

Study of the Structural and Optical Properties of $\text{Bi}_2\text{O}_3\text{:Cu}$ Thin Films as a Function of Different Doped Ratios

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Abstract

Thin films of pure bismuth oxide (Bi_2O_3) and doped with copper (0.2,4,6 %) were deposited on glass substrates by using a pulsed laser deposition device (PLD) with a power of (600mj) at room temperature and under low pressure (10-3mbar) ,The X-ray diagnostic results of bismuth oxide films doped and undoped with copper showed that they are of a monocrystalline structure and of cubic type. By analyzing these curves, it became clear the location of the peak around the angle of 27 degrees at the level (111), but the value of the optical energy gap increased by increasing the distortion rates and it has a high permeability.

Keywords — Bismuth oxide, Copper, Structural Properties, Optical Properties

Introduction :

Pulsed laser deposition (PLD) technology is increasingly utilized to prepare a variety of thin films and the simplest action of a pulsed laser deposition (PLD) device is to vaporize the target material to be deposited on glass substrates by shining a high-intensity beam of laser light on it [1] , By collecting this vapor on glass substrates installed above the target where the thin film is produced on them. Of all the technologies, PLD ranks as one of the most successful, due to its high controllability and relatively low costs compared to other technologies [2,3]. There is growing interest in transparent conductive oxides (TCO) due to the use of these films in various devices such as infrared detectors, solar cells, photodiodes, gas sensors and liquid crystal displays [4]. Electrical and optical properties make TCO materials a highly attractive material for technological applications [5]. Due to its unique properties, bismuth trioxide (Bi_2O_3) is among the most important TCOs, since it has a large energy gap, a high conductivity of oxygen ion, notable optical conductivity, and proper photoluminescence [6]. Optical coatings, electronic ceramics, solid oxide fuel cells, gas sensors, optoelectronic equipment, superconductors, elevated-temperature catalysts, and optical coatings are all applications of Bi_2O_3 [7]. Bi_2O_3 has five essential polymorphisms referred to as: $\delta\text{-Bi}_2\text{O}_3$ (cubic), $\omega\text{-Bi}_2\text{O}_3$ (triangular), $\alpha\text{-Bi}_2\text{O}_3$ (monoclinic), $\beta\text{-Bi}_2\text{O}_3$ (tetragonal) and $\gamma\text{-Bi}_2\text{O}_3$ (body-centered cubic) [8,9]. Since $\beta\text{-Bi}_2\text{O}_3$ has the smallest energy gap (~ 2.4 eV), it absorbs most strongly in the visible region of light. Moreover, the performance of this phase was superior to that of others in terms of motivation [10,11]. As one of the few metal elements that does not have a silver or gray natural color, pure copper has an orange-red color, and when exposed to air, it acquires a reddish tint. Copper is characterized by being a soft metal, malleable and retractable and has a very large electrical and thermal conductivity. Therefore, copper is used in many fields,

including as a heat and electricity conductor, in building materials, and as an alloys' component. Copper forms a layer of brown and black copper oxide with atmospheric oxygen, which protects the base metal from further corrosion. Addition, copper is slowly reacting with oxygen in the atmosphere but it does not react with water[12].

The practical part:

Bismuth oxide powder of high purity (99.99%) impregnated with high purity copper (99.8%) was pressed with a hydraulic press with a compressive strength of (10^2) bar to make tablets with a weight of (3g) copper-doped Bi_2O_3 , where pulsed laser deposition of targets produced copper-doped Bi_2O_3 thin films on glass substrates. The Nd: YAG pulsed laser with a wavelength (1064 nm) was employed as an energy source. At a frequency of (6 Hz) and the power was set to the target at 600 mJ) for the wholly samples. It was decided to maintain a 3 cm distance between the glass substrate and the target. The chamber was primary discharged to a base pressure of less than (10^{-3} mbar) using a turbo molecular pump, thin films were deposited by shining laser pulses on the disk where the number of pulses $N=150$ was applied at room temperature.

Results and discussion:

1- X-ray diffraction results:

The diagnostic results showed the X-ray technique of bismuth oxide membranes doped and undoped with copper and (0, 2, 4, 6) it has a monocrystalline structure of the cubic type, and through the analysis of these curves, it became clear the location of the peak (Peak) around the angle of 27 degrees at the level (111), which is the predominant growth direction for all prepared thin film, as in Figure (1). The distance between the Crystal levels (d_{hkl}) was calculated by the relation

$$n\lambda = 2d_{hkl}\sin\theta_B$$

Where the dislocation density and the number of crystals were calculated according to the relationships, respectively.

$$v = a_0^2 \cdot c_0$$

Calculate the average crystal size using the Debye-Scherrer method according to the relationship

$$D_{av} = K\lambda / \beta \cos\theta_B$$

It was shown that the grain size decreased upon doping, but it increased as the doping percentages increased, which are shown in Table (1).

Sample	2 θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} SD	Dave (nm)	hkl	a_0 (Å)	$\delta \cdot 10^{-18}$ nm ⁻²	$N_o \cdot 10^{-18}$ nm ⁻²
Bi_2O_3 -pure	27.3	0.1873	3.2641	3.19327	43.6	111	4.896	0.00052	0.0042
Bi_2O_3 -Cu (2%)	27.3	1.52	3.2641	3.19327	5.4	111	4.896	0.03456	2.2495
Bi_2O_3 -Cu(4%)	27.2	1.33	3.2759	3.19327	6.1	111	4.913	0.02647	1.5080
Bi_2O_3 -Cu(6%)	27.1	1.19	3.2842	3.19327	6.9	111	4.926	0.02120	1.0806

Table (1): Structural parameter values of undoped and copper-doped bismuth oxide films

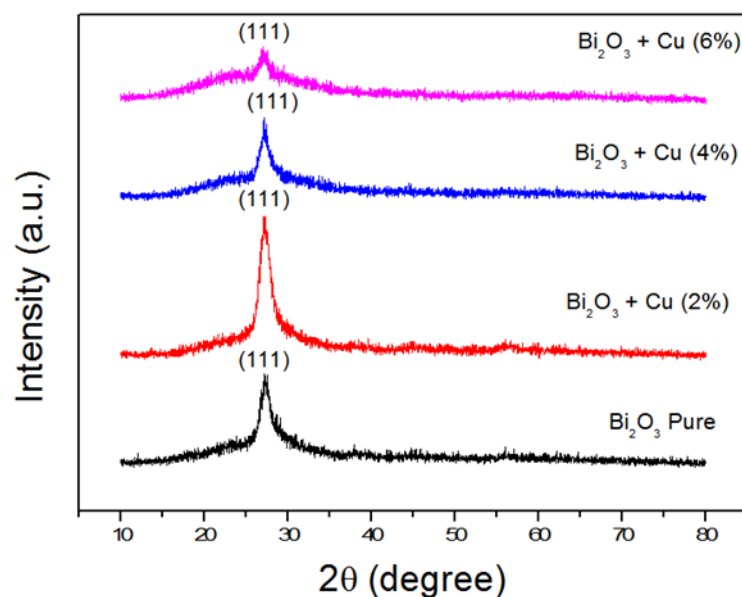
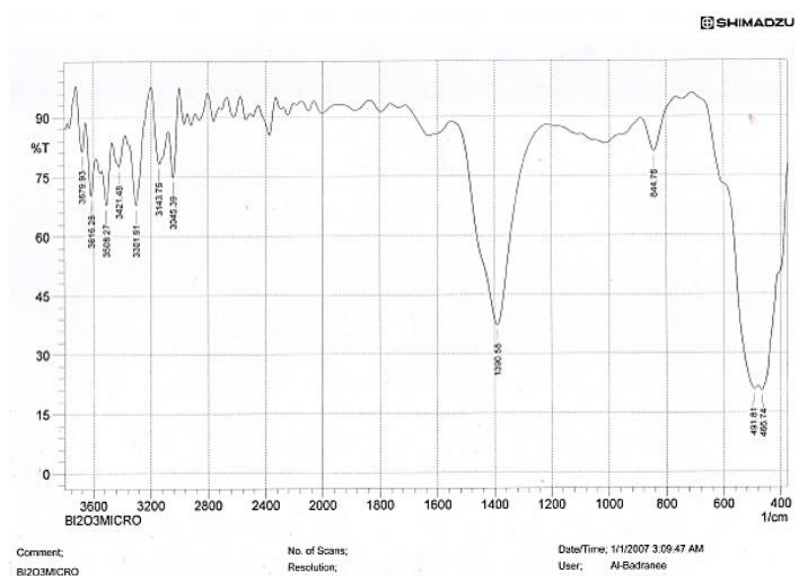
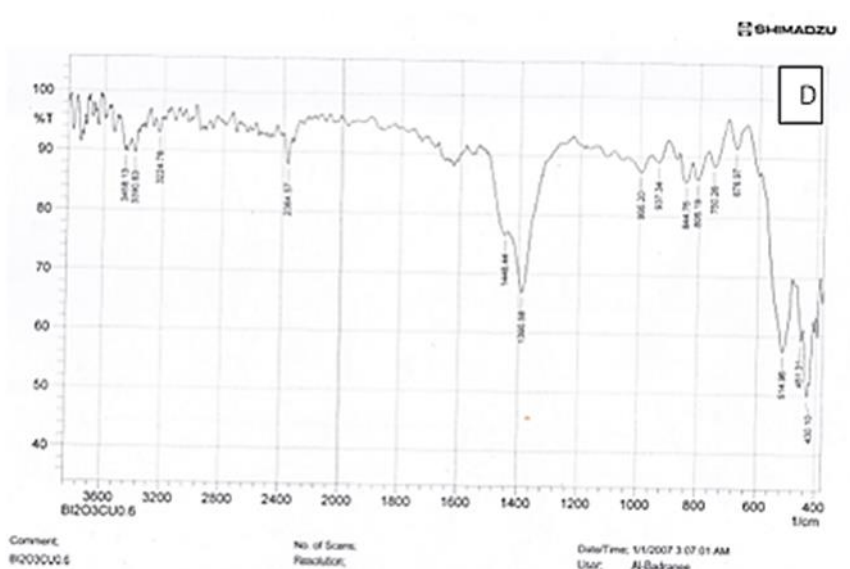


Figure (1): X-ray diffraction of copper-doped and un doped films

2- FTIR Results:

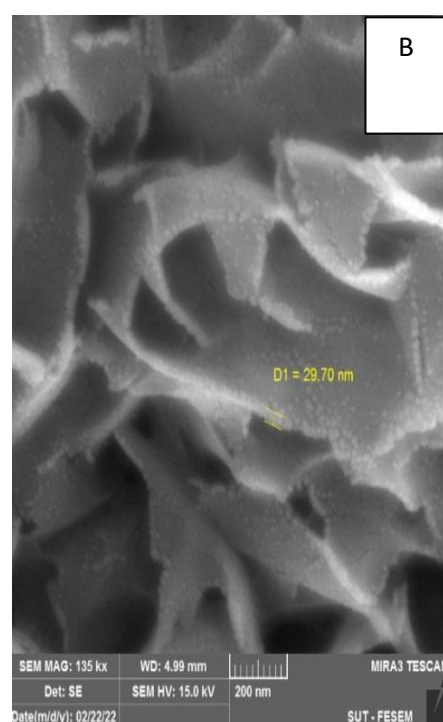
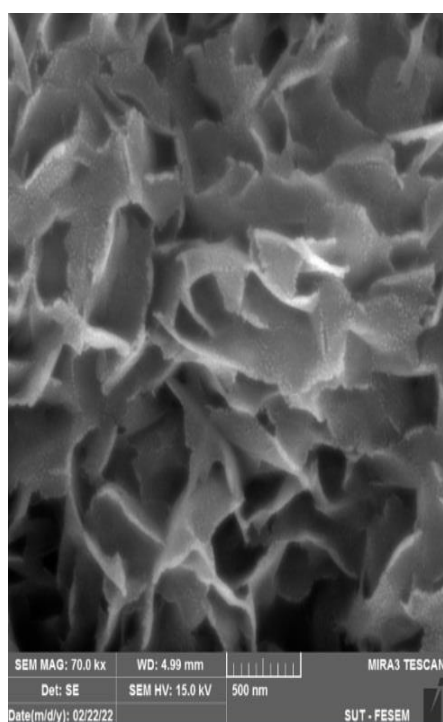
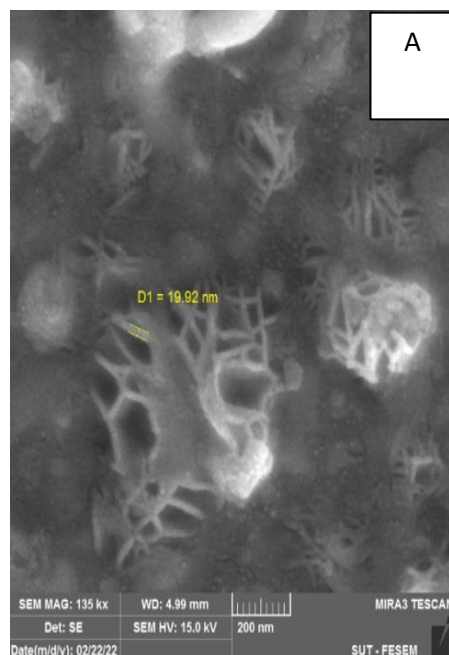
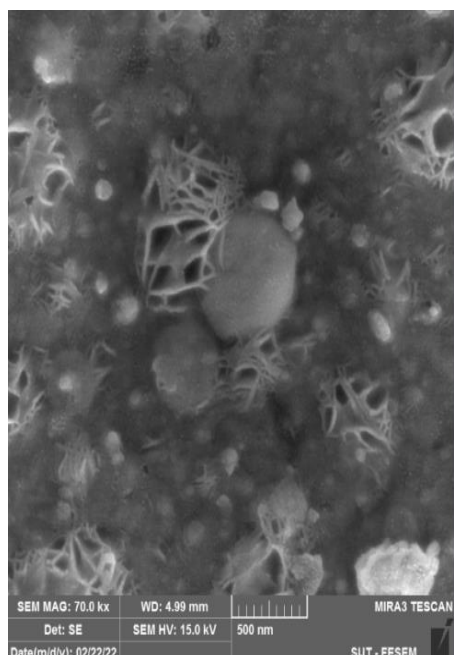
While the (FTIR) results of the copper-doped bismuth oxide films showed in different doping ratios within the measurement range ($400\text{--}4000\text{ cm}^{-1}$), by measuring the transmittance spectrum as a function of wave number, as shown in Figure (2), which showed some of the vibrational bonds of the prepared films. The absorption peaks at wave number (500 cm^{-1}) showed the presence of (Bi_2O_3). A wide absorption range is observed at ($3500\text{--}3000\text{ cm}^{-1}$) representing the extended vibrations of the (O-H) bonds of the prepared films. A strong bond of the (C-O) bond was recorded at wave numbers (1455,1400) due to the defects caused by the addition of Cu particles. The presence of the extended C-N vibrations was observed at 1438 .





3- The results of scanning field electron microscopy (FE-SEM) examinations of the prepared films:

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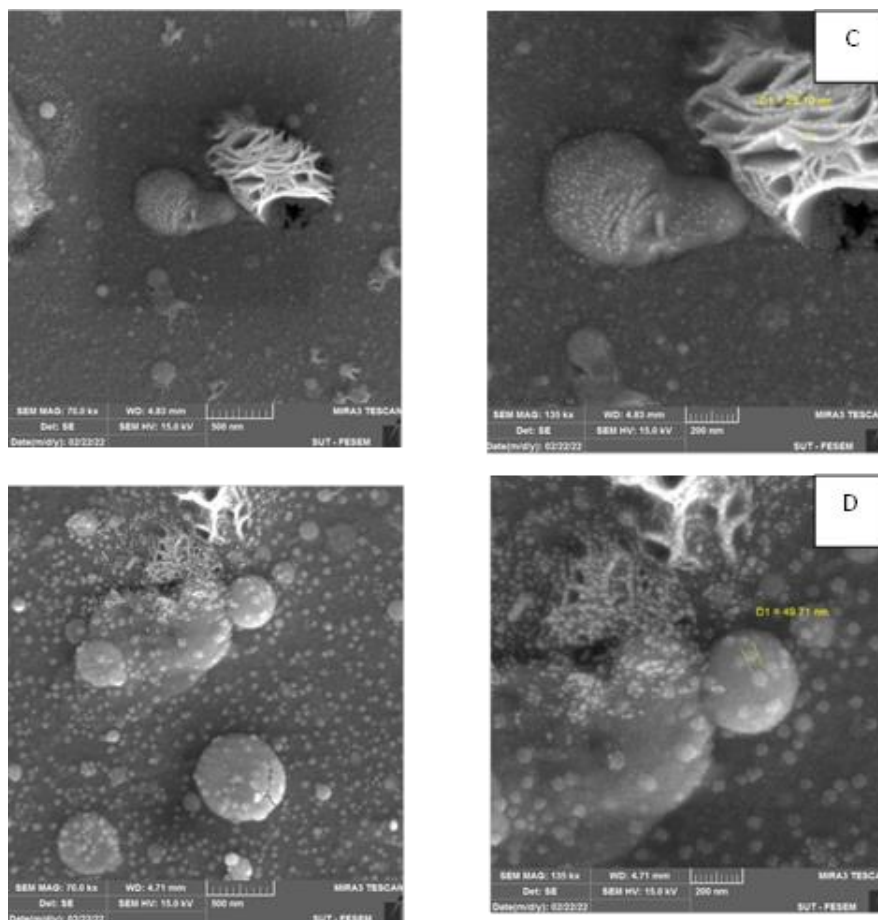


Figure 3: FE-SEM images of un doped and copper-doped thin film
 (A) pure bismuth oxide (B) Bismuth oxide doped with 2%
 (C) doped bismuth oxide by 4% (D) bismuth oxide doped 6%

4- Results of optical measurements of undoped and copper-doped bismuth oxide films:

(4-1) Permeability:

Figure 4 elucidates the transmittance spectrum in terms of the wavelength within the range (300-900 nm) for pure bismuth oxide films and copper-doped films with percentages (6,4,2), the transmittance spectrum of undoped bismuth oxide films has a transmittance (~30%) Vaccination greatly increases permeability

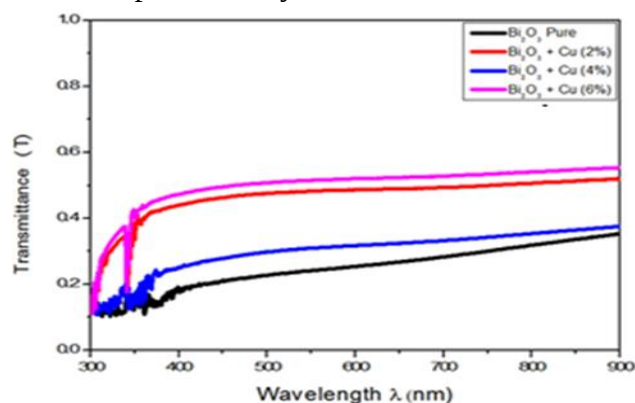


Figure (4) transmittance spectrum of pure bismuth oxide doped with copper

(4-2) Absorption:

Figure (5) displays the change of absorbance in terms of photon energy, for undoped bismuth oxide films doped with copper at percentages (6, 4, 2). All films show strong absorption in the ultraviolet region, with the modification of the excitation peak appears in the grafted films, and we note that the absorbance values decrease with increasing grafting

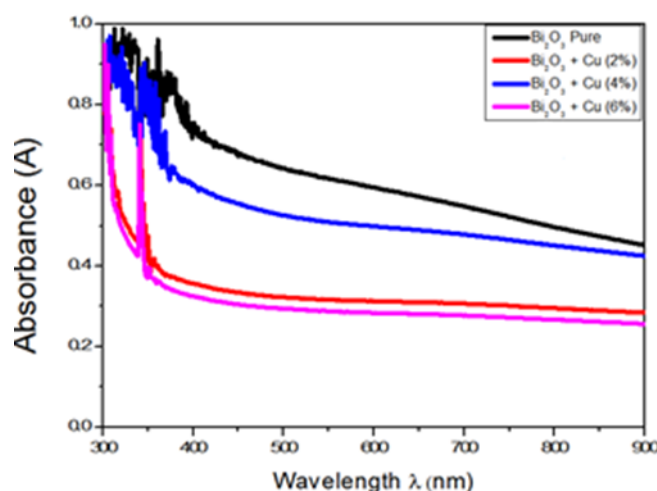


Figure (5) Absorbance of pure and copper-doped bismuth oxide

(4-3) Energy Gap:

The optical energy gap of the permissible direct electronic transitions was calculated for the undoped bismuth oxide films grafted with copper in different doped ratios, and it was found that the energy gap values increase with the grafting rate by 2% and reach eV 3.79 as it appeared in Table No. (2) and Figure (6) and then decreases About this value with an increase in the vaccination rate, as its value ranged between (2.75 eV) and (3.79 eV).

Sample	E_g (eV)
Bi_2O_3 -pure	2.75
Bi_2O_3 -Cu (2%)	3.79
Bi_2O_3 -Cu(4%)	3
Bi_2O_3 -Cu(6%)	3.75

Table No. (2): Energy gap values of undoped bismuth oxide films dotted with copper in different doped ratio.

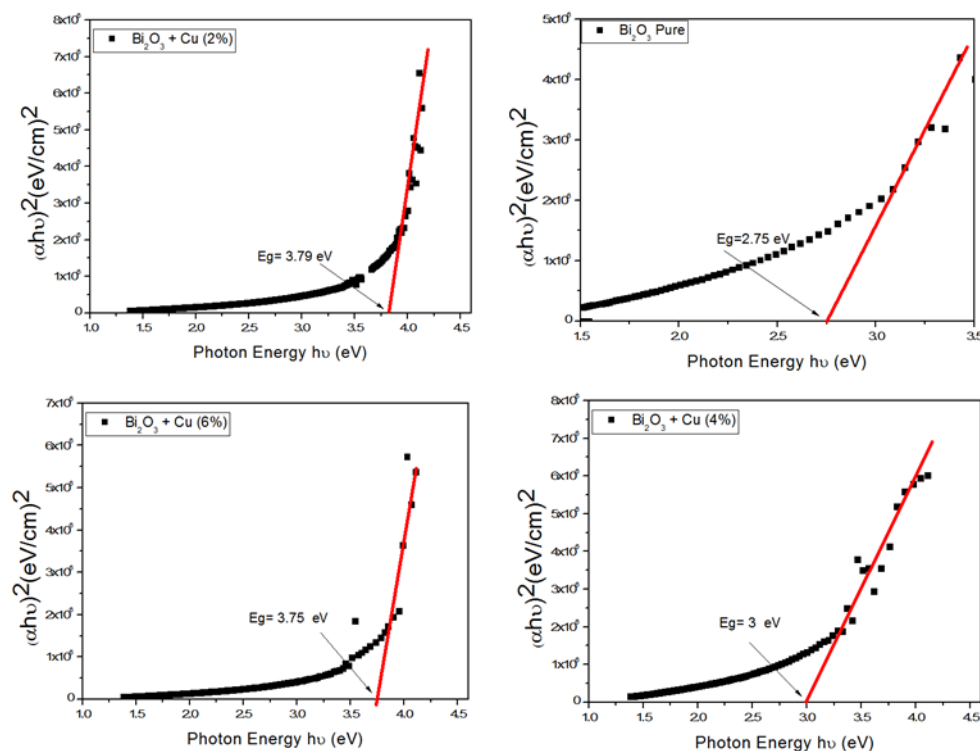


Figure (6) shows the energy gap of undoped bismuth oxide films dotted with copper in different doped ratios.

Conclusion:

1-The addition of the defect did not affect the nature of the crystal structure, as it remained of a monocrystalline structure in the prevailing direction (111), but its effect appeared in the positions of the peaks and their intensity, improving the crystal structure, except for the proportion (4% , 6%), which had the opposite effect .

2- the optical energy gap value is increased by increasing the doped ratios and all thin film have high permeability.

3-the results of FE-SEM showed that the thin film consist of spherical shapes and contain three-dimensional pyramidal structures "like a flower" with the presence of amorphous nanoparticles, representing the grafting material (copper) and effectively connected to the surface of Bi₂O₃.

4- FTIR tests of the prepared thin film showed that the absorption peaks in the wavelength number (500 cm⁻¹) are the presence of (Bi₂O₃). A wide absorption range was observed at (3500-3000 cm⁻¹) representing the extended vibrations of the (O-H) bonds of the prepared thin films.

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