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Effect of Silver Doped Nanostructured ZrO2 Thin Films on Some physical properties

Abstract: - Disengage and silver-doped ZrO2 samples with different percentages of Silver content (2%,4%) are grown via spray pyrolysis. XRD has demonstrated that the pinnacle of the maximum force compares to the favored direction (111) for ZrO2 films at 4% of silver. The Grain size for unadulterated ZrO2 molecule is (13.02 -14.62) nm with ZrO2: 4% Ag, though the dislocation density boundary diminishes from 58.98 to 46.67, though the strain (%) boundary expanded from 26.61 to 23.70, AFM examines uncovered a smooth surface Rrms harshness esteems decline from 7.68 nm to 3.23 nm from ZrO2 to ZrO2: 4% Ag. Besides, the Roughness Average saw in the scope of 685 nm to 4.12 nm with Undoped ZrO2 and ZrO2: 4% Ag subsequently. The particle size saw in the scope of 69.30 nm to 51.02 nm with ZrO2 and ZrO2: 4% Ag subsequently. The maximum transmittance value of the pure sample is 90%, which decreases by silver doping increase. The minimum transmittance value for 4% Silver doping is 70 %. Band gaps of Undoped ZrO2, ZrO2: 2% Ag and ZrO2: 4% Ag films were 5.26 eV, 5.20 eV and 5.14 eV, respectively. Doping with silver raises the absorption coefficient while lowering the optical constants

Keywords: ZrO2, silver, spray pyrolysis technique, Structural, AFM.

1. Introduction

Zirconia thin films are highly intriguing since they are used in various domains, including the biological and optical sciences [1]. Thin metal oxide films, such as those formed of ZrO_2, and AlO_2, are essential for optical applications like antireflective coatings, and microelectronic devices [2]. Huge broadband gap, strong dielectric coefficient, and thermal durability are only a just some zirconia's remarkable properties [3,4]. ZrO_2 thin film has the ability to absorb photons through two inter-band transitions (direct at 5.87 eV and indirect at 5.22 eV, respectively) [5-7]. Numerous techniques, including treatment, doping, and molarity change, among others, can increase ZrO_2 applications [8]. Zirconia is a great material for aesthetic farming and plays a significant part in dental materials, such as implanted teeth, because of its delicate white appearance [9]. Several methods for depositing ZrO_2 were employed, like; pulsed laser deposition [10], Plasma spraying [11], sol-gel [12-15], electrochemical deposition [16], thermal evaporation method [17] DC magnetron sputtering [18], dip coating [19], RF sputtering deposition [20], and spray pyrolysis method [21-25]. Zirconium oxide thin films were

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formed in this paper using a spray pyrolysis process at varied Ag doping, to study the physical characteristics of ZrO_2 and ZrO_2: Ag.

2. EXPERIMENTAL

Thin films of both materials were produced using spray hydrolysis. Disengage and silver-doped ZrO_2. $ZrCl_2$ from Fluke, which is 99.99% pure, was delivered as 0.1 M of silver homogenous and dissolved in distilled water. In order to stop Zirconia hydroxide from forming, one to two drops of HCl were added. Similar to that, silver-doped films were produced using an aqueous solution of $AgCl_2.6H_2O$. ZrO_2 sheets were supported on a substrate made of slide glass microscope. After that, the substrate is put on the plate and gradually warmed up until the deposition temperature is obtained. The prepared solution was sprayed with a glass nozzle onto the substrate using air as the carrier gas while being maintained at 450 ^oC. The experiments were carried out with multiple films doped at the same conditions, using a tip held at an offset of 30 cm above the surface of the substrate to guarantee the accuracy of the results. The circumstances above were discovered to be ideal in terms of the films' quality. Layer-grown materials adhered well to their supports. By using the optical interference method, the thickness was (325-350) nm. the XRD was employed to determine film structure. AFM is employed to study film surface. Shimadzu UV-VIS-NIR spectrophotometer was utilized to assess transmission and absorption.

3. RESULTS AND DISCUSSIONS

Fig. 1 provides the XRD patterns of the disengage ZrO2 and ZrO2: Ag films in line with JCPDS card number 27.0997. Every structure has a dispersion peak that is approximately 30.39°, 35.24°, 50.52°, and 60.18°, that correlate to the favored directions (111), (200), (220), and (222), correspondingly [26, 27].

Grain size (D) was evaluated via Scherer's formula [28-30]:

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

Where β is (FWHM) and λ is the operating X-ray wavelength (1.5406Å). The acquired data are given in Table 1. It shown that the Grain size for unadulterated ZrO_2 molecule is about (13.02 -14.62) nm with ZrO_2: 4% Ag. the same behavior was noticed in references [31,32].

The dislocation density (δ) is employed by Eq. (2) [33-35]:

$$\delta = \frac{1}{D^2} \qquad (2)$$

The strain (ε) is determined by Eq. (3) [36-38]:

$$\varepsilon = \frac{\beta cos\theta}{4} \qquad (3)$$

Table 1 presents the outcomes. Dislocation density drops from 58.98 to 46.67 nm with the addition of silver. By boosting the quantity of silver, the strain is reduced [39–40]. Fig. 2 shows the fluctuation of FWHM, D, and against Silver concentration.

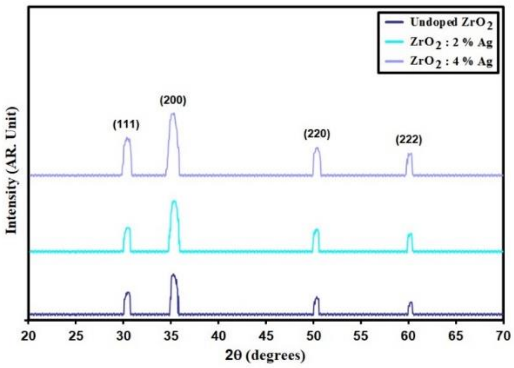

Fig.1. XRD styles of grown films.

Samples	2 q (°)	(hkl) Plane	β (°)	E_g (eV)	D (nm)	dislocation density (δ) ($\times 10^{14}$) (lines/m^2)	strain (ε) ($\times 10^{-4}$)
Undoped ZrO_2	35.24	200	0.64	5.26	13.02	58.98	26.61
ZrO_2: 2% Ag	35.21	200	0.61	5.2	13.66	53.59	25.36
ZrO_2: 4% Ag	35.18	200	0.57	5.14	14.62	46.67	23.7

TABLE 1. *D*, E_g and structural coefficient of deposit films.

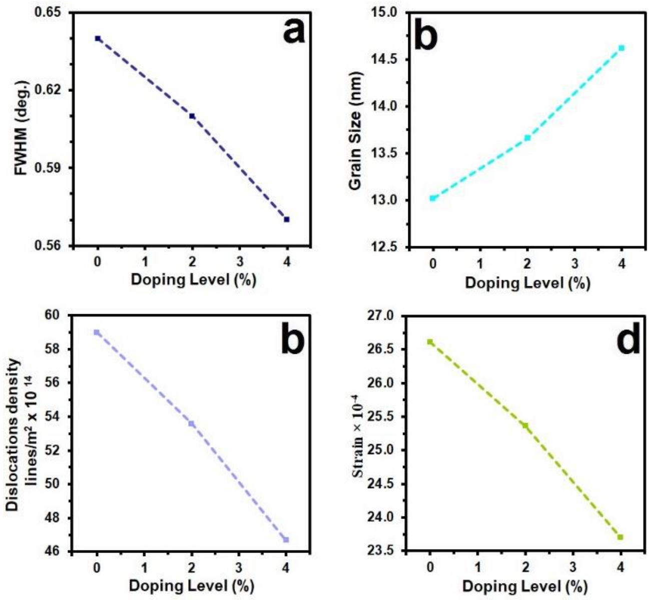

Fig.2. P_{st} of intended films.

The shape of the specimen was obtained with the help of AFM. Utilizing the ZrO2 and ZrO2:Ag films' average dimension of particles (Pav), roughness of the surface (Ra), and the root mean square smoothness (rms). The values of these parameters are listed in Table 2, and Fig. 3 depicts the granules that are present in films but scattered in some regions. The median particle size, roughness average Ra, and rms values of (69.30, 52.68, and 51.02) nm, (6.85, 5.68, and 4.12) nm, and (7.68, 6.89, and 3.23) nm, respectively, were all significantly affected by the presence of silver dopant [41–43]. Table 2 displays the rise in PAFM and Pav for AFM parameters due to Silver presence.

TABLE 2. P_{AFM} of grown films.

Samples	P_v nm	R_a (nm)	Rms (nm)
Undoped ZrO_2	69.3	6.85	7.68
ZrO_2: 2% Ag	52.68	5.68	6.89
ZrO_2: 4% Ag	51.02	4.12	3.23

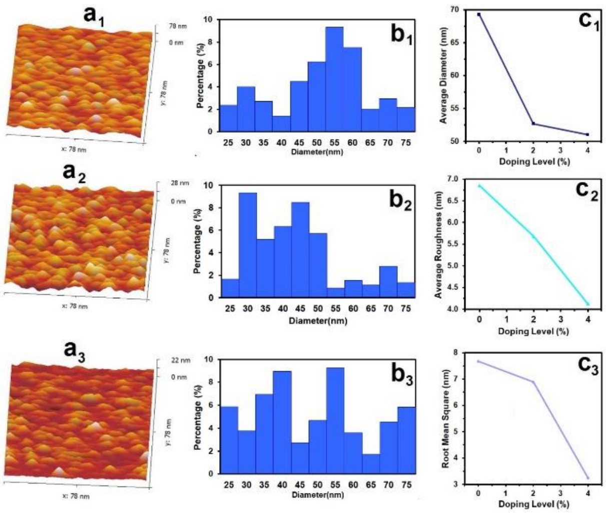

Fig. 3. AFM acquaintance of the intended films

When the produced films' transmittance (T) vs wavelength was measured, it was discovered that the average transmittance of ZrO2 for the disengage ZrO2 films was over 75%. However, the transmittance fell as the doping percentage rose. This shows how the inclusion of silver doping agent significantly altered the visual attributes of the coatings. The reduction in permeability can be due to a boost in light dispersion brought on by the creation of bigger particles as a result of the silver dopant. The ZrO2 films are very transparent and suited for a variety of optical applications, according to the T findings overall [44-46].

The absorption coefficient (α) was determined via the relation [47-49]:

$$\alpha = (2.303 \times A)/t \quad (4)$$

Where the film thickness is (t). As seen in Fig. 6, the silver concentration increases A, indicating that the films' optical properties, notably their capacity to absorb light, were impacted by the silver disengage [50,51].

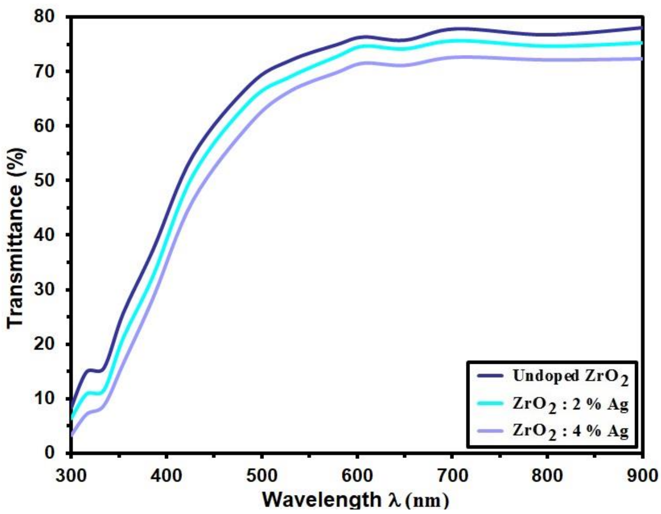

Fig. 4 Transmittance of the grown films.

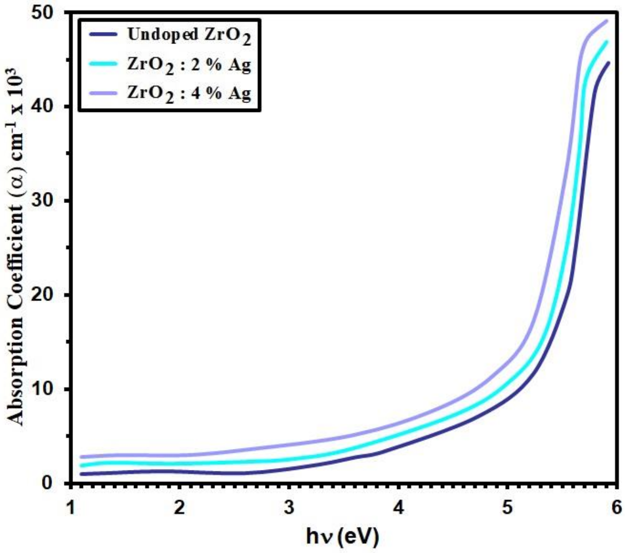

Fig. 5 Absorption coefficient of grown films.

Using the relationship below, the optical bandgap E_g was measured. [52-54]:

$$(\alpha h\nu) = B\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (5)$$

Where B is constant, $(\alpha h\upsilon)^2$ Vs. (hυ), are displayed in Fig. 4. Optical bandgap declined from 5.26 to 5.14 eV as the 4% Silver [55, 56].

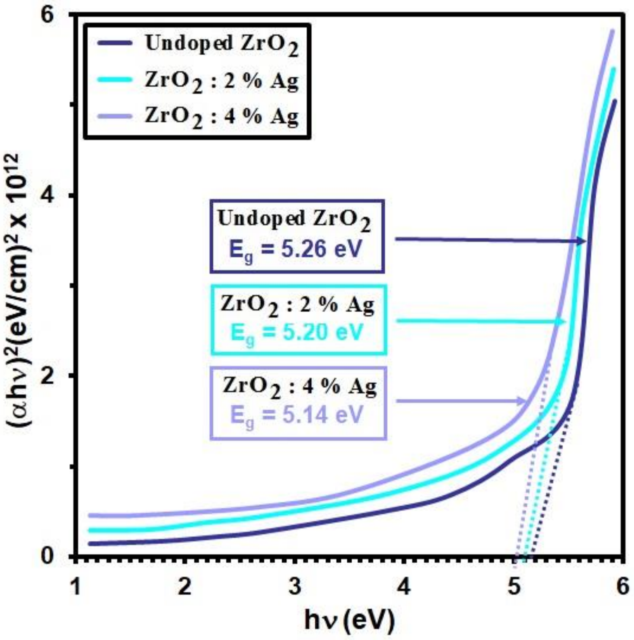

Fig. 6 $(\alpha h\upsilon)^2$ Vs. (hυ) of the intended films.

The refractive index (n) was calculated via the relation [57-59]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (7)$$

R stands for reflectivity. The relationship of n of ZrO2 and ZrO2 is seen in Fig. 7: When comparing the wavelength of Ag films to the additive silver content, it can be shown that n decreases with increasing silver content. This might be attributed to an increase in optical absorption in the visible and ultraviolet area [60].

The extinction coefficient (k)) is determined using the relation [61-63]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (7)$$

Where, λ is the wavelength. From Fig. (8) we can easily obtain k of the ZrO_2 and ZrO_2: Ag films k decrease as the additive silver increased [64, 65].

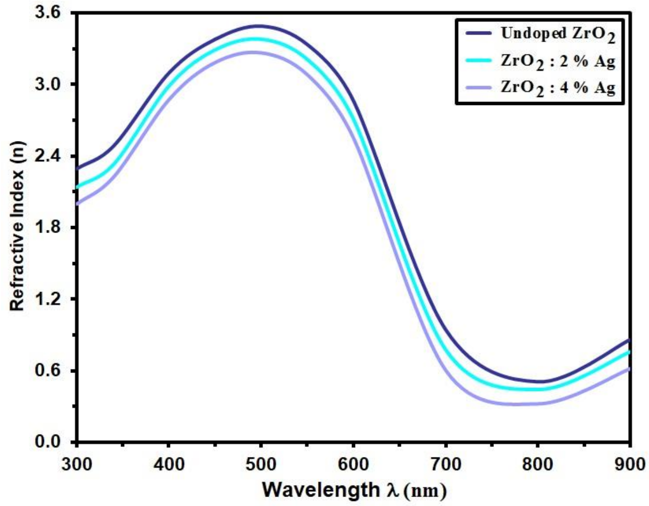

Fig. 7 refractive index for grown films.

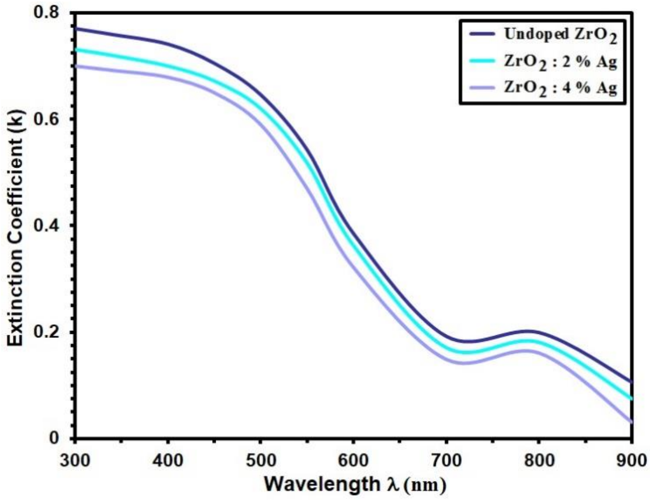

Fig. 8 extinction coefficient of the grown films.

4. CONCLUSION

By using the aerosol distillation process, ZrO2 and argent enriched ZrO2 of various concentrations were effectively synthesized; the XRD findings show a dominating signal across (111). Although the strain value increased from 58.98 to 46.67, the number of dislocations at the barrier shrank from 26.61 to 23.70. The average grain size for the disengage ZrO2 molecule was (13.02-14.62) nm with ZrO2: 3% Ag. For ZrO2, ZrO2:2% Ag, and ZrO2:4% Ag, the average particle sizes are observed in the range of (69.30), (52.68) and (51.02) nm, respectively. The spectrum gap, elimination coefficients, and reflective index for the range of silver doping described here drop as the silver doping increases transmission%, whereas the absorbance coefficient rises for the range of silver doping shown here.

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