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# The doping effect on the properties of zinc oxide (ZnO) thin layers for photovoltaic applications

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## ARTICLE INFO

### Article history:

Received 28 January 2015

Received in revised form

19 February 2015

Accepted 20 February 2015

Available online 29 March 2015

### Keywords:

Thin layer

New material

Solar cell

Photovoltaic

## ABSTRACT

In this study, we experimentally elaborated Copper- and Indium-doped Zinc Oxide (Cu: ZnO and In: ZnO) thin films at different temperatures ( $T_1 = 480$  °C and  $T_2 = 520$  °C), the doping ratio were varied between 0% and 8%. Using a low cost solution-based chemical deposition, we have developed a ZnO thin film deposition process that offers fine-control of the surface morphology. It consists in spraying a volatile compound of the material to be deposited on a substrate maintained at high temperature to cause a chemical reaction in order to form at least one solid product. Therefore, the proposed ZnO doped layer is highly promising for applications for the next-generation solar cells.

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## Introduction

In the last decades, the development of materials using thin layers has contributed to the expansion of the electronics and optoelectronics performance. Moreover, the new open field of low cost and unbreakable large area photovoltaic devices implies the use of small size devices as an available cheap solution. The thin layers can be elaborated from a wide range of compositions such as conductive materials, insulators, semiconductors and polymers [1–3]. It is found that physical properties are closely related to the deposition parameters, mono or multilayer films can be synthesised with different thicknesses, typically from one monolayer to few hundred micrometres [4,5]. The Zinc Oxide (ZnO) semiconductors were

currently studied; various methods have been used to synthesis ZnO-based thin layers. However, a big progress on the synthesis techniques of thin films and the results indicate the possibility of converting the conductivity of the semiconductor n-type to p-type. The nanotechnology revolution has given him a place among the master race materials for optoelectronic applications; this is due to the multiple benefits that we present in this work. Transparent conductive oxides (TCO) are remarkable materials in many areas. The existence of their dual properties, electrical conductivity and transparency in the visible range, making them ideal candidates for applications in optoelectronics, photovoltaic or electro chromic windows [6–9]. Sponge-like ZnO thin film shows promising prospects as Li-ion battery anode [10]. Dye-sensitized solar cells with an energy storage function are demonstrated

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<http://dx.doi.org/10.1016/j.ijhydene.2015.02.075>

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by modifying its counter electrode with a poly ZnO nanowire array composite. This simplex device could still function as an ordinary solar cell with a steady photocurrent output even after being fully charged [11].

At the vanguard of these materials, the (ZnO) is a semiconductor oxide which presents very interesting properties. In nature, it is ruby red in colour and is found abundantly in minerals, while artificially prepared is colourless or white. If the properties of natural ZnO have long been known, the researchers focused in recent years on the ZnO obtained artificially. ZnO is a potential candidate for the UV-emitting systems as it possesses at room temperature a large gap (3.37 eV) and a large exciting binding energy (60 meV) [6]. It is also an excellent optics in high performance photovoltaic devices, such as the HIT structure or CIGS based thin layers [1].

### Study of the optical properties

TCO ZnO is transparent in the visible and near infrared field. This later is considered as “twin” of gallium nitride. It can be used for potential applications in the fields of photovoltaic, light emitting diodes for illumination, transparent conductive oxides, photonics or sensors (Fig. 1.) The main advantage of ZnO-based devices is due to its components which are non-toxic and very abundant on earth. This is an important advantage because it reduces production costs. It can also be found in nature in the form of powder or solid crystal. It is in the form of mineral [12].

It was shown that is possible to have an n-type ZnO with many elements such as Al [1], Ga [2] In [3], etc. orp-type doping which remains, meanwhile, still controversial. The advent of p-type ZnO will open the door to transparent electronics the formation's reaction of stoichiometric ZnO [13].



The measure of transmission (T) is done by placing the sample at the entrance to the sphere (position 1 in Fig. 2). The

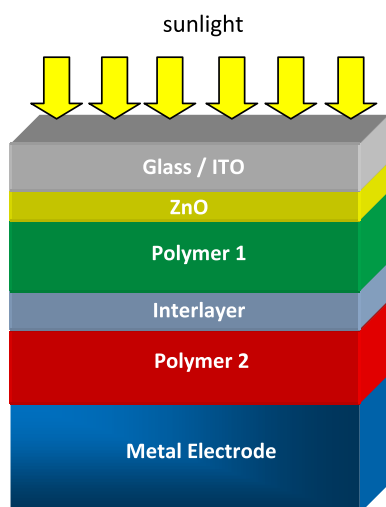


Fig. 1 – Structure of a solar cell made of material and the ZnO thin layers.

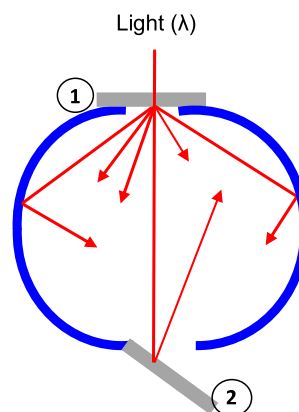


Fig. 2 – Schematic illustration of the Sub-Split-Step Fourier method distribution.

light produced by the source passes first through the sample and the sphere harvest as well as the light that was transmitted through the sample. The sphere harvests as well as the light that was transmitted through the sample. The reflectance measuring R is done by placing the sample in place of a small square of the sphere wall, located as opposed to the entrance of this one (position 2 in Fig. 2).

It is important to note that these measurements of T and R were performed on ZnO films deposited on a glass substrate. The light when it passes through the sample, it passes through several media having different refractive indices, in the following order: air/ZnO/glass/air. We can grossly evaluate the proportion of light that is reflected at these interfaces, using equation (2).

$$R = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2 \quad (2)$$

R: part of the reflected light when it passes between two media of refractive index  $n_2$  and  $n_1$ . If we consider that the reflections that occur when the light passes in each medium, and we take  $n_{\text{air}} = 1$ ,  $n_{\text{glass}} = 1.5$  and  $n_{\text{ZnO}} = 2$ , the part of the light reflected to different interfaces is about 17%. This calculation does not take into account the different roughness of the interfaces, which may also influence R. Therefore the R and T measurements performed with the spectrometer to the ZnO layers deposited on a glass substrate does not fully correspond to values of the transmitted and reflected light in a solar cell.

### Optical transmission

The optical characterizations were based on the transmission spectra in the visible-UV. Indeed, as has been detailed in the previous section, the operation of the spectra allows us to calculate the optical gap. Figs. 3–6 combined transmission spectra in the range of 250–1000 nm, the films prepared with the two dopants Cu and In. Even though the general shape of the spectra is the same, they are composed of two parts:

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