Characterization of ZnO thin films elaborated by cathodic sputtering with different oxygen percentages: investigation of surface energy.

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Abstract. In this work, transparent thin films of Zinc Oxide (ZnO) were elaborated by RF sputtering with different oxygen percentages (10%, 20%, 30%, 50%). A structural (X-ray Diffraction) and morphological (Atomic Force Microscopy) study was carried out to investigate the influence of the elaboration conditions. A high roughness was obtained for the ZnO film deposited with 50% of O2 under 100w RF power, and the roughness increased with increasing O2 rate. The physicochemical properties were characterized by the calculation of surface energy, the results showed that the surface of the ZnO thin films are governed by short-range forces, i.e. the dispersive component (LW) is larger than the polar component (AB). The calculation of the interaction energy ($\Delta G_{int}$) has shown that the surfaces of ZnO films are hydrophobic ($\Delta G_{int} < 0$) and the degree of hydrophobicity increases with increasing oxygen percentage.

Introduction

For many years, zinc oxide (ZnO) has been a major contributor to the development of various fields. It is found in tyre manufacturing, ceramics and chemical industry, manufacture of special glasses, etc. It is a non-toxic compound to the environment, which is also of interest in the pharmaceutical field [1]. Zinc oxide has interesting electrical and optical properties, because of its high transparency and its relatively wide energy band gap ($\approx 3.26$ eV) [2]. This makes it a good candidate for applications in optoelectronics applications [3]. From a chemical point of view, ZnO has a high binding energy (O-Zn) [4,5].

In particular, materials produced in the form of thin films have physicochemical properties that differ in many points compared to massive materials. Due to their good physical properties, thin films of zinc oxide are mainly used in the production of solar cells [6-9]. They are also found as highly sensitive chemical sensors in gas detectors [10], light-emitting diodes and transistors [11-14], overvoltage protection devices [15-17] and photodetectors [18].

Different technological processes can be used to deposit ZnO as thin films. We can note the chemical methods that consist to elaborate the material by chemical reaction or decomposition of molecules such as: pyrolysis spray technique [19], sol-gel technique [20]. There are also some
physical methods that consist to elaborate the film by extraction of the material from a target like: thermal evaporation [21], laser ablation (PLD) [22] and cathodic sputtering [23-25].

The physicochemical properties, particularly wetting, characterized by surface energy, are used in many processes with very varied applications. In this work, we describe the interfacial interactions of Zinc oxide thin films by calculating the surface energy using the droplet technique. These thin films are produced using RF sputtering by changing the Oxygen rate in order to optimize the influence of the deposition parameters.

Experimental

1. Deposition of ZnO thin films

As presented in previous work [26,27], ZnO thin films were developed by RF sputtering in an ALCATEL SC451 deposition system equipped with an ALCATEL ARF 601 RF generator operating at 13.56 MHz. They were deposited using a high-purity metal target Zn with a diameter of 10 cm in a mixture of argon oxygen gas. Before deposition, the glass substrates were ultrasonically cleaned in acetone and isopropyl alcohol to remove any impurities and rinsed with distilled water. The spraying was carried out in a gas mixture Ar / O2 under an RF power of 100W. The films were deposited with different oxygen percentages (10%, 20%, 30% and 50%) for 30 min.

2. Characterization technique

2.1. X-ray diffraction

The X-ray diffraction (XRD) technique can mainly identify phase formation, grain size and film stress state. The X-ray diffraction spectra were collected using the Philips X’ Pert MPD device. The radiation source was from CuKα= 1,541 Å. The whole system is controlled by software allowing the automation of measurements, with an acceleration voltage of 40 kV and a current of 30 mA.

2.2. Atomic force microscopy

In this work, we used the Nanosurf Easyscan 2 AFM device to extract topographic parameters from ZnO thin films. It is an atomic force microscope system that can perform nanoscale measurements of the topography and several other properties of a sample. The EasyScan 2 AFM system is a modular scanning probe system that can be classified for more measurement capabilities. The main parts of the basic system are the EasyScan 2 AFM scanning head, the AFM sampling step, the EasyScan 2 controller with the AFM Basic module and the EasyScan 2 software.

2.3. Measuring the contact angle

Contact angle measurements were made using a goniometer (GBX instruments, France) using the droplet method. Three to six measurements of the contact angle were made on each surface of the substrates of ZnO thin films obtained with different oxygen percentages. The liquids used in this study (Table 1) cover a wide range of surface tensions. Diiodomethane being non-polar, water and Formamide are polar [28].
Table 1. Values of the total free surface energy and its components as a result of interaction of \( lw \) and \( ab \) used in the investigation of contact angle of liquids at a temperature of 20°C [mJ/m\(^2\)].

| Liquid         | \( \gamma_L \) | \( \gamma^L_{lw} \) | \( \gamma^L_{ab} \) | \( \gamma^L_+ \) | \( \gamma^L_- \) |
|---------------|-----------------|---------------------|---------------------|-----------------|-----------------|
| Water         | 72.8            | 21.8                | 51.0                | 25.5            | 25.5            |
| Formamide     | 58.0            | 39.0                | 19.0                | 2.28            | 39.6            |
| Diiodomethane | 50.8            | 50.8                | \( \approx 0 \)     | \( \approx 0 \)  | \( \approx 0 \)  |

3. Determination of Surface Energy

3.1. The young equation

In 1805, Thomas Young [29] defined the contact angle of a drop of liquid on an ideal solid surface by the mechanical balance of the drop under the action of three interfacial tensions:

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \tag{1}
\]

Where \( \gamma_{lv}, \gamma_{sv}, \) and \( \gamma_{sl} \) represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and \( \theta \) is the contact angle.

3.2. The Van Oss acid-base method

This approach initiated by Van Oss and COLL. [30] takes into account molecular interactions via electron donor/acceptor processes that involve the complementary properties of liquid and solid. The surface energy is then written:

\[
\gamma = \gamma^{lw} + \gamma^{ab} \tag{2}
\]

Where \( \gamma^{lw} \) is the contribution of Lifshitz-Van der Waals (LW) forces and \( \gamma^{ab} \) is the contribution of acid-base interactions (AB).

According to the Van ossl model, polar interactions occur when an electron acceptor (+) encroaches on an electron donor (-). The geometric mean is therefore formed from the respective opposite parts. For the calculation of surface energy, at least three liquids are required: one dispersive liquid and two polar liquids according to the Lewis scale [27]. The surface energy equation is then written:

\[
\frac{(\cos \theta + 1)/2}{\gamma_L} = \left( \frac{\gamma^{lw}_L \gamma^{lw}_w}{(\gamma^L_+ \gamma^L_-)^{1/2}} \right)^{1/2} / \gamma_L + \left( \frac{\gamma^L_+ \gamma^L_-}{(\gamma^L_+ \gamma^L_-)^{1/2}} + (\gamma^L_+ \gamma^L_-)^{1/2} / \gamma_L \right) \tag{3}
\]

Where \( \theta \) is the contact angle measured, \( \gamma^{lw} \) is the der Waals Van free energy component, \( \gamma^+ \) is the electron acceptor component, \( \gamma^- \) component is the electron donor and the indexes (S) and (L) denote respectively solid surface and the liquid phase.

3.3. Hydrophobicity

According to van Oss [32] the hydrophobicity of a given material (i) can be defined in terms of the variation of the free energy of interaction between two moieties of that material immersed in water (w). The free energy comprises a polar (AB) and a non-polar (LW) component and the variation of the total free energy is given by:

\[
\Delta G_{iw} = -2(\gamma^L_+ \gamma^L_- - \gamma^{lw}_L \gamma^{lw}_w)/2 + 2(\gamma^L_+ \gamma^L_- - \gamma^{lw}_L \gamma^{lw}_w)/2 \tag{4}
\]

When the value of \( \Delta G_{iw} \) turns is negative (the free energy of interaction between molecules is attractive) it means that the solid surface has less affinity for water than among themselves, meaning
that they have a hydrophobic character. On the contrary, solid surface are hydrophilic when this value is positive \( \Delta G_{\text{w}} > 0 \).

4. Results and discussions

4.1. Structural properties

The results of X-ray diffraction analysis of Zinc oxide thin films deposited on glass substrates with different oxygen percentages are shown in Figure 1. We observe that all deposited ZnO thin films have a hexagonal polycrystalline structure of the Würzite type. These films have a preferential orientation along the c-axis of the mesh perpendicular to the substrate surface.

In all spectra, the samples have only one peak, which appears at an angle close to 34.2° corresponding to the ZnO peaks (002). This observation applies only to the four percentages of oxygen used in the deposition of ZnO films.

![X-ray diffraction spectra of ZnO thin films.](image)

Figure 1: X-ray diffraction spectra of ZnO thin films.

4.2. Topographic Properties

Surface of Zinc oxide thin films is characterized by atomic force microscopy. The images obtained from the four samples are presented in Figures 2 and 3. It is observed that the oxygen rate has a direct influence on the surface topography of the ZnO thin films. This variation in oxygen percentage caused different topographies.
Figure 2: 2D AFM images of the surfaces of ZnO films

Figure 3: 2D AFM images of the surfaces of ZnO films
The Esayscan 2 image analysis software of the Nanosurf Flex AFM atomic force microscope was used to extract the roughness parameters. Figure 4 shows the variation of the RMS roughness $Ra$ and $Sa$. The increase in the percentage of oxygen during the deposition of ZnO thin films caused a change in the roughness of the surfaces studied, which explains why the change in the percentage of oxygen influences the structure and topography of the substrate surface.

![Figure 4: Ra and Sa roughness of ZnO films obtained at different oxygen percentages.](image)

**4.3. Physicochemical properties**

The surface energy of ZnO thin films was determined from contact angle measurements using different liquids (Water, Formamide and Diodomethane) on the sample surfaces used in this study, by applying the acid-base theory.

The results of contact angles values, different surface energy components and free interaction energy ($\Delta G_{\text{int}}$) are grouped in Table 2. Figure 5 shows in the same time the evolution of water contact angle and total surface energy according to the variation of the oxygen percentage under a fixed RF power (100w). we observe that the values of the contact angle increase and surface energy decrease with increasing oxygen rate. this means the influence of the elaboration conditions on physicochemical properties. in addition, the increase in oxygen rate has caused an increase in the hydrophobic character of ZnO thin films, i.e. the water contact angle increases.

**Table 2. Values of the contact angle and surface energy components [mJ/m²]**

| Substratum     | Contact Angle ($^\circ$) | Surface Energy Component (mJ/m²) | $\Delta G_{\text{int}}$ |
|----------------|--------------------------|---------------------------------|------------------------|
|                | $\theta_W$ | $\theta_F$ | $\theta_D$ | $\gamma^{LW}$ | $\gamma^+$ | $\gamma^-$ | $\gamma^{AB}$ | $\gamma^{Tot}$ |            |
| ZnO (10% $O_2$) | 80,9      | 74,4      | 48,2      | 35,3        | 0,9        | 14,6       | 7,4        | 42,7        | -23,39     |
| ZnO (20% $O_2$) | 85,3      | 76,6      | 51        | 33,7        | 0,5        | 12         | 5,8        | 39,5        | -30,13     |
| ZnO (30% $O_2$) | 88,4      | 73        | 43,5      | 31,04       | 0,2        | 11         | 3,00       | 34,04       | -33,54     |
| ZnO (50% $O_2$) | 96,8      | 80,9      | 63        | 26,8        | 0,1        | 4,2        | 2,8        | 29,6        | -57,32     |
Figure 5: Evolution of water contact angle and surface energy according to O\textsubscript{2} rate

Figure 6 shows the surface energy values LW and AB of the ZnO thin films obtained by RF sputtering at 100 w power with different oxygen percentages (10%, 20%, 30% and 50%). The surface energy of ZnO films is decreased as the percentage of oxygen increases.

On the other hand, the dispersive component of the surface energy of the different samples is larger than the acid-base component. For example, the surface of the thin film ZnO 10%, the dispersive component (LW) represents 85.32% of the total surface energy, while the polar component (AB) only represents 14.68% of the total energy.
Figure 6: Surface energy, dispersive (LW) and acid-base (AB) of ZnO thin films

We also find that the apolar component decreases when the percentage rate of oxygen is increased. This explains the polar nature of oxygen, which tends to minimize surface energy as its concentration increases.

![Graph showing surface energy, dispersive, acid and base component of ZnO thin films](image)

Figure 7: Surface energy, dispersive, acid and base component of ZnO thin films

As the ZnO thin films have a very important non-polar component (Figure 7), it can be said that their surface is governed by the long-range Van der Waals forces. The acid component of the surface energy is practically negligible, while the value of the dispersive part is very important.

Figure 8 shows the result obtained from the hydrophobicity of the different samples. The degree of hydrophobicity expressed in terms of free energy of interaction ($\Delta G_{\text{int}}$) increases as the oxygen concentration increases during the deposition of ZnO thin films. The results show that these films are hydrophobic and the film obtained with 50% oxygen has a very high interaction energy which is equal to about -57 mJ/m2.
Conclusion
In this work, we deposited films of zinc oxide (ZnO) on glass substrates by RF sputtering under different experimental conditions (fixed sputtering pressure 100w, percentage of reactive gas (O2) in the gas mixture (Ar/O2) varied between 10% and 50%). We have carried out several series of samples that we have subsequently characterized on the structural, topographical and physico-chemical plans.

The results were found by successively varying the parameters. We have shown that deposition parameters such as power and relative oxygen and argon concentrations are of crucial importance to the internal structure of the deposited films.

we found in this study that the resulting thin films of ZnO were hydrophobic and governed by long-range forces (Van der Waals intermolecular interaction forces). The results also showed that the increase in oxygen concentration typically increased the roughness values and decreased the surface energy.

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