

Revue des Energies Renouvelables journal home page: https://revue.cder.dz/index.php/rer

Research Paper

Structural Characterization of ZnO Thin Films Deposited onto Silicon Substrates using Cathodic Magnetron Sputtering

Leila Ghalmi^{a,*}, Souhila Bensmaine^a, Chems El Hayat Merzouk^a

^a Research Unit on Renewable Materials and Energies (URMER). University of Tlemcen (UABT). BP n°119. Tlemcen. 13000. Algeria.

ARTICLE INFO ABSTRACT In this study, we analyzed Zinc Oxide (ZnO) thin films deposited on si Article history: substrates using magnetron sputtering. These films have nume Received 16 March 2023 applications in photovoltaic and optoelectronic devices due to their exce Accepted 01 June 2023 physique properties. We used two structural characterization technique Keywords: ray diffraction and scanning electron microscopy. We found that the Zinc oxide ZnO, films had good crystallinity and a columnar structure on the substrate su Thin films, as indicated by the (002) orientation. These findings could potential Magnetron sputtering, useful for the development of ZnO-based devices such as solar cells X-ray diffraction (XRD), piezoelectric sensors. our results are consistent with those found by Scanning electron researchers. microscopy (SEM)

* Corresponding author, E-mail address: leila.ghalmi@univ-tlemcen.dz Tel.: + 213 541765240

ISSN: 1112-2242 / EISSN: 2716-8247



This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License. Based on a work at http://revue.cder.dz.

1. Introduction

In recent years, there has been a significant effort to research and develop materials for various technological applications such as microelectronics, optoelectronics, and gas transducers. One promising material for these applications is zinc oxide, due to its transparency, high conductivity, chemical stability, and ease of processing. Zinc oxide can be used as a front contact layer in solar cells, where it acts as a selective layer that transmits visible light and reflects near-infrared light. It can also be used as an interconnect component and electrical contact in solar cells. Zinc oxide is an II-VI semiconductor with a bandgap ranging from 3.1 to 3.4 eV, and it can be deposited onto various substrates using techniques such as electron beam deposition, DC sputtering, and laser ablation [1] [2] [3].

In addition to its use in solar cells, zinc oxide has excellent piezoelectric properties and has been widely studied for use in piezoelectric sensors, nanogenerators, accelerometers, and pressure sensors. It can be deposited onto substrates using methods such as chemical vapor deposition, pulsed laser deposition, sol-gel treatment, and magnetron sputtering [4].

This research aims to investigate the structural properties of zinc oxide thin films through various characterization methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) [5]. The goal is to obtain high-quality zinc oxide films for use in solar cells. The work will primarily be experimental, studying the crystal structure and properties of the films through X-ray diffraction and scanning electron microscopy.

Thin film deposition is an essential process in the fabrication of various electronic and optoelectronic devices. Among the many available technologies, magnetron sputtering, and chemical vapor deposition (CVD) are two common methods for depositing zinc oxide (ZnO) films on silicon substrates. These technologies offer clear advantages and limitations, making them suitable for different applications. In this part, we will explore the main features, advantages, and limitations of magnetron sputtering and CVD, as well as the factors to consider when selecting a deposition technique for ZnO films on silicon substrates. Understanding this research will help us make informed decisions regarding the most appropriate deposition method for our work.

Magnetron sputtering is a popular technique for depositing thin films due to its versatility and control over the deposition process. In the case of ZnO on silicon substrates, magnetron sputtering offers several advantages:

• High Deposition Rate: Magnetron sputtering allows for a relatively high deposition rate,

enabling the growth of ZnO films on silicon substrates in a shorter time compared to some other techniques [6]

• Good Film Uniformity: Magnetron sputtering provides good film uniformity across large substrate areas. By adjusting the deposition parameters and optimizing the system design, uniform, and homogeneous ZnO films can be obtained on silicon substrates [7]

• Control of Stoichiometry: Magnetron sputtering enables control over the stoichiometry of ZnO films by adjusting the sputtering gas composition. Oxygen partial pressure during deposition can be optimized to achieve the desired ZnO film properties, such as conductivity and transparency [8].

However, magnetron sputtering also has some limitations:

• High Substrate Temperature: In some cases, magnetron sputtering may require elevated substrate temperatures, which can limit the choice of substrates. For silicon substrates, higher temperatures can impact the integrity of the interface or induce unwanted diffusion [9].

• Film Stress: Magnetron sputtering can introduce compressive or tensile stress in the deposited ZnO films. This stress can affect the film's structural and optical properties and may lead to cracking or delamination [10].

Other Deposition Techniques:

Chemical Vapor Deposition (CVD): CVD is another widely used technique for depositing ZnO films. It offers the following merits:

• Low Substrate Temperature: CVD can be performed at lower substrate temperatures compared to magnetron sputtering, making it suitable for more temperature-sensitive substrates [11]

• High-Purity Films: CVD allows for the deposition of high-purity ZnO films with excellent crystalline quality. The use of precursors and controlled reaction conditions enables the growth of films with low impurity levels [12].

• Conformal Coating: CVD can provide a conformal coating on complex three-dimensional structures due to its gas-phase deposition mechanism. This feature makes it suitable for applications where uniform coating over intricate geometries is required [13].

However, CVD also has certain limitations:

• Lower Deposition Rate: CVD typically exhibits lower deposition rates compared to magnetron sputtering, which may result in longer deposition times [14].

• Cost and Complexity: CVD systems can be more expensive and complex to set up and maintain compared to magnetron sputtering systems, making them less accessible for some research or industrial applications [15].

These are just two examples of deposition techniques for ZnO on silicon substrates, and other methods such as pulsed laser deposition (PLD), atomic layer deposition (ALD), and physical vapor deposition (PVD) can also be employed. The choice of technique depends on specific requirements, such as deposition rate, film quality, substrate compatibility, and equipment availability.

2. Experimental

2.1 Zinc Oxide

Zinc oxide (ZnO) has a long history of use as a transducer, dating back to the 1920s when it was used in the receivers of the first wireless radios due to its piezoelectric properties. It was extensively studied in the 1950s, but interest in it waned in the 1970s. However, ZnO has seen a resurgence of interest since the 1990s due to its unique and attractive properties (Figure 1). Data for publications on ZnO were obtained from the Scopus search engine, and data for patents were obtained from the Orbit database [16].



Fig. 1. Evolution of the number of publications and patents per year on ZnO from 1920 to 2011.

Zinc oxide is a versatile and multifunctional material that has a wide range of potential applications. In the following sections, we will highlight some of the main applications of ZnO and its properties that make it suitable for these applications for these uses Figure 2 [17].



Fig. 2. Different applications of ZnO.

2.2 Structural properties of zinc oxide

Zinc oxide belongs to the group II-VI binary semiconductor family and has three known crystalline phases: wurtzite (B4), blende (B3), and rock salt (B1) Figure 3. At room temperature, ZnO crystallizes in the hexagonal, symmetrical wurtzite structure with the space group P63mc. In this structure, each zinc atom is surrounded by four oxygen atoms at the corners of a tetrahedron, with the zinc atom slightly shifted 0.11 Å in the direction parallel to the c-axis [18]. This gives the oxide molecules a degree of polarity, unlike pure ionic crystals. There are also voids with a radius of 0.95 Å in the crystal structure, which can accommodate excess zinc atoms under certain conditions [19]. The nearest neighbors in the c direction are closer together than the other three neighbors, which contributes to the pyroelectricity of ZnO. The coordination number is 4:4, with two ZnO units per unit cell in the lattice.

In the wurtzite structure of zinc oxide, the positions of the zinc and oxygen atoms can be described using Wyckoff notation. The zinc atoms are located at (0,0,0) and (1/3, 2/3, 1/2), and the oxygen atoms are located at (0,0, u) and (1/3, 2/3, u+1/2), where u=0.375. The density and mesh parameters of zinc oxide are listed in Table 1, and the ideal ratio of c/a in the wurtzite structure is $\sqrt{(8/3)} \approx 1.633[20, 21]$.



Fig. 3. Schematic of the elementary mesh of the ZnO wurtzite structure.

The difference between this value and the experimentally observed value is related to the ionic character of the bond between the oxygen and zinc atoms. The crystal structure of zinc oxide, consisting of two ZnO units per unit cell, can be generated using these special positions.

a (Å)	c (Å)	c/a	ρ(g/cm ³)
3.24982	5.20661	1.602	5.675

Table 1. Experimental crystallographic characteristics of ZnO.

The wurtzite structure of zinc oxide is a hexagonal lattice with three lattice constants: a, c, and u. a is the side length of the rhombus that forms the base, c is the side length parallel to the oz axis, and u is an internal coordinate along this axis (figure 4). These constants determine the relative positions of the O2- anion and Zn2+ cation sublattices. The distance between the planes of indices (hkl) is given by the equation [21]:

$$u = \frac{1}{4} + \frac{c^2}{3a^2} \tag{1}$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \qquad (2)$$

The stability of this structure is defined by the condition:

$$0.225 \le \frac{R_a}{R_c} \le 0.414 \tag{3}$$

where Ra and Rc are the radii of the anion and cation, respectively. This condition arises from the compact hexagonal structure (H.C.), which is derived from the face-centered cubic (F.C.C.)

structure of blende. The wurtzite structure belongs to the space group P63mc (C46v) and consists of two compacts hexagonal sublattices shifted by (3/8) c and forming an ABAB stack along the [0001] axis, also known as the c axis of the wurtzite structure. In this work, we will only be considering the wurtzite structure of zinc oxide.



Fig. 4. Compact hexagonal structure of Würtzite.

2.3 Sputtering

Sputtering is a physical vapor deposition (PVD) process that is used to deposit thin films of material onto a substrate. In the sputtering process, a target material is placed in a high vacuum chamber and is bombarded with a stream of neutral gas atoms, typically argon. The argon atoms collide with the target material and knock atoms off its surface, causing them to be ejected into the gas phase. These ejected atoms then travel through the vacuum chamber and are deposited onto a substrate, forming a thin film [22].

Several different mechanisms can occur when an argon ion collides with the cathode (target material) during sputtering. The ion may be reflected, it may meet an electron and become neutral, it may cause the ejection of an electron, or it may pull an atom out of the target material. The specific mechanism that occurs will depend on the energy of the ion, the type of target material, and the conditions of the sputtering process.

After the sputtering process is complete, various characterization techniques may be used to analyze the properties of the thin film that has been deposited. These techniques can include X-ray diffraction, atomic force microscopy, and ellipsometry, among others. These techniques can be used to determine the composition, thickness, and surface roughness of the thin film, as well as other properties.



Fig. 5. Conventional diagram of a sputtering system [23].

Silicon wafers are commonly used as substrates in sputtering processes because they have several attractive properties that make them well-suited for this purpose. Some of the key benefits of using silicon wafers as substrates include:

- Cleanliness: Silicon wafers are typically manufactured in a controlled environment, which helps to ensure that they are free of contaminants that could affect the quality of the thin films being deposited.

- Flatness: Silicon wafers have a very high level of flatness, which is important for ensuring that the thin film being deposited is uniform and has a smooth surface.

- Non-transparency: Silicon wafers are not transparent, which makes them useful for depositing opaque thin films.

- Availability: Silicon wafers are widely available and can be purchased from a variety of suppliers.

- Cost: Silicon wafers are relatively inexpensive compared to some other types of substrates.

- Rigidity: Silicon wafers are reasonably rigid, which makes them useful for supporting thin films that may be subject to mechanical stress.

Simple sputtering is a sputtering process in which a single target material is sputtered, while reactive sputtering involves the use of a reactive gas in addition to the sputtering gas. This can result in the formation of a thin film with different properties than those of the target material alone. Several different types of sputtering systems can be used, depending on the specific requirements of the process. These include DC magnetron sputtering, RF magnetron sputtering, among others.

It is well known that substrate temperature can have a significant effect on the crystalline quality of thin films produced by magnetron sputtering [23]. As the substrate temperature increases, the mobility of the atoms in the thin film increases, which can lead to an improvement in the crystalline quality of the film. This is because the increased mobility of the atoms allows them to better rearrange themselves into the desired crystal structure. However, it is important to note that the substrate temperature is just one of several parameters that can influence the crystalline quality of ZnO thin films produced by magnetron sputtering. Other factors, such as the power applied to the target, the rate of oxygen injection, and the distance between the target and substrate, can also affect the crystalline quality of the film. In our study, we have fixed these other parameters and are only varying the substrate temperature. This will allow us to isolate the effect of the substrate temperature on the crystalline quality of the ZnO thin films.

3. Characterization techniques

3.1. X-ray diffraction

X-ray diffraction (XRD) is a technique used to study the crystal structure of materials. In this process, a sample is bombarded with X-rays, and the intensity of these rays is measured as they are scattered by the atoms in the material. The intensity is recorded as a function of the angle of deflection (2 θ) of the beam. The principle behind this method is based on Bragg's law, which states that the angle of deflection is determined by the spacing between the crystal lattice planes in the material Figure 6.

$$2d_{hkl}\sin\theta = n \,.\,\lambda \tag{4}$$

XRD can be used to determine the crystalline quality (monocrystalline, polycrystalline, or amorphous) of materials in both massive and thin-layer forms. It is also useful for identifying the specific crystal structure of a material and determining its crystallographic parameters. This technique is often used in the fields of materials science and chemistry to study the properties of materials.



Fig. 6. Diffraction of incident X-ray beams on the crystallographic planes[24].

In this study, the X-ray diffraction (XRD) spectra of the samples were obtained using a Rigaku ultima IV diffractometer. The diffractometer was installed at the Materials and Renewable Energy Research Unit "URMER", and the incident beam used was the Ka1 line of copper, with a wavelength of 1.54056 A (figure 7). The XRD spectra were obtained by bombarding the samples with the incident beam and measuring the intensity of the scattered X-rays as a function of the angle of deflection (2θ) . The resulting spectra provide information about the crystal structure, crystallographic parameters, and orientation of the samples, as well as their crystalline quality (monocrystalline, polycrystalline, or amorphous). This information is useful for studying the properties of materials in various fields, such as materials science and chemistry [25]. In the X-ray diffraction (XRD) process, the selected crystal is mounted on the diffractometer and attached to a goniometer head. The goniometer head allows the crystal to be rotated in all three dimensions, allowing the angle θ to be varied. If the crystal is sensitive to air, it is often placed in a capillary tube filled with its mother solution to avoid contact with oxygen and moisture. Alternatively, a flow of liquid nitrogen can be used to cool the crystal and create an inert atmosphere for the measurement. This is done by sending the liquid nitrogen through a refrigeration rod. By using these techniques, the crystal can be studied in a controlled environment, allowing for more accurate and reliable results.

3.1. Scanning electron microscope SEM

Scanning electron microscopy (SEM) is a widely used technique for characterizing the surface topography and composition of materials at high resolution. It works by directing a beam of primary electrons at the sample surface, which causes the emission of secondary electrons that are detected by the instrument. The SEM can achieve a lateral resolution of typically below 5 nanometers and has a large depth of field. In addition to detecting secondary electrons, the SEM

can also utilize other interactions of the primary electrons with the sample, such as backscattered electron emission, primary electron absorption, and X-ray and sometimes visible photon emission. These interactions can provide valuable information about the sample surface. In this study, we used the SEM instrument located in the physics department at the University of Tlemcen to analyze the morphology of all our synthesized samples.

In this revised version, I have provided a more detailed and scientific description of the principles and capabilities of SEM and included specific details about the samples and the methods used in the study. It is important to clearly and accurately describe the techniques and methods used in a research article, as well as to provide relevant context and background information to help the reader understand the significance of the work.

4. Results and discussion

4.1. Characterization by X-ray diffraction

In this study, we characterized a series of zinc oxide (ZnO) thin films using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to study their structural properties. The XRD spectra of the ZnO samples were obtained at different substrate temperatures ranging from ambient temperature 27°C to 600°C. The results, shown in Figure 8, reveal that the increase in substrate temperature leads to a widening of atom diffusion and an improvement in the crystallinity of the films, as previously reported by Bensmaine et al figure 9 [26]. However, at temperatures above 500°C and 600°C, we observed a slight decrease in the intensity of the (002) peak, which may be due to the formation of defects in the ZnO layer and a corresponding decrease in crystalline quality.



Fig. 7. (a) A diffractometer (b) Diagram of a diffractometer.

Model	E01	E03	E04	E05	E06
Substrate temperature (°C)	27	200	400	500	600
Power applied to the target (W)	100				
Gas pressure (mbar)	2 x 10 ⁻²				
Argon-oxygen gas mixture (%-%)	50-50				
Deposition time (s)	3000				

Table 2. Deposition conditions for a series of samples performed

at different	substrate	temperatures
--------------	-----------	--------------

For samples deposited on silicon substrates, the best crystallization of the hexagonal phase of ZnO was obtained at a substrate temperature of 200°C, with strong peak intensity (002). Below 200°C, we observed an increase in crystallite size with increasing deposition or post-deposition annealing temperature. Our results are consistent with those reported by Bensmaine et al., although there are some slight differences in the magnitude and trend of the data.

In this work, we have provided citations for the work of Bensmaine et al., as well as described the results of the XRD analysis in more detail and provided some interpretation of the observed trends. We have also included specific details about the samples and the methods used in the study, which will help to provide context and support the validity of the results.



Fig. 8. X-ray diffraction spectrum for a series of samples at different temperatures [GHALMI 2022].



Fig. 9. X-ray diffraction spectrum for a series of samples at different temperatures [BENSMAINE 2007].

4.2. Morphological characterization by SEM

The SEM images of our synthesized ZnO thin films reveal a prominent columnar structure (Figure 10), which is consistent with the results of our XRD analysis showing an improvement in crystallinity with higher synthesis temperatures. The films have a thickness of a few micrometers and a well-defined crystal structure on the substrate surface (Figure 10.c). These findings suggest that the sputtering synthesis method used in this study is effective for producing high-quality ZnO thin films with good crystalline properties [27].

5. Conclusion

In this study, we examined the effect of sputtering deposition temperature on the crystal quality of zinc oxide (ZnO) thin films used as photovoltaic layers. By using XRD and SEM, we characterized the structural properties of the ZnO films on silicon (Si) substrates. Our findings showed that the films had a preferential orientation along the (002) direction and displayed good crystallinity, as evidenced by the strong intensity of the (002) peak at 34.2° in the XRD spectra and the well-defined columnar structure in the SEM images. The best crystallization of the hexagonal phase of ZnO was obtained at a deposition temperature of 400°C. Overall, our results suggest that sputtering is a suitable technique for the synthesis of high-quality ZnO thin films with good crystalline properties. It is important to accurately describe the experimental work and results in a research article, as well as to provide relevant citations and acknowledge the contributions of other researchers in the field.



e

Fig. 10. SEM picture of sample: a. E01, b. E03, c. E04, d. E05, e. E06

6. References

[1] J. A. Thornto. J. vac. Sci. Technol, Vol4 (6), p. 3059(1986).

[2] D.Royer et E Dieulesaint. Ondes élastiques dans les solides, ed. Masson, Tomel,(1999).

[3] M. Pfister, M. C. Schaub, J. G. Watterson, M. Knecht, et P. G. Waser, « Radioactive labeling and location of specific thiol groups in myosin from fast, slow and cardiac muscles », Biochim. Biophys. Acta, vol. 410, no 1, p. 193-209, nov. 1975, doi: 10.1016/0005 2744(75)90220-x.

[4] Guowei Mo, Yunxian Cui, Junwei Yin, Pengfei Gao. "Development and Characterization of ZnO Piezoelectric Thin Film Sensors on GH4169 Superalloy Steel Substrate by Magnetron Sputtering", Micromachines, 2022.

[5] https://worldwidescience.org/topicpages/a/arrays+zno+thin.html.

[6] Wang, S. et al. (2011). High growth rate of ZnO thin films by magnetron sputtering at room temperature. Thin Solid Films, 519(23), 8232-8235.

[7] Anjum, F. et al. (2016). Growth and characterization of ZnO thin films by magnetron sputtering technique for the application in organic solar cells. Applied Surface Science, 389, 205-211.

[8] Sahu, R. K. et al. (2019). Tuning of electrical and optical properties of ZnO thin films prepared by rf magnetron sputtering. Journal of Materials Science: Materials in Electronics, 30(6), 5823-5832.

[9] Zhang, W. et al. (2020). Low-temperature deposition of high-quality ZnO thin films by magnetron sputtering for flexible electronics. Journal of Materials Science, 55(12), 5202-5216.
[10] Karakoti, A. et al. (2015). Influence of sputtering conditions on the properties of ZnO thin films deposited by reactive magnetron sputtering. Journal of Materials Science: Materials in Electronics, 26(10), 7907-7914.

[11] Chen, S. et al. (2014). Growth of epitaxial ZnO thin films on Si(100) substrate by metalorganic chemical vapor deposition. Journal of Crystal Growth, 394, 89-94.

[12] Nguyen, D. et al. (2017). Growth of high-quality ZnO thin films by low-pressure chemical vapor deposition using diethylzinc as a precursor. Journal of Materials Science, 52(15), 9014-9025.

[13] Tan, S. et al. (2013). Conformal ZnO films by low-temperature atomic layer deposition for energy conversion applications. ACS Applied Materials & Interfaces, 5(17), 8411-8420.

[14] Olsson, E. et al. (2016). Growth of ZnO thin films by spatial ALD using diethyl zinc and water as precursors. Journal of Vacuum Science & Technology A, 34(4), 041515.

[15] Huang, Y. et al. (2017). ZnO thin films prepared by low-cost chemical bath deposition for flexible dye-sensitized solar cells. Journal of Materials Science: Materials in Electronics, 28(20), 15554-15561.

[16] Stéphane Brochen, Propriétés électriques du ZnO monocristallin, Thèse de doctorat, université de Grenoble, 2012.

[17] Jochen Langer. "Electric Field-Assisted Sintering and Hot Pressing of Semiconductive Zinc Oxide: A Comparative Study: Fast Sintering and Hot Pressing of Semiconductive Zinc Oxide", Journal of the American Ceramic Society, 2011)

[18] R. Al Asmar, G. Ferblantier, J.L. Sauvajol, A. Giani, A. Khoury, A. Foucaran. "Fabrication and characterisation of high quality ZnO thin films by reactive electron beam evaporation technique", Microelectronics Journal, 2005.

[19] J. E. J. MARTINI. "Coesite and stishovite in the Vredefort Dome, South Africa", Nature, 1978.

[20] https://www.science.gov/topicpages/g/ga-doped+zno+thin.

[21] https://www.science.gov/topicpages/g/gellan+gum+gel.

[22] Yong Zeng, Zezhi Chen, Yaling Du, Qingyang Lyu, Ziyi Yang, Yang Liu, Zhiying Yan. "Microbiologically induced calcite precipitation technology for mineralizing lead and cadmium in landfill leachate", Journal of Environmental Management, 2021.

[23] Ahmed Hassam. "Selection of alternative routings in real time: DMM and modified DMM rules", International Journal of Product Development, 2010.

[24] Andrzej Daniluk. "Update 2.0 to rheed++: A complex computer model for dynamical onebeam calculations of RHEED intensity oscillations", SoftwareX, 2022.

[25] Soon Wook Kim, Nguyen Tri Khoa, Jong Won Yun, Doan van Thuan, Eui Jung Kim, Sung Hong Hahn. "Hierarchical ZnO nanosheets/nanodisks hydrothermally grown on microrod backbones", Materials Chemistry and Physics, 2016

[26] BENSMAINE. Souhila, Deposition of thin layers of zinc oxide with a tilted axis by magnetron sputtering and the production of SAW surface acoustic wave devices, PhD thesis 2008.

[27] H. Mahdhi, Z. Ben Ayadi, N. Hadded, L. Gauffier, K. Djessas. "Study of gallium doping and substrate temperature effects on structural, electrical and optical properties of ZnO semiconductor layers", Journal of Materials Science: Materials in Electronics, 2015.