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Characterizations of sprayed TiO_2 and Cu doped TiO_2 thin films prepared by spray pyrolysis method

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TiO_2 and TiO_2:Cu films were deposited by spray pyrolysis (SP). X-ray diffraction reveals that deposited films have a polycrystalline structural. The AFM image of the surface reveals that roughness and root mean square affected by doping. Optical transmission of films was found to decrease from 94 % to 84 % with the as the doping percentage increase to 3. Optical bandgap (E_g) of TiO_2 thin film was 3.947eV. The bandgap is shifted to lower energies upon doping.

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1. Introduction

TiO_2 is n-type semiconductor with a bandgap of 3.2 eV and 3.0 eV [1-3]. Anatase can be formed at 300°C [4]. Anatase phase of TiO_2 is the most efficient for photocatalysis [5-7]. Optical properties and electronic structure of TiO_2 can be tuned by injecting with transition elements [8-10]. Cu has features over all transition metals for TiO_2 doping [11-15], because the atomic radii of Cu (86 pm) and TiO_2 (74.5 pm) are close to each other, so Cu will replace Ti into crystal lattice [16]. Also TiO_2: Cu displays low electron-hole recombination rate, it acts as trapping center for photoelectrons [17]. Different methods were applied for the prepare of TiO_2 films, like sol–gel [18, 19], RMS [20, 21], PLD [22], SP [23], solvothermal method [24], thermal evaporation [25], ion beam sputtering [26]. The (SP) method has unparalleled properties like large-area coating, costless, controllable, therefore they applied to prepare the deposited films seeking for their physical properties.

2. Experimental

TiO_2 and TiO_2: Cu films were grown by SP. A solution contains 0.05 M of Ti $(CH_3COO)_2{\cdot}2H_2O$ and 100 ml of deionized water DW was utilized to maintain the solution. 0.1M of $(Cu(NO_3)_2.3H_2O)$ resolved in DW as a dopant with volumetric percentage 1 and 3. Table 1 offers the optimal status. Gravimetric measurements were employed for estimating the film thickness, the results were 350± 35 nm. Transmittance spectra was obtained via Shimadzu

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spectrophotometer. XRD is utilized to gain film structure, whilst the AFM is gained to set films morphology.

Table 1. Optimal terms of the intended films.

Base temperature	450°C
Base to spout distance	29cm
Spraying rate	5 mL/min
Spraying time	8 S
Pause interval	1 min

3. Results and discussions

Fig.1. displays XRD styles, all films offer pure anatase phase with preferred orientation along (202) at 2θ = 36.52 fitted with JCPDS card no 89-4203. The crystallite size *D* minimize with the increment of Cu. This could be due stress inspired by difference in ionic radii [27]. Figures 2 (a, b, c, and d) represents (FWHM) β, Crystallite size, Microstrain ε and the dislocation density δ due to doping weight ratios. D were determined by using Debye-Scherrer formula given by the equation (1) [28-30] and illustrated in Table 2:

$$D = \frac{K\lambda}{\beta cos\theta}(nm) \tag{1}$$

where, K = 0.94, λ = 1.5407 Å, and θ = diffraction angle. δ was estimated using relation (2) [31-33]:

$$\delta = \frac{1}{D^2}\left(\frac{lines}{m^2}\right) \tag{2}$$

The microstrains (ε) was determined using relation 3 [35-36]:

$$\varepsilon = \frac{\beta cos\theta}{4} \tag{3}$$

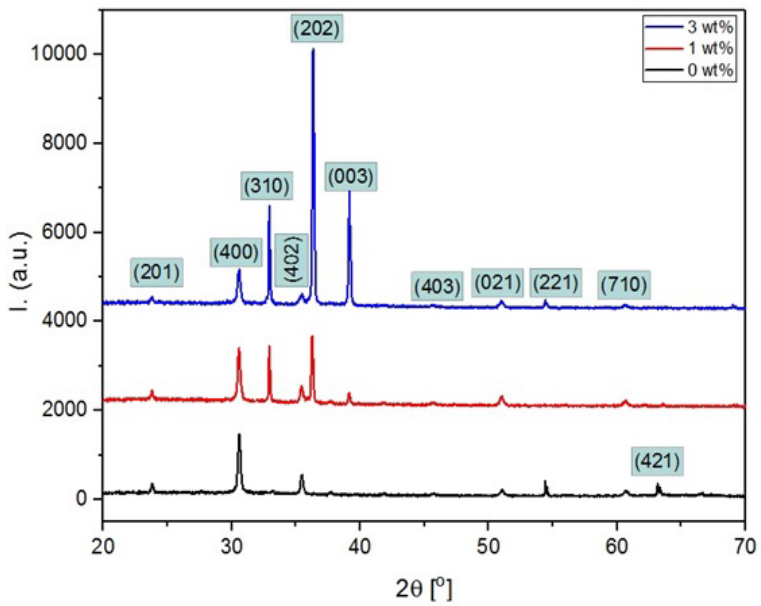

Fig. 1. XRD pattern of grown films.

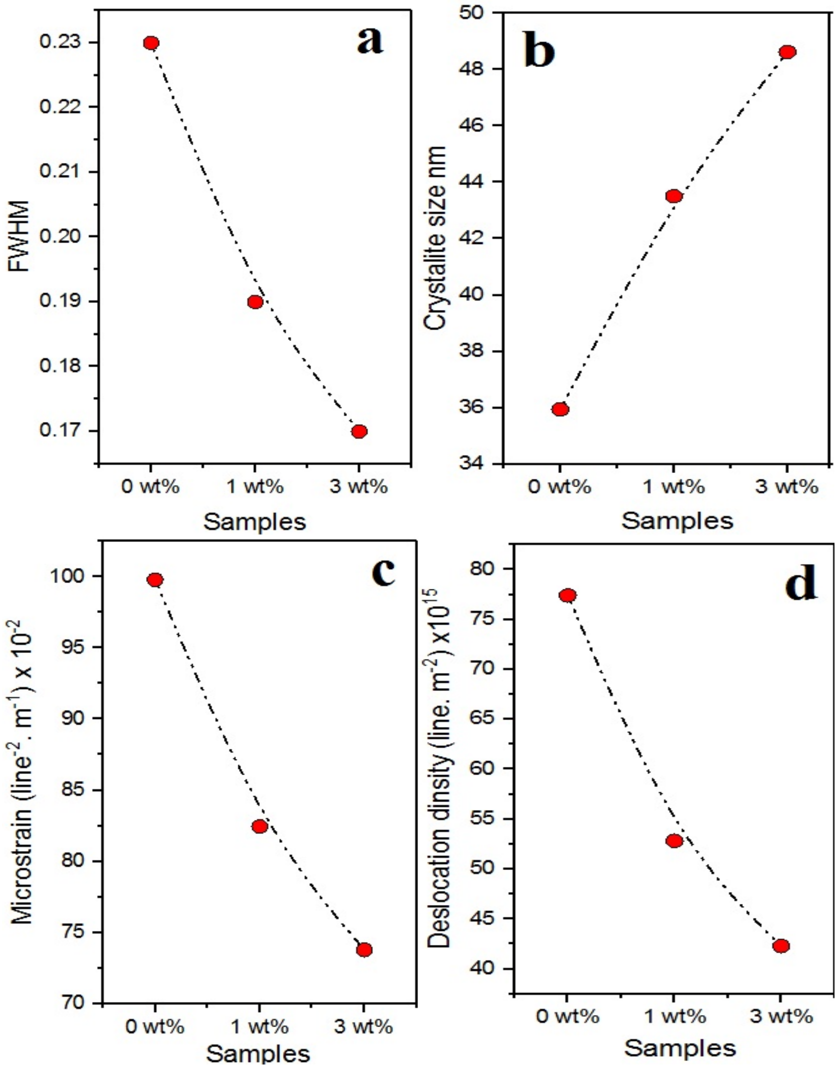

Fig. 2. Structural Parameters (Spar) of grown films.

Table 2. S_{par} of intended films.

Samples wt %	(hkl) Plane	2Θ (°)	FWHM (°)	(D) (nm)	ε (Line^{-2}·m^{-1}) ×10^{-2}	(δ) (Line. m^{-2}) ×10^{15}	d (Å)	
							Standard	Calculated
0	(202)	36.52	0.23	35.94	0.998	0.774	3.51	3.53
1	(202)	36.52	0.19	43.50	0.824	0.528	3.51	3.53
3	(202)	36.52	0.17	48.62	0.737	0.422	3.51	3.53

4. Topography surface analysis

Figures (3, 4 and 5) show the surface morphologies of the deposited films. It can be seen by AFM images that the films were noncompact morphology and non-cracks and offered a granular nanostructure with grain size ~ 100 nm. Surface average roughness (R_a) increased with Cu dopant concentration. R_a and root mean square (R_{rms}) of intended films are offered in Table 3. R_{rms} and R_a are affected by doping. As can be seen that Cu content was more than its solubility in TiO_2, so formation of CuO is possible, leading to higher roughness [37].

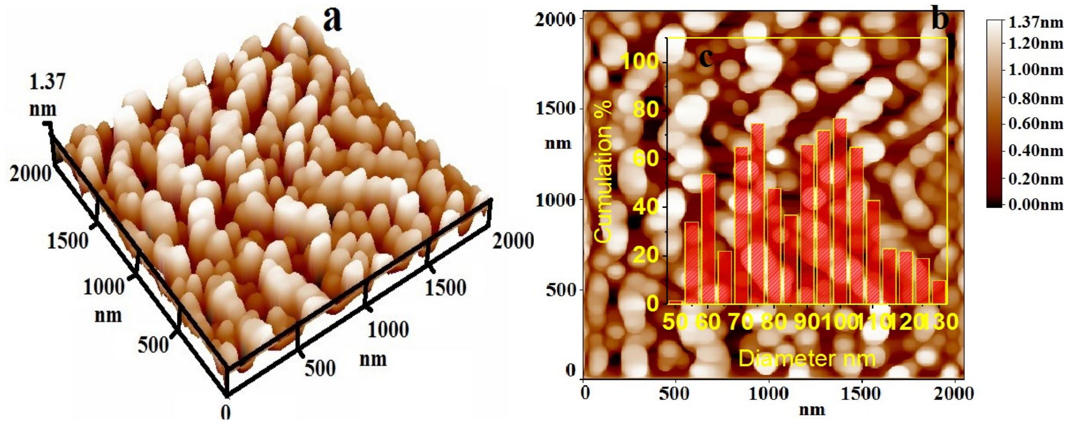

Fig. 3. AFM images of TiO_2 thin films.

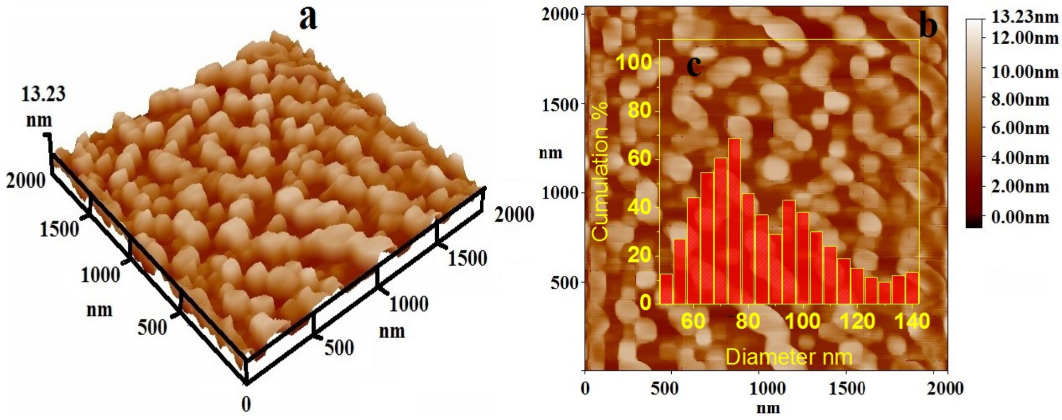

Fig. 4. AFM images TiO2:1% Cu

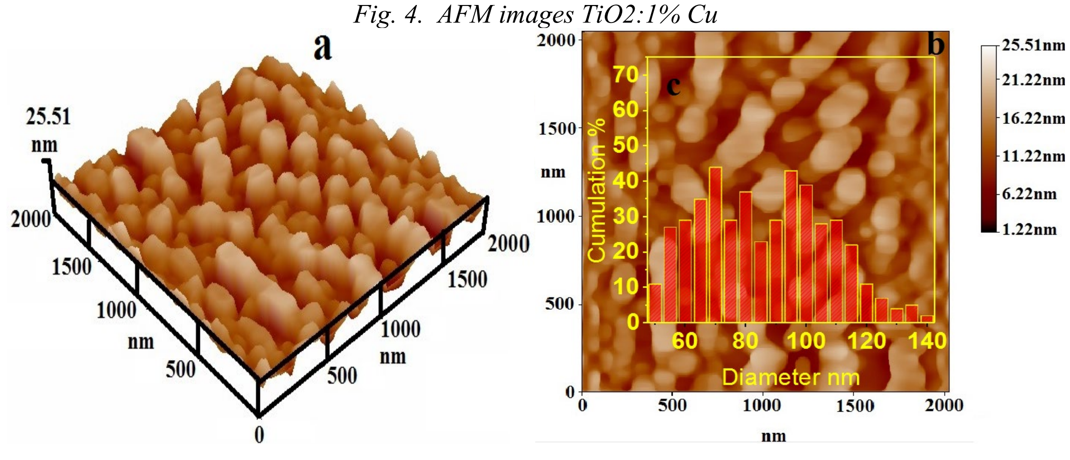

Fig. 5. AFM images TiO_2:3%Cu.

Table 3. Average particle size, Ra and Rrms for pure and Cu doped TiO_2.

Samples Wt %	**D nm**	**R_a nm**	**R_{rms} nm**
0	70	1.37	2.09
1	80	13.23	0.39
3	100	25.51	3.43

5. Optical properties analysis

Experimental measurements are commonly presented in relation to the percentage transmittance (T), as defined in Equation [38-40]:

$$T\% = \frac{I}{I_o}\% \tag{4}$$

Where I_o and I is the initial light intensity, the light intensity following its passage through the specimen. Fig. 6. Display the difference in transmittance T upon wavelength of undoped TiO_2 and TiO_2: Cu thin films. It is seen from Fig. 6, that films prepared at 3% Cu doping show a transmission of greater than 80 % in Vis and NIR area. It is found that transmittance decreases with the increase of Cu due to an increment in amorphous nature of doped films [41].

The absorption coefficient (α) is gained from Eq. 5 [42-44]

$$\alpha = 2.303(A/T) \tag{5}$$

Fig.7. display α that was slowly increased in the high wavelength and then sharply increased near the absorption edge. Hence, the α value depends on Cu doping and decreases as Cu content rises. The variation of absorption might be due to defect centers [45].

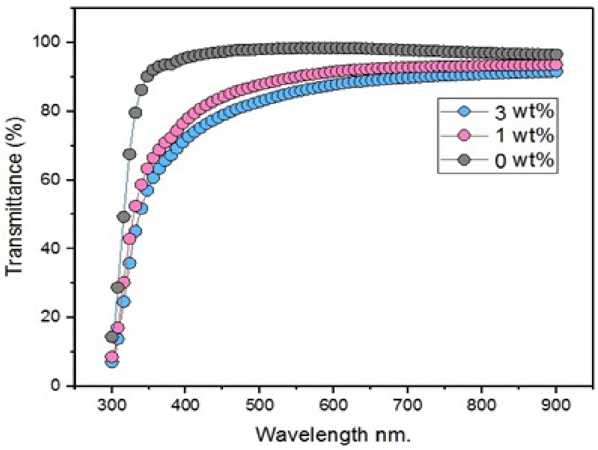

Fig. 6. Transmitance of the deposited films

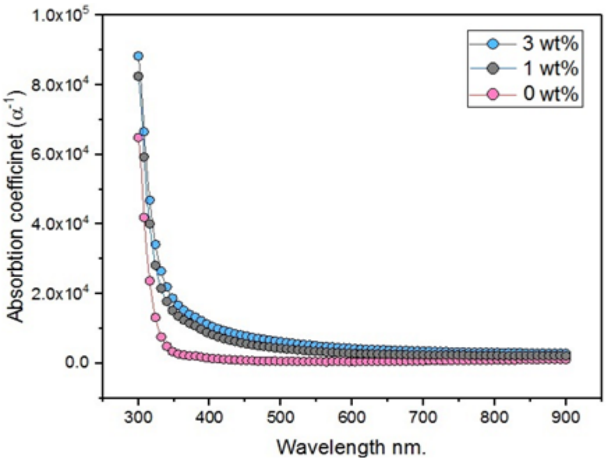

Fig. 7. α of the grown films.

The energy gap E_g is obtained by Tauc's relation [46-48].

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \tag{6}$$

Where A is a constant, $h\nu$ is photon energy. E_g was obtained from Fig. 8, Their value is 3.974 eV, which agrees with the reported values. For 1 % and 3% Cu doping the direct bandgap of the film was (3.947and 3.86) eV [49, 50]. So it is clear that for Cu doping affect bandgap value of TiO_2 thin films. These values were agreed with the reported values [51, 52].

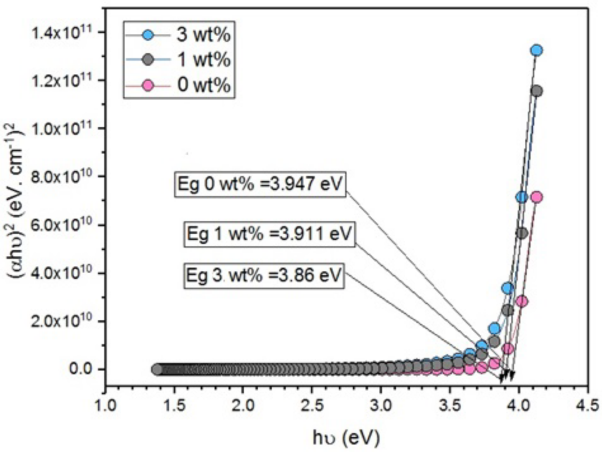

Fig. 8. Direct band gaps of the deposited films films.

6. Conclusion

Pure TiO_2 and TiO_2:Cu films are deposited by SP technique. XRD styles display anatase phase with preferred peak (202) at 2θ = 36.52°. The AFM image reveals that the R_a and RMS affected by Cu dopant. Direct transition offers a reduce in bandgap from 3.947 eV to 3.86 eV.

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