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Magnetic behaviour and DCEMS study of SnO_2 films implanted with ^{57}Fe

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Abstract Fe implanted SnO_2 films (5×10^{16} and 1×10^{17} ^{57}Fe ions/cm^2) characterized by conversion electron Mossbauer spectroscopy (CEMS) are reviewed. The substrate temperatures affect the growth of precipitated iron oxides. The Fe ion implanted film at room temperature (RT) shows no Kerr effect and no magnetic sextet in CEM spectra. The SnO_2 film implanted with ^{57}Fe at the substrate temperature of 300 °C show a small Kerr effect although the magnetic sextet is not observed, but post-annealing results in the disappearance of the Kerr effect. This magnetism is considered to be due to defect induced magnetism. Some samples were measured by CEMS at 15 K. SnO_2 (0.1 at %Sb and 3 at %Sb) films, implanted at 500 °C and the post-annealed samples, show RT ferromagnetism due to formation of clusters of magnetite and maghemite, respectively. The layer by layer analysis of these films within 100 nm in thickness has been done by depth sensitive CEMS (DCEMS) using a He + 5 % CH_4 gas counter. The structures and compositions of Fe implanted SnO_2 films, and the effects due to post-annealing were investigated.

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1 Introduction

The origin of magnetic interactions in diluted magnetic semiconductors (DMS) is an interesting issue from the viewpoint of a basic problem in dilute magnetism and from the viewpoint of the application to spintronics [1, 2]. We have reported different types of magnetic phenomena in the case of Fe doped SnO_2 powders, prepared by sol-gel method [3], and made it clear that defects in DMS contribute to enhance the saturation magnetization. We have also studied the phonon or vibration density of states (VDOS) of ^{57}Fe doped SnO_2 and TiO_2 with the rutile type structure using synchrotron radiation [4]. The binding force of nearest neighbors in rutile SnO_2 is stronger than that in rutile TiO_2.

Further, thin films of $Sn^{57}_{1-x}Fe_xO_{2-\delta}$ have been implanted at room temperature (RT) with 1×10^{17} ^{57}Fe ions/cm^2, and at 300 °C with 5×10^{16} and 1×10^{17} ^{57}Fe ions/cm^2 [5]. The as-implanted samples at RT and the post-annealed samples did not show any optical electromagnetic effect (Kerr effect). The sample implanted with 1×10^{17} Fe ions/cm^2 at substrate temperature of 300 °C showed the Kerr effect, but the effect disappeared after post-annealing at 400 °C. We have also shown that the bulk magnetization is enhanced by introducing Sb^{5+} in the Fe doped SnO_2 powder [6]. The SnO_2 (0.1 %Sb) films implanted with ^{57}Fe at a substrate temperature of 500 °C showed relatively large RT ferromagnetism as compared with SnO_2 (3 % Sb) films [7]. In this paper, the SnO_2 and SnO_2 (0.1 %Sb and 3 %Sb) films, implanted with ^{57}Fe and post-annealed, were re-investigated by low temperature CEMS or DCEMS using a back-scattered type of gas flow counter.

2 Experimental

SnO_2 films containing 0 %, 0.1 % and 3 % Sb with thickness of 200 nm were prepared on quartz glass by using DC sputtering in O_2 flow, and were implanted with 5×10^{16} ^{57}Fe ions/cm^2 at room temperature (RT), 300 °C and 500 °C in vacuum, using an acceleration energy of 100 keV. From TRIM calculations, it is expected that the iron atoms are located at about 40 nm in depth with the maximum concentration of 5 at % Fe. The implanted sample was post-annealed step by step at 400 °C, 500 °C, 600 °C, 700 °C and 800 °C for several hours. XRD of SnO_2 film showed the rutile structure without any impurity phase. Polar Kerr effect was measured with magnetic circular dichroism (MCD) mode. Three CEM spectra were simultaneously observed from different depths by discriminating the resonance electrons with three energy regions (2–6.5 keV, 6.5–11 keV, and 11–20 keV) using a homemade He + 5 % CH_4 gas counter [8, 9]. This method provides roughly a layer by layer analysis of thin films. That is DCEMS, whereas conventional CEM spectra obtained by detecting all emitted electrons are specifically called integral CEM spectra (ICEMS). CEM spectra of some samples were measured at 15 K using a H_2 proportional counter [10]. Doppler

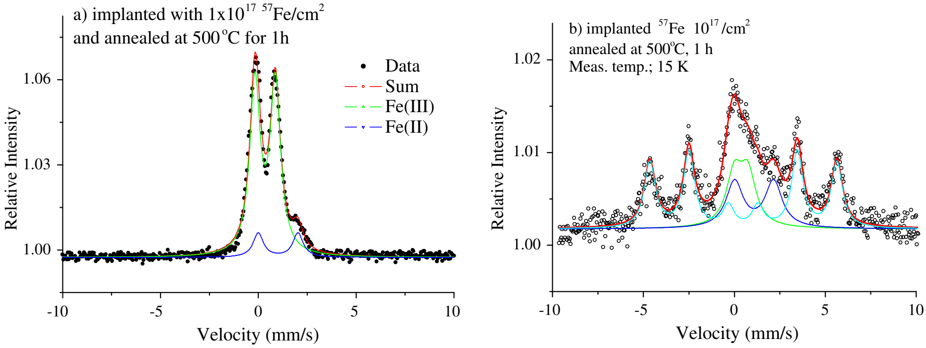

Fig. 1 RT and 15 K CEM spectra of SnO_2 film implanted with ^{57}Fe and annealed at 500 °C for 1 h

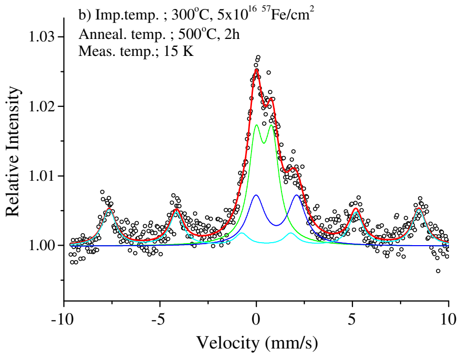

Fig. 2 15 K CEM spectrum of SnO_2 implanted with 5×10^{16} $^{57}Fe/cm^2$ at the substrate temperature of 300 °C, and post annealed at 500 °C for 2 h

velocity was calibrated with standard α-Fe foil at RT and a γ source of $^{57}Co/Cr$ matrix was used.

3 Results and discussion

SnO_2 film implanted with 1×10^{17} $^{57}Fe/cm^2$ at RT and the post-annealed sample did not show polar Kerr effect. RT and 15 K CEM spectra of ^{57}Fe implanted at RT and post-annealed at 500 °C are shown in Fig. 1. RT CEM spectrum of the post-annealed sample show only doublets of paramagnetic Fe(II) and Fe(III) species, but a broad magnetic sextet (magnetic field (B_{hf}) = 32 T, isomer shift (δ) = 0.49 mm/s, FWHM (Γ) = 0.74 mm/s) was observed at 15 K. From the IS and the B_{hf} values it is clear that the small clusters of high spin Fe(III) oxide are formed. The doublet of Fe(III) are due to super-paramagnetic components at RT. CEM spectrum collected at 15 K of as-implanted SnO_2 did show almost the same as the RT CEM spectrum, but by post-annealing, the magnetic sextet of the Fe(III) oxide appeared at 15 K. This suggests that the clusters of Fe oxide become larger by post-annealing.

SnO_2 implanted with ^{57}Fe at the substrate temperature of 300 °C, showed the Kerr effect, which disappeared upon post annealing [5]. The magnetic sextets were

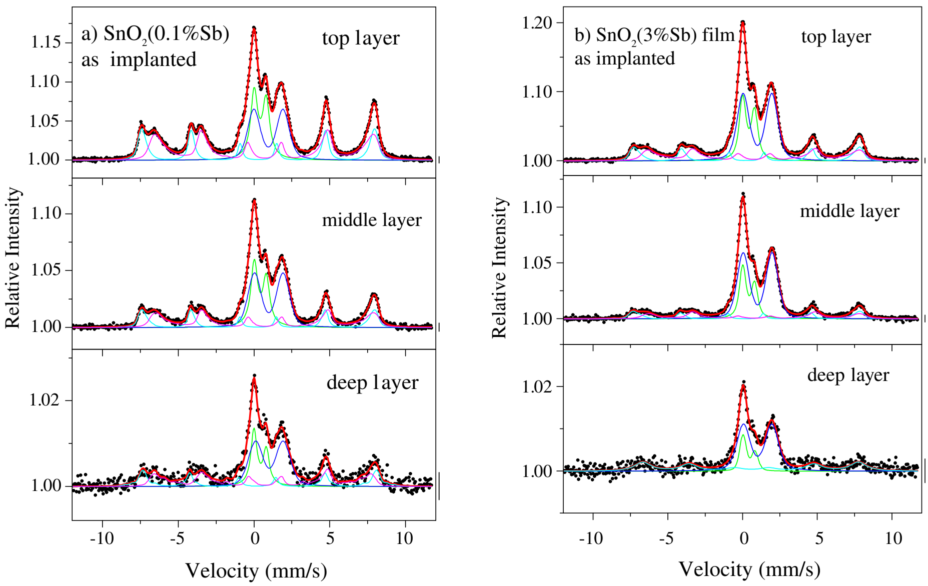

Fig. 3 DCEM spectra of SnO_2 (0.1 %Sb) and SnO_2 (3 %Sb) films implanted with 5×10^{17} ^{57}Fe at the substrate temperature of 500 °C

not clearly observed in the ^{57}Fe CEM spectra of SnO_2 film implanted with 1×10^{17} $^{57}Fe/cm^2$ at RT before and after annealing. This suggests that the number of magnetic defects produced in oxygen vacancy decrease by absorption of oxygen due to post-annealing in air atmosphere. The SnO_2 film implanted with 5×10^{16} $^{57}Fe/cm^2$ showed a broad sextet with small intensity, in addition to two doublets, although the Kerr effect was not observed. After post-annealing, the CEM spectrum of the sample measured at 15 K is shown in Fig. 2. The largest hyperfine field observed is considered to be due to clusters of hematite. The increase of the substrate temperature seems to result in formation of larger clusters.

SnO_2 (0.1 %Sb or 3 %Sb) films, implanted with ^{57}Fe at substrate temperature of 500 °C were studied. Kerr rotation curves were measured by MCD mode at light wavelength $\lambda = 300$ nm. Kerr rotation angles of the SnO_2 (0.1 %Sb) film are larger than that of SnO_2 (3 %Sb) [7]. In this case, Kerr effect of a film post-annealed at 400 °C and at higher temperatures showed larger hysteresis than before annealing. Another compound is considered to be produced in the film upon annealing. DCEM spectra of these samples as implanted at substrate temperature of 500 °C are shown in Fig. 3. The spectra of as-implanted SnO_2 films were decomposed into 4 subspectra of two doublets and two sextets. For SnO_2 (0.1 %Sb), the doublets with small isomer shift ($\delta = 0.39(1)$ mm/s, $\Delta = 0.77(2)$ mm/s, $\Gamma = 0.61(2)$ mm/s, Int. = 21.7 %) and large isomer shift ($\delta = 0.94(1)$ mm/s, $\Delta = 1.92(2)$ mm/s, $\Gamma = 0.78(2)$ mm/s, Int. = 27.7 %) are assigned to paramagnetic Fe^{3+} and Fe^{2+} species, respectively. Two broad sextets ($\delta = 0.31$ mm/s, $B_{hf} = 47.7$ T, and $\delta = 0.62$ mm/s, $B_{hf} = 43.7$ T) can be assigned to Fe^{3+} in tetrahedral site A and $Fe^{2.5+}$ in octahedral site B of magnetite clusters, respectively. The area ratio of the two sextets was 16.9 % and 33.8 %, respectively.

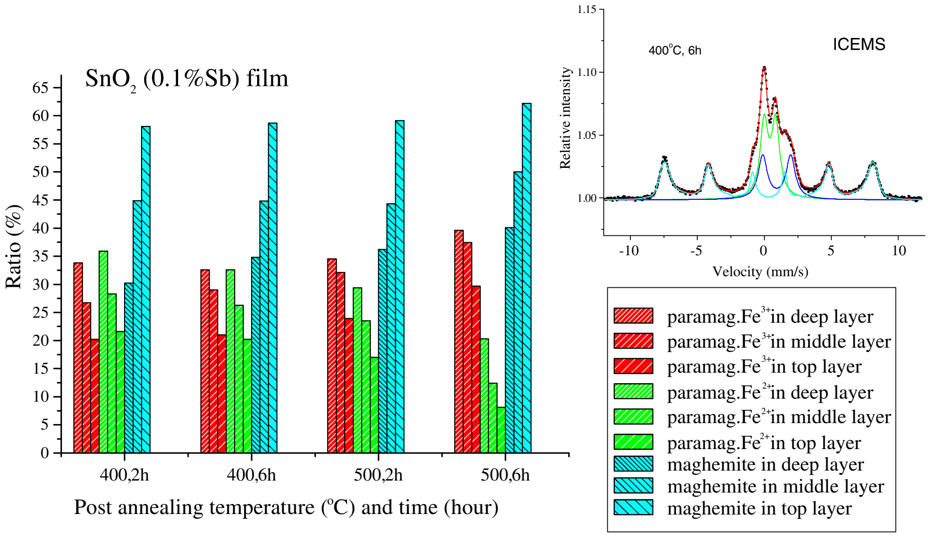

Fig. 4 Area intensity ratios of Fe species produced in the three layers of SnO_2 (0.1 %Sb) films annealed at 400 °C and 500 °C for various hours. Inset: typical ICEM spectrum of SnO_2 (0.1 % Sb) films with, implanted with 5×10^{16} Fe ions at a substrate temperature of 500 °C, and post-annealed at 400 °C for 6 h

The broadening of these peaks and the reduced hyperfine field (B_{hf}) values are due to finely dispersed grains of Fe oxides.

DCEM spectra obtained by detecting the electrons in the high energy region reflect the top layer of the film as shown in Fig. 3. The relative area of the magnetite in top layer is large as compared with those of the middle and the deep layers of the SnO_2 films. This shows that a large amount of magnetite with relatively large grain sizes is located in the top layer. For the SnO_2(3 %Sb) implanted film, similar results are obtained although the relative intensity of the sextets are small. It is considered that the clusters are harder to grow in Sb rich SnO_2 because Sb^{5+} ions with small ionic radius are substituted at the sites of Sn^{4+} in the rutile structure.

Two magnetic sextets of magnetite changed into one broad sextet with small tails towards lower velocities after post-annealing. The magnetic sextet of the post-annealed samples can be assigned to finely dispersed maghemite (γ-Fe_2O_3) because of the Mossbauer sextet with (δ) = 0.31–0.33 mm/s, quadrupole shift (2ε) = 0.01–0.02 mm/s, and the maximum B_{hf} = 47.5 T as shown in Fig. 4. Therefore, the Kerr effect observed for the annealed samples is due to finely dispersed γ-Fe_2O_3.

With increasing the annealing temperature and time, the magnetic fields increased somewhat, by 1 T, at post annealing at 500 °C for 6 h. The doublet intensity of paramagnetic Fe^{2+} decreased and the doublet intensity of Fe^{3+} increased with annealing, especially on the top layer. These relationships for layer by layer SnO_2 films, annealed at high temperatures, are shown in Fig. 4. The sample annealed at 500 °C for 6 h showed a high intensity of γ-Fe_2O_3. It is considered that the grains of γ-Fe_2O_3 are somewhat grown while paramagnetic Fe^{2+} species are oxidized. Therefore, it is suggested that large amounts of γ-Fe_2O_3 are formed by annealing at higher temperatures because the Fe^{2+} species remained when annealed at 500 °C.

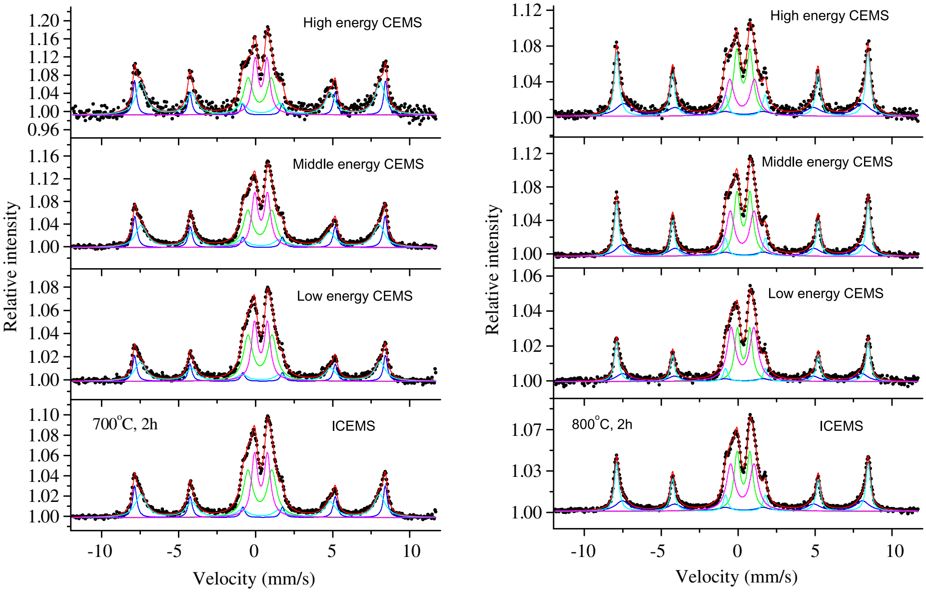

Fig. 5 DCEM spectra of SnO_2 (3 %Sb) implanted with 5×10^{16} $^{57}Fe/cm^2$, and annealed at various temperatures. 1. Sextet1; α-Fe_2O_3, $H_{in} = 51$ T, IS = 0.37 mm/s, $2\varepsilon = -0.18$ mm/s, $\Gamma = 0.34$ mm/s. 2. Sextet2; γ-Fe_2O_3, $H_{in} = 48$ T, IS = 0.32 mm/s, $2\varepsilon = -0.04$ mm/s, $\Gamma = 0.90$ mm/s

It is found that paramagnetic Fe^{2+} and Fe^{3+} species remain as many fine oxides in deep layers of SnO_2 films.

In the case of SnO_2 (3 %Sb) implanted and annealed, Kerr rotation angles are observed mainly due to the fine maghemite produced in the SnO_2 films. The annealing up to 700 °C is effective for transparent and ferromagnetic films. The annealed sample at 800 °C does not show any Kerr effect because weak ferromagnetic hematite (α-Fe_2O_3, $B_{hf} = 51$ T, IS = 0.37 mm/s, $2\varepsilon = -0.18$ mm/s, $\Gamma = 0.34$ mm/s) is produced from maghemite although the ratio of paramagnetic or superparamagnetic Fe^{3+} species does not increase so much. Mössbauer parameters of the sextet with low intensity and low hyperfine field ($B_{hf} = 48.4$ T, $\delta = 0.34$ mm/s, $2\varepsilon = -0.13$ mm/s, and $\Gamma = 1.06$ mm/s) as shown in Fig. 5 are somewhat different from those of maghemite for the annealed sample at 700 °C ($B_{hf} = 47.8$ T, and $\delta = 0.33$ mm/s, $2\varepsilon = -0.03$ mm/s, $\Gamma = 0.9$ mm/s). The hematite peaks can be distinguished from the maghemite peaks because the quadrupole shift's values are close to −0.2 mm/s. The area ratios of the sextets with high magnetic field and low magnetic field were almost the same among DCEM spectra of top, middle, and deep layers of the annealed sample at 800 °C. Therefore, the sextet with low hyperfine field for the annealed sample at 800 °C is considered to be a tailing part of fine particle of hematite in SnO_2 film produced by annealing at high temperatures.

The maghemite in SnO_2 (3 %Sb) implanted with ^{57}Fe is relatively stable against heating up to 700 °C. We want to mention that insulating SiO_2 glass implanted with ^{57}Fe shows ferromagnetic behavior [11]. Metallic Fe clusters are included in insulating SiO_2 together with Fe^{2+} and Fe^{3+} species. Ferromagnetism is obtained even for annealing up to 950 °C. It is due to ferromagnetic ε-Fe_2O_3 produced in cavities of SiO_2. It is reported that ε-Fe_2O_3 is useful for absorption of electromagnetic waves with high frequency because of the large coercivity [12]. The small cavities of insulating SiO_2 play an important role to form ε-Fe_2O_3. The Fe implantation and post-annealing of SiO_2 is expected to induce absorption of electromagnetic waves.

4 Conclusions

SnO_2 films implanted with ^{57}Fe were measured by CEMS at 15 K. It was confirmed that the longer annealing time and the higher temperature of SnO_2 substrate film during ion implantation, resulted in the precipitation of larger clusters. SnO_2 (0.1 %Sb and 3 %Sb) films doped with 5×10^{16} ^{57}Fe ions/cm^2 at 500 °C show bulk ferromagnetism at RT. Post-annealing enhanced somewhat the bulk magnetism. The phenomena are attributed mainly due to the formation of magnetite for as-implanted sample and of maghemite for the post-annealed samples, respectively. DCEMS showed that relatively large clusters of magnetite and maghemite are formed on the topmost layer of the implanted region, and large amounts of paramagnetic Fe^{2+} are located in deep layers. It is found that a paramagnetic Fe^{3+} species with large Δ is produced by heating at high temperatures. The implanted and annealed SnO_2 layers are not intrinsic DMS, but have the potential to be transparent and magnetic conductive films.

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References

1. Coey, J.M.D., Venkatesan, M., Fitzgerald, C.B.: Nat. Mater. **4**, 173 (2005)
2. Punnoose, A., Hays, J., Thurber, A., Engelhard, M.H., Kukkadapu, R.H., Wang, C., Shutthanandan, V., Thevhuthasan, S.: Phys. Rev. B **72**, 054402 (2005)
3. Nomura, K., Barrero, C.A., Sakuma, J., Takeda, M.: Phys. Rev. B **75**, 184411 (2007)
4. Rykov, A.I., Nomura, K., Sakuma, J., Barrero, C., Yoda, Y., Mitsui, T.: Phys. Rev. B **77**, 014302 (2008)
5. Nomura, K., Reuther, H.: Hyperfine Interact. **191**, 159 (2009)
6. Nomura, K., Barrero, C.A., Kuwano, K., Yamada, Y., Saito, T., Kuzmann, E.: Hyperfine Interact. **191**, 25 (2009)
7. Nomura, K., Iio, S., Hirose, Y., Németh, Z., Yamamoto, K., Reuther, H.: J. Nucl. Radiochem. Sci. **11**, 1 (2010)
8. Nomura, K., Okubo, T., Nakazawa, M.: Spectrochim. Acta B **59**, 1259 (2004)
9. Nomura, K., Iio, S., Ujihira, Y., Terai, T.: Industrial applications of the Mossbauer effect. In: Gracia, M., Marco, J.F., Plazaola, F. (eds.) AIP, CP, vol. 765, pp. 108 (2005)
10. Fukumura, K., Nakanishi, A., Kobayashi, T.: Nucl. Instrum. Methods B **86**, 387 (1994)
11. Nomura, K., Reuther, H.: J. Radioanal. Nucl. Chem. **287**, 341 (2011)
12. Jin, J., Hashimoto, K., Ohkoshi, S.: J. Mater. Chem. **15**, 1067 (2005)