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Electrical properties of high purity tin dioxide doped with antimony

KEIZO UEMATSU
Faculty of Engineering, Nagaoka Institute of Technology, Nagaoka, Niigata, Japan
NOBUYASU MIZUTANI, MASANORI KATO
Faculty of Engineering, Tokyo Institute of Technology, O-Okayama, Meguro-ku, Tokyo, Japan

The electrical conductivity of high purity tin dioxide doped with antimony was studied at temperatures of 900 to 1200° C and partial pressures of oxygen between 10^{-8} and 1 atm. For specimens having a dopant concentration over 1×10^{19} Sb cm^{-3}, the electrical conductivity decreased slightly with temperature and independent of oxygen partial pressure. The electrical conductivity of specimens having a dopant concentration under 1×10^{18} Sb cm^{-3} increased with temperature and with decreasing partial pressure of oxygen. The significance of the dopant and the thermally created defects is discussed.

1. Introduction

Stannic oxide is an important oxide semiconductor and its properties have been well understood over the temperature regions for practical applications [1–10]. It has a wide band gap and one of the highest mobilities of the carrier (electrons) among oxides. Its semiconducting properties can be controlled by doping with antimony and/or fluorine [11–13]. Heavily doped thin films are widely used as transparent electrodes. Ceramics having less or no dopant and fine porous microstructures can be applied as gas sensors [14–24].

Much less is known about the property change which occurs at high temperature during heat treatment procedures. The formation of donor states associated with non-stoichiometry of stannic oxide was studied only for limited conditions on undoped single crystals [25], for which the achievement of equilibrium in the lower temperature region was doubtful for the reason stated in the following text. Variations of the oxidation states of dopants are also seen [26–30]. Poor property control limits the application of this material at a more advanced level.

The objective of the present study is to clarify the relation between temperature, oxygen partial pressure and the equilibrium semiconducting properties of stannic oxide doped with a wide concentration range of antimony. The specimens were prepared from very pure starting material. The dopant concentrations studied were 0.0004 to 0.4 wt % (1×10^{17} to 1×10^{20} Sb cm^{-3}), which is the typical level required for semiconductors for advanced applications [31]. We hope the knowledge obtained in this study will enable a more advanced design of function in stannic oxide.

2. Experimental procedure

High purity metallic tin (99.999%) was dissolved in hydrochloric acid, and precipitated as stannic oxalate by adding an aqueous solution of oxalic acid. After washing with distilled water and drying, the precipitate was heated at 300° C for 10 h in air and then at 700° C for 10 h in air for decomposition to stannic oxide. For doping the specimens, a measured amount of antimony oxide chloride dissolved in an aqueous solution of tartaric acid was added to the oxide powder, mixed, dried and again heated at 700° C for 10 h in air. Doped stannic oxides having nominal antimony concentrations of 1×10^{17}, 3×10^{17}, 1×10^{18}, 1×10^{19} and 1×10^{20} Sb cm^{-3}, and also undoped stannic oxide were prepared. (One-quarter of the added dopant was lost in processing as will be explained in the following text). The powders were formed into rods (2 mm × 4 mm × 30 mm) and isostatically pressed at 1000 kg cm^{-2}. The rods were placed in a recrystallized alumina Tumman tube, buried in oxide powder of the same composition and sintered at 1400° C for 16 h in air. Scanning electron microscopic examination showed that samples had a porous microstructure with interconnecting rod-like grains of a size of about 2 μm. The electrical conductivities were measured by the four-point d.c. method. Fine platinum electrodes (0.1 mm diameter) were attached to the specimen with a small amount of platinum paste. The current was supplied by a constant-current power source through a fixed resistance. The voltage drops across the resistance and the inner electrodes of the specimen were measured with a recorder (internal resistance 10 MΩ) to determine the current and the resistance of the specimen, respectively. The reading was averaged after changing the current direction. For heating the specimen an electric furnace with pyromax heating wire and a recrystallized alumina muffle tube was used. The temperature was controlled with a Pt–13 Rh Pt thermocouple and on–off type temperature controller, and measured with a Pt–13 Rh Pt thermocouple placed near the centre of the specimen. The oxygen partial pressure was controlled by CO_2–O_2 and CO–CO_2 mixtures, prepared either by mixing carbon dioxide and oxygen or by passing carbon dioxide through a zirconia oxygen pump, and was measured

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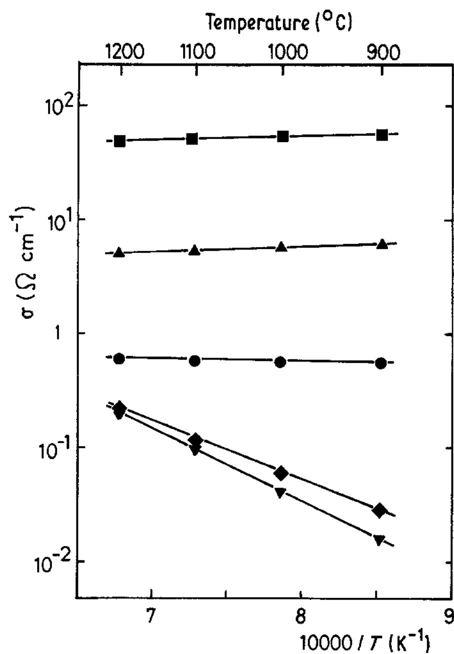

Figure 1 Effect of temperature on the electrical conductivities of specimens having various dopant concentration at P_{O_2} = 1 atm. (▼) Undoped, (◆) $3 \times 10^{17}\,cm^{-3}$, (●) $1 \times 10^{18}\,cm^{-3}$, (▲) $1 \times 10^{19}\,cm^{-3}$, (■) $1 \times 10^{20}\,cm^{-3}$.

with a zirconia cell placed near the specimen. The oxygen pressure in the atmosphere was also checked with zirconia oxygen cells in the gas entering and coming out of the furnace tube. In the following text, results on the specimen having the dopant concentration $1 \times 10^{17}\,Sb\,cm^{-3}$ were not presented for clarity of the figures. These results always lie between those for specimens having no dopant and $3 \times 10^{17}\,Sb\,cm^{-3}$.

3. Results

Fig. 1 shows changes of electrical conductivity with temperature at the oxygen partial pressure, P_{O_2} = 1 atm for specimens having various dopant concentrations. The specimens having higher dopant concentrations showed a slight decrease of conductivity with increasing temperature. The conductivities also decreased approximately 1/10 with the corresponding decrease in dopant concentration for specimens having dopant concentrations of 1×10^{20}, 1×10^{19} and $1 \times 10^{18}\,Sb\,cm^{-3}$. In reducing the dopant concentration from 1×10^{18} to $3 \times 10^{17}\,Sb\,cm^{-3}$, the conductivity decreased more than 1/3. At lower dopant concentrations, the conductivity in the lower temperature region was low, but increased significantly with increasing temperature.

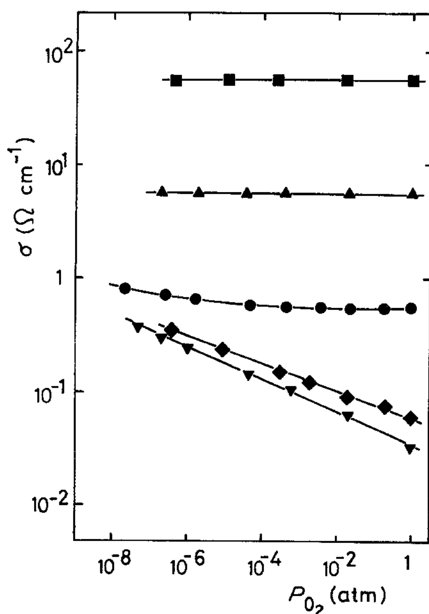

Figure 2 Effect of partial pressure of oxygen on the electrical conductivities at 1000° C. (▼) Undoped. (◆) $3 \times 10^{17}\,cm^{-3}$, (●) $1 \times 10^{18}\,cm^{-3}$, (▲) $1 \times 10^{19}\,cm^{-3}$, (■) $1 \times 10^{20}\,cm^{-3}$.

Fig. 2 shows the effect of P_{O_2} on the electrical conductivity for various specimens. In the measurements, the lower end of the P_{O_2} range was limited by the dissociative evaporation of the specimen. No conductivity change with P_{O_2} was found within experimental certainty for specimens containing more than $10^{19}\,Sb\,cm^{-3}$. At the dopant concentration $10^{18}\,Sb\,cm^{-3}$, the conductivity changed slightly with P_{O_2}. This effect of P_{O_2} on conductivity was found to increase with increasing temperature, but is not shown in this figure. At dopant concentrations below $3 \times 10^{17}\,Sb\,cm^{-3}$, the conductivities changed markedly with P_{O_2} but only slightly with dopant concentration. This slight difference in conductivity decreased further with increasing temperature, and no appreciable difference was found at 1200° C among specimens having dopant concentration below $3 \times 10^{17}\,Sb\,cm^{-3}$. For all these specimens, the slope of the log P_{O_2} against log σ plot was approximately 1/8.

Throughout the above measurements, considerable equilibration periods were required to obtain reproducible results. At 1200° C, the conductivities were measured at least 30 min after the P_{O_2} on the specimen became constant. Longer equilibration periods were necessary with decreasing temperature. At 900° C, a few days were necessary after the P_{O_2} on the specimen became constant. Thereafter, no significant change of conductivity was found in 10 days.

Table I shows the result of semiquantitative chemical analysis of the specimen. The major impurities were iron and molybdenum. The antimony content was also determined quantitatively in a separate chemical analysis for specimens initially doped with $1 \times 10^{20}\,Sb\,cm^{-3}$. The antimony found in the sintered specimen was $0.78 \times 10^{20}\,Sb\,cm^{-3}$, which was approximately 3/4 of the initial content. This difference may be due to the evaporation of antimony during sintering. For other specimens, reliable analysis of antimony was impossible. In the following analysis, antimony concentrations in these specimens were assumed also to be 3/4 of the starting composition. The basis of this assumption is that the vapour pressure of antimony in solid solution and the evaporative loss of antimony should both be proportional to the antimony concentration for a dilute solid solution in which Henry's law is followed.

4. Discussion

The constant conductivity at any P_{O_2} in the specimens having high dopant concentrations suggests that the carrier concentrations are constant in these specimens. Concentrations of donors created by the antimony doping are much higher than those of thermal origin.

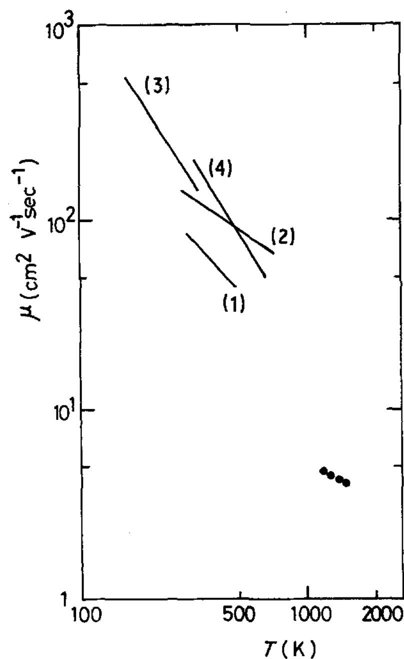

Figure 3 Carrier mobility in high purity tin dioxide. (●) This study; (1) Kohnke [5]; (2) Marley and Dockerty [4]; (3) Nagasawa *et al.* [8]; (4) Fonstad and Rediker [9].

To test this assumption, the mobility of carriers was estimated by assuming that each antimony atom forms one donor state, that donor states are exhausted in the temperature region considered, and that the effect of microstructure can be neglected. Fig. 3 shows the temperature dependence of carrier mobility determined in this study. Also included in this figure for reference are those determined by Hall measurements [4–9]. The mobilities determined in this study were found on the extrapolation of the Hall mobility. Considering the difference in the method of measurement, the uncertainty in the dopant concentration and the porous microstructure, the agreement was very good which strongly supports the above assumption. The slight decrease of conductivity with increasing temperature in Figs 1 and 2 for specimens having more than 1×10^{19} Sb cm^3 was clearly due to the decrease of mobility with increasing temperature.

The lower conductivity than expected for the specimens having 3×10^{17} Sb cm^{-3} in the low temperature

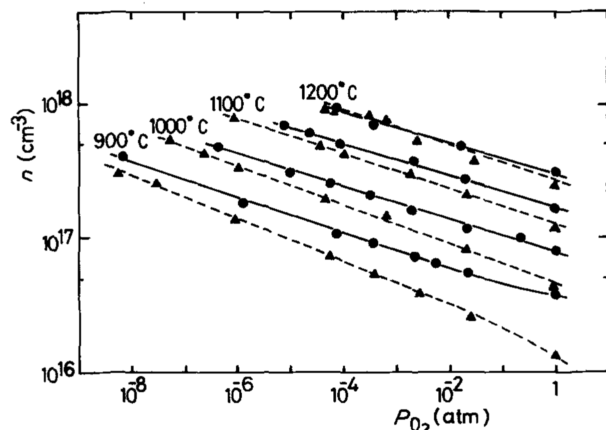

Figure 4 Effect of partial pressure of oxygen on the defect concentration in tin dioxide. (▲) Undoped, (●) doped with 3×10^{17} Sb cm^{-3}.

TABLE I Chemical analysis of specimens*

Element	Intensity
Al	+
B	± to +
Cu	± to +
Fe	+ to ++
Mo	++ to +++
Mn	± to +
Nb	± to +
Ni	± to +
Pb	+ to ++
Sb	+++
Si	+ to ++
Sn	Strong

*Spectroscopic analysis: no other element found.

region of Fig. 1 suggests that the effect of antimony dopant may be compensated by the residual impurities. The starting material used in this study has only 99.999% purity, and the concentration level of dopant corresponds to approximately 0.001% which is close to the concentration level of impurities in the starting material. Elements having a valency of less than three are inherently dominant among elements and they act as acceptors to compensate the donors created by antimony doping.

The marked increase of conductivity with decreasing P_{O_2} in Fig. 2 for specimens having no or little dopant content strongly suggests that donor states related to the defects of thermal origin are dominant. Fig. 4 shows the P_{O_2} dependence of defect concentration which was calculated by assuming that the mobilities were the same for specimens having different dopant concentrations and that all donor states were ionized. A significant increase of donor concentration with decreasing P_{O_2} is apparent in this figure for all temperatures. Further, the convergence of donor concentration at 1200° C for specimens having less than 3×10^{17} Sb cm^{-3} suggests that donors related to native defects of thermal origin may be dominant in this condition. The slope in Fig. 4 was approximately 1/8 which is clearly different from the 1/6 found by Samson and Fonstad [25]. They reached this conclusion through conductivity measurements for only a limited P_{O_2} range (0.01 to 1 atm) on single-crystalline specimens. Our careful re-examination of their data suggests that the results can be better expressed with the slope 1/8. They also reported very short equilibration times (several minutes) at above 1100° C. This result clearly disagrees with the present results. The long equilibration time required even on porous specimens having fine grains shows that a significantly longer time should be necessary for equilibration in single crystals. The doubly ionized oxygen vacancy model proposed by Samson and Fonstad [25] is doubtful. Construction of a reasonable defect model to account for the slope of 1/8 is not attempted at the present stage, since the results obtained in this study are still influenced by the unknown impurities. Specimens having a still higher purity are necessary to clarify the defect structure of this material.

The present results clearly show that provided high purity starting materials of 99.999% are used, the

electrical properties of tin dioxide can be controlled down to donor levels of approximately $7 \times 10^{17} cm^{-3}$. This is a very important region for semiconductor applications. The Debye length estimated by a simple analysis is long enough to create a wide energy barrier and to develop interesting properties at interfaces [31]. The present results may give the impression that provided a starting material having still higher purity is used, better control may be possible for the defect concentration. Unfortunately, this seems to be incorrect. Considering the formation of native defects of thermal origin and their low equilibration rates, it may be difficult to control the donor level at $1 \times 10^{17} cm^{-3}$ even in ultra-pure starting materials.

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