



## Research Paper

# Thickness dependent growth of low temperature atomic layer deposited zinc oxide films



Z. Montiel-González<sup>a,b,\*</sup>, O.A. Castelo-González<sup>a</sup>, M.T. Aguilar-Gama<sup>a</sup>, E. Ramírez-Morales<sup>a</sup>, H. Hu<sup>a</sup>

<sup>a</sup> Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Temixco, Morelos 62580, Mexico

<sup>b</sup> CONACYT-Centro de Investigación en Materiales Avanzados S.C., Unidad Monterrey, PIIT, Apodaca, Nuevo León 66628, Mexico

## HIGHLIGHTS

- Polycrystalline columnar ZnO thin films deposited by ALD at low temperatures.
- Higher deposition temperature leads to a greater surface roughness in the ALD ZnO films.
- Higher temperature originates larger refractive index values of the ALD ZnO films.
- ZnO thin films were denser as the numbers of ALD deposition cycles were larger.
- XPS analysis reveals mayor extent of the DEZ reaction during the ALD process.

## ARTICLE INFO

### Article history:

Received 21 December 2015

Revised 4 August 2016

Accepted 2 September 2016

Available online 6 September 2016

### Keywords:

Atomic layer deposition

Zinc oxide thin films

Thickness dependent growth

Spectroscopic ellipsometry

## ABSTRACT

Zinc oxide films are promising to improve the performance of electronic devices, including those based on organic materials. However, the dependence of the ZnO properties on the preparation conditions represents a challenge to obtain homogeneous thin films that satisfy specific applications. Here, we prepared ZnO films of a wide range of thicknesses by atomic layer deposition (ALD) at relatively low temperatures, 150 and 175 °C. From the results of X-ray photoelectron spectroscopy, X-ray diffraction and Spectroscopic Ellipsometry it is concluded that the polycrystalline structure of the wurtzite is the main phase of the ALD samples, with OH groups on their surface. Ellipsometry revealed that the temperature and the deposition cycles have a strong effect on the films roughness. Scanning electron micrographs evidenced such effect, through the large pyramids developed at the surface of the films. It is concluded that crystalline ZnO thin films within a broad range of thickness and roughness can be obtained for optic or optoelectronic applications.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Zinc oxide is a wide bandgap ( $E_g \approx 3.3$  eV) semiconductor, transparent for infrared and visible radiation. Numerous applications of this II–VI compound have been proposed or realized in the form of thin films. For example, n-doped ZnO with high electron mobility is a good candidate as transparent conductive electrode [1], whereas the intrinsic ZnO has been used as buffer layer in solar cells [2,3] and transistors [4]. Moreover, the high absorption coefficient at photon energies larger than 3.3 eV makes ZnO suitable as UV radiation protective layer for organic solar cells

(OSCs), if its deposition temperature can be low enough during manufacturing [5].

Thin films of ZnO can be prepared by solution methods such as spray pyrolysis, sol-gel, and chemical bath deposition. During the preparation of electronic devices, these methods can only be used for the first layers because the solution itself might damage the former deposited materials. Physical methods like pulsed laser and sputtering are widely used for metal oxide deposition, although they require high vacuum, and the temperature could be too high for organic substrates. An important alternative is the chemical vapor deposition (CVD) methods, e.g. atomic layer deposition (ALD), among others. In ALD, two precursors are feed to a reaction chamber in a sequential way, so they react separately with the substrate to form an atomic layer of the desired compound. Because of the reactions are superficial and self-limiting, the ideal ALD leads to a homogenous composition and good thickness uniformity of the grown film. As a result, several properties of the ALD ZnO films

\* Corresponding author at: CONACYT-Centro de Investigación en Materiales Avanzados S.C., Unidad Monterrey, PIIT, Apodaca, Nuevo León 66628, Mexico.

E-mail addresses: [zemog@ier.unam.mx](mailto:zemog@ier.unam.mx), [zeuz.montiel@cimav.edu.mx](mailto:zeuz.montiel@cimav.edu.mx) (Z. Montiel-González).

have been found to be better than those of films obtained with other methods like metal organic CVD [6] and sputtering [7].

The incorporation of ALD layers into solar cells technology has also been studied, mainly to improve their efficiency or substituting hazardous materials such as cadmium sulfide. Applications and prospects of ALD films for photovoltaics have been summarized in a recent review [8]. In particular, 0.1–100 nm of ZnO [9,10] or 150 nm of ZnO:Al thin films [11] have been used as electron selective layers or transparent conductive oxides, respectively, in OSCs. In this work, crystalline ZnO films, from 90 to more than 500 nm thick, were deposited by ALD at 150 and 175 °C. These are suitable temperatures for further application in several types of solar cells (e.g. OSCs, CIGS, etc.), where values under 200 °C are mandatory to avoid degradation [8]. The effect of the ALD deposition temperature and the number of cycles, on the thickness and roughness of the films were observed by Scanning Electron Microscopy (SEM) and confirmed through the analysis and numerical fitting of their ellipsometric spectra. A typical behavior of the complex refractive index was also determined as a function of the deposition cycles for ZnO samples deposited at both temperatures.

## 2. Experimental details

ZnO thin film deposition was carried out in a Savannah-200 ALD system of Cambridge NanoTech Inc., with diethylzinc (DEZ, Aldrich 52%) as the metal precursor and deionized water as the oxygen source. The films were deposited on p-type silicon (1 0 0) wafers (c-Si) and Corning® glass. The glass slides were washed with neutral alkaline soap and cleaned in an ultrasonic bath with water and acetone for 10 min each. c-Si pieces of  $2 \times 2 \text{ cm}^2$  were immersed in a 5% HF solution during 90s to remove the native oxide. Then the substrates were placed into the heated ALD chamber at 150 or 175 °C, depending on the case. Ultrapure  $\text{N}_2$  (99.9999%) was used as purging gas and it was kept at a flow rate of 20 sccm (cubic centimeters per minute at standard temperature and pressure). The film formation consisted of sequential pulses of: DEZ (0.2 s),  $\text{N}_2$  (2 s),  $\text{H}_2\text{O}$  (0.6 s) and  $\text{N}_2$  (2 s), which form a deposition cycle of 4.8 s. Films of 400, 800, 1200, 1600 and 2000 cycles were prepared in this work.

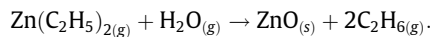
X-ray diffraction (XRD) patterns of samples deposited on c-Si were obtained with a Rigaku DMAX-2200 X-ray diffractometer at glancing angle of 0.5°. The crystal size of each sample was calculated through the Scherer formula, in which the instrumental widening was determined with the  $\text{LaB}_6$  standard. The Williamson-Hall (W-H) method was not used to estimate the crystal size and microstrain, since the XRD peaks of the samples could not be fitted as Lotentzian profiles. SEM cross section micrographs were taken in a Hitachi FE-SEM 5500 microscope. X-ray photoelectron spectroscopy (XPS) measurements were made in a Perkin Elmer PHI 5100 equipment. The chemical analysis by XPS was calibrated by taking the carbon 1 s peak (284.6 eV) as reference. The specular reflectance and transmittance spectra of ZnO on glass were obtained with a spectrophotometer Jasco V-670 in a wavelength range from 240 to 840 nm.

Spectroscopic ellipsometry (SE) measurements of ZnO/c-Si samples were made with a Horiba Jobin Yvon UVISSEL DH10 Phase Modulated ellipsometer, in the photon energy range of 1.5–5.0 eV at angle of incidence of 70°. The experimental data of SE are a set of measurements of the  $\Psi$  and  $\Delta$  angles which are related to the complex reflectance ratio ( $\rho$ ) as follows [12]:  $\rho = r_p/r_s = \tan \Psi \exp(i\Delta)$ , where  $r_p$  and  $r_s$  are the complex Fresnel coefficients of the studied system (e.g. air/ZnO film/c-Si substrate), for polarization parallel ( $p$ ) and perpendicular ( $s$ ) to the plane of incidence. Moreover, the Fresnel coefficients at each interface are functions of both the intrinsic material properties (e.g. complex refractive index) and

the structural parameters (e.g. thickness and roughness). Therefore,  $\Psi$  and  $\Delta$  data implicitly contain the information of real refractive indices ( $n$ ) and extinction coefficients ( $k$ ) of air, ZnO and c-Si, as well as the thickness of the ZnO film ( $d$ ). To determine the values of  $n$ ,  $k$  and  $d$  of ZnO from  $\Psi$  and  $\Delta$ , a model dependent analysis has to be performed by fitting model parameters to minimize the mean square root error between the experimental and model-calculated  $\Psi$  and  $\Delta$  spectra, evaluated through a figure of merit ( $\chi^2$ ) based on the Levenberg-Marquardt algorithm [12].

## 3. Results and discussion

The stoichiometric reaction between DEZ and  $\text{H}_2\text{O}$  in an ALD cycle is assumed to be [13]:



Ideally, after the surface reaction the unique solid product should be a ZnO monolayer on the substrate. However, the XPS spectra of the obtained ZnO thin films suggest non stoichiometric ZnO and the presence of carbon and oxygen peaks. Fig. 1a gives the survey of XPS spectra of two ZnO samples deposited at 150 and 175 °C after 2000 cycles. For both samples Zn and O are identified. The presence of C could be the contamination from the sample handling, and also from the incomplete reaction of DEZ.

Fig. 1(b) shows the high resolution XPS spectra of the Zn 2p doublet with binding energies at  $\sim 1023.3$  and  $\sim 1045.5$  eV, those could be assigned as Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> binding states of ZnO, respectively [14–16]. In the literature, the binding energy of Zn 2p<sub>3/2</sub> of a bulk ZnO is reported as  $1022.0 \pm 0.4$  eV [14]. Due to the reaction of  $\text{H}_2\text{O}$  during the ALD process, the slight shift to higher energy of the Zn 2p<sub>3/2</sub> signals in the final products suggests the presence of hydroxide species, as observed precisely in ZnO compound [17].

Fig. 1c gives the high resolution XPS spectra of O1s that contain two signals: the 530.8 eV signal is attributed to Zn–O bond [18–20]. The second, at 532.5 eV, is related to chemisorbed oxygen [18] or superficial hydroxyl groups [19,20]. As will be seen in the following XRD analysis and the bandgap determinations, the crystalline ZnO phase predominates in the ALD samples. The higher intensities of 532.5 eV signals suggest that the OH groups should be on the surface of ALD samples.  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the ambient also contribute to these signals.

Finally, Fig. 1(b) and (c) clearly show an increase in the ZnO related signals with the deposition temperature, which is explained by an increase in completion or extension of the reaction of the Zn precursor during the ALD process.

To confirm the formation of the crystalline ZnO phase in the ALD films, Fig. 2a and b shows XRD patterns of all the films deposited at both temperatures (Fig. 2a and b). The diffraction peaks coincide quite well with the crystalline planes of the hexagonal wurtzite (PDF#36-1451), with the differences in the preferential orientation: the (1 0 0) plane (at  $2\theta = 31.8^\circ$ ) has the maximum intensity in those ALD films, while for the wurtzite, it is the (1 0 1) plane (at  $2\theta = 36.2^\circ$ ) with the maximum value. Only the wurtzite phase exists in the ALD films; no other crystalline zinc compound was found in this case. In the same figures, the effect of the deposition temperature on the diffraction patterns of the products is observed in the relative intensities of a couple of crystalline planes; the intensities of the (0 0 2) and (1 0 3) planes of the samples deposited at 175 °C are greater than those of the films deposited at 150 °C. It suggests that the temperature promotes changes in the crystalline orientation, as it is well documented in the literature [21,22]. The absolute intensity of each diffraction peak increases with the deposition cycles, which is an indication of increment in the crystallite population, but not necessarily of

Download English Version:

<https://daneshyari.com/en/article/4991886>

Download Persian Version:

<https://daneshyari.com/article/4991886>

[Daneshyari.com](https://daneshyari.com)