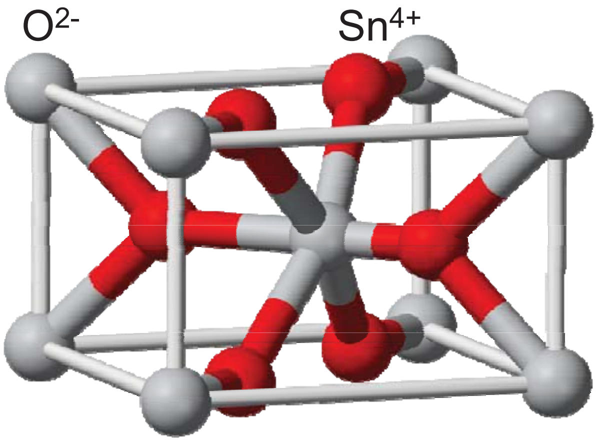
(Sn,Al)O_x Films Grown by Atomic Layer Deposition

June 29th 2011

Jaeyeong Heo, Yiqun Liu, Prasert Sinsermsuksakul, Zhefeng Li,
Leizhi Sun, Wontae Noh, and Roy G. Gordon

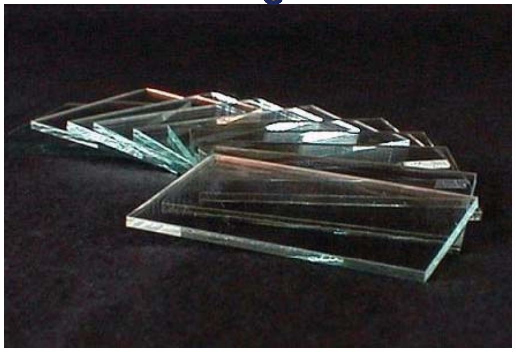
Harvard University, Cambridge, MA, USA

Transparent Conducting Oxide (TCO) -SnO_2

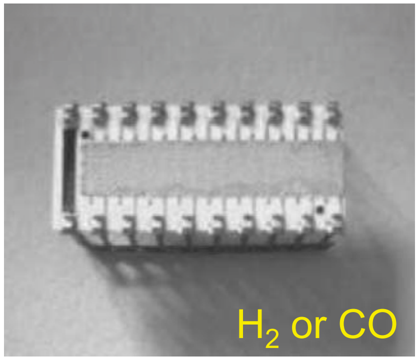


- Transparency and conductivity with high stability
- Crystal structure: Rutile (tetragonal)
- n-type semiconductor with E_g 3.6 eV

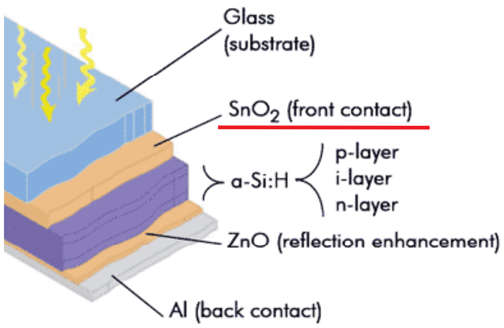
FTO-energy conserving window



Gas Sensors



Photovoltaics



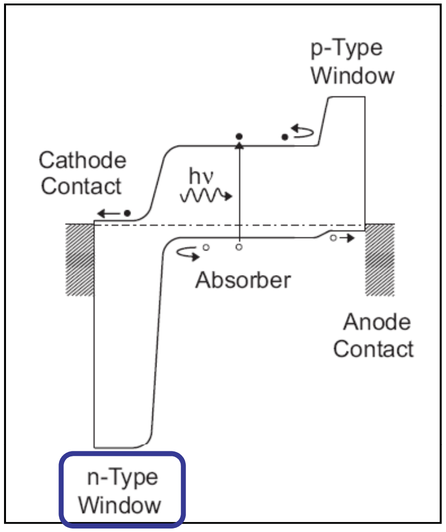
The Gordon Lab

Jaeyeong Heo

Higher resistivity oxide

(1) Hole blocking layer for solar cells

$10^{-2} \sim 10^{0}$ ohm·cm



(2) AOS TTFT for displays

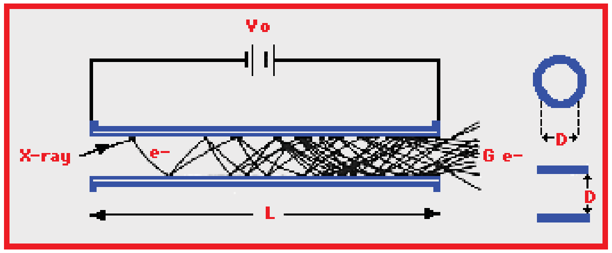
$10^{0} \sim 10^{6}$ ohm·cm

Device Structure	TOS(IGZO) TFT + AM-OLED (Top Emission)
Panel size	11.7-inch (297mm) diagonal
Mobility	11.5 cm^2/Vs
V_{th}	0.27V
S-factor	0.3V/dec
Resolution	960 RGB x 540
Brightness	600 cd/m^2
Contrast	> 1000000 : 1(Dark)
Number of colors	10 bit RGB
Color saturation	> 100% (NTSC)

SONY (SID 2010)

(3) Microchannel electron multiplier plates

$10^{6} \sim 10^{8}$ ohm·cm

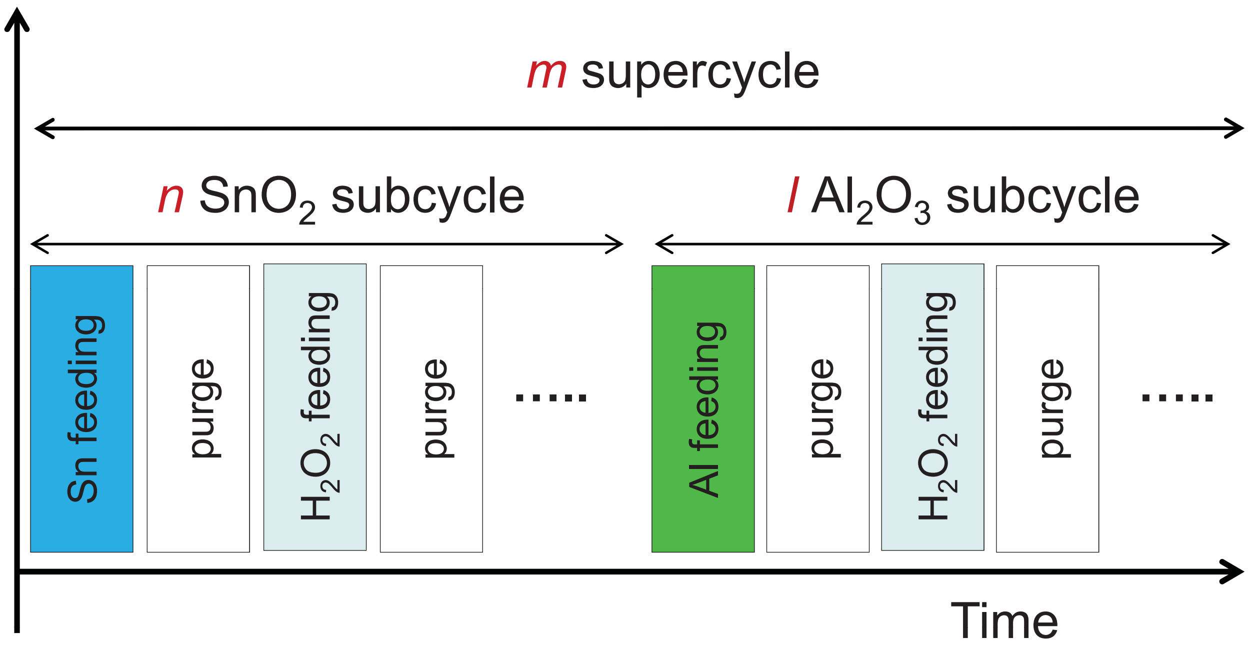


The possibility of controlling film's resistivity over a wide range

→ forming (Sn,Al)O_x composite materials by ALD

Chemisorption behaviors ⟷ Properties of materials

(Sn, Al)O_x supercycle



- exp. set -

m (n, l)
300(1,0) (SnO_2)
3(99,1)
12(24,1)
30(9,1)
33(8,1)
38(7,1)
75(3,1)
60(3,2)
60(2,3)
400(0,1) (Al_2O_3)

t: ~40-50 nm

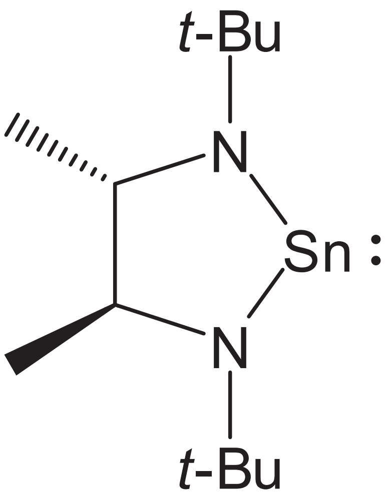
- Temperature: 120 °C
- Sn precursor: CAT(II)
- Al precursor: TMA
- Oxidant: 50 wt.% H_2O_2
- Purge: 30-60s

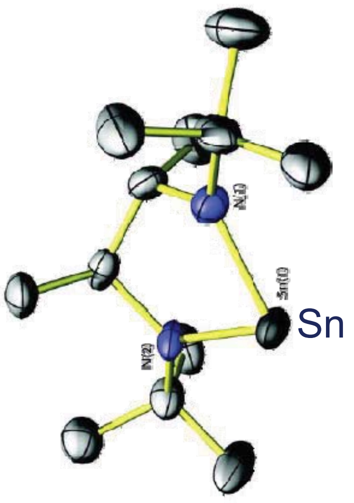
Notation: m(n,l)

ex. 30(9,1): 30 × supercycles [$9 \times SnO_2 + 1 \times Al_2O_3$]

Jaeyeong Heo

Cyclic amide tin (II)

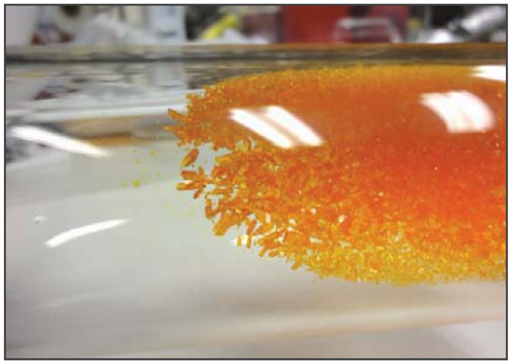


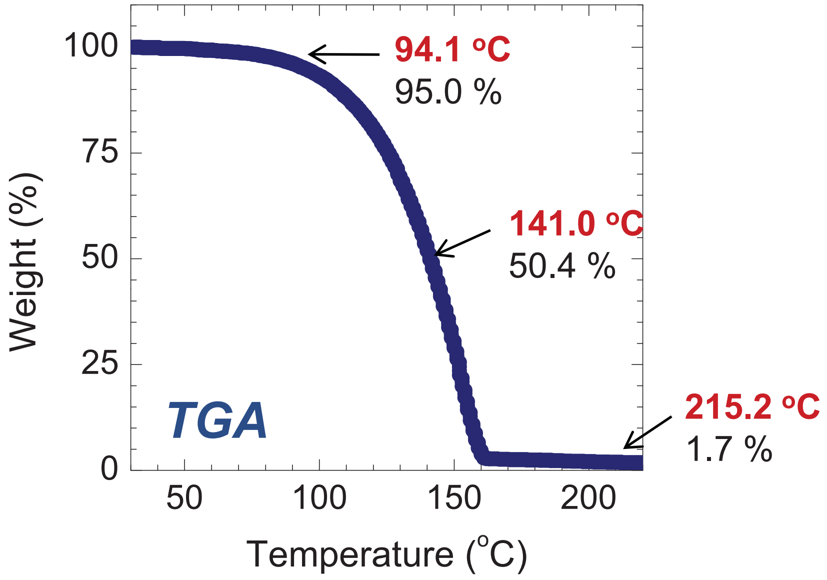


1,3-bis(1,1-dimethylethyl)-4,5-dimethyl-(4R,5R)-1,3,2-diazastannolidin-2-ylidene
(CAS # 1268357-44-3)

- Sn-N distance is 2.02 Å
- N-Sn-N angle is 82.7 °
- Planar five-member ring

Picture



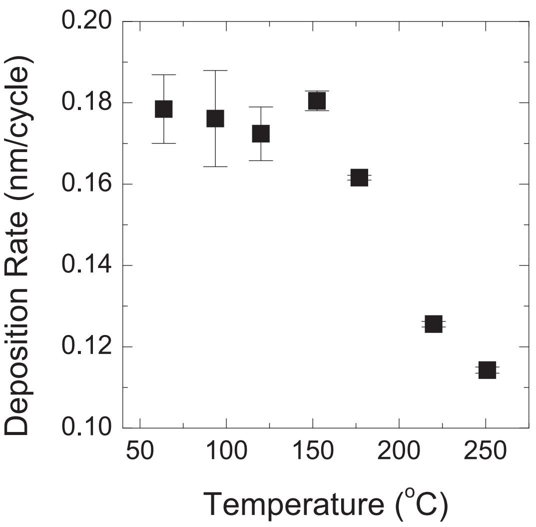


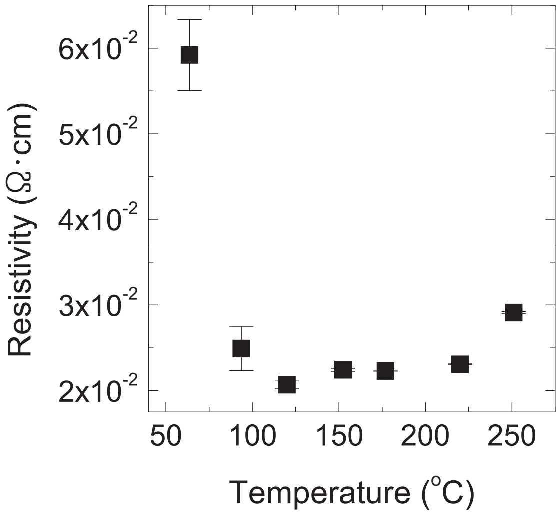
- Clean evaporation w/o residue
- Vapor pressure: 0.42 Torr @40°C

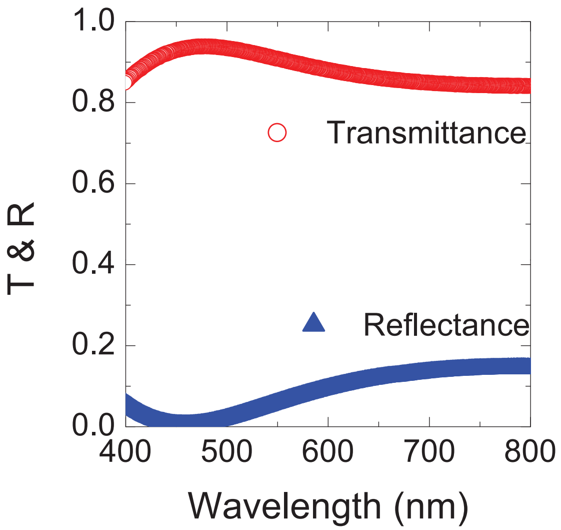
**Dr. Adam S. Hock & Dr. Sang Bok Kim*

Jaeyeong Heo

ALD SnO_2 results







- G/R: 0.175 nm/cycle @ 50°C
- Resistivity: 2×10^{-2} ohm·cm
- Mobility: 7 $cm^2/V \cdot s$
- C.C: ~10^{20} #/cm^3
- Transmittance: 87.8%
- No C and N impurities

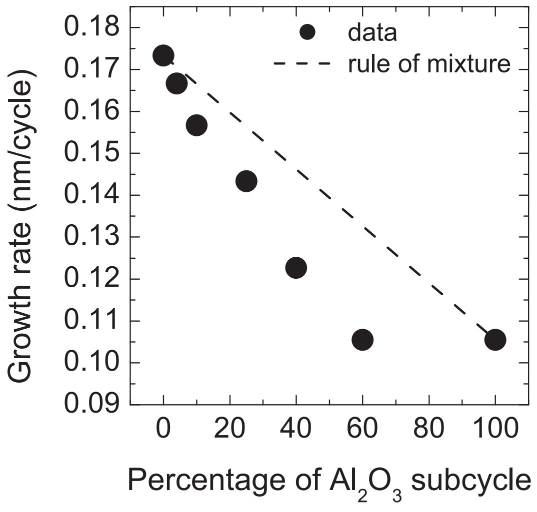
J. Heo *et al*. *Chem. Mater.* **22**, 4964 (2010).

The Gordon Lab

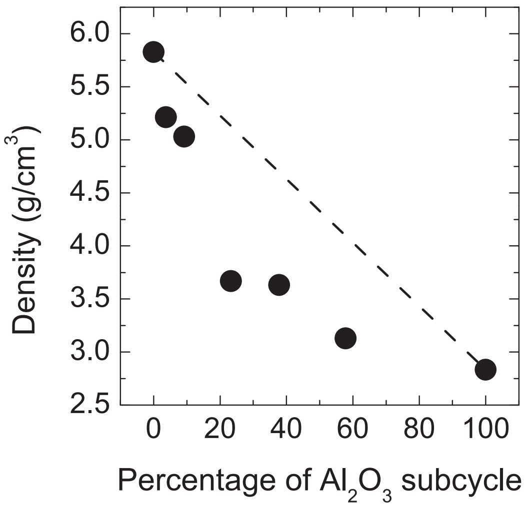
Jaeyeong Heo

Basic composite films' properties

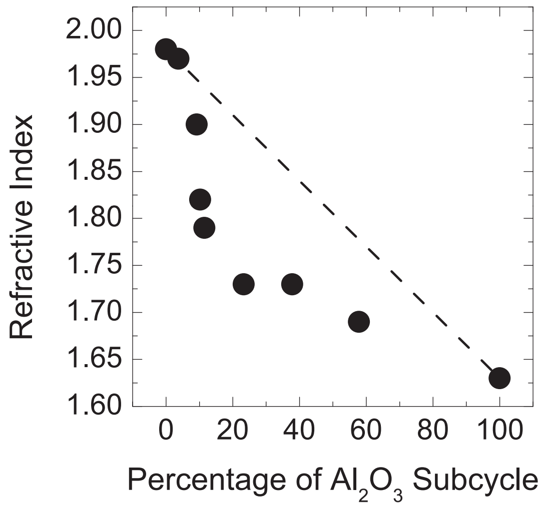
Growth rate



Density



Refractive index



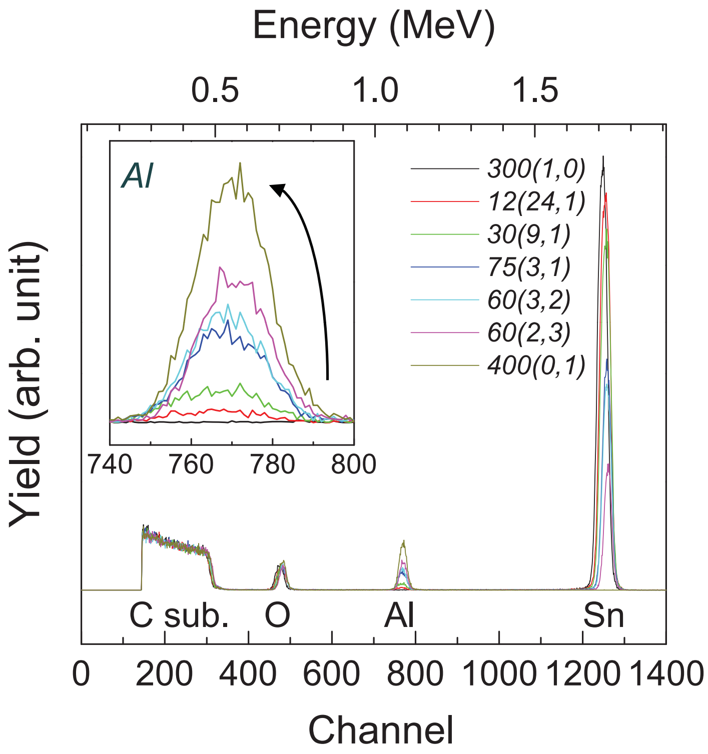
- G/R, film density, and refractive index deviates from the expected plot (rule of mixture)
- Percentage of Al_2O_3 subcycle ~20% → *~50 at.% Al*

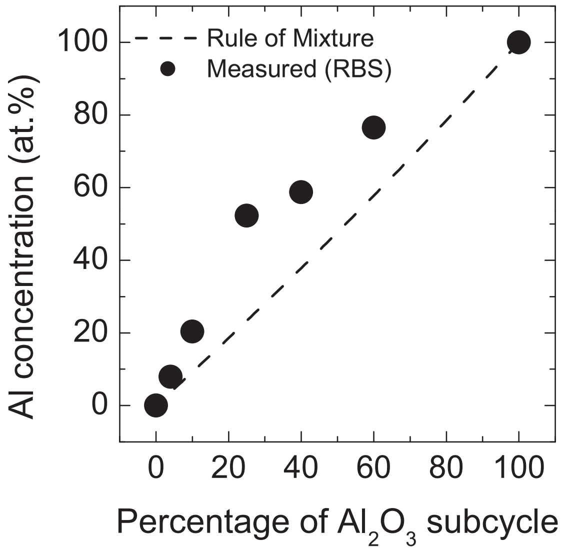
J. Heo et al. *J. Phys. Chem. C* **115**, 10277 (2011).

The Gordon Lab

Jaeyeong Heo

Composition analysis $(Sn,Al)O_x$ - RBS





Rule of Mixture

$$\text{Al content } (\%) = \left[\frac{\rho_{\text{Al}} \times \%\,\text{Al}_2\text{O}_3}{(\rho_{\text{Al}} \times \%\,\text{Al}_2\text{O}_3 + \rho_{\text{Sn}}(100 - \%\,\text{Al}_2\text{O}_3)}\right] \times 100$$

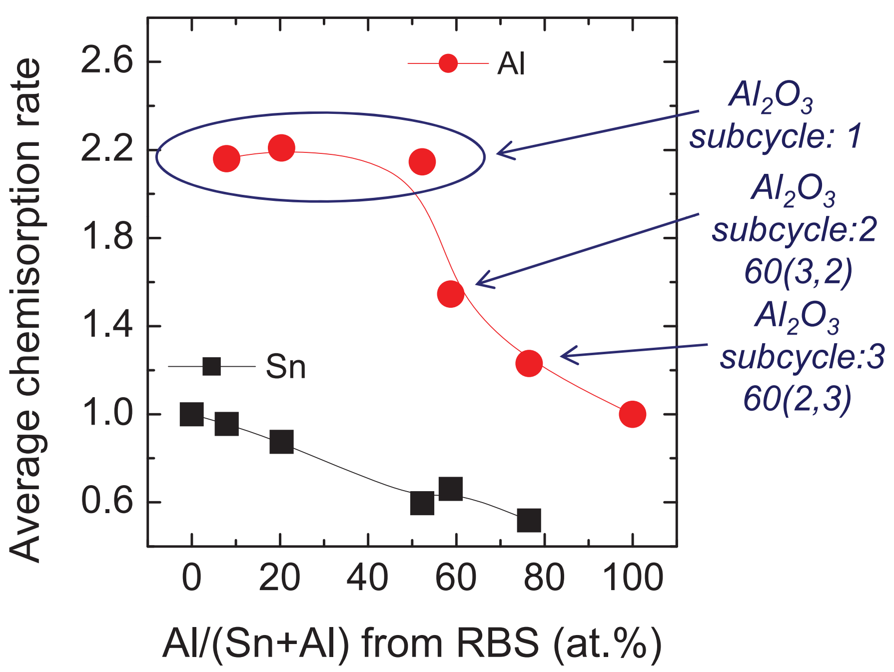
ρ: area density of cations per cycle, %( ): percentage of subcycle

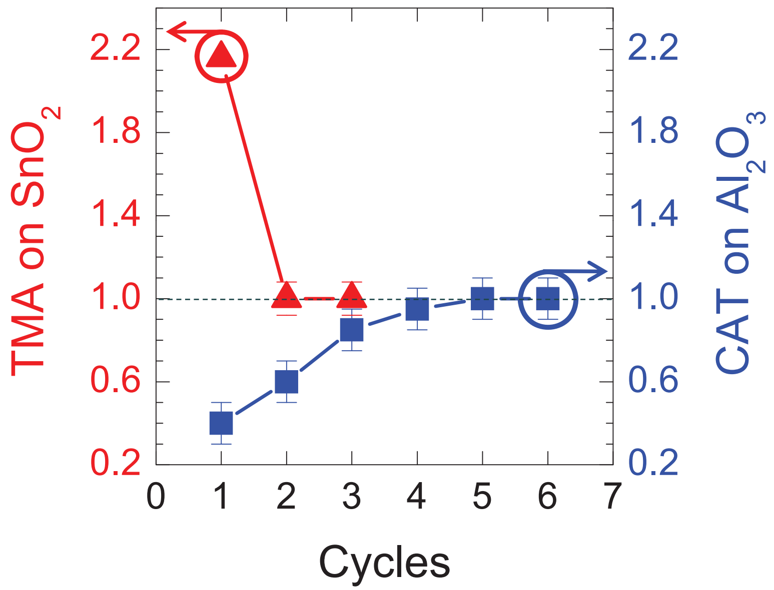
Higher Al concentration than expected over the entire range

The Gordon Lab

Jaeyeong Heo

Chemisorption analysis by RBS





1) TMA

- 1st: ~2.2 times enhancement on SnO_2
- 2nd: Return to its own chemisorption

2) CAT

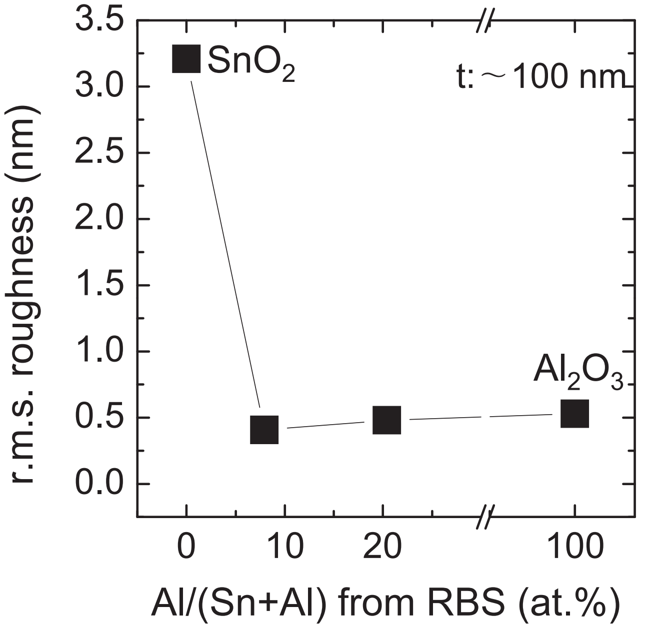
- ~5 cycles for full recovery

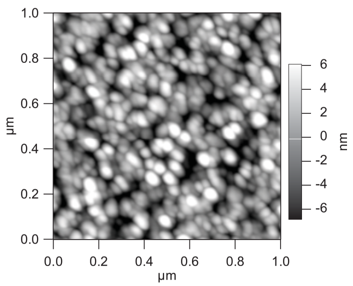
J. Heo et al. *J. Phys. Chem. C* **115**, 10277 (2011).

The Gordon Lab

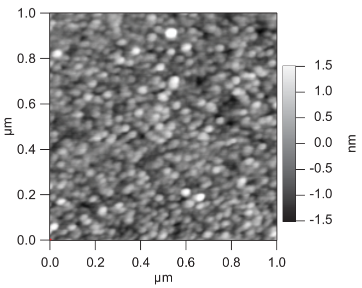
Jaeyeong Heo

What's happening? - TMA on SnO_2





SnO_2



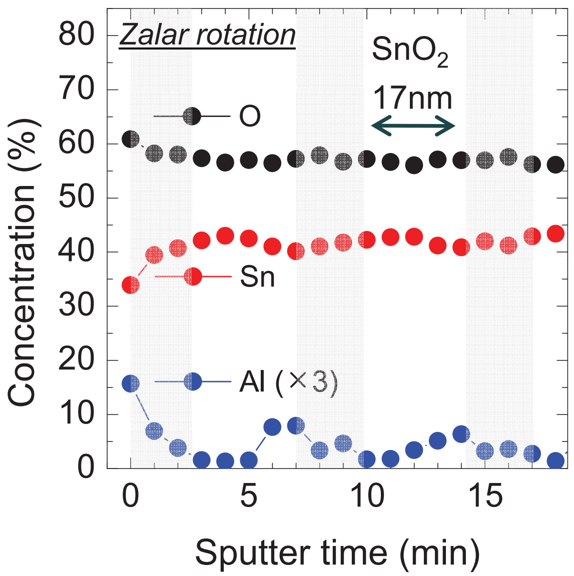
$(Sn,Al)O_x$
7.9% Al

1) Surface area: Smaller R_{rms}

2) # of –OH: SnO_2:33° Al_2O_3:47°

3) Monolayer diffusion of Al?

3(99,1) - ~2% Al

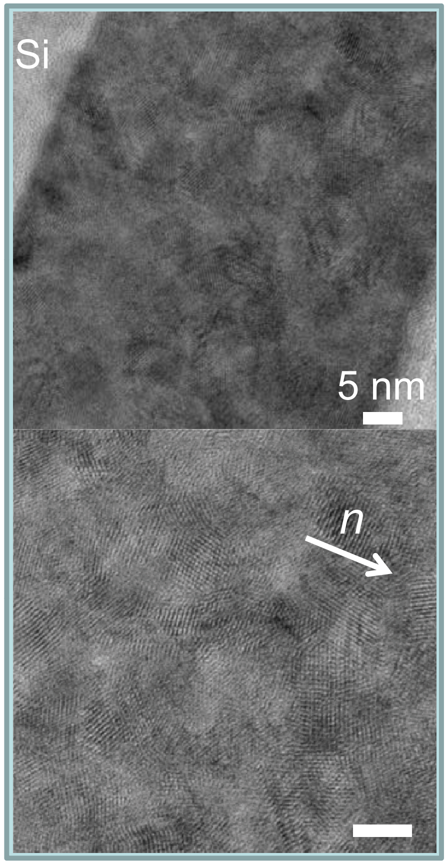


- Tailing → minor diffusion
- Nanolaminate Al distribution

Jaeyeong Heo

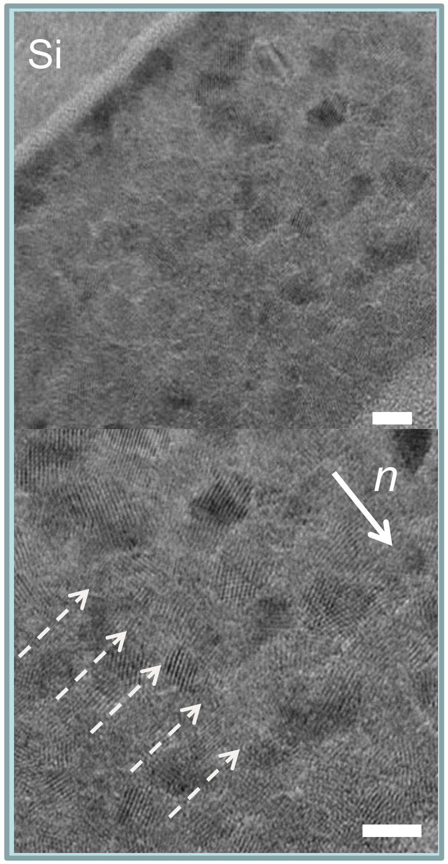
Microstructure of composite films

SnO_2



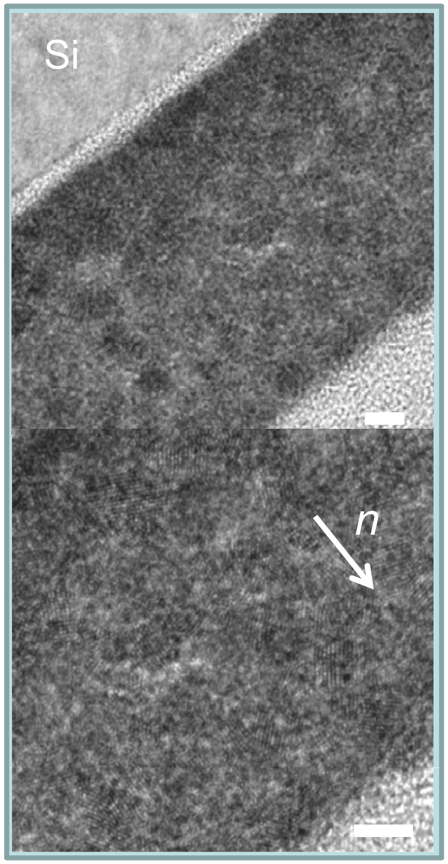
Polycrystalline

12(24,1) - **7.9% Al**



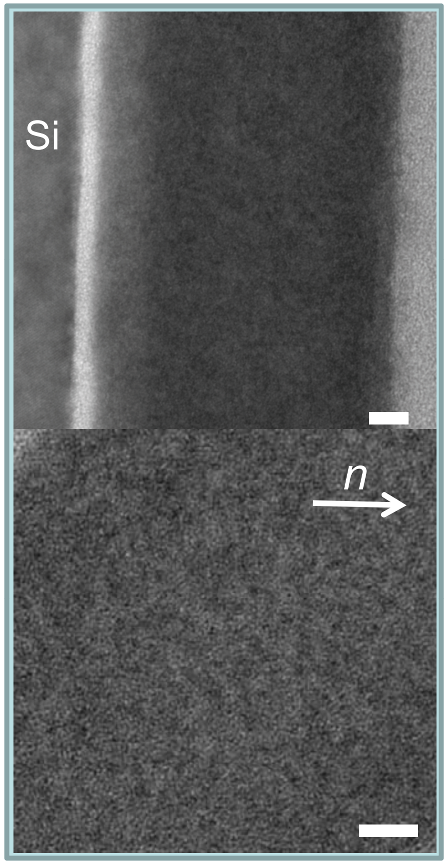
Polycrystalline
Nanolaminate

30(9,1) - **20.4% Al**



Less crystallized

75(3,1) - **52.3% Al**

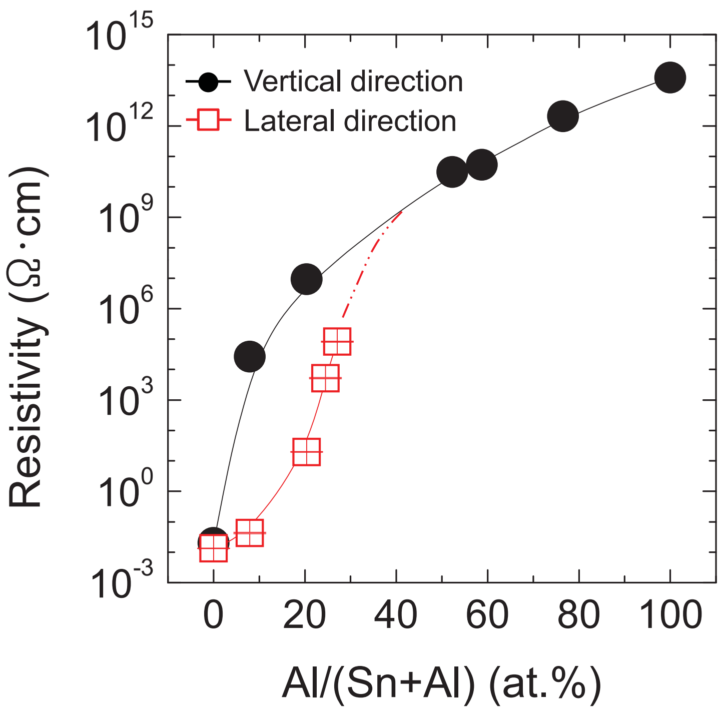


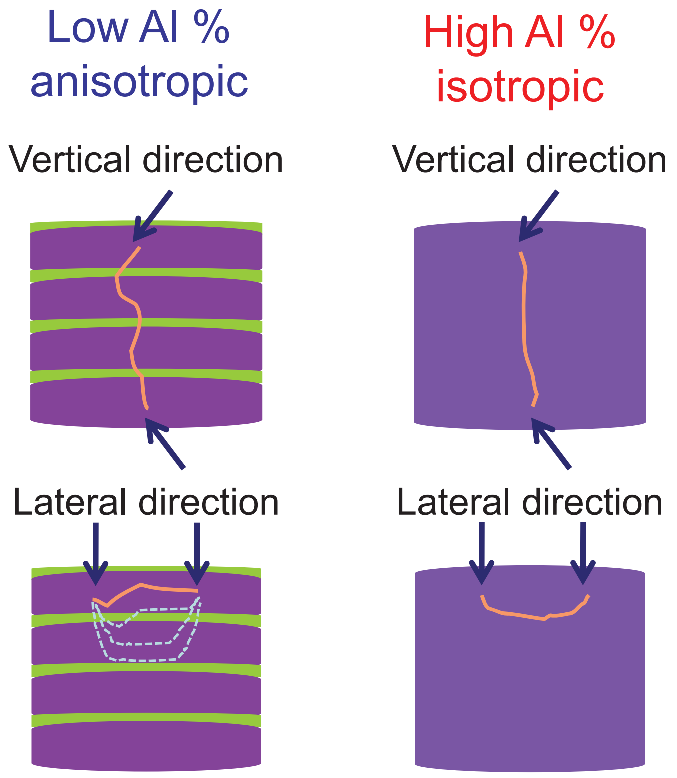
Amorphous

The Gordon Lab

Jaeyeong Heo

Electrical properties of composite films





- Electrical anisotropy
- Less Al: nanolaminate distribution of resistive Al_2O_3
- More Al: well mixed/ amorphous
- Resistivity change over 15 orders of magnitude

Jaeyeong Heo

Summary

Macroscopic properties of $(Sn,Al)O_x$ composite films were studied.

Chemisorption behaviors govern films’ microstructures and electrical properties.

Nanolaminated Al distribution for small Al concentrations.

Controlled adjustment of film’s electrical resistivity over more than 15 orders of magnitude was achieved.

Acknowledgements

(1)Camille and Henry Dreyfus Postdoctoral Program

(2)Air Force Office of Scientific Research (FA9550-09-C-0075)

(3) Center for Nanoscale Systems

(NSF award no. ECS-0335765)

- Group members
- Dr. Harish Bhandari
- Dr. Sang Bok Kim