Physical Properties of Nanostructured CuO Thin Films Doped by Titanium

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Abstract

Undoped CuO and CuO: Ti were grown employing spray pyrolysis deposition SPD . XRD patterns reveal films with predominant peak via (002), increasing with increasing doping. The grain size increases from 13.27 nm to 17.37 nm as Titanium content increases. AFM indicates the appearance of nanostructure with a decrement in particle size and porosity via doping increment. The transmittance is above ٥٠ % in the visible area for the intended films. The bandgap is decreased from (1.85 to 1.75) eV. The investigated optical constants decrease with the increase of Titanium content.

Keywords: CuO Thin Films, Ti, XRD, AEM, Optical bandgap.

الخصائص الفيزيائية لأغشية اوكسيد النحاس ذات التركيب النانوي المشوب بالتيتانيوم

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الملخص

تم تنمية اوكسيد النحاس واوكسيد النحاس المشوب بالتيتانيوم باستخدام الترسيب بالتحلل الحراري. اثبتت أنماط حيود الاشعة السينية بان الاغشية لها قمه سائدة بالاتجاه (٠٠٢) ونزداد بزيادة التشويب. ازداد معدل الحجم الحبيبي من ١٣,٢٧ نانومتر الى ١٧,٣٧ نانومتر بزيادة محتوى التيتانيوم. اثبتت نتائج مجهر القوة الذرية وجود تراكيب نانوية مع نقصان في حجم الجسيمات والمسامية بزيادة تركيز الشائب. كانت النفاذية اكثر من ٥٠ % في المنطقة المرئية ولكافة الاغشية. قلت فجوة الطاقة من ١,٨٥ الى ١,٧٥ الكترون فولت. لقد وجد بان الثوابت البصرية قلت بزيادة محتوى التيتانيوم.

الكلمات المفتاحية: أغشية أوكسيد النحاس الرقيقة، التيتانيوم ، حيود الاشعة السينية ، مجهر القوى الذرية ، فجوة الطاقة البصرية.

Introduction

Cupric oxide (CuO) has garnered a lot of interest in recent decades because of its environmental acceptability, low cost of manufacturing, and ability to be easily produced and thermodynamically stable[1-3]. Copper oxides materials are used in p-n junction diodes due to its semiconductor behaviour [4-6]. In addition of using these materials in semiconductor applications, it's also useful for heterogeneous catalysts [7, 8], microwave dielectric materials and solid-state gas sensor[9,10].The elements of cupric oxide constituents are non-toxic and its abundant. Because of these advantages get considerable attention to be used in several applications such as power sources and photovoltaic devices [11]. Hsin-ChunLu et al. found that CuO bandgap is (1.3-2.1eV) [12]. There are several techniques such as RF magnetron sputtering [13], CSP [14], SILAR [15], CBD [16], electrodeposition [17] and sol-gel techniques [18]. thermal evaporation [19] PLD [20] and plasma based ion implantation and deposition [21]. In this work, we used CSP technique because of the simple requirement and reproducibility [22-24]. The doping or annealing method is used to modify CuO thin film properties such as structural, morphology, and optical [25, 26]. In this work, we adopted the doping technique to examine the change in CuO films' structural, morphology and optical properties by doping with Titanium.

Experimental

To prepare CuO thin films, 0.1 M of CuO was resolved in 1:1 deionized water and ethanol. Copper trichloride ($CuCl_3$) (provide by PubChem India) was used as doping agent was resolved in deionized water. Drops of HCl were acceded the solution to make it clear. On a glass slide substrate, a Ti-doped CuO thin layer was deposited using CSP technique. The substrate was 400 degrees Celsius, and the distance between the spout and bases was 28 centimeters. To avoid cooling, the spraying period was extended to 60 seconds and the spray rate was set to 4 ml/min. Nitrogen was used as carrier gas. The gravimetric method was employed to obtain film thickness, their values were 320 ± 25 nm. The structural properties were obtained by XRD. AFM (AA3000 Scanning Probe Microscope) were utilized to study surface of the deposited samples. Absorbance spectra were taken in wavelength area of 300-900 nm employing UV-Visible spectrophotometer (UV Spectrophotometer Shimadzu Model UV-1800).

Results and Discussions

Fig. 1. Offers measured XRD spectra of the intended films. ICDD card no. (05-0661) employed for fitting the prepared films were polycrystalline. Peaks shown at (002), (112), (220) and (202) planes. Strong peak is mainfest toward (002). The recorded data showed that the intensity peaks increase with Ti doping, improving the films crystallinity. Scherrer formula was employed to obtain mean crystallite size (D) for the [002] diffraction peak [27]

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

Where λ is X-rays wavelength used, β and θ are (FWHM) and diffraction angle respectively. The acquired data is gained in Table 1. It showed that *D* increases from 13.27 to 17.37 nm as Titanium concentration increases.

The dislocation density (δ) is estimated via the relation [28]:

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

δ decreases from 56.78 to 33.64

The strain (ε) showed by the formula [29]:

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

The value of ε increases with increasing Cu concentration. Table 1 shows the obtained structural coefficients S_c Fig. 2 symbolizes S_c against Titanium content.

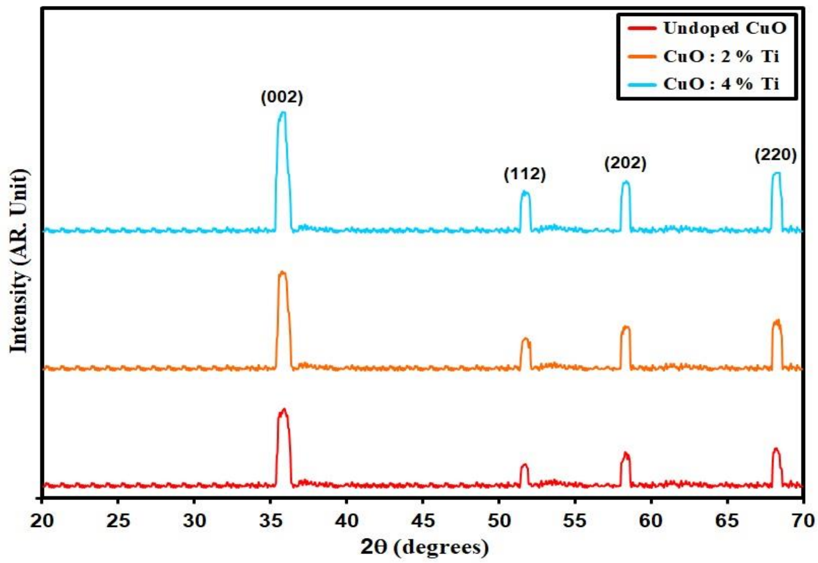

Fig.1. XRD styles of grown samples.

Table 1. *D*, optical bandgap and S_c of grown thin films.

Sample	2 θ (º)	(hkl) Plane	FWHM (º)	E_g (eV)	*D*(nm)	δ (× 10^{15}) (lines/m^2)	*ε* (×10^{-3})
Undoped CuO	35.92	002	0.59	1.85	13.27	56.78	26.12
CuO: 2% Ti	35.61	002	0.55	1.81	15.17	43.45	22.84
CoO: 4% Ti	35.35	002	0.51	1.75	17.37	33.64	19.95

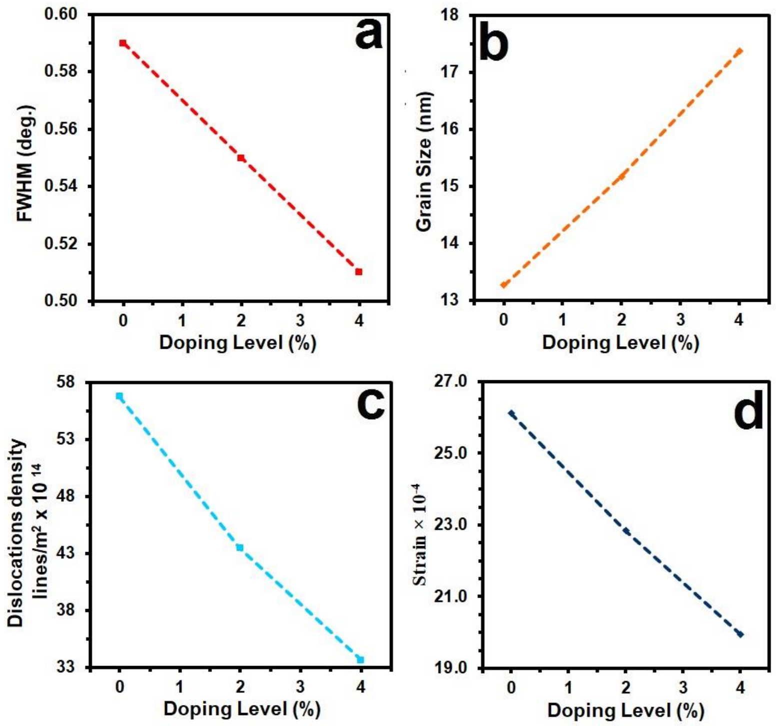

Fig.2. S_c of the grown thin films.

Fig. 3 offers AFM images of intended films. films display pyramidal shape. The particle size T_p of the deposited films was in the domain of 80.36,69.75 and 51.81 nm for the (Undoped CuO, CuO:2% Ti, CuO:4% Ti) respectively. RMS values show increment from 7.73 to 3.29 nm with Ti. The surface roughness R_a values were increase from 5.91-3.17 nm. AFM parameters against CuO dopant demonstrated in Fig. 3 (a_3, b_3 and c_3).

Ra and Rrms are affected by Titanium concentration. The values of AFM parameters P_{AFM} are represented in Table (2).

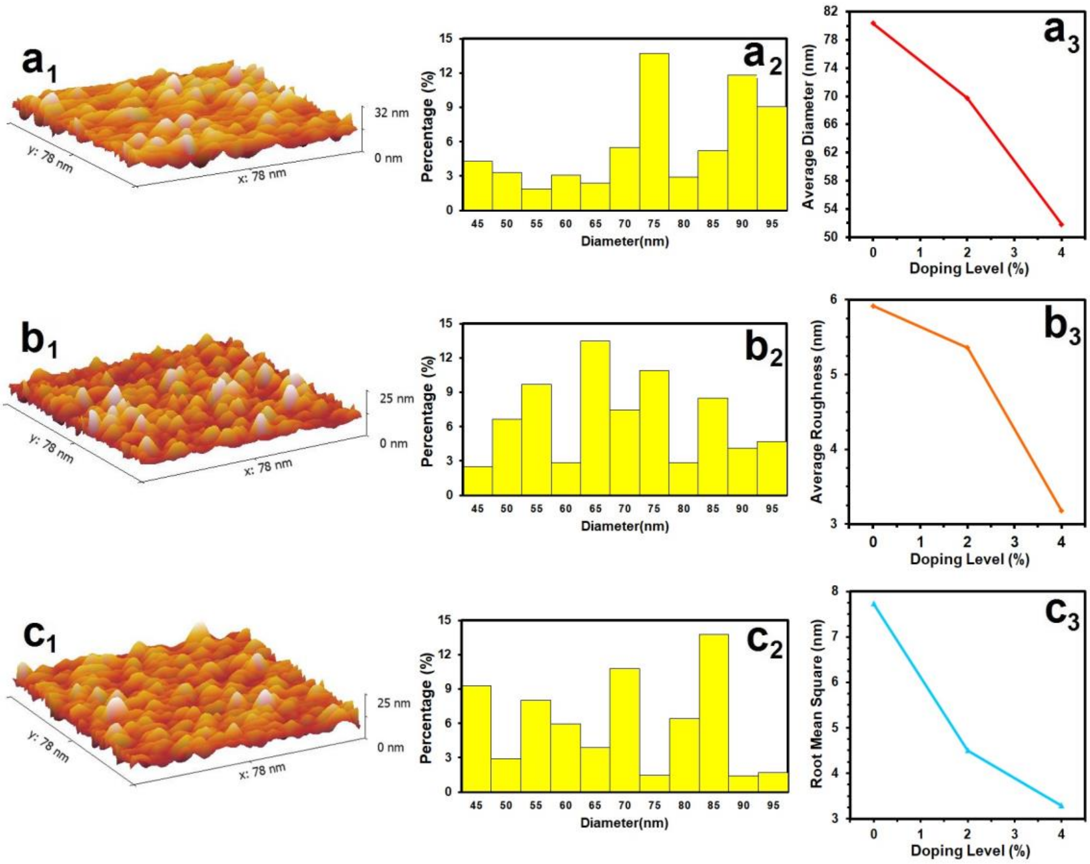

Fig.3. AFM images (a_1, b_1 and c_1), granularly distributed (a_2, b_2 and c_2) and diversity of P_{AFM} against doping (a_3, b_3 and c_3).

Table 2. P_{AFM} of the intended thin films.

Specimen	**T_p nm**	**R_a (nm)**	**R. M. S. (nm)**
Undoped CuO	80.36	5.91	7.73
CuO: 2% Ti	69.7	5.36	4.50
CoO: 4% Ti	51.81	3.17	3.29

Fig. 4 displays the transmittance (T) of deposited films. T is decreased with increasing Titanium content and was over 60% for CuO films.Transmittance edge moves across longer wavelength by Titanium content increases, which mentions a decrement in bandgap of grown films. The decrease in transmittance films doped with 2 and 4 at. % content may be due to the integration of extra Titanium in the CuO lattice.

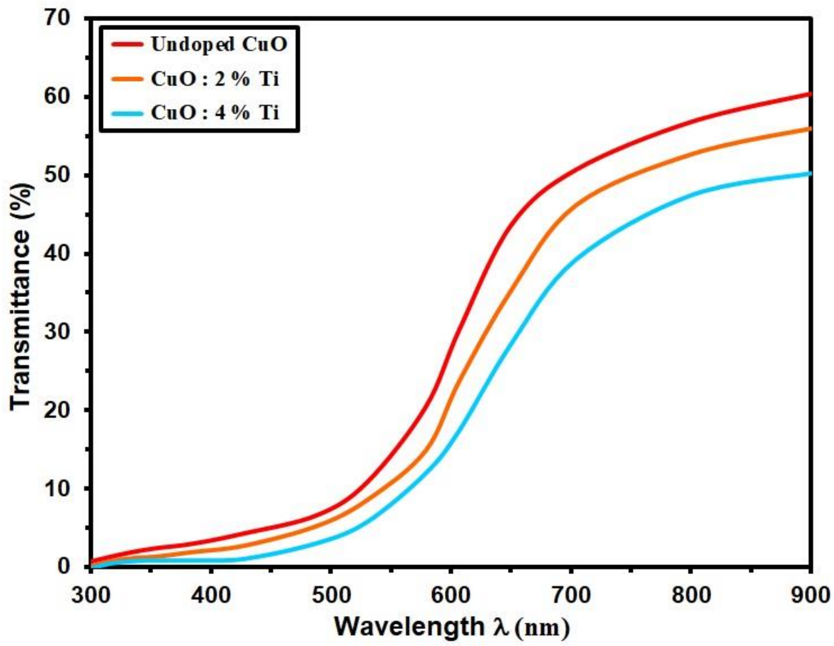

Fig. 4: T of the intended films.

Fig. 5 offers a graph of absorption coefficient (α), which was evaluated by Eq.(1) [30]:

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

Where A represents absorbance and d film thickness. The calculated absorption coefficient of CuO film using equation (4) is depicted in Fig. (5). The results show an increase in the absorption coefficient beyond absorption edge region, then it decreased. In addition, the figure showed ($\alpha \geq 10^4 cm^{-1}$), leading to an increase in the occurrence of direct transitions.

The following formula is used to calculate the band gap [31]:

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

Where (hν) is photon energy, (B) Constant .

Fig. 6 represents the variation of $(\alpha\, h\nu)^2$ with hν, which shows the allowed direct transition electronic. Undoped CuO thin film recorded 1.85 eV band gap value, and the doped Titanium with (2 and 4 wt%) recorded 1.81 ,1.75 eV.

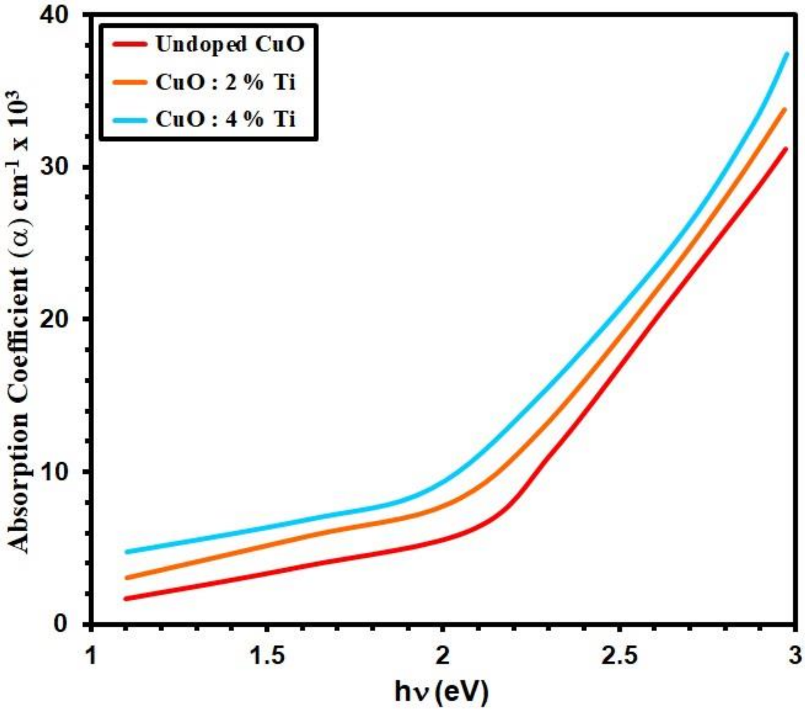

Fig. 5: α of the intended films.

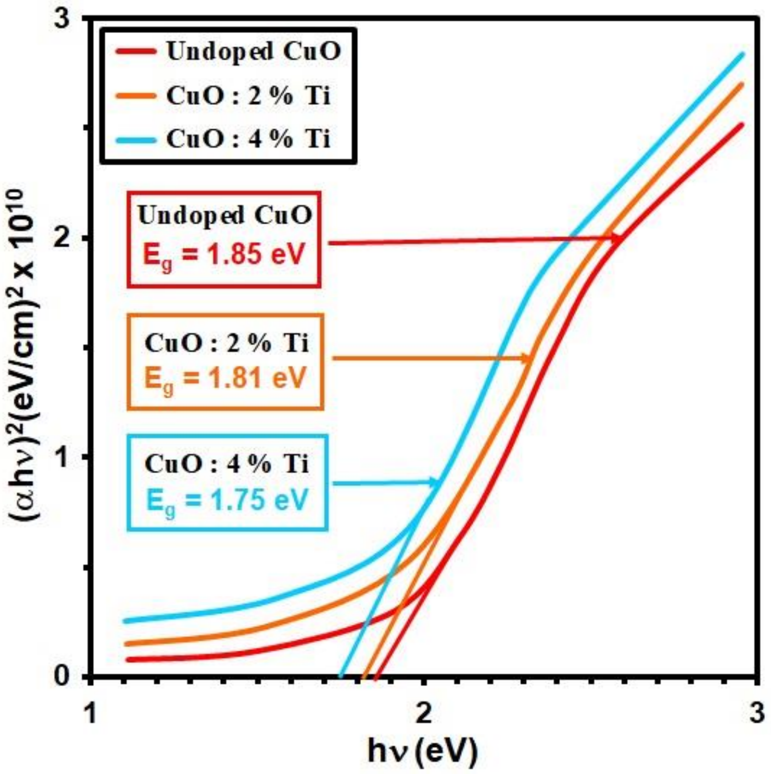

Fig. 6: $(\alpha h\nu)^2$ versus hν for CuO with different Ti doping.

The data of the optical spectrum is used to calculate the extinction coefficient (κ) and refractive index (n).

The parameters κ and n are calculated using the following formulas (6). (7) [32-34]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad \textbf{(6)}$$

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

Where R is the reflectance.

Fig. (7) reveals K of CuO thin film. In the UV range, the extinction coefficient increases whereas it will decrease after this region. The change in K values is due to photons' absorption [35]. Fig. (8) represents the change in refractive index of CuO film versus the wavelength. the refractive index increases with wavelength. According to the achieved data, the maximum value of n is (3.6).

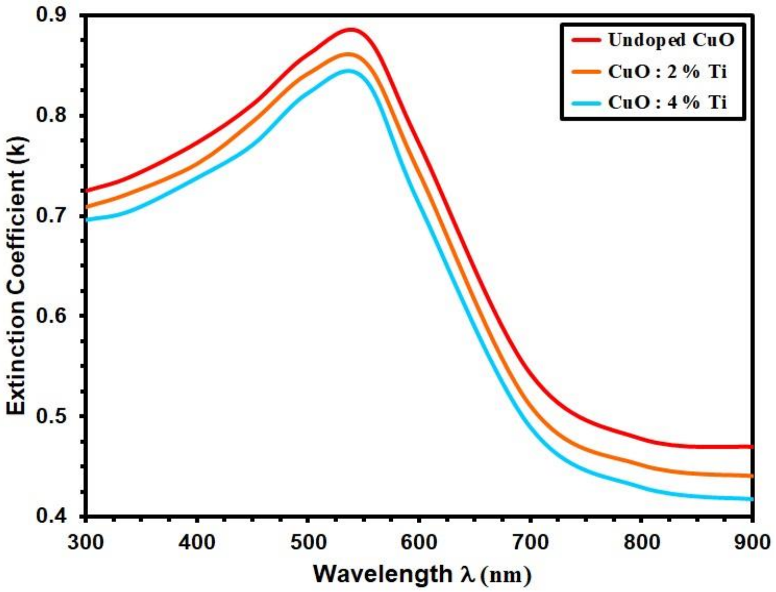

Fig. 7: K of intended films.

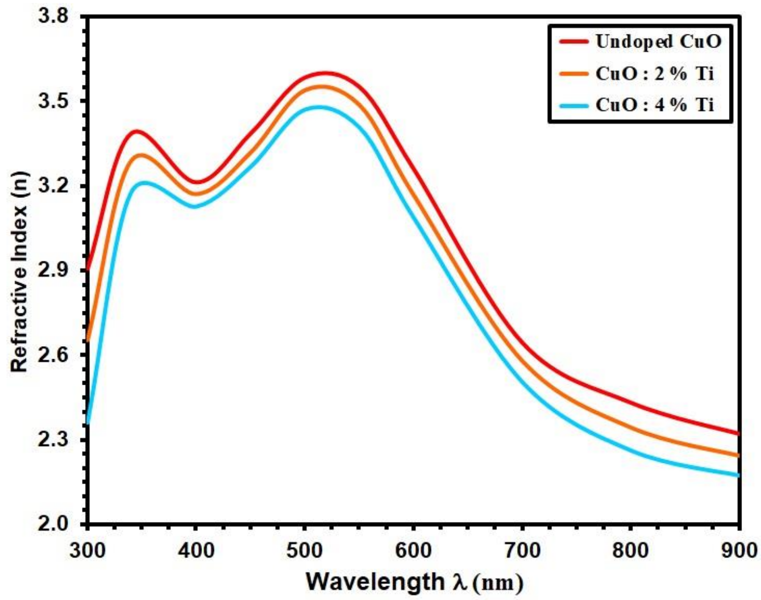

Fig. 8. n of the intended films

Conclusion

The Ti-doped CuO films were grown by varying doping using the chemical spray pyrolysis technique. XRD styles displayed that films have (002) dominant peak. The grain size was (13.27- 17.37) nm with CuO:4% Ti, whereas the strain (%) parameter increased from (26.12-19.95) × 10^{-4}. AFM shows that grain size was monitored in the domain of 80.36,69.75 and 51.81 nm for the (CuO, CuO:2% Ti, CuO:4% Ti) respectively. The transmittance in UV–VIS area decreased with increasing of Titanium content and was over 6% transmittance at Undoped CuO films. Absorption coefficient increase increases with increasing dopant concentration in the visible region. Undoped CuO thin film recorded 1.85 eV band gap value, and the doped Titanium with (2 and 4 wt%) recorded 1.81 ,1.75 eV. K and n decrease with increasing Ti for all samples.

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