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Structural and Electrical Specification of ZrO_2 Nano Thin Film Prepared by PLD

Suroor H. Taha[1,*] and Thamir A. Jumah[2]

[1,2]Department of Physics, College of Science, Al-Nahrain University, Baghdad, Iraq

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Abstract

Zirconium dioxide was prepared as a thin film by using pulse laser deposition (PLD). Subsequently, the films had been thermally treated by annealing process at temperature 450 °C. The structural and electrical parameters of thin films were investigated. As-deposited films were amorphous and had a large surface density of ablated particles. The Annealing process resulted change the phase from amorphous to polycrystalline. The X-ray diffraction of all these films has a polycrystalline structure with two different phases named tetragonal and monoclinic. Hall measurements indicate that the charge carriers of all these films were p-type. In addition, the Hall coefficient suffers some change with thin film thickness. The AC results measured showed the films have resistance and capacitance properties. The AC conduction is dominated by hole cattier.

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*Corresponding author: suroorhekmat@yahoo.com

1. Introduction

Thin film can be characterized as a thin solid layer of deposition material, their thickness is among between a few nanometers to may be many micrometers or more. As known, the structure of thin films like such material is divided into amorphous and crystalline structure depending on the preparation and boundary conditions as well as the material type and nature. Films and thin films include two main parts: the deposition layer and the base substrate. Subsequently, another field of application science is called material science which involved thin film deposition [1]. In recent years, thin films have pulled the attention of researchers and scientists and have been a subject of dense research and expansion. Thin film innovation is a developed field including a wide scope of uses for example bio-systems and optical communications [2]. Recently, thin films have had a great development of preparing methods include chemically and physically techniques. Thin films are widely used in different fields of application such as optical devices, energy storage, and chemical deposition and for radiation attenuation techniques. In recent, a large portion of the innovations are utilized for limiting the materials into nano-size just as nano-thickness prompting the development of new and one of a kind practices of such materials can be obtained in optical, electrical, optoelectronic, bio technique, dielectric applications, etc. [1]. Zirconia is one of the important ceramics material due to specific property that is used as a biomaterial that has a promising future and has a unique feature called transformation toughening, due to its high mechanical strength and fracture toughness, which can give it higher strength compared to other type's ceramics. Zirconia also has unique characteristics such as optical, electrical, thermal, and mechanical; making it a good choice for thermal barrier coating, structural materials, semiconductor materials and solid oxide fuel cell electrolytes. Due to its stable photochemical properties, it is directly applicable to photonics. Zirconia implants are becoming increasingly important in the field of dental medicine due to their good mechanical properties, biocompatibility and for aesthetic reasons [3]. ZrO_2 is classified as a semiconductor because it has a p-type wide band gap and tends to become more conductive with increasing temperatures. ZrO_2 is also an important dielectric material for potential application as an insulator in transistors in future nano-electric devices. The fully stabilized ZrO_2 nanoparticles are also well suited for high temperature energy conversion systems, attributed to its high oxygen ion transport capabilities and long-term stability [4-6].

The crystal structure of ZrO_2 significantly influences its physical properties. Furthermore, pure zirconia has three crystal phases at different temperatures: monoclinic, tetragonal, and cubic. Generally, at very high temperatures above 2370 °C the material has a cubic structure. At intermediate temperatures range (1150–2370 °C), it has a tetragonal structure [7]. At low temperatures (below 1150 °C) the material transforms to the monoclinic structure which is a thermodynamically stable phase [4-6]. However, appearance of both cubic and tetragonal metastable phases at low temperatures (LTP) has been observed by numerous authors depending on the precursors, the condition of preparation, the particle size and the presence of impurities and dopants. Several techniques for producing zirconium oxide ZrO_2, such as sol/gel method, vapor phase method, pyrolysis, spray pyrolysis, hydrolysis, hydrothermal, pulse laser deposition (PLD) and microwave plasma [8]. Among these methods, pulsed laser deposition (PLD) is a simple, flexible and fast to prepare high quality thin films from metals, semiconductors and insulators [9,10].

In this work, ZrO_2 thin films have been fabricated by pulsed laser deposition (PLD) mostly using Nd:YAG laser. The films were prepared by reactive laser ablation of a pure zirconium target under (2×10^{-2} mbar) vacuum. The purpose of this project is to specification and characterization the performed thin films of zirconia dioxide.

2. Material and Methodology

2.1 Material preparation

Commercially available Zr (99.99 % purity) powder was compacted into a circular disk pellet of 2.5 cm in diameter and 0.4 cm thickness by a hydraulic press under 4 ton pressure. The ZrO_2 film is deposited on glass substrates by virtue of pulsed laser deposition technique.

2.2 System set-up

Q-switched Nd:YAG laser operating at different energies (600, 700 and 800) mJ and laser fluency (500 np). The operation condition is the following; laser wavelength (1064) nm (pulse width 10 ns) repetition rate (6 Hz). The system chamber was evacuated (2×10^{-2} mbar). The distance between the target- substrate was 2cm. The angle between the horizontal target surface and the gun nozzle was 45^o.

2.3 Annealing process

Atmospheric furnace was used to perform the annealing process, the annealing temperature was selected at 450 ^oC for half hour. One benefit of this type of furnace is to enrich the oxygen.

2.4 Thickness Measurement

The thickness of the prepared films was measured by optical finger technique. The thickness was found to be (106, 119 and 228) nm.

2.5 Structural Analysis

The structural analysis of the films was studied by virtue of XRD (PAN Alytical co., Made in Hollanda) with the operation condition, CuKα radiation with wavelength 1.5406 A^o, voltage = 45.0 (kV), current = 40.0 (mA) at 2-theta from 20 to 80 degree. The crystallite size (D) was calculated for (0 1 1) reflections of t-zirconia, using the following Scherrer formula with an accuracy of ±3 nm:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad \ldots(1)$$

where λ is the wavelength of X-rays used, θ is the angle of diffraction and β is the full width at half maximum (FWHM). [11]

2.6 Electrical analysis

Measurements of Hall Effect had been done by using (iRASOL, HSR-24AC) system. When the current flowing in a thin plate of a conducting or semiconducting material, it creates a potential difference (Hall voltage) on opposite sides of the thin sheet, these consider the main principle of the Hall Effect work. Hall voltage was created by applying a magnetic field (B = 5000 Gauss) perpendicular to the Hall element. When applying a magnetic field (B) with perpendicular direction on the electric field, then yields a current and generation transverse electric voltage given by when I is called the hall current, V_H is called hall voltage, and R_H called Hall Coefficient. From Eq. (2) it can be calculate Hall coefficient value, and the sign of Hall coefficient determines the type of carrier. [12]

$$R_H = \frac{V_H}{I}.\frac{t}{B} \qquad \ldots(2)$$

In addition to the type of carrier, where the signal is a negative semiconductor coefficient, the type of n-type and if positive, the type of p-type as the following equations; [12,15]

$$R_H = \frac{-1}{n.e}, \text{ for } n\text{-type} \qquad \ldots(3)$$

$$R_H = \frac{1}{p.e}, \text{ for } p\text{-type} \qquad \ldots(4)$$

where e is the electron charge. To calculate the conduction by the following equation if the conduction is due to one carrier's type e.g. electrons: [12,15]

$$\sigma_n = qn\mu_n, \text{ for } n\text{-type} \qquad \ldots(5)$$

$$\sigma_p = qp\mu_p, \text{ for } p\text{-type} \qquad \ldots(6)$$

and from the result of conduction can be measure the Hall mobility by the Eq. (8); [12,16]

$$\mu_H = \frac{\sigma}{n.e} \qquad \ldots(7)$$

$$\mu_H = \sigma|R_H| \qquad \ldots(8)$$

3. Results and Discussion

3.1. X-ray analysis

The crystal structure and crystal orientation of ZrO_2 thin films are studied carefully. The deposited film and thin film had been prepared by pulse laser deposition (PLD) technique at energies range (600, 700, and 800) mJ for get layer thickness (106, 119, 228) nm respectively, which are annealed at a temperature 450 ^oC in an atmospheric furnace for half hour. The structural of the deposited layers were analytical by virtue of X-ray diffraction (XRD) technique. The effect of annealing temperatures ZrO_2 on the structure of the films is also discussed. Figure 1 shows that the films at ambient temperature were amorphous. After the annealing process, the films have a polycrystalline structure which shows in Figure 2.

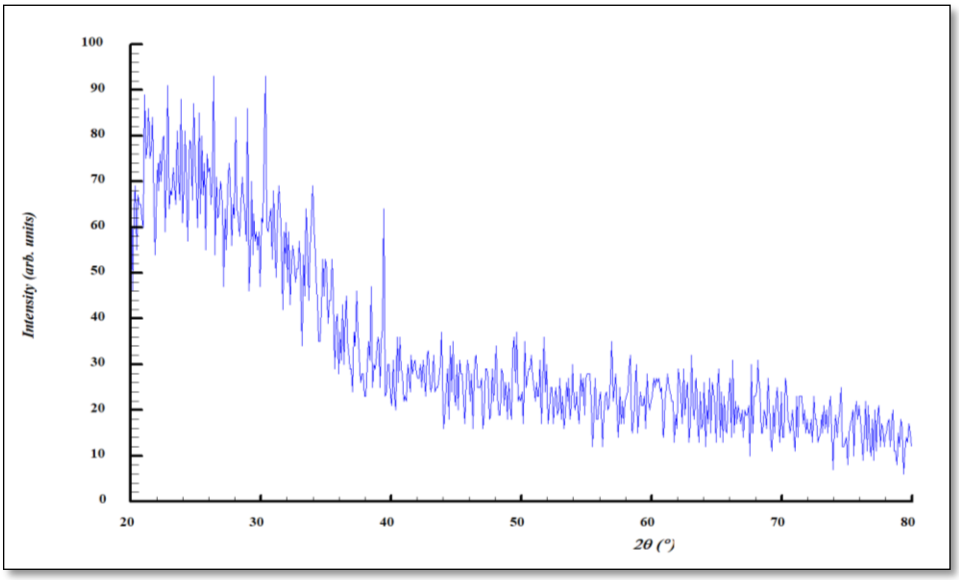

Figure 1. The XRD spectrum of ZrO_2 thin films deposited at E = 600 mJ with ambient temperature.

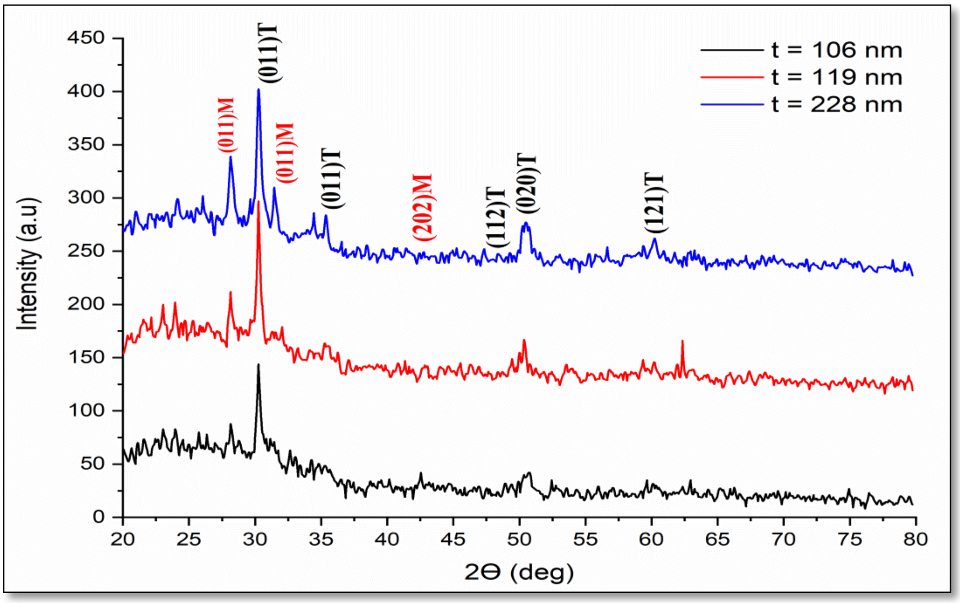

Figure 2. The XRD spectrum of ZrO_2 thin films at different thickness at Ta = 450 °C.

When the temperature is 450 °C, thin films structure were transformed into crystalline films. It is clear that the amount of annealing temperature has significant influence on the structure of the films. According to Crystallography Open Database (COD ## 0.21-1010912, 0.08-1525706) these figures have substantial sharp diffraction peaks at 30.12° (011), 50.3° (112) and 60.2° (121). The conclusion from the identification of the crystalline phases that have mix of two phases are tetragonal and monoclinic phase of the ZrO_2 thin films and has desired orientation along the (011) direction at 30.12° [13]. These figures also show that the highest peaks were obtained by achieving annealing process where the heat treatment increases of the plane intensity and thus increases of the crystallite size. With increasing annealing temperatures on the prepared films, the desired orientation along (011) plane increases, suggesting that the annealed process improved the crystalline structure as the small crystals joined together due to heated treatment. Table 1 shows the structural parameters, crystallite size and inter-planar spacing of ZrO_2 thin films with 450 °C annealing temperature. The phase transition from amorphous to crystalline with an increase in the grain size. The films produced by PLD are amorphous and the reason for the PLD technique contains small and medium sized particles in the resulting films. Using the Scherer's formula to calculate the crystallite size. At thicknesses of 106, 119, and 228 nm, the crystallite size increased as the thickness increased. These contrasting card results indicate that the phase formation in zirconia is more complex and depends on the method of deposition process conditions, energy of the deposition, annealing temperature etc. This result agreement with the Sha Zhao, Fei Ma studied [14], S. Sayan, N. V. Nguyen and etc., [15], Farida Rebib, Ange lique Bousqet and etc., [16].

Table 1. Structural parameters for XRD results for ZrO_2 thin films with different energies deposition and different thickness at 450 °C annealing temperature.

Ta(°C)	*E* (mJ)	*t* (nm)	2θ (Deg.)	Hkl	FWHM (Deg.)	d(Å)	Crystallite size(nm)
450	600	106	30.332	(011)	0.3347	2.9468	25.68
	700	119	30.332	(011)	0.2793	2.9468	30.78
	800	228	30.233	(011)	0.2939	2.9563	29.24

3.2. Hall effect measurement

Hall coefficient (R_H), Hall mobility (μ_H), electrical conductivity (σ), and carrier concentration (n_H) have been determined from Hall measurements for ZrO_2 thin films in which prepared by PLD technique on glass substrate at energy range (600,700,800) mJ and different thickness (106,119,228) nm respectively, which are annealed at 450 °C for half hour. From Hall measurements appear that charge carriers of all these films were *p*-type (i.e., the conduction is dominated by holes). Figures 3 and 4 shows the variation of Hall mobility and carrier's concentration as a function of thickness. Table 3.2 shows with increasing the thickness of films the carrier concentration is increasing due to the concentration of the defect in the film increasing as the thickness increases, resulting in an increase in the charge carrier. While increases in thickness resulted in a decrease in Hall mobility. The relationship between n_H and μ_H is inverse. As a result, the electrical conductivity will decrease, as shown in Figure 5.

Table 2. Hall Effect measurements for ZrO_2 thin film with different thickness of films.

Ta (°C)	Thickness (nm)	R_H (m^{-3} C^{-1})	$n(cm)^{-3}$	σ $(\Omega.cm)^{-1}$	μ_H (cm^2/V.s)	Carrier type
450	106	4.93×10^3	1.27×10^{15}	1.68×10^1	8.27×10^{04}	P
	119	3.19×10^3	1.95×10^{15}	9.22×10^0	2.94×10^{04}	P
	228	1.92×10^3	3.26×10^{15}	4.86×10^0	9.31×10^{03}	P

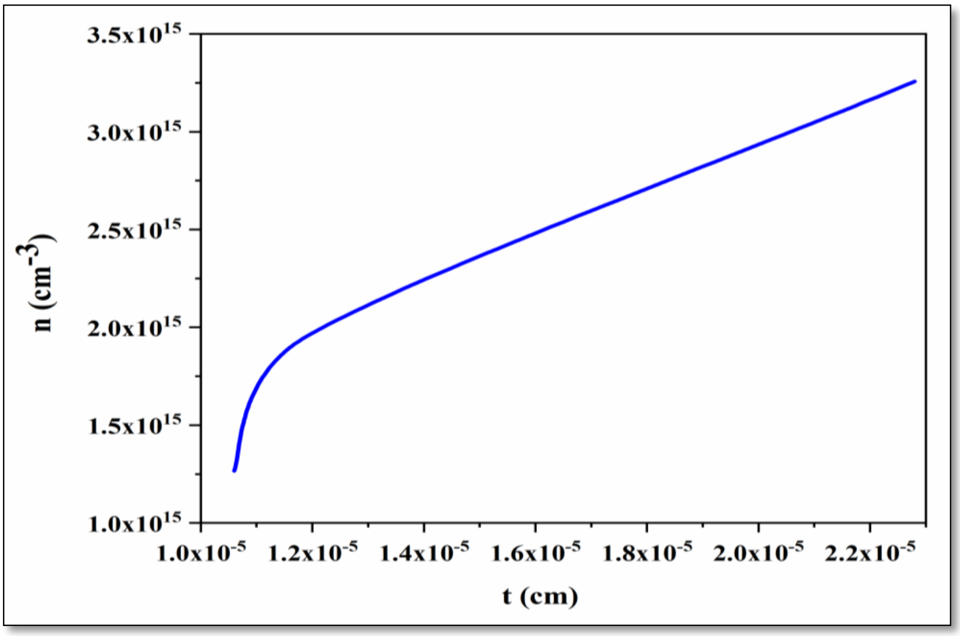

Figure 3. Variation of carrier concentrations (*n*) function of thin films thickness.

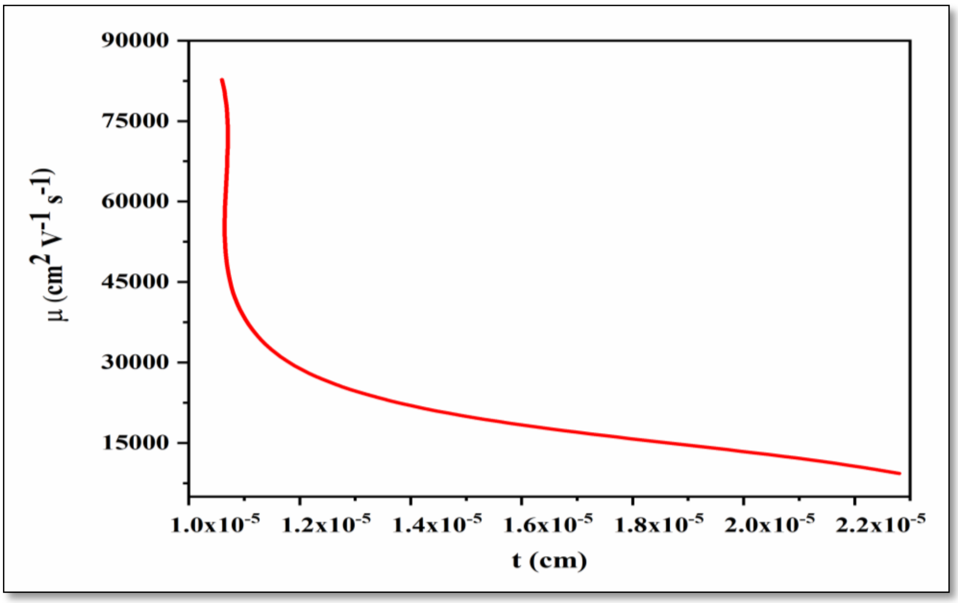

Figure 4. Variation of Hall mobility (μ_H) function of thin films thickness**.**

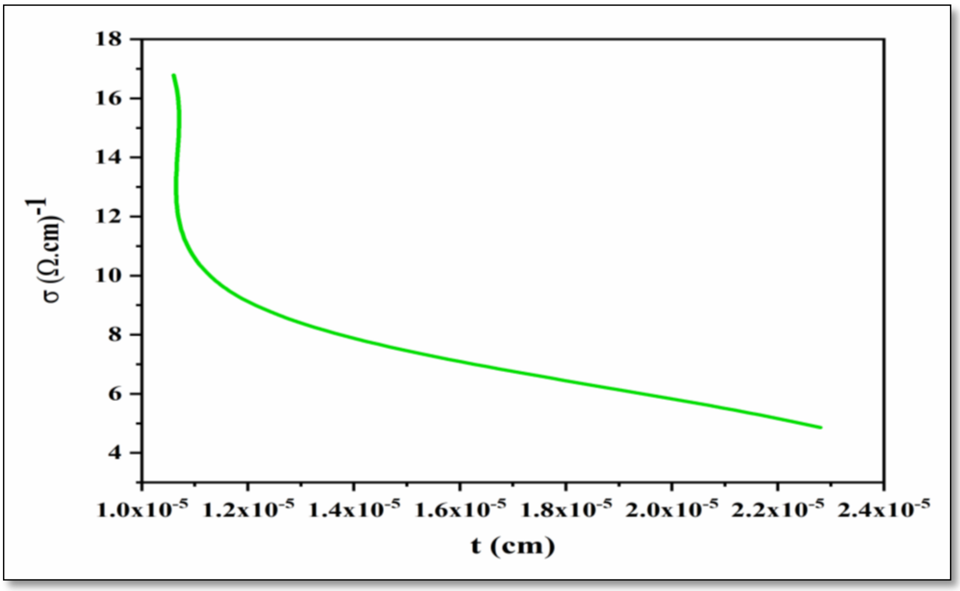

Figure 5. Variation of electrical conductivity (σ) function of thin films thickness.

4. Conclusion

1- The deposition technique has an influence parameter for obtaining efficient results in structural and electrical properties.
2- Both structural and electrical properties are enhanced by virtue of annealing treatment in a condition of Oxygen enriched.
3- Due to the annealing process, the thin film became more denser and therefore the transmittance will be decreased.

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