Electronic conduction of tin oxide thin films prepared by chemical vapor deposition

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SnO_2 thin films having low resistivity were prepared by chemical vapor deposition. Conductivity, its dependence on temperature, and Hall effect of films were measured. Examination of the surface morphology by scanning electron microscope showed that the SnO_2 thin films are made up of many grains. Experimental results were discussed by the grain-boundary model. The carrier transport mechanism across a grain boundary is the tunnel effect rather than the thermionic emission.

INTRODUCTION

Tin oxide thin films have been widely applied to transparent conductors in photoelectric conversion devices, for example, gas discharge display, amorphous silicon solar cells, and liquid-crystal display devices, etc.[1] Although most of the effort has been devoted to the deposition of SnO_2 thin films having low resistivity and high transparency, their physical properties such as electronic conduction mechanism had not been understood enough. Recently the conduction mechanism was explained by carrier transport across a grain boundary due to the thermionic emission,[2,3] based on the polycrystalline semiconductor model developed by Seto[4] and Orton.[5] The model has been useful in many kinds of polycrystalline materials[6-9] as well as polysilicon films.[4] According to the model the conductivity and mobility are proportional to grain size, but in their papers on SnO_2 polycrystalline the grain size of the thin films was not taken into account in discussing electronic properties.

In this paper, SnO_2 thin films are prepared at temperatures from 300 to 550 °C by the chemical vapor deposition (CVD) method. The conductivity, Hall effect, and grain size of films are measured. From the consideration where the conductivity is associated with the grain size, it is found that the tunnel effect is dominant over the thermionic emission.

EXPERIMENT

A schematic diagram of the CVD setup for the preparation of tin oxide thin films is shown in Fig. 1. The liquid $SnCl_4$ (purity 99.999%) kept at 25 °C was vaporized with nitrogen gas flow (0.3 ℓ/min) and the gas flow was mixed with oxygen gas flow (3 ℓ/min) on the way to a reaction chamber. The reaction of $SnCl_4$ with O_2 can be represented by

$$SnCl_4(g) + O_2(g) \rightarrow SnO_2(s) + 2Cl_2(g).$$

The reaction chamber was composed of a glass vessel and a quartz plate on a heater. SnO_2 thin films were deposited onto substrates on the quartz plate at temperatures from 300 to 550 °C. The substrate was a 3000-Å thermally grown silicon dioxide layer on an n-type ⟨100⟩ silicon wafer. The dependence of conductivity on temperature between 130 and 350 K was measured by the four probe method. The thickness of SnO_2 thin films in this study was always 5000 Å. The Hall effect was measured at 0.5 mA in a 5000-G magnetic field and the Hall voltage was always proportional to the magnetic field and the current. The surface morphology and the grain size of films were examined by using scanning electron microscope.

EXPERIMENTAL RESULTS

Figure 2 shows the variation of conductivity and carrier concentration at room temperature as a function of deposition temperature. From the polarity of the Hall voltage, all SnO_2 films were n-type semiconductor. The carrier concentration in Fig. 2 is calculated from

$$n = -1/(qR_H),$$

where R_H is the Hall coefficient and q is the electron charge. The conductivity and carrier concentration increase initially with the increase of the deposition temperature and begin to decrease above 450 °C. The conductivity of the film deposited at 450 °C shows a considerably high value, i.e., $9.35 \times 10^2 \Omega^{-1}\,\mathrm{cm}^{-1}$, though the film is not doped intentionally. The surface morphology of films shown in Fig. 3 indicates that SnO_2 thin films prepared by the CVD method

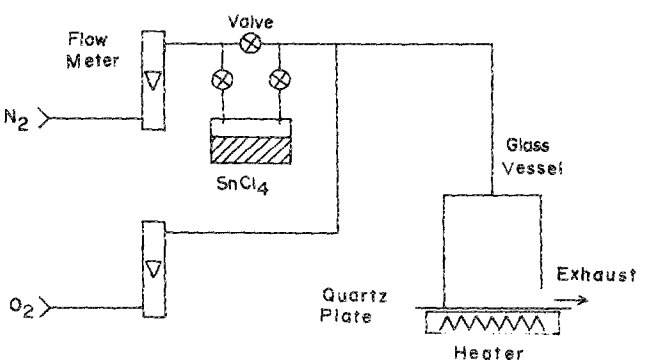

FIG. 1. Schematic diagram of the CVD setup for the deposition of tin oxide films.

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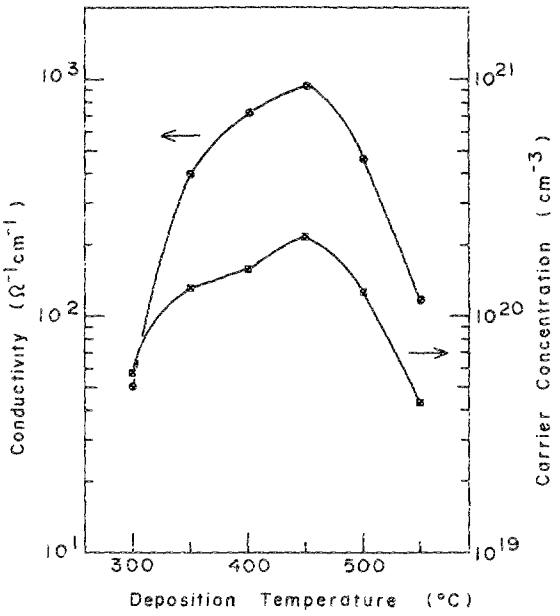

FIG. 2. Conductivity and carrier concentration at room temperature as a function of deposition temperature.

are made up of grains and the grain size tends to increase with the deposition temperature. Average grain size of films is obtained and the values are listed in Table I. The temperature dependence of the conductivity is shown in Fig. 4. It is found constant over the temperature range 130–350 K.

TABLE I. Values of average grain size L, potential barrier height V_B, depletion layer width l_2, and interfacial gap state density Q_t with different deposition temperatures T_s.

T_s (°C)	L (Å)	V_B (eV)	l_2 (Å)	Q_t (cm^{-2})
300	1000	0.085	28.1	1.60×10^{13}
350	1800	0.085	18.7	2.42×10^{13}
400	1500	0.065	14.7	2.33×10^{13}
450	2300	0.092	15.0	3.26×10^{13}
500	2300	0.088	19.1	2.45×10^{13}
550	1700	0.062	27.9	1.19×10^{13}

DISCUSSION

Figure 5 shows the idealized structure of a polycrystalline film.[4] Figure 5(a) shows a polycrystalline material composed of grains joined together through grain boundaries. For simplicity, the grain is assumed to be a square having a grain size of L cm. At the grain boundaries there are a large number of disordered states, then interfacial gap states are formed and filled with electrons, as shown in Fig. 5(b). The negative charge is localized at the grain boundaries, as shown in Fig. 5(c). The charge neutrality condition requires that depletion layer develops in the grain adjacent to the grain boundaries. This is represented in the following:

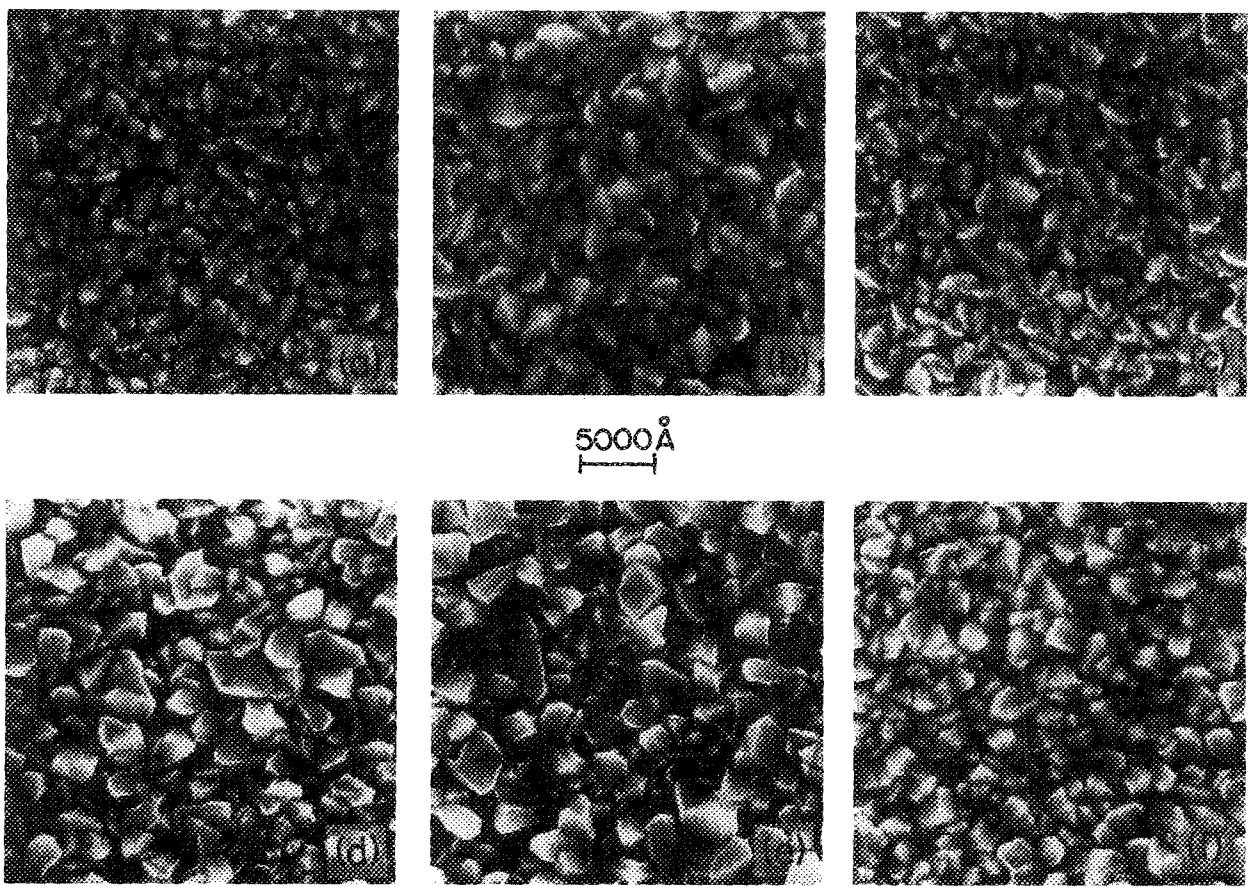

FIG. 3. Scanning electron micrographs of tin oxide films prepared at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, (f) 550 °C.

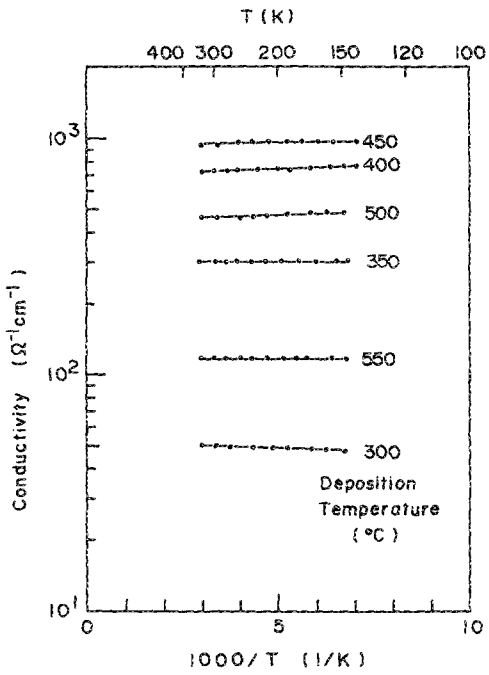

FIG. 4. Conductivity of tin oxide films as a function of reciprocal temperature.

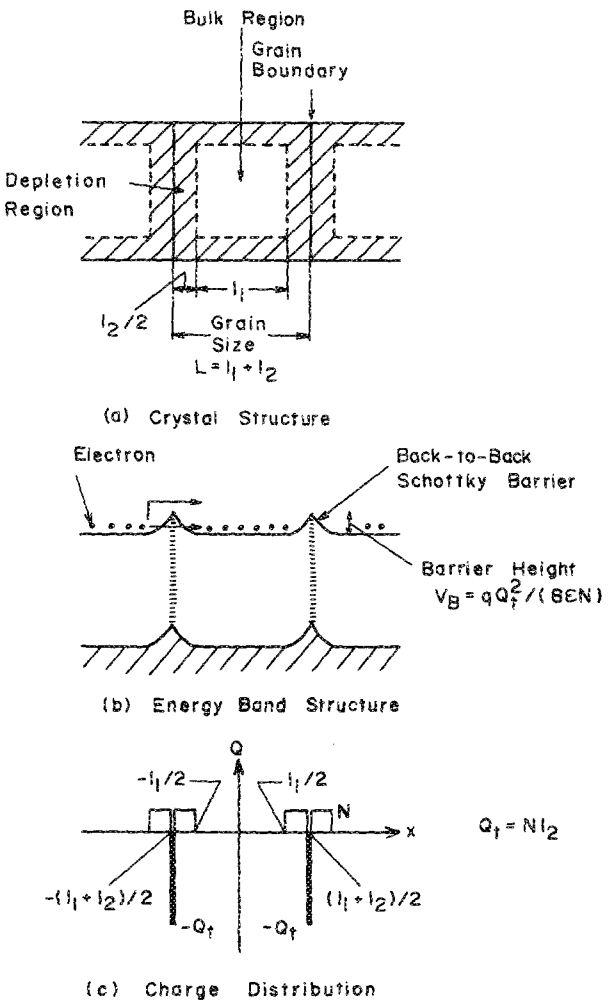

FIG. 5. (a) Model for the crystal structure of polycrystalline films. (b) Energy-band structure. (c) Charge distribution within the grain and at the grain boundary.

$$Q_t = Nl_2, \tag{1}$$

where Q_t is the gap state density at grain boundaries, N the donor concentration in the bulk region, and l_2 the depletion layer width.

The SnO_2 thin films in this study were not doped intentionally as mentioned before. But in the present samples produced by the $SnCl_4$ decomposition, chlorine atoms should be incorporated into the SnO_2 lattice, yielding donor levels.[10] In fact the chlorine atoms, the quantity of which decreased with increasing deposition temperature, were found by means of x-ray microanalyzer. The deposition temperature dependence of the carrier concentration similar to that shown in Fig. 2 has been reported and explained by Jousse.[3] At lower deposition temperatures, the quantity of chlorine is large, but the doping efficiency should be decreased in part of the amorphous phase, while at higher deposition temperatures the quantity of chlorine as donor source decreases.

At the grain boundaries a back-to-back Schottky barrier is formed, as shown in Fig. 5(b). The extension of the depletion layer in the bulk of the grain is divided into two cases, depending on whether (a) $Q_t > NL$ or (b) $Q_t \lesssim NL$.[5] In the former case, the depletion layer extends throughout the grain. In the latter case, only part of the grain is depleted of carriers. As our SnO_2 film has a higher carrier concentration and a large grain size, the depletion layer width must be much smaller than the grain size, i.e., $l_2 \ll L$, as is in case (b). This can be verified by calculational results listed in Table I. From the Poisson's equation, the barrier height is given as

$$V_B = qQ_t^2/8\epsilon N, \tag{2}$$

where ϵ is the dielectric constant of SnO_2.

Orton and Powell[5] have suggested that for polycrystalline thin films included in case (b), where $l_2 \ll L$, Hall coefficient R_H obtained from experiments is approximated to that in the bulk region R_1,

$$R_H \simeq R_1 \equiv -1/qn_1 \tag{3}$$

and the carrier concentration in the bulk region n_1 is almost equal to the donor concentration N:

$$N \simeq n_1. \tag{4}$$

The carrier concentration, shown in Fig. 2, represents that in the bulk region and the concentration of the donor levels, which should be produced by chlorine autodoping.

We have assumed that the conductivity of films is governed by the carrier transport across the potential barrier at grain boundaries due to the thermionic emission. The conductivity by the thermionic emission over the back-to-back Schottky barrier, σ_{th}, is given as[5]

$$\sigma_{th} = [Lq^2n_1/(\sqrt{2\pi m^* kT})]\exp(-qV_B/kT), \tag{5}$$

where m^* is the effective mass of carrier, k the Boltzmann constant, and T the absolute temperature. It should be noted that σ_{th} is proportional to grain size. In Eq.(5), four unknown quantities, i.e., L, n_1, m^*, and V_B are involved. The average grain size determined from the scanning electron photographs can be given as L in Fig. 5. n_1 is almost equal to the carrier concentration in Fig. 2, as indicated by Eq. (3). Jousse[3] has proposed $m^* = 0.15m_0$, where m_0 is the free-electron mass for the polycrystalline SnO_2. The value of V_B

can be estimated from the experimental results shown in Fig. 2, by using Eq. (5). For the film deposited at 450 °C, V_B is 0.141 eV, which is too large. If $V_B = 0.141$ eV, a significant temperature dependence of conductivity would appear. When we calculate the conductivity at 150 K compared with that at 300 K,

$$\sigma_{150\ \mathrm{K}}/\sigma_{300\ \mathrm{K}} = 6\times 10^{-3} \quad \text{for} \quad V_B = 0.14\ \text{eV}.$$

This is inconsistent with the experimental results because the conductivity of our samples is almost constant over the temperature range.

The constant conductivity in Fig. 4 suggests that the tunnel effect plays a major role in the carrier transport across the barrier. When we assume the potential barrier to be a rectangle of the height V_B and the width l_2, the tunnel current can be obtained easily. Following Holm,[11] the tunnel current density J_{tun} for a very small applied voltage V across a barrier is given by

$$J_{\mathrm{tun}} = [q^2V(\sqrt{2m^*V_B})/(h^2l_2)] \times \exp[-4\pi l_2(\sqrt{2m^*V_B})/h], \quad (6)$$

where h is the Planck constant. The conductivity by the tunnel effect σ_{tun} becomes

$$\sigma_{\mathrm{tun}} = [Lq^2(\sqrt{2m^*V_B})/(h^2l_2)] \times \exp[-4\pi l_2(\sqrt{2m^*V_B})/h]. \quad (7)$$

This equation indicates that σ_{tun} is proportional to grain size as is in Eq. (5), but independent of temperature. Four unknown quantities, i.e., L, m^*, V_B, and l_2, must be determined in Eq. (7). But L and m^* have been already estimated. If we solve equations of Eqs. (1), (2), and (7) simultaneously, and $\epsilon = 12\epsilon_0$,[3] where ϵ_0 is the dielectric constant of free space, then it becomes possible to obtain these values. For the film prepared at 450 °C, V_B, l_2, and σ_{tun} are plotted as a function of Q_t in Fig. 6. As indicated by Eqs. (1) and (2), V_B and l_2 show parabolic and linear dependence, respectively, and σ_{tun} decreases with an increase in Q_t. The value of conductivity obtained in the experiment yields Q_t, according to the results of Fig. 6. Similarly for the other samples, the values of Q_t, V_B, and l_2 are calculated and listed in Table I. It should be noted that all the SnO_2 films in this study satisfy the conditions $Q_t < NL$ and $l_2 \ll L$. The values of V_B in Table I, compared with those of other polycrystalline materials,[5] are reasonable. And from Eq. (2), Q_t is proportional to the square root of donor concentration, and this trend is found in Table I and also in the paper on polysilicon films.[4]

The electronic properties of SnO_2 thin films prepared by the CVD method can be explained consistently by the tunnel effect.

CONCLUSIONS

Tin oxide (SnO_2) thin films were prepared by the CVD method. The conductivity and carrier concentration of films

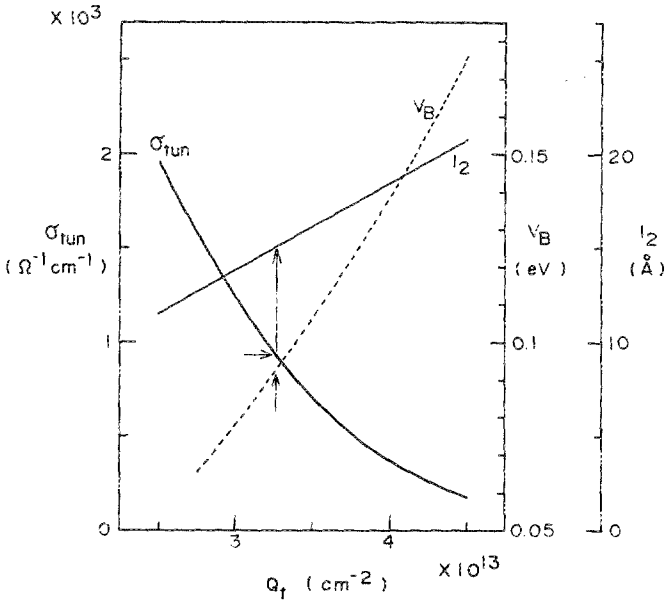

FIG. 6. Variation of the conductivity by the tunnel effect σ_{tun}, potential barrier height V_B, and depletion layer width l_2 with interfacial gap state density Q_t. The value that corresponds to the experimental one is illustrated by arrows.

significantly depend on the deposition temperature. The sample prepared at 450 °C shows the highest conductivity of films. It was observed by scanning electron microscope that the SnO_2 thin film consists of a large number of grains and the grain size tends to increase with deposition temperature. The experimental results were discussed based on the grain boundary model. The tunnel effect across the grain boundary is dominant compared with the thermionic emission.

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