57Fe implantation effect of Sb doped SnO2 films

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Abstract. We implanted 57Fe with 5x1016 ions/cm2 into SnO2 films containing 0.1% Sb and 3% Sb at the substrate temperature of 500°C in vacuum. As a result, four kinds of subspectra were observed in the depth selective CEM spectra by using a back scattered type of gas counter. Two doublets are assigned to paramagnetic Fe3+ and Fe2+ species and two sextets are assigned to site A and site B of magnetite. Magnetite formation was found to prefer the top layer, whereas paramagnetic Fe2+ species were included in the deeper layer of the films. SnO2 (with 0.1% and 3% Sb) films doped with 5x1016 57Fe ions/cm2 at 500°C and post-annealed at 400°C for 6 h showed bulk ferromagnetism at room temperature although the 57Fe implanted SnO2 (3% Sb) film showed smaller Kerr effect than the 57Fe implanted SnO2 (0.1% Sb) film. This phenomenon was attributed mainly to the amount of magnetite in the as prepared samples and to the maghemite in the post-annealed samples, respectively, in addition to magnetic defects.

1. Introduction
The origin of magnetic interactions in diluted magnetic semiconductors (DMS) is attracting a great attention as a basic problem in magnetism and as an application of spintronics [1-2]. We have reported different types of magnetic source in case of Fe doped SnO2 powders, prepared by sol-gel method [3], and also the phonon density of states of rutile type structures of SnO2 and TiO2 [4]. It is clear that defects in DMS can also contribute to saturation magnetization. On the other hand, thin films of Sn1-x57FexO2-δ have been implanted at room temperature with 1x1017 Fe ions/cm2, as well as at 300°C with 5x1016 and 1x1017 Fe ions/cm2 [5]. The as implanted samples at room temperature and post-annealed samples did not show any Kerr effect, but the sample implanted with 1x1017 Fe ions/cm2, while heated at 300°C, showed Kerr effect although the magnetic sextets were not clearly observed in the 57Fe conversion electron Mössbauer (CEM) spectra. Kerr effect disappeared after the post-annealing. This suggests that the number of magnetic defects decreases by absorption of oxygen due to annealing in air atmosphere [5]. We have also showed that the bulk magnetization is enhanced by introducing Sb in the Fe doped SnO2 powder [6]. This time we tried to implant the Sb doped SnO2 films with 57Fe at high substrate temperature. It was found that the films show Kerr effect, and we have also characterized the surface products on the films by conversion electron Mössbauer spectroscopy (CEMS) using a gas counter.
2. Experimental
SnO2 films containing 0.1% Sb and 3% Sb with thickness of 200nm were prepared on quartz glass by using DC sputtering in O2 flow and were implanted with 5x10^{16} ^{57}Fe ions/cm^2 at the substrate temperature of 500°C in vacuum, using the acceleration energy of 100 keV. From TRIM calculations of implantation conditions of 5x10^{16} Fe ions/cm^2, 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 post-annealed at 400°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 (2-6.5keV, 6.5-11keV, and 11-20 keV) using homemade Mössbauer system and He + 5% CH4 gas counter [7,8]. This method provides the rough depth profile of layers of interest. Doppler velocity was calibrated with standard α-Fe foil at room temperature and a γ source of ^{57}Co/Cr matrix was used.

3. Results
To obtain the bulk ferromagnetism, Kerr rotation curves were measured by MCD mode at λ=300 nm for SnO2 (0.1%Sb) film and (b) SnO2 (3%Sb) film, implanted with ^{57}Fe at substrate temperature of 500°C. As shown in Figure 1, it is clear that Kerr effect of both samples was observed, and the Kerr rotation angles for 0.1% Sb doped SnO2 films were larger than that for 3%Sb doped SnO2 films.

CEM spectra of these samples are shown in Figure 2. CEM spectra obtained by detecting emitted electrons with the high energy regions reflect the top layer. These spectra were decomposed to 4 subspectra of two doublets and two sextets. The Mössbauer parameters of the sample with 0.1% Sb are listed in Table 1. The doublets with small isomer shift (δ = 0.39 mm/s) and large isomer shift (δ = 0.94 mm/s) are assigned to paramagnetic Fe^{3+} and Fe^{2+} species, respectively. Two broad sextets with δ = 0.31 mm/s and δ = 0.62 mm/s can be assigned to Fe^{3+} at site A and Fe^{2.5+} at site B of magnetite because the area ratio of the two sextets is almost 1:2. The broadening of these peaks is considered to be due to the fine grain size of the particles. Only the relative area of the components in CEM spectra were found to differ between the SnO2 films with 0.1% Sb and 3% Sb. In the case of 0.1 % Sb doped SnO2 film, the relative area of the ferromagnetic magnetite phase was larger than in 3% Sb doped SnO2 films. This result is in accordance with the larger Kerr effect of the former sample.

As shown in Table 1, the subspectra area intensities of magnetite were 63.6%, 48.9% and 34.7% in high energy, middle energy, and low energy CEM spectra of 0.1%Sb doped SnO2 film, respectively, whereas the subspectra area intensities of paramagnetic Fe^{3+} were 18.5%, 28.9% and 40%, respectively. These suggest that magnetite layers are produced rather in upper layers of implanted regions, and that paramagnetic species prefer the deep layers of implanted regions of SnO2 films.

Kerr effect of these films annealed at 400°C for 6 hours showed the same hysteresis as before the annealing treatment. In the case of implantation at 300°C, Kerr effect was observed, but disappeared.
by post annealing [5]. However, Kerr effect was found to remain in the present case even after annealing. The CEM spectra measured after the heat treatment are shown in Figure 3. The magnetite phase with 2 sextets, found in the case of the as prepared samples, changed into one broad sextet with small tailing towards lower velocities in both samples. After annealing, the magnetic subspectra can be fitted with a sextet showing a small distribution of magnetic hyperfine fields. The isomer shift and quadrupole splitting of the sextet show roughly 0.31-0.33 mm/s and 0 mm/s values, respectively, while the maximum of the hyperfine fields is around 47.5 T. Therefore, the magnetic subspectra of the post annealed samples are considered to be due to one component of fine $\gamma$-Fe$_2$O$_3$. The doublet intensity of Fe$^{2+}$ decreased more in top layer than in deep layer after annealing.

Figure 2. Depth selective CEM spectra showing the change of the quantity of magnetite in different depths of SnO$_2$ films with 0.1% Sb (left) and 3% Sb (right), implanted with 5x10$^{16}$ Fe ions at a substrate temperature of 500°C. ICEMS indicates the integrated CEM spectra.

| Doublets Area Int. | Sextets | Top layer | Middle layer | Deep layer | ICEMS |
|--------------------|---------|-----------|--------------|------------|-------|
| (%)                | $\delta$ (mm/s) | $\Delta$ (mm/s) | $\Gamma$ (mm/s) | $\delta$ (mm/s) | $\Delta$ (mm/s) | $\Gamma$ (mm/s) | $\delta$ (mm/s) | $\Delta$ (mm/s) | $\Gamma$ (mm/s) |
| 17.9 %             | 0.39 (3) | 0.75 (4) | 0.59 (3) | 22.4 % | 0.32 (1) | 47.6 (4) | -0.01 (1) | 0.46 (2) |
| 18.5 %             | 0.85 (2) | 1.94 (4) | 0.82 (5) | 41.2 % | 0.60 (1) | 43.5 (1) | -0.09 (2) | 0.97 (3) |
| 22.3 %             | 0.39 (1) | 0.76 (2) | 0.59 (2) | 16.1 % | 0.31 (1) | 47.6 (1) | 0.01 (2) | 0.46 (3) |
| 28.9 %             | 0.93 (1) | 1.93 (2) | 0.79 (2) | 32.7 % | 0.63 (1) | 43.7 (1) | -0.09 (2) | 1.04 (4) |
| 25.3 %             | 0.39 (3) | 0.82 (6) | 0.62 (6) | 10.3 % | 0.31 (3) | 48.5 (3) | 0.03 (8) | 0.37 (14) |
| 40.0 %             | 0.99 (3) | 1.97 (5) | 0.72 (5) | 24.4 % | 0.64 (4) | 43.9 (4) | 0.07 (8) | 0.78 (14) |
| ICEMS               | 21.7 % | 0.39 (1) | 0.77 (2) | 0.61 (2) | 16.9 % | 0.31 (1) | 47.7 (1) | -0.00 (1) | 0.46 (2) |
| 27.7 %             | 0.94 (1) | 1.92 (2) | 0.78 (2) | 33.8 % | 0.62 (1) | 43.7 (1) | -0.07 (2) | 0.99 (3) |
4. Conclusions
SnO$_2$ (with 0.1% and 3%Sb) films doped with 5x10$^{16}$ $^{57}$Fe ions/cm$^2$ at 500°C and post-annealed at 400°C for 6 h showed bulk ferromagnetism at room temperature. This phenomenon was attributed mainly due to formation of ferromagnetic magnetite for as prepared samples and of maghemite for the post-annealed samples, respectively, rather than magnetic defects. Including more Sb in SnO$_2$ film was found to decrease the amount of magnetite produced. It is further found that on the top layers of the implanted region, magnetic components were apt to produce at the substrate temperature of 500°C and in high vacuum.

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