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Influence of Bismuth Dopant on Physical Properties of nanostructured TiO_2Thin Films

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Abstract:
Nano structured TiO2 was prepared utilizing spray pyrolysis deposition (SPD). The characterization of the deposited films was studied with Bi dopant. The XRD analysis indicated that films are polycrystalline with a preferred orientation along (110) direction. The AFM analysis shows a porous morphology structure. The optical properties were obtained by UV–visible spectro photometer, which show that these films were highly transparent above 80% at the wavelength more than 700 nm with a slightly influenced upon Bi content. The energy gap was shifted from 3.1to 2.6 eV, versus doping.

Keywords: *Bi:TiO2, SPD, Optical, structure, topographical.*

I. INTRODUCTION

Titanium oxide (TiO_2) is a n-type semiconductor with wide energy bandgap of 3.2. TiO_2show pleasant properties like transparency to visible light, high refractive index and a low absorption coefficient. [1-3]. TiO_2 has three main crystalline structures: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). Rutile is commonly stable at high temperatures [4].The phase conversion from anatase to rutile relys on film growth process, which might be influenced by defect concentration, grain boundary concentration, and particle packing [5, 6].It is found that the optical properties and electronic structure of TiO_2 is modified under the doping of transition elements. These transition metals minimize the rate of recombination of hole-electron pairs, and improve the "interfacial charge transfer efficiency"[7,8]. There are several TiO_2 thin film deposition techniques including sol–geldeposition[9],spraypyrolysis[10],pulsedlaserdeposition[11], e-beamevaporation[12],chemicalvapordeposition[13],andreactivemagnetronsputtering[14].In this paper pure Titanium dioxide and doping with Bismuth 2% and 4% thin films prepared in the simple and low cost of CSP in order to study their optical, structural and Morphology.

II. EXPERIMENTAL

Titanium dioxide (TiO_2) and Bismuth (Bi) -doped TiO_2 thin films were prepared by CSP method. The aqueous solution containing 0.05 M of Titanium acetate (Ti $(CH_3COO)_2 \cdot 2H_2O$) and 100 mL of deionized water was used to obtain the matrix solution. To prepare the doping material

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0.1M of cupric nitrate trihydrate ($Bi(NO_3)2.3H_2O$) to dissolve in deionized water of dopant as a volumetric percentage 2 and 4., which kept constant during the deposition process for TiO_2 and Bi doped TiO_2. Substrate temperature was kept at 450°C during deposition process. Nitrogen was used as a carrier gas, distance between substrate and nozzlewas kept at 29 cm. spraying time , spraying rate and the time interval between two spray process were 8 s, 5m L/min and 1 min respectively.

Film thickness was obtained by Gravimetric technique and was about 350± 30 nm. Transmittance and Absorbance spectra were recorded via Shimadzu double beam spectrophotometer. Structural parameters were analyzed by X-ray diffractometer (Shimadzu, model: XRD-6000, Japan) using CuKα radiation. AFM (AA 3000 Scanning Probe Microscope) was utilized to study deposited thin films surface.

III. RESULTS AND DISCUSSION

XRD patterns of pure and Bi doped TiO_2thin films are displayed in Fig. 1.Thefilmsexhibitpolycrystallinetetragonalcrystals tructure. The diffraction peaks observed in XRD patterns of all the films corresponds to (110), (200), (201) and (203) planes of the typical tetragonal crystal structure of TiO_2 thin filmscompared withJCPDS card no 00-021-1236. The diffractionpeakswereindexedtosrilankiteplanesand Birelativepeaks werenotobserved implying that Bi was doped into TiO_2 lattice. At doping of Bi the intensity of (110) plane increases which may be due to increase in the mobility of titanium and oxygen atoms which led to the increase in the nucleation of crystallization phase of srilankite TiO_2.The crystallite size (*D*) of the sample was calculated from full width at half maximum (FWHM) β of the (110) peak of anatase TiO_2 by Debye Scherrer equation [15, 16].

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \qquad -----1$$

Where λ (1.54060 Å) is X-ray wavelength. The Dislocation density (δ) was calculated by using relation [17]:

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

The micro strains (ε) were caused by crystalline defects and determined using the following relation 3 [17, 18]:

$$\varepsilon = \frac{\beta cos\theta}{4}(lines^{-2}.m^{-1}) \qquad -----3$$

The variation of *D* and lattice parameters with dopant Bi was calculated and the findings are recorded in Table 1,which assure that *D* full in the category of nano. The Crystallite size of the plane (110) increases with the increase of concentration doping of Bi. Theim proving in the crystallinity of the films are confirms decreasing in defects. This also confirms from the grainsize, which is increased by increasing the concentration doping in Bi.

Table1: Structural data of TiO_2 with different Bi doping by (SPD).

Bi (%) Doping	**(hkl) Plane**	**2Ɵ (Deg.)**	**Lattice constant (Å)**	**FWHM (Deg.)**	**D (nm)**	**(ε) (Line^{-2}·m^{-1}) ×10^{-4}**	**(δ) (Line. m^{-2}) ×10^{15}**

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			a	b	c				
0	-110	24.93	5.45	9.18	5.14	0.88	9.17	38.64	11.883
			a	b	c				
2	-110	24.93	5.45	9.18	5.14	0.86	9.41	37.64	11.277
			a	b	c				
4	-110	24.93	5.45	9.18	5.14	0.8	10.05	35.24	9.883

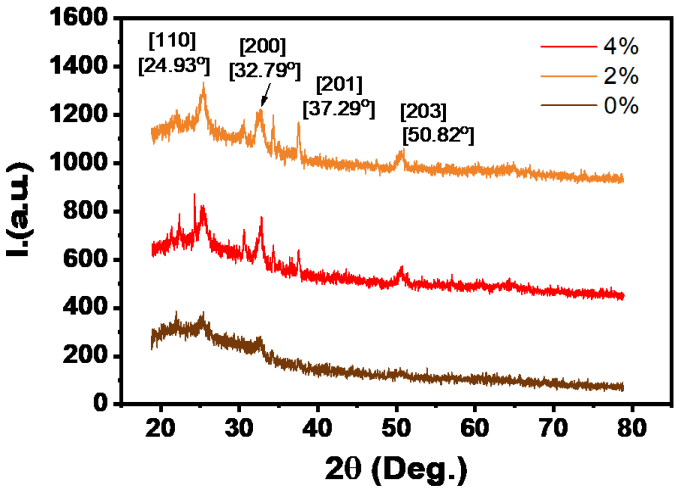

Figure 1. XRD pattern of pure TiO_2 films and 2% and 4% Bi doping concentrations.

The surface morphologies of pure TiO_2 and different concentration Bi doping films are illustrated in Fig. 2. The surface morphology of the pure TiO_2 film was composed of different grain size with average diameter 92.44 nm, average roughness (Ra) 1.07 nm and the root mean square (R. M. S) 1.3 nm. In addition, it was found that the films deposited at 2 % and 4 % Bi doping were increase slightly in average diameter (97.45-123.47) nm, Ra and R. M. S were getting the same behaviors in addition to that some grains was sharp as shown in Fig. 2. The increased values of Ra and RMS of the films, indicating its good polycrystalline structure at the surface make these films suitable in solar cell applications [19]. The R.M.S and average roughness (R_a) of prepared films are shown in Table 2. As can be seen the R_{rms} and R_a follow the dopant.

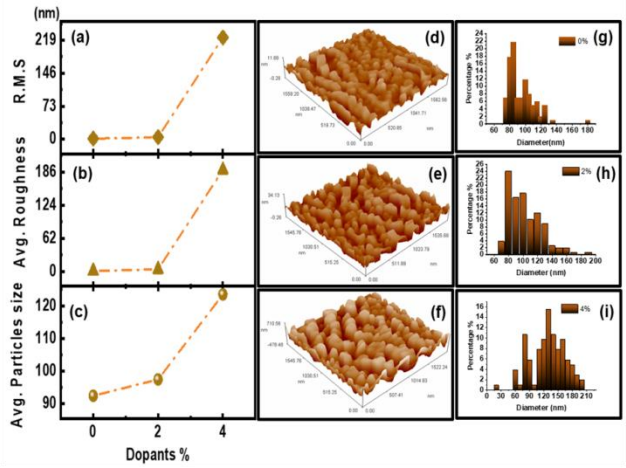

Figure 2. a. AFM image of pure TiO_2 thin films. e. and f. AFM images of the doped Bi: TiO_2 2% and 4%.

Table 2: surface morphologyof TiO_2 with different Bi doping by (SPD).

mn doping (%)	Avg. Diameter (nm)	R_a (nm)	R. M. S. (nm)
0	92.44	1.07	1.3
2	97.45	4.07	4.64
4	123.47	19	22.5

Transmittance spectra of the films are obtained by UV-Vis spectrophotometer in the wavelength range between 200 to 900 nm Fig.3.It is clear that when the concentration doping increases then transmittance slightly decreases. The films show high transmittance above 80%at wavelength more than 700 nm. Since the calculated energy band gaps of pure films are approximately 3.1 eV. Therefore, these ils absorbs photons with wave lengthless than 400nm, according to the

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relationλ(nm)=1240/E_g(eV). All these films show high absorption in the wavelength below than 600nm. When thewavelengthoflightincreasedfrom550nm,thenitst ransmittanceincreases.Upto 600nm, the maximum obtained transmittance is 80%. Therefore,these films can be used for the protection of optoelectronic devices from UV radiations.

The absorption coefficient (α) for each wavelength was calculated from equation (4) [20]:

$$\alpha = 2.303(A/T) \qquad -----4$$

Fig. 4 shows absorbance spectra of the deposited samples. It was clear that absorbance increased via increase Bi content, and that films after doping have values of absorption coefficient (α >10^4 cm^{-1}) this means that the direct transition is possible to occur. Bi dopant altered local lattice symmetry and defect, which could modulateabsorbance and material properties[21].

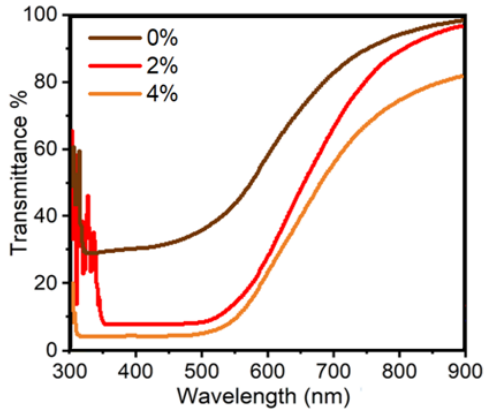

Figure 3.Transmittance with wavelength of pure and 2% and 4%Bi: TiO_2 thin films.

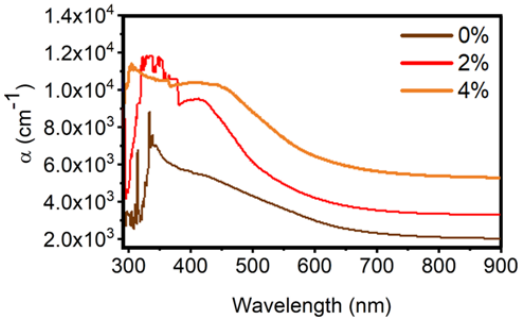

Figure 4. Absorption coefficient with wavelength of pure and 2% and 4% Bi:TiO_2 thin films.

The optical energy bandgap of pure TiO_2 and doped Bi thin films are calculated by the following Tauc's relation [22, 23].

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^n \qquad -----5$$

Where n equalto ½ or for direct transition. A is a constant quantity,E_g is the bandgap energy, h ν is photon energy. Optical bandgap energy is determined by plotted a graph between $h\nu$ and $\alpha h\nu$[24] as shown in Fig. 5. Thecalculatedbandgapenergyforpure TiO_2 anddopedof Bi2% and 4% thin filmsare3.1,2.8and2.6 eV,respectively.Thisdecreasebandgapisduetothe increaseindopingofthefilmswhich is according to the literatures [25-27].

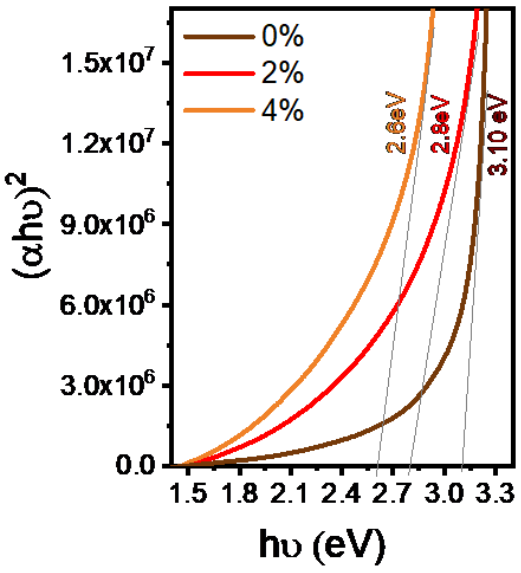

Figure 5. Indirect bandgaps of pure and 2% and 4%Bi: TiO_2 thin films.

IV. CONCLUSIONS

The structure, optical properties, and surface morphology of nanostructure $TiO_2$and different Bi dopant concentrations films deposited by CSP were investigated. XRD results display polycrystalline structure . All films show high transmittance above 80% in the visible region.

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Bandgap decrease with increase in doping of films. The films deposited at 2% and 4% Bi doping were increase slightly in average diameter (97.45-123.47) nm. The Ra and R. M. S follow the average diameter.

V. ACKNOWLEDGMENTS

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