Electrical and optical properties of tin oxide-based thin-films prepared by streaming process for electrodeless electrochemical deposition (SPEED)

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Introduction
- Transparent conducting oxides (TCOs) are wide-bandgap semiconductors with relatively high free electron concentration and are increasingly used in photovoltaic (PV) devices and as electrodes, structural templates, and diffusion barriers.
- Among TCOs, indium tin oxide (ITO) is most widely used but because of scarcity of In and its high price, there is high demand to replace it with a similar but less expensive TCO.
- Fluorine-doped tin oxide (FTO) is a promising candidate due to its chemical stability, electrical conductivity, optical transparency, and thermal stability.

Experimental
- Main precursors are: tin IV chloride (the Sn source) and ammonium fluoride (the F source).
- A reservoir of reagent solution is maintained at a temperature sufficiently low to inhibit homogeneous reactions.
- The solution was nebulized into droplets by an ICP/MS nozzle, which produces droplets in the size range 5 - 15 μm, as these droplets were sprayed onto the heated substrate.

Thin-film deposition by SPEED
SnO2:F is deposited by SISOM’s proprietary SPEED deposition method on borofloat glass:

- The fluorine doping reaction is:
  \[ \text{[Sub]} \text{Sn(OH)}_{3}^{2+} + 4\text{NH}_4\text{F} + 3\text{OH} \rightarrow \text{[Sub]} \text{SnF}_4 + 4\text{H}_2\text{O} + 4\text{NH}_3 \]
- Growth of SnF4 molecules occurs randomly during film deposition and increase the conductivity of the SnO2 film, because F acts as an electron donor when it occupies the O lattice site.
- Oxygen vacancies are formed by the direct adsorption of the tin complex, [SnLn]p+(4+) onto the heated substrate, according to:
  \[ \text{[Sub]}\text{[SnLn]}^{p+(4+)} + m\text{OH} \rightarrow \text{[Sub]} \text{Sn} + m\text{(OHL)} \]
- The Sn on the SnO2 lattice without the corresponding oxygen leads to the oxygen vacancy. The Sn/oxygen-vacancy pair acts as an electron donor that further increases the film conductivity. This method of doping has been reported to be less effective than that based on F impurities.

X-ray diffraction (XRD)
XRD 2-theta measurement for a FTO film, where reflections from (110), (200), (211), (310) and (301) planes of tetragonal SnO2 are observed. No peaks of any other crystal or phase are observed.

Hall measurements
- 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 $6 \times 10^4$ Ω·cm, Hall mobility 8.3 cm²/V·s, and carrier concentration $1 \times 10^{21}$ cm⁻³.
- FTO film grown by SPEED method at 460 °C has a sheet resistance of 21 Ω/sq with average transmittance of 93% in the visible range, which leads to very good Haacke’s Figure of merit, $\Phi = 0.023$.
- Most commercial ITO and FTO coated glasses have values in the range 0.009 to 0.020, and our FTO film is superior to these.

FTO morphology: Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

- The SEM image reveals a dense nanostructure apparently devoid of cracks and voids. Grains of all FTO samples have about 100 nm lateral dimensions.

Optical transmission and bandgap
- An unpolarized, normal-incidence transmittance spectrum collected at room temperature for a typical SPEED-grown FTO film in the wavelength range 250 to 1000 nm.
- FTO film exhibits average transmittance of 93% in the visible range.

- By plotting $(\alpha h \nu)^2$ vs hν and extrapolating the linear portion to zero, the bandgap can be estimated to be 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.

Conclusion
- Low-cost SnO2:F (FTO) thin films were successfully grown using SPEED technique. All FTO samples deposited have shown high transmittance with average of about 93% beyond 350 nm wavelength, which is good for transmitting the solar spectrum.
- SPEED deposited FTO films also possess excellent structural properties and adhesion to the substrate surface. FTO is already known to be stable under a wide range of chemical treatments and thermal stress, which makes them desirable in solar cell and sensing applications.
- The direct bandgap was spectroscopically determined to be 4.0 eV. Excellent electrical properties, including resistivity of $6 \times 10^4$ (Ω·cm) and Hall mobility of 8.3 (cm²/V·s) and Haacke’s figure of merit of 0.023 were found for the best sample. These characteristics are comparable to other TCO candidates for replacing ITO.