Low temperature spark plasma sintering of tin oxide doped with tantalum oxide

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Tantalum oxide-doped, nano-sized tin oxide powder was consolidated by spark plasma sintering by systematically varying the sintering temperature, heating rate, holding time at the sintering temperature, and doping amount. The relative densities of the TaO_{2.5}-doped SnO₂ sintered specimens increased with the increasing sintering temperature from 800 to 1000°C, but were almost independent of the heating rate and holding time in the ranges from 30–90°C/min and 5–120 min, respectively. The DC electrical conductivity, in contrast, reached a maximum value at the sintering temperature of 900°C, but decreased at 1000°C due to decomposition of the SnO₂. In addition, a faster heating rate and shorter holding time resulted in a higher electrical conductivity of the TaO_{2.5}-doped SnO₂ specimens due to the solution of Ta⁵⁺ in the SnO₂ and formation of a metastable compound.

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1. Introduction

Tin oxide (SnO₂) is an n-type semiconductor with a wide energy band gap and limited electrical conductivity.^{1)–6)} SnO₂ ceramics doped with aliovalent cations, such as Sb, have been extensively investigated to improve the electrical conductivity; i.e., n-type carriers supplied by oxygen vacancies through the substitution of Sb⁵⁺ for Sn⁴⁺.^{7)–9)} However, it is difficult to fabricate fully densified SnO₂ by conventional sintering methods, partly due to its high vapor pressure at high temperatures.^{10)–13)} Sintering aids, such as CuO, Li₂CO₃, and ZnO, have been found to enhance the sinterability of the SnO₂ ceramics, but the sintering aids often inhibit the electrical conductivity.^{14)–16)} In recent years, spark plasma sintering, SPS (or electric current-assisted sintering; ECAS), in which a green compact is directly heated by pulsed DC electric current under compressive stress,^{17),18)} has been successfully used for producing dense SnO₂ materials at relatively lower temperatures and in shorter sintering times.^{19),20)} In fact, fully- densified, Sb⁵⁺-doped SnO₂ with a good electrical conductivity has been consolidated by the SPS technique.^{21)–25)} Nevertheless, antimony is a toxic element, therefore, the development of alternative SnO₂ materials with similar properties, but from non-toxic resources, is required. Another candidate as a donor for SnO₂ is tantalum oxide (Ta₂O₅). Ta₂O₅ is known to be a non-toxic material with an excellent corrosion resistance,^{26),27)} and acts as an n-type dopant in SnO₂ to decrease the electrical resistivity by increasing the carrier concentration.^{28)–31)} Ta⁵⁺-doped SnO₂ thin films with an excellent electrical conductivity have been developed,³²⁾ but a polycrystalline body fabricated by SPS has not yet been reported. The present research was undertaken to investigate the influence of the SPS on the sinterability and electrical conductivity of the TaO_{2.5}-doped SnO₂ powder by varying the most relevant process parameters, i.e., sintering

temperature, heating rate, holding time at the sintering temperature, and doping amount.

2. Experimental procedure

TaO_{2.5}-doped SnO₂ polycrystalline ceramics were prepared by first mixing powders of SnO₂ (Nanotek Co., 99.9% purity, 21 nm) and Ta₂O₅ (Rare metallic Co., 99.9% purity, <5 μm) to obtain samples having the doping level from 0.5 to 5 mol%. The TaO_{2.5}-doped SnO₂ materials were produced by mixing in ethanol for 1 h at 2000 rpm using a planetary centrifugal mixer (AR-250; Thinky Co., Japan), then drying at 70°C for 48 h. The dried powders were then sifted through a 60-mesh sieve for granulation.

Using a spark plasma sintering machine (LABOX-315CS; Sinterland Co., Japan), the powder was heated to the desired sintering temperature in a carbon die having an inside diameter of 15 mm. All the sintering experiments were carried out in a vacuum (20 Pa) at a uniaxial compressive pressure of 80 MPa. The temperature was measured by a thermocouple attached to a non-through hole (1 mm diameter and 5 mm depth) in the side of the carbon die. The carbon die was covered with carbon heat insulation to avoid heat dissipation from the external surface of the die. The effects of the main process parameters, such as (i) sintering temperature, (ii) heating rate, and (iii) holding time at the sintering temperature, were systematically analyzed for the 1 mol% TaO_{2.5}-doped SnO₂ in order to determine the optimum sintering conditions for enhancement of the densification and electrical conductivity. First, the sintering temperature was varied at 800, 900 and 1000°C by setting a constant heating rate of 90°C/min and holding time of 5 min [Fig. 1(a)]. Next, the heating rate was varied at 30, 50 and 90°C/min, while the sintering temperature and holding time were held constant at 900°C and 5 min, respectively [Fig. 1(b)]. Third, the holding time at the sintering temperature was varied at 5, 30, and 120 min, while the sintering temperature and heating rate were kept constant at 900°C and 90°C/min [Fig. 1(c)]. Finally, the doping amount was varied at 0 (undoped), 0.5, 1, 2, 3 and 5 mol% of TaO_{2.5}, holding

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Fig. 1. Temperature profiles of the present sintering experiments. Effects of (a) sintering temperature, (b) heating rate and (c) holding time at sintering temperature.

the sintering temperature to 900°C, the heating rate to 90°C/min, and the holding time to 5 min.

The final density of the sintered body was measured by Archimedes method. The theoretical density of SnO_2 has been reported to be 7.02 g/cm³.³³⁾ The microstructure of the fracture surfaces of the sintered bodies was inspected using a scanning electron microscope (SEM, SU-8000; Hitachi, Japan). The electrical conductivity was measured at room temperature by a four-probe method using a DC Voltage/Current Source/Monitor (6240B; ADC Co., Japan). For the conductivity measurements, bar-shaped samples with the typical cross-section of about 2×3 mm² and length of 10 mm were produced from the sintered pellet by cutting using a diamond isometric blade followed by polishing to a mirror state with diamond paste. The phase analysis of the produced samples was carried out by X-ray diffraction (Rigaku, Ultima III, 30 mA, 40 kV) using Cu-k α radiation at a scan speed of 4°/min and scan step of 0.02° over the 2θ range of 20–80°.

3. Experimental results

The relative density and DC electrical conductivity of 1 mol% $\text{TaO}_{2.5}$ -doped SnO_2 as a function of sintering temperature at the constant heating rate of 90°C/min and holding time of 5 min are shown in Fig. 2. With the increasing sintering temperature from 800 and 1000°C, the relative density increased from 85.3 to 95.2%. The relative density of more than 90% can be obtained in 1 mol% $\text{TaO}_{2.5}$ -doped SnO_2 by SPS at the sintering temperature

Fig. 2. Relative density and DC electrical conductivity of 1 mol% $\text{TaO}_{2.5}$ -doped SnO_2 sintered bodies as a function of sintering temperature at a constant heating rate (90°C/min) and holding time (5 min).

Fig. 3. Effect of sintering temperature at constant heating rate (90°C/min) and holding time (5 min): (a) gas pressure in the sintering chamber during sintering experiments, and (b) weight loss of sintered bodies to green compacts at different sintering temperatures.

of less than 900°C. The electrical conductivity increased with the increasing sintering temperature from 800 to 900°C, but decreased when the temperature increased from 900 to 1000°C.

The changes in the gas pressure in the sintering chamber during the sintering experiments at different sintering temperatures are presented as a function of the specimen temperature or testing time in Fig. 3(a). As can be seen, the gas pressure when the sintering temperature was 1000°C shows two major peaks; the first one was seen from around 100 to 700°C, and the second one from around 950°C. The second peak was observed only at

Fig. 4. X-ray diffraction patterns of the 1 mol% TaO_{2.5}-doped SnO₂ bodies sintered at 800, 900, and 1000°C for 5 min with the heating rate of 90°C/min.

the sintering temperature of 1000°C, but was not seen at the temperatures of 800 and 900°C. In a previous study, a mass spectroscopy analysis during the thermogravimetric measurement revealed the desorption of H₂O, OH⁻ and CO₂ bonded on the surface of the SnO₂ particles at temperatures from around 250 to 650°C.³⁴⁾ At a higher temperature, SnO₂ showed a peritectic decomposition according to the following reaction,³⁵⁾ SnO₂ (s) → SnO (g) + 1/2 O₂ (g). The weight loss of the sintered bodies to the green compacts of the 1 mol% TaO_{2.5}-doped SnO₂ specimens at the different sintering temperatures is shown in Fig. 3(b). The weight loss is remarkable in the body sintered at 1000°C in comparison to the specimens sintered at 800 and 900°C. The vacuum down at 1000°C in the present material must result from the decomposition of SnO₂. The decreased electrical conductivity in the specimen sintered at 1000°C is probably related to the decomposition of SnO₂. In fact, metallic thin film was precipitated on the surface of the carbon punches after the SPS process at 1000°C; a part of decomposed tin oxide must precipitate as metal tin. The higher sintering temperature can effectively enhance the densification, but the sintering temperature should be lower than 1000°C in order to increase the electrical conductivity of the sintered body.

The XRD patterns of the 1 mol% TaO_{2.5}-doped SnO₂ bodies sintered at 800, 900, and 1000°C for 5 min with the heating rate of 90°C/min are shown in Fig. 4. The major diffraction lines in the materials were assigned to the tetragonal SnO₂ phase.³³⁾ The specimens sintered at 900 and 1000°C contained Ta₂Sn₂O₇³⁶⁾ as a minor phase. In addition, the material sintered at 1000°C exhibited weak diffraction lines assigned to tetragonal tin.³⁷⁾ The presence of tin probably resulted from precipitation of Sn contained in the decomposed tin oxide gas.

The relative density and electric conductivity of the 1 mol% TaO_{2.5}-doped SnO₂ bodies as a function of the heating rate at the constant sintering temperature of 900°C and holding time of 5 min are depicted in Fig. 5. The relative density insignificantly increased with the increasing heating rate, merely changing from 91.5 to 93.1%. In contrast, the conductivity remarkably increased with the increasing heating rate from 50 to 90°C/min.

The profiles of the density and electric conductivity of the 1 mol% TaO_{2.5}-doped SnO₂ bodies as a function of the holding

Fig. 5. Relative density and DC electrical conductivity in 1 mol% TaO_{2.5}-doped SnO₂ sintered bodies as a function of heating rate under constant sintering temperature (900°C) and holding time (5 min).

Fig. 6. Relative density and DC electrical conductivity in 1 mol% TaO_{2.5}-doped SnO₂ sintered bodies as a function of holding time under constant sintering temperature (900°C) and heating rate (90°C/min).

time at the sintering temperature are depicted in Fig. 6. The sintering temperature and heating rate were 900°C and 90°C/min, respectively. The relative density was almost independent of the holding time, showing about 93% at the different holding times from 5 to 120 min. The electric conductivity, in contrast, decreased with the increasing holding time from 5 to 30 min.

Based on the above results, the sintering temperature, heating rate, and holding time should be 900°C, 90°C/min, and 5 min, respectively, to improve both the relative density and electrical conductivity of the 1 mol% TaO_{2.5}-doped SnO₂. The doping amount dependence was evaluated from 0.5 to 5 mol% of TaO_{2.5} by employing a combination of the process parameters. The doping amount dependences of the density and electric conductivity of the 0–5 mol% TaO_{2.5}-doped SnO₂ bodies are presented in Fig. 7. The density of the undoped SnO₂ was 93.6%. The relative density slightly decreased with the increasing doping amount from 0.5 to 3 mol%, and significantly declined to 86.0% by 5 mol% TaO_{2.5}-doping. The electrical conductivity of the undoped specimen was $2.6 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$. The conductivity slightly increased by the 0.5 mol% TaO_{2.5}-doping, and remarkably increased to $7.5 \Omega^{-1} \text{cm}^{-1}$ by the 1 mol% TaO_{2.5}-doping. However, the conductivity decreased with the increasing doping amount beyond 2 mol%. As for the doping effect on the electrical conductivity, the optimum doping level is about 1 mol% TaO_{2.5}.

Fig. 7. Relative density and DC electrical conductivity in TaO_{2.5}-doped SnO₂ specimens sintered at 900°C for 5 min under a constant heating rate (90°C/min) as a function of doping amount from 0 mol% (undoped) to 5 mol%.

Fig. 8. X-ray diffraction patterns of the SnO₂ bodies doped with 0–5 mol% TaO_{2.5} sintered at 900°C for 5 min at the heating rate of 90°C/min.

The XRD patterns of the SnO₂ bodies doped with 0–5 mol% TaO_{2.5} sintered at 900°C for 5 min with the heating rate of 90°C/min are shown in Fig. 8. The major diffraction lines in the present materials were assigned to the tetragonal SnO₂ phase.³³⁾ The SnO₂ bodies doped with 0.5–3 mol% TaO_{2.5} contained Ta₂Sn₂O₇³⁶⁾ as a minor phase. In the 3 mol% TaO_{2.5}-doped SnO₂, the diffraction peaks of Ta₂O₅^{38),39)} were identified as another minor phase. In the 5 mol% TaO_{2.5}-doped SnO₂, Ta₂O₅ appears as the second phase instead of Ta₂Sn₂O₇ as shown in the Fig. 8. The reduction of the electric conductivity by more than 3 mol% TaO_{2.5}-doping was probably related to the precipitation of Ta₂O₅.

Figure 9 shows SEM images of the fractured surfaces of the SnO₂ materials doped with (a) 0 mol% (undoped), (b) 0.5 mol%, (c) 1 mol%, (d) 2 mol%, (e) 3 mol%, and (f) 5 mol% TaO_{2.5} sintered at 900°C for 5 min with the heating rate of 90°C/min. The present materials exhibited bimodal microstructures, consisting of grains with the grain sizes of less than 50 nm and more than 100 nm, while the grain sizes seemed to slightly increase with the increased doping amount of TaO_{2.5}. The fine grain sizes

Fig. 9. Typical SEM images of fracture surfaces of sintered SnO₂ bodies doped with (a) 0 mol% (undoped), (b) 0.5 mol%, (c) 1 mol%, (d) 2 mol%, (e) 3 mol% and (f) 5 mol% TaO_{2.5}.

in the specimens resulted from the initial nano-sized particle size and low sintering temperature.

4. Discussion

Among the present sintering conditions, the highest DC electrical conductivity of $7.5 \Omega^{-1} \text{cm}^{-1}$ was achieved for the 1 mol% TaO_{2.5}-doped SnO₂ sintered at 900°C for 5 min with the heating rate of 90°C/min. The sintering densification was enhanced by the increased sintering temperature, but because of the decomposition of SnO₂ at around 1000°C, the electrical conductivity deteriorated by increasing the sintering temperature to 1000°C. The shorter holding time and faster heating rate resulted in a higher electrical conductivity of the SnO₂ specimens, while the relative density was almost independent of the two processing parameters. The holding time and heating rate effects on the conductivity must be related to the phase composition of the sintered bodies.

Table 1 summarizes the previously reported electrical conductivity data of the Sb₂O₅-doped SnO₂ ceramics produced by SPS.^{21)–25)} The reported electrical conductivity of the Sb₂O₅-doped SnO₂ depends on the chemical composition and sintering conditions, ranges from 4 to $176 \Omega^{-1} \text{m}^{-1}$. The conductivity in the present 1 mol% TaO_{2.5}-doped SnO₂ was within the range of those of the Sb₂O₅-doped SnO₂ materials. It should be noted that the doping amount in the present material was lower than the Sb-doped SnO₂ materials. Ta⁵⁺ is therefore a useful dopant element with a low toxicity for the improvement of the electrical conductivity in SnO₂. It is known that the electrical conductivity in SnO₂ is improved by a solution of Ta⁵⁺ in SnO₂.^{28),40)} In a previous study of the electric properties in the Ta₂O₅-doped SnO₂–CuO varistor system, the increased conductivity was explained in terms of the dissolution of Ta⁵⁺ in the SnO₂; both the substitutional and interstitial position of Ta⁵⁺ in SnO₂ should be associated with a decrease in the oxygen anion vacancy concentration and an increase in the electron concentration.^{28),40)} Ta-doping therefore enhances the electric conductivity of SnO₂.

According to the equilibrium phase diagram of the SnO₂–Ta₂O₅ system,^{41),42)} the solubility of Ta₂O₅ in SnO₂ is less than a few mol% at temperatures lower than 1300°C. There is no stable compound in the SnO₂–Ta₂O₅ eutectic system, but a number of metastable compounds has been reported.^{42),43)} Sn₂Ta₂O₇ is a

Table 1. Electrical conductivity of Sb₂O₅-doped SnO₂ ceramics sintered by SPS reported in the literature^{21)–25)}

Chemical composition	Sintering condition			Electrical conductivity / $\Omega^{-1}\text{cm}^{-1}$	Relative density /%	Ref.
	Sintering temperature /°C	Heating rate /°C/min	Compressive stress /MPa			
SnO ₂ + 18 mol% Sb ₂ O ₃	890	Not given	40	4	92.44	21
SnO ₂ + 10 at% CuSb ₂ O ₆	890	Not given	40	7.39	99.06	22
SnO ₂ + 10 at% Sb	1000	100	40	12.66	97.7	23
SnO ₂ + 12 at% Sb	1000	100	40	176	97.5	24
(with post-annealing at 800°C)						
SnO ₂ + 1.5 at% Sb ₂ O ₅	980	100	40	58.86	96.5	25
SnO ₂ + 1 mol% Ta ₂ O ₅	900	90	80	7.47	92.9	Present study

metastable compound which can be generated from a mixture of SnO and Ta₂O₅ at 1000°C in a vacuum.⁴³⁾ In the present materials, the metastable compound must be produced by the SPS due to the high heating rate, low sintering temperature and short holding time. The electrical properties of Sn₂Ta₂O₇ have not been reported, but the compound would be a semiconductor based on the following results. The energy band gap of Sn₂Ta₂O₇ is theoretically estimated to be 3.0 eV,^{44)–46)} which is lower than that of SnO₂ (=3.6 eV).^{1),2)} In addition, a Mössbauer study of Sn₂Ta₂O₇ indicated that both Sn⁴⁺ and Sn²⁺ were presented in the compound.⁴⁷⁾ Sn₂Ta₂O₇ could therefore exhibit a better electrical conductivity than SnO₂. In contrast, Ta₂O₅ is a dielectric material with a poor electrical conductivity.^{46),48)} The higher sintering temperature, lower heating rate and longer holding time of the SPS processes led to the formation of Ta₂O₅ as the stable second phase, resulting in the reduced conductivity. The high heating rate and short holding time of the present SPS must yield the solution of Ta and the formation of the metastable compound, both of which probably enhance the electrical conduction of SnO₂. In addition to the minor phases, grain boundary segregation of Ta⁵⁺ would be another factor to determine the specimen conductivity; if the electrical conduction through the grain boundaries contributes to a major part of the total conductivity in the present materials, it is possible that the grain boundary segregation of TaO_{2.5} could significantly influence the specimen conductivity. Further investigation regarding effects of small amount of TaO_{2.5}-doping on microstructure and conductivity is required to reveal the effect of the grain boundary segregation.

It has been widely accepted that surface diffusion and evaporation-condensation processes substantially contribute to mass transport during the sintering and grain growth of SnO₂.^{34),49)} It has also been pointed out that a reducing atmosphere and aliovalent cation-doping have significant influence on the mass transport phenomena, but it remains unclear whether the oxygen anion^{34),49),50)} or tin cation^{51),52)} is the rate-controlling species. In a previous investigation of the Nb₂O₅-doping effect on the diffusion coefficient in SnO₂, for instance, it has been concluded that the rate-controlling species of the diffusion in SnO₂ can change depending on the doping amount.⁵²⁾ The effects of the Ta-doping on the sintering densification and grain growth in the present materials are unclear at present. Further investigation on the mass transport phenomenon, such as isothermal grain growth in a fully-densified material, is required for the elucidation of the Ta-doping effect on the microstructure of SnO₂.

5. Conclusions

The present study investigated the sinterability and electrical conductivity resulting from densification of TaO_{2.5}-doped SnO₂ compacts by SPS as a function of the sintering temperature,

heating rate, holding time, and doping amount. The results are summarized as follows:

1. The sintering densification was enhanced by the increasing sintering temperature from 800 to 1000°C. The electrical conductivity, however, was reduced by increasing the sintering temperature to 1000°C due to the decomposition of the SnO₂ at around 1000°C.
2. The relative density was almost independent of the heating rate and holding time in the examined ranges. The shorter holding time and faster heating rate resulted in a higher electrical conductivity of the SnO₂ specimens.
3. Among the present materials, the highest DC electrical conductivity of 7.5 $\Omega^{-1}\text{cm}^{-1}$ was achieved in 1 mol% TaO_{2.5}-doped SnO₂ sintered at 900°C for 5 min with the heating rate of 90°C/min. The high electrical conductivity must be a consequence of the low sintering temperature, high heating rate and shorter holding time.
4. The SnO₂ bodies doped with 0.5–3 mol% TaO_{2.5} contained metastable Ta₂Sn₂O₇ as the second phase, and stable Ta₂O₅ was produced instead of Ta₂Sn₂O₇ in the 5 mol% TaO_{2.5}-doped SnO₂. The high heating rate and short holding time must lead to the solution of Ta⁵⁺ and formation of a metastable compound.

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