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# Doped-Fluorine on Electrical and Optical Properties of Tin Oxide Films Grown by Ozone-Assisted Thermal CVD

**J. W. Bae,[a] S. W. Lee,[b] and G. Y. Yeom[a]**

[a]*Department of Materials Science and Engineering, SungKyunKwan University, Suwon, 440-746 South Korea*
[b]*Korea Electric Testing Institute, 692-8, Keumjung-dong, Kunpo, Gyeonggi-do, Korea*

Transparent conductive fluorine-doped tin oxide (FTO, $SnO_2$:F) films were grown using a low-pressure metallorganic chemical vapor deposition (LP-MOCVD) with tetramethyltin (TMT), oxygen containing 2.96 mol % ozone ($O_3$), and hydrofluoric acid (HF) as a dopant. Using ozone contained oxygen instead of pure oxygen, the substrate temperature could be reduced by ~100°C while maintaining a growth rate similar to that of tin oxide film. Growth rate of FTO film increased with the flow rate of TMT, however, adherence strength between the film and glass decreased. Resistivity of FTO thin films decreased with the TMT and HF flows over most of ranges investigated, while the resistivity increased rapidly with respect to excessive flow of the TMT over 300 sccm. Optical transmittance of FTO film was about 80% at 550 nm, and the variation as a function of HF flow rate was not significant. FTO film prepared at an optimum condition showed a minimum resistivity of $1.09 \times 10^{-3}$ Ω cm, a mobility of 19 $cm^2/Vs$, and a carrier concentration of $3.05 \times 10^{20}$ $cm^{-3}$.
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Transparent conductive oxide (TCO) films have widely been employed as an optical transparent electrode in display devices and photovoltaic cells or other opto-electronic devices such as electroluminescent display, and solid-state imagers.[1,2] The most used materials are zinc oxide (ZO), indium-tin oxide (ITO), and tin oxide (TO). In comparison to TO, ZO and ITO have the highest conductivity, but are chemically unstable in plasma or at high temperature. The development trends for TCO can be compressed into the high conductivity, transmittance, and chemical and thermal stability. From the viewpoint of these requirements, TO ($SnO_2$) has many possibilities. TO is an electrical conductor with high conductivity with a good transparency in the visible spectral range and an excellent reflectivity to infrared wavelength. Also, TO has the highest chemical stability among the TCO materials. Although undoped tin oxide has been employed as a transparent electrode in the field of electrochemical devices, doped tin oxide would be better due to its higher conductivity. It is well known that the high conductivity of TO films is caused by both intrinsic defects (oxygen vacancy) and dopants (F, Sb, etc.).[3-5] Therefore, the unique method to obtain high-quality transparent conductor is to induce electron degeneracy by introducing nonstoichiometry and appropriate dopants in the films.

Tin oxide films have been produced by a number of techniques such as spray pyrolysis, dc (or radio-frequency, rf)-sputtering, and chemical vapor deposition (CVD).[6-9] Of the above techniques, organometallic CVD processes offer several advantages such as good control of film properties and relatively high growth rate on the order of $1 \times 10$ nm $S^{-1}$.[10] Tetramethyltin [TMT; $(CH_3)_4Sn$] is one of the volatile organotin sources, and that has good stability in air and moisture.[11] Hydrofluoric (HF) has a bright future as a fluorine source because it is common, relatively inexpensive, and has a good reactivity. As the n-type dopant, chlorine and the heavier halogens are so large that they distort the lattice structure and cause additional electron scattering in the conduction band, resulting in the reduction of electron mobility, which subsequently decreases the conductivity. On the other hand, fluorine produces the least scattering because it is not large enough to cause the distortion and the scattering, leading to no degradation.[12,13] Oxygen containing a few mol % ozone was employed instead of pure oxygen. The better activity of ozone may give rise to the higher growth rate of tin oxide film at a relatively lower substrate temperature.

In this paper, the properties of tin oxide films grown using thermal CVD with TMT, HF, and oxygen containing a few mol % ozone were discussed. Oxygen containing ozone is employed to reduce the growth temperature.

## Experimental

The growth of fluorine-doped tin oxide film was carried out in a vertical cold-wall low-pressure CVD (LPCVD) system. And the films were grown onto soda-lime-silicate (SLS) glasses. Source materials were TMT, HF, and oxygen containing 2.96–5.1 mol % ozone. To prevent the condensation of TMT, the mass flow controller (MFC) and gas line linked with TMT container were heated and kept constant at 40°C by a commercially available temperature controller. In addition, the temperature of 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. Hydrofluoric acid used as the F-doping material was put into the showerhead without a carrier gas by keeping the temperatures of HF container and gas line constant at 90 and 60°C, respectively. Flow rates of HF were varied from 40 to 140 sccm. Flow rates of oxygen containing ozone and TMT were 2 slm and 150-300 sccm, respectively. Oxygen containing ozone was fed into the showerhead with TMT and HF-acid. Ozone ejected from the pump was removed by passing a furnace maintained at 600°C. Working pressure and substrate temperature were kept constant at 7 Torr and 350°C, respectively. To investigate the effects of post annealing on electrical properties of fluorine-doped tin oxide (FTO) films, the films were annealed at 450°C for 30 min in nitrogen, pure oxygen, and oxygen containing 2.69 mol % ozone atmospheres, respectively. Changes of electrical properties before and after annealing were observed with a Hall measurement system.

Film thickness of FTO film was measured using a depth profilometer. Prior to measuring the growth rate, the FTO film was etched using wet etchant. Adhesion strength between the films and the substrate was examined using a scratch tester. The composition of the film was analyzed by X-ray photoelectron spectroscopy (XPS). The electrical properties of tin oxide film such as resistivity, carrier concentration, and mobility were measured by a Hall measurement system. The UV-spectrophotometer was utilized to measure the optical transmittance of the film.

## Results and Discussion

Figure 1 shows the growth rates and the resistivities of fluorine-doped tin oxide thin films as a function of TMT flow rate. The growth temperature and the flow rates of oxygen containing 2.96 mol % ozone and hydrofluoric acid were fixed at 350°C and 300 and 100 sccm, respectively. As shown in the figure, the growth rate increased with the increase in the TMT flow rate, indicating a typical chemically active process; however, the rate was saturated at the flow rate of 300 sccm and higher. The resistivity of the films decreased with the TMT flow rate upto 250 sccm, and increased

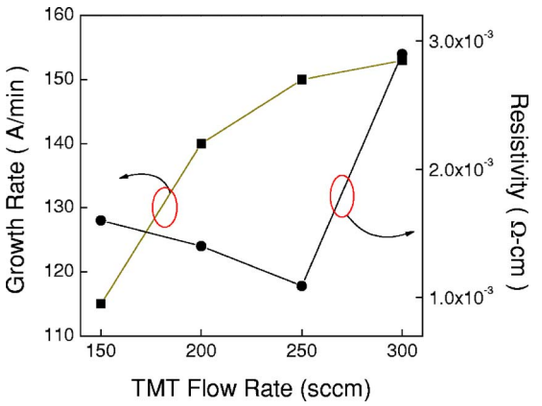


**Figure 1.** (Color online) Growth rate and resistivity of FTO films as a function of TMT flow rate (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, HF of 100 sccm, and substrate temperature of 350°C).

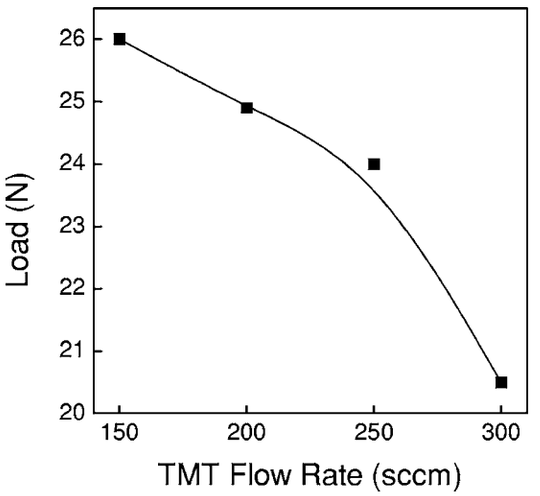


**Figure 2.** Adhesion strength between the grown FTO films and the glasses as a function of TMT flow rate (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, HF of 100 sccm, and substrate temperature of 350°C).

rapidly at the flow rate of 300 sccm. Note that there is an optimum flow rate of TMT, 250 sccm in this study. From our previous study,[14] the required minimum substrate temperature to grow undoped tin oxide film by using a pure oxygen was 350°C, however, as oxygen containing a few mol % ozone instead of pure oxygen was used, the minimum temperature could be reduced by 200°C and, a growth rate higher than 620 Å/min at 400°C. We noted that ozone may decompose into reactive oxygen atom, that is, oxygen radical ($O^*$) and oxygen molecule at the temperature above 200°C, and the oxygen radical reacts with TMT. The continuous reaction of the radical with the decomposed TMT radicals finally produces reactive tin atom which can be easily react with oxygen or oxygen radical to form $SnO_x$ ($x$ = 1–2). The reaction with the growth temperature above 200°C can be described as

$$O_3 \rightarrow O_2 + O^* \quad [1]$$

$$Sn(CH_3)_4 + xO^* \rightarrow Sn(CH_3)^*_{4-x} + xCH_3O^*,\ x = 1\text{–}4 \quad [2]$$

Although the addition of ozone in pure oxygen increases the decomposition rate of TMT, which helps in decreasing an optimum substrate temperature to grow tin oxide and increasing a growth rate at the same growth temperature, the use of a high flow rate of TMT may be limited because the possible bending of soda lime glass along with enhanced outdiffusion of sodium from the glass toward the grown film at high temperature. Using a larger amount of TMT requires higher substrate temperature. High flow rate of TMT at a fixed substrate temperature leads to the degradation of physical and electrical properties of the grown films as shown in Fig. 1 and 2.

Figure 2 shows the adhesion strength between the grown tin oxide film and the glass substrate as a function of TMT flow rate measured using a scratch tester. The growth conditions were the same as with Fig. 1. The adhesion strength decreased with the increase in TMT flow rate, and the change was prominent at the flow rate of 300 sccm. This implies that the bonding strength between reactants was not enough to form normal tin oxide at the overflow of TMT. This TMT-reaction-limit-process may lead to the excessive oxygen deficiency in the tin oxide films and the weak adhesion between the films and glasses. These result in the degradation in the electrical properties of the film such as resistivity and mobility. In this experiment, a TMT flow rate of 250 sccm was determined to be optimum amount at the substrate temperature of 350°C.

With a fixed TMT flow rate at 250 sccm, an optimum amount of HF used as a dopant source was investigated at the substrate temperature of 350°C and with the oxygen containing 2.96 mol % ozone of 300 sccm. The variation in resistivity as a function of HF flow rate is shown in Fig. 3. Resistivity decreased continuously with the HF flow rate until it reached at 100 sccm, and the further increase led to the degradation of the electrical property. At high flow rate over 100 sccm, the chance for the reaction between the HF and the TMT radical decreases, and the surplus HF acts as contamination in the FTO film, resulting in the increase of resistivity and the whitish residue on surface of the films. The variation of fluorine composition in the FTO thin film was investigated using X-ray photoelectron spectroscopy (XPS), and the results are shown in the Fig. 4. As shown in the figure, atomic percentages of fluorine and oxygen in the films continuously increased and decreased with HF flow rate while the amount of tin in the film was kept constant. The decrease in the resistance can be attributed to an increase in donor concentration in the film at the proper growth temperature, and the subsequent increase with fluorine concentration, after reaching a minimum, can be ascribed to an increase in disorders due to excessive fluorine atoms not contributing as donors, which is just reducing the mobility without donating an electron to conduction band. Note that a proper F-doping concentration to obtain a minimum resistance exists for the tin oxide film growth using an ozone-CVD.

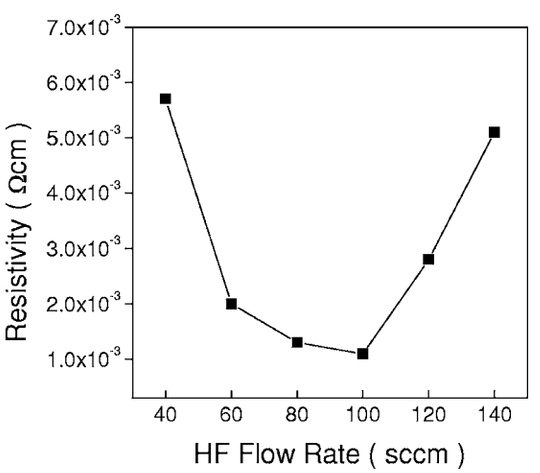


**Figure 3.** Resistivity of FTO films as a function of HF flow rate (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, TMT of 250 sccm, and substrate temperature of 350°C).

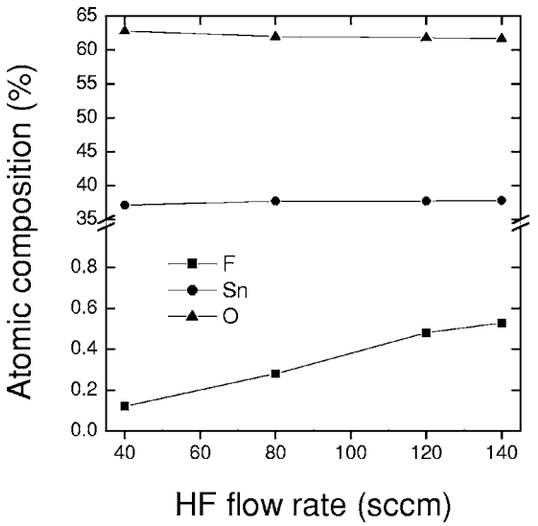


**Figure 4.** XPS spectra of FTO films as a function of HF flow rate (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, TMT of 250 sccm, and substrate temperature of 350°C).

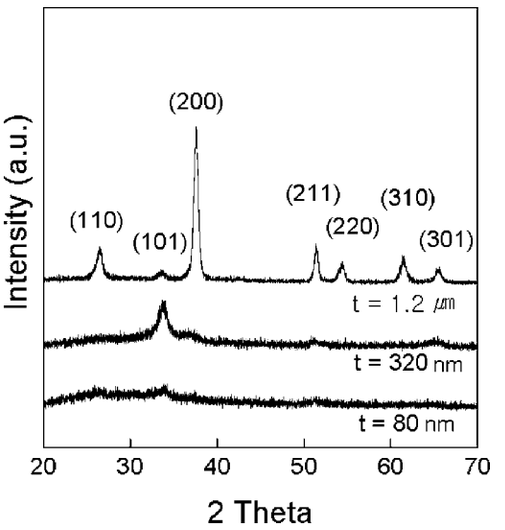


**Figure 6.** XRD spectra of FTO films as a function of grown thickness (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, TMT of 250 sccm, HF of 100 sccm, and substrate temperature of 350°C).

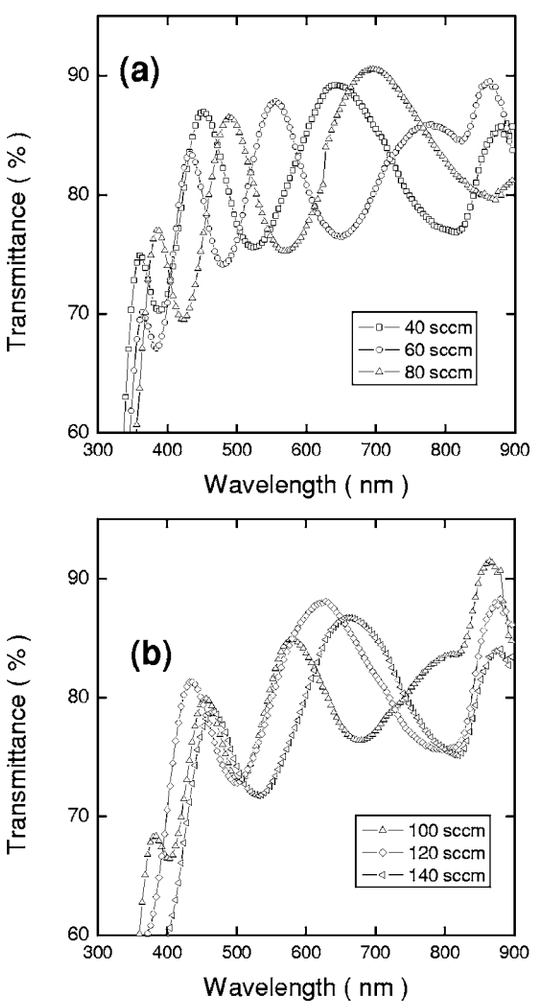


**Figure 5.** Optical transmittance of FTO films as a function of HF flow rate (growth conditions: oxygen containing 2.96 mol % ozone of 300 sccm, TMT of 250 sccm, and substrate temperature of 350°C).

However, the variation in the transmittance of FTO films as a function of HF flow rate was not significant over the UV and visible wavelength regions as shown in Fig. 5. In Fig. 5, growth parameters were the same as used for the Fig. 3, and the growth thickness was kept same near 4000 Å for all of films with the deviation below 10%. As shown in the figure, optical transmittance between 75 and 86% at 550 nm could be obtained. In general, transparent conductive oxide requires an optical transmittance more than 80% at 550 nm with a film thickness of 1000 Å; therefore, the FTO films grown using oxygen containing ozone and HF as a dopant source seems to be useful to any optical devices.

Figure 6 shows the X-ray diffraction data measured for different thickness of FTO films. The growth temperature, the flow rate of oxygen containing 2.96 mol % ozone, TMT, and hydrofluoric acid were fixed at 350°C and 300, 250, and 100 sccm, respectively. As the thickness of FTO film increased up to 1.2 μm, the preferred orientations were changed from (101) to (200). This is different from our previous study[14] on the XRD measurement for undoped-tin oxide films grown using pure and ozone contained oxygen gases. According to the study, tin oxide film having a thickness around 1.0 μm showed both (110) and (211) preferred growth orientation for the pure oxygen-tin oxide and (211) orientation for the ozone-tin oxide.

Table I shows the changes in resistivity, mobility, and carrier concentration of FTO films as a function of post-annealing conditions. The annealing temperature was kept at 450°C for 30 min. The

**Table I. Variations in resistivity, mobility, and carrier concentration of FTO films for three different annealing ambient. The annealing temperature was kept at 450°C for 30 min.**

| | Before annealing | $N_2$ annealing | $O_2$ annealing | $O_3$ annealing |
|---|---|---|---|---|
| Resistivity ($\times 10^{-3}$ Ω cm) | 1.16 | 1.37 | 1.6 | 2.1 |
| Mobility ($cm^2/Vs$) | 18 | 22.3 | 25.7 | 28 |
| Carrier conc. ($\times 10^{20}$ $cm^{-}$) | 2.97 | 2.05 | 1.52 | 1.02 |
| Measurement errors (%) | ±6 | ±2.5 | ±2.7 | ±2.4 |

growth conditions are the same as with Fig. 6. Carrier concentrations were decreased for all of annealing conditions even though the mobilities were increased. In particular, in the cases of the annealing conditions using pure oxygen and oxygen containing ozone, the degradation of electrical property was bigger than that of nitrogen anneal. Note that the increase in the mobility is one of reasons for higher conductivity of FTO film in general; however, the electrical property of FTO film obtained in this study seems to be more dependent upon the carrier concentration of the film. It is well known that the concentration of tin oxide film originates from oxygen vacancies donating two electrons per vacancy to conduction band and dopants creating one electron per atom. Therefore, the variation in the electrical conductivity of FTO films obtained in this study appears to be more related to sensitivity to the annealing process using oxygen ambient, which is leading to the reduction of oxygen vacancies in the films through the re-oxidation process.

## Conclusion

The effects of TMT and HF flow rates on the growth rate, physical and optical properties, and electrical properties of tin oxide thin films grown using a low-pressure metalorganic chemical deposition have been investigated. At excessively high flow rates of TMT and HF, the films showed higher resistivity and lower transmittance and adhesion strength. In particular, the flow rate of HF over 120 sccm led to the whitish residue on the grown film due to the insufficient reaction between TMT radicals and HF molecules. Annealing in oxygen ambient caused the more significant reduction in the electrical conductivity of FTO film. It can be ascribed to the reduction of oxygen vacancy donating electrons to conduction band due to the additional reaction between SnO$x$ ($x \neq 2$) and oxygen during the anneal processes.

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