Mössbauer study of \(\text{SnO}_2\) powders doped with dilute \(^{57}\text{Fe}\) prepared by a sol-gel method \(^\ast\)

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SnO\(_2\) powders, doped with various \(^{57}\text{Fe}\) contents were prepared by a sol-gel method, and annealed finally at 500 °C and 650 °C. These samples were characterized by Mössbauer spectroscopy, vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) to investigate the relationship of magnetic properties, grain sizes, annealing temperatures and Mössbauer parameters. The particle sizes of SnO\(_2\) powders reduced to less than 100 nm with the increase of Fe contents up to 5%. Rutile SnO\(_2\) was the only phase obtained for all samples. Room temperature Mössbauer spectra suggest the presence of two different paramagnetic iron sites for all samples and one magnetically relaxed species for those samples with the lowest iron concentrations. The magnetization increased with the Fe content, but was reduced for the samples annealed at 650 °C perhaps due to a segregation of \(\alpha\)-Fe\(_2\)O\(_3\) doped with tin.

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1 Introduction

Diluted magnetic semiconductors (DMS) have been currently developed because of their potential applications in spintronics as a new device – spin FET. Unfortunately, GaAs, GaN, and InP doped with transition metals only show ferromagnetism below room temperature. It was recently found that DMS transparent films of TiO\(_2\), doped with Co show ferromagnetic properties at room temperature [1]. Min Lee et al. reported that the ferromagnetic behavior of Ti\(_{1-x}\)\(^{57}\text{Fe}_x\)O\(_2\) increases with the decrease of \(^{57}\text{Fe}\) doping amount [2]. The Fe-doped TiO\(_2\) films produced by PLD were studied by conversion electron Mössbauer spectrometry (CEMS) [3]. These films contained metallic Fe and paramagnetic Fe(III). Ogale et al. reported that Co-doped SnO\(_2\) showed a high temperature ferromagnetism with a giant cobalt moment [4]. Deposited films of SnO\(_2\) doped with Fe showed remarkably strong ferromagnetism, for which a novel ferromagnetic exchange mechanism is introduced [5]. Optical transparency, electrical conductivity and ferromagnetism are essential properties of a new attractive DMS. Chemically synthesized powders


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of p-type SnO and n-type SnO$_2$, doped with Fe have been studied [6]. The authors suggest close relationship between the structural and magnetic properties of Co-doped SnO$_2$ nanoparticles [7]. Increasing the Co doping concentration to 1% leads to a rapid expansion of the lattice and significant structural disorder. The magnetic and structural properties of synthesized powders depend on the conditions of preparation.

We have prepared powders of SnO$_2$, doped with various amounts of $^{57}$Fe by a sol-gel method, which provides uniform grains, and investigated the effect of annealing temperature and increasing iron content on the magnetic and structural properties of the final products.

2 Experimental

Various compositions of Sn$_{1-x}$$^{57}$Fe$_x$O$_2$ ($x = 0.005, 0.01, 0.03, 0.05,$ and $0.1$) were obtained by a sol-gel method. Several mol. % of Fe$^{2+}$ citric acid solutions were mixed with ethylene glycol solutions of bisacetylacetatedichloro Sn$^{4+}$. The mixed solutions were evaporated at $80^\circ$C, calcinated at about $200^\circ$C, and finally annealed at $500^\circ$C and $650^\circ$C for 2 hours. All thermal treatments were performed in air. The products were measured by XRD, VSM, SEM, and Mössbauer spectrometry. The Mössbauer spectra measured at room temperature (RT) were decomposed into two doublets, magnetically relaxed and sharp sextet components. The Mössbauer Doppler velocity was calibrated by $\alpha$-Fe.

3 Results and discussions

Average particle sizes of SnO$_2$ powders as a function of Fe content, estimated from observations of scanning micrographs, are shown in Fig. 1. The particle sizes became smaller with a higher Fe doping and were less than about 100 nm in a

![Fig. 1. Average particle sizes of SnO$_2$ powders as estimated from SEM images.](image-url)
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diameter for almost all samples doped with more than 3 mol. % Fe. These results indicate that Fe doping disturbs the growth of SnO$_2$ particles. These results are in agreement with the results of chemically synthesized powders [7]. Typical XRD patterns are shown in Fig. 2. The prepared powder samples were confirmed to have the rutile structure of SnO$_2$, but iron compounds were not clearly detected by XRD. The crystallinity of SnO$_2$ was improved at a high temperature. Mean crystal sizes of almost all SnO$_2$ grains, estimated from FWHM of (110) peaks were in the range of 26–32 nm. For example, the crystal sizes ranged from 26 nm for SnO$_2$ doped with 10 mol. % Fe to 32 nm for SnO$_2$ doped with 0.5 mol. % Fe, annealed at 500°C. For small Fe doping, the particle sizes determined from XRD and SEM do not agree, but for high Fe doping, the results from both techniques agree. The small particles observed by SEM are considered to be magnetically single domain. The lattice parameters are shown in Fig. 3.

Fig. 2. Typical XRD patterns of Sn$_{0.95}^{57}$Fe$_{0.05}$O$_2$ annealed at a) 650°C and b) 500°C.

XRD peak intensity of SnO$_2$ annealed at 500°C decreased with Fe doping. The peak positions slightly shifted to lower angles with the increase of Fe contents. For the samples annealed at 500°C, the $c$ lattice parameter is observed to decrease with increasing Fe content, whereas with the exception of samples $x = 0.05$ and 0.1, the unit cell remains essentially constant along the $a$ axis. On the other hand, for the samples annealed at 650°C, the $c$ lattice parameter is observed to decrease with increasing iron content, whereas the $a$ lattice parameter decreases up to $x = 0.5$, and then increases. These results suggest that iron has replaced tin in the SnO$_2$ structure.

As shown in Fig. 4, the shapes of the magnetization curves suggest the pres-
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Fig. 3. Dependence of lattice parameters of SnO$_2$ rutile structure on Fe doping for different annealing temperatures.

ence of ferromagnetic and paramagnetic components. Fig. 4b) shows the magnitude of magnetization at the largest magnetic fields of 5 kOe. The magnetization of Sn$_{1-x}$Fe$_x$O$_2$ annealed at 500 $^\circ$C increases with the increase of Fe contents, and showed maximum of 0.0619 emu/g for $x = 0.1$. At the annealing temperature of 650 $^\circ$C, ferromagnetism was reduced. The detailed analysis will be performed in a forthcoming paper.

Fig. 4. a) Typical magnetization curves of Sn$_{1-x}$Fe$_x$O$_2$ ($x = 0.1$) annealed at 500 $^\circ$C and 650 $^\circ$C, and b) dependence of magnetization at the largest fields on the Fe content.

Mössbauer spectra of Sn$_{1-x}$Fe$_x$O$_2$ annealed at 500 $^\circ$C are shown in Fig. 5. Weak broad sextets are observed in MS spectra of Sn$_{1-x}$Fe$_x$O$_2$ with a low Fe content in addition to paramagnetic components. Previous work, using non-enriched $^{57}$Fe samples, has only identified one doublet and one sextet [6], but in the present work, we discerned two doublets and one broad sextet because the paramagnetic peaks were asymmetric. The relative intensity of this sextet seems to increase with the decrease of Fe doping. Paramagnetic doublet D1 (isomer shift
δ = 0.36–0.37 mm/s, quadrupole splitting ΔEQ = 0.69–0.83 mm/s, peak width Γ = 0.5–0.8 mm/s) is assigned to octahedral Fe(III) substituted at Sn(IV) sites, and paramagnetic doublet D2 (δ = 0.41–0.46 mm/s, ΔEQ = 1.56–2.07 mm/s, Γ = 0.5–0.8 mm/s) is tentatively ascribed to distorted Fe(III) sites, because large ΔEQ values reflect the disordered oxygen configuration. The δ values of D2 are a little larger than for the high-spin Fe(III). The D2 site is perhaps produced by oxygen defects and the surface of the grains may contain a lot of oxygen defects. The neutralization by an existence of valence state 3+ results in oxygen defects. The broad sextets come from the paramagnetic relaxation of spin-lattice interaction.

Fig. 5. RT Mössbauer spectra of Sn1−xFeO2 annealed at 500°C for 2 hrs as a function of the Fe content.

Paramagnetic doublets D1 (δ = 0.36 mm/s, ΔEQ = 0.81–0.91 mm/s, Γ = 0.5–0.82 mm/s) and D2 (δ = 0.3–0.34 mm/s, ΔEQ = 1.6–2.3 mm/s, Γ = 0.5–0.82 mm/s) were observed for samples annealed at 650°C. The isomer shifts of D2 for samples annealed at 650°C showed high-spin Fe(III), which were different from those of D2 for samples annealed at 500°C although ΔEQ values were similar with each other. The peak width Γ of both doublets increased with the decrease of the Fe contents. This suggests weak magnetic interactions at low concentrations of Fe. This interpretation is in agreement with the reported Fe diffusion from the inner core to the outer shell of the particles with increasing temperature [7].

Magnetic sextet (δ = 0.38 mm/s, ε = −0.18 mm/s, Bhf = 51 T, Γ = 0.41 mm/s) was clearly observed in Mössbauer spectra of samples with x ≥ 0.05, annealed at 650°C as shown in Fig. 6, although the presence of iron oxides could not be clearly recognized by XRD. The parameters of this sextet are indeed similar to that of
α-Fe₂O₃ doped with Sn. This suggests that perhaps several percent of iron oxides are segregated in the surface layers of SnO₂ grains by annealing at high temperatures. Coey et al. [5] proposed that this sextet comes from the Fe-doped SnO₂. If this oxide is Sn-doped α-Fe₂O₃, the magnetic behavior can be weakened due to the weakly ferromagnetic behavior of α-Fe₂O₃, segregated at high temperatures. At low Fe content, line-width of doublets was large, and magnetic relaxation peaks appeared. These components are considered to be due to paramagnetic relaxation when the relaxation time of the spin-lattice interaction is longer than the nuclear excitation-relaxation time (about 10⁻⁷ s).

![Mössbauer spectra of Sn₁₋ₓFeₓO₂](image)

Fig. 6. RT Mössbauer spectra of Sn₁₋ₓFeₓO₂ annealed at 650 °C for 2 hrs as a function of Fe content.

It is clear that the ΔE₀ and Γ of doublets become broad at low content of Fe for samples annealed at 500 °C and 650 °C. A strong sextet of α-Fe₂O₃ was observed at a high concentration of x = 0.15 and annealing at 650 °C. It suggested that a long annealing of samples doped with a high Fe content promotes the segregation of α-Fe₂O₃. Large broadened peaks observed in Mössbauer spectra are due to paramagnetic relaxation, observed at very low concentration of doped Fe, and magnetic interactions were observed at a relatively high concentration of doped Fe. From these results, it is considered to be important that Fe ions are embedded into SnO₂ matrix as much as possible and do not segregate as weakly ferromagnetic α-Fe₂O₃. The large magnetization, as recently reported by Ogale et al. [4], was not obtained for these samples prepared by a sol-gel method, because the powders were composed of small particles.
4 Summary

SnO\textsubscript{2} doped with various amounts of Fe were prepared by a sol-gel method. Although segregated iron oxides were not clearly recognized by XRD, dilute Fe species doped in SnO\textsubscript{2} were easily characterized by Mössbauer spectrometry. When increasing the Fe contents, it is found that the particle size decreases, the intensity of the hematite sextet for the samples annealed at 650°C increases, and the weak broad sextet disappears. Magnetic relaxation and paramagnetic peaks were observed in Mössbauer spectra of those samples, which showed relatively high magnetization. The valence state of doped Fe was high-spin Fe\textsuperscript{3+}. It seems that a guideline for preparation of DMS materials is obtained, although these results are tentative. Transparent DMS films are expected to be obtained by a pulse-laser deposition using a target of correspondingly doped powders.

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