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Synthesis and characterization of Zinc Oxide thin films deposited by Spray Pyrolysis technique for possible applications in solar cells

Síntesis y caracterización de películas delgadas de Óxido de Zinc depositadas por la técnica de Spray Pirolisis para su posible aplicación en celdas solares

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Abstract

In the present study, the synthesis and characterization of ZnO thin films deposited at 300, 350 and 400°C using the Ultrasonic Spray Pyrolysis technique, as a possible candidate for electron transport layer (ETL) in solar cells is reported. X-ray diffraction (XRD) analysis revealed that the films have a hexagonal wurtzite phase with a preferential orientation (101) with good polycrystallinity. The mean crystallites size based on the Debye-Scherrer model was calculated, indicating that the size of the crystals decreases as the deposition temperature increases. The optical characterization of the material showed a high transmittance in the visible region (85-99%) with which the optical band gap (3.06-3.29 eV) was determined. The thickness, surface roughness and optical constants (n and k) were determined by Spectroscopic Ellipsometry using the Gaussian oscillator model. Hall Effect revealed a low resistivity of 1-4 Ω cm and a high mobility of charge carriers (304 cm^2/Vs) in the films. Due to all these properties, ZnO is considered an ideal material for optoelectronic applications, as well as a material with potential to be used as ETL in solar cells.

ZnO, Spray Pyrolysis, Solar cell

Resumen

En el presente estudio, se reporta la síntesis y caracterización de películas delgadas de ZnO depositadas a 300, 350 y 400°C mediante la técnica de Spray Pirolisis Ultrasónico, como posible candidato de capa transportadora de electrones (ETL) en celdas solares. El análisis de difracción de rayos X (XRD) reveló que las películas tienen una fase hexagonal wurtzita con una orientación preferencial (101) con una buena policristalinidad. Se calculó el tamaño medio de los cristalitos en base al modelo de Debye-Scherrer, indicando que el tamaño de los cristales disminuye a medida que aumenta la temperatura de depósito. La caracterización óptica del material mostró una alta transmitancia en la región visible (85-99%) con lo cual se determinó la banda prohibida óptica (3.06-3.29 eV). El espesor, la rugosidad de la superficie y las constantes ópticas (n y k) se determinaron mediante Elipsometría Espectroscópica utilizando el modelo de oscilador Gaussiano. Efecto Hall reveló una baja resistividad de 1-4 Ωcm y una alta movilidad de portadores de carga (304 cm^2/Vs) en las películas. Por todas estas propiedades, el ZnO se considera un material idóneo para aplicaciones optoelectrónicas, así como un material con potencial para utilizarse como ETL en celdas solares.

ZnO, Spray Pirolisis, Celda solar

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1. Introduction

Zinc oxide is a transparent n-type semiconductor with a direct band gap of ~3.37 eV and an exciton energy of 60 meV at room temperature [1, 2] due to its unique physical characteristics, it is considered a material with excellent optical and electrical properties, further it is non-toxic and inexpensive due to its abundance in the nature [3, 4]. Others positive properties include high electrochemical and thermal stability [4, 5]. For all these properties, the ZnO has generated special interest between the researchers for its use in optoelectronic devices.

The main crystalline structures that ZnO presents are the hexagonal wurtzite and zincblende [6, 7, 8]. ZnO films have been obtained by various techniques such as sputtering [9, 10], electron beam evaporation [11], spin coating, chemical vapor deposition, sol-gel [8] and ultrasonic spray pyrolysis (USP). [6, 12]. In the present study, the ZnO thin films have been deposited by SPU technique due to its low cost, simplicity (no high vacuum requirement, deposition shorts times), versatility and deposition uniformity [6].

The objective of this work is synthesized and characterized ZnO thin films deposited by Ultrasonic Spray Pyrolysis technique as possible candidate for electron transport layer (ETL), integral part in solar cell, which offers the electron contact selectivity and mitigates recombination phenomena for enhanced device performance by its relatively high electron mobility, environmental stability, and transmissivity in the visible region [8, 13, 14].

There are many studies using ZnO in solar cells, such as ZnO nanowires, ZnO nanorods, ZnO nanoparticles and ZnO films, [14, 15, 16] that help improve device performance. Nevertheless, in these studies, the complexity of the methods, the high temperature sintering process, the sophisticated, time-consuming processing used for the obtained of the ETL are the disadvantage principal.

For all this reason, we considered that the ZnO thin films obtained by SPU technique have a big potential to be used as ETL in solar cells.

2. Description of the method

The ZnO was synthesized at a deposited temperature (Td) of 300, 350 and 400°C by the Ultrasonic Spray Pyrolysis technique. The thin films were deposited on glass and n-type silicon substrates, orientation (1 0 0), with a resistivity of 1-10 Ω cm.

The precursor solution was obtained using a molarity of 0.2 M of zinc acetate dihydrate [$Zn\ (CH_3COO)_2 \cdot 2H_2O$] ≥98% dissolved in 50 ml methanol. The flow rate of solution was of 0.5 ml/min. The nozzle to substrate distance was 15 cm and diameter of nozzle was 2 cm. The deposition time was of 10 minutes for all samples.

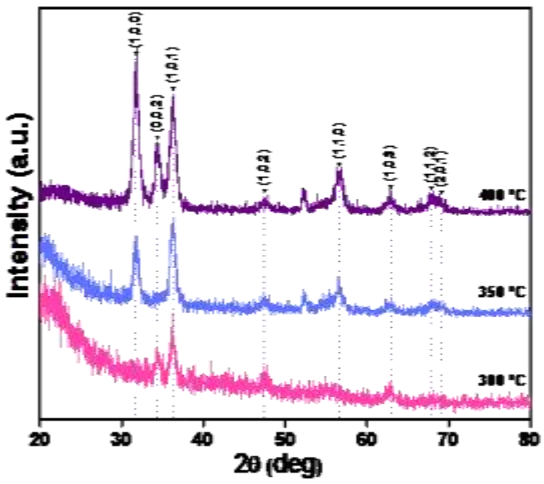
The structural properties were investigated by X-ray Diffraction (XRD), a Diffractometer Bruker model D8 Discover equipped with ray X tube of Cu Kα radiation (λ=1.54059 Å), operated to 40 kV and 40 mA was used. The XRD patterns of ZnO thin films were recorded at grazing incidence measurements with an angle θ-2θ of 1°

The optical properties were investigated by UV-Vis Spectroscopy, a Spectrophotometer Perkin Elmer 330, speed 120nm/min was used. Spectroscopic ellipsometry (SE), J.A. Woollam, M-2000DI. The ellipsometric parameter (amplitude Ψ and phase Δ) were acquired using an incidence angle of ~70 in a 193-1690nm spectral range.

The electrical properties were obtained by Hall Effect Measurement System, HMS-5000 at room temperature with a Magnetic Flux density of 0.5T.

3. Results

Graph 1 show the XRD patterns of ZnO thin films obtained at 300, 350 and 400°C. According to the peak positions matched in the (00-036-1451) PDF database the ZnO films have a hexagonal wurtzite structure with a preferential orientation (101). As the films were processed at different temperatures (300, 350, 400°C) the intensity of the XRD peaks were increased.



Graph 1 XRD patterns of ZnO thin films obtained at 300, 350 and 400°C

The observed XRD profile allow calculating the average crystallite size from peak (101). The X-ray diffraction peak broadening acquired in a diffractometer is due to the instrumental and the physical factors (as the crystallite size). The breadth that depends solely on the physical factors is extracted by subtracting the instrumental broadening factor from the experimental line profile according to [17]:

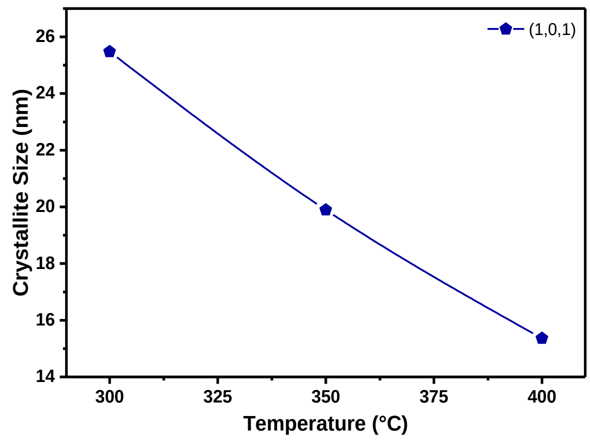
$$\beta = B\left(1 - \frac{b^2}{B^2}\right) \text{ (rad)} \quad (1)$$

2θ is the diffraction angle. B and b are the breadths of the peak from the XRD pattern at the same position of the experimental and reference sample respectively. The average diameter of the crystallites was calculated using Scherrer equation:

$$L = \frac{D\lambda}{\beta cos\theta} \quad (2)$$

where θ is the Bragg angle, λ is the X-ray wavelength (CuKa radiation) = 1.54056 Å, L is the crystal size, and D is the shape factor which is approximately the unity.

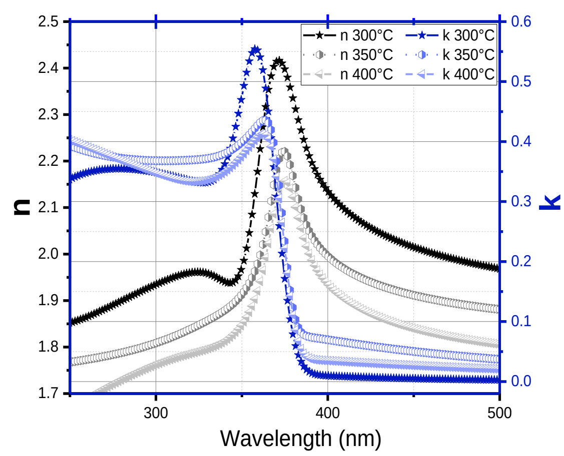
Graph 2 shows crystallite size by Scherrer equation of ZnO thin films obtained at 300, 350 and 400°C. The size of the obtained crystallites decreases as the temperature increases; however, the number of crystallites increases as indicated by the change in the intensity of the peaks.



Graph 2 Crystallite size by Scherrer equation of ZnO thin films obtained at 300, 350 and 400°C

ZnO thin films were characterized by Spectroscopic Ellipsometry (SE), which is a frequently used optical characterization method for materials and nanoscale systems. It is based on measuring the change in the polarization state of a linearly polarized beam of light reflected from the sample surface. The ellipsometry spectra obtained from the Ψ and Δ parameters are fitted with an appropriate optical model for nanostructure thin film, and thus, rich information including surface roughness, film thickness, and optical constants of the nanomaterial are revealed [18].

Graph 3 show the complex refractive index (n and k) of ZnO thin films deposited at 300, 350 and 400°C. To obtain the optical properties the Gaussian oscillator model was used by the Complete EASE software.



Graph 3 Complex Refractive index (n and k) of ZnO thin films obtained at 300, 350 and 400°C

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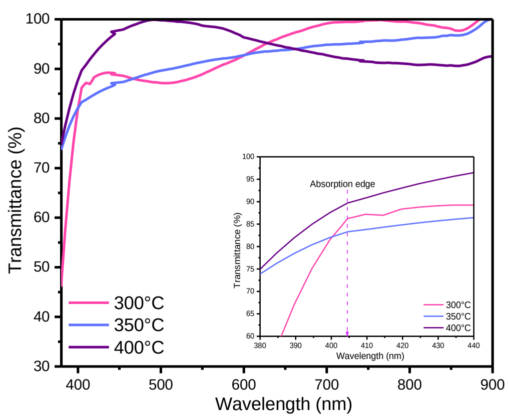
Table 1 show the thickness, surface roughness, complex refractive index (n and k) of the ZnO samples deposited at 300, 350 and 400°C.

Td (°C)	Thickness (nm)	Roughness (nm)	n@370 nm	k@360 nm
300	205±2.05	29.28±1.12	2.4	0.54
350	128.81±0.80	28.33±0.230	2.2	0.43
400	121.23±1.59	12.01±1.98	2.11	0.41

Table 1 Values of thickness, surface roughness, complex refractive index (n and k) of ZnO samples deposited at 300, 350 and 400 °C

The thicknesses and roughness of the films decrease as the temperature increases even though the deposition time was constant. All the films showed a refractive index (n) greater than 2 in λ equal to 370nm (see table 1 and graph 3). Both, n and k increase towards lower energies, however for wavelengths greater than 370 nm these parameters tend to decrease, observing this behavior for all films. These changes in the optical properties can be associated with variations in the crystal structure and superficial morphology of the ZnO films [19, 20].

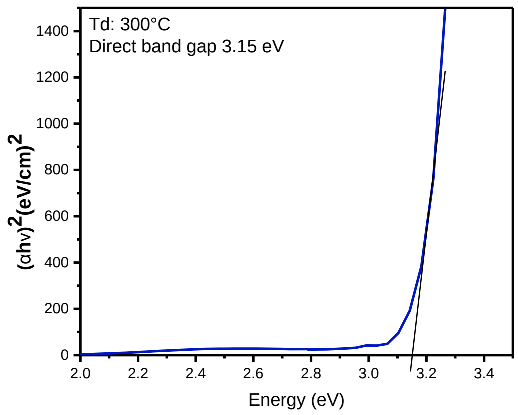
Graph 4 show the Transmittance spectra of the ZnO thin films. The optical characterization of the material showed a high transmittance in the visible region (85-99%). The figure inset in the graph 4 shows the absorption edge (404nm) of the samples.



Graph 4 Transmittance spectrum of ZnO thin films obtained at 300, 350 and 400°C. Inset absorption edge

Graph 5 shows the band gap calculated by means of transmittance spectrum and the relationship known as Tauc plot [21], considered a direct transition. The band gap (Eg) obtained was of 3.15 eV for the sample deposited at 300°C, which has a shift towards lower energies.

For the case of the samples deposited at 350°C the Eg was of 3.06 eV and for the sample deposited at 400°C was of 3.29 eV.



Graph 5 $(\alpha h\nu)^2$ versus energy (hv). Example to obtain the Eg approximated value by using the relationship known as Tauc plot of ZnO thin film deposited at 300 °C

The electrical properties of the ZnO thin films were obtained by Hall Effect measurement system, which revealed a low resistivity of 1-4 Ω cm for all samples and a relativity high electron mobility of charge carriers of 304 cm^2/Vs in the films.

4. Analysis

From XRD analysis, which revealed that the ZnO thin films have a hexagonal wurtzite phase with a preferential orientation (101) and that the mean crystallites size decreases of 25nm to 15mn as the deposition temperature increases of 300 to 400°C, it is confirmed that the polycrystallinity of the films increases with the increases of the deposition temperature.

Also, it is observed that the film deposited at 400°C has other preferential orientation (100) with a FWHM like peak corresponding to the orientation (101), indicating two possible orientations, which results very interesting in its electrical properties. It could be confirmed in a work to future by an electrical characterization more complete and its conduction mechanisms (current-voltage curves in condition of darkness).

Thicknesses and surface roughness of the films decrease of 200 to 120 nm and of 29 to 12 nm, respectively, as the temperature increases, which are related with the crystallite and grain size.

These results confirm that the thickness of the films can be controlled through the deposit temperature, which is important aspect for the use of the material as ETL [14], since it has been reported that at a lower thickness, there is a mitigated recombination phenomena for enhanced device performance [22, 23].

From optical characterization, the samples showed a high transmittance in the visible region (85-99%), which is optimal for the application as ETL. In relation with the change in the value of the band gap, it could be modulated with the change of the deposition temperature.

The electrical measurements, which revealed a low resistivity of 1-4 Ω cm and a relativity high electron mobility of charge carriers of 304 cm2/Vs in all the films. This is an expected results due to the material nature.

Due to all these properties, ZnO thin films are considered a material with a big potential for to be used as ETL in solar cells.

5. Conclusions

In conclusion, highly transparent ZnO thin films were successfully prepared by the Ultrasonic Spray Pyrolysis technique on glass and n-type silicon substrates at 300, 350 and 400 °C, using solution of zinc acetate dihydrate. The X-ray diffraction analysis showed that films are polycrystalline nature with hexagonal wurtzite phase (preferential orientation (101)), in addition, the crystallites size is estimated of 25 to 15 nm. Optical measurements show that the films possess high transmittance over 85 % in the visible region and sharp absorption edge near 400 nm. The film has a direct band gap with an optical value of 3.06 to 3.29 eV which is close to the previously reported value (3.37 eV). Electrical results revealed a low resistivity of 1-4 Ω cm and a relativity high electron mobility of charge carriers of 304 cm2/Vs in all the films.

The properties of the ZnO thin film can be controlled through the deposit temperature, which allowed found the best characteristics for obtained the electron transport layer as integral part of the solar cell.

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