Multilayer composite AZO / AGZO thin films for transparent conductive electrodes

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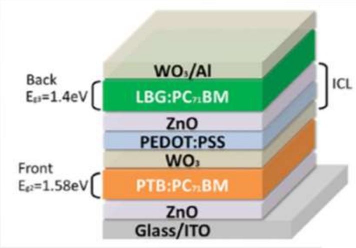
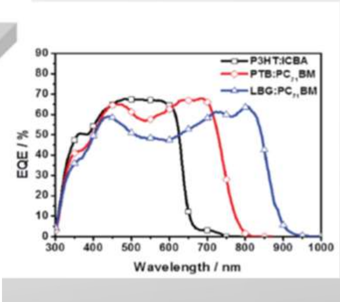
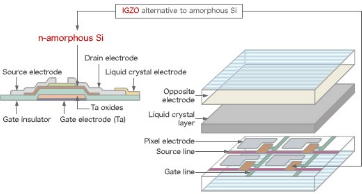
TRANSPARENT CONDUCTIVE OXIDES (TCOs)

- **Applications -**
  - flat panel displays, and touch screens, energy efficient windows
  - Photovoltaic cells (PVCs) – esp. thin film, multilayer PVCs
  - Transparent electronics for communications & computing (TFTs)
- **Challenges -**
  - Material criticality – scarce input materials (Indium Tin Oxide)
  - Process cost – physical deposition methods are slow and coating large areas accurately is expensive.
- **Research goals – TCO materials for Solar PV**
  - Minimise materials criticality issues – scarcity, cost, toxicity of input materials.
  - Use a low cost solution based process, while optimising TCO performance.

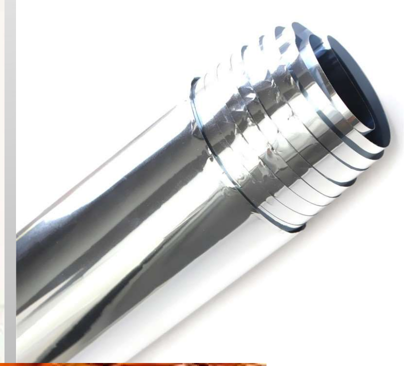






TRANSPARENCY AND CONDUCTIVITY RARELY COINCIDE

- **Transparency**
- In insulators like glass, light propagates by localised (bound) electrons.
- In a good conductor, free electrons ***absorb and reflect*** light
- Plasmons (free electrons oscillating en masse) cause reflection of light at energies below the resonance peak
  - Plasmon peak frequency $f_p \propto \sqrt{n_e}$ - so high carrier density makes metal reflect visible light (**e.g. in Gold $\boldsymbol{f_p}$ is in UV due to high $\boldsymbol{n_e}$**)
- **Electrical conductivity**
- Conductivity - carrier density and mobility $\sigma = n_e . e . \mu_e$
- n_e is increased by doping with extra-valent impurities (eg swapping a Zn^{2+} ion with an Al^{3+})
- Mobility depends on various scattering mechanisms related to defects, impurities, and other discontinuities in charge distribution.

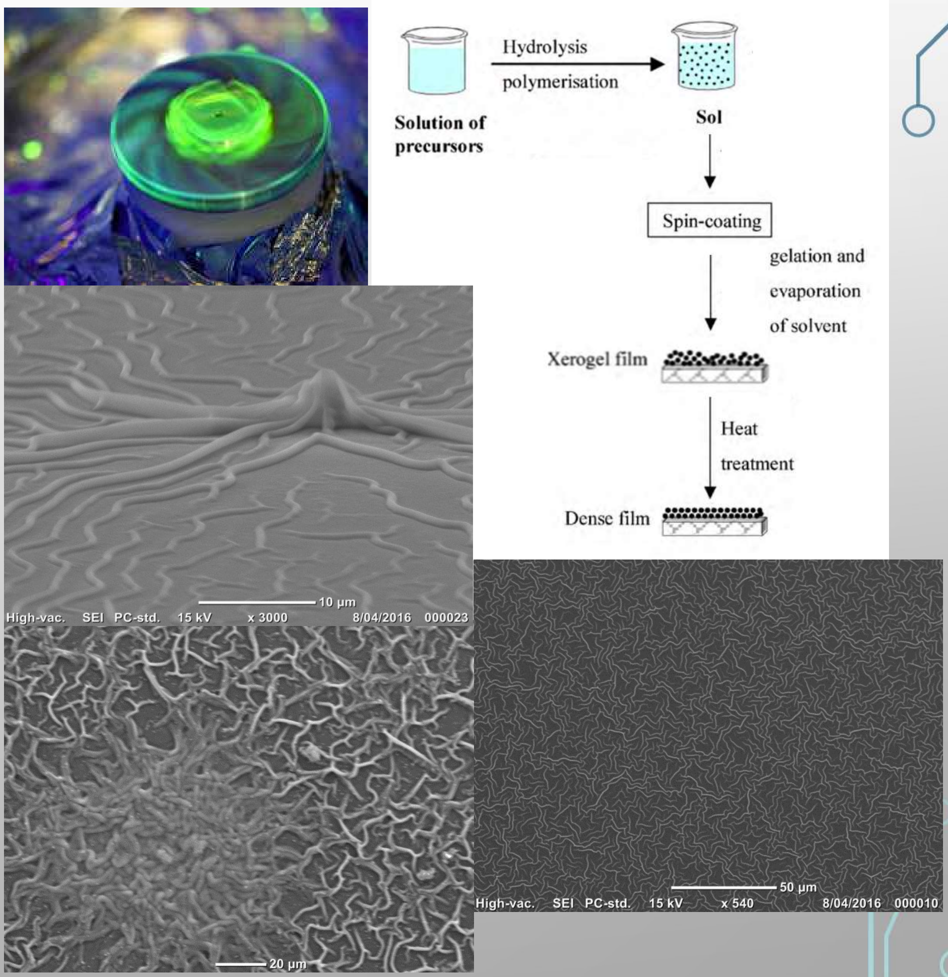


SOL-GEL / SPIN-COAT PROCESS

- Sol-gel process
  - Colloidal solution based coating process – low cost.
  - High disorder is inherent in the process – low conductivity.
  - Shrinkage and microstrain during drying and annealing.
  - Poor conductivity compared to physical deposition methods (e.g. Pulsed Laser , Magnetron Sputtering).

But large areas by physical deposition
is slow – costly, and consistency is difficult

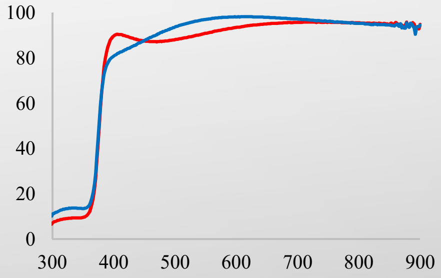
- Spin coating method
  - gelation occurs on spinning substrate
  - spin rates around 3000 rpm, 20-30 seconds
- Thermal annealing
  - Various temperatures / duration / ramp rates
  - Atmosphere – oxidising / inert / reducing

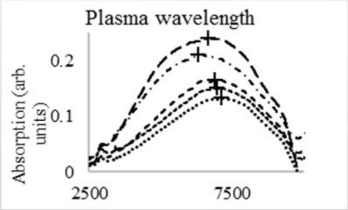


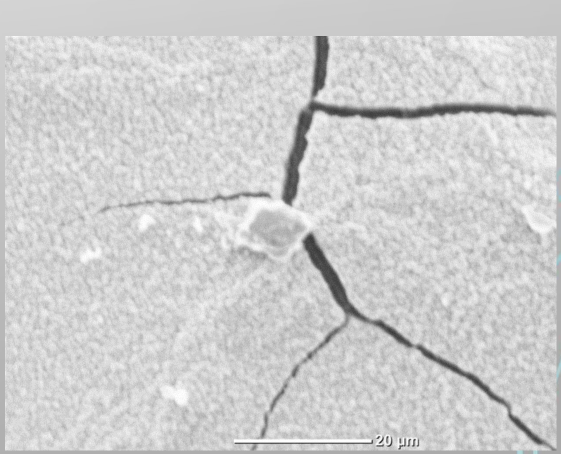
OPTICAL PROPERTIES

- **Transmission spectra – upper & lower bounds**
  - **IR edge** is bound by plasmon resonance absorption
    (λ_p = plasma wavelength $\approx$ IR absorption peak)
  - **UV edge** is bound by absorption due to electronic transitions
    - determined by the material's energy band structure - i.e. by the periodic charge distribution in the crystal lattice.
    - **Carrier density** also effects Band gap – **Burstein moss effect,** and band gap narrowing due to many body effects at high carrier density.
  - **In the visible range,** various defects in the film can result in scattering of light and degradation of transparency.
  - **Impurities and defects** can also generate extra electron states which are inside the host matrice's forbidden gap – these can result in absorption and tailing at the UV edge.

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0\varepsilon_\infty m^*}} \longrightarrow \lambda_p \propto \frac{1}{\sqrt{n_e}}$$

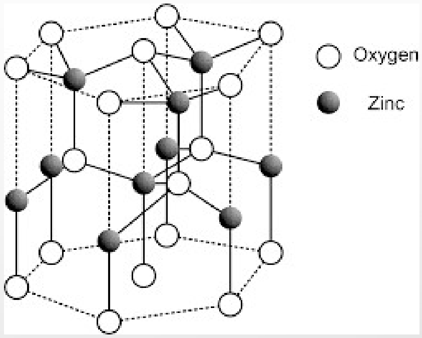




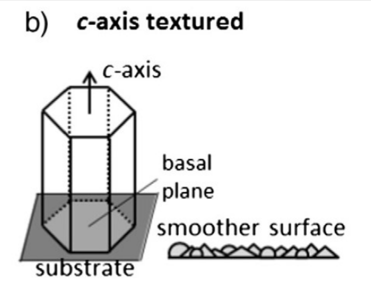


ELECTRICAL PROPERTIES

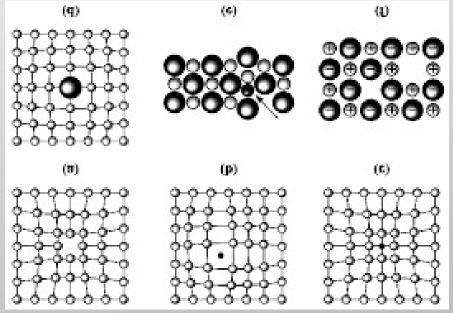
- **Carrier density (n_e)**
  - **Need $n_e \geq \sim 2.0x10^{19} cm^{-3}$** for metallic type conduction (below this density, hopping conduction dominates due to large separation between carriers).
  - **Need $n_e \leq \sim 5.4x10^{21} cm^{-3}$** plasma resonance impinges on the lower end of visible range. (Au: $n_e \sim 5x10^{22} cm^{-3}$)
  - Carriers from ionised dopant atoms, crystal defects, unintentional doping (N, H).
- **Carrier mobility (μ_e) –**
  - the absence of scattering from phonon (thermal) scattering, ionised impurities, point defects, dislocations, grain boundaries, internal and external surface scattering.

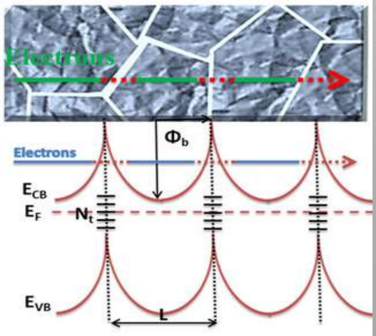


Stashans 2011



Fanni 2013





Bikowski & Ellmer 2014

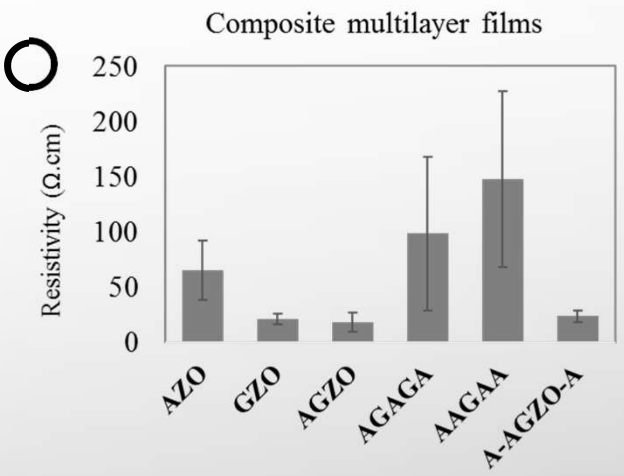
ZnO BASED TCOs – AZO, GZO, AGZO

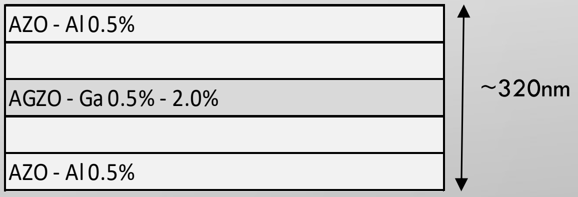
Investigate ZnO with Al and/or Ga doping.

1. **Multilayer films**

AZO, GZO, AGZO, AGAGA, AAGAA, A-AGZO-A

- A-AGZO-A similar performance to AGZO, with less Ga




AZO - Al 0.5%

AGZO - Ga 0.5% - 2.0%

AZO - Al 0.5%

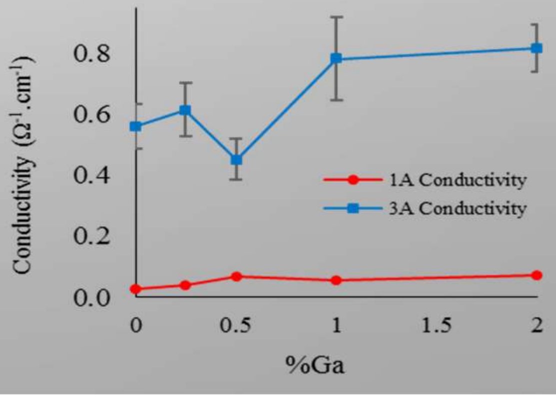
~320nm

2. **A-AGZO-A – variable Ga** content 0 - 2%

- investigate optimal Ga concentration in A-AGZO-A films.

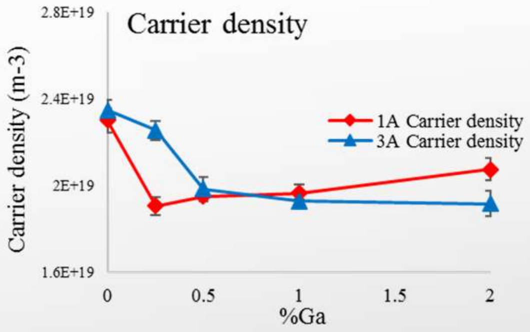
3. **LAYER-BY-LAYER annealing process** - multilayer TCOs

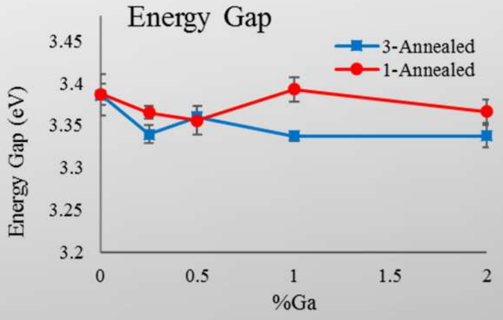
- 10x improved resistivity with multi-annealing

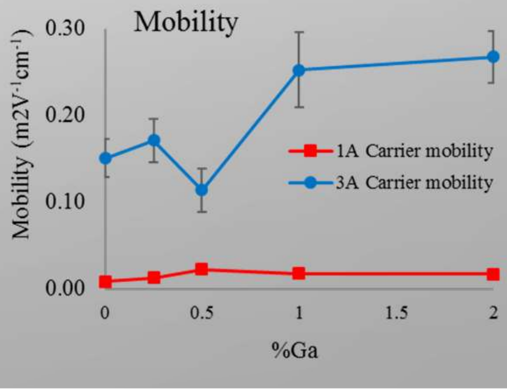


LAYER-BY-LAYER ANNEALING

- Comparing a single thermal annealing treatments to layer-by-layer (x3).
- Each treatment – 1 Hr, 530°C, under N_2 atmosphere.
- Carrier concentration – little change.
- Energy Gap – little change
- Mobility – improved approx. 11-18x
- Anomalous poor mobility in 0.5% Ga samples

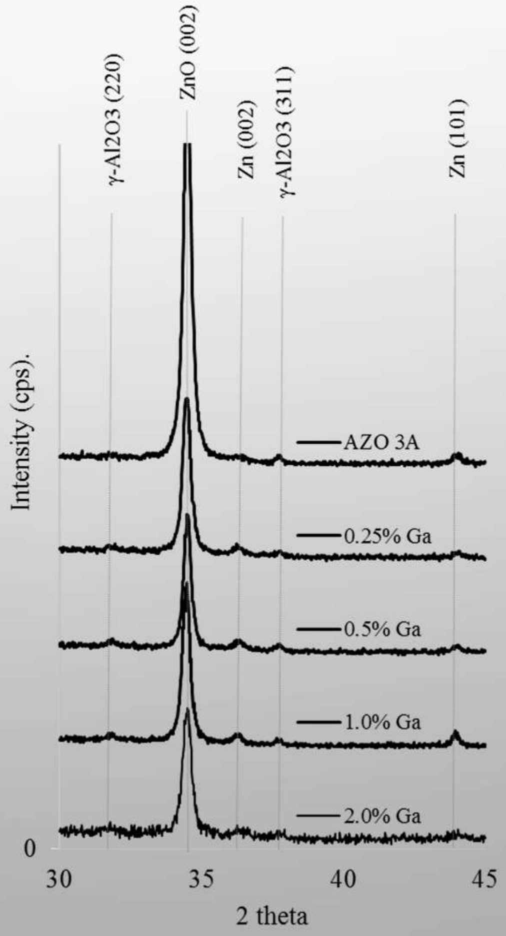


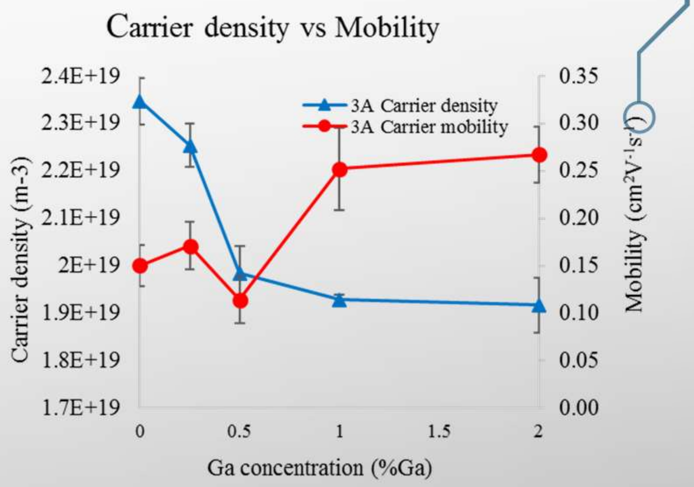


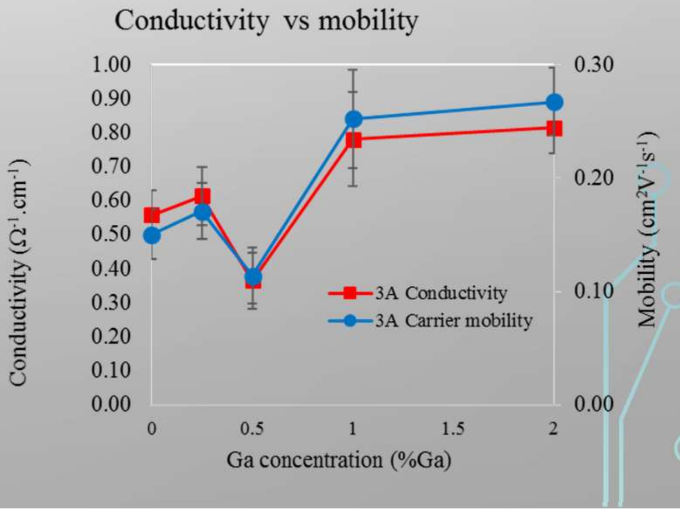


CARRIER DENSITY AND MOBILITY – LAYER BY LAYER

- As Ga concentration increased
  - crystal structure degrades and
  - carrier concentration reduces
  - indicating the proliferation of trap states associated with clustering of displaced Zn atoms and excess Al_2O_3
- In the multi-annealed films, metallic Zn and Al_2O_3 phases appear, which reduces doping efficiency, degrades crystal structure.
- Declining carrier density effectively reduces scattering centres, which improves mobility

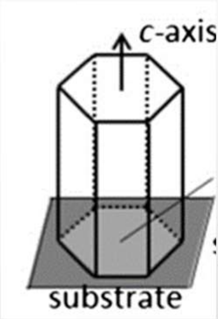


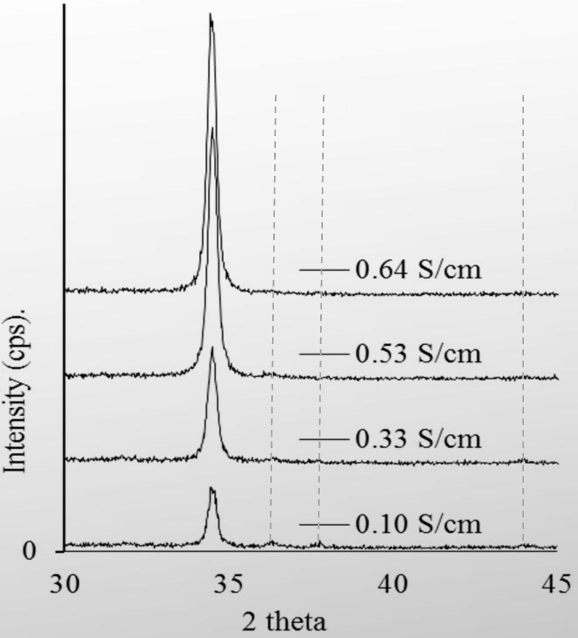


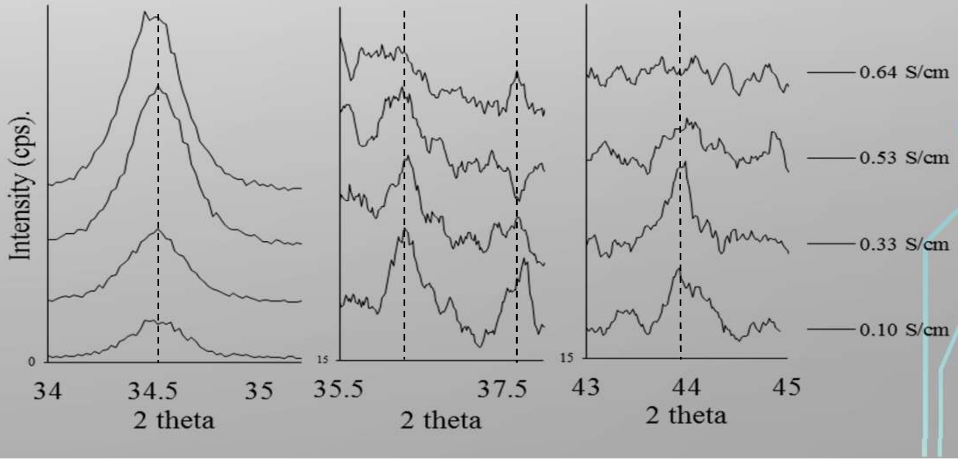


THE UNDERPERFORMER - 0.5% Ga

- Anomalous behaviour in the sample set with 0.5% Ga
  - Drop in carrier density
  - Large drop in mobility
- Mobility is proportional to percentage of hexagonal crystal phase
- Poor crystallinity is accompanied by emergence of other phases – Al_2O_3 and Zn
- Scattering occurs at internal surfaces between different structures.
- Solubility limit of Al and Ga in ZnO ~0.3%
- Differences in crystal structure may be due to high sensitivity to temperature and ramp rates during annealing.





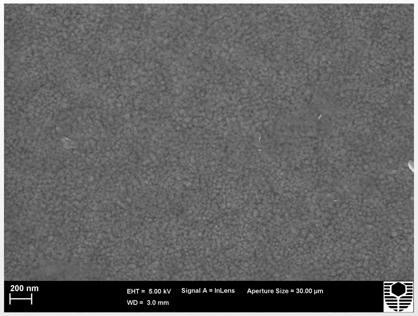


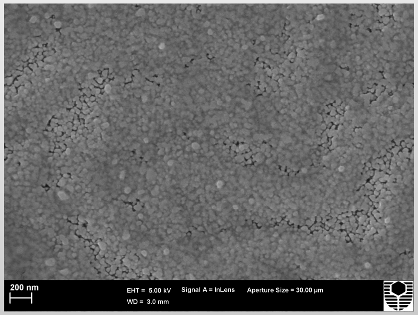
ISOTROPIC CONDUCTIVITY AND MORPHOLOGY

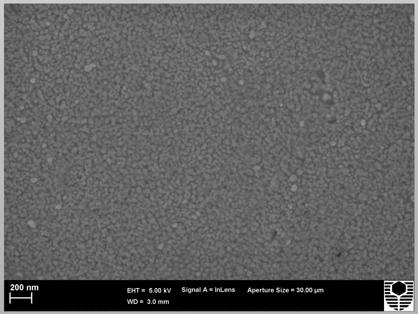
- Carrier density was very consistent across all thin films and sits near the threshold for metallic conduction:

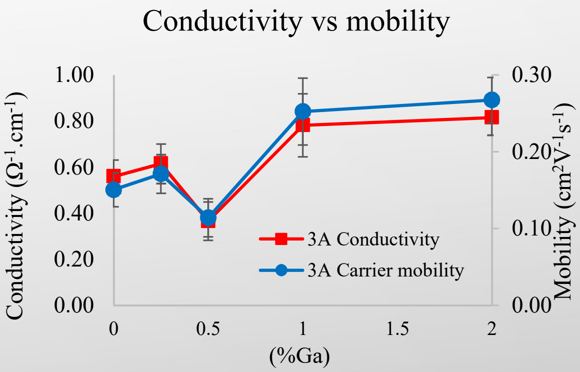
  $1.9 \times 10^{19} \text{cm}^{-1} > n_e > 2.3 \times 10^{19} \text{cm}^{-1}$

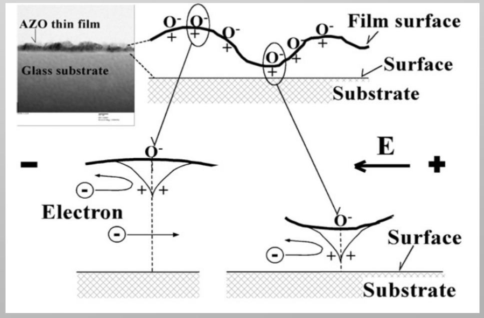
- **Electron mobility** determines electrical conductivity in these processes.
- Incomplete annealing of sol-gel films may leave behind remnants of the xerogel film with regions of high porosity and valleys where the film thins considerably (average thickness is around 320nm) (Kozuka et al. 2000).
- Surface adsorption of O_2 in the valleys generates local potential barriers which reduce the cross-sectional area of the conductor (Minami 2008).











(Minami 2008)

CONCLUSIONS

- We can use composite multilayer films to improve TCOs and reduce materials cost.
- Layer-by-layer annealing process improves mobility significantly in co-doped multilayer films.
- BUT
  - Narrow window of conditions for high conductivity and transparency.
    - Need a narrow range of carrier density ~ 2×10^{19} - 5×10^{21}
    - Need low defect / dislocation density, and other scattering centres
    - Need low porosity and surface roughness << film thickness
    - High energy gap Eg > ~3.3eV
  - Sol-gel based processes – highly sensitive to process settings e.g.
    - Film thickness > high internal strain > high dislocation density > poor mobility
- Multivariate statistical analysis may be useful in refining process parameters.

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