Electrical Properties of Oriented SnO_2 Thin Films

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Electrical properties of (001) and (110) oriented SnO_2 films with SnO_2 crystallites oriented in the same direction as the rutile TiO_2 substrates, were investigated. The oriented films exhibited relatively low electric conductivities of 10^{-2} – 10^1 Scm^{-1} (carrier concentrations of 10^{16} – 10^{19} cm^{-3} and mobilities of 0.3 – $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in comparison with polycrystalline films used as transparent conducting coatings. No anisotropy of the conductivity was noticeable in spite of the alignment of the SnO_2 particles along a particular crystallographic axis.

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配向性 SnO_2 薄膜の電気的性質

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1. Introduction

Oriented SnO_2 thin films have been prepared on the (001) and (110) planes of rutile TiO_2 single crystals by chemical vapor deposition. SnO_2 crystallites composing the film had the same crystallographic orientation as the rutile substrates^{1),2)}. The present work was undertaken in an attempt to contribute to the knowledge of the electrical properties of SnO_2 films, especially when the SnO_2 particles in the films oriented in a definite direction. Electrical properties of transparent conducting SnO_2 films have been studied due to their applications as heat mirrors, display systems and solar cells³⁾⁻⁵⁾. These films, however, are polycrystalline. Little work has been done with oriented SnO_2 films.

2. Experimental

The oriented SnO_2 films were prepared on the (001) and (110) planes of rutile TiO_2 single crystals by chemical vapor deposition described previously^{1),2)}. The depositions were carried out at a temperature of 900° – 1300°C for 1 h ((001) SnO_2 films) and 1.5–2.5 h ((110) SnO_2 films). The deposition times were turned out to be optimum for the preparation of the conducting films. Electrical measurements were made in air at room temperature. Indium was applied as the Ohmic contact to the SnO_2 films. The electric

conductivity (σ) along the particular crystallographic axes of the SnO_2 films was measured by the 4-probe method. The van der Pauw's technique was also used to measure the conductivity, the carrier concentration (n) and the mobility (μ)

Electrical properties of the films deposited at 1100°C were mainly measured because the SnO_2 particles in the films were distinct in shape and orientation.

3. Results and discussion

The appearances of the SnO_2 films deposited on the (001) planes of rutile TiO_2 , as revealed by the scanning electron microscope, are shown in Fig. 1. The same microscope was used to measure the film thickness in specimen cut and observed at a 90° angle. SnO_2 films were 7–20 μm thick. The crystallographic axes of the SnO_2 particles determined from the back Laue reflection camera are also shown in Fig. 1. The representatives of measured electrical properties are shown in Table 1 and the variation of the conductivity vs. the deposition temperature in Fig. 2. Although the conductivity varied from sample to sample, it appeared that increasing deposition temperature tended to increase the conductivity. No conducting film was obtained below 1000°C . Higher conductivity of the SnO_2 films deposited at higher temperature seems to be due to their

Fig. 1. (001) SnO_2 films deposited on (001) TiO_2 at 1300°C (a), 1100°C (b), 900°C (c) for 1 h. SnCl_4 flow rate: 1.3 ml min^{-1} .

Table 1. Electric properties of (001) SnO_2 films deposited on (001) TiO_2 at 1100° and 1300°C (*) for 1 h. SnCl_4 flow rate: 1.3 ml min^{-1} .

Sample	$\sigma \times 10^2 \Omega^{-1}\text{cm}^{-1}$			μ^{***} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	n^{***} cm^{-3}
	[100]	[010]	[110]		
121-2	6	10	5	16	5×10^{16}
	13.2***				
200	80	63	69	X	X
	31***				
307	8	8	9	15	3×10^{16}
	7.7***				
11*	22***			7	2×10^{17}
120*	530	810	490	6	9×10^{18}
	860***				
130*	410***			11	2×10^{18}

***: measured by van der Pauw's method

higher carrier concentrations (Table 1). The mobility little varied with the deposition temperature in spite of such a drastic change in the appearance of the film as shown in Fig. 1. The conductivities along the [100] and [010] axes were reasonably consistent with each other. Further, they are comparable not only to the conductivity along the [110] axis but also those obtained by van der Pauw's method which gives the average value over all directions of the films. No anisotropy of the conductivity was observed for these films.

Figure 3 shows the morphology and the crystallographic axes of a (110) SnO_2 film. The representative electrical properties of (110) SnO_2 films were shown in Table 2. The conductivities of the (110) SnO_2 films were similar to those of the (001) SnO_2 films whereas

Fig. 2. Electric conductivities of (001) SnO_2 films deposited on (001) TiO_2 at various temperature for 1 h (○) and 4 h (●). SnCl_4 flow rate: 1.3 ml min^{-1} .

Fig. 3. (110) SnO_2 films deposited on (110) TiO_2 at 1100°C for 2.5 h. SnCl_4 flow rate: 0.3 ml min^{-1} .

Table 2. Electric properties of (110) SnO₂ films deposited on (110) TiO₂ at 1100° and 1300°C (*) for 1.5 and 2.5 h (**). SnCl₄ flow rate: 0.3 ml min⁻¹

Sample	$\sigma \times 10^2 \Omega^{-1} \text{cm}^{-1}$			μ^{***} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	n^{***} cm^{-3}
	[001]	[111]	[110]		
228 ^{***}	87	-	-	X	X
	9 ^{***}				
229 ^{***}	93	86	140	0.7	4×10^{18}
	43 ^{***}				
414 ^{***}	23	28	43	0.3	1×10^{18}
	6 ^{***}				
310 ^{***}	-	-	8	X	X
	7 ^{***}				
316-1	140 ^{***}			4	2×10^{18}
2282	72 ^{***}			8	6×10^{17}
314 [*]	1×10^3 ^{***}			3	3×10^{19}

*** : measured by van der Pauw's method

their appearances were different from each other. The (110) films seemed to have more or less higher carrier concentration but lower mobility than the (001) films. The high deposition temperature increased the conductivity as well as in the case of the (001) films. Although the alignments of the SnO₂ particles along the [001], [111] and [110] directions appeared to be different from each other, the anisotropy of the conductivity was not noticeable in the (110) films.

Anisotropy of the conductivity in SnO₂ single crystals has been found to be small ($\sigma_{[100]}/\sigma_{[001]} = 1.2$ at 300 K)⁶⁾. On the other hand, Suzuki et al. found that the predominantly oriented (101) films of SnO₂ polycrystalline films showed the highest conductivity, which was supposed to be

due to the effects of the grain boundary or the film texture^{7),8)}. Those effects on the anisotropy of the conductivity seemed to be little in the oriented (001) and (110) films prepared in this experiment.

The reported value of the mobility in SnO₂ single crystals is about 200-300 cm² V⁻¹ s⁻¹ while doped and undoped polycrystalline films used as transparent conducting films have a carrier concentration of 10¹⁸-10²¹ cm⁻³ and mobility about one order of magnitude smaller than in single crystals^{3),4)}. The oriented films in this experiment had relatively low carrier concentrations and low mobility even in comparison with polycrystalline films. It seems that the high deposition temperature in this experiment (most conducting films were usually deposited at about 500°-600°C), reduced the oxygen vacancies and/or interstitial Sn in the SnO₂ films.

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