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PREPARATION AND STUDY OF THE STRUCTURAL AND OPTICAL TRAITS OF AG: ZRO_2 NANOSTRUCTURE THIN FILMS PREPARED VIA SPIN COATING: EFFECT OF SPIN SPEED ON THIN FILMS PROPERTIES

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ABSTRACT

Thin films of silver: zirconium oxide (Ag: ZrO_2), prepared using the spin coating method (SCM) with 2% silver nitrate (Ag NO_3) and 1% zirconium nitrate (Zr (NO_3) 4) on glass substrate at room temperature, with different spin speeds (1000, 2000 and 3000) rpm. X-ray diffraction (XRD) and Field Emission scanning electron microscopy were used to investigate the structural properties of the grown silver films. The optical properties of these thin films were distinguished by UV-vis spectroscopy. The films' polycrystalline nanostructure was revealed by X-rays, and the grain size shrank with increasing spin speed (from 1000 to 3000 rpm). The scanning electron microscope showed that the average particle size also decreases from (80.7 - 42.67) nm with an increase in the spin speed from (1000 - 3000). and Uv-vis spectroscopy showed that the transparency of the films increases, while the absorbance, coefficient attenuation, and absorption coefficient of the films decrease when the spin speed increases.

Keywords: (Ag: ZrO_2) thin film, spin coating (SC), nanostructure thin film, structural properties, optical properties.

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1. INTRODUCTION

Metal thin films, such as silver and aluminum, have gained popularity as for microelectronic devices for a variety of applications, including contact electrodes in solar cells and gas sensors, organic light-emitting diodes, heat-reflecting mirrors, anti-reflective coatings, and flat-panel displays [1-3]. Because of their numerous industrial and medical applications, silver thin films have been extensively researched[4]. Ag thin films can also achieve unique electrical and optical properties to make them perform better in optical devices compared to other metal films [5]. It is also a good option for electrical contacts in high-temperature superconducting devices and as interconnectors inside electronic devices. [4].

Among the advantages of applying silver thin films on electronic devices are the following (low manufacturing cost, high uniformity across the flat base, good adhesion to the base, thermal stability, low specific resistance, and low particulate pollution) [6]. Several methods, including magnetic sputtering, plasma jet ,thermal evaporation, and chemical bath deposition, were used to create silver films [7,8].

A thin film of zirconium oxide (ZrO_2) has received great attention from researchers because of its distinctive mechanical, electrical, and optical properties, such as a low thermal conductivity at room temperature, a high refractive index, high oxidation resistance, and a high melting temperature of 2680 °C [9-11]. It is also one of the most important transition metal oxides that have a relatively large energy gap of 5.2 to 5.79 eV [12]. ZrO_2 has been used in a variety of applications, including CD reader heads, gas sensors, solid oxide fuel cells, memory devices, and bioceramics [13-15]. Also, ZrO_2 has several crystal structures that are monoclinic, cubic, and tetragonal, and these structures play an important role in the dielectric properties of the material [8-11].

Several chemical and physical deposition techniques are used to produce high-quality ZrO_2 thin film, including the sol-gel method, thermal evaporation, magnetic sputtering, and pulsed ion beam evaporation [16-19]. Numerous industrial and manufacturing sectors employ the sol-gel spin coating method, which involves three critical steps: first-solution deposition on the substrate, second-stage high-speed rotation, and third-stage drying [20]. The parameters of spin coating are very important in stable thin film deposition. These parameters include the type of substrate, type of solvent, solution viscosity, spin time, and spin speed [21-24]. The range of spin speed is important to achieve the required thickness as it is possible to produce very homogeneous thin films when it exceeds 1000 rpm. It is also possible to obtain homogeneous films at 500 and 600 rpm if the process is done more carefully, as the most common coating devices reach 8000 rpm [25].

The main objective of this research is to study the effect of the spin coating speed on the structural and optical properties of the prepared films

2. EXPERIMENTAL PART

For deposition of Ag: ZrO_2 thin films, silver nitrate powder (Ag NO_3), zirconium nitrate powder (Zr $(NO_3)_4$), NaOH, and sodium hydroxide with a purity of 99% were used for each of them and glass substrate. All of them were purchased from Sigma Aldrich, USA.

The solution was prepared by placing Ag NO_3 and Zr (NO_3) 4 in a 2:1 ratio, respectively, in 100 ml of

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deionized water on a magnetic stirrer, then adding 1 M NaOH to the solution drop by drop to set the pH of the solution at 9. Blending the solution continues for two hours at 60 °C to form a gel. Then drops of the solution are placed on a glass substrate for 30 min after cleaning, removing impurities, and drying them. After that, the substrate on which the solution is deposited is placed inside the spin coating system for 50 sec at room temperature, and the spin speed is changed (1000, 2000, and 3000) rpm. Gray-color thin films of high uniformity and adhesion were obtained with thicknesses of (106, 90, and 83) nm for each spin speed (1000, 2000, and 3000) rpm, respectively, as the relationship is inverse between them, as the increase in the speed will decrease the thickness. Thickness was measured through the optical interferometer technique.

The structural properties of the prepared thin films were analyzed by an X-ray diffraction device (Rigaku) and Field Emission Scanning Electron Microscope (FESEM) Hitachi model S-4160 operating at 30 kV, while the optical properties were analyzed by UV-visible spectrophotometer (Union space international Uv1601) has spectral range 300-900 nm.

3. RESULTS AND DISCUSSIONS

3.1 X-Ray Diffraction Result

Figure-1 shows the X-ray diffraction pattern of Ag: ZrO_2 thin films with different spin coating speeds prepared by the spin coating method. The diffraction pattern shows the following crystal planes (111), (200), (202), and (311) of Ag taken from JCPDS card number 04-0783 and at diffraction angles of (2θ = 38.24º, 44.44º, 64.56º and 77.52º), respectively. As for the crystal planes (111), (200), (202), and (311) they are for ZrO2 and at diffraction angles (2θ= 30.24º, 35.48º, 50.80º and 60.20º) taken from JCPDS card No. (17-0923), respectively. The figure also shows that all the prepared thin films have a polycrystalline nanostructure with the same diffraction pattern. Table-1 shows the values of the structural parameters of the prepared films. We notice a decrease in the particle size when the spinning speed is increased from 1000 to 3000 rpm. This result shows a modification in the structural properties of the films as increasing the speed increases the centrifugal force and thus increases the spread of the gel on the substrate to form uniform Ag: ZrO_2 thin film, Since the thickness decreases with the increase in the spin speed, and since the crystal size is the thickness of the nano- thin film, so the process of collecting the particle decreases with the decreasing thickness. Therefore, the increase in the spin speed decreases the crystal size. This is agreed with [26].

The value of crystallite size (D) is calculated via Debye–Scherer's formula shown by Equation (1).

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

Whereas (D) is the crystallite size (nm), λ is the wavelength of x-ray -Cu-Kα radiation (0.15406 nm), θ is the diffraction angle (degree), and β is the Full Width at Half Maximum (FWHM) of peak

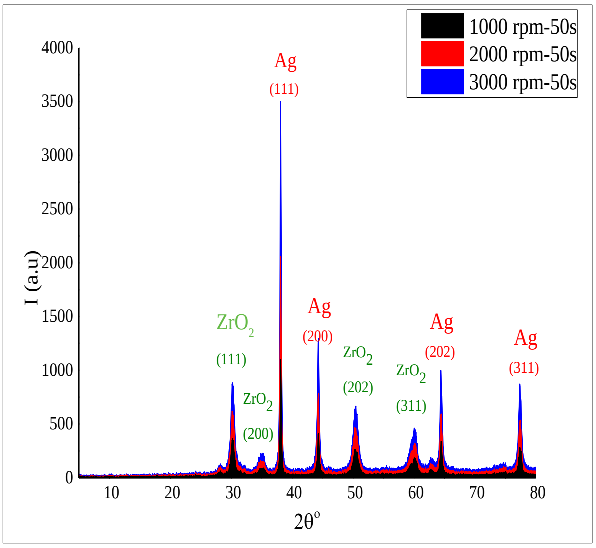

Figure-1. X-ray diffraction pattern of Ag: ZrO_2 films prepared by spin coating and at different spin speeds (1000, 2000, and 3000) rpm.

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Table-1. Structural parameters of Ag: ZrO_2 films prepared by spin coating and at different spin speeds obtained from XRD patterns.

Samples at different spin speed coating	Type of particle	2θ (degree)	crystallite size (D) (nm)	hkl
At 1000 rpm	ZrO_2	30.24	105.20	111
	ZrO_2	35.48	100.31	200
	Ag	38.24	111.15	111
	Ag	44.44	107.63	200
	ZrO_2	50.80	101.77	202
	ZrO_2	60.20	98.85	311
	Ag	64.56	105.02	202
	Ag	77.52	102.65	311
At 2000 rpm	ZrO_2	30.24	80.76	111
	ZrO_2	35.48	76.92	200
	Ag	38.24	85.38	111
	Ag	44.44	82.30	200
	ZrO_2	50.80	77.69	202
	ZrO_2	60.20	75.83	311
	Ag	64.56	80.1	202
	Ag	77.52	78.46	311
At 1000 rpm	ZrO_2	30.24	62.12	111
	ZrO_2	35.48	59.16	200
	Ag	38.24	65.67	111
	Ag	44.44	63.31	200
	ZrO_2	50.80	59.76	202
	ZrO_2	60.20	58.33	311
	Ag	64.56	62.61	202
	Ag	77.52	60.35	311

3.2 Scanning Electron Microscope (SEM)

Figure-2 shows the analytical images of the Ag: ZrO_2 thin film deposited by (FE-SEM) at different spin speeds. The figure shows that the prepared thin films have a granular nanostructure and islands-shaped agglomeration, and this is due to the nature of the overlapping of silver and zirconium oxide. The images also show some luminous assemblies and granules that indicate silver. It also shows that when the speed increases, Due to the increase in centrifugal force and the substance spreading on the substrate surface as spin speed increases, these particles spread. It appears as in Figure-2a that the composition is large and spherical granules, and the granular size begins to decrease as in Figure-2b when the spin speed increases to 2000 rpm and in Figure-2c at the spin speed 3000 rpm, we notice a more decrease in granular size with the close of the particles between them that agree with [27, 28]. This result is similar to the results of X-ray diffraction. Table-2 shows the average particle size of the prepared Ag: ZrO_2 thin films with different spin speeds.

Table-2. The value of the average grain size for Ag: ZrO_2 films prepared by spin coating and at different spin speeds was obtained from FESEM images.

Samples at different spin speed coating	Average grain size D (nm)
At 1000 rpm	80.7
At 2000 rpm	61.92
At 3000 rpm	42.67

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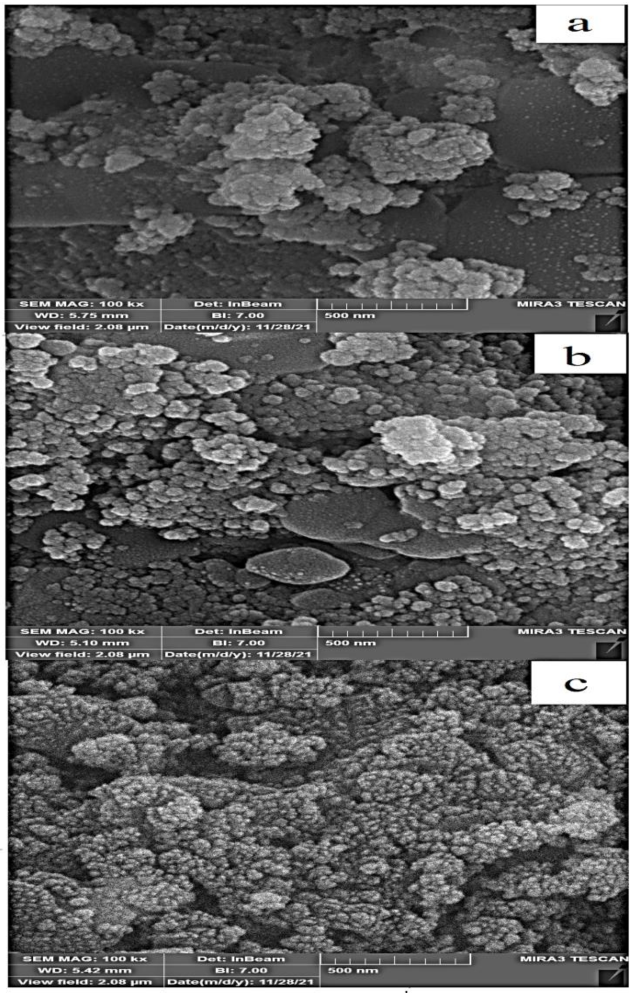

Figure-2. FE-SEM images of Ag: ZrO_2 films prepared by spin coating and at different spin speeds.

3.3 Optical Properties

Figure-3 shows the optical properties of Ag: ZrO_2 thin films deposited at different spin speeds. it shows that the transmittance of these nanostructure films is low, and this is due to the effect of the metallic silver material, as one of the characteristics of the metal thin films is that it is low transmittance and also shows an increase in it when the spin speed increases, as it increases from 9% to 15%. Contrary to all the absorbance curves, absorbance coefficient and coefficient attenuation decrease with the increase in the spinning speed from (2-5), (13-2) and (4-6), respectively. Those agree with [28]

As a result of the increase in spin speed, which led to a decrease in the thickness of the thin films, and according to the relationship of thickness with absorbance based on Lambert's law, the decrease in thickness leads to a decrease in the absorbance and an increase in the transmittance of the films depending on the inverse relationship between them.

Also, as a result of the direct relationships of the absorbance with the attenuation coefficient and the absorption coefficient, it is clear that they decrease with the decrease in absorbance. Also, the film thickness decreases and the light scattering decreases when the rotation speed is increased

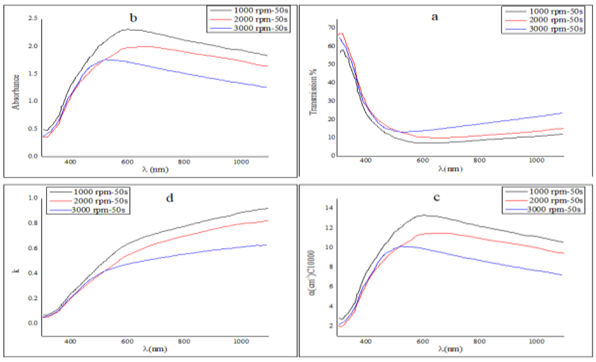

Figure-3. Optical properties of Ag: ZrO_2 at different spin speeds.

4. CONCLUSIONS

In this study, the spin coating was used to create Ag: ZrO_2 nanostructure thin films at various spin speeds. The findings were as follows:

a) The films' thickness is measured using the optical interferometer technique, and it drops from 103 to 85 when the spin speed is increased from 1000 to 3000 rpm.

b) According to X-ray diffraction results, the films have a polycrystalline nanostructure and many of the characteristic peaks of zirconium oxide and silver are present. The crystal size of the films decreases while the peak intensity increases with increasing spin speed.

c) It was found through FE-SEM that the thin Ag: ZrO_2 films have a granular structure and the appearance of crystal islands and that the rate of their particle size decreases with the increase of the close between the grains when the spinning speed increases, and this is consistent with the results of X-ray diffraction.

d) By Uv-visible spectroscopy to find out the optical properties, the transmittance of the films is low due to the presence of silver, but it increases with increasing spin speed, unlike each of the absorbance curves, absorption coefficient, and attenuation coefficient, the decreased with increasing spin speed.

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