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^{119}Sn CEMS study of Sb doped SnO_2 film

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Abstract Sb doped SnO_2 films prepared by DC sputtering and heating were characterized by ^{119}Sn conversion electron Mössbauer spectrometry (CEMS). An asymmetric doublet was observed in the Mössbauer spectra of 1 %, 3 %, and 10 % Sb doped SnO_2 films. The peak ratios of doublets are considered to be due to the columnar crystal growth on the substrate. With the doping level of Sb, both the isomer shift (δ) and the quadrupole splitting (Δ) increased. After annealing, δ increased and Δ decreased for each sample. These results suggest the followings. The electron doping of the SnO_2 lattice by pentavalent Sb induces the increase of the electron density at the Sn^{IV} nucleus. The annealing process leads to more

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complete accommodation of the Sb dopant that results in more effective electron doping and therefore increasing isomer shift for tin. Simultaneously, the distortion of the lattice caused by Sb is relaxed and the quadrupole splitting decreases.

Keywords ^{119}Sn Mössbauer spectroscopy · Sb doped SnO_2 · Structural information

1 Introduction

Transparent and conductive films are useful for solar cell and light devices applications, catalysis, gas sensors, etc.. We have studied earlier the magnetic properties of SnO_2 films doped with iron [1], as well as the magnetic properties and defect structure of SnO_2 doped with Fe and Sb using conversion electron Mössbauer spectrometry (CEMS) [2] and even depth selective ^{57}Fe CEMS [3]. We have also performed theoretical *ab initio* calculations on these systems [4]. Sb doped SnO_2 films are frequently used as a base film for various applications. In this study, these oxide films were analysed by ^{119}Sn CEMS. We focused on the effect of Sb doping on DC sputtered and annealed SnO_2 films.

2 Experimental

1 %, 3 % and 10 % Sb doped SnO_2 films (the percentage value refers to the molar ratio of Sb to Sn) on quartz glass substrate were prepared by DC sputtering, and annealed at 500°C for 2 hours in air. ^{119}Sn conversion electron Mössbauer (CEM) spectra were recorded by a conventional Mössbauer spectrometer (WISSEL Co.) with a flowing gas (96 % He + 4 % CH_4) proportional counter (RANGER Co.) at room temperature using a $CaSnO_3$ source. The incident gamma rays were perpendicular to a sample plane. The Doppler velocity was calibrated by measuring standard α-Fe with a ^{57}Co(Rh) source, and the tin isomer shifts are given relative to $CaSnO_3$. The Mössbauer spectra were evaluated by least-square fitting using the MOSSWINN program.

3 Results and discussion

The ^{119}Sn CEMS spectra of SnO_2 films with and without annealing showed the envelope of an asymmetrical doublet. We have evaluated these CEM spectra by three kinds of possible restrictions; 1) one doublet with the same intensity and the same line width of the two peaks, 2) one doublet with the same intensity and different line widths of two peaks and 3) one doublet with the different intensities and the same line width of the two peaks. The lowest chi square was obtained for the third case. Thus the final evaluation was done by constraining the line width (FWHM) of the two lines of the doublet to be the same while there was no constraint on the intensities. Let us note here, that SnO_2 films are considered uniform and polycrystalline films, composed of oriented columnar SnO_2 crystals.

With increasing Sb dopant concentration, δ and Δ increased as shown in Table 1 and Fig. 1. The doping with Sb^{5+} influences the electric density around Sn nucleus. Since the

Table 1 ^{119}Sn CEM parameters of Sb doped SnO_2 films before and after annealing at 500°C for 2 hours

Sample characterisation		^{119}Sn Mössbauer parameters			
Doping rate	treatment	δ (mm/s)	Δ (mm/s)	W (mm/s)	P_1/P_2 ratio
1 %Sb	as-deposited	0.014± 0.004	0.56± 0.005	0.83± 0.008	1.25± 0.031
1 %Sb	annealed	0.016± 0.014	0.52± 0.016	0.86± 0.024	1.20± 0.106
3 %Sb	as-deposited	0.021± 0.015	0.57± 0.017	0.84± 0.029	1.24± 0.108
3 %Sb	annealed	0.034± 0.022	0.49± 0.024	0.84± 0.035	1.46± 0.220
10 %Sb	as-deposited	0.045± 0.007	0.64± 0.008	0.86± 0.014	1.06± 0.037
10 %Sb	annealed	0.075± 0.014	0.60± 0.016	0.85± 0.026	1.20± 0.090

valence state of Sb is higher than that of Sn in the lattice, charge compensation requires higher electron density at the Sn^{IV} centers. Indeed, the increased δ means the increase of electron density around the ^{119}Sn nucleus. The increased Δ means that the electric field gradient at the ^{119}Sn nucleus increases with Sb doping rates, obviously due to the distortion caused to the lattice structure. From these results, it is considered that doped Sb atoms are substituted at Sn sites and/or incorporated at the interstitial sites. Thus, it is confirmed that Sb doping into SnO_2 is effective in this range.

After annealing at 500°C for 2 hours, δ increased, while Δ decreased for each sample. Larger Sb doping level resulted in larger increase of δ. It is considered that annealing in air brings up the rutile structure with substitutionally accommodated Sb^{5+} and reduces the amount of interstitial Sb and oxygen vacancies. This suggests that the crystal structure of rutile shows the smallest distortion of electron density distribution around Sn atoms.

In the case of so-gel synthesized Sb doped SnO_2 [5], the valence states were observed as Sb^{3+}, Sb^{5+}, and Sn^{4+} by Mössbauer spectroscopy. Since, in DC sputtering, oxygen loss and therefore reduction of Sb^{5+} to Sb^{3+} may occur, it would also be reasonable to consider that Sb^{3+} transforms into Sb^{5+} by annealing in air, and that all Sb atoms are well incorporated in the lattice structure of rutile SnO_2 in the sputtered film. However, large initial (i.e.,. as-deposited) amount of Sb^{3+} is not reasonable to assume because it would not explain the electron doping effect of the rutile lattice indicated by the increase of tin isomer shift.

The asymmetry ratio (Peak1/Peak2) of the doublet decreased after annealing the films except 3 % Sb doped SnO_2, of which the electric resistivity was the smallest among these samples. We need to consider the orientation of columnar SnO_2 crystals on the substrate, which affects the carrier electron density, not only the doping effects. These columnar films are composed from polycrystalline SnO_2, and may be considered as pseudo-single crystals. This explains the texture origin of the doublet asymmetry. On the other hand, the asymmetry of the peaks may also be due to Goldanskii-Kariyagin effect but it is unlikely due to the close to cubic structure of SnO_2.

Distinction between the two origins experimentally (variation of the geometry or the temperature) in CEMS technique is not simple, so it needs future studies.

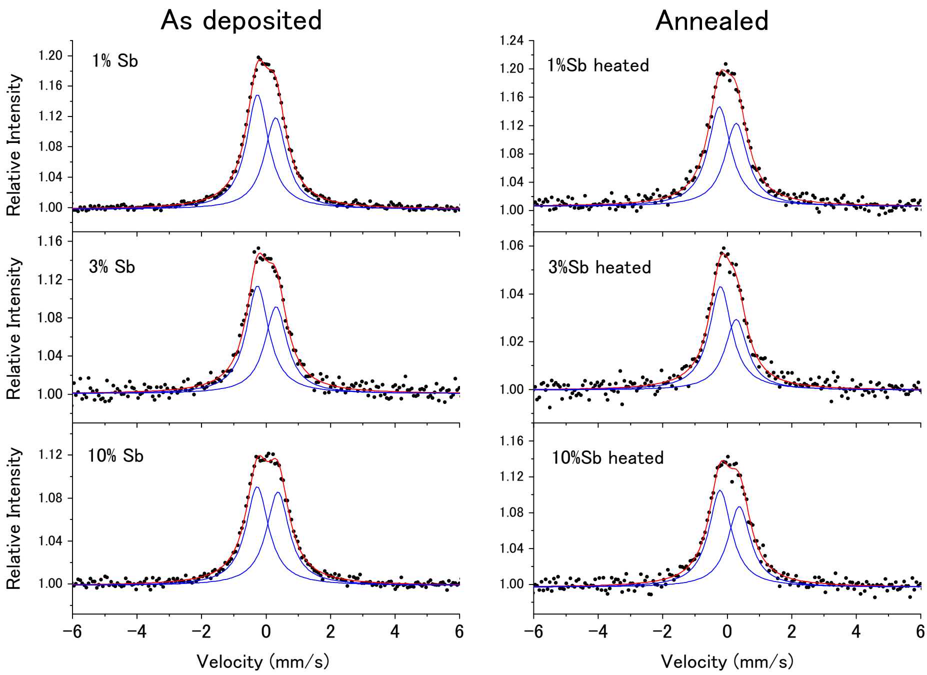

Fig. 1 ^{119}Sn CEM spectra of Sb doped SnO_2 films: as deposited film and annealed film

4 Conclusion

SnO_2 films doped with 1 %, 3 % and 10 % Sb concentrations and post annealing effect were characterized by ^{119}Sn CEMS.

With the doping rate of Sb, both δ and Δ values increased. After annealing, δ increased and Δ decreased for each sample. These findings suggest that the electron doping by Sb induces the increase of the electron density at the Sn^{IV} nucleus. Annealing in air at 500 ^{o}C brings up Sb atoms more perfectly incorporated in the lattice structure of SnO_2, and the distortion of the rutile lattice is relaxed. The asymmetry of the doublet can be explained as a texture effect due to columnar SnO_2 crystal growth in the film.

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References

1. Nomura, K., Reuther, H.: Hyperfine Interact. **191**, 159–165 (2009)
2. Nomura, K., Nemeth, Z., Reuther, H.: J. Phys. Conf. Ser. **217**, 01218 (2010)
3. Nomura, K., Iio, S., Hirose, Y., Németh, Z., Yamamoto, K., Reuther, H.: J. Nucl. Radiochem. Sci. **11**, 1–5 (2010)
4. Mudarra Navarro, A.M., Rodríguez Torres, C.E., Cabrera, A.F., Weissmann, M., Nomura, K., Errico, L.A.: J. Phys. Chem. C **119**, 5596–5603 (2015)
5. Grzeta, B., Tkalcec, E., Goebbert, C., Takeda, M., Takahashi, M., Nomura, K., Jaksic, M.: J. Phys. Chem. of Solids **765-772**, 63 (2002)