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ZnO-based Transparent Conductive Oxide Thin Films

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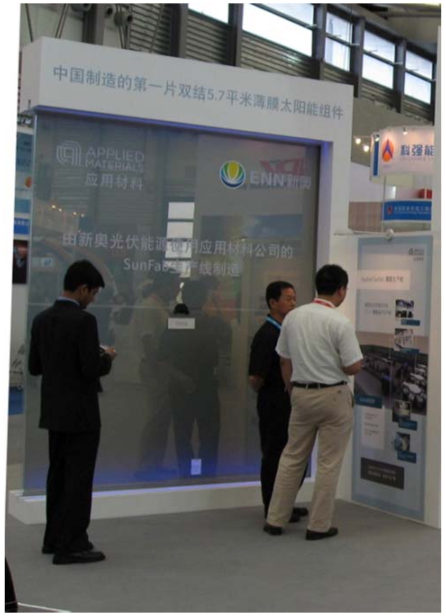
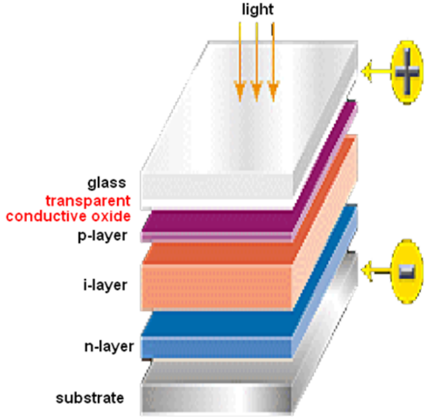
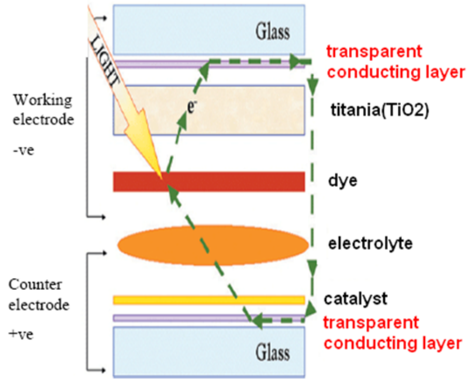
Rapid developments of thin film PV industry and technology



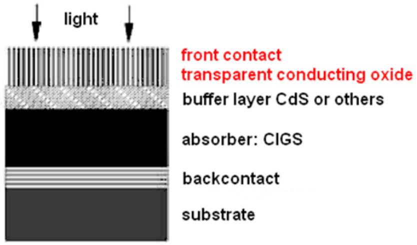
a-Si solar cell structure



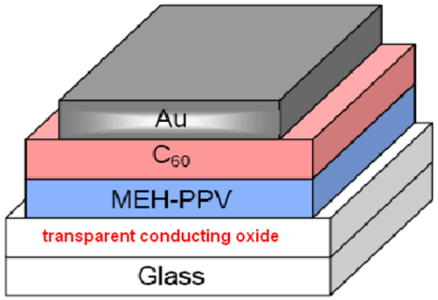
Dye-sensitized solar cell structure



CIGS solar cell configration



a sample structure of organic solar cell



Transparent Conductive Oxides for Thin Film Solar Cells

Liquid Crystal Display

Thin Film Solar Cells

Light emitting diodes

Transparent Thin Film Transistors

Traditional TCO such as FTO and ITO can not satisfy the rapid development of this field.

ZnO-based TCO is promising and attracted much attention: Cheap, high performance, etc

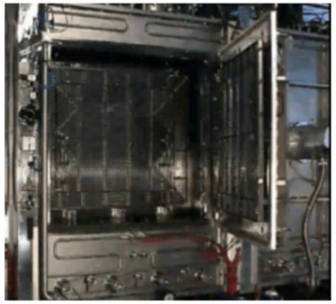
" Good TCO can turn poor light absorbers into reasonable solar cells and bad TCO can turn good light absorbers into poor solar cells "

Transparent Conductive Oxides for Thin Film Solar Cells

Zinc-Oxide as TCO

LEYBOLD OPTICS

TCO (~ 500 nm) sputtering



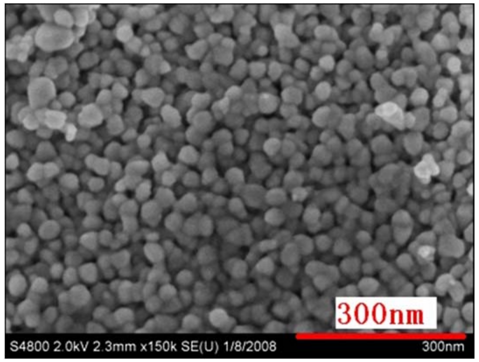
ILA900
- Vertical In-Line system
- Precise temperature uniformity
- High process uniformity

PEGASUS
- Vertical In-Line system
- Single side sputtering
- High throughput production system
- Smallest clean-room footprint

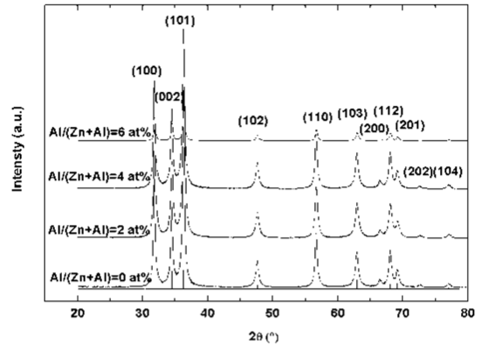
Boron: ZnO
Light scattering capability
Thicker film & lower transparency

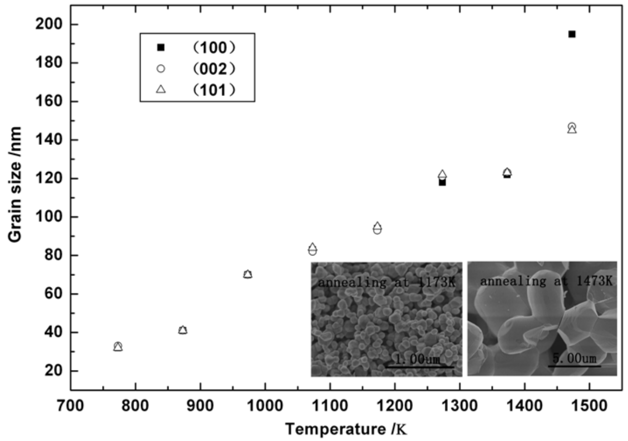
AZO/GZO
Better conductivity
No side effect
Lower deposition rate

Our ZnO-based Nano-powder Technology



Al contents in the starting materials/%	*Al contents by ICP/%*
Al/(Zn+Al)=0 at%	Al/(Zn+Al)=0.02 at%
Al/(Zn+Al)=2 at%	Al/(Zn+Al)=1.95 at%
Al/(Zn+Al)=4 at%	Al/(Zn+Al)=3.54 at%
Al/(Zn+Al)=6 at%	Al/(Zn+Al)=5.34 at%

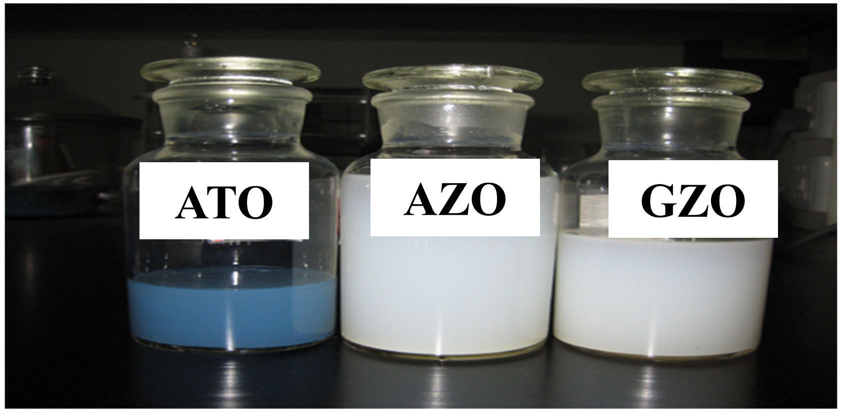




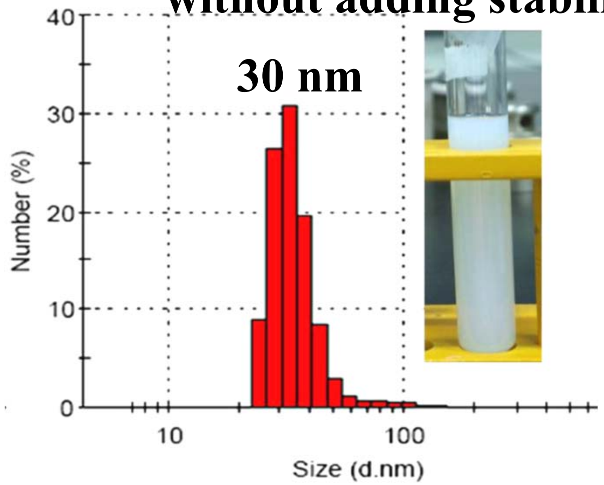
Samples	Resistivity ρ/Ω·cm
ZnO	17
2at% AZO	4.2
4at% AZO	4.1
6at% AZO	1.2

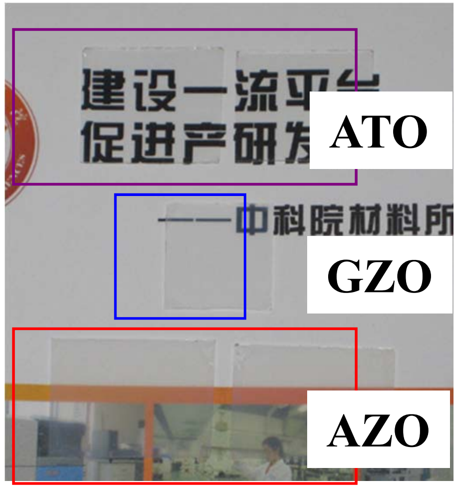
Zhang and Song et al, J. Sol Gel Sci & Tech (2009), J. Mater. Sci (2011)

ZnO-based Nanopowder Dispersion and Coatings



High concentration dispersion (>35%) without adding stabilizer





87.6%

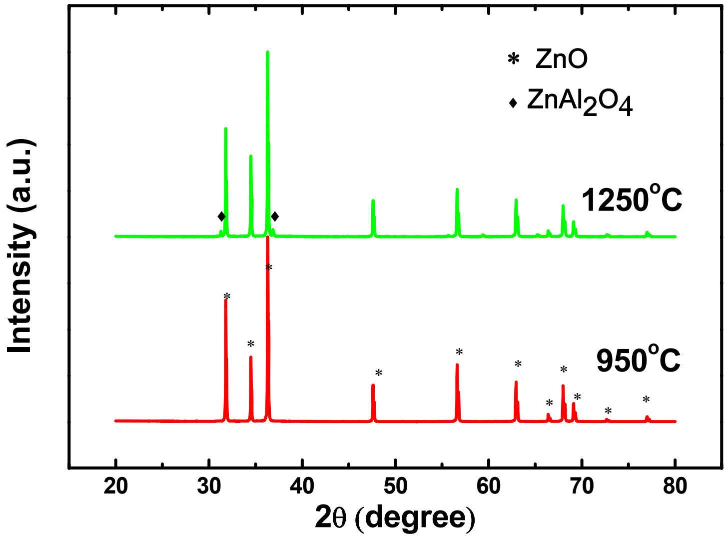
86.2%

92.3%

	Powders resistivity (Ω·cm)	Film resistivity (Ω·cm)
AZO	4	12
ATO	10^{-3}	4×10^{-2}

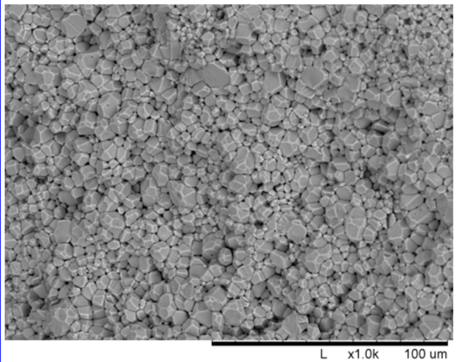
Zhao & Song et al, J. Am. Ceram. Soc. (2010)

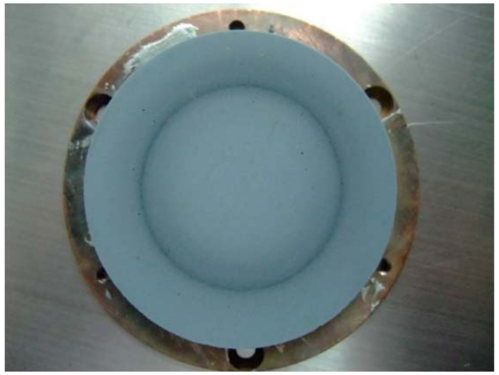
Our ZnO-based Sputtering Target Technology

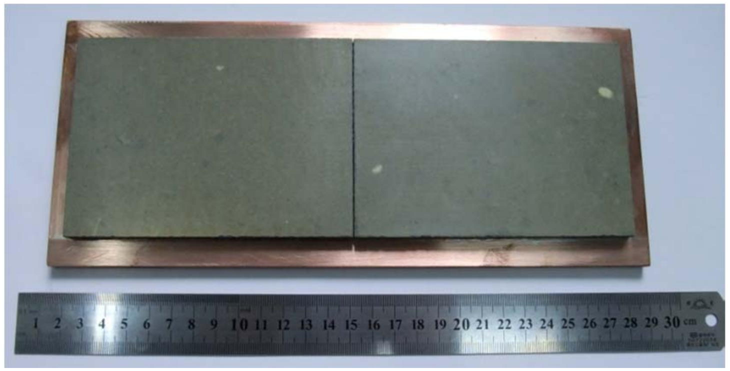


AZO ceramic sputtering target

- ✓ Single phase structure
- ✓ Ultrahigh density (>99.5%) & low sintering temperature
- ✓ High purity (> 99.99%)
- ✓ Low resistivity for DC sputtering
- ✓ Small grain size for fast deposition

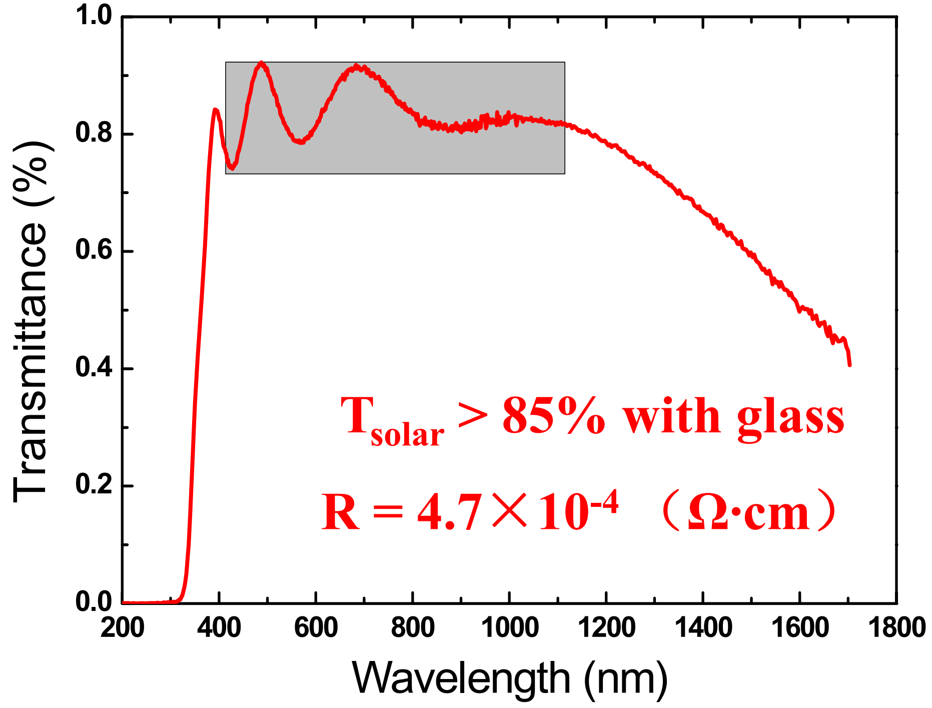






Zhang and Song et al, Inter. J. Appl. Ceram. (2011) and Inter. J. Appl. Ceram (2012)

Our AZO TCO Thin Films Made by DC Sputtering



For reference:

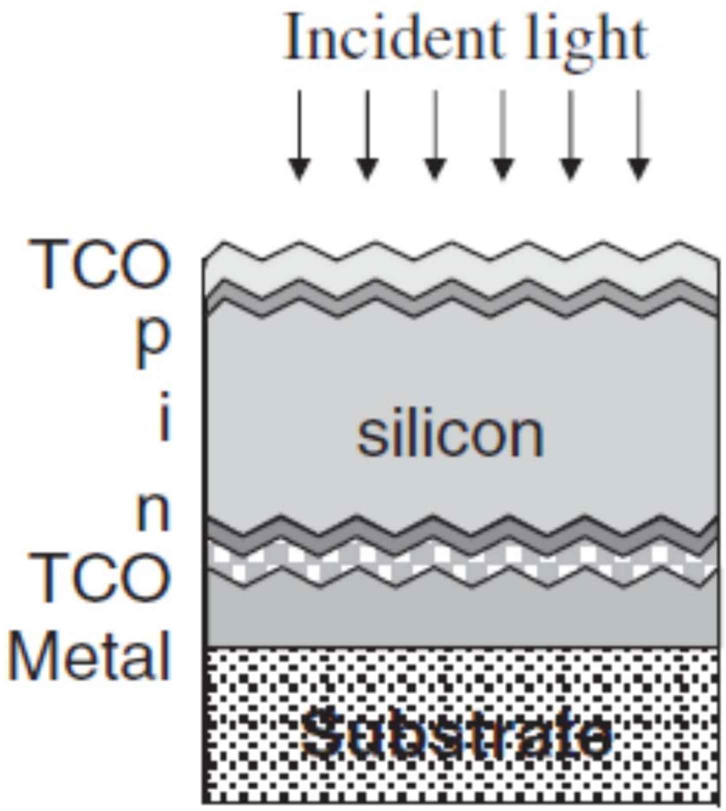
Indium tin oxide TCO:

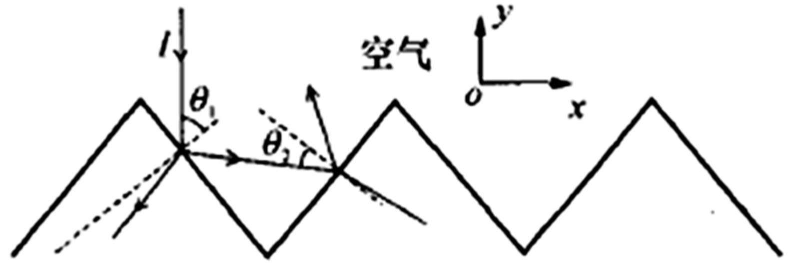
- ✓ $T_{solar} \approx 85\%$ with glass
- ✓ $R \approx 1\sim5 \times 10^{-4}$ Ω.cm

Fluorine doped tin oxide TCO:

- ✓ $T_{solar} \approx 80\%$ with glass
- ✓ $R \approx 1\sim5 \times 10^{-3}$ Ω.cm

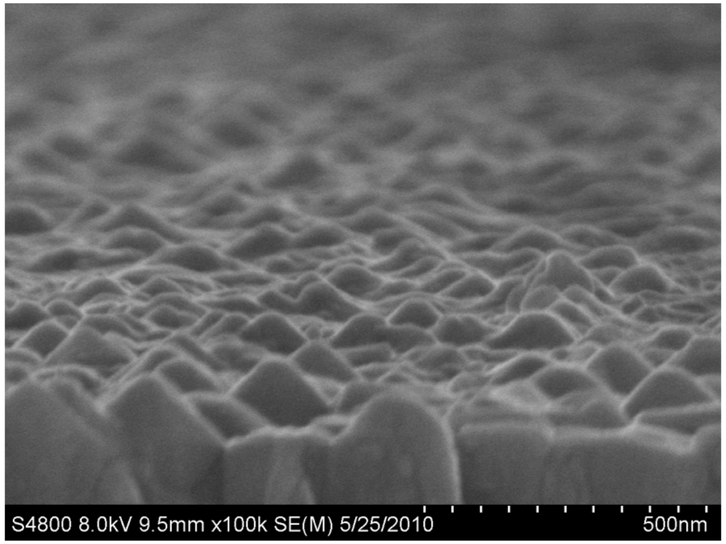
Surface Morphology Control: Enhanced Light Scattering

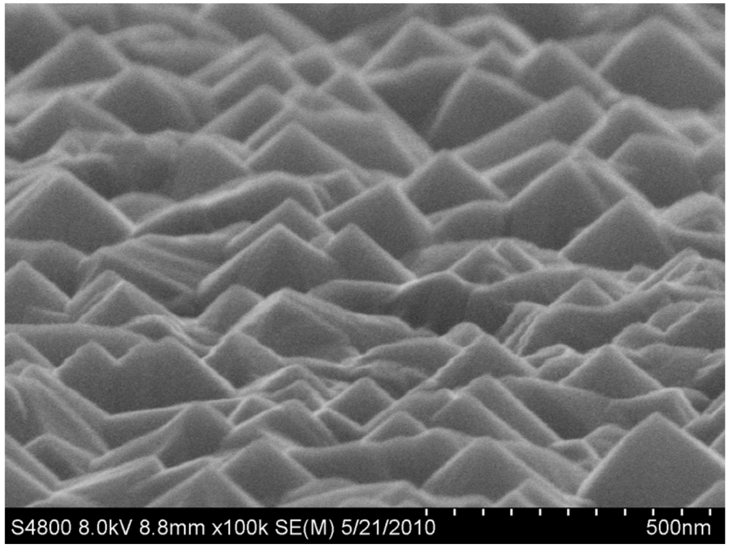


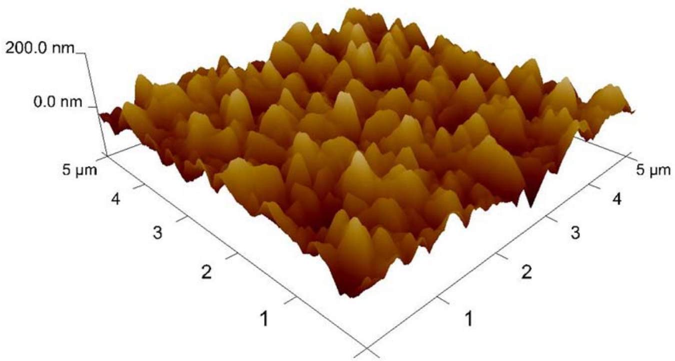


By modifying the surface roughness of TCO thin films, the transmittance angle of light can be changed. This can largely enhance the light absorption in Si-based thin film solar cells.

Surface Morphology Control: Enhanced Light Scattering

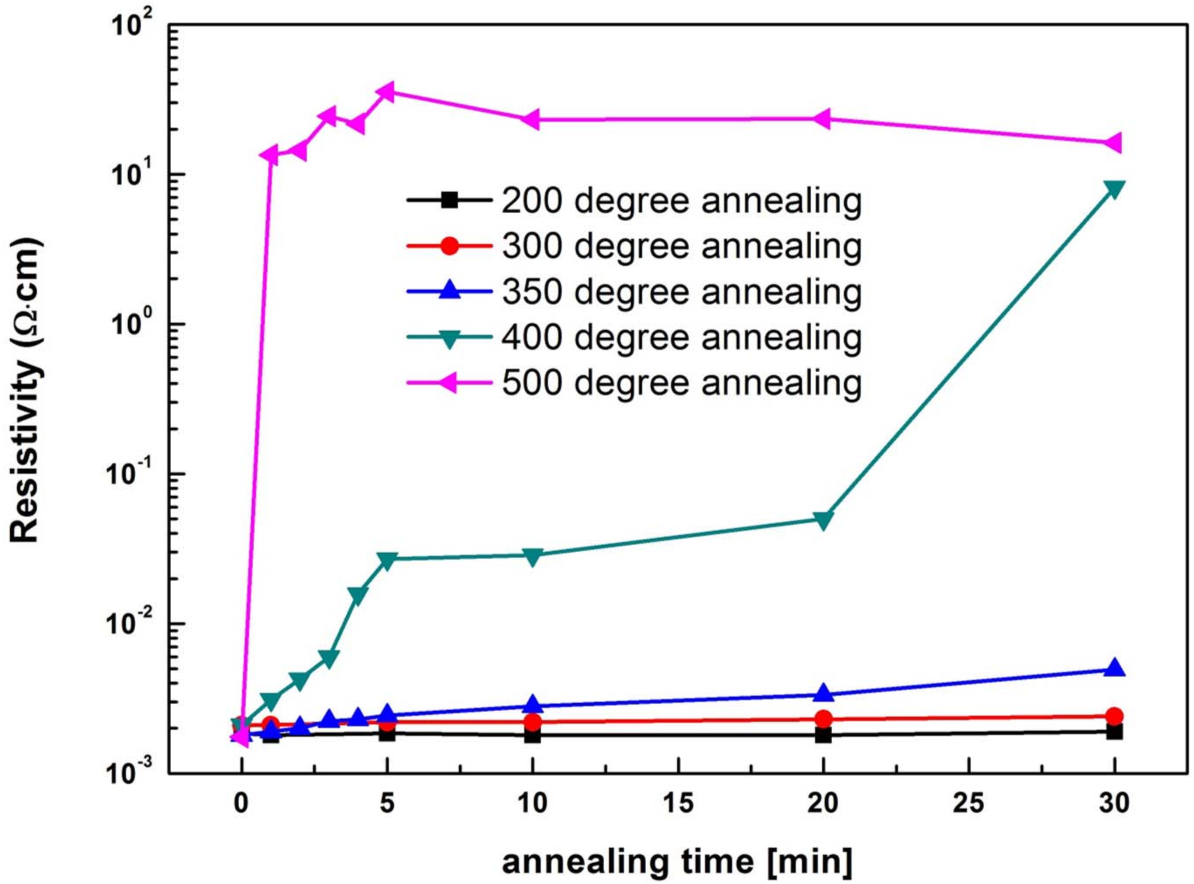






A kind of pyramid-like structure can be achieved directly using DC sputtering of ultra-dense and fine grain size AZO targets. The surface roughness can be more than 40 nm.

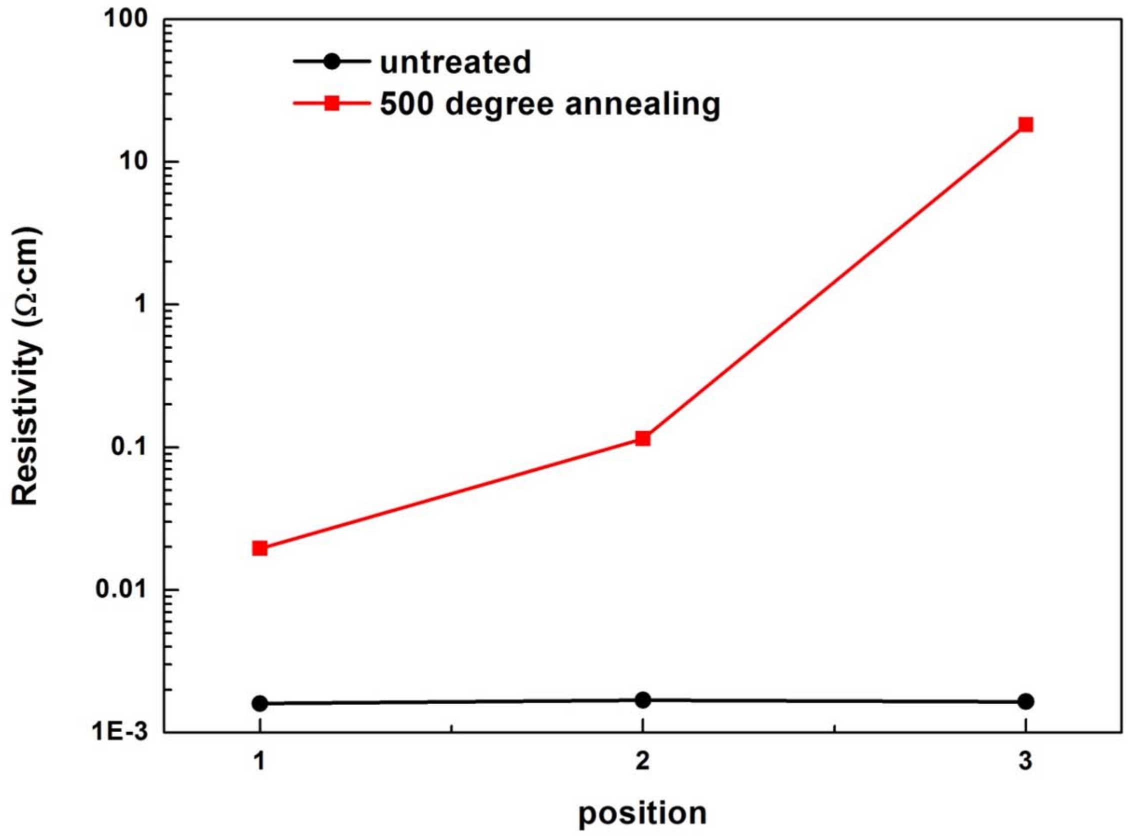
AZO thermal stability



AZO thin films were stable in air up to 300 ºC.

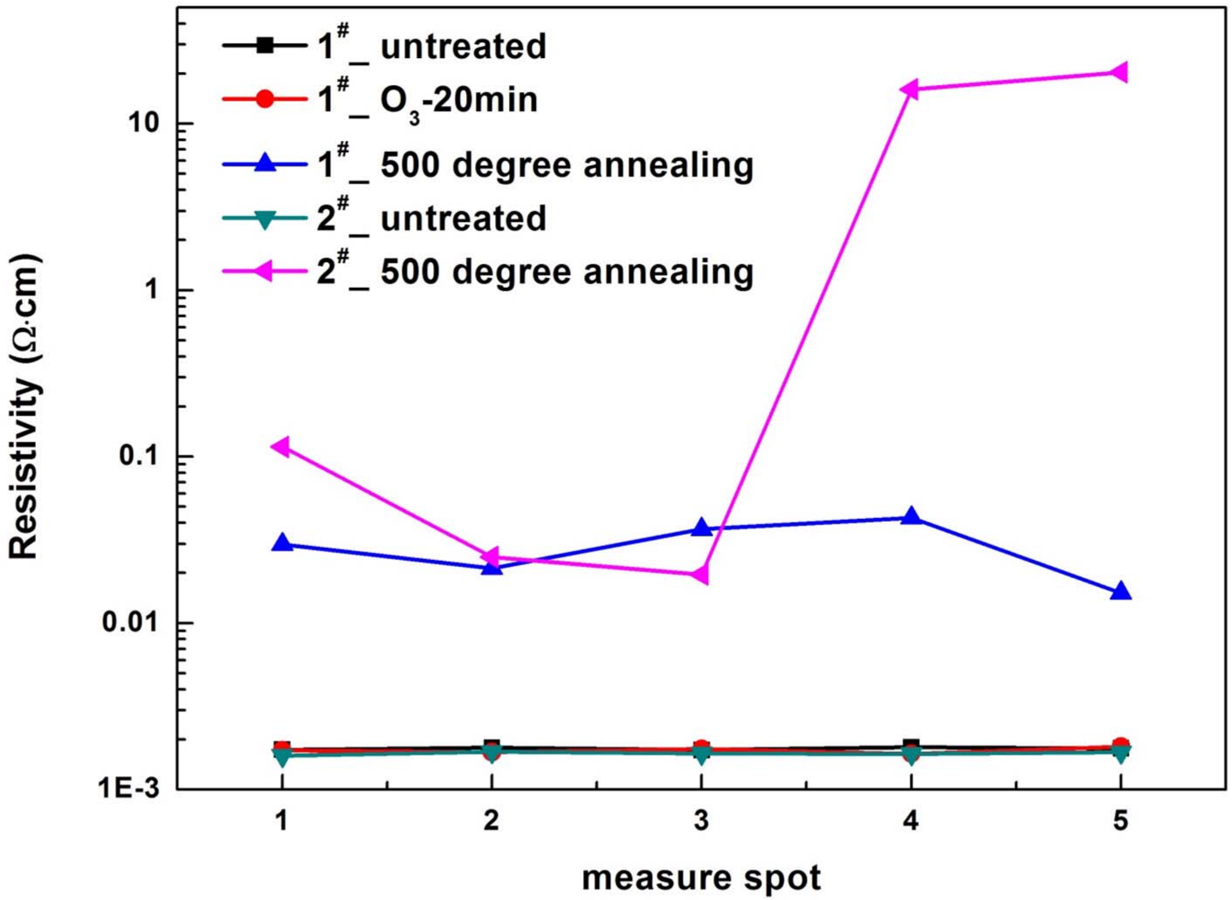
It's resistivity increased significantly when heated at 500 ºC in air.

Inhomogeneous resistivity after heating



The resistivity of AZO could be quite different after heating. It could be different about four orders of magnitudes with in 10 × 10 cm^2.

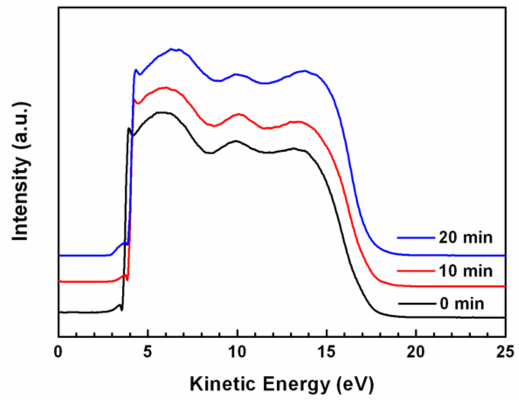
Effects of UV-ozone treatments

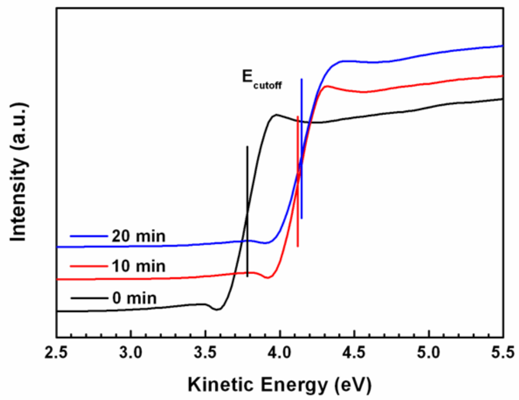


UV-ozone treatments could improve the large area homogeneity of AZO films after heating.

The overall degradation of conductivity was reduced for AZO thin films after heating.

Work Function Control of ZnO-based TCOs

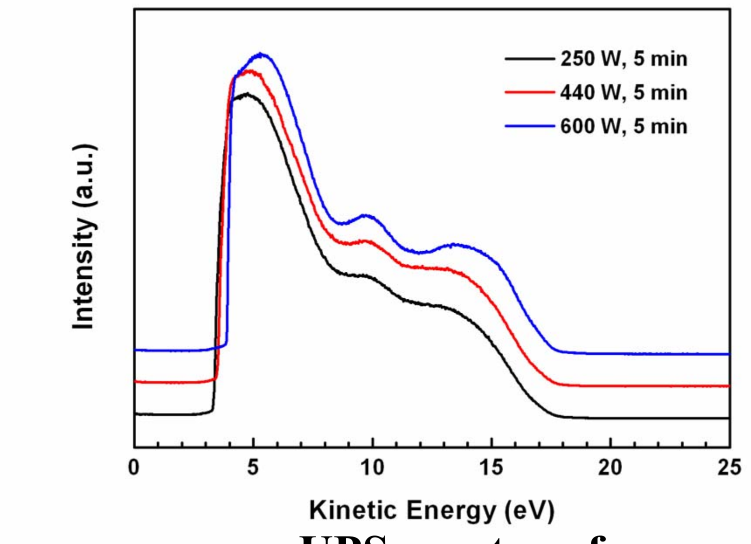


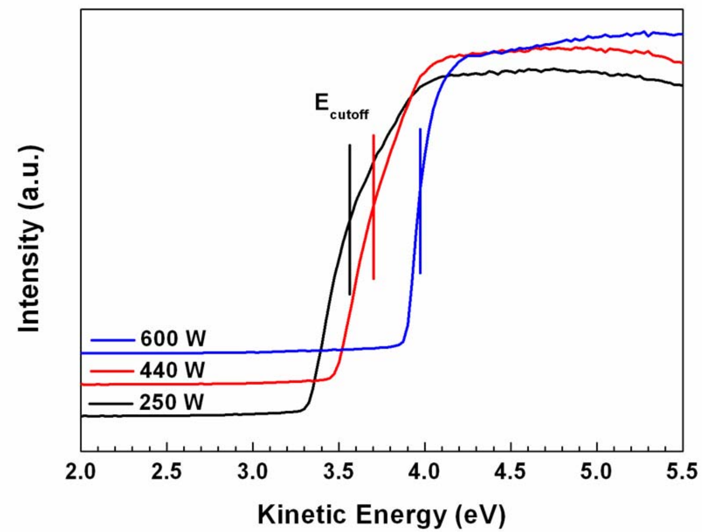


(a) UPS spectra of UV-ozone treated AZO ; (b) secondary electron cut-off

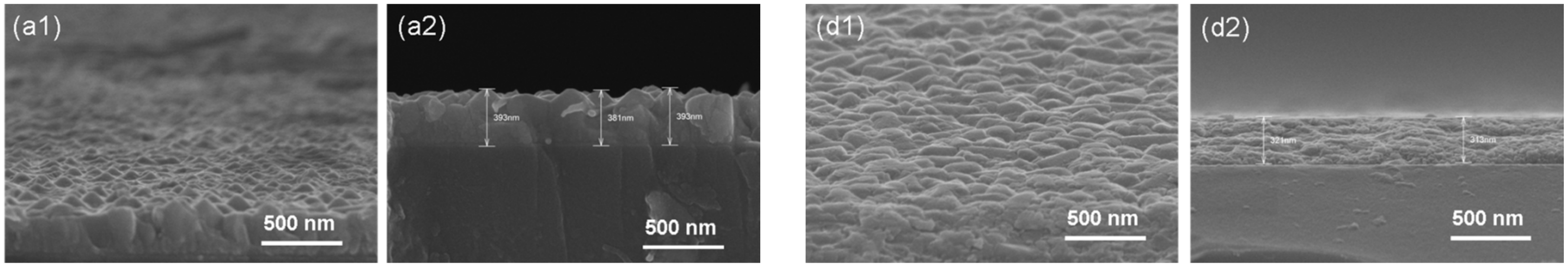
UV-ozone treatment time	Zn (%)	O (%)	Al (%)	C (%)	$[O_{ZnAl}]/([Zn]+1.5[Al])$	Φ (eV)
0 min	22.62	38.63	2.09	36.66	0.69	3.70
10 min	28.47	44.06	1.60	25.86	0.83	4.03
20 min	25.78	43.49	2.32	28.41	0.96	4.02

Work Function Control of ZnO-based TCOs





UPS spectra of oxygen plasma treated AZO surfaces



Though WF increased, the roughness and the film thickness decreased after oxygen plasma treatments.

Summary

- ✓ A complex sol-gel method was developed for large scale production of ZnO-based nano powders;
- ✓ Very high concentration of ZnO-based dispersions were successfully prepared without adding impurities;
- ✓ AZO sputtering targets with high density and without $ZnAl_2O_4$ phase can be made at low sintering temperature;
- ✓ AZO thin films with high optical and electrical properties can be made from our own sputtering targets;
- ✓ The optical, electrical properties, surface properties and thermal stability are crucial for the applications in thin films solar cells. These properties can be tailored either in the fabrication process or in the surface treatment process.
- ✓ Future work needed: Durability and stability in various environments, multilayer structures for better performance; NIR transmittance; poly-Si growth; flexible substrates; large area production; etc

Thank you for your attention!