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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 ZrO₂, and AlO₂, 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]. ZrO₂ 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 ZrO₂ 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

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depositing ZrO₂ 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 formed in this paper using a spray pyrolysis process at varied Ag doping, to study the physical characteristics of ZrO₂ and ZrO₂: Ag.

2. EXPERIMENTAL

Thin films of both materials were produced using spray hydrolysis. Disengage and silver-doped ZrO₂. ZrCl₂ 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 AgCl₂.6H₂O. ZrO₂ 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 °C. 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]:

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

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 ZrO₂ molecule is about (13.02 -14.62) nm with ZrO₂: 4% Ag. the same behavior was noticed in references [31,32].

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

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

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

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

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.

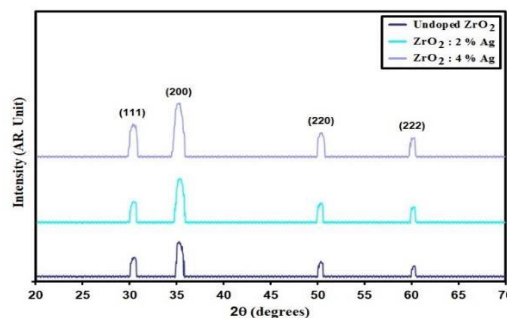


Fig.1. XRD styles of grown films.

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.

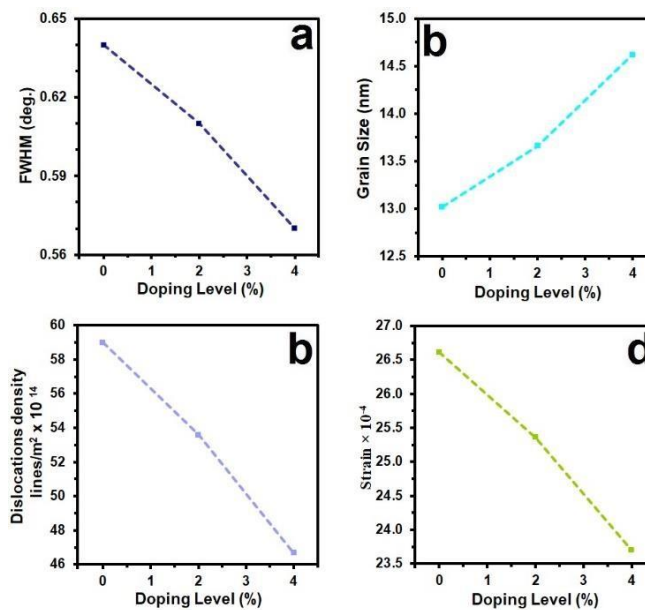


Fig.2. P_{st} of intended films.

The shape of the specimen was obtained with the help of AFM. Utilizing the ZrO₂ and ZrO₂:Ag films' average dimension of particles (P_{av}), roughness of the surface (R_a), 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 R_a , 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 P_{av} 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

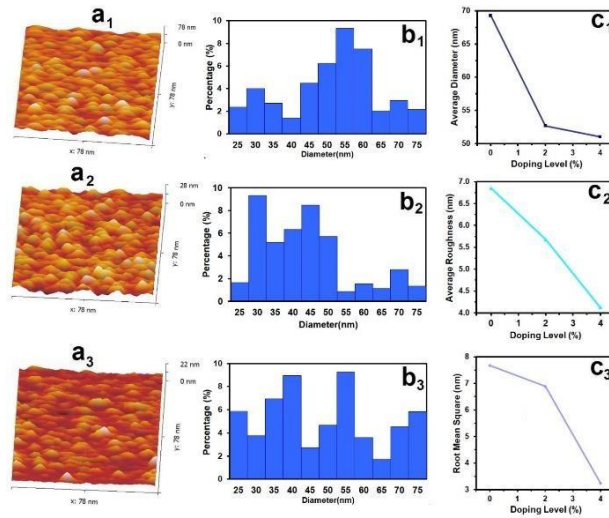


Fig. 3. AFM acquaintance of the intended films

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].

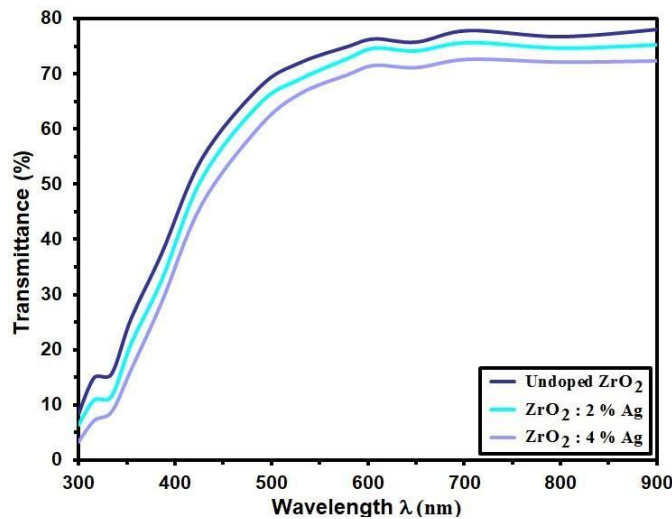


Fig. 4 Transmittance of the grown films.

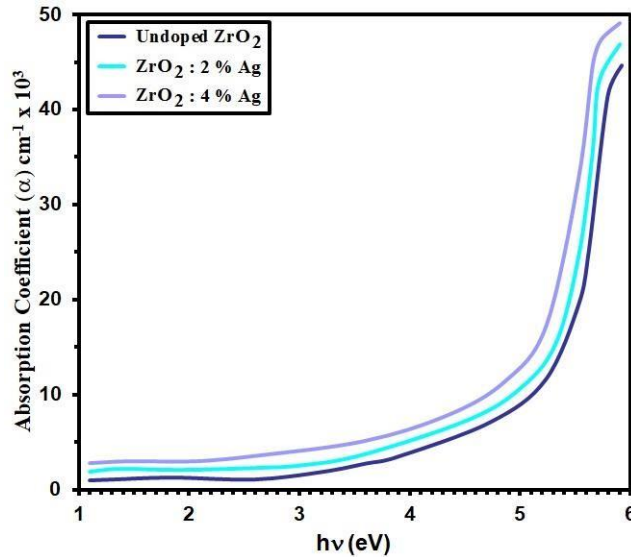


Fig. 5 Absorption coefficient of grown films.

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

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

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

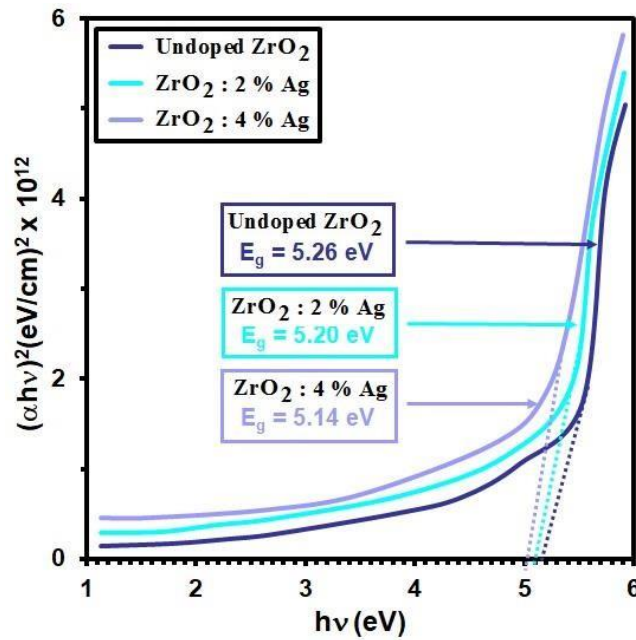


Fig. 6 $(\alpha h\nu)^2$ Vs. $(h\nu)$ of the intended films.

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

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

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]:

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

Where, λ is the wavelength. From Fig. (8) we can easily obtain k of the ZrO₂ and ZrO₂: Ag films k decrease as the additive silver increased [64, 65].

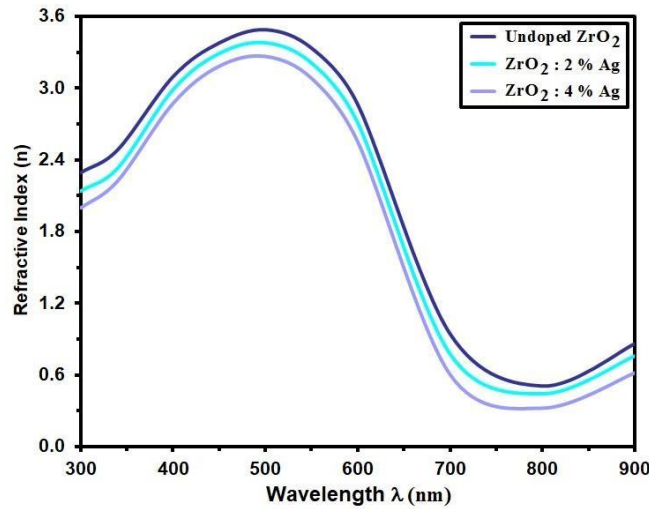


Fig. 7 refractive index for grown films.

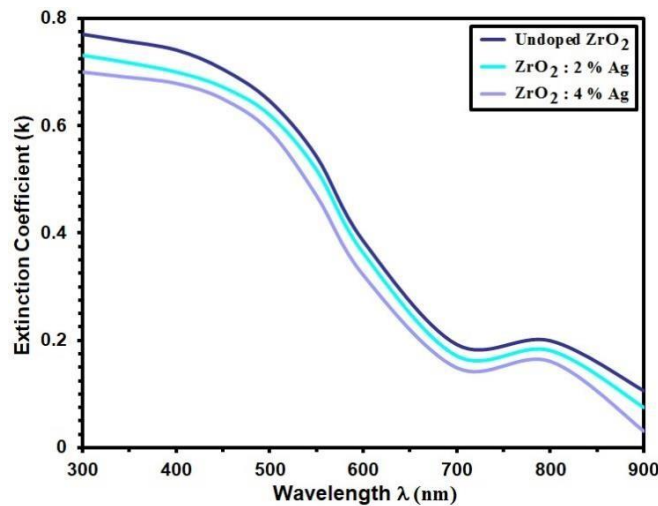


Fig. 8 extinction coefficient of the grown films.

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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