural defects with two localized carriers near the surface of SnO_2 film were calculated using a quantum-mechanical approach, and a magnetic triplet state was found to be the ground state in the vicinity of the SnO_2 surface.

Fig. 6 Thermo-magnetic curves of milled SnO_2 powder after 1 hour and 60 days in air at room temperature.

4. CONCLUSION

The SnO_2 nano-particles with oxygen vacancies were prepared by the mechanical milling (MM) method using planetary ball mill, and clear magnetic hysteresis was observed at room temperature. The saturation magnetization M_s at 300 K were 7.8×10^{-2} , 4.6×10^{-1} and 6.0×10^{-1} emu/mol for the milled samples at 100, 200 and 300 rpm, respectively. Thus a larger magnetic moment can be obtained in the nano-powder prepared by mechanical method than by chemical method.

The confirmation of oxygen vacancies are planned for the present samples by the photo-luminescence measurements [9], and TEM observations. The experimental results shall be reported in the near future.

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