Growth and fabrication of dye sensitized solar cells on multilayer transparent conductive films

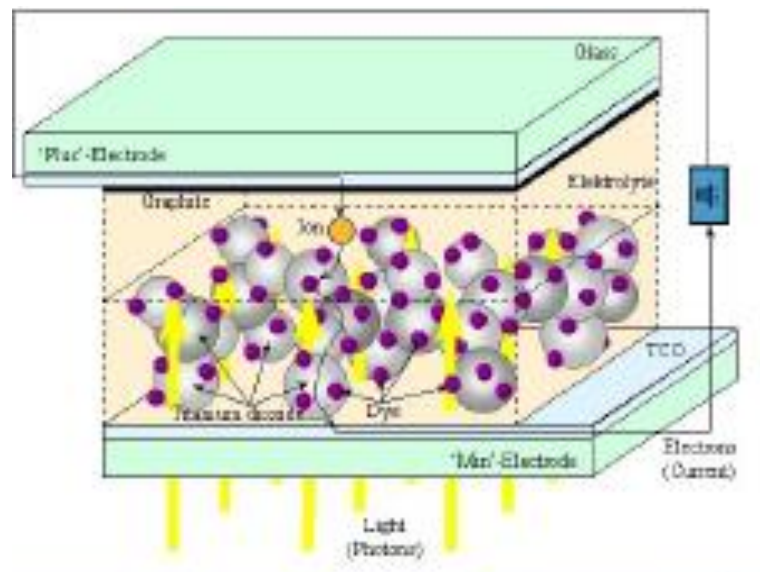
Dipti R. Sahu

Department of Natural and Applied Sciences, Namibia University of Science and Technology, Windhoek, Namibia

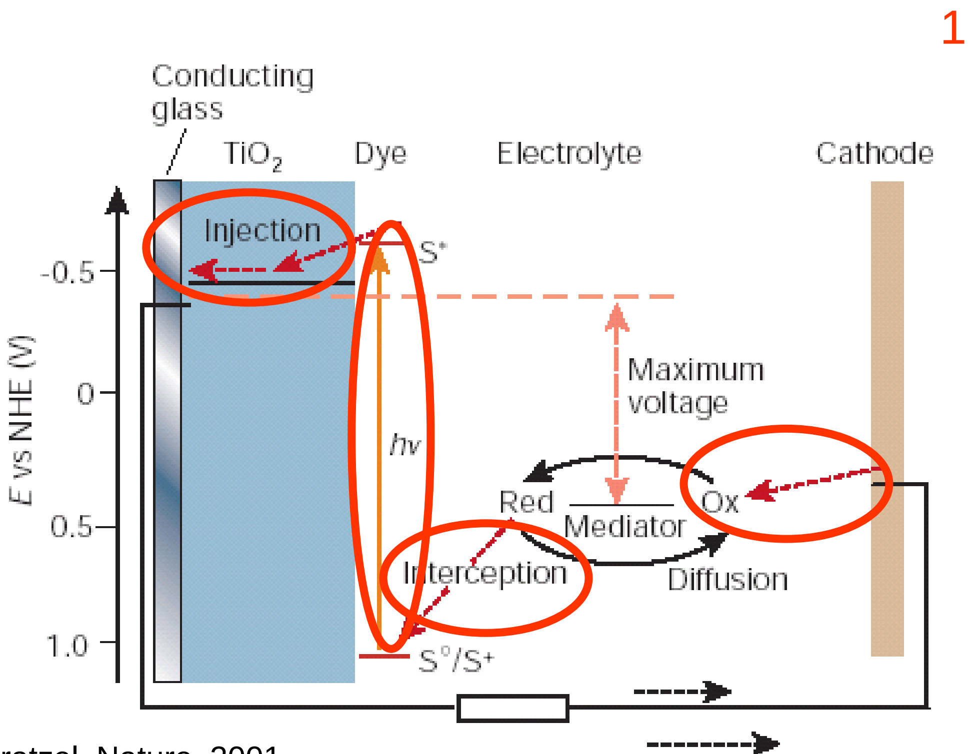
Email: dsahu@nust.na

Dye Sensitized Solar Cell (DSSC)

- Easy to be fabricated
- Low cost
- Friendly to the environment
- Photo voltage is significantly less sensitive to light intensity variation than that of conventional solar cells



Principle of Dye-Sensitized Solar cells



Gratzel, Nature, 2001

1.Absorption

$$S + h\nu \rightarrow S^*$$

2. Electron injection

$$S^* \rightarrow S^+ + e^-(TiO_2)$$

3. Regeneration

$$2S^+ + 3I^- \rightarrow 2S + I_3^-$$

4. Cathode:

$$I_3^- + 2e^-(Pt) \rightarrow 3I^-$$

Low photocurrent could be the result of

1. **Inefficient light harvesting by the dye**
2. **Inefficient charge injection into TiO_2**
3. **Inefficient collection of injection electron**

Enhancement of injected electron collection

- **Multilayer nanocrystalline films with the structure of transparent conducting oxide/metal/transparent conducting oxide**
  - **ZnO/Ag/ZnO**
  - **Al-ZnO/Ag/Al-ZnO**

Transparent Conductor

- A thin film is Transparent to visible light (220 -1100 nm) and conducting to electricity is called a Transparent Conductor

- The basic Electromagnetic Theory does not permit a material to be both conducting and transparent simultaneously.
  - For example : Copper or Silver cannot be transparent
  - $NaCl$, CaF_2, In_2O_3, TiO_2 cannot conduct !

The basic Physics of TCO Films:

- Maxwells Equations demand that NO MATERIAL CAN BE BOTH Transparent (to visible light) and Conducting (to electricity)

So How to get a Transparent Conductor ?

- All Metal Oxides are Transparent
- All Metals are conducting
- Mix a Metal Oxide and a Metal !!

  Modify a transparent material for electrical conduction.

The TCO Thin films are

- Wide band gap materials
- Oxygen deficient
- Just by varying oxygen content in the film (JUST ONE ELEMENT), the TCO can be made to exhibit:
  - Metallic
  - Semiconducting
  - Insulating Properties !!

Metal Oxides have a large Optical Band Gap

Examples:

Indium Oxide (In_2O_3)

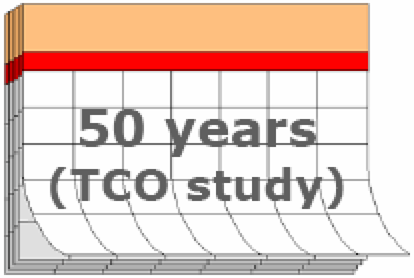
Zinc Oxide (ZnO)

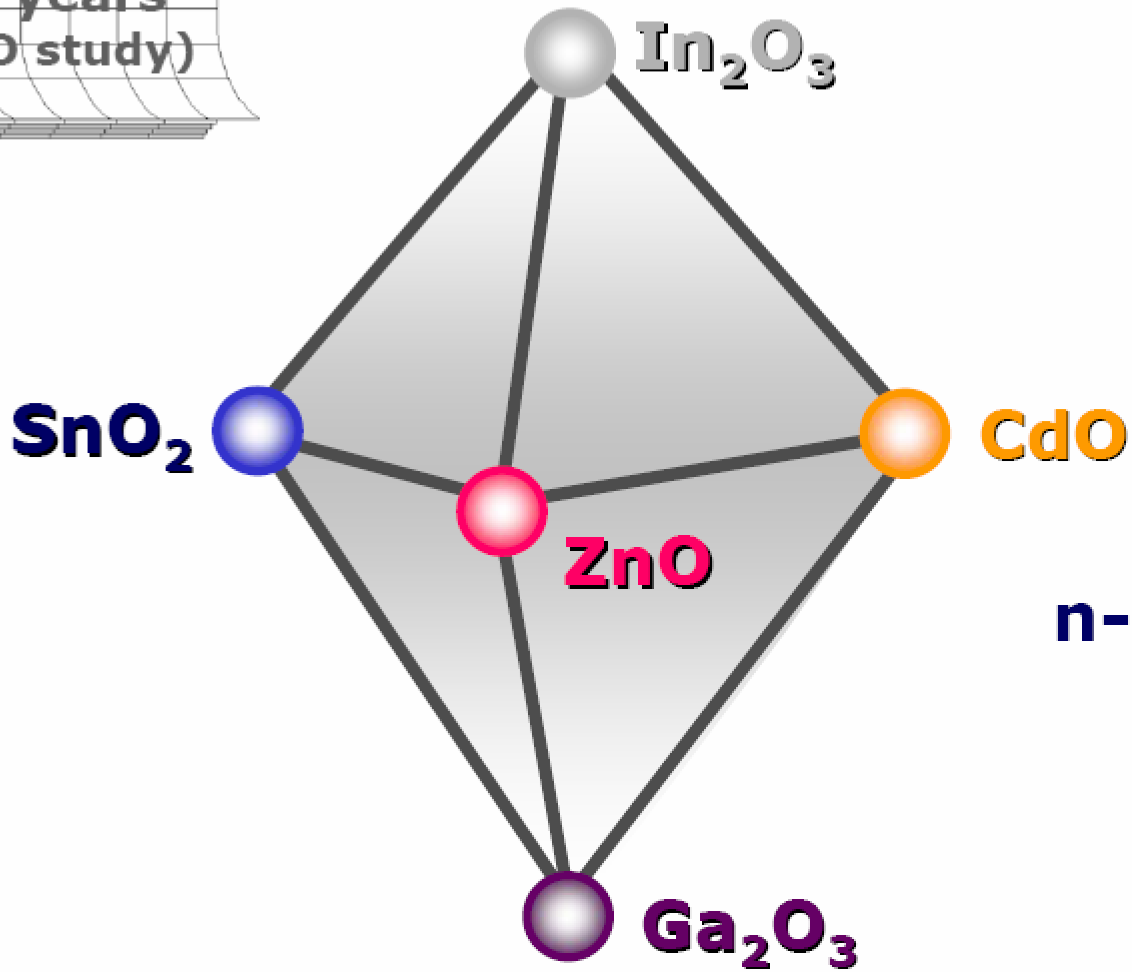
Tin doped Indium Oxide (ITO)

and many more: all are metal oxides

- Metal oxides are transparent to visible light (220 – 1100 nm). The optical band gap is 3.1 - 6.0 eV
- They are all insulators
- They are all stable inorganic materials

Transparent conducting oxides





1980 …

n-type TCOs, with good electrical properties.

Transparent Conductive Oxide Requirements

Layer resistivity R as small as possible

→ Thickness d as large as possible

→ Doping n and mobility μ as large as possible

Transmission T as large as possible

→ Thickness d as small as possible

→ Doping n as small as possible

Why Multilayer with Metal interlayer

1. Very low sheet resistance

2. High optical transparency in the visible range

3. Relatively lower thickness than single layer TCO films

4. Better durability than single layer metal films.

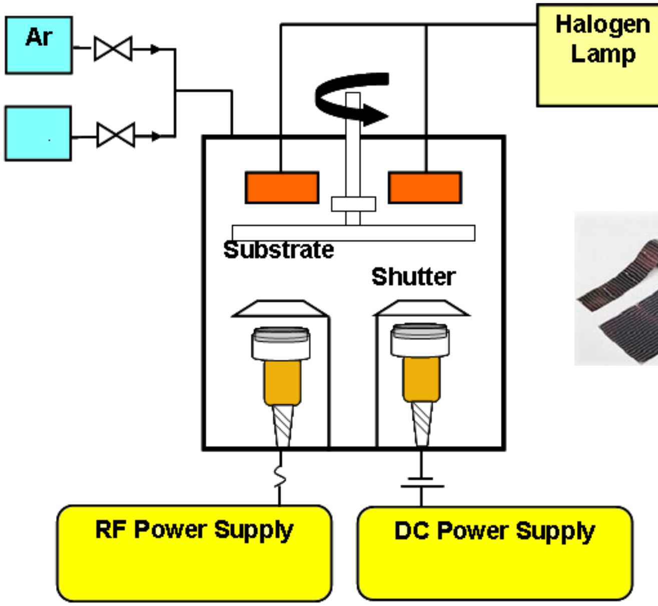
Why ZnO/Ag/ZnO

- ZnO is a transparent conductive oxide with a wide band gap (> 3.3ev)
- Transparent in the wavelength region 350 to > 800nm and Wavelength cutoff depends on the charge carrier concentration.
- Non toxicity, low cost, material abundance, high stability against hydrogen plasma and heat cycling.
- Avoid series resistance effect.
- Thin Ag film had good optical and electrical properties ,Ag has highest conductivity of all metals.

To get improved cost effective transparent conductive material we chose ZnO based TCO with Ag as interlayer.

Transparent Conducting Oxide Thin Film

- **Al-doped ZnO (AZO)**
- **ZnO/Ag/ZnO multilayer**
- **AZO /Ag/AZO multilayer**

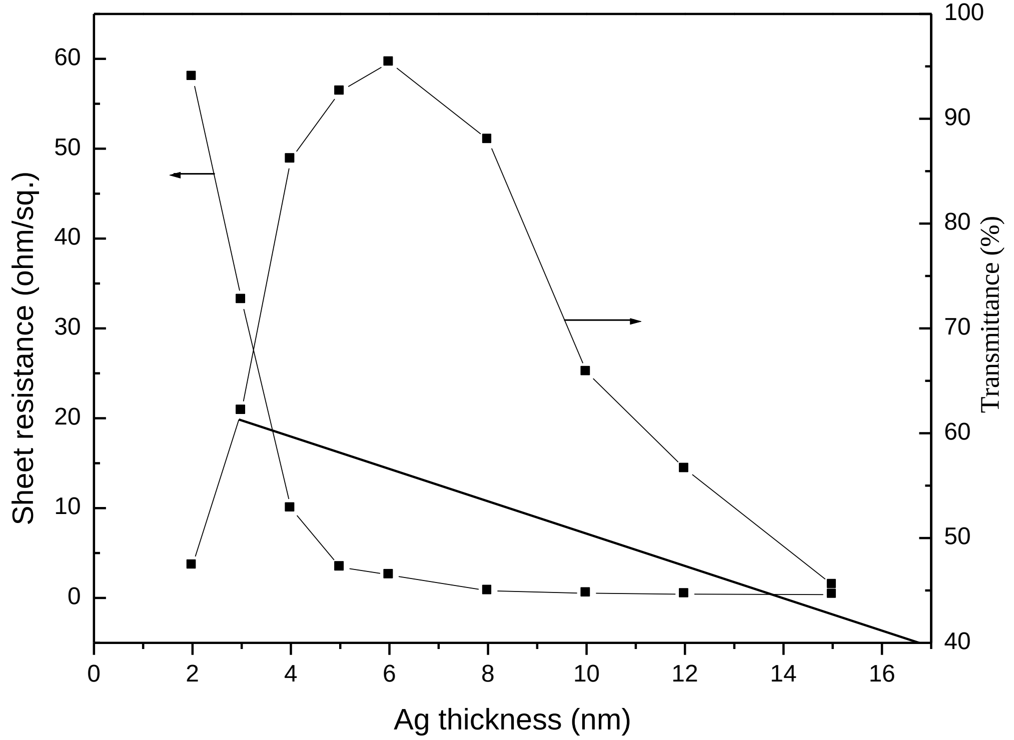


Preparation Conditions :

- Target : ZnO (RF Sputtering), Ag (DC Sputtering)
  - AZO (sintered 2 wt % Al_2O_3 doped with ZnO: E-beam evaporation)
- Pressure: 6×10^{-3} T,
- Substrate Temp Variation : RT to 300°C
- Ar atmosphere: Variation from 20 to 50 sccm)

Transparent electrode for Dye Sensitized Solar Cells

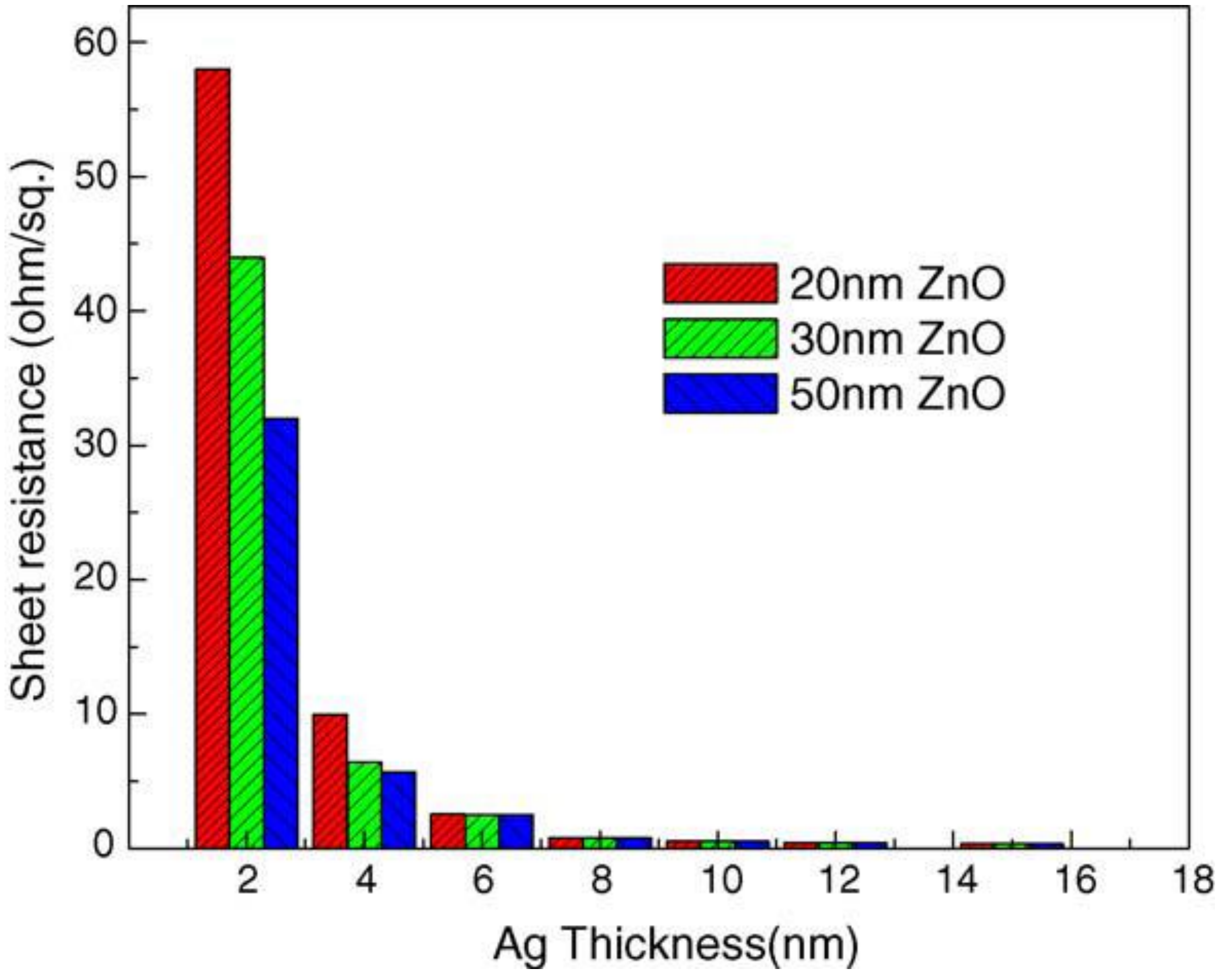
ZnO/Ag/ZnO (ZnO =20nm and Ag =6nm)



Transmittance = 90 % & Sheet resistance (R_s) = 3 Ω/sq.

$$\rho = 1.4 \times 10^{-5}\ \Omega.cm$$

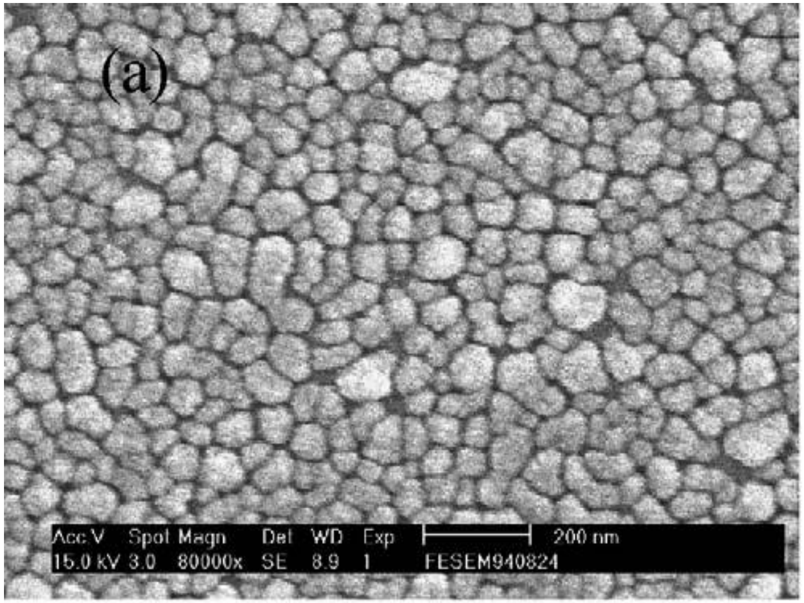
ZnO/Ag/ZnO multilayer

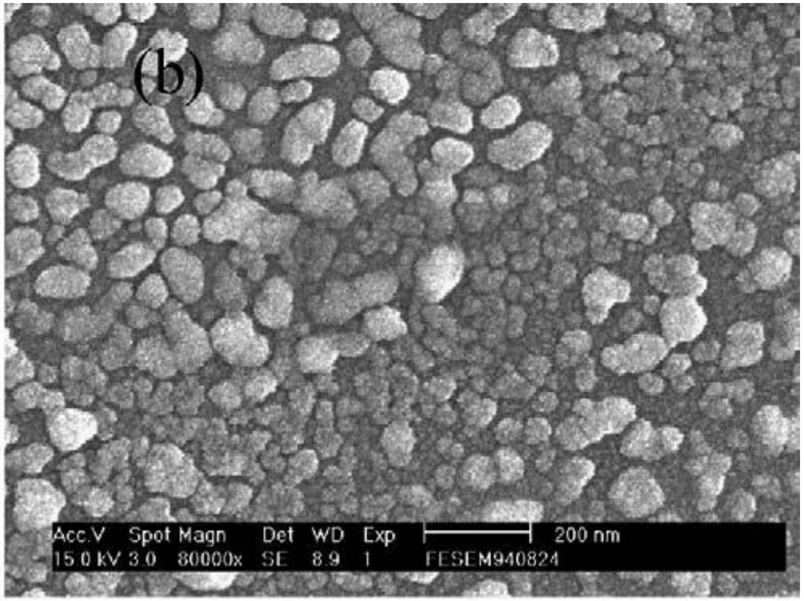


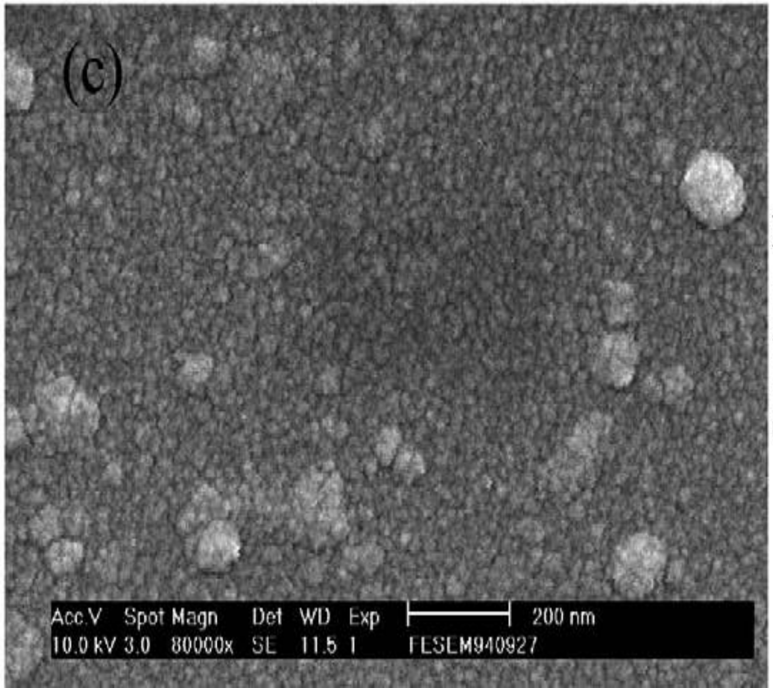
Maximum transmittance 90% and Sheet resistance 3Ω/sq.

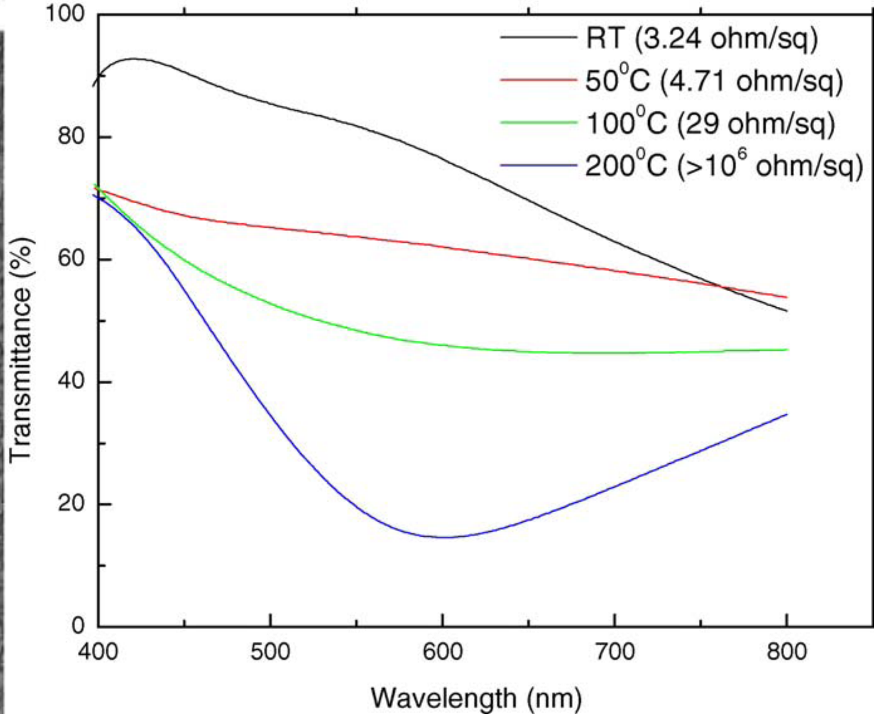
(Thickness of film : 46nm)

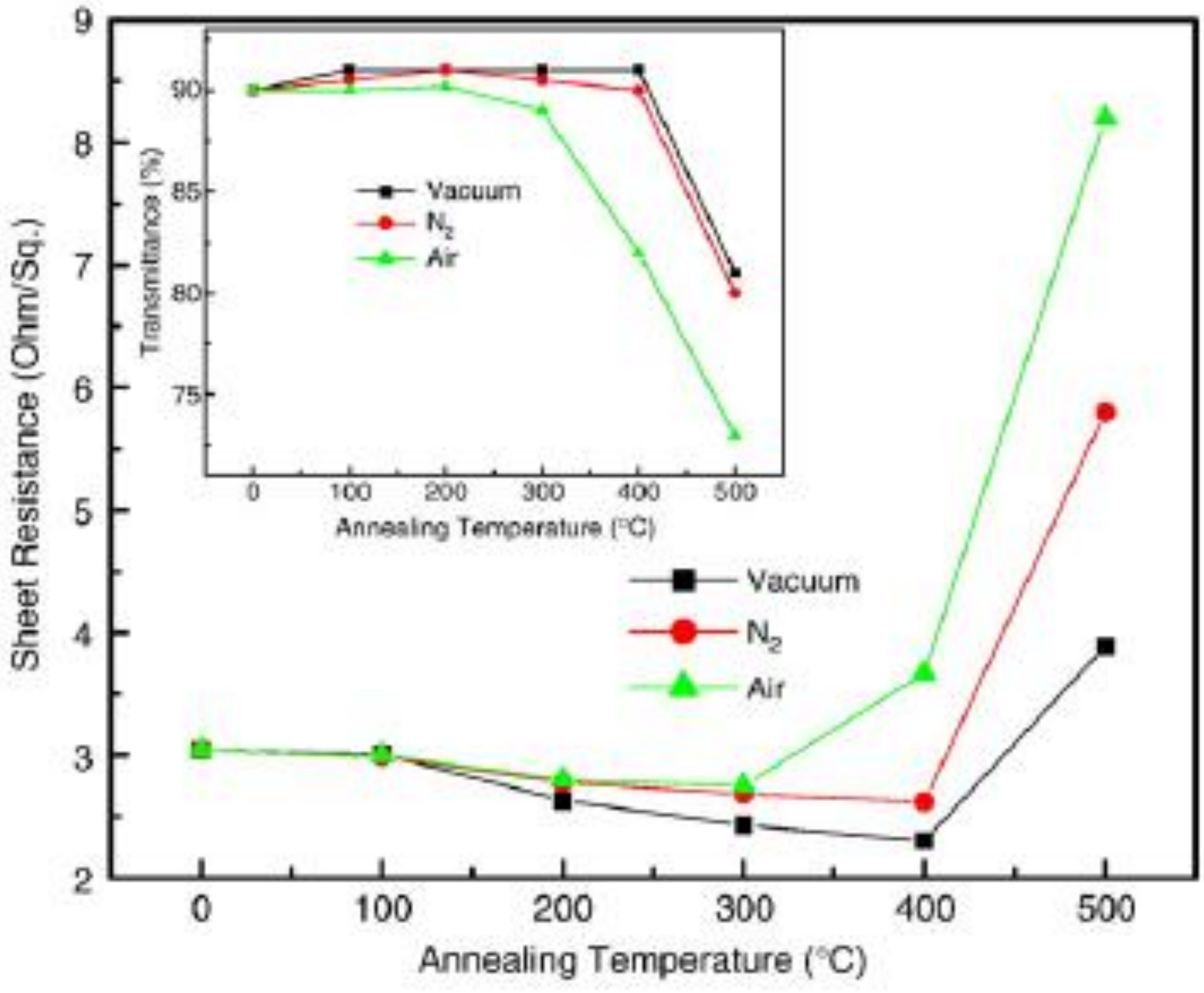
Effect of Ag film





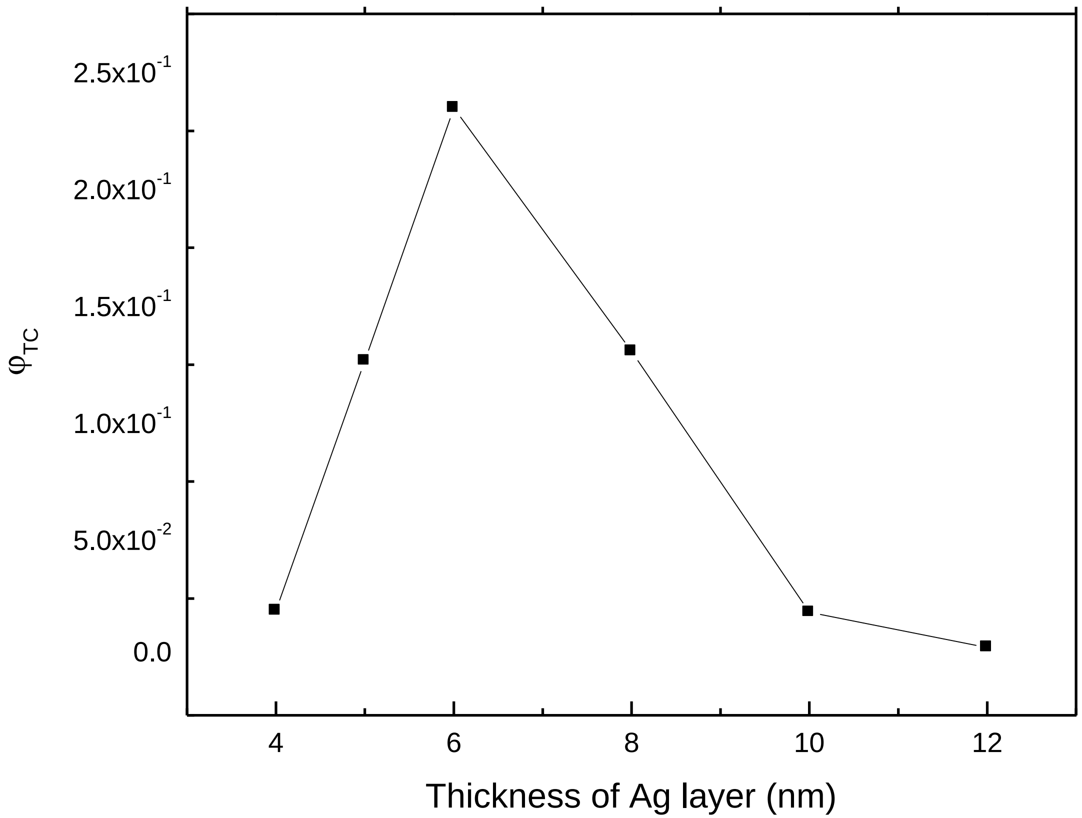






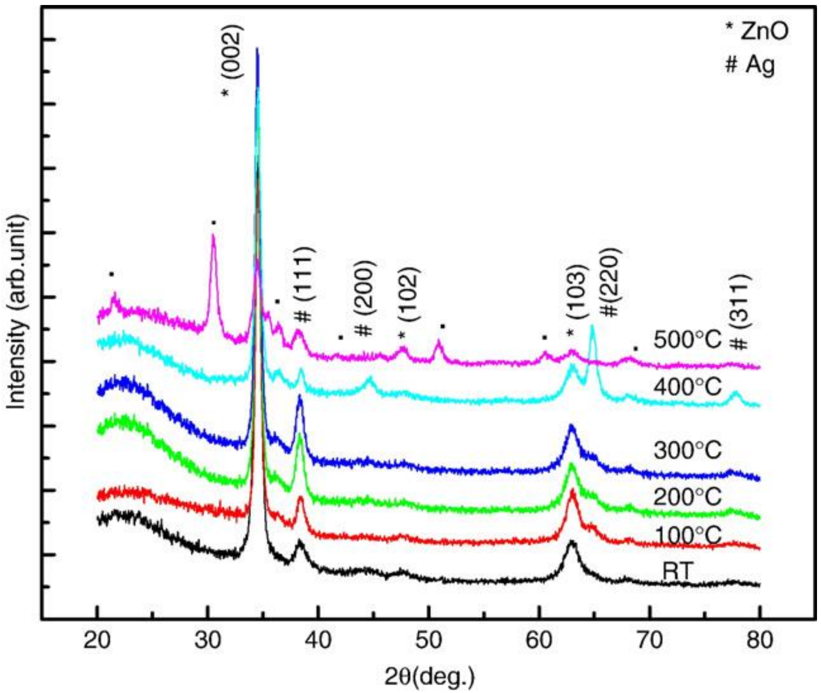
Thermal stability up to 400^{0}C in all atmosphere
---- Suitable TCO for DSSC

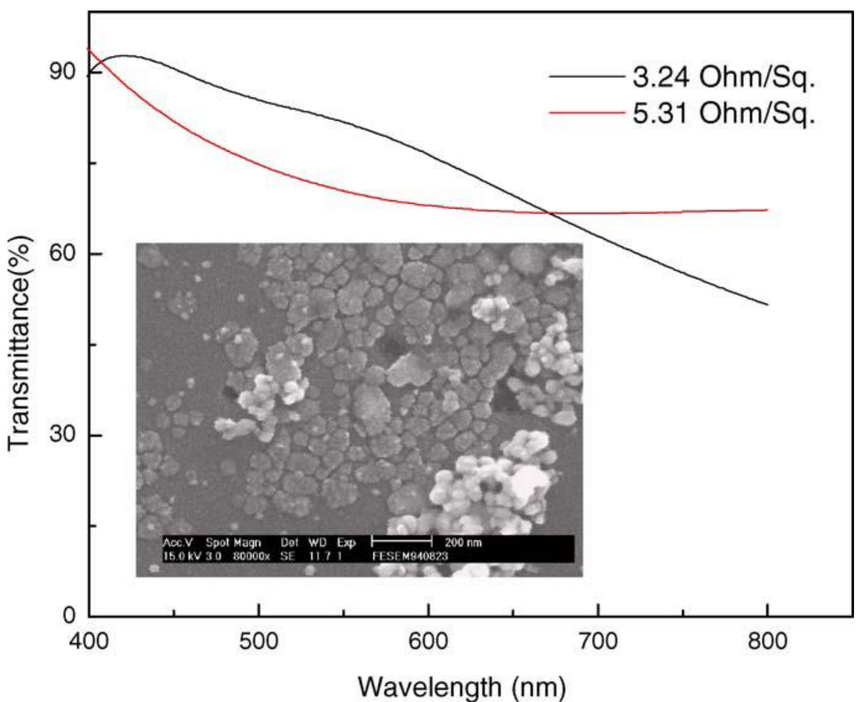
Figure of Merit ($\varphi = T^{10}/R_{Sh}$)

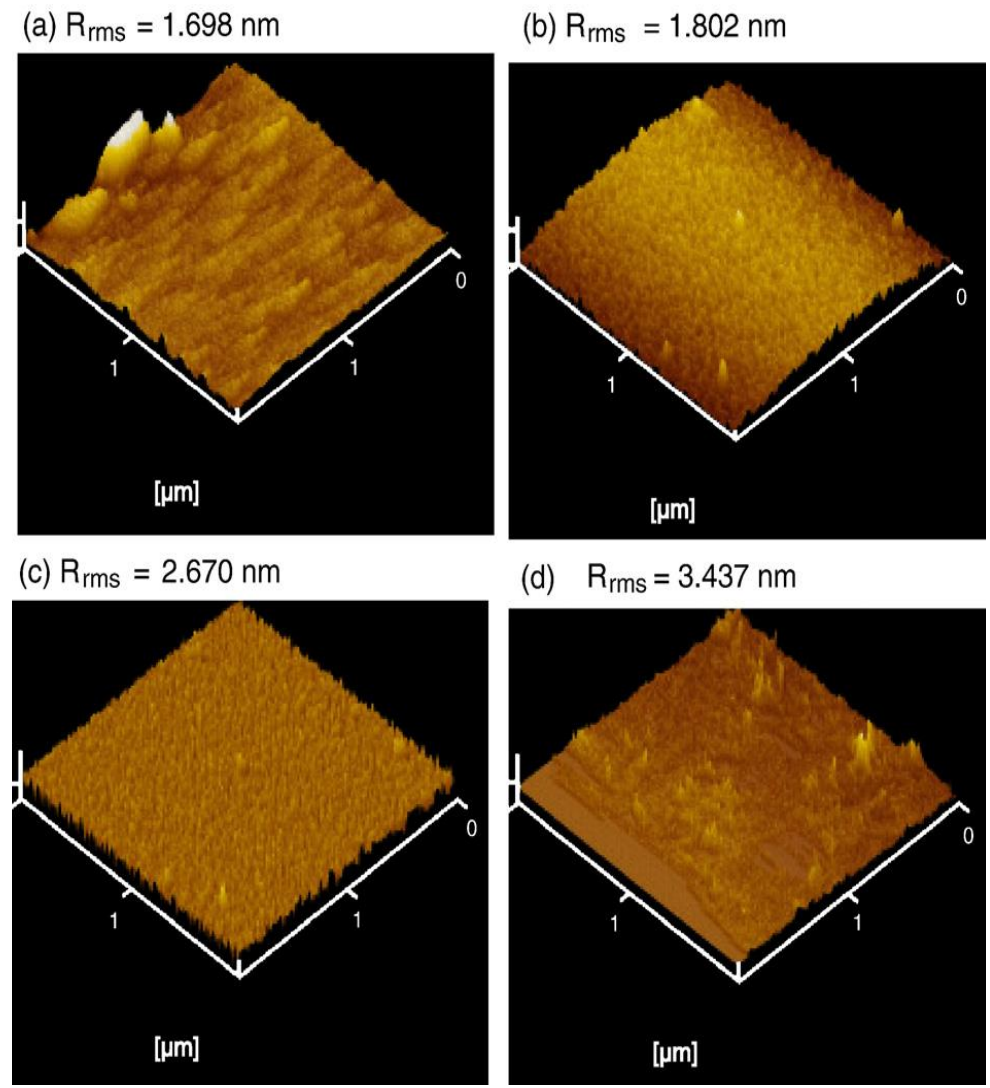


$\varphi_{TC} = 2.36\times10^{-1}\ \Omega^{-1}$ higher than the maximum of existing conductive oxide films and multilayers.

$\varphi_{TC} = 2 \times 10^{-2}\ \Omega^{-1}$, Liu et al ,Thin Solid Films,441(2003)200

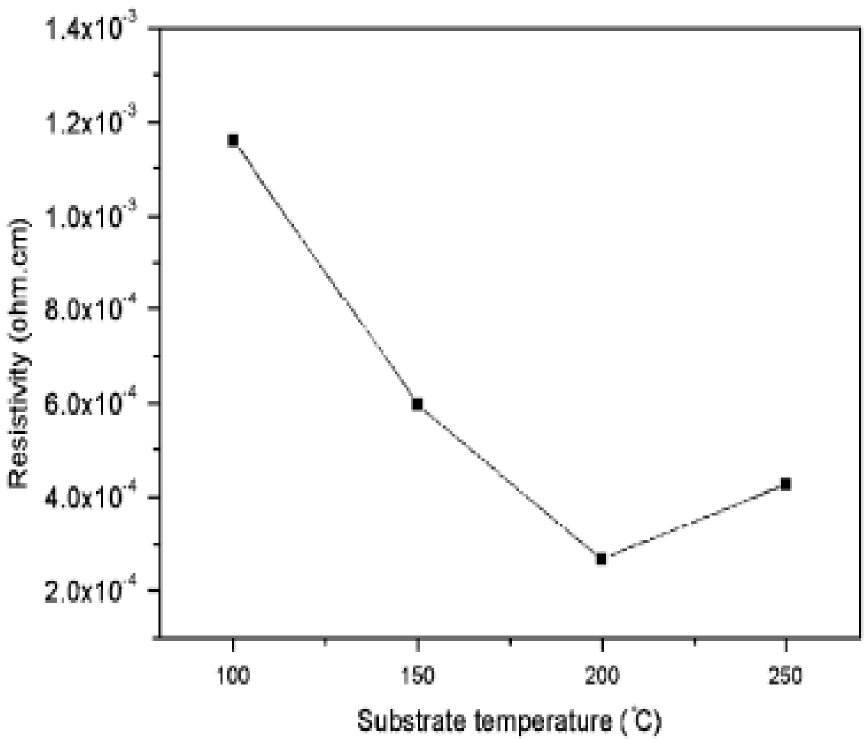


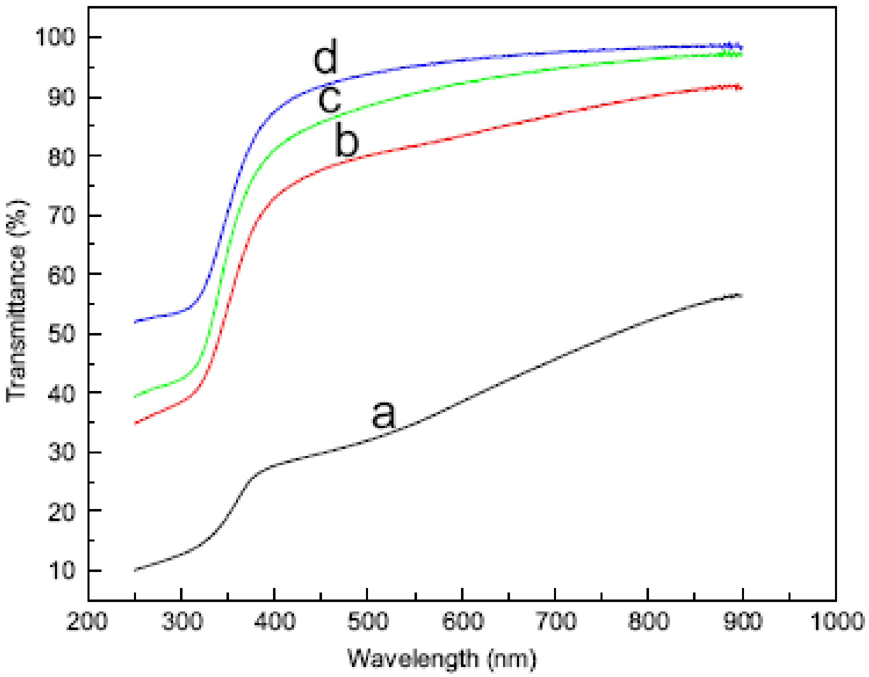




$\rho = 1.4 \times 10^{-5}\ \Omega.cm$

Al doped with ZnO (AZO)

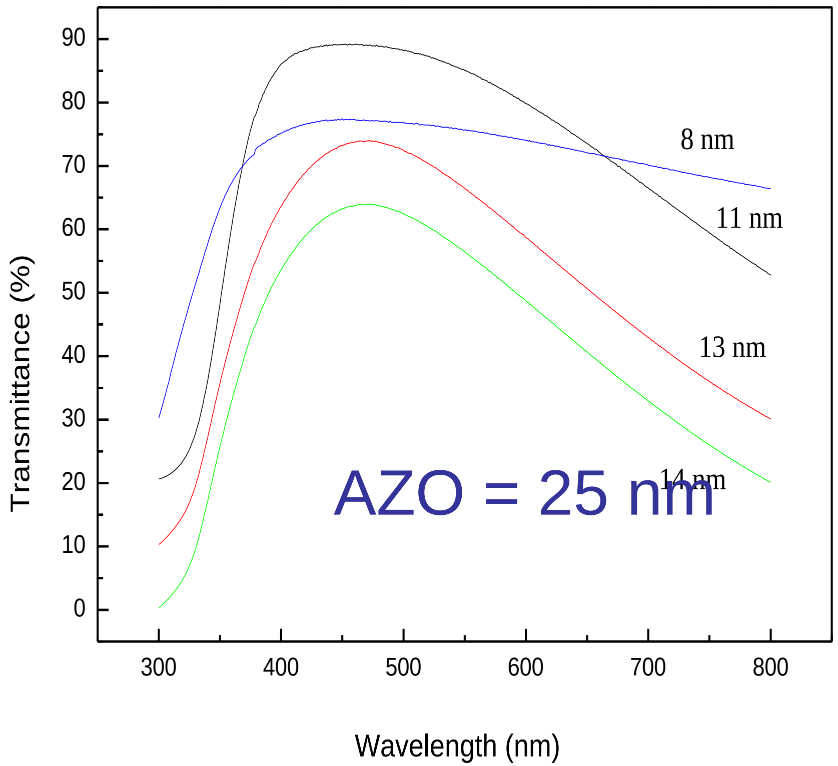


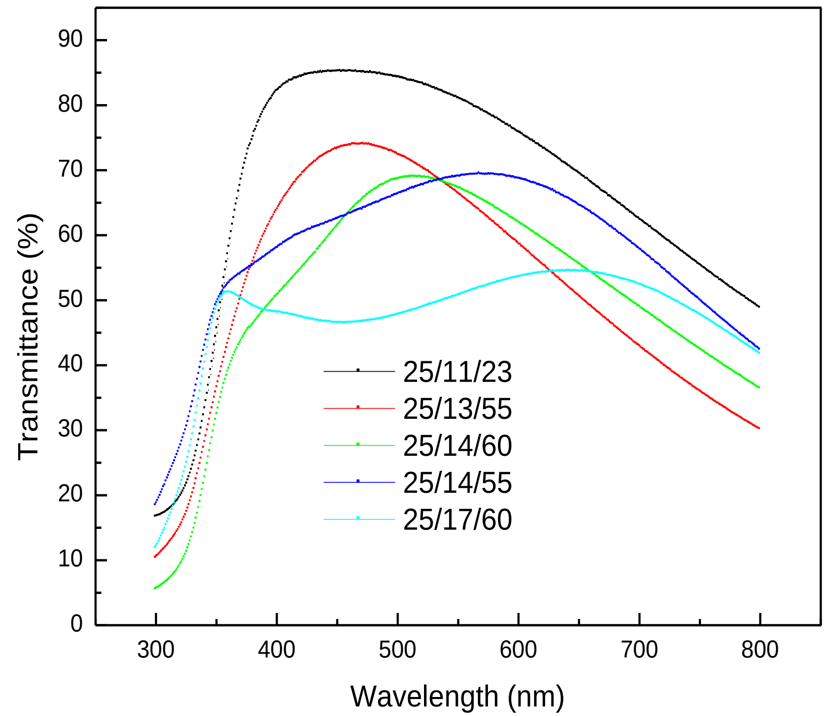


a. 100^0C (b) 150^0C (c) 200^0C (d) 250^0C substrate temperature

Resistivity: 2.5×10^{-4} Ω.cm and Transmittance > 80%

AZO / Ag / AZO multilayer





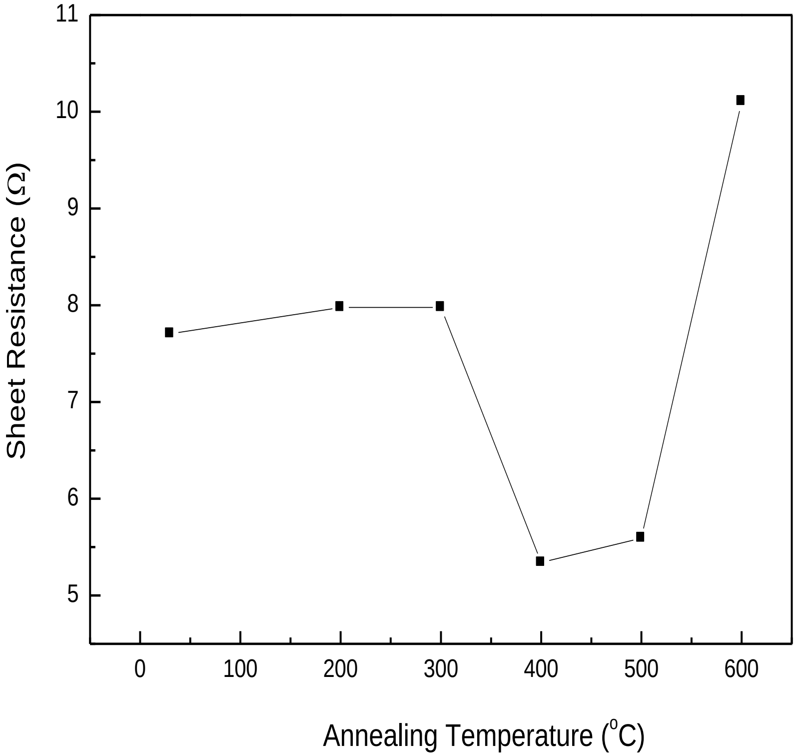
Importance of Ag layer thickness for maximum transmission

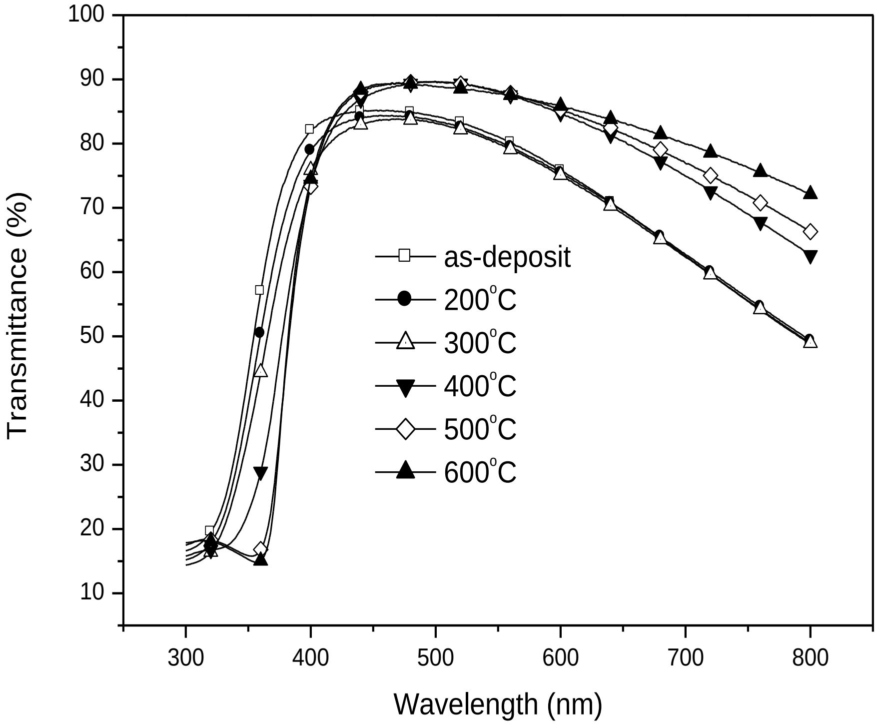
Optimum thickness11 nm : T > 80 %

Al-doped (AZO) /Ag/AZO multilayer

AZO = 25nm and Ag =11nm

Transmittance = 90 % & R_s = 5.34 Ω/sq.





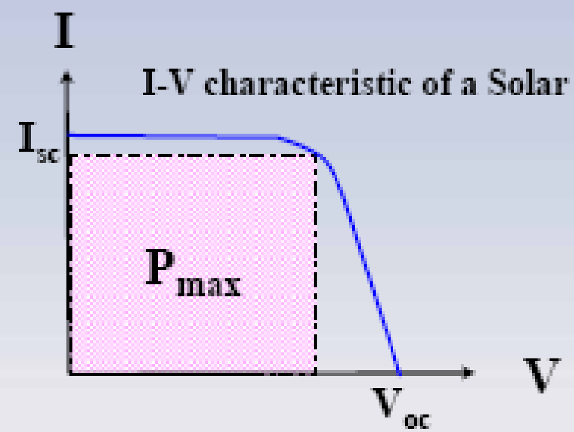
Thermal stability up to 500^0C

AZO/Ag/AZO shows better properties up to 500^0C where as ZnO/Ag/ZnO multilayers shows up to 400^0C.

Fabrication of Dye Sensitized Solar cell (DSSC)

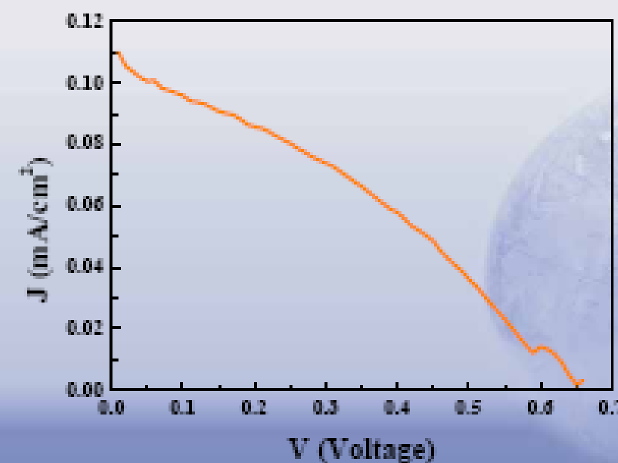
Photoelectrochemical Performance

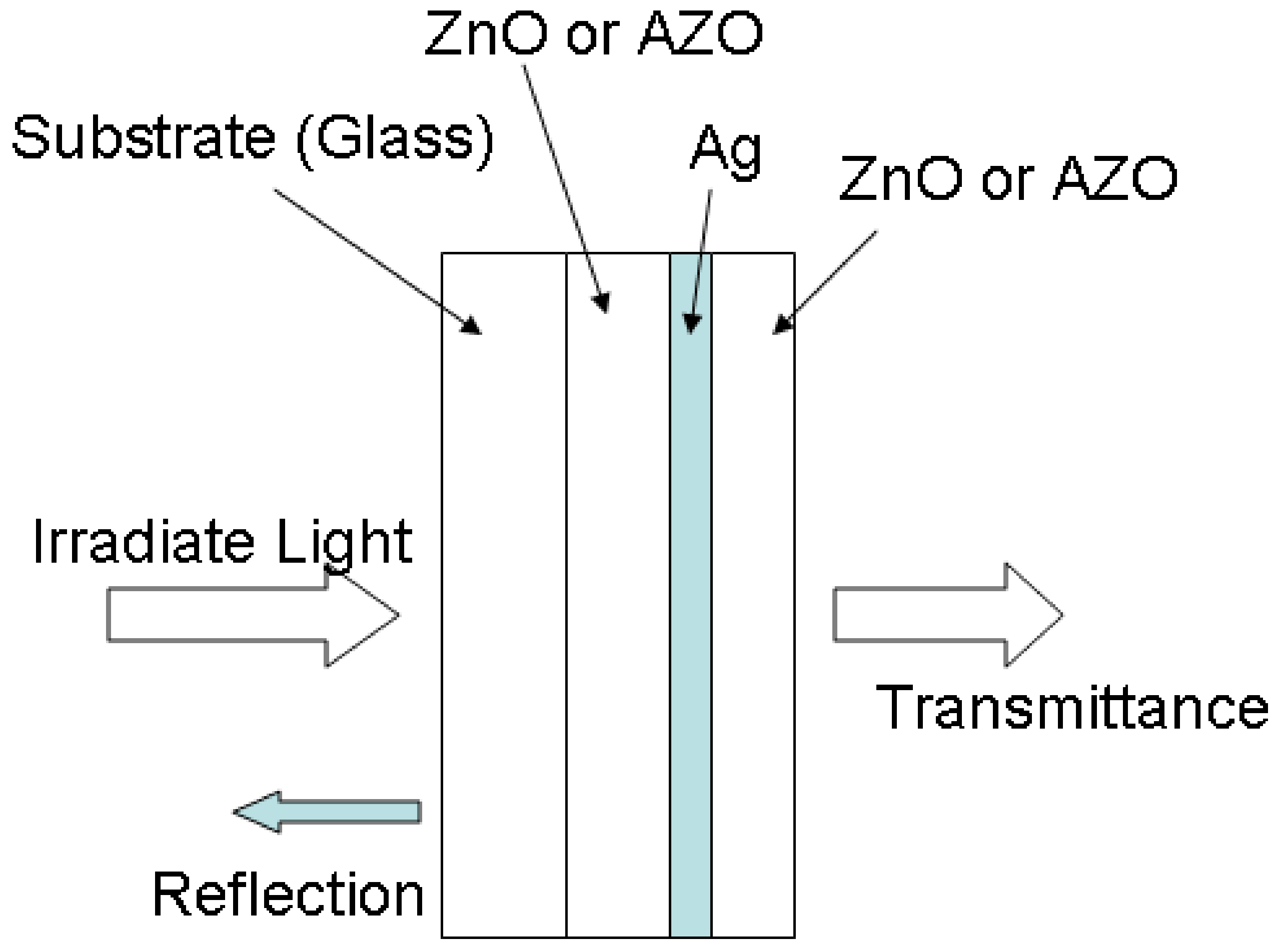
- Fill Factor(F.F.) $= \dfrac{P_{max}}{I_{sc} \times V_{oc}}$
- Conversion Efficiency $= \dfrac{F.F \times (I_{sc} \times V_{oc})}{I_{light}}$



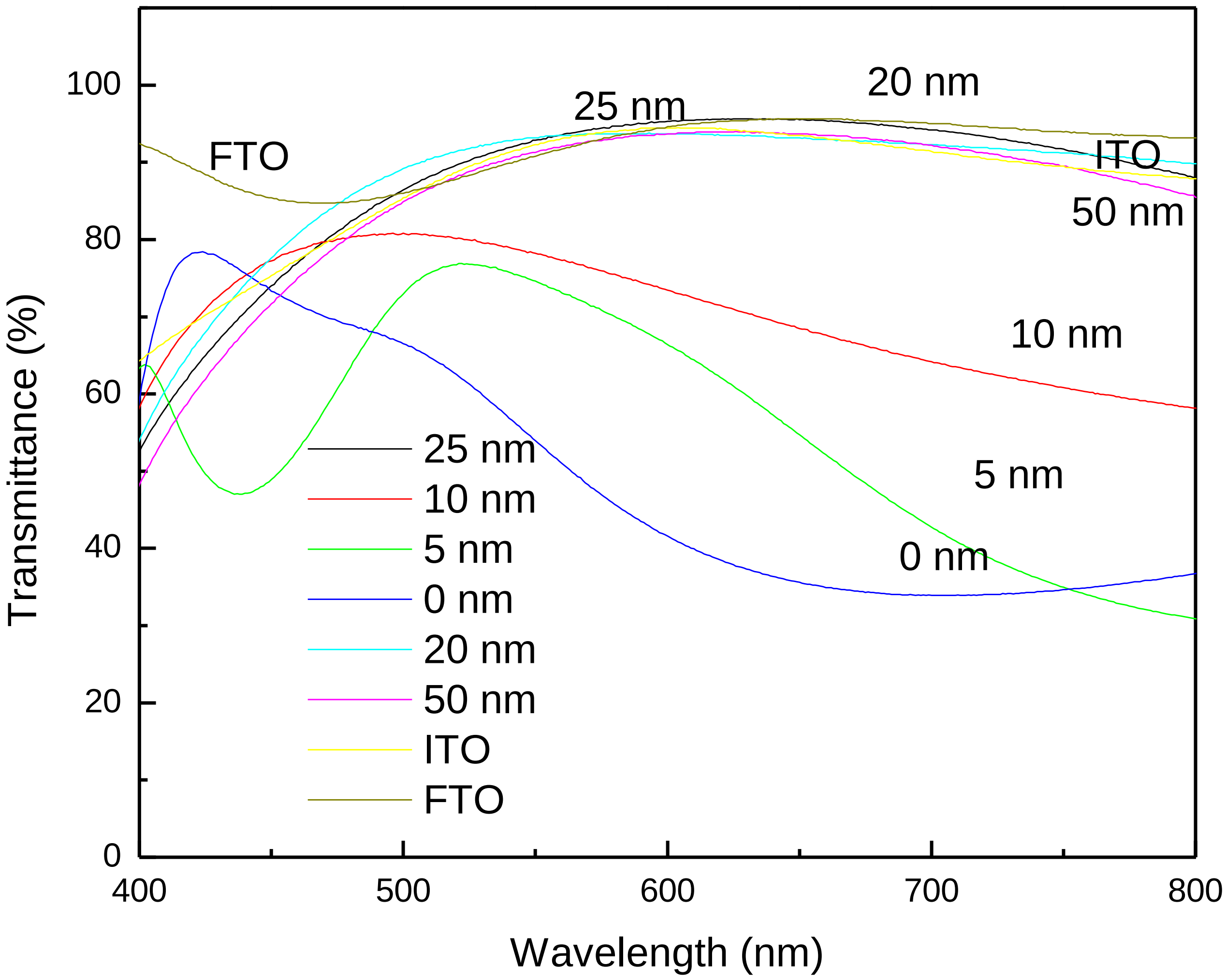
- I-V characteristic measurement of TiO_2 nanorods solar cell

I_{sc} = 0.1(mA)
V_{oc} = 0.66 (V)
F.F.= 0.34
η = 0.032%

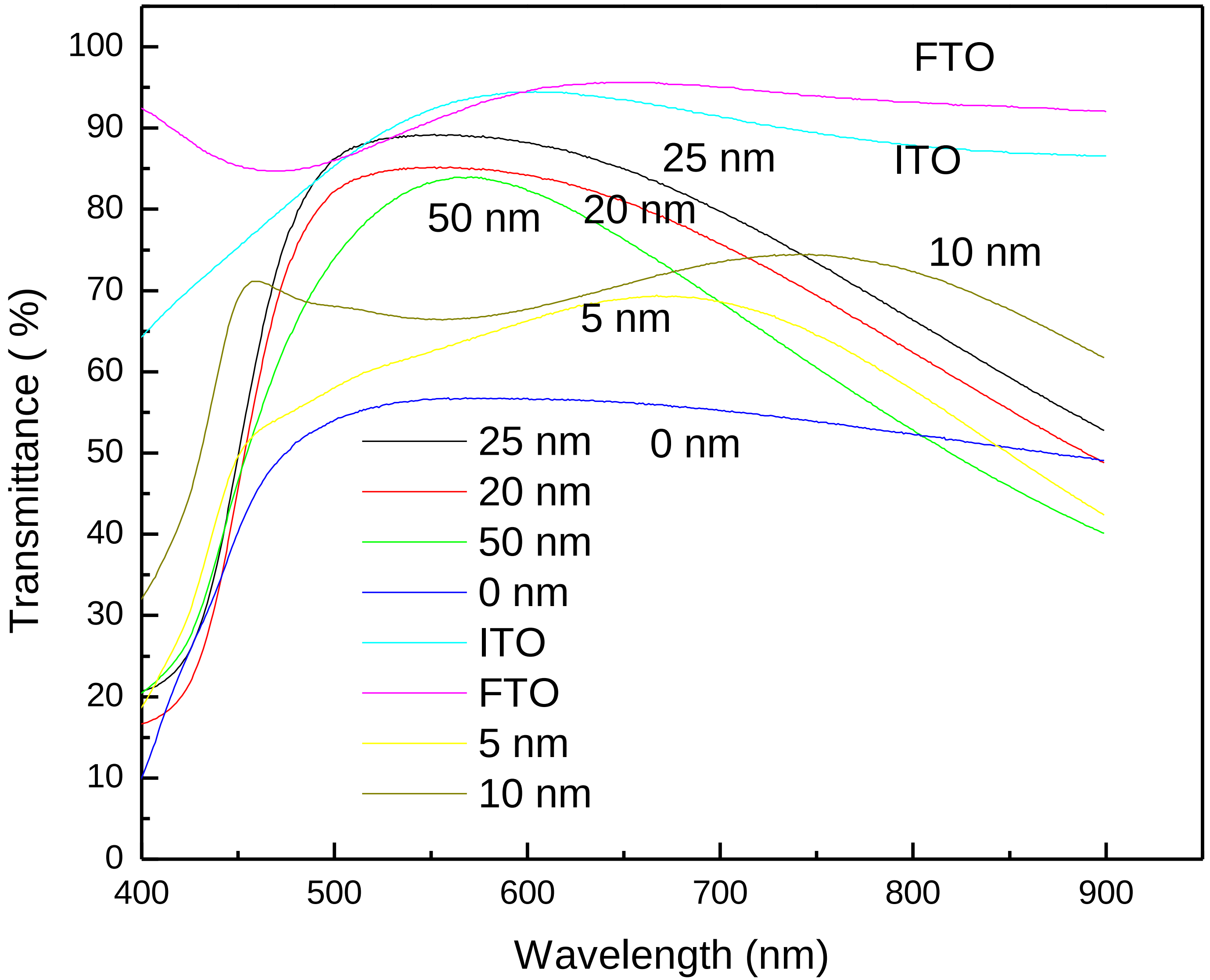



ZnO or AZO
Substrate (Glass)
Ag
ZnO or AZO
Irradiate Light
Transmittance
Reflection

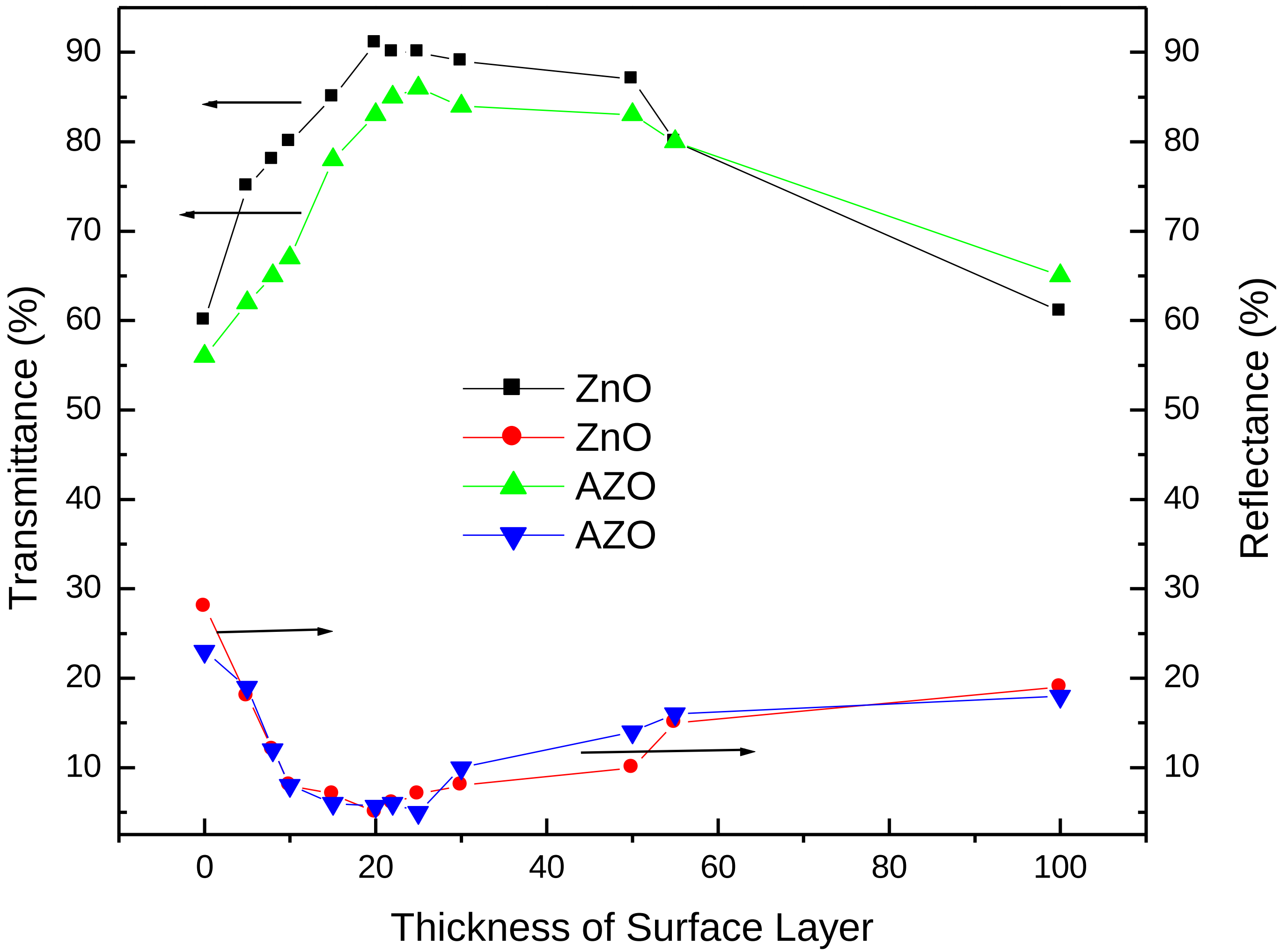
ZAZ Multilayer with different thickness of ZnO surface Layer



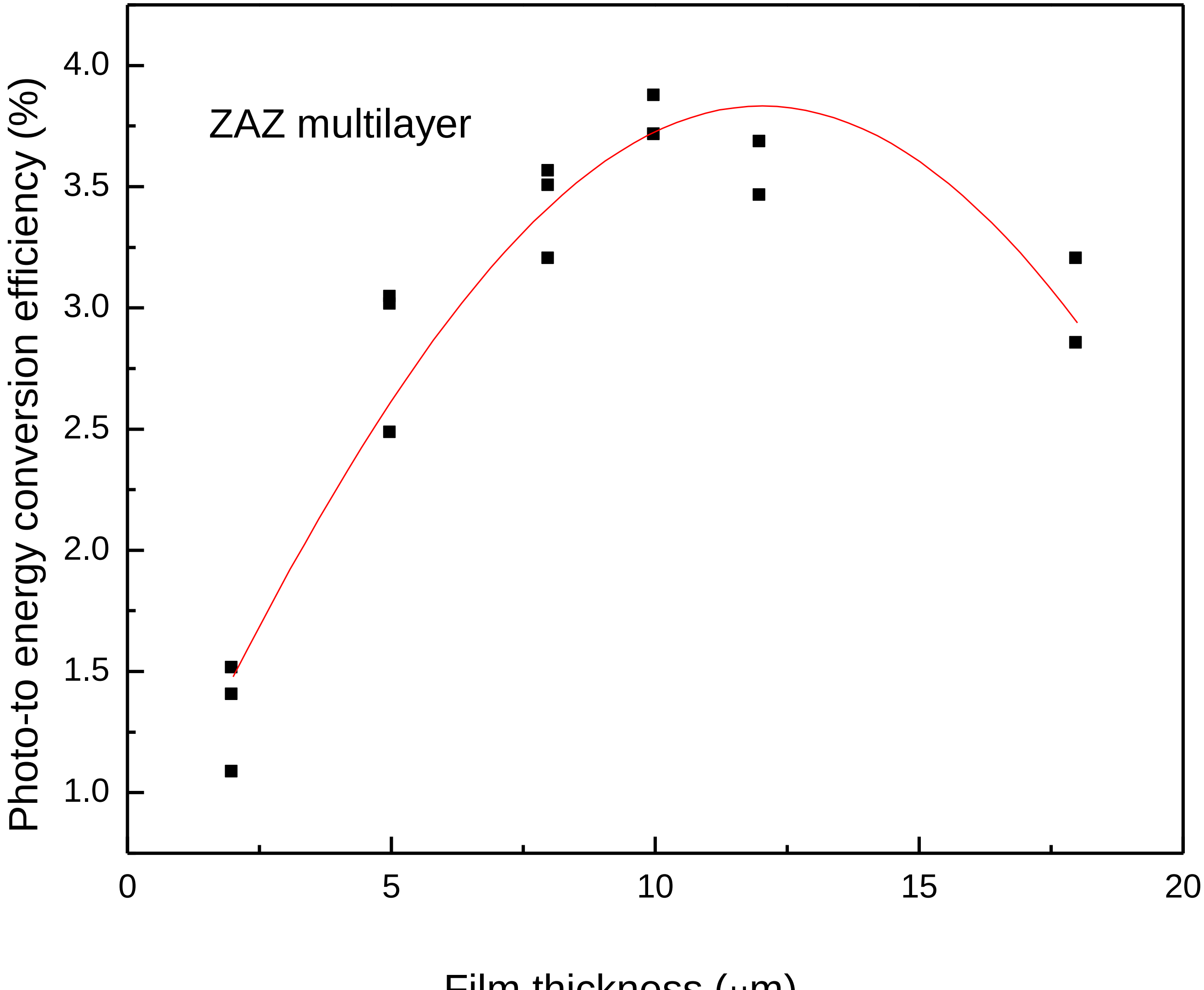
AAA Multilayer with different thickness of AZO surface Layer



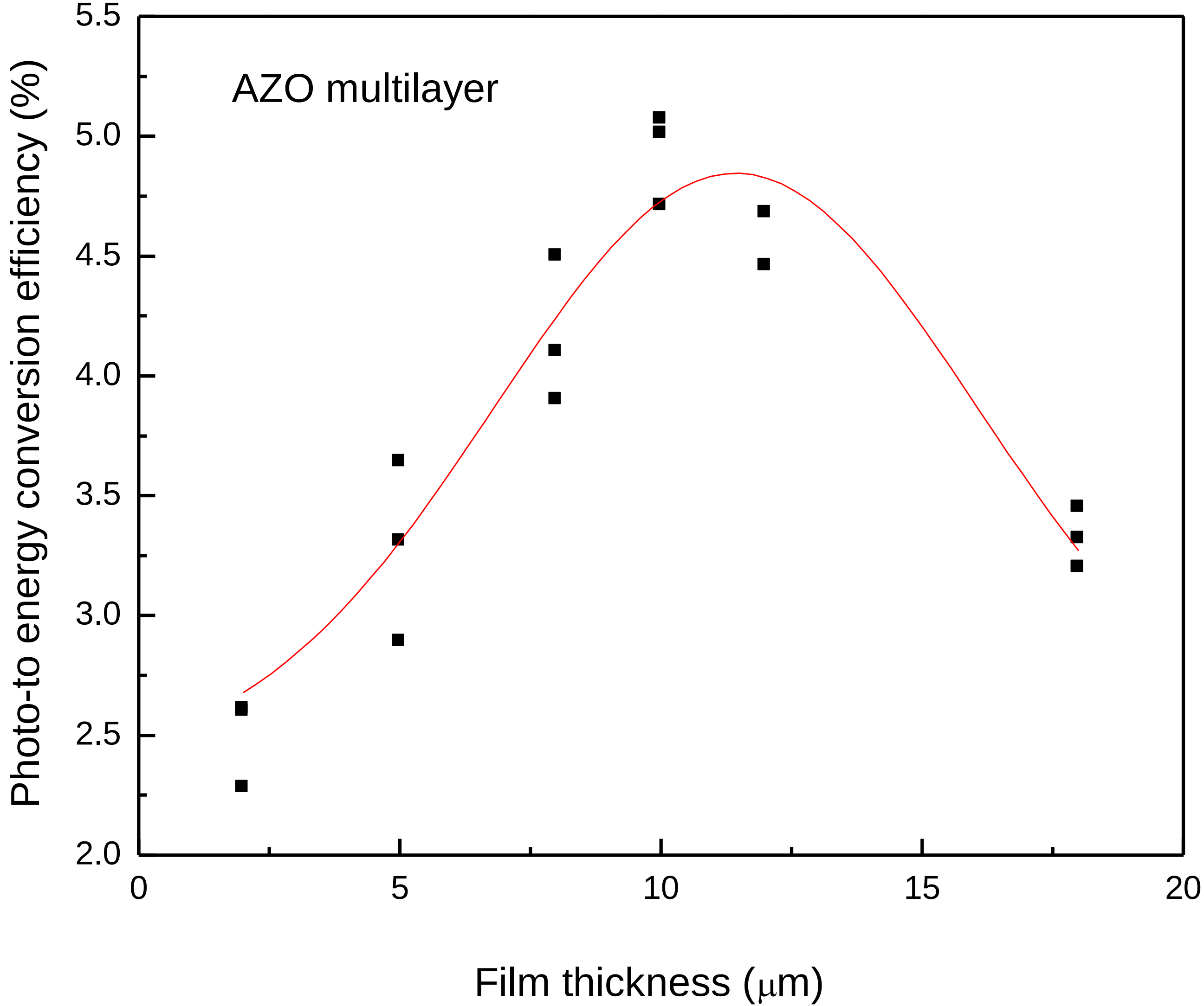
Maximum Transmittance Vs Thickness of Surface layer



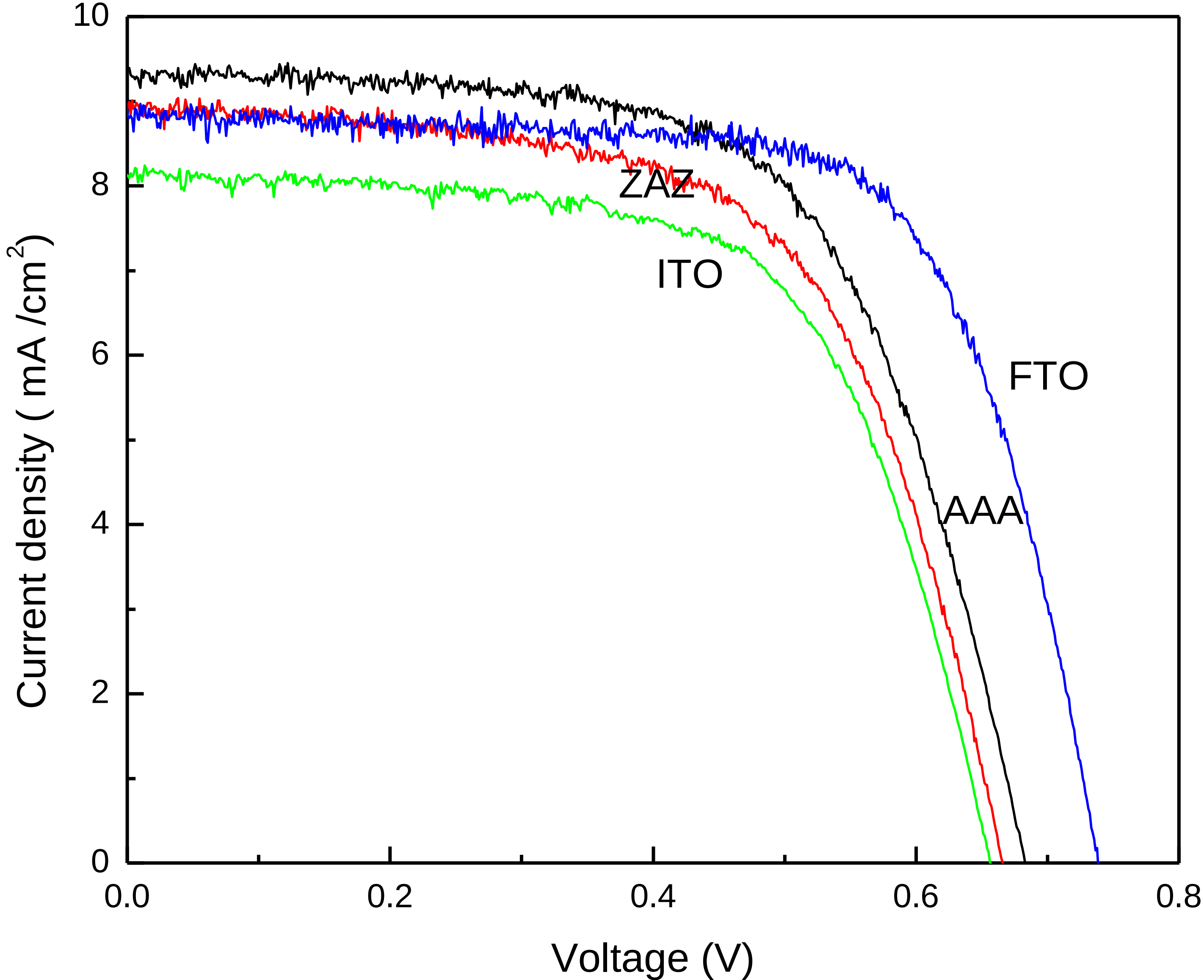
Light to energy conversion efficiencies of the DSSC with the thickness of the mesoporous TiO2 layer grown on ZAZ



Light to energy conversion efficiencies of the DSSC with the thickness of the mesoporous TiO_2 layer grown on AAA



The current (I)- Voltage(V) graph of the DSSC fabricated with ZAZ,AAA, ITO and FTO glass

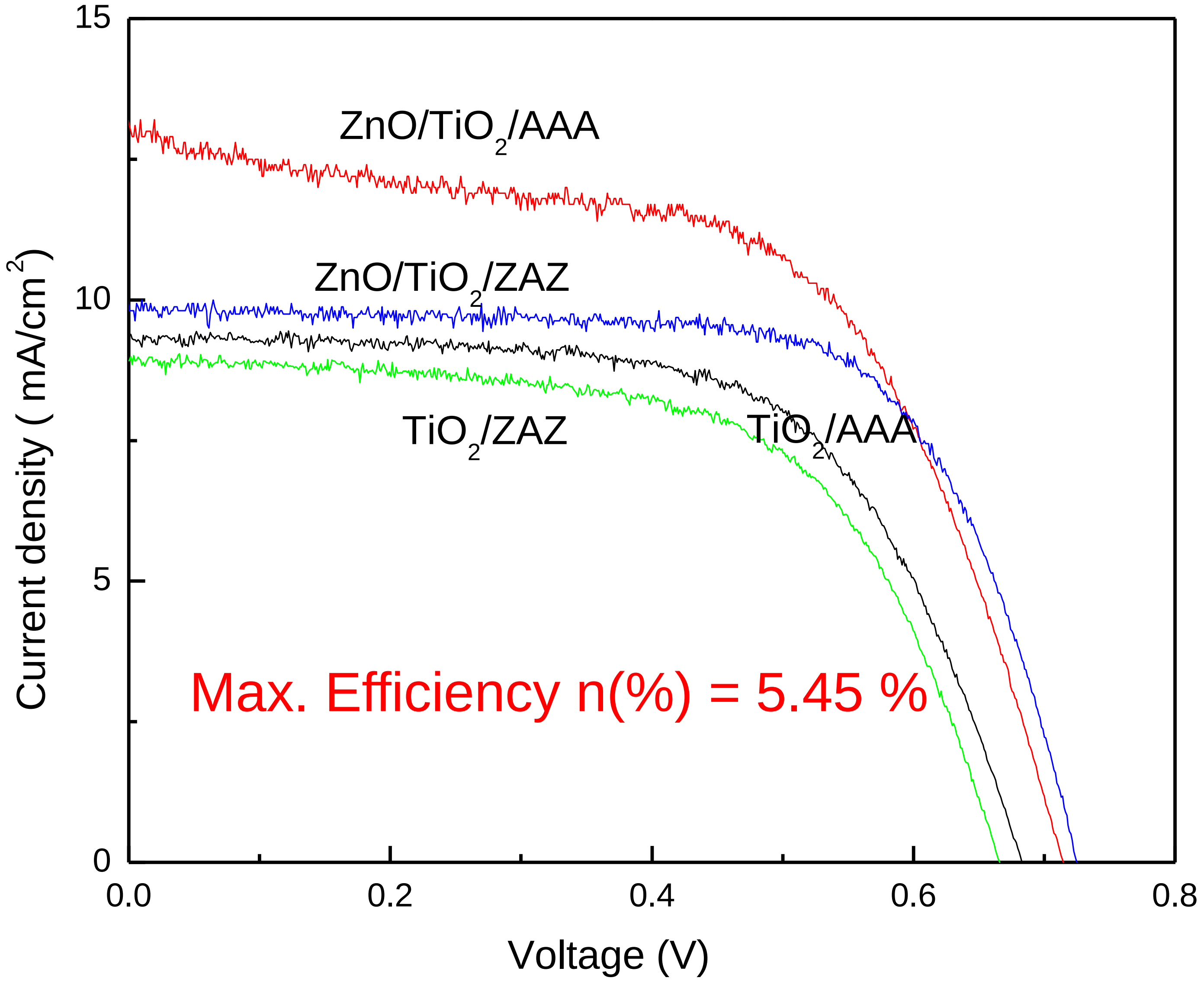


I-V Characteristics of DSSC fabricated using FTO, ITO, ZAZ, AAA and the mesoporous TiO_2 electrodes. Measured under AM 1.5 (100 mW cm^{-2})

	FTO	ITO	ZAZ	AAA
Jsc ($mAcm^{-2}$)	9. 36 (8.9-9.84)	8.92 (8.1-8.83	9.12 (8.9-9. 23)	**9. 84 (9.14- 10.2)**
V_{OC}	0.725 (0.66-0.73)	0.63 (0.66-0.69)	0.67 (0.66-0. 71)	0.72 (0.69-0.73)
FF	0.69 (0.66-0.71)	0.64 (0.61-0.64)	0.63 (0.62- 0. 68)	0.69 (0.67-0.69)
n%	4.68 (3.87-5.1)	3.59 (3.2-3.89)	3. 84 (3.64-4.45)	4. 89 (4.26-5.13)

Data are based on the averages of the dye sensitized cell samples; ranges of data are shown in parentheses

The I-V characteristics of DSSC with bare TiO_2 and ZnO/TiO_2 film electrodes on ZAZ and AAA.



Design of Devices and Circuits

Conclusions

- Suitable multilayer TCO electrode with sheet resistance of 7 □/sq and transmittance of more than 85 % are synthesized for fabrication of DSSC.

- The DSSC on AAO covered with ZnO/TiO_2 film yielded an overall cell efficiency 5.45 %.

- This developed multilayer TCO can be used as transparent electrode for making improved DSSC or plastic DSSC.

Thank you for your attention