

## Spectroscopic Ellipsometry study of ZnO thin films

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The demand for low cost, high performance optoelectronic devices leads to the development of more efficient transparent conductive oxide (TCO) thin films as transparent electrodes for thin film solar cells, photothermal conversion systems, gas sensors, optical position sensors, acoustic wave transducers, liquid-crystal displays, etc...

From all the TCO materials studied during recent years, zinc oxide (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties, its high chemical and mechanical stability and, owing to its abundance in nature, it is a lower cost material compared with the most currently used TCO materials ITO and SnO<sub>2</sub>. However, undoped ZnO thin films are not stable, especially at high temperatures. Doping the zinc oxide can reduce this disadvantage. Additionally doping leads to an increase in the conductivity of the ZnO thin films. Doping of ZnO is achieved by replacing Zn<sup>2+</sup> atoms with elements of higher valency such as indium, aluminium, and gallium.

These type of oxide materials can be produced by several techniques such as sputtering, thermal evaporation, spray pyrolysis, electrodeposition or sol-gel methods.

In this study the MM-16 Liquid Crystal Modulation Ellipsometry (LCME) was used to characterise material properties such as thickness and optical properties.

### Sample preparation

ZnO thin films were prepared by the sol-gel method. Zinc acetate dihydrate was used as starting material and dissolved in ethanol and monoethanolamine as a solvent and complexing agent, respectively. For doped films, aluminium nitrate was used and the Al/Zn molar ratio was varied from 1 to 3%. The precursor solution

was deposited by up to nine separate spin coating procedures at 3000 rpm for 30s, according to the intended number of layers. Doped and undoped films were pre-heated at 300°C (10min) after each coating and finally, heat treated at 550°C for 2 hours. [Prepared by LIMHP – Paris 13 University].

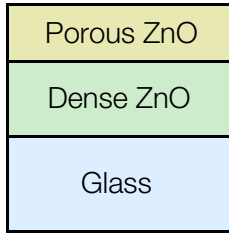
### Results

Ellipsometric measurements were collected at an angle of incidence of 70° across the spectral range 430-850 nm. SE measures the ellipsometric angles  $\Psi$  and  $\Delta$  as defined by the fundamental equation of ellipsometry (1), where  $r_p$  and  $r_s$  are the Fresnel reflection coefficients, parallel and perpendicular to the plane of incidence, respectively:

$$\rho = \frac{r_p}{r_s} = \tan\Psi * e^{i\Delta} \quad (1)$$

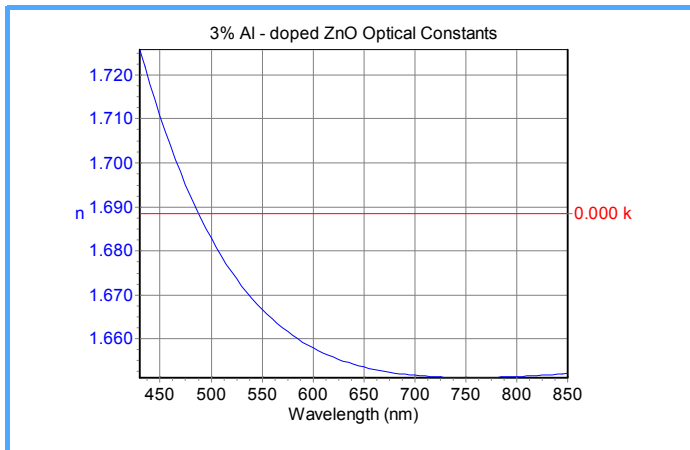
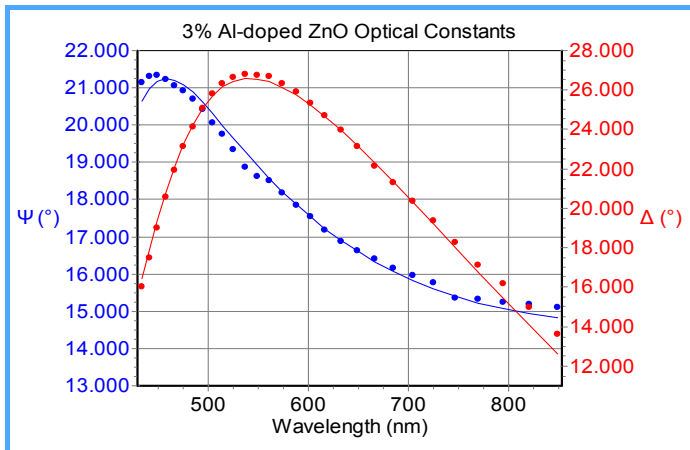
Both thickness and optical properties were extracted from the SE data analysis. The fitting process is used to adjust the theoretical data to experimental data. The optical constants of the samples have been determined using the new-amorphous dispersion formula.

For each sample, and in this study the number of layers varies from 2 to 9, the optical constants are accurately described with a two-layer model which is illustrated below.



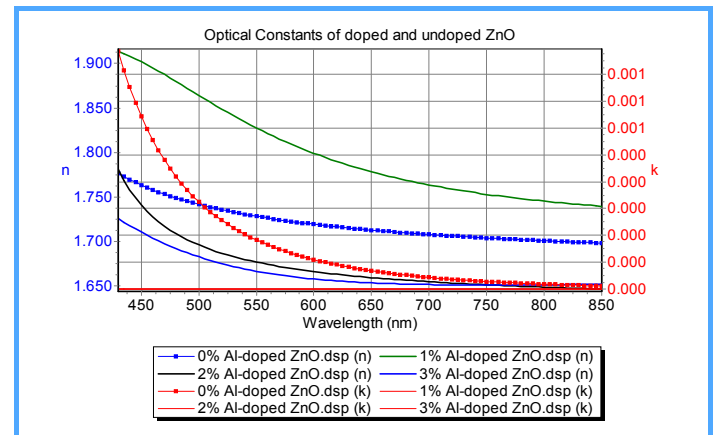
The model takes into account a dense ZnO layer at the bottom of the structure with a porous layer above. The presence of the porous layer in the model gives a significant improvement to the  $\chi^2$  value when compared to the single layer model. For each sample the porous layer thickness has an average value close to 50 nm.

The data presented below are for samples with 3 deposition cycles.



The figure below shows that the refractive index decreases when doping concentration increases from 1 to 3% Al. On the other hand, the refractive index of pure ZnO film is situated among those of doped films with 1 and 2% aluminium.

Sample reference	Dense layer thickness (Å)	Porous layer thickness (Å)
Undoped ZnO	1268	548
1% Al - doped ZnO	1128	610
2% Al - doped ZnO	1231	315
3% Al - doped ZnO	1510	484



## Conclusion

The sensitivity of the MM-16 Spectroscopic Ellipsometer is such that characterisation of different doping concentrations of Al in ZnO is possible. Further to this the MM-16 LCME allows the highest sensitivity and precision of the ellipsometric angles across the full range  $[0^\circ, 360^\circ]$ , even when  $\Delta$  is close to  $0^\circ$ , and this performance is essential when characterising thin transparent films.