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_2. 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^{2+} 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 Phase Modulated Spectroscopic Ellipsometry (PMSE) 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 preheated at 300°C (10min) after each coating and finally, heat treated at 550°C for 2 hours. [Prepared by LIMHP – Paris 13 University].

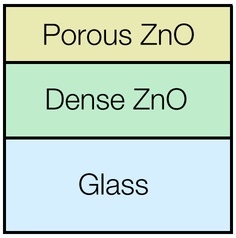
Results

Ellipsometric measurements were collected at an angle of incidence of 70° across the spectral range 310-1700 nm. SE measures the ellipsometric angles Ψ and Δ as defined by the fundamental equation of ellipsometry (1), where rp and rs are the Fresnel reflection coefficients, parallel and perpendicular to the plane of incidence, respectively:

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

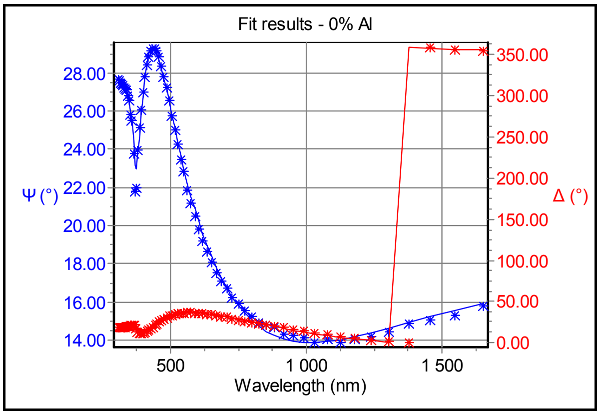
A large spectral range has been chosen for accurate characterisation of the ZnO thin films as they exhibit strong absorption in the FUV range. Both thickness and optical properties were extracted from the SE data analysis simultaneously. The spectroscopic measurements exhibit two different parts. Between 310-1700 nm, the ZnO layer is transparent introducing interference fringes, whilst at higher energies the film becomes completely absorbing. The fitting process is used to adjust the theoretical data to the experimental data. The optical constants of the samples have been determined using the new-amorphous dispersion formula.

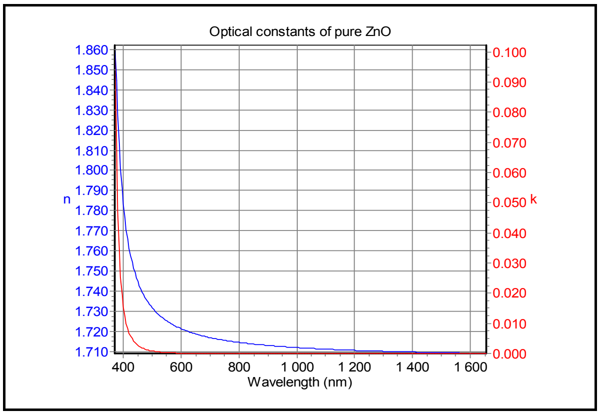
For each sample, and in this study the number of layers varies from 2 to 9, the optical constants are accurately described with a two-layer model which is illustrated below.



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 following table 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)	Dense layer	
			Refractive index at 632.8 nm	Refractive index at 1.55 µm
Undoped ZnO	1229	561	1.719	1.709
1% Al - doped ZnO	1108	659	1.772	1.748
2% Al - doped ZnO	838	515	1.691	1.689
3% Al - doped ZnO	1544	404	1.667	1.664

Conclusion

The sensitivity of Spectroscopic Ellipsometry is such that characterisation of different doping concentrations of Al in ZnO is possible. Further to this the UVISEL PMSE allows the highest sensitivity and precision of the ellipsometric angles across the full range [0°, 360°], even when Δ is close to 0°, and this performance is essential when characterising thin transparent films.

Bibliography

- «Properties of pure and Al-doped ZnO Thin Films synthesized by soft chemistry», L. Znaidi, S. Ben Yahia, J. P. Gaston, J. Kurdi, J. F. Guillemoles (submitted).
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