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## UV PHOTORESPONSE OF ZnO FILMS MEASURED OVER LONG PERIODS

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### Resumen

El ZnO es un material semiconductor tipo n con una alta energía de ligadura excitónica (60 meV) y un bandgap directo de 3,37 eV. Esta última característica hace que se lo considere un material fotoconductor, apto para la detección UV.

La fotoconductividad es una propiedad importante en los sólidos por medio de la cual la conductividad global de la muestra cambia debido a la radiación incidente. En general esta propiedad es un proceso complejo que incluye la generación y recombinación de portadores de carga y su transporte a los electrodos. En el caso del ZnO, la interpretación de la fotoconductividad resulta particularmente difícil por el hecho que, además de los mencionados, ocurren simultáneamente otros procesos, entre ellos la absorción y desorción de oxígeno sobre la superficie.

En el presente trabajo se estudió la fotorespuesta de films de ZnO nanoestructurados obtenidos por el método de sol-gel y depositados por spin-coating, para tiempos largos de exposición a la radiación o en oscuridad.

En los gráficos obtenidos de resistencia vs. tiempo se observa que, tanto en el pasaje desde la oscuridad hacia la iluminación UV, como a la inversa, hay un efecto de cambio de tendencia en el comportamiento de la curva luego de un período de horas. La mayoría de los trabajos existentes en literatura se relacionan con las características de dispositivos detectores de UV en tiempos muy breves de exposición-oscuridad (no mayores a algunos minutos). En los trabajos existentes con mediciones a tiempos largos no se hace mención a este comportamiento. Se discuten posibles mecanismos involucrados.

## Abstract

ZnO is an n-type semiconductor material with a high exciton binding energy (60 meV) and a direct bandgap of 3.37 eV. This last characteristic makes it considered a photoconductive material, suitable for UV detection.

Photoconductivity is an important property in solids whereby the overall conductivity of the sample changes due to incident radiation. In general, this property is a complex process that includes the generation and recombination of charge carriers and their transport to the electrodes. In the case of ZnO, the interpretation of photoconductivity is particularly difficult due to the fact that, in addition to the aforementioned effects, other processes occur simultaneously, including the absorption and desorption of oxygen on the surface.

In the present work, the photo response of nanostructured ZnO films obtained by the sol-gel method and deposited by spin-coating, was studied for long times of exposure to radiation or in the dark.

On the resistance vs. time curves, it is observed that, both in the passage from darkness to UV illumination and vice versa, there are changes in the behavior of the curve after a period of hours. Most of the existing works in the literature are related to the characteristics of UV detection devices in very short exposure-dark times (no longer than a few minutes). In the existing works with measurements at long times, there is no mention about this behavior. Possible mechanisms involved are discussed.

**Palabras clave:** ZnO; películas nanocristalinas; fotoconductividad; UV.

**Keywords:** ZnO; nanocrystalline films; photoconductivity; UV.

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## 1. Introduction

ZnO is a semiconductor material with a high exciton binding energy (60 meV) and a direct bandgap of 3.37 eV. This last characteristic makes it a photoconductive material, suitable for UV detection<sup>1</sup>, as well as a promising candidate for photonic devices in the UV spectral range at room temperature<sup>2</sup>. It is used in device systems such as photodetectors, gas sensors, photoemission and field emission devices, and Schottky diodes.

Undoped ZnO typically exhibits n-type conductivity, which many authors often associate with oxygen vacancies. However, first principles calculations showed that oxygen vacancies are not associated with shallow donor levels, but rather with deep levels<sup>3</sup>. The origin of n-type conductivity to this day remains a matter of debate. The presence of this and other native defects in the crystal, such as zinc interstitials or involuntary impurities, play a very important role in the

electrical properties of the material, both directly and through the interaction of the material with the surrounding atmosphere.

The interpretation of photoconductivity in ZnO is not simple at all, because many aspects of a semiconductor are involved simultaneously: optical absorption, carrier recombination kinetics, defects that control the useful life and transport properties, and among the most important, the absorption and desorption of oxygen on the surface<sup>1,4,5</sup>.

According to the theory, it would be expected that as soon as the lighting is interrupted, the conductivity drop very rapidly; but in ZnO this is known not to happen. On the contrary, the decay process is very slow and it is governed by surface effects such as absorption and desorption of oxygen gas<sup>4,6</sup>.

An understanding of all these processes would allow the development of more stable and reliable devices.

## **2. Materiale y Methods**

### ***2.1 Synthesis of the films***

For the synthesis of the films, a precursor solution was prepared using zinc acetate dihydrated  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (ZAD) (Merck) as organic precursor agent, absolute ethanol (EtOH) (Merck) as solvent and acetic acid (HAC) (Merck) in aqueous solution to promote hydrolysis, in the following molar ratios:  $\text{Zn} / \text{EtOH} = 0.012$ ;  $\text{HAC} / \text{Zn} = 0.01$  (in a 0.08M aqueous solution).

The solution was kept under reflux and with constant thermal stirring at 67 °C for 1 hour. After 24 hours of aging at room temperature, the solution was deposited on quartz substrates by spin-coating technique. After each deposit, the samples received a drying treatment at 200 °C for 10 min. There were made as many deposits as the desired number of layers. Finally, the samples received a final heat treatment at 450 °C for 3 hours.

## **2.2 Structural and morphological characterization**

The samples were characterized by grazing incidence X-ray diffraction (GIXRD) (incidence angle  $\alpha_i = 1^\circ$ ) using a conventional Phillips PW 3710, Cu-K $\alpha$  (1.54056 Å) equipment.

The observation of the films was carried out in a Kar Zeiss FESEM DSM 982 Gemini scanning microscope, belonging to the Advanced Microscopy Center, FCEyN, UBA.

## **2.3 Electrical characterization**

The electrical characterization of the films was carried out by the four-point method, for which, on the ZnO films, four rectangular, parallel and equidistant Au electrodes were made. Such electrodes were deposited by sputtering, using an *ad hoc* matrix of our own design (built in the laboratory).

The measurements were made by mounting a system in a tube oven at 50 °C in order to keep the film in absolute darkness and isolated from any source of external light excitation, avoiding at the same time fluctuations in room temperature and humidity. The resistivity of a sample is determined from the injection of a current  $I$  between the external electrodes and the measurement of the voltage  $V$  between the internal electrodes.

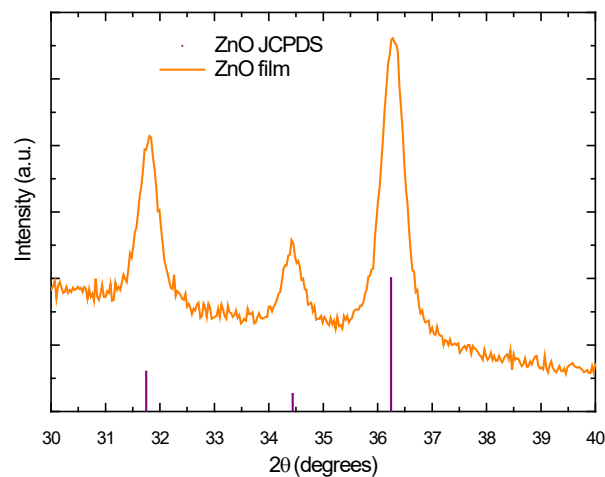
## **2.4 Photoconductivity Measurements**

For the photoconductivity study, a source of UV LEDs with wavelength  $\lambda = 395$  nm was constructed, which was mounted above the sample.

In this work, only the results obtained corresponding to a 12-layer film are shown. In the measurements presented, the periods of both darkness and illumination were greater than 15 hours, with records at 10-minute intervals.

### 3. Results

In Figure 1 it can be seen the GIXRD diffractogram corresponding to the ZnO film, in the  $2\theta$  range between  $30^\circ$  and  $40^\circ$ , where the main peaks corresponding to the reflections of the (100), (002) and (101) planes of the hexagonal wurtzite structure of ZnO appear <sup>7</sup>.

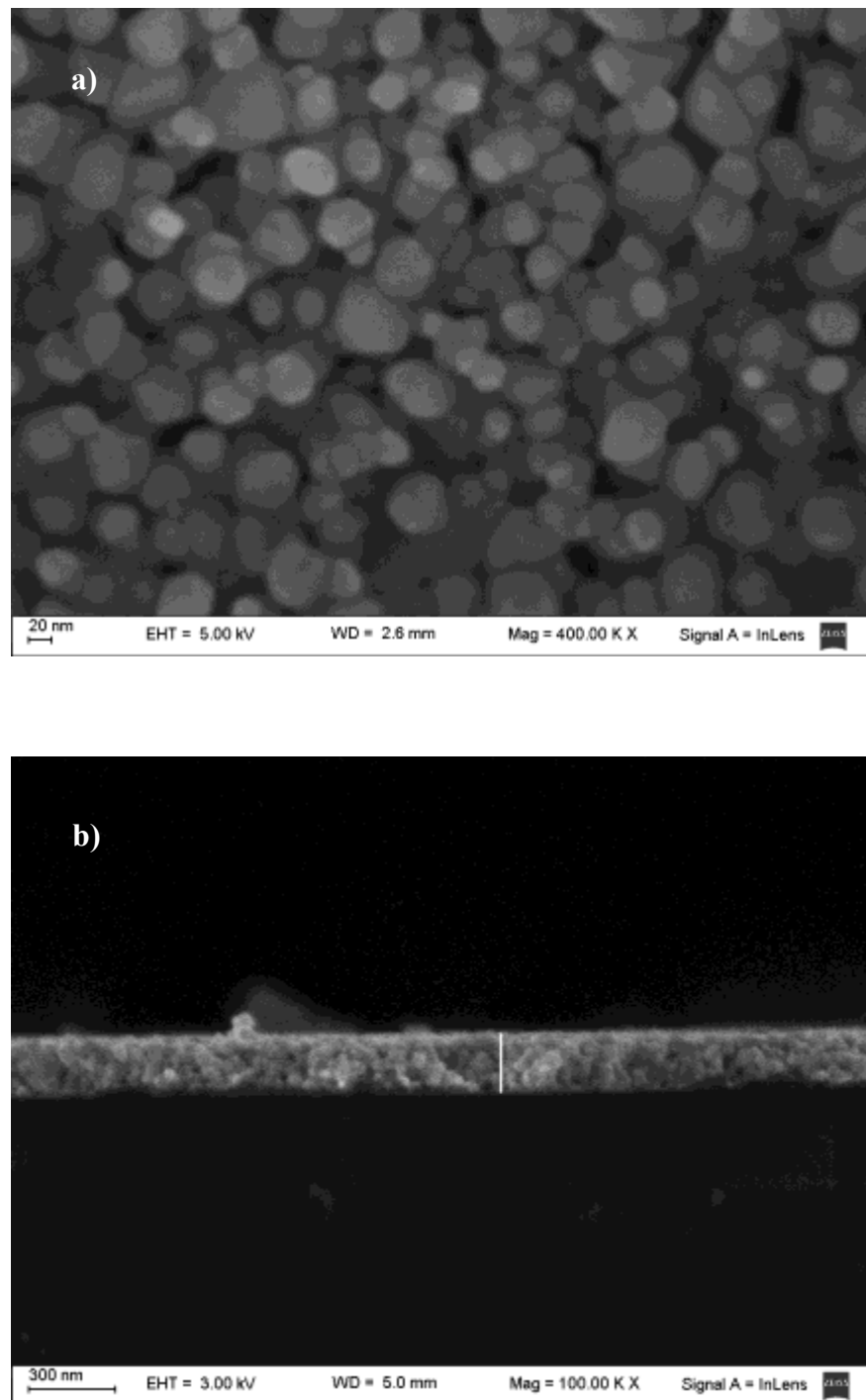


**Figure 1.** GIXRD diffractogram corresponding to the 12 layers ZnO sample

Figure 2 corresponds to FESEM micrographs of the studied ZnO sample: image a) shows the topography of the surface film, while image b) presents the profile. It can be seen a continuous film with a uniform thickness of about 220 nm, made up of nanometric particles.

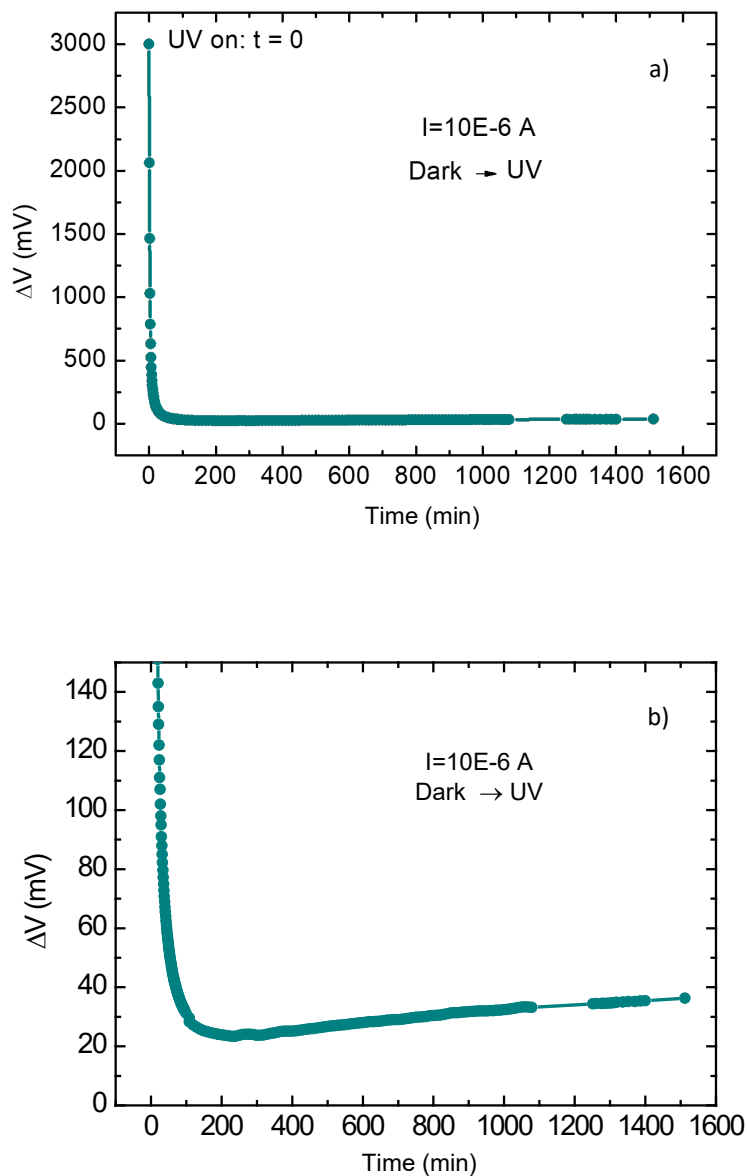
Graphs presented in Figures 3 and 4 correspond to photoconductivity measurements. Ordinates axis represents variation of voltage ( $\Delta V$ ) with UV illumination, which corresponds, according to Ohm's Law, to a linear variation of sample resistance.

Figure 3a) shows that, after several hours of darkness and when lighting at  $t = 0$ , the resistance drops drastically. In the enlargement of the graph (fig. 3b) it can be observed that at 4 hours a minimum appears, reaching 0.8% of the value in the dark, after which the resistance grows smoothly until reaching 1.2% at 25 hours.



**Figure 2.** FESEM micrograph of the ZnO sample studied: a) Surface image; b) Profile image.

In fig. 4.a), after several hours of illumination, at  $t = 0$  the UV source is turned off. At first, the resistance begins to grow until reaching a maximum (corresponding to 50V) at  $t = 6$  hours, after which, it decrease smoothly till 12% of the reached value.

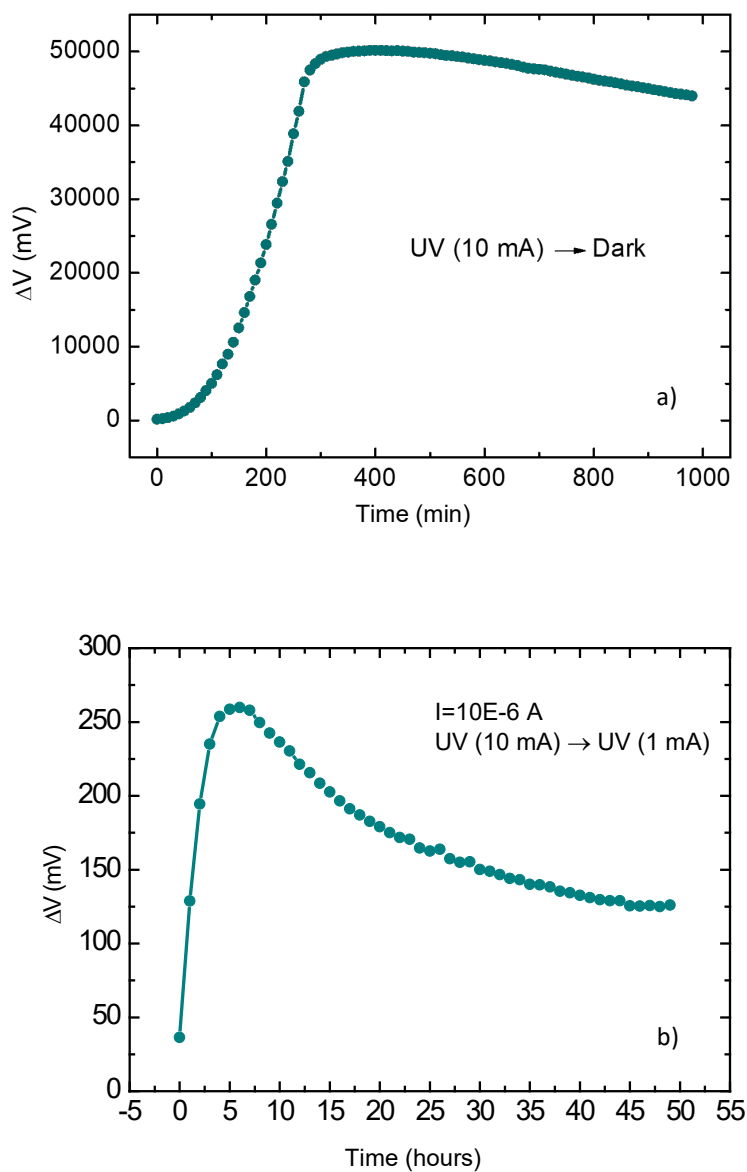


**Figure 3.** a) Voltage variation during the Dark  $\rightarrow$  UV transition; b) Zoom in of fig. 3a).

In fig. 4.b), after illuminating the sample for several hours with a certain intensity (feeding LEDs with 10mA), at  $t = 0$  the power of the source is lowered (feeding LEDs with 1mA). Resistance grows to a maximum at 6 hours and, again, declines at a slow rate, reaching the 55% of this value at  $t = 49$  hours.

It can be observed that the response speed is faster when it is illuminated or the illumination is increased than when the lighting is interrupted or simply dimmed. In the first case, the response

times are in the order of seconds or minutes, while when lighting decreases it can be minutes or hours.



**Figure 4.** a) Voltage variation during the UV  $\rightarrow$  dark transition. b) Voltage variation as UV illumination intensity is lowered from UV (10mA) to UV (1mA)

Similar results to those presented in these figures were obtained in other ZnO studied samples. It is important to note that these observations are not reported in the existing literature for long-time photoconductivity measurements.



#### 4. Discussion

Photoconductivity curves show that so in the passage from dark to UV as viceversa, there is a change in the behavior of the curve after a period of 4 and 6 hours respectively. This effect also appears at 6 hours when the intensity of UV lighting is decreased.

This suggests the competition of at least two processes, with their characteristic times, and acting in opposite directions.

The interpretation of photoconductivity in ZnO is particularly complex due to the fact that different processes occur simultaneously.

There is a fast response associated with processes such as transitions between bands.

On the contrary, adsorption and photodesorption processes of oxygen on the surface of the sample <sup>2</sup> due to the presence of defects, show a slow behavior. These processes occur as follow:

- In the absence of light, ZnO adsorbs O<sub>2</sub> from the surrounding air due to the presence of surface states. The O<sub>2</sub> captures a free electron from the crystal, remaining as a charged ion (O<sup>2-</sup>) and generating a region of charges near the surface, that is, a potential barrier that reduces electrical conduction.

- When illuminating with UV, an electron-hole pair (e<sup>-</sup>-h<sup>+</sup>) is produced: e<sup>-</sup> contributes to conduction while h<sup>+</sup> is captured by O<sup>2-</sup>, the latter being released (photodesorption). The e<sup>-</sup> trapped by the O<sup>2-</sup> will return to the interior of the ZnO, also contributing to conduction and causing, in turn, a decrease in the barrier, also favoring conductivity.

- When the lighting is removed, the O<sub>2</sub> are readsorbed on the surface until the balance is restored.

This process is slower than photodesorption.

Intrinsic defects of ZnO (oxygen vacancies and interstitial zinc) play a key role in the response to UV. ZnO tends to lose oxygen and thus become non-stoichiometric. Its n-type conduction is due to such intrinsic defects that they act as donors in the ZnO matrix. After a sufficiently long time during which the structural relaxation of the network takes place, some oxygens move towards the surface and can form surface states. Then the oxygen vacancies that remain in regions close to

the surface, act by supplying electrons to the  $O^{2-}$  which is found as an adsorbate (increasing the electrical resistance as already mentioned). These surface states increase the density of adsorbed  $O^{2-}$ . These extra oxygens can be incorporated into the network filling the vacancies and even creating zinc interstitials.

## 5. Conclusions

The difference in response speed when turning on and when lighting is interrupted could be interpreted as follows: when ZnO is exposed to ultraviolet light, a large number of unpaired electrons are generated through the surface, resulting in a rapid increase in photocurrent, whereas once UV exposure is turned off, it takes longer to discharge these photogenerated electrons. Probably these slow processes, take about hours to reach equilibrium.

But, in addition, another extra process should be acting, in a weaker way, at even longer times and in the opposite direction, being the one that generates the presence of these soft changes in behavior. More studies should be carried out aiming to determine if the observed characteristic times are related to the dynamics of the defects and the relaxation of the ZnO network.

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