Tin Oxide Films Deposited by Ozone-Assisted Thermal Chemical Vapor Deposition

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Transparent conductive tin oxide (TO, SnO_2) films have been prepared by low pressure metal organic chemical vapor deposition (LP-MOCVD) from various mixtures of tetramethyltin (TMT) with oxygen and oxygen containing 2.96 to 5.1 mol% O_3. The properties of TO films have been changed with the gas flow rate (oxygen, oxygen containing ozone) and the substrate temperature. The use of oxygen containing ozone instead of pure oxygen reduced substrate temperature significantly and the resistivity while maintaining the same growth rate. The films prepared using ozone showed resistivity ranging from 10^{-2} to 10^{-3} Ωcm, and ranging mobility from 10.5 to 13.7 cm^2/Vs.

KEYWORDS: tin oxide, TMT, ozone, CVD, oxygen vacancy

1. Introduction

Transparent conductive oxide (TCO) films have been widely employed as an optical transparent electrode in display devices and photovoltaic cells or other optoelectronic devices such as electroluminescent displays and solid-state imagers.[1,2] Tin oxide has been produced by a number of techniques such as spray pyrolysis, DC (or rf) sputtering, and chemical vapor deposition (CVD).[3–6] Among these techniques, the organometallic CVD technique offers several advantages such as good control of film properties and relatively high growth rate of the order of 1–10 nm/s. The most widely used materials for TCO film fabrication are zinc oxide (ZO), indium-tin oxide (ITO), and tin oxide (TO). Compared to TO and ZO, ITO has the highest conductivity, but is the most chemically unstable.

The trend in TCO development can be summarized into high conductivity, high transmission, and chemical stability. From the viewpoint of these requirements, TO has many possibilities. TO is an electrical conductor that has high conductivity as well as good transparency in the visible spectral range and excellent reflectivity in the infrared range. TO also has the highest chemical stability.

It is well known that the high conductivity of TO is caused by both intrinsic defects (oxygen vacancy) and dopants (F, Sb, etc.).[7–9] Therefore, a unique method to obtain a high-quality transparent conductor is to induce electron degeneracy by introducing nonstoichiometry and appropriate dopants. In this study, the effects of deposition temperature and oxygen/ozone flow rate on the conductivity and optical properties of films grown by LP-MOCVD using tetramethyltin [TMT; $(CH_3)_4Sn$] and oxygen containing ozone are investigated. We used TMT as the source of Sn because it is one of the volatile organotin sources and has good stability in air and moisture.

2. Experiment

The deposition of tin oxide was carried out in a vertical cold-wall LPCVD system. Soda-lime-silicate (SLS) glass was used as the substrate. Source materials were TMT, oxygen, and oxygen containing 2.96–5.1 mol% ozone. To prevent the condensation of TMT, the mass flow controller (MFC) and the gas lines linked with the TMT container were heated and maintained at 40°C by a commercially available temperature

controller. The temperature of the TMT container was maintained at 23°C by a thermostat. As a result of above two controlled temperatures, the adequate flow of TMT vapor could be obtained without using a carrier gas. Oxygen or oxygen containing ozone was also carried to the showerhead with TMT. The flow rates of oxygen (or oxygen containing O_3) and TMT were 100–500 sccm and 6–35 sccm, respectively. To compare the physical, electrical, and optical characteristics of tin oxide films grown with pure oxygen and oxygen containing ozone, tin oxide films were deposited under the deposition condition shown in Table I and at various deposition temperatures from 200°C to 450°C.

The thickness of the deposited tin oxide films was measured using a step profilometer after etching tin oxide films partially with a mixture of HCl (50%) and Zn powder. The chemical composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS). Crystallinity and other structural properties were measured by X-ray diffraction (XRD) analysis. The electrical properties such as resistivity, carrier concentration, and mobility were analyzed using a four-point probe and Hall measurement. A UV spectrophotometer was used to measure the optical transmission of the films.

3. Results and Discussion

Figure 1 shows the growth rate of tin oxide as a function of growth temperature. The growth temperature of tin oxides grown using pure oxygen and TMT (O_2–SnO_2) ranged from 350°C to 450°C and that of tin oxides using oxygen containing a few mole percent (3–5) of ozone and TMT (O_3–SnO_2) ranged from 200°C to 400°C. As shown in the figure, the growth rates were increased exponentially with increasing substrate temperature, indicating a typical chemically active process; however, the growth rates for O_3-SnO_2 were much higher than those for O_2–SnO_2. In the case of O_2–SnO_2, no noticeable growth of tin oxide was detected when the substrate temperature was below 300°C and a growth rate of 10 Å/min was obtained when the substrate temperature was raised to 350°C. Relatively high growth rates of 110 Å/min and 360 Å/min could be obtained at 400°C and 450°C, respectively. However, the use of a high substrate temperature is limited due to the possible bending of and enhanced diffusion of Na into the soda lime glass substrate, in addition to
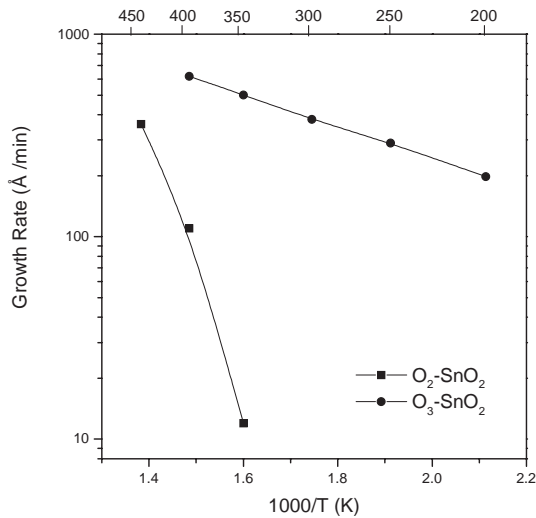
Fig. 1. Growth rates of tin oxides grown with pure oxygen (O_2–SnO_2) and with oxygen containing ozone (O_3–SnO_2)as a function of growth temperature (TMT: 8 sccm, oxygen: 300 sccm, oxygen containing 2.96 mol% ozone: 300 sccm)
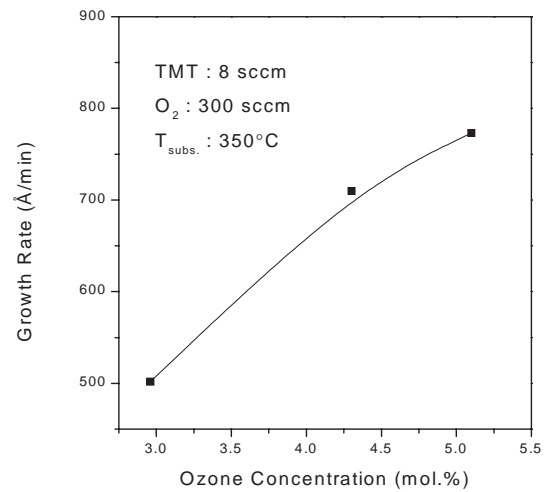

Fig. 2. Growth rates as a function of ozone concentration for tin oxides grown with oxygen containing ozone.

Fig. 3. XRD spectra of O_2–SnO_2 films grown at 400°C. Other growth parameters are listed in Table I.

a reduction of process throughput. When oxygen containing 2.96 mol% ozone instead of pure oxygen was used as shown in Fig. 1, tin oxide growth rates higher than 100 Å/min could be obtained even at 200°C and, at a substrate temperature of 400°C, a growth rate of 620 Å/min was obtained. Therefore, by introducing ozone, the substrate temperature could be reduced significantly at the same growth rate of tin oxide.

Figure 2 shows the effect of ozone concentration in oxygen on the growth rate of O_3-SnO_2. Ozone concentration was varied from 2.96 mol% to 5.1 mol% in 300 sccm oxygen while the substrate temperature was set at 350°C and the TMT flow rate was fixed at 8 sccm. As shown in the figure, as ozone concentration in oxygen increased, the growth rate of O_3–SnO_2 increased linearly. It is known that ozone decomposes into reactive oxygen atom (O^*) and oxygen molecule above 200°C, and the decomposed reactive oxygen atom reacts with TMT at temperatures above 200°C, as shown below.

$$Sn(CH_3)_4 + xO^* \rightarrow Sn(CH_3)^*_{4-x} + xCH_3O^* \quad x = 1\text{–}4$$

The continuous reaction of O^* with the decomposed TMT radicals finally produces reactive Sn^* which can easily react with oxygen to form SnO_x. Therefore, the addition of ozone in oxygen and an increase in its concentration will increase the growth rate of SnO_2. The addition of ozone in oxygen also changed the physical properties and electrical properties of the grown tin oxides.

Figure 3 shows the X-ray diffraction data measured for different thicknesses of O_2–SnO_2. The growth conditions are listed in Table I. When the thickness of O_2–SnO_2 was less than 2400 Å, the film showed (110) preferred orientation; however, as the thickness of O_2–SnO_2 increased, the (211) preferred orientation showed up in addition to the (110) preferred orientation. However, in case of O_3-SnO_2, the films showed both (110) and (211) preferred orientations when the film is thin and, as the film thickness is increased, the film showed only the (211) preferred orientation. The results are shown in Fig. 4. Figure 4 also shows the effect of substrate temperature on the film structure for O_3–SnO_2 films of similar thickness. When the substrate temperature was in-

creased from 300°C to 400°C, the film showed more (110) preferred orientation and better crystallinity even though the crystallinity of O_3–SnO_2 is generally worse than that of O_2–SnO_2. Therefore, the increase in substrate temperature improved the crystallinity and the growth rate of O_3–SnO_2.

The electrical properties of O_3–SnO_2 were measured using the four-point probe methods and the Hall measurement system, and the results are shown in Table II. For comparison, the electrical properties of O_2–SnO_2 were also measured. The growth conditions for both of the films are the
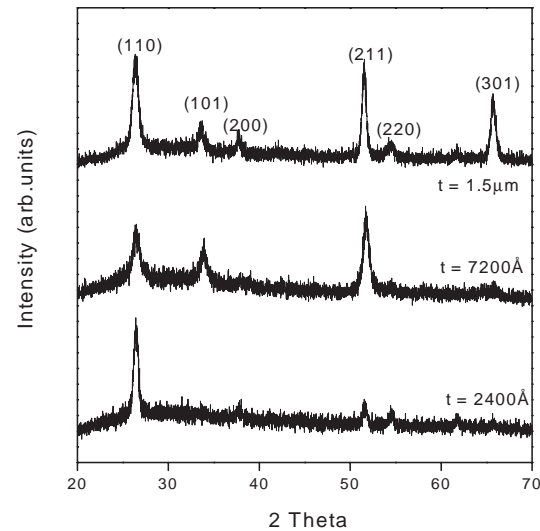
Table I. Standard deposition conditions used to deposit tin oxide in the experiment.

	O_2–SnO_2	O_3–SnO_2
O_2 flow rate	300 sccm	300 sccm
O_3 concentration	—	2.96 mol.%
TMT flow rate	8 sccm	8 sccm
Working pressure	7 Torr	7 Torr

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sames, as shown in Table I. The substrate temperature chosen for O_2–SnO_2 was 400°C and that for O_3–SnO_2 was 350°C, which showed the lowest resistivities in our experimental conditions. The lowest resistivity at a certain temperature is due to a balance between the loss of carrier concentration caused by the improvement of stoichiometry as discussed below and the increase in mobile carrier concentration with improved crystallinity with increasing substrate temperature, as shown in Fig. 4. As shown in Table II, the carrier mobility and concentration of O_3–SnO_2 were much higher than those for O_2–SnO_2 ; because of this, the resistivity of O_3–SnO_2 (10^{-2}–10^{-3} Ωcm) was about ten times lower than that of O_2–SnO_2 (10^{-1}–10^{-2} Ωcm).

The optical properties of O_3–SnO_2 deposited at 350°C were measured using a spectrophotometer for the different film thicknesses and the results are shown in Fig. 5. Other growth parameters are the same as those shown in Table I. As shown in the figure, an optical transmission higher than 80% could be obtained at an optical wavelength of 550 nm for films up to 4400 Å thick and up to 75% for films 5900 Å thick. The thickness of the transparent conductive oxide generally used in optical devices ranges from 2000 Å to 3000 Å and requires an optical transmission of at least 80%; therefore, the O_3–SnO_2 fabricated in our experiment appears to be applicable to real optical devices.

The high conductivity of the transparent conductive oxide

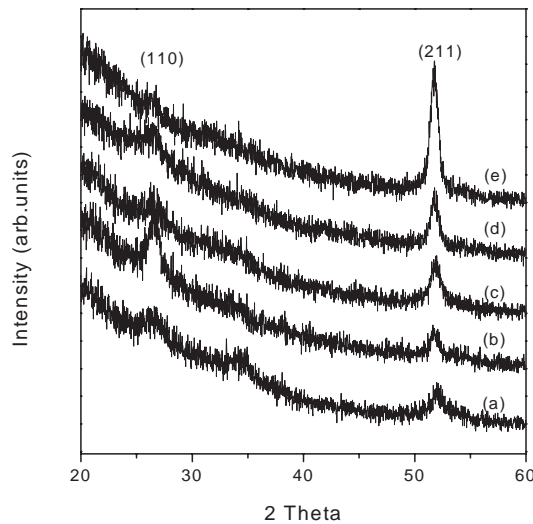is known to originate from the nonstoichiometry of the oxide, and oxygen deficiency in the oxide is responsible for the conductivity.[10] The composition ratios of grown O_2–SnO_2 and O_3–SnO_2 were measured by X-ray photoelectron spectroscopy (XPS) and the results are also shown in Table II. The O/Sn ratio of O_2–SnO_2 ranged from 1.856 to 1.933 while that of O_3–SnO_2 ranged from 1.64 to 1.678; therefore, more oxygen vacancies were observed for O_3–SnO_2. When x mole of oxygen vacancies exists in SnO_2, x mole of SnO is formed with 1-x mole of SnO_2; therefore, a nonstoichiometric oxide consisting of $Sn_{1-x}^{4+} Sn_x^{2+} O_{2-x}^{2-}$ is formed. The X mole of oxygen vacancies and x mole of Sn^{2+} induce $2x$ mole of carrier concentration in the SnO_x thin film; thus the film shows high conductivity.[9] From the O/Sn ratios measured XPS, x is calculated to range from 0.067–0.144 for O_2–SnO_2 and 0.322–0.36 for O_3–SnO_2. The free electrons from the oxygen vacancies will be $2x$ and the ratio of free electrons between O_3–SnO_2 and O_2–SnO_2 ranges from 2.5 to 4.8; therefore, there are more free electrons for O_3–SnO_2. The ratio of carrier concentration between O_3–SnO_2 and O_2–SnO_2 in Table II ranges from 3.0 to 4.3, and the ratio of carrier concentration shows a similar trend with the ratio of oxygen vacancies. Therefore, the high conductivity of the grown O_3-SnO_2 is attributable to high concentration of oxygen vacancies in the film as measured by XPS.

The use of an organic compound for chemical vapor deposition can induce carbon contamination in the grown film due to the carbon in the gas source. Using XPS, the remaining
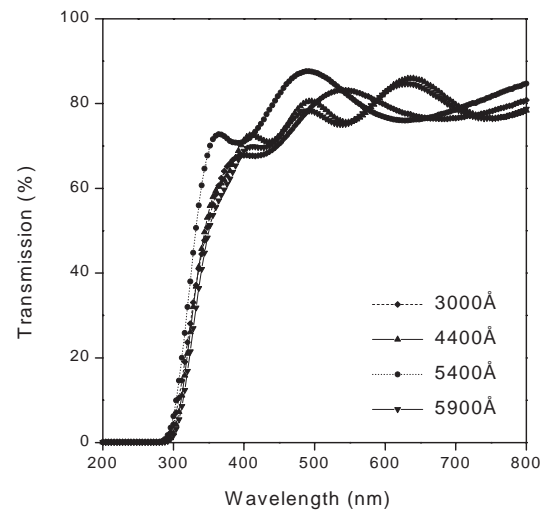

Fig. 4. XRD spectra of O_3–SnO_2 films grown with oxygen containing 2.96 mol% ozone: (a) 300°C: 4700 Å, (b) 400°C: 5500 Å, (c) 350°C: 4800 Å, (d) 350°C: 6500 Å, and (e) 350°C: 8200 Å. Other growth parameters are listed in Table I.

Fig. 5. Variation of the optical transmission of O_3–SnO_2 films grown with oxygen containing 2.96 mol% ozone as a function of thickness (substrate temperature: 350°C). Other growth parameters are listed in Table I.

Table II. Hall measurement data, four-point probe data, and XPS data measured for O_2–SnO_2 grown at 400°C and O_3–SnO_2 at 350°C. Other growth conditions are listed in Table I.

Measurement	Unit	O_2–SnO_2 (T_{sub}: 400°C)	O_3–SnO_2 (T_{sub}: 350°C)
Hall measurement	μ (cm^2/V$_S$)	0.4–2.5	10.5–13.7
	ρ (Ωcm)	10^{-1}–10^{-2}	10^{-2}–10^{-3}
	Carrier conc. (/cm^3)	3–5 × 10^{19}	9 × 10^{19}–3 × 10^{20}
4-point probe	R_s (Ω/□)	470–1650	157–256
XPS	O/Sn	1.856–1.933	1.64–1.678
	C/Sn	0.24–0.246	0.105–0.150

carbon content was also investigated for both O_2–SnO_2 and O_3–SnO_2 and the result also is shown in Table II. Much lower carbon concentration was obtained for O_3–SnO_2 compared to that for O_2–SnO_2, possibly due to the reaction between reactive oxygen atom from ozone and TMT. Therefore, the oxygen atom from ozone is believed to not only decompose TMT more rapidly but also react with carbon in the TMT more actively to form volatile by-products such as CO and CO_2.[11]

4. Conclusion

The effects of ozone on the growth rate, physical and optical properties, and electrical properties of SnO_2 thin films grown by low-pressure metal organic chemical deposition using TMT and oxygen have been studied. The use of a few mole percent (3–5) of ozone in oxygen instead of pure oxygen in growing SnO_2 increased the growth rate; therefore, the substrate temperature could be reduced significantly at the same growth rate. O_3–SnO_2 deposited at 350°C with 2.96 mol% of ozone showed higher carrier mobility and carrier concentration than O_2–SnO_2 deposited at 400°C with pure oxygen; therefore, it exhibited lower resistivity than to O_2–SnO_2. The

lower resistivity of O_3–SnO_2 appears to be related to the higher concentration of oxygen vacancies in SnO_x film as measured by XPS. Due to the poorer crystallinity of the film deposited at lower temperature and more SnO phase deteriorating the optical transmission of O_3–SnO_2, the optical transmission of O_3–SnO_2 was not the highest, however; an optical transmission higher than 80% required in optical devices could be obtained for films with less than 4000 Å in thickness.

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