International Journal of Applied Glass Science 4 [3] 242–247 (2013)
DOI:10.1111/ijag.12016

INTERNATIONAL JOURNAL OF
Applied Glass
SCIENCE

Oxygen Distribution of Fluorine-doped Tin Oxide Films Coated on Float Glass along Depth Before and After Heat Treatment

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Fluorine-doped tin oxide (FTO) films were deposited on float glass to create low-emissivity glass (low-E glass) by atmospheric pressure chemical vapor deposition (APCVD). Heat treatments were carried out to assess its antioxidant properties. The surface morphology, crystal structure, and the oxygen and tin concentrations in the FTO films were investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), Auger electron spectrometer (AES), and X-ray photoelectron spectroscopy (XPS), respectively. The results indicated that the electrical properties determined by the four-point probe method remained constant up to 600°C with increasing temperature. The FTO films exhibited nonstoichiometry with a ratio of [O]/[Sn] >2 on the top surface and <2 in the film. The sheet resistance of the film strongly depended on the oxygen concentration on the film surface. When the heating temperature reached 700°C, the sheet resistance increased rapidly from 9.4 to 86.7 Ω/□ with a concomitant increase in the oxygen concentration on the top surface.

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Introduction

Tin dioxide (SnO_2) is an important oxide material that combines low electrical resistance with high optical transparency in the visible light spectrum. These properties are valuable in a number of applications: electrode materials, solar cells, light-emitting diodes, flat panel displays, and other optoelectronic devices in which an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area[1,2] SnO_2 materials are also transparent to visible light but reflect infrared light, which is responsible for today's use of SnO_2 as an energy-conserving material. SnO_2-coated architectural windows allow light but not heat to transmit in and out of buildings.[3–5]

Pure SnO_2 is an insulator and does not possess significant conductivity. However, its conductivity can be increased when free electrons are introduced into SnO_2 through F, Sb, and Cu doping.[6,7] In recent years, fluorine-doped tin oxide (FTO) films have attracted increasing attention. They have been deposited onto float glass by atmospheric pressure chemical vapor deposition (APCVD) to create low-E glass, which is used in buildings to save energy. Its mid- and far-infrared reflectivity (2.5~25 μm) is approximately 80%. FTO films can also effectively prevent heat transfer between the indoors and the outdoors.[8,9]

Fluorine-doped tin oxide films are wide band-gap semiconductors (>3.4 eV) whose specific electrical and optical properties are strongly dependent on the surface chemical composition, oxygen vacancies (i.e., oxygen deficiency), and the amount of doping material. In many cases, heat treatment is essential to imbue the as-deposited products with high strength. The preparation processing involves heating the material near to its softening point (approximately 680°C) in the furnace. The flat glass is then subjected to a rapid, even cooling of its surface, with the compression stress in the outer part and tension stress in the inner part, to increase the glass strength for windows. Generally speaking, SnO_2 films are stable and durable. However, its electrical properties decrease during heat treatment for as-of-yet unknown reasons. As there is an increasing demand for these materials, it is necessary to understand the chemical evolution of FTO films on glass.

The preparation of tin oxide films doped with fluorine, and their optical/electrical properties have been reported recently. Jow-Lay Huang *et al.* investigated the effects of annealing on the properties of antimony tin oxide thin films deposited by RF reactive magnetron sputtering[10] M. Kwoka *et al.* studied the XPS depth profiling of L-CVD SnO_2 thin films[11] Despite the tremendous amount of research conducted on FTO films, there are relatively few studies on the relationship between the oxygen content and the optical-electrical properties of SnO_2 films deposited by the CVD technique during heat treatment. In particular, little is known about the quantified difference of oxygen distribution between top surface and deep layer.

In this work, FTO films were deposited onto soda–lime–silica float glass by CVD in the tin bath of a float glass production line. Subsequently, heat treatments were performed in a resistor muffle furnace. The electrical properties were analyzed by four-point probe method. The surface morphology and crystal structure of the film were investigated by SEM and XRD. The concentration and distribution of oxygen and tin along depth were analyzed by Auger electron spectrometry (AES) and XPS. A comparison was made between the electrical properties and the oxygen content in the film before and after heat treatment.

Experimental

The samples studied in this work were low-E glass prepared by depositing fluorine-doped tin oxide onto a moving (380–500 m/h) hot soda–lime–silica glass (~600°C) ribbon using mono-butyl tin trichloride ($C_4H_9SnCl_3$, MBTC) and trifluoroacetic acid (CF_3COOH, TFA) as the precursors for Sn and F, respectively, in the CVD deposition. A 4 min heat treatment in air was carried out at different temperatures from 20 to 700°C in the laboratory resistor muffle furnace (SX2-4-10) at a heating rate 5°C/s and then cooled in the furnace to room temperature. The heating unit is the resistance wire on two sides of the furnace, including a thermocouple thermometer. The glass is heated in the middle, and the temperature measurement points are located at the two sides of the furnace. The glass and the thermocouple thermometer are separated by some distance. Therefore, it is worth noting that the space temperature inside the furnace may be a little higher (approximately 20°C) than the substrate temperature.

The structure and morphology of the films were studied by X-ray diffraction (XRD, D/max-2500/PC)

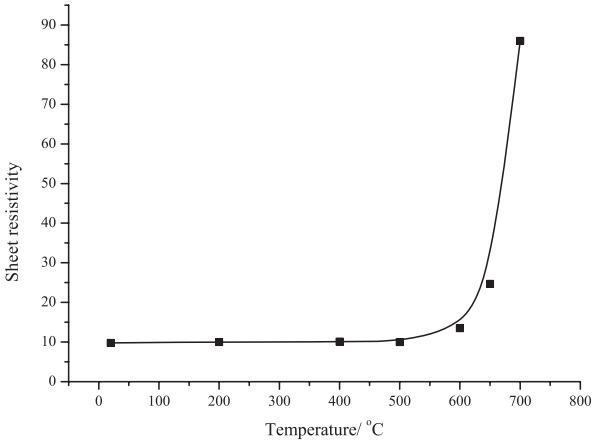

Fig. 1. Sheet resistance (Ω/□) of films under heat treatment in air.

and field-emission scanning electron microscopy (FESEM, S4800). The electrical properties were analyzed by four-point probe method. The atom percentages of oxygen and tin were determined by AES (PERKIN- ELMER-PHI Model 660) and XPS (ESCALAB250) using Ar-ion bombardment. The main analysis parameters were as follows: AlKα = 1486.6 eV, 150 W, spot size 500 μm, pass energy 50.0 eV, energy step size 0.05 eV, MgKα = 1253.6 eV, and ion gun description: 2 kV beam, 2 μA sample current, 1×10^{-7} mbar. The oxygen and tin atom percentages can be calculated based on the integrated intensity I_O/I_{Sn} determined for the SnO_2 powder of known composition.

Results and Discussion

Electrical Properties of Samples

The electrical properties, as shown in Fig. 1, indicate that the sheet resistance (R_s) remains almost unchanged (9.4 Ω/□) as the temperature increases to 600°C, after which it begins to increase. As the space temperature in the resistor furnace increases to 700°C, the sheet resistance (R_s) of the thin film increases dramatically to 86.7 Ω/□. Here, sheet resistance is specified in units of "ohms per square," indicating the particular coating resistance within the square area. These results imply that the electrical properties of FTO films remain remarkably stable when the temperature is below 600°C. The change in electrical properties begins at 600°C. A sharp increase in the sheet resistance occurs when the temperature reaches 700°C. The emissivity of FTO film may decline above 600°C, and losing effectiveness may occur at 700°C.

Surface Morphology and Structure

Field-emission scanning electron microscopy (SEM) and XRD were used to analyze the surface morphology and structure, respectively. The surface SEM morphologies of the as-deposited and postheated FTO films are shown in Fig. 2. The surfaces of the films are smooth, and large polyhedron-like grains (approximately 100–200 nm) are distributed over small round grains (20–30 nm). There is no obvious difference in grain sizes in the as-deposited and postheated FTO films.

As observed from the XRD analysis (Fig. 3), the films are polycrystalline with a mainly tetragonal SnO_2 phase. There are no notable changes in the diffraction pattern of the films after heat treatment. The films exhibit a preferred orientation, with the (211) plane parallel to the surface. With increasing heating time, the preferred orientation with the (211) plane becomes more obvious.

Oxygen Concentration Distribution in the Sample During Heat Treatment

To further interpret the origin of the variation in the electrical properties of FTO low-E glass, heat treatment experiments based on the processing parameters were performed with the temperature between 600 and 700°C for 150~300 s. The oxygen content in the film surface during the heating process was analyzed quantitatively by XPS (Fig. 4) and AES (Fig. 5).

The XPS results reveal that the oxygen concentration on the top surface differs from that of the inner surface. For instance, the oxygen concentration for the as-deposited sample is 68% on the film surface but approximately 50% in the inner film. A constant composition can be obtained after etching for 20 s (approximate depth of 15 nm). The FTO film can be divided into three parts: the top surface, near surface, and deep layer. The changes in oxygen concentration occur only in the top surface before and after heat treatment. The oxygen content is 68% for the as-deposited sample and increases to 83% after heat treatment (700°C for 200 s). Apparently, oxygen adsorption and diffusion from the air lead to a higher concentration of oxygen in the top surface. Meanwhile, the oxygen content in the

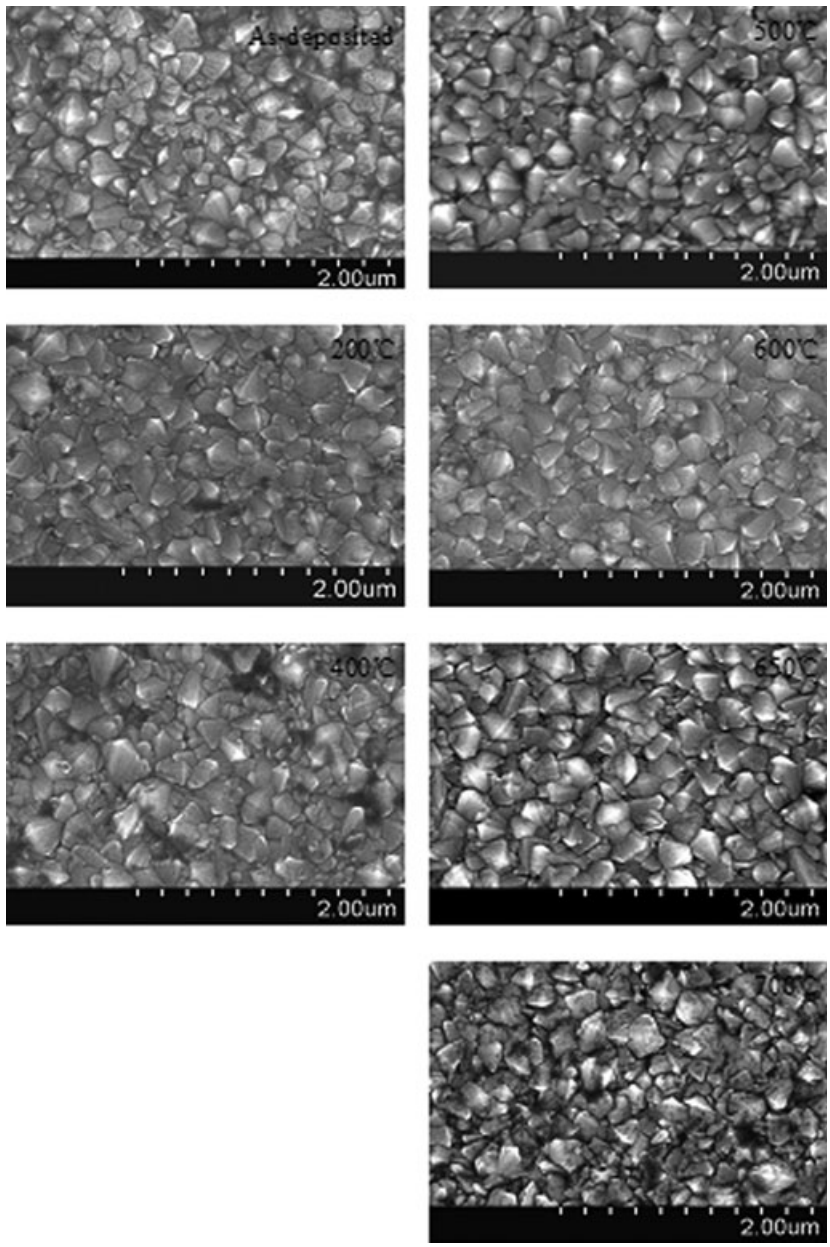

Fig. 2. Scanning electron microscopy micrographs of FTO films thermally annealed at different temperatures.

deep layer of the film changes little. The [O]/[Sn] atom ratios calculated from the XPS data confirm that the tin oxide in the film is in a nonstoichiometric state (Table I) and should be described as SnO_x, where x is below 2 in the deep layer and above 2 in the top surface. The [O]/[Sn] ratios increase sharply to 5.29 after heat treatment from 2.28 for the as-deposited sample. However, the ratio in the near surface increases only slightly after heat treatment and remains unchanged for etching times up to 490 s. The change in the oxygen content in the film subjected to a higher temperature is very similar to the steep rise exhibited by the electrical properties (Fig. 3). This feature hints that the sheet resistance of film depends strongly on the surface oxygen concentration.

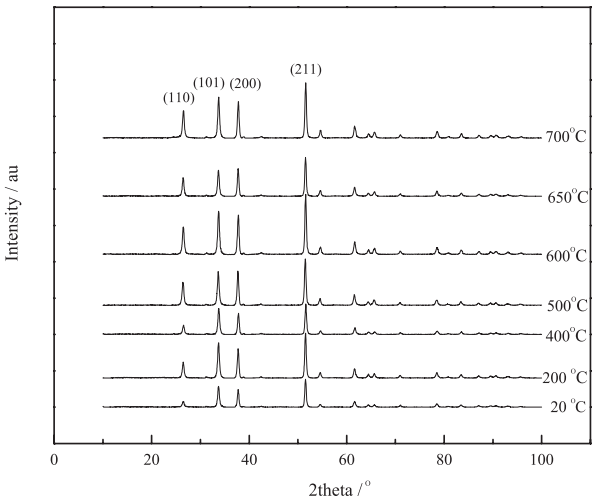

Fig. 3. X-ray diffraction patterns of the Fluorine-doped tin oxide films heated at different temperatures.

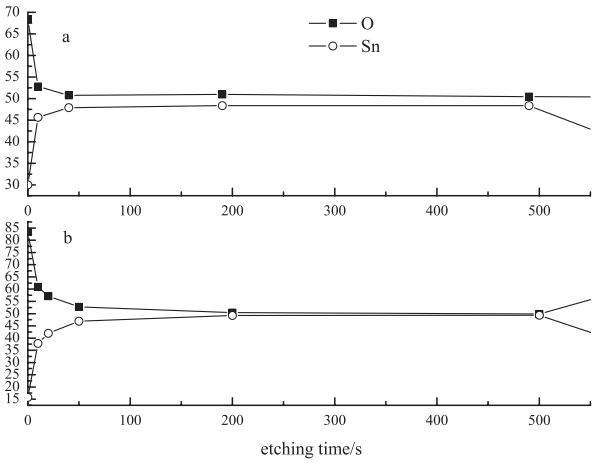

Fig. 4. Oxygen distribution in SnO_2: F film depth analyzed by X-ray photoelectron spectroscopy (a: as-deposited sample, b: after heat treatment at 700°C).

AES results also demonstrate that the oxygen atom percent in top surface increases from 61% of the as-deposited value to 77% after heat treatment (700°C for 200 s). However, the oxygen content only increases in the top layers (etching time <10 s, approximate depth of 15 nm), not the deeper film (see Fig. 5).

It is well known that the properties of SnO_2 thin films strongly depend on their deviation from stoichiometry, the nature and amounts of dopants and impurities,

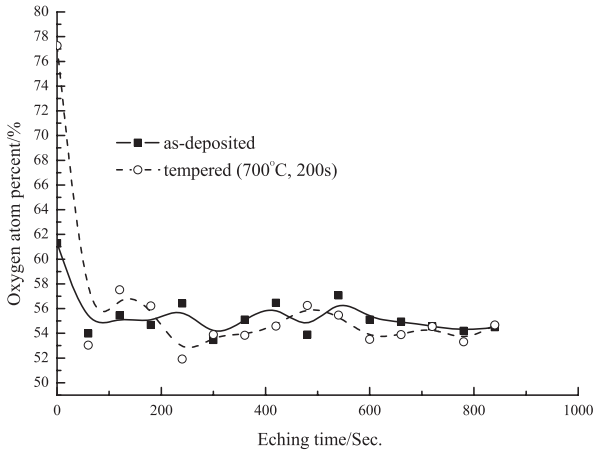

Fig. 5. Depth-composition profiles of O and Sn analyzed by Auger electron spectrometry.

Table I. Atomic Ratio of [O]/[Sn] in Fluorine-doped Tin Oxide Films on Low-E Glass Before and After Heat Treatment

	[O]/[Sn]	
Etching time (s)	**As-deposited sample**	**After heat treatment (700°C)**
0	2.28	5.29
10	1.16	1.61
40	1.06	1.36
190	1.05	1.12
490	1.04	1.02

and film microstructure. All of these properties depend on the deposition methods, parameters, and postdeposition processing. This type of nonstoichiometric FTO film was prepared in a tin bath with an oxygen deficit of a float glass production line. Apparently, the [O]/[Sn] atomic ratio will most likely approach 2.0 during heat treatment. Oxygen diffusion from the air during heat treatment leads to a higher concentration of oxygen in the top layers. With increasing oxygen content, the oxygen vacancies and carrier concentration in the top layers will decrease. Correspondingly, the surface resistance increases significantly. Notably, the oxygen content is in excess ($x > 2$) in the top layers, most likely due to bridge oxygen introduced from the ambient atmosphere.

It has been proposed that the adsorbed oxygen transitions into various oxygen anionic species, transferring an electron from SnO_2 to the chemisorbed oxygen according the following processes[1]:

$$O_2(gas) \leftrightarrow O_2(ad) \leftrightarrow O_2^{2-}(ad) \leftrightarrow O^-(ad) \leftrightarrow O^{2-}(ad) \leftrightarrow O^{2-}(lattice)$$

The conductivity decreases with increasing temperature, which can be interpreted in terms of the conversion of chemisorbed O_2^- into O^- (O^{2-}) and thus additional acceptance of electrons from the tin oxide by oxygen adsorbates.

Conclusions

Low-E glass was prepared by coating FTO film onto float glass using on-line CVD. Heat treatment experiments were carried out in air. The sheet resistance remained constant until 600°C, then increased steeply from 9.4 to 86.7 Ω/□ as the temperature increased to 700°C. The FTO films were polycrystalline with a SnO_2 tetragonal structure. The observed SEM morphology and XRD pattern changed little before and after the heat treatment. The oxygen atom concentration in the top surface was higher than that of the deep layer both before and after heat treatment. There was a sharp increase of oxygen content in the top surface after heat treatment. The [O]/[Sn] ratio increased from 2.28 to 5.29 after heat treatment. The change in the [O]/[Sn] ratio was similar to that of the conductivity, which was almost unchanged until 600°C, after which it increased quickly. The decrease in the oxygen vacancies and carrier concentration with temperature increased the resistance because of the oxygen adsorbates. The sheet resistance of the film depends strongly on the oxygen concentration on the top surface.

Acknowledgments

The work was supported by the National Natural Science Foundation of China under grant No. 50972126 and by the Group of Electrochemical Engineering, EPFL, Lausanne, Switzerland.

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