Optical and Electrical Properties of Tin Oxide-Based Thin Films Prepared by Streaming Process for Electrodeless Electrochemical Deposition

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ABSTRACT

Transparent conducting thin-films of SnO_2: F were grown on preheated glass, Al_2O_3 coated glass, and quartz substrates by Streaming Process for Electrodeless Electrochemical Deposition (SPEED). Stannic chloride ($SnCl_4$) and ammonium fluoride (NH_4F) dissolved in a mixture of deionized water and organic solvents were used as precursors. The preheated substrate temperature was varied between 440 and 500 °C. High quality SnO_2:F films were grown at all the substrate temperatures studied. The resulting typical film thickness was 250 nm. X-ray diffraction shows that the grown films are polycrystalline SnO_2 with a tetragonal crystal structure. The average optical transmission of the films was around 93% throughout the wavelength range 400 to 1000 nm. The lowest electrical resistivity achieved was 6×10^{-4} Ω-cm. The Hall measurements showed that the film is an n-type semiconductor, with carrier mobility of 8.3 cm^2/V-s, and carrier concentration of 1×10^{21} cm^{-3}. The direct bandgap was determined to be 4.0 eV from the transmittance spectrum.

INTRODUCTION

Transparent conducting oxides (TCOs) are wide band-gap semiconductors with relatively high free-electron concentration, which arises either from defects or extrinsic dopants with shallow levels near the conduction band edge [1, 2]. TCOs are increasingly used in photovoltaic (PV) devices and as electrodes, structural templates, and diffusion barriers.

Indium tin oxide (ITO) is the most widely used TCO [3, 4] because of its high electrical conductivity and optical transparency. The expense of indium (In) motivates the search for alternative TCOs. Fluorine-doped tin oxide (FTO, or SnO_2: F) is promising due to its chemical stability, electrical conductivity, optical transparency, and thermal stability, especially in high-temperature hydrogen-containing environments for gas sensing applications [5].

The microstructural, electrical, and optical properties of FTO are sensitive to deposition technique and conditions [6, 7]. Streaming Process for Electrodeless Electrochemical Deposition (SPEED) [8-11], which was developed by SISOM Thin Films LLC, is a high-rate uniform deposition technique that uses water-soluble precursors to rapidly coat the substrate with nanoparticle-based films. SPEED has its foundation in chemical bath deposition (CBD) [8-10] and is distinct from spray pyrolysis. To be pyrolysis, there must be a thermochemical decomposition of organic material at elevated temperatures (> 400 °C) in the absence of oxygen.

Indeed, the Greek root "lysis" means "separating". Organic solvents are used, and the products of the decomposition then react to form a film. In contrast, SPEED is a pure heterogeneous reaction between two reactants at a surface, using water as the primary solvent. Without the need to thermally decompose anything, SPEED is capable of growing materials at much lower substrate temperatures than is spray pyrolysis.

There are no fundamental limits to the achievable film thickness. SPEED allows high-quality film growth on large area hydrophilic rigid or flexible substrates, at lower temperature than the traditional spray pyrolysis, using environmentally friendly water-soluble primary chemicals and very flexible chemistry formulation for binary or more complex compound materials growth. Here we report application of SPEED to grow FTO films.

EXPERIMENT

The main precursors in the reagent solution are 0.4 M tin IV chloride (the Sn source) and ammonium fluoride (the F source, at 20% of the Sn concentration). The chemicals (Alfa Aesar) were dissolved in a mixed solvent of water, ethanol, isopropanol, and methyl propanol. Deionized water (20% by volume) is one of the main requirements in SPEED chemistry [8], serving as both solvent and oxygen source. The ethanol, isopropanol, and methyl propanol are mainly complexing agents for Sn ions. The complexing capabilities of the mixed solvents controls solution stability and shelf life.

A reservoir of the solution is maintained at a temperature sufficiently low to inhibit homogeneous reactions. The solution was nebulized into droplets (5 - 15 μm size range) by an inductively coupled plasma mass spectrometry (ICP-MS) nozzle and sprayed onto the heated substrate. Before deposition, the 5.0 cm × 5.0 cm substrates were cleaned thoroughly with industrial soap, rinsed with deionized water followed by acetone, then rinsed again with deionized water, and hot-air dried. The film deposition was done by scanning the surface of the vacuum-chucked substrate with the sprayer in cycles. A proportional-integral-derivative (PID) controlled heater maintained the substrate temperature at 440, 460, 470, or 500 °C. Fig 1 presents a photograph of the SPEED system during deposition.
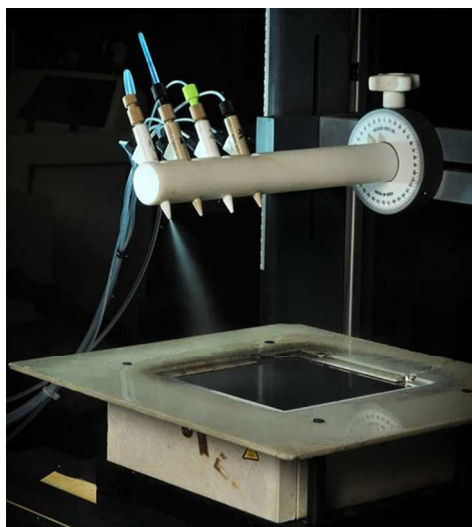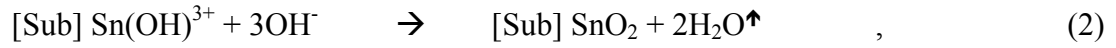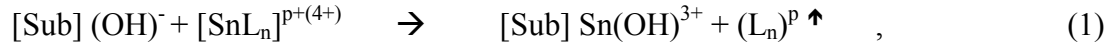

Figure 1 Photograph of SPEED spray head.

SPEED processes and chemistries, have their foundation in chemical bath deposition (CBD) [8-10] and they are designed to ensure film growth takes place via heterogeneous reaction
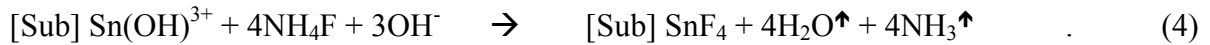
only.–A process requirement is a hydrophilic substrate that attaches OH⁻ ions, which serve as heterogeneous-reaction nucleation sites. The local electrical field created by the adsorbed OH⁻ to the substrate attracts the positively charged complex to initiate the electrochemical reaction process without an external electrical field, which eliminates the need for electrodes. Similar to what we have in CBD [9], the reactions that summarize the film growth are:

$$[\text{Sub}]\,(\text{OH})^- + [\text{SnL}_n]^{p+(4+)} \quad \rightarrow \quad [\text{Sub}]\,\text{Sn(OH)}^{3+} + (\text{L}_n)^p \uparrow \quad , \tag{1}$$

$$[\text{Sub}]\,\text{Sn(OH)}^{3+} + 3\text{OH}^- \quad \rightarrow \quad [\text{Sub}]\,\text{SnO}_2 + 2\text{H}_2\text{O} \uparrow \quad , \tag{2}$$

where L is the ligand supplied by the organic solvents, [Sub] is the heated substrate, p is the charge of the ligand L, and n is the number of ligands involved in the Sn/L coordination. The upward arrows signify reaction byproducts that are decomposed and volatilized. The substrate kT must exceed the heterogeneous reaction activation energy and be sufficient to decompose and volatilize the reaction byproducts. Formation of attached SnO_2 in Eq. (2) is followed by site regeneration according to

$$[\text{Sub}]\,\text{SnO}_2 + \text{OH}^- \rightarrow [\text{Sub}]\,\text{SnO}_2(\text{OH})^- \tag{3}$$

The attachment of fresh OH⁻ from a freshly sprayed precursor initiates the next growth cycle, which continues thus layer-by-layer. The high concentration of OH⁻ nucleation sites causes lateral grain growth competition, leading to nanoparticle morphology of the resulting film. The fluorine doping reaction is

$$[\text{Sub}]\,\text{Sn(OH)}^{3+} + 4\text{NH}_4\text{F} + 3\text{OH}^- \quad \rightarrow \quad [\text{Sub}]\,\text{SnF}_4 + 4\text{H}_2\text{O} \uparrow + 4\text{NH}_3 \uparrow \quad . \tag{4}$$

Growth of SnF_4 molecules occur randomly during growth. F on the O lattice site is a donor. Oxygen vacancies occur via adsorption of the tin complex $[\text{SnL}_n]^{p+(4+)}$ according to

$$[\text{Sub}]\,[\text{SnL}_n]^{p+(4+)} + m\text{OH}^- \quad \rightarrow \quad [\text{Sub}]\,\text{Sn} + m(\text{OHL}_n) \uparrow \tag{5}$$
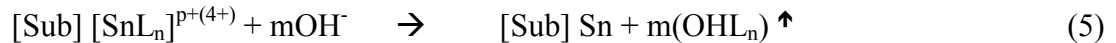
With solvent ligands, the adsorbed complex undergoes hydroxyl-ion-assisted reduction to form attached Sn [12], which paired with the oxygen vacancy acts as an donor [6].

X-ray diffraction (XRD, Panalytical Empyrean) system in asymmetric out-of-plane geometry (with 30 kV, 40 mA, Cu K_α radiation at $\lambda = 0.1540598$ nm) characterized the fabricated films for 2θ values from 20 to 80 degrees with incidence angle $\alpha = 15$ deg with respect to the substrate plane. Scanning electron microscopy (SEM, Zeiss Ultra 55) characterized morphology. A spectrophotometer (Perkin-Elmer Lambda 900) collected transmittance T from 200 to 1000 nm wavelength with Al_2O_3-coated borofloat glass as reference. Absorption coefficient was calculated according to Beer's law, $\alpha = (1/d)\ln(1/T)$, with film thickness d from cross-sectional SEM. The optical bandgap of the material was deduced from the absorption spectrum. Resistivity, mobility, and carrier concentration were evaluated by Hall measurements (MMR technologies) at room temperature in a Van der Pauw four-point probe configuration using indium contacts and a magnetic induction of 0.65 T.

RESULTS

Transparent and conductive films were grown only when the substrate was at least 400 °C, where the heterogeneous reaction for SnO_2 is activated, and the reaction byproducts are decomposed and volatilized. Most depositions occurred at 440 to 500 °C, where grown films appear uniform and shiny and adhere strongly. These films are scratch resistant due to the heterogeneous film growth mechanisms and high crystallinity, since higher cohesive strength is associated with smaller free volume [13, 14]. Films grown on quartz have lower resistance than films grown on borofloat glass. Substrate interactions, such as the compensating in-diffusion of B, were blocked by pre-coating borofloat glass with Al_2O_3 by SPEED, creating an impurity diffusion barrier.

Fig. 2 (a) presents an SEM micrograph of a film grown at 460 °C, revealing dense nanostructure devoid of cracks and voids. Grains for all samples have about 100 nm lateral dimensions. Fig. 2 (b) presents a cross-sectional SEM image, where both Al_2O_3 and SnO_2:F layers are evident with thicknesses 150 and 250 nm, respectively.
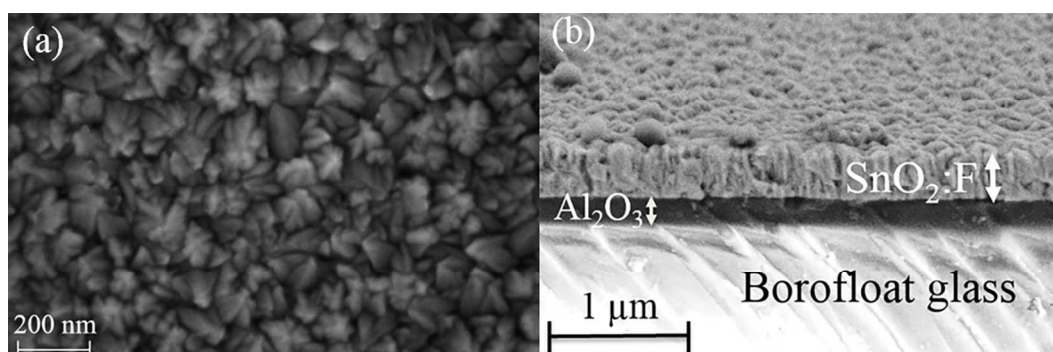

Figure 2. (a) SEM micrograph of the FTO film grown at 460 °C, (b) SEM cross section of FTO film.

Fig. 3 presents XRD with reflections from (110), (200), (211), (310) and (301) planes of tetragonal SnO_2 [13]. No peaks of any other crystal or phase are observed.
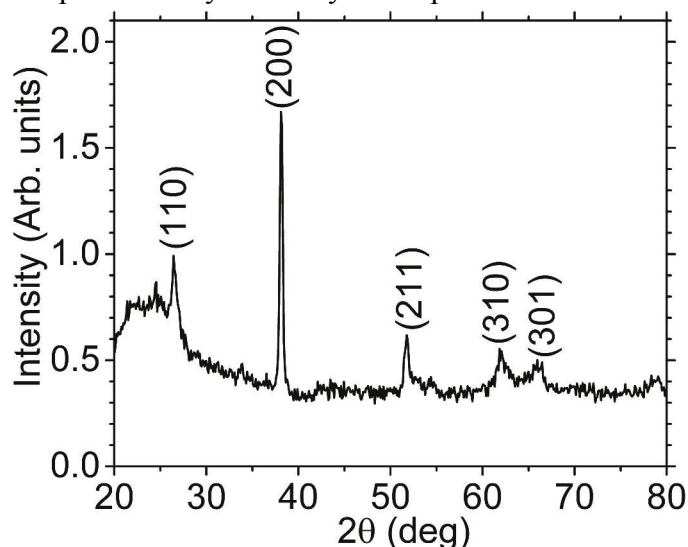

Figure 3. XRD of FTO film grown by SISOM's SPEED technique at 460 °C.

Fig. 4 (a) presents an unpolarized, normal-incidence transmittance spectrum collected for a typical film. The film microstructure (Fig. 2 (a)) is smaller than the incident wavelength, so little scattering is expected. FTO film exhibits average transmittance of 93% in the visible, and there is a sharp short-wavelength cut-off due to fundamental absorption [15]. These attributes agree well with the earlier reports for FTO [14-16].

The absorption coefficient α is related to the incident photon energy by

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \qquad (6)$$

where C is a constant characteristic of the medium, E_g is the direct bandgap energy, and hν is the photon energy [17]. By plotting $(\alpha h\nu)^2$ vs hν and extrapolating the linear portion to zero, we obtain the bandgap, as shown in Fig. 4 (b). The bandgap values of all films are around 4.0 eV. This value is in agreement with previous reports that the bandgap of FTO is in the range 3.9 - 4.6 eV [6]. The bandgaps of Al_2O_3 and the glass substrate are significantly larger, so that they do not contribute to the absorption in Fig. 4 (a).
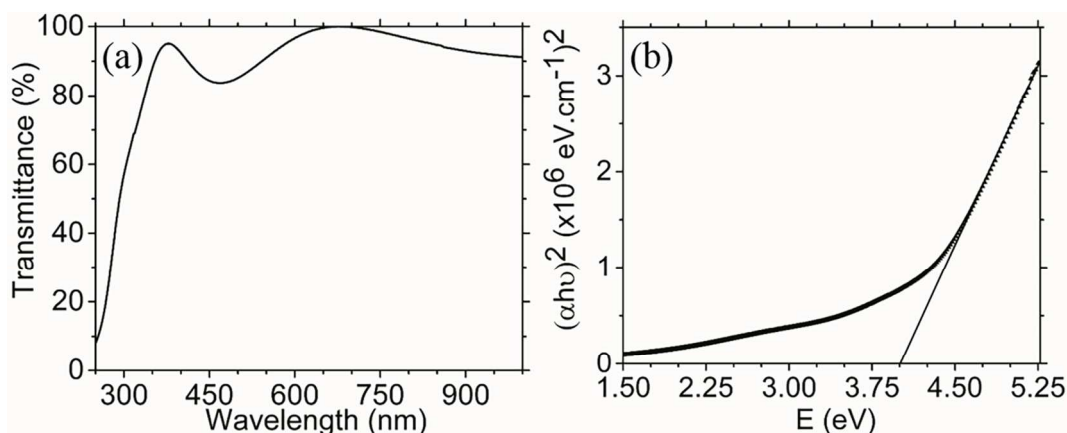

Figure 4. (a) Transmission spectrum of typical SPEED-grown SnO_2:F film on Al_2O_3 coated glass, (b) Plot of $(\alpha h\nu)^2$ as a function of photon energy (hν) used to estimate the optical bandgap of SPEED-grown FTO thin-film.

The Hall coefficients are negative for all films, confirming their n-type conductivity. The best results achieved for the 250 nm thick film are an electrical resistivity of 6×10^{-4} Ω-cm, Hall mobility 8.3 cm^2/V-s, and carrier concentration 1×10^{21} cm^{-3}.

Haacke's figure of merit [18] for the photovoltaic application of transparent conducting films is $\varphi = T^{10}/R_s$, where T is the transmittance in the visible range and R_s is the sheet resistance. FTO film grown by SPEED at 460 $^\circ$C has a sheet resistance of 21 Ω/sq with average transmittance of 93% in the visible range, which leads to $\varphi = 0.023$ S. This is comparable to numbers reported for FTO films fabricated by spray pyrolysis [6, 18]. The value 0.071 obtained for the sputtered TCO Cd_2SnO_4 is one of the highest known [18], and experimental FTO films grown by CVD have reached that value [6]. However, most commercial ITO and FTO coated glasses have values in the range 0.0009 to 0.020, and our FTO film is superior to these. The spray-pyrolysis-grown FTO sample with the same thickness as ours of Ref. [6] had the lower value 0.018, since our sample has higher transmittance and comparable sheet resistance relative to that sample.

CONCLUSIONS

SPEED has yielded high performing TCO films and has numerous practical advantages over other electrodeposition and self-assembly techniques for fabricating inorganic thin films. In contrast to SPEED, usual electrodeposition techniques require electrical contact to the substrate, have poor control over current distribution that practically limits substrate size, and are usually limited to single-element material deposition. Spray pyrolysis usually requires organic solvents and temperatures above 400 ^{o}C and gives high impurity levels that lead to films with porosity and cracks.

In contrast, SPEED uses water as solvent and carefully selected simple ligands which allow impurity free films to grow at substrate temperatures in the range 100-500 ^{o}C, and which effectively give reaction byproducts that are readily volatilized or washed away with no residue left behind. Spin-coating results in films with very high level of impurities, which are difficult to get rid of in post-spin bake, cure, and sintering; and it cannot be scaled to very large substrates. Traditional chemical bath deposition, on the other hand, is a slow process and it has high and wasteful homogenous reaction, which limits achievable thickness; moreover it can only be used in growing a very limited number of inorganic compound films.

Low-cost SnO_2: F (FTO) thin films were successfully grown using SPEED technique. All films have high transmittance with average of about 93% beyond 350 nm wavelength, which is good for transmitting the solar spectrum. The FTO films are also highly crystalline and adhere strongly to the substrate. The direct bandgap was spectroscopically determined to be 4.0 eV. Excellent electrical properties, including resistivity of 6×10^{-4} (Ω-cm) and Hall mobility of 8.3 (cm^2/V-s) were measured. FTO is already known to be stable under a wide range of chemical treatments and thermal stress, which makes it attractive for solar cells and sensors.

ACKNOWLEDGMENTS

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