Low Temperature Atomic Layer Deposition of Tin Dioxide, SnO$_2$

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Outline

Earth-abundant, non-toxic transparent conductor: SnO$_2$

ALD process for SnO$_2$
- new tin precursor
- growth per cycle

SnO$_2$ film properties
- composition
- structure
- optical properties
- electrical properties
- applications

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SnO₂: Transparent Conductor and Heat Mirror

High visible transmission (high bandgap \((E_g \sim 4.1 \text{ eV})\)

High electrical conductivity (high electron concentration and mobility)

High environmental stability

Constituent elements are non-toxic and abundant

Known ALD processes require high temperatures, > 200 °C

or produce impure films (C, N), amorphous, low conductivity
Tin(II) Cyclic Stannylene as ALD Precursor

\[
\text{t-Bu} \quad \text{N} \quad \text{N} \quad \text{t-Bu} \quad \text{Sn}
\]

N\textsuperscript{2},N\textsuperscript{3}-di-tert-butyl-butane-2,3-diamido-tin(II)

Hydrocarbon ligand \rightarrow high volatility (30 Torr at 60 °C)

Chelate structure \rightarrow thermal stability

Sn-N bonds \rightarrow reactive to hydrogen peroxide, H\textsubscript{2}O\textsubscript{2}

Synthesis and properties described by Adam Hock, Wednesday 14:15
ALD Process for SnO$_2$

Source temperature: 40 °C
Substrate temperature: 120 °C
Growth per cycle: 0.18 nm
Induction period: only a few cycles
ALD Saturation Curves

Increasing doses of cyclic stannylene precursor for tin

Increasing doses of oxygen precursor, hydrogen peroxide

Refractive index ~ 1.94 for saturated growth (3 doses)

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Temperature Dependence of Growth

ALD window from 50 to 150 °C
SnO$_x$ Composition

Rutherford Backscattering Spectroscopy (RBS)

No C or N in film

SnO$_2$ for 2-3 doses
X-Ray Photo-Electron Spectroscopy (XPS)

No impurities detected (C, N) inside film
Smooth Morphology of SnO$_2$ Films

400 cycles => 71 nm

AFM
RMS roughness = 2 nm
< 3 % of thickness

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Step Coverage

Uniform thickness in holes with aspect ratio 50:1, grown at 50 °C
Polycrystalline Rutile Structure of SnO$_2$ Films

TEM

Si

SnO$_2$

5 nm

X-Ray Diffraction (XRD)

Intensity (arb. unit)

2Theta($^\circ$)

20 25 30 35 40 45 50 55 60

(101) (200) (211) (302)

(110) (101) (200) (301)

electron diffraction

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SnO$_2$ has Very Little Visible Absorption

Film 100 nm thick

Band gap 4.13 eV
Electrical Properties

Resistivity minimum for stoichiometric SnO₂ (2 to 4 doses)

N-type semiconductor by Hall measurements

- electron concentration ~ $10^{20}$ cm⁻³
- electron mobility ~ 6 cm² V⁻¹ s⁻¹

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Resistivity vs. Deposition Temperature

minimum resistivity 0.02 Ω-cm when deposited at 120 °C
Proposed Mechanism

Ligand exchange of Sn precursor with hydroxylated surface

Oxidative addition of hydrogen peroxide
Summary

SnO$_2$ is transparent semiconductor made of earth-abundant, inexpensive, non-toxic elements

ALD from a cyclic tin(II) amide and H$_2$O$_2$ $\Rightarrow$ SnO$_2$

Smooth films of pure, stoichiometric, polycrystalline SnO$_2$

High optical transparency and electrical conductivity

Successfully used in several applications:
  organic solar cells (with Alan Heeger, UCSB)
  conducting and protective coatings for plastics
    (with Michelle Schulberg, Physical Sciences Inc.)
  electron multipliers (Philippe deRouffignac, Arradiance, to be presented on Wednesday at 13:30)

another possible application: thin-film transistors on plastic
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