

Characterization of ^{57}Fe Implanted and Annealed SnO_2 (3 % Sb) Films by Depth Selective Conversion Electron Mössbauer Spectroscopy (DCEMS)

K. Nomura,*^a S. Iio,^a Y. Hirose,^b Z. Németh,^{a,c} K. Yamamoto,^d and H. Reuther^e

^a School of Engineering, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656 Japan

^b School of Science, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656 Japan

^c Institute of Chemistry, Eötvös Loránd University, Pázmány P. s. 1/A, 1117 Budapest, Hungary

^d Research Center, Asahi Glass Co.Ltd, 1150 Hazawa-cho, Kanagawa-ku, Yokohama, 221-8755 Japan

^e Forschungszentrum Dresden-Rossendorf e.V., Institut für Ionenstrahlphysik und Materialforschung, Postfach 510119, D-01324 Dresden, Germany

Received: December 1, 2009; In Final Form: February 9, 2010

SnO_2 (3 % Sb) films were implanted with 5×10^{16} ^{57}Fe ions/cm² at the substrate temperature of 500 °C, and annealed at temperatures between 400 °C and 800 °C. These films were characterized by depth selective conversion electron Mössbauer spectroscopy (DCEMS) using a back scattered type of a gas proportional counter, and measured by a Kerr effect magnetometer. Kerr effect measurements of the SnO_2 films showed ferromagnetism at room temperature. The Mössbauer spectra of the as-implanted films consisted of paramagnetic doublets of Fe^{3+} and Fe^{2+} species and two broad sextets, which showed site A and site B of fine grain magnetite. The Kerr rotation angles increased step by step with post-annealing up to 700 °C. This phenomenon was attributed mainly to ferromagnetic maghemite produced by post-annealing. It was found from DCEMS analysis that the maghemite with relatively large grains exists more in top layer than deep layer.

1. Introduction

The origin of magnetic interactions in diluted magnetic semiconductors (DMS) is an interesting issue as a basic problem in magnetism and its possible application in spintronics.^{1,2} We have reported different types of magnetic source in case of Fe doped SnO_2 powders, prepared by sol-gel method and post annealing³, and also the phonon density of states (DOS) of rutile type structures of SnO_2 and TiO_2 .⁴ The dilution and clustering of doping Fe species can be estimated by Mössbauer spectra and phonon DOS. We have clarified that the diluted Fe species probe the phonon DOS in SnO_2 more faithfully than in TiO_2 . When a large magnetization was obtained for diluted Fe doped SnO_2 , a magnetic relaxation with broad lines was observed in room temperature Mössbauer spectra. However, when the small magnetization was observed, no magnetic component was found in Mössbauer spectrum. In the latter case, the magnetization disappeared by annealing for long time.³ It is clear that defects in DMS can also contribute to enhance the saturation magnetization.

On the other hand, thin films of $\text{Sn}_{1-x}\text{Fe}_x\text{O}_{2-\delta}$ have been implanted at room temperature with 1×10^{17} Fe ions/cm² and at 300 °C with 5×10^{16} and 1×10^{17} Fe ions/cm², with an implantation energy of 100 keV in each case.⁵ The as-implanted samples at room temperature and post-annealed samples did not show any Kerr effect, but the sample implanted with 1×10^{17} Fe ions/cm² at substrate temperature of 300 °C showed Kerr effect although the magnetic sextets were not so clearly observed in the ^{57}Fe conversion electron Mössbauer (CEM) spectra. Kerr effect disappeared after annealing. This suggests that the number of magnetic defects decreases by absorption of oxygen due to annealing in air atmosphere.⁵ We have also shown that the bulk magnetization is enhanced by introducing Sb^{5+} in the Fe doped SnO_2 powder.⁶ We have tried to prepare ^{57}Fe implanted SnO_2 films (containing 0.1 %Sb and 3 % Sb) at the substrate

temperature of 500 °C, which showed Kerr effect.⁷ The Kerr effect did not disappear after annealing.

In the present work, the SnO_2 (3 % Sb) films annealed at various temperatures are characterized by depth selective conversion electron Mössbauer spectroscopy (DCEMS) using a back-scattered type of gas flow counter in order to study especially the effect of post annealing.

2. Experimental

SnO_2 (3 % Sb) films with thickness of 200 nm were prepared on quartz glass by DC sputtering, and implanted with 5×10^{16} ^{57}Fe ions/cm² at the substrate temperature of 500 °C in vacuum, using an energy of 100 keV.⁸ From TRIM calculations of implantation conditions of 5×10^{16} Fe ions/cm², the iron profile peak is expected to be located at about 40 nm depth with a maximum Fe concentration of 5 at. %. Some samples were step by step post-annealed at 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C. Polar Kerr effect of these samples was measured with magnetic circular dichroism (MCD) mode. Three CEM spectra were simultaneously observed on each sample 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 homemade Mössbauer system and He + 5 % CH_4 gas flow counter.^{9,10} This method provides the rough depth profile of layers of interest, which is named as DCEMS. In contrast to DCEMS, conventional CEMS, which detects all electrons, is called in this article Integrated CEMS (ICEMS). Doppler velocity was calibrated with standard α -Fe foil at room temperature and a γ source of $^{57}\text{Co}/\text{Cr}$ matrix was used.

3. Results and Discussion

In order to confirm whether the bulk ferromagnetism appeared or not, polar Kerr rotation curves were measured by MCD mode for SnO_2 (3 % Sb) film, implanted with ^{57}Fe at substrate temperature of 500 °C, and annealed at 400 °C for 6 hours and further at 500 °C for 6 hours. As shown in Figure 1,

*Corresponding author. E-mail: k-nomura@t-adm.t.u-tokyo.ac.jp

it is clear that the Kerr rotation angles at light wave length of $\lambda = 300$ nm for SnO_2 (3 % Sb) films increased with the increase of annealing temperatures. In order to know the origin of ferromagnetism at room temperature and the effect of annealing on the ferromagnetism, three CEM spectra with different energies were measured step by step on the as-implanted sample after annealing at 400 °C for 2 hours and for 4 hours, and further at 500 °C for 2 hours and 4 hours. The Mössbauer parameters of the as-implanted SnO_2 (3 % Sb) film and the post-annealed one at 400 °C for 2 hours are listed in Tables 1 and 2, respectively.

DCEM spectra were obtained by detecting emitted electrons with the high, middle, and low energy regions, which reflect the top, middle, and deep layers, respectively. These spectra were decomposed to four subspectra of two doublets and two sextets. The doublets with small isomer shift ($\delta = 0.39$ mm/s) and large isomer shift ($\delta = 1.00$ mm/s) are assigned to paramagnetic Fe^{3+} and Fe^{2+} species, respectively. Two broad sextets with $\delta = 0.33$ mm/s and $\delta = 0.64$ mm/s can be assigned to Fe^{3+} at tetrahedral site A and $\text{Fe}^{2.5+}$ at octahedral site B of magnetite (Fe_3O_4) because the area ratio of the two sextets is almost 1:2 in the middle energy CEMS. The broadening of these peaks is considered to be due to the fine grain size of the iron compounds.

As shown in Table 1, the subspectra areas of magnetite were 34 %, 30 %, and 21 % in high energy, middle energy, and low energy CEM spectra of 3 % Sb doped SnO_2 film, respectively, whereas the subspectra areas of paramagnetic Fe^{2+} were 33 %, 48 % and 54 %, respectively. These suggest that magnetite layers are produced rather in upper layers of implanted regions, and that paramagnetic Fe^{2+} species prefer the deep layers of implanted regions of SnO_2 films.

Kerr effect of the films after annealed at 400 °C for 6 hours showed the larger rotation angles compared to that before the annealing treatment. In the case of implantation at substrate temperature of 300 °C, only a small Kerr effect was observed for the as-implanted film, and it disappeared by post annealing.⁵ However, in the present case Kerr effect was observed even after annealing. The CEM spectra were measured after the heat treatment at 400 °C for 2 hours. The magnetite peaks (two sextets with different isomer shifts), found in the case of the as-prepared samples, changed into two sextets with similar isomer shifts, quadrupole splitting values of near-zero quadrupole shift values, and different ratios as shown in Table 2. Those sextets can be considered as a superposition of several sextets with small tailing towards lower velocities. The magnetic components of samples annealed up to 500 °C were analyzed by using hyperfine field distributions. The magnetic

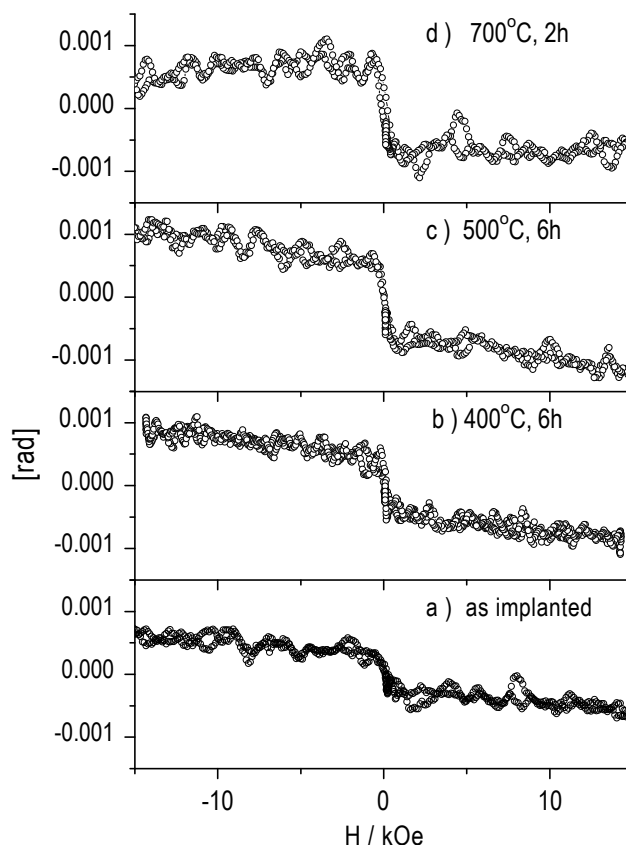


Figure 1. Polar Kerr rotation curves of SnO_2 (3 % Sb) film, implanted with ^{57}Fe at substrate temperature of 500 °C (a), post-annealed at 400 °C for 6 hours (b), at 500 °C for 6 hours (c), and at 700 °C for 2 hours (d) measured by MCD mode at $\lambda = 300$ nm.

subspectra of the heated samples can be fitted with a small distribution of magnetic hyperfine fields as shown in Figure 2. Therefore, the magnetic subspectra of the post-annealed samples up to 500 °C are considered to be due to one component of fine maghemite ($\gamma\text{-Fe}_2\text{O}_3$). It is understood that the maghemite is easily produced from magnetite by heating at 400 °C because of the same spinel structure of magnetite and maghemite. The magnetic hyperfine field distributions are shown in Figure 2. With increasing the annealing temperature and time, the maximum probability of hyperfine fields increased a little and the hyperfine field increased by 1 T. This suggests that the grain size of fine maghemite increased a little with increase of

TABLE 1: Mössbauer parameters of SnO_2 (3 % Sb) film, implanted with 5×10^{16} Fe ions/cm²

Doublets				Sextets				
Area ratio (%)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Area ratio (%)	δ (mm/s)	B_{hf} (T)	2ϵ (mm/s)	Γ (mm/s)
Top layer								
22.8%	0.38 (1)	0.74 (2)	0.59 (2)	18.6%	0.33 (1)	47.1 (1)	-0.03 (2)	0.60 (3)
32.9%	0.97 (1)	1.97 (2)	0.76 (2)	25.6%	0.64 (1)	42.7 (2)	-0.05 (3)	1.00 (5)
Middle layer								
22.9%	0.39 (1)	0.74 (2)	0.63 (2)	9.6%	0.32 (1)	47.4 (1)	-0.02 (2)	0.49 (4)
48.1%	1.00 (1)	1.98 (1)	0.72 (2)	19.5%	0.64 (1)	43.3 (1)	-0.14 (3)	1.06 (5)
Deep layer								
25.4%	0.38 (3)	0.73 (5)	0.70 (6)	11.0%	0.34 (6)	46.4 (3)	0.1 (2)	0.5 (3)
53.8%	1.03 (1)	2.03 (2)	0.68 (3)	9.8%	0.6 (1)	43.0 (9)	-0.0 (3)	0.9 (4)
ICEMS								
23.2%	0.39 (1)	0.73 (1)	0.62 (1)	12.4%	0.33 (1)	47.2 (1)	-0.02 (2)	0.55 (4)
44.5%	1.00 (1)	1.99 (1)	0.72 (1)	19.8%	0.64 (2)	43.1 (2)	-0.08 (3)	1.00 (5)

CEMS spectra were fitted assuming two doublets and two sextets. (δ : isomer shift, Δ : quadrupole splitting, 2ϵ : quadrupole shift, B_{hf} : hyperfine field, Γ : line width at half maximum peak)

TABLE 2: Mössbauer parameters of ^{57}Fe implanted SnO_2 (3 % Sb) film, annealed at 400 °C for 2 hours

Doublets				Sextets				
Area ratio. (%)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Area ratio (%)	δ (mm/s)	B_{hf} (T)	2ε (mm/s)	Γ (mm/s)
Top layer								
28.0%	0.40 (1)	0.79 (2)	0.59 (1)	28.9%	0.32 (3)	47.4 (1)	-0.00 (2)	0.82 (3)
30.7%	0.90 (1)	2.04 (2)	0.96 (2)	12.5%	0.31 (1)	42.1 (2)	-0.09 (3)	1.0 (1)
Middle layer								
28.5%	0.41 (1)	0.80 (2)	0.64 (1)	19.0%	0.35 (1)	47.6 (1)	-0.00 (2)	0.79 (4)
45.7%	1.00 (1)	2.02 (1)	0.77 (2)	6.8%	0.39 (3)	42.3 (1)	-0.13 (6)	0.9 (1)
Deep layer								
25.7%	0.42 (3)	0.82 (3)	0.62 (4)	12.4%	0.36 (4)	47.8 (4)	0.09 (9)	0.8 (2)
55.4%	1.01 (1)	2.01 (2)	0.75 (2)	6.5%	0.3 (1)	43. (1)	-0.1 (3)	0.9 (1)
ICEMS								
28.2%	0.41 (1)	0.81 (1)	0.63 (1)	19.5%	0.34 (1)	47.6 (1)	0.01 (1)	0.78 (4)
44.0%	0.99 (1)	2.02 (1)	0.79 (1)	8.3%	0.35 (2)	42.5 (4)	-0.10 (5)	0.9 (1)

The CEM spectra were fitted by assuming two doublets and two sextets.

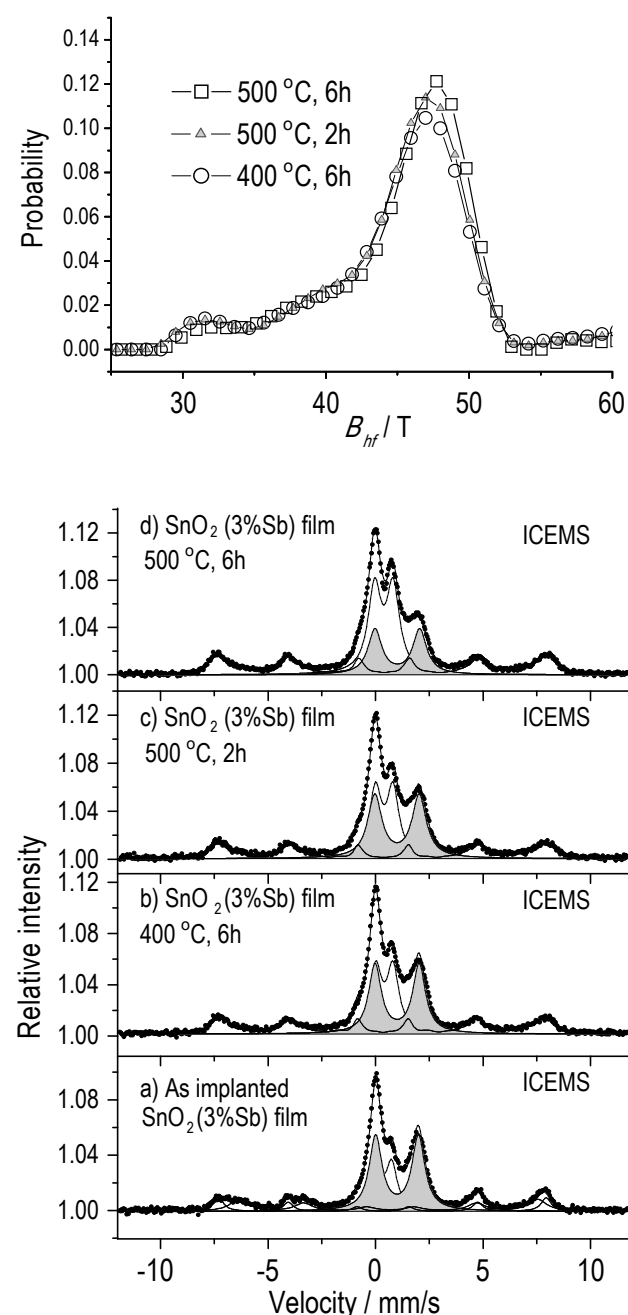


Figure 2. ICESM spectra of the samples: as implanted, annealed at 400 °C for 6 hours, at 500 °C for 2 hours and for 6 hours, and the hyperfine field distributions of fine maghemite produced by heating the ^{57}Fe implanted SnO_2 (3 % Sb) films at each temperature.

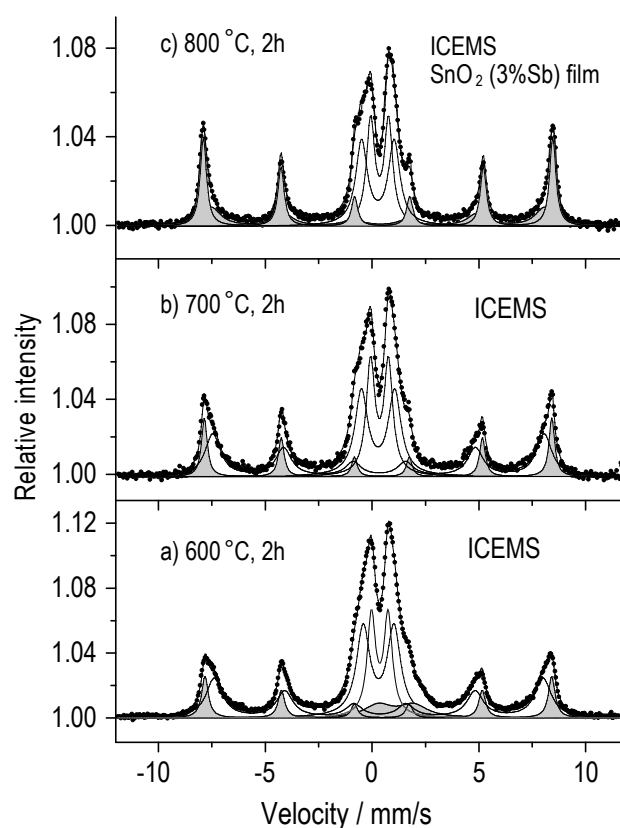


Figure 3. ICESM spectra of the samples annealed at each temperature of 600 °C (a), 700 °C (b), and 800 °C (c) for 2 hours.

annealing temperature and time.

When heating above 600 °C, the sextet due to hematite ($\alpha\text{-Fe}_2\text{O}_3$, with the estimated values: $\delta = 0.38$ mm/s, $2\varepsilon = -0.19$ mm/s, $B_{\text{hf}} = 50.5$ T, $\Gamma = 0.35$ mm/s) was observed in addition to that of the maghemite ($\delta = 0.33$ mm/s, $2\varepsilon = -0.04$ mm/s, $B_{\text{hf}} = 47.9$ T, $\Gamma = 0.9$ mm/s) as shown in Figure 3. The doublet peaks of Fe^{2+} almost disappeared, although some small Fe^{2+} peaks remained only in the deepest layer, and two kinds of paramagnetic Fe^{3+} peaks ($\delta = 0.34\text{--}0.37$ mm/s, $\Delta = 0.77\text{--}0.85$ mm/s, $\Gamma = 0.44\text{--}0.49$ mm/s and $\delta = 0.26\text{--}0.33$ mm/s, $\Delta = 1.35\text{--}1.51$ mm/s, $\Gamma = 0.65\text{--}0.90$ mm/s) were clearly observed as shown in Figure 4. The component with large isomer shifts may be superparamagnetic $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$, while the other with lower isomer shifts and large quadrupole splitting may be dilute Fe^{3+} in SnO_2 matrix.

The area ratios of paramagnetic Fe^{3+} components, paramagnetic Fe^{2+} component, magnetic maghemite, and hematite; produced in top surface, middle, and deep layers of the samples heated step by step in air; are shown in Figure 5. The area ratio of paramagnetic Fe^{3+} increased a little in deep layers but decreased in top layers with heating at high temperature ranges of 600–800 °C. The difference of area ratios of maghemite between layers was relatively large in case of heating at low temperatures of 400–500 °C, but decreased with the further increase of heating temperature. This suggests that the fine grains of maghemite are growing by heating.

The Kerr rotation angles observed for the annealed samples are considered to attribute mainly to the fine maghemite produced in the SnO_2 films, and annealing up to 700 °C is found to be effective as transparent and ferromagnetic film. However, heating at 800 °C was not good for room temperature ferromagnetism because weak ferromagnetic hematite was produced from maghemite while the ratio of paramagnetic or superparamagnetic Fe^{3+} species was not so much increased. The annealed sample at 800 °C did not show any Kerr effect, and the Mössbauer parameters of the sextet with low intensity and low hyperfine field ($B_{\text{hf}} = 48.4$ T, and $\delta = 0.34$ mm/s, $2\epsilon = -0.13$ mm/s, $\Gamma = 1.06$ mm/s) as shown in Figures 3 and 4 were different from those for the annealed sample at 700 °C ($B_{\text{hf}} = 47.8$ T, and $\delta = 0.33$ mm/s, $2\epsilon = -0.03$ mm/s, $\Gamma = 0.9$ mm/s), which latter is corresponding to maghemite. The hematite peaks can be distinguished from the maghemite peaks because the quadrupole shift's values are different. 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 at the annealed sample at 800 °C is considered to be a tailing part due to fine particle of hematite in SnO_2 film produced by annealing at the high temperatures, not maghemite.

The magnetic peaks observed by Fe ion implantations and post-annealing at high temperatures can be assigned to sextets due to magnetite and maghemite, and clearly distinguished

from the magnetic relaxation peaks observed in dilute Fe doped SnO_2 powders.

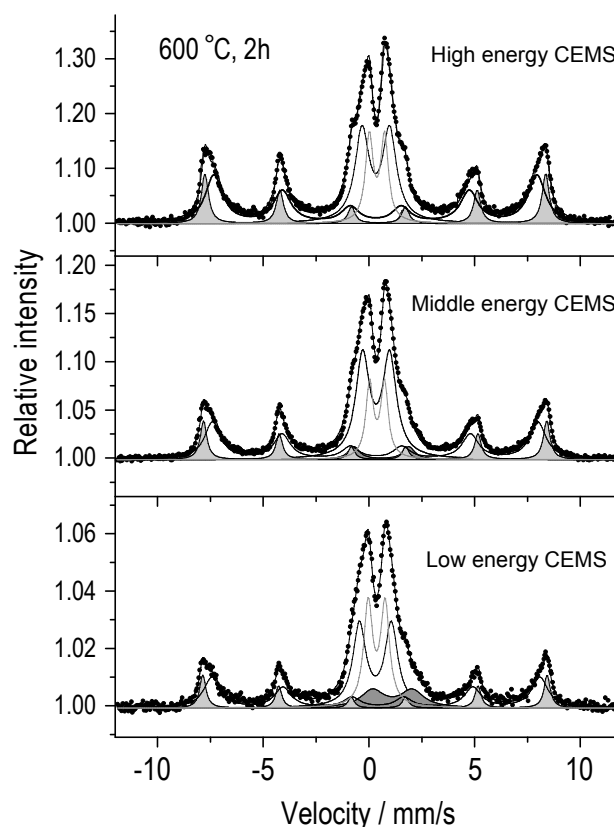


Figure 4. DCEM spectra of ^{57}Fe implanted SnO_2 (3 % Sb) sample, annealed at 600 °C for 2 hours. High energy CEMS: top layer, Middle energy CEMS: middle layer, Low energy CEMS: deep layer.

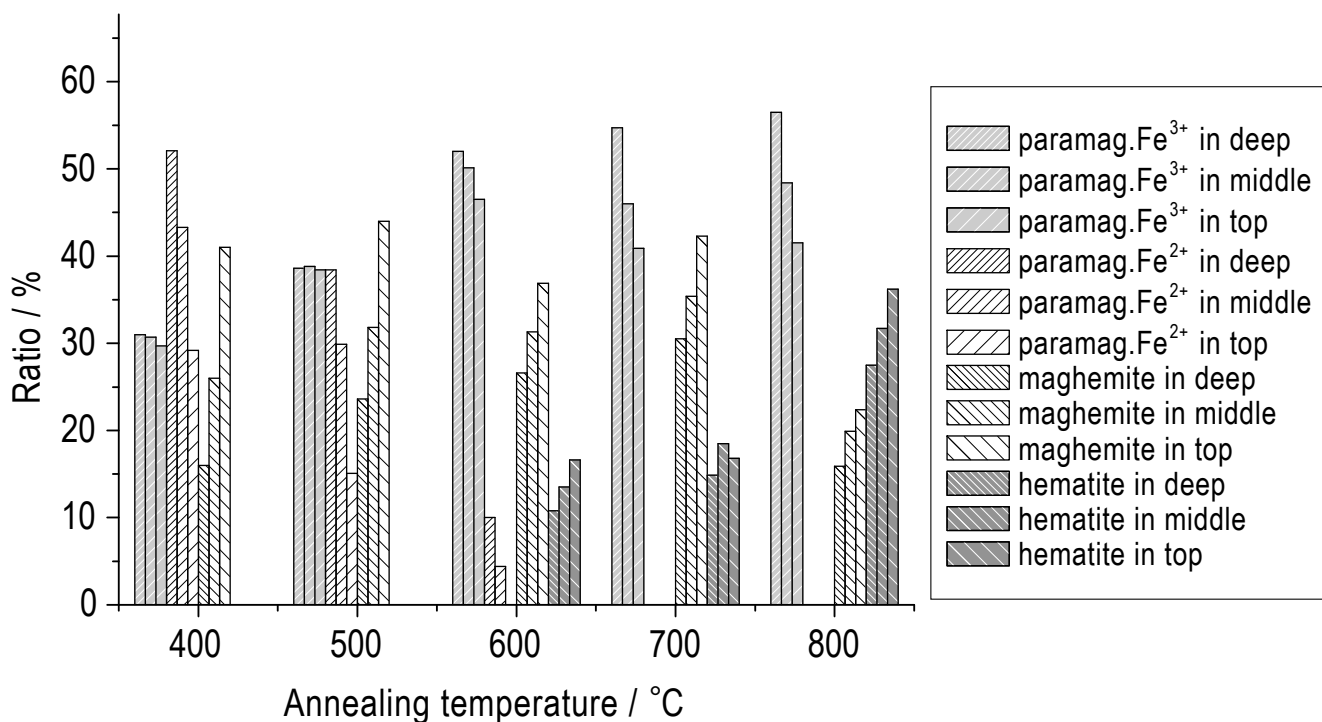


Figure 5. Ratios of four divided Fe species produced in top, middle, and deep layers of SnO_2 film implanted with ^{57}Fe , annealed step by step at 400 °C for 6 h, 500 °C for 6 h, 600 °C for 2 h, 700 °C for 2 h, and 800 °C for 2 h. Two paramagnetic Fe^{3+} species observed for the samples heated at the higher temperatures than 600 °C are summed up. The ratio of maghemite for the heated sample at 800 °C may be a part of fine hematite.

4. Conclusions

SnO_2 (3 % Sb) film doped with 5×10^{16} ^{57}Fe ions/cm² at substrate temperature of 500 °C with an energy of 100 keV was post-annealed step by step from 400 °C to 800 °C. These samples except the one heated at 800 °C showed Kerr effect, that is, bulk ferromagnetism at room temperature. The Kerr rotation angles increased with the increase of annealing temperature up to 700 °C. The room temperature ferromagnetic phenomena were attributed mainly to maghemite produced from magnetite and mixed Fe^{3+} and Fe^{2+} oxides by post-annealing. It was found from DCEMS analysis that the maghemite with relatively large grains exists more in top layer than in deep layer. The transparent magnetic films at room temperature were obtained by implantation at substrate temperature of 500 °C and post-annealing up to 700 °C although these films were not intrinsic dilute magnetic semiconductors.

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