Mössbauer Studies of Reactively Deposited Tin Oxide Films

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The oxidation state of SnO_x films prepared by reactive deposition was studied by Mössbauer spectroscopy. All the amorphous films deposited below the substrate temperature of 350°C were composed of Sn^{2+} and Sn^{4+} , which ratio depended on the substrate temperature and oxygen pressure. With increasing oxygen pressure, the Sn^{4+} content in the films was increased to be saturated with the film composition of $\text{SnO}_{1.5}$, while it was decreased at higher substrate temperatures. The crystallized films deposited at $350\sim 420^\circ\text{C}$ were also composed of Sn^{2+} and Sn^{4+} , and the Sn^{2+} content was markedly decreased at higher substrate temperatures. The values of quadrupole splitting and isomer shift of tin ions in the films were discussed.

1 Introduction

Tin oxide films are of great technological interest as transparent electrodes¹⁾ or gas sensors²⁾. This is because the films are n-type semiconductors with a band gap of about 4eV ¹⁾. The electroconductive nature of the films is due to oxygen vacancies, and thus is closely connected to the structure of films.

Tin oxide films can be prepared by reactive deposition³⁻⁵⁾. The dependence of the film structure on the deposition conditions have been studied by X-ray diffraction. Above the oxygen pressure of 0.1Pa , amorphous or tin dioxide films are deposited, depending on the substrate temperature, while below 0.1Pa , films are of lower oxide such as $\text{SnO}^{4)}$. We further investigated the film structure using Sn^{119} Mössbauer effect. This paper describes the influence of the oxygen pressure and substrate tempera-

ture on the oxidation state of films.

2 Experimental procedures

Films were deposited in a conventional high vacuum chamber evacuated with an oil diffusion pump. The substrates were placed about 20cm from an evaporation source. After the vacuum chamber was evacuated below $6\times 10^{-4}\text{Pa}$, tin (purity, 99.999%) was evaporated from an alumina crucible and the oxygen gas (purity, 99.995%) was introduced to the desired pressure. The oxygen pressure during deposition was in the range $7\times 10^{-2}\sim 0.7\text{Pa}$. The substrate temperature was kept between 50 and 420°C , and the deposition rate was at about $1\text{\AA}/\text{s}$. The films were deposited about $5500\text{\AA}$ thick on Al foils.

Mössbauer effect measurements were made at a liquid nitrogen temperature. Barium stannate BaSnO_3 was used as a source of γ -radia-

tion. The spectra of pure SnO_2 and SnO were also measured as the reference. All the Mössbauer spectra were analyzed by fitting to Lorentzian lines, using a least-squares fitting program. The Sn^{2+} and Sn^{4+} contents in the films were determined from the relative intensities of Sn^{2+} and Sn^{4+} lines. The systematic error in these cation contents was expected because of a difference in the recoil free fractions of Sn^{2+} and Sn^{4+} .

3 Results and discussion

Figure 1 shows examples of Mössbauer spectra for the films deposited at various oxygen pressures and substrate temperatures. The solid lines in the figure represent a least square fit to the data. The spectra of the films were mainly composed of Sn^{2+} and Sn^{4+} lines. The line width of Sn^{2+} was in the range 0.91~1.03mm/s, nearly independent of the lattice form and the oxidation state of films, while that of Sn^{4+} was 0.81~1.10mm/s. The value of Sn^{4+} was slightly larger for the highly oxidized amorphous films.

Figure 2 shows the dependence of the Sn^{4+} ratio to the total tin ions in the films on the oxygen pressure. The substrate temperature was 50 and 250°C. The film deposited at 250°C and at 9.3×10^{-2} Pa was crystallized SnO , and the others were amorphous⁴³. The Sn^{4+} content in the films deposited at 50°C was increased as the oxygen pressure increased upto about 0.25 Pa. The number of oxygen molecules adsorbed on the substrate is increased at the higher oxygen pressures, resulting in the higher oxidized films. Above 0.25Pa, the Sn^{4+} content was saturated at about 75%. From the gravimetric analyses, the saturated composition of films is approximately $\text{SnO}_{1.5}$ ⁴⁴. The results indicate that the oxidation state of $\text{SnO}_{1.5}$ is not ex-

Fig.1 Mössbauer spectra of films deposited at various oxygen pressures and substrate temperatures. a: 7×10^{-2} Pa, 50°C. b: 0.65 Pa, 50°C. c: 0.24 Pa, 250°C. d: 0.24 Pa, 370°C. e: 0.24 Pa, 420°C

ceeded at room temperature by reactive deposition. At the higher substrate temperature of 250°C, the Sn^{4+} content in the films was also increased with increasing oxygen pressure. However, the values were lower compared to those of films deposited at 50°C, and the value of 75% was nearly attained at about 0.7 Pa. At the higher substrate temperature, the number of oxygen molecules adsorbed on the substrate is decreased, resulting in a lower oxidized state of films. Such an effect of the substrate temperature on the oxidation of films is also

Fig.2 Dependence of the Sn^{4+} content on the oxygen pressure (Po_2). The substrate temperature is (a) 50°C and (b) 250°C .

reported for silicon oxide films⁷⁾.

Figure 3 shows the dependence of the Sn^{4+} content in the films on the substrate temperature. The oxygen pressure during deposition was about 0.24 Pa. The films deposited below 350°C were amorphous, while those deposited at and above 350°C were crystallized with a rutile-like structure. The Sn^{4+} content in the amorphous films was decreased with increasing substrate temperature because of a decrease in the number of oxygen molecules adsorbed on the substrate. On contrast, the Sn^{4+} content in the crystallized films was markedly increased at the higher substrate temperatures, and reached the value of about 91% at 420°C , very close to a SnO_2 composition. At the higher oxygen pressure of 0.7 Pa and at 420°C , the Sn^{4+} content was slightly larger at about 94%. Although the number of O_2 ad molecules on the substrate will be further decreased above 300°C , the O_2 and Sn particles adsorbed on the substrate will be energetically much activated. This results in a higher reactivity between oxygen and tin particles, and thus the highly oxidized films are grown in a crystallized form at the higher substrate temperatures.

Fig.3 Dependence of the Sn^{4+} content on the substrate temperature (T_s) at 0.24 Pa.

Figure 4 shows the dependence of the isomer shift and quadrupole splitting of Sn^{4+} on the Sn^{4+} content in the amorphous or crystallized films. The isomer shift and quadrupole splitting of Sn^{4+} in the amorphous films were close to the values for the pure SnO_2 (isomer shift, 0.08 mm/s; quadrupole splitting, 0.55 mm/s). The results indicate an octahedral coordination of the oxygen for the Sn^{4+} in the films. The slightly larger values of the quadrupole splitting at the higher Sn^{4+} contents will be due to an increased asymmetry of the octahedron for the highly oxidized films. Collin et al. have also reported the larger quadrupole split-

Fig.4 Dependence of isomer shift (Is) and quadrupole splitting (Qs) of Sn^{4+} on the Sn^{4+} content in amorphous (○, △) and crystallized films (●, ▲).

Fig.5 Dependence of isomer shift(Is) and quadrupole splitting(Qs) of Sn^{2+} on the Sn^{4+} content in amorphous (○, △) and crystallized films (●, ▲).

ting of Sn^{4+} in the amorphous films than that in the SnO_2 crystal⁹⁾.

Figure 5 shows the dependence of the isomer shift and quadrupole splitting of Sn^{2+} on the Sn^{4+} content. The isomer shift of Sn^{2+} in the amorphous films were nearly close to the value of 2.59mm/s for the pure Sn_2O_3 ⁹⁾ or to the value of 2.63mm/s for the pure SnO , though the value was somewhat larger at the higher Sn^{4+} content. The quadrupole splitting of Sn^{2+} in the amorphous films were very close to the value of 1.96mm/s for the pure Sn_2O_3 ⁹⁾, but much larger than the value of 1.36mm/s for the pure SnO . The results suggest that the oxygen coordination for Sn^{2+} in the amorphous films is similar to that in the Sn_2O_3 crystal, nearly independent of the oxidation state of films. For the oxygen coordination in the Sn_2O_3 , details have not yet been reported.

The isomer shift and quadrupole splitting of Sn^{4+} in the crystallized films were in good agreement with those for the pure SnO_2 crystal. For the Sn^{2+} , the isomer shift and quadrupole splitting were very

close to those for the pure Sn_2O_3 .

4 Summary

Valence state of tin ions in the reactively deposited SnO_x films were analyzed by Mössbauer spectroscopy. Both the amorphous and crystallized films were composed of Sn^{2+} and Sn^{4+} . With increasing oxygen pressure, the oxidized degree of the amorphous films was increased to be saturated at the film composition of $\text{SnO}_{1.5}$, while it was decreased at the higher substrate temperatures. The crystallized films was markedly oxidized at the higher substrate temperatures. The film composition was nearly SnO_2 at 420°C. The values of the isomer shift and quadrupole splitting of Sn^{2+} and Sn^{4+} in the amorphous films suggested the oxygen coordinations for Sn^{2+} and Sn^{4+} similar to those in Sn_2O_3 crystals, nearly independent of the film composition.

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