DEPOSITION OF CuS, ZnS AND THEIR STACKED LAYERS THIN FILMS BY CHEMICAL SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT: *In this study, CuS, ZnS, and stacked layers of (CuS/ZnS and ZnS/CuS) thin films with solution molarity of (0.1 M) have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (400 ^oC). The thickness of the prepared thin films was about (350 ± 30) nm measured by gravimetric method. Various characterization techniques have been used to investigate the structural and optical properties of the prepared thin films. The XRD results showed that the CuS film has a polycrystalline nature with covellite-hexagonal structure and preferred orientation along (103) plane, and the ZnS film has a polycrystalline wurtzite-hexagonal structure with preferred orientation along (0010) plane, While the CuS/ZnS and ZnS/ CuS stacked layers thin films have a polycrystalline structure and mixture phase of covellite-hexagonal and wurtzite-hexagonal. The crystallite size of the prepared samples were (14.04, 13.95, 14.12 and 12.82) nm for CuS, ZnS and their stacked layers CuS/ZnS and ZnS/CuS respectively. AFM results showed homogenous and smooth thin films. FESEM results showed the formation nanostructures with different shapes, such as cauliflower, semi spherical, hexagonal, and in the form of plates and rods. The UV-Visible-NIR absorbance spectra were recorded in the range of (300- 900) nm to investigate the optical characteristics. The results have shown that the absorption coefficient value is ($\alpha > 10^4$ cm^{-1}) of all prepared thin films, which this in turn proved that the prepared thin films are likely to have direct electronic transitions. The values of the optical energy gap were (2.12, 3.34, 2.62 and 3.20) eV for CuS, ZnS, and their stacked layers CuS/ZnS and ZnS/CuS respectively.*

Keywords: CuS, ZnS, Stacked Layers, Structural Properties, Optical Properties, Nanostructures

1. INTRODUCTION

Copper sulfides (Cu_xS, x = 1–2) are significant binary compounds as they are of great concern due to their wide range of applications in optical and electrical devices, such as photo thermal conversion, electro-conductive electrodes, microwave shielding coatings, solar control coatings, dye-sensitized solar cells, potential nanometer-scale switch, cathode materials in lithium rechargeable batteries and some chemical sensing applications [1-6]. They are well known to form a wide variety of non-stoichiometric and mixed phases, of which at least five species are known to be stable at room temperature: covellite (CuS) in the sulfur-rich region; and anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$), and chalcocite (Cu_2S) in the copper-rich region [7]. Zinc sulfide (ZnS) thin film is a promising material for its use in various application devices. In opto-electronics, it can be used as light emitting diode in the blue to ultraviolet spectral region due to its wide band gap of 3.7 eV at room temperature [8]. In the area of optics, ZnS can be used as a reflector and dielectric filter because of its high refractive index (2.35) and its high transmittance in the visible range, respectively [9,10]. Several techniques such as molecular beam epitaxy [11] and MOCVD [12] have been used to produce ZnS thin films with adequate properties (high crystallinity, low resistivity and high transmittance). In the present study, (CuS, ZnS, and their stacked layers CuS/ZnS and ZnS/CuS) thin films are deposited by chemical spray pyrolysis method at 400^oC. The films are characterized by X-ray diffraction (XRD), AFM, FESEM and UV-Vis-NIR spectroscopy and the results were discussed to investigate their possible applications.

2. EXPERIMENTAL DETAILS

Thin films of CuS and ZnS were deposited on glass substrates (Soda lime glass) using a homemade chemical spray pyrolysis system. Distilled water was used to prepare the precursor solutions by dissolving 0.1 M of $Cu(CH_3COO)_2.H_2O$ (99 % purity, from Alpha Chemika-India) and 0.1 M of $SC(NH_2)_2$ (99 % purity, from Central Drug House (P) Ltd. New Delhi - India) to deposit the CuS thin film layer; and 0.1 M of $Zn(CH_3COO)_2.2H_20$ (99.9% purity, from Sharlo-Spain) and 0.1 M of $SC(NH_2)_2$ to deposit the ZnS thin film layer. These aqueous solutions were magnetically stirred for 10 min, and then the resultant solutions were sprayed on the glass substrates which were kept at temperature of 400 ^oC. To prepare CuS/ZnS (or ZnS/CuS) stacked layers thin films, CuS (or ZnS) thin film was first grown on glass substrates and ZnS (or CuS) thin film was later deposited on the first thin film. The thickness of the prepared thin films was about (350 ± 30) nm measured by gravimetric method. Other deposition conditions such as spray nozzle substrate distance (30 cm), spray time (10 s), spray interval (2 min) and pressure of the carrier gas (1.5 bar) were kept constant during the deposition process. The prepared films were characterized by X-ray diffraction (Burker D8 Advance, CuKα line, 1.54056 Å), Atomic Force Microscopy (AFM) using scanning probe microscope type (SPM- AA3000, Contact mode, supplied by Angstrom, Advanced Inc), Field Emission Scanning Electron Microscopy (FESEM) (MIRA3,TE-SCAN) and UV-VIS-NIR spectrophotometer (Shimadzu, UV- 1800).

3. RESULTS AND DISCUSSION

3.1 X- ray diffraction analysis

Figure (1) shows the patterns of X-ray diffraction of CuS and ZnS thin films. It can be observed that the positions of the XRD peaks of CuS film are located at angles ($2\Theta\sim$ 29.28^o, 31.78^o, 32.84^o, 47.82 ^{o} and 59.4^o) corresponding to the planes (102), (103), (006), (107) and (116) respectively which belong to the covellite-hexagonal structure with the preferred orientation of (103). These peaks are consistent with the International Center for Diffraction Data (ICDD) card number (06-0464). The appearance of several peaks in the XRD pattern indicates that the film has a polycrystalline structure. These results are in agreement with the results reported by other studies [13,14]. From the same figure, it can be noticed that the peaks positions of the ZnS film are located at angles (2Θ ~ 28.6^o, 47.76^o and

56.6°) corresponding to the planes (0010), (110) and (1110) respectively which are attributed to the wurtzite-hexagonal structure with the preferred orientation of (0010). These results are in agreement with the International Center for Diffraction Data (ICDD) card number (12- 0688) and are similar to the reported ones by other studies [15,16].

Figure (2) shows the X-ray diffraction patterns of the stacked layers (CuS/ZnS and ZnS/CuS) thin films, where the figure indicates that the films have polycrystalline structure with mixture phases of the hexagonal phase of CuS assigned by the (+) symbol, and the hexagonal phase of ZnS assigned by the (*) symbol. The stacked layers (CuS/ZnS and ZnS/CuS) thin films have the preferred orientations (103) and (0010) respectively, and when comparing the results of the peaks positions with the International Center for Diffraction Data (ICDD) for both compounds, it can be concluded that the results are close. We can notice also a decrease in the full width at half maximum (FWHM) of the peaks belong to CuS/ZnS film compared with that of ZnS/CuS film which may be attributed to the copper ions on the top layer of the CuS/ZnS film, and we can notice that the CuS phase is clearly seen in both films, which can be attributed to that the bonding force between sulfur ions and copper ions is stronger than the that between sulfur ions and zinc ions [17].

The interplanar spacing (d) was calculated using Bragg's equation [18]:

$$n\lambda = 2d\sin\theta \qquad \text{...... (1)}$$

And for hexagonal unit cell, the lattice constants (a_o, c_o) are given by [19]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a_o^2}\right) + \frac{l^2}{c_o^2} \qquad \text{...... (2)}$$

Where (h, k, l) are the Miller indices. From the Table (1), it is clear that the values of the lattice constants of CuS and ZnS film are in agreement with the values of the (ICDD) standard cards for both materials; (a_o=3.792 Å, c_o= 16.34 Å) and (a_o= 3.82 Å, c_o=31.20 Å); respectively. From the table, it can be observed also that the values of the lattice constants of the (CuS)/(ZnS) and (ZnS)/(CuS) thin films are shifted from their values of (CuS) and (ZnS) films and from their values in the (ICDD) standard cards. This deviation is due to the replacement of the two compounds ions with each other, since the diameter of copper ions is (0.73 Å), which is greater than the diameter of zinc ions is (0.60 Å) [16].

The crystallite size of the prepared thin films was calculated by Scherrer's formula given by the following equation [16]:

$$D = \frac{K\lambda}{\beta\cos\theta_B} \qquad \text{...... (3)}$$

Where D is the crystallite size, λ is the X-ray wavelength of CuKα Line radiation, β is the full width at half maximum (FWHM) and θ is the Bragg's angle. Table 1 shows that the crystallite sizes are (14.04 nm) and (13.95 nm) for CuS and ZnS thin films respectively, and their values were (14.12 nm) and (12.82 nm) for CuS/ZnS and ZnS/ CuS thin films respectively. The texture coefficient $Tc_{(hkl)}$for all samples have been calculated from the X-ray data using the well-known formula [20]:

$$Tc_{(hkl)} = \frac{I_{(hkl)}/I_{o(hkl)}}{\frac{1}{N}\sum I_{(hkl)}/I_{o(hkl)}} \qquad \text{...... (4)}$$

Where $I_{(hkl)}$ is the measured intensity, $I_{o(hkl)}$ taken from the ICDD data and (N) is the number of peaks in the experimental pattern. The texture coefficient is calculated for crystal plane (103) and (0010) of the prepared thin films. The values of the texture coefficient for all samples are shown in Table (1) and it can be noticed that its values for CuS and ZnS films are less than one, which indicates that there are more than one preferred orientations, whereas its values for CuS/ZnS and ZnS/CuS thin films are greater than one, which indicates that the crystal growth of the two films are within the preferred orientations (103) and (0010) only.

3.2 AFM analysis

The surface morphology of the thin films deposited on glass substrates is carried out using AFM. The size of scanned area was (2×2) μm^2. Figure (3) shows uniform, homogeneous, with pinholes or cracks and having a large number of grains. The grain size of thin films is in the range of several tens of nanometers which indicates the crystalline nature of the films. The average roughness value, the grain size, and root mean square roughness of all films are shown in Table (2).

3.3 FESEM analysis

The surface topography of the deposited material of the prepared thin films was studied using (FESEM), which scans the surfaces with high magnification and high precision. The images of all films with magnification of (100KX) and (200KX) are shown in figure (4). It can be observed that the CuS film grew in the form of cauliflower and semi spherical nanostructures with an average particle size of (52.6 nm). These structures are composed of many packed grains, and the appearance of large scale grains on the surface of the film can be clearly seen, while the images of the ZnS film show the formation of nanostructures in the form of plates and rods packed and arranged above each other with an average particle size of (46.2 nm). Moreover, the images of the stacked layers (CuS/ZnS and ZnS/CuS) thin films show regularly arranged cauliflower nanostructures with an average particle size of 30.9 nm and 24.6 nm respectively. Similar nanostructures were previously recorded in other reports [14, 15, 21-23].

3.4 Optical studies

The optical properties of the prepared thin films have been investigated by using UV-Vis-NIR absorbance spectra in

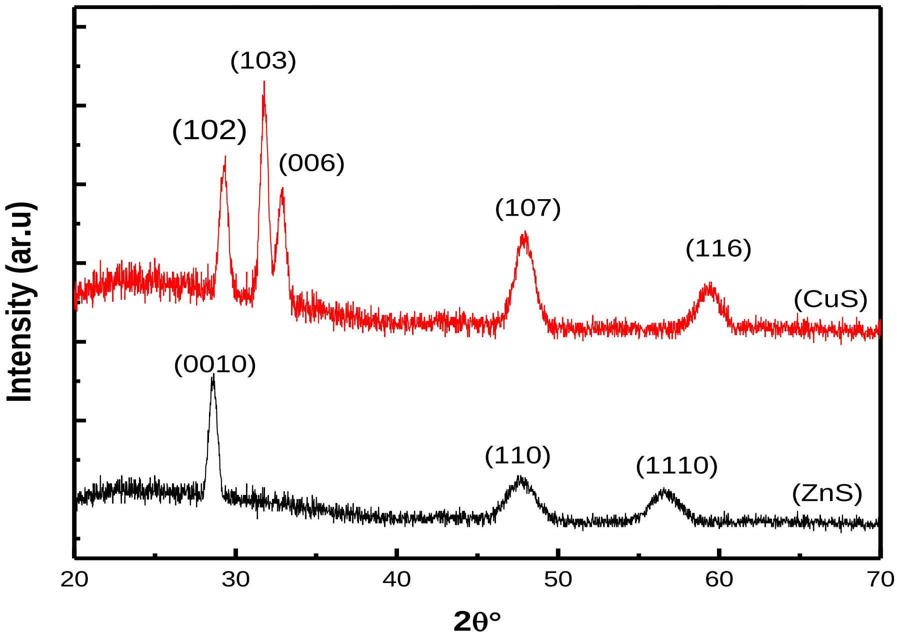


Fig. (1): X-ray diffraction patterns of the CuS and ZnS thin films.

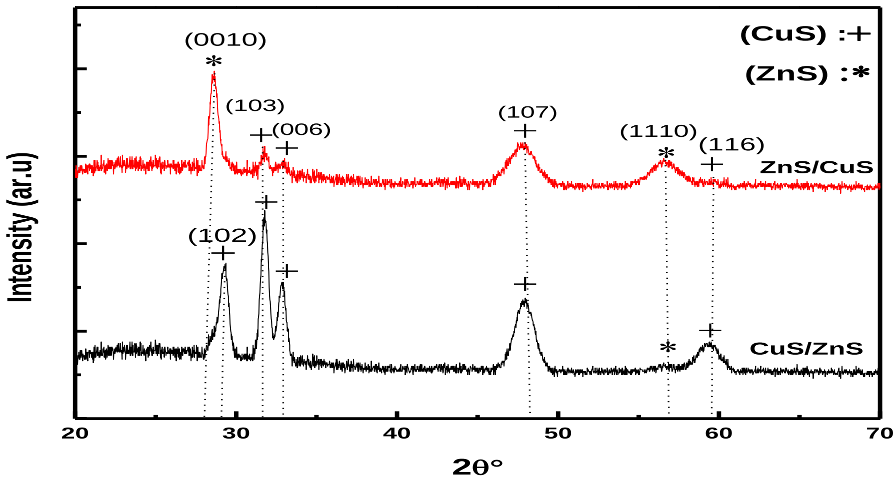
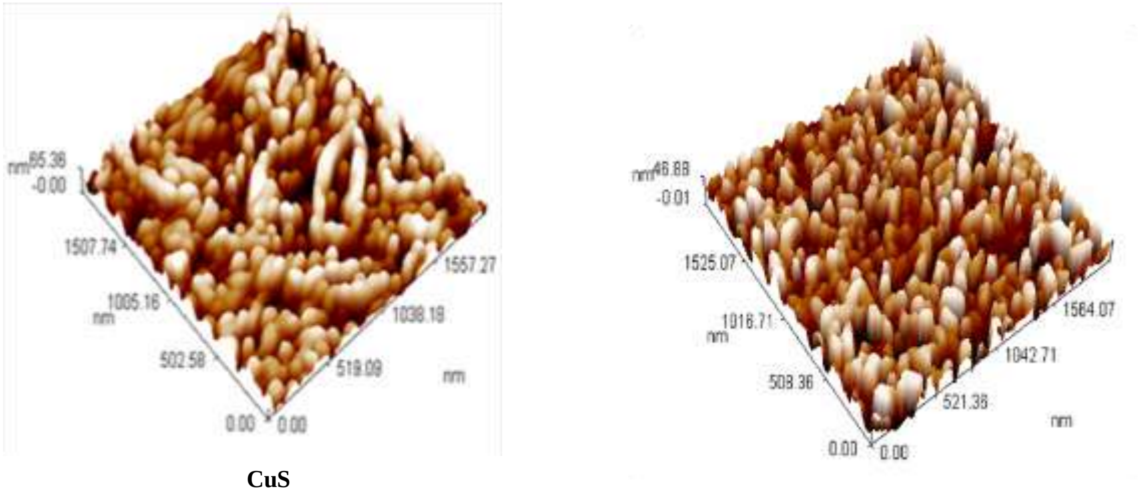


Fig. (2): X-ray diffraction patterns of the stacked layers (CuS/ZnS and ZnS/CuS) thin films.

Table (1): Structural parameters of the (CuS), (ZnS) and their stacked layers (Cus/Zns and ZnS/CuS) thin films.

Sample	CuS	ZnS	CuS/ZnS	ZnS/CuS
hkl	103	0010	103	0010
2θ (deg)	31.78	28.6	31.8	28.6
d_{hkl} (Å)	2.8132	3.1198	2.8122	3.1198
FWHM (deg)	0.5882	0.5876	0.5853	0.6395
Lattice constant (a_o) (Å)	3.795	3.818	3.83	3.80
Lattice constant (c_o) (Å)	16.34	31.20	16.37	31.19
D (nm)	14.04	13.95	14.12	12.82
$T_{c(hkl)}$	0.81	0.94	1.74	1.91

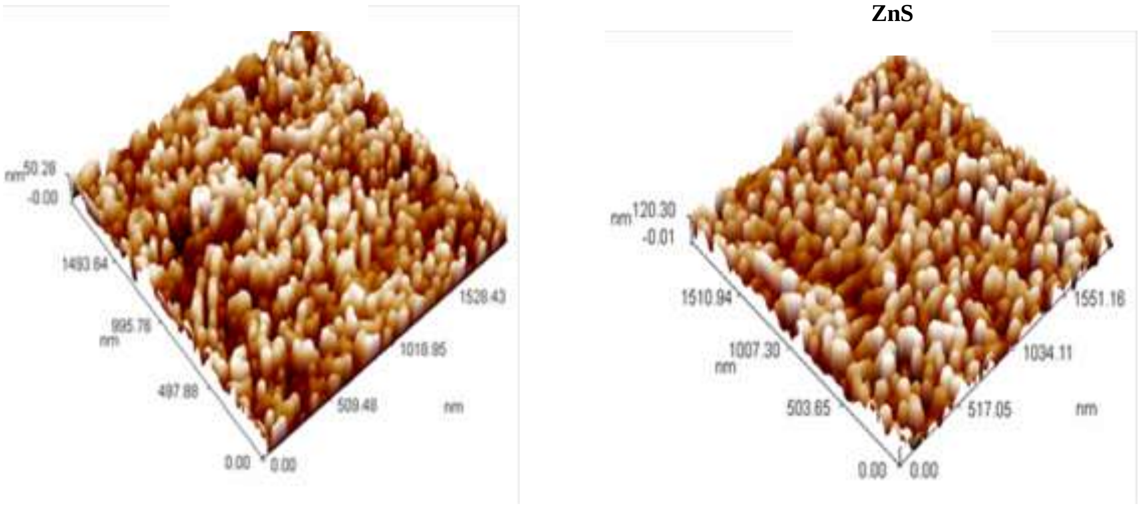


CuS

CuS

CuS

ZnS



CuS/ZnS

CuS/ZnS

Fig. (3): AFM images of the (CuS), (ZnS) and their stacked layers (CuS/ZnS and ZnS/CuS) thin films.

Table (2): Average roughness, root mean square roughness, and grain size of the (CuS), (ZnS) and their stacked layers (Cus/ZnS and ZnS/CuS) thin films.

Sample	Surface roughness (nm)	RMS (nm)	Grain Size (nm)
CuS	11.7	13.5	68.73
ZnS	15.3	17.8	103.78
CuS/ZnS	6.4	7.5	83.52
ZnS/CuS	5.2	6.8	74.04

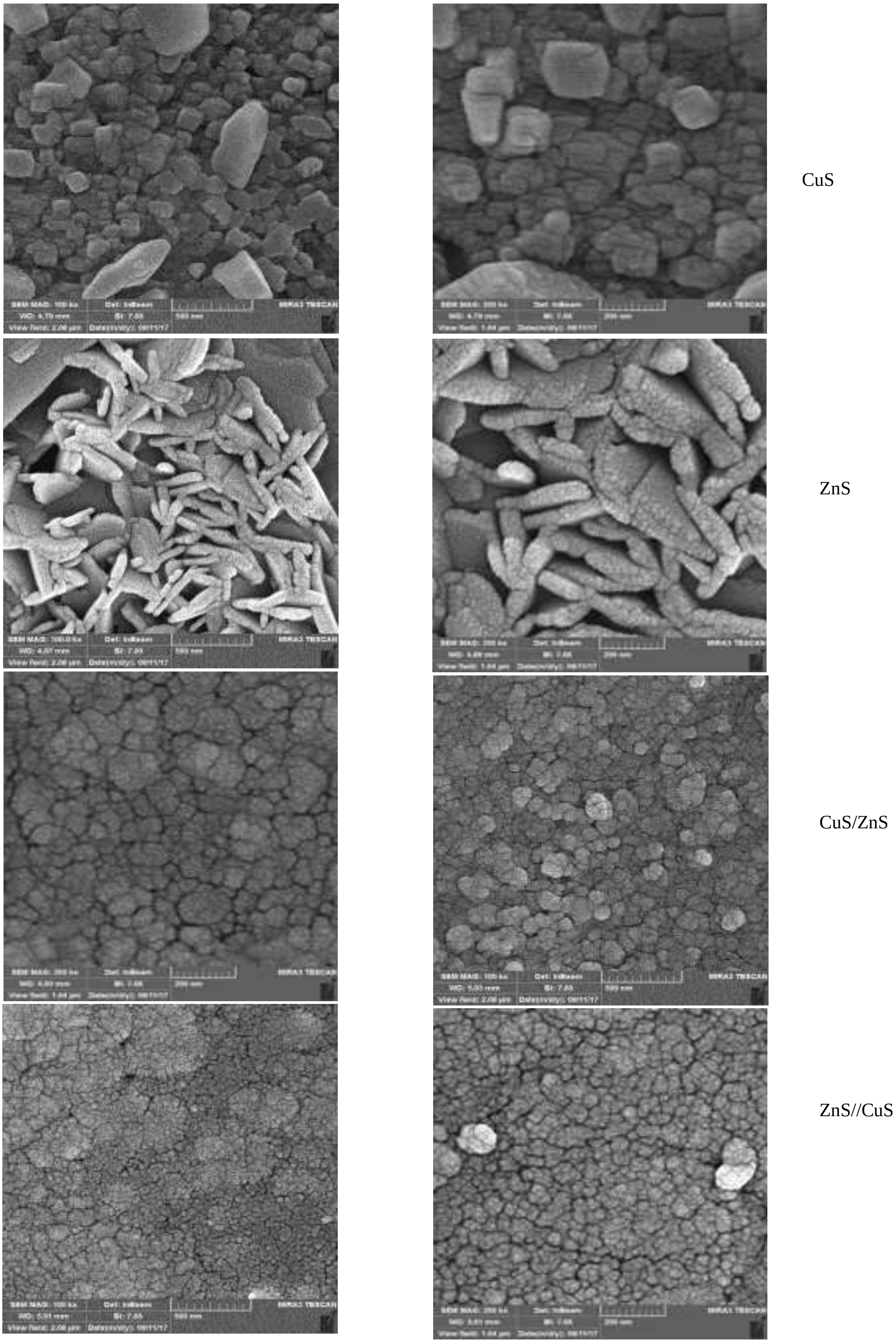


Fig. (4): FESEM images of (CuS), (ZnS) and their stacked layers (CuS/ZnS and ZnS/CuS) thin films.

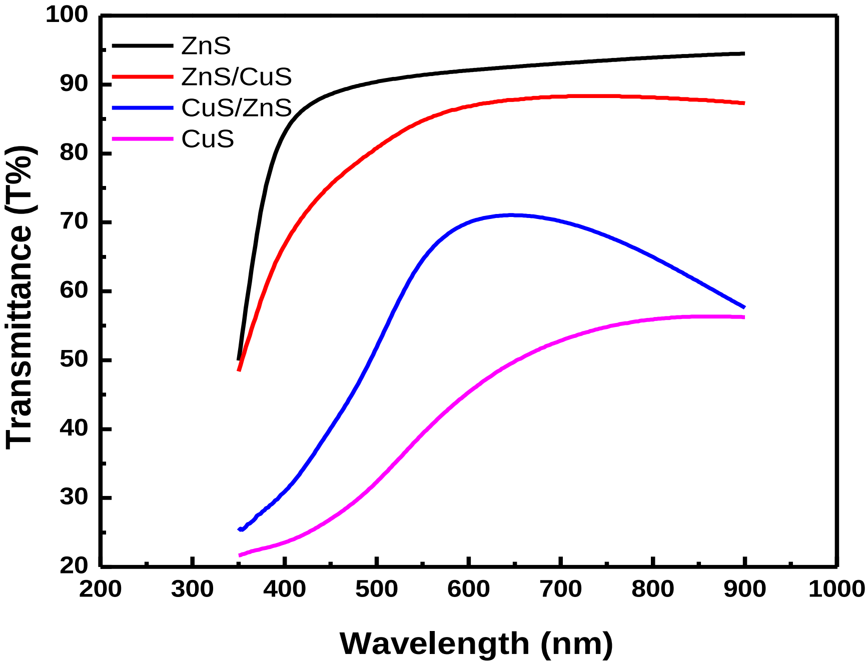


Fig. (5): The transmittance as a function of wavelength of (CuS), (ZnS) and their stacked layers (Cus/ZnS and ZnS/CuS) thin films.

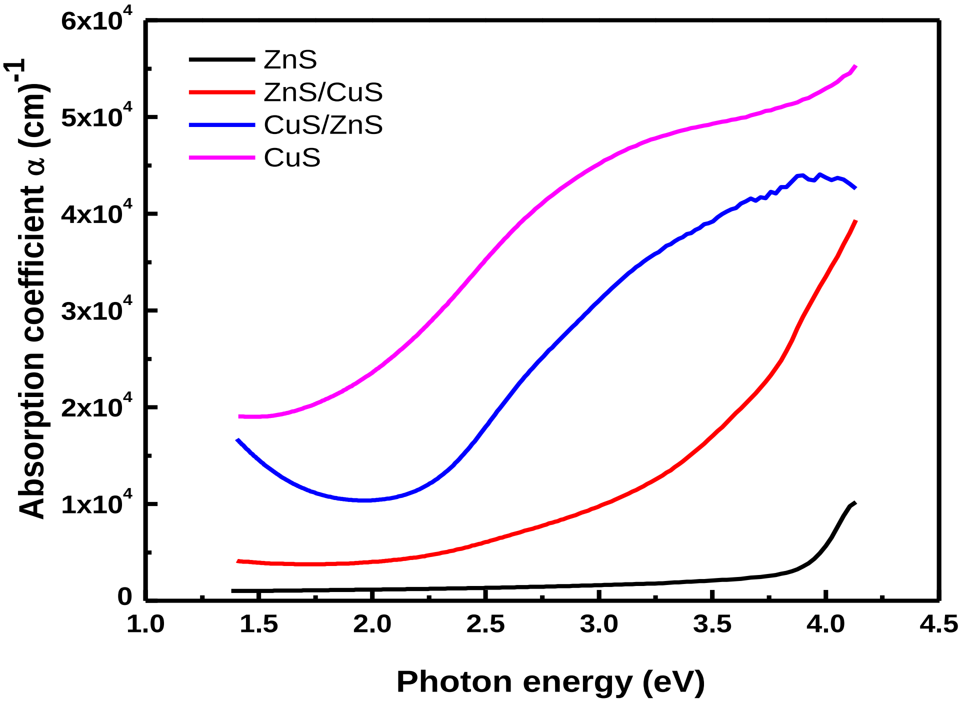


Fig. (6): The relationship between the absorption coefficient and the photon energy of (CuS), (ZnS) and their stacked layers (CuS/ZnS and ZnS/CuS) thin films.

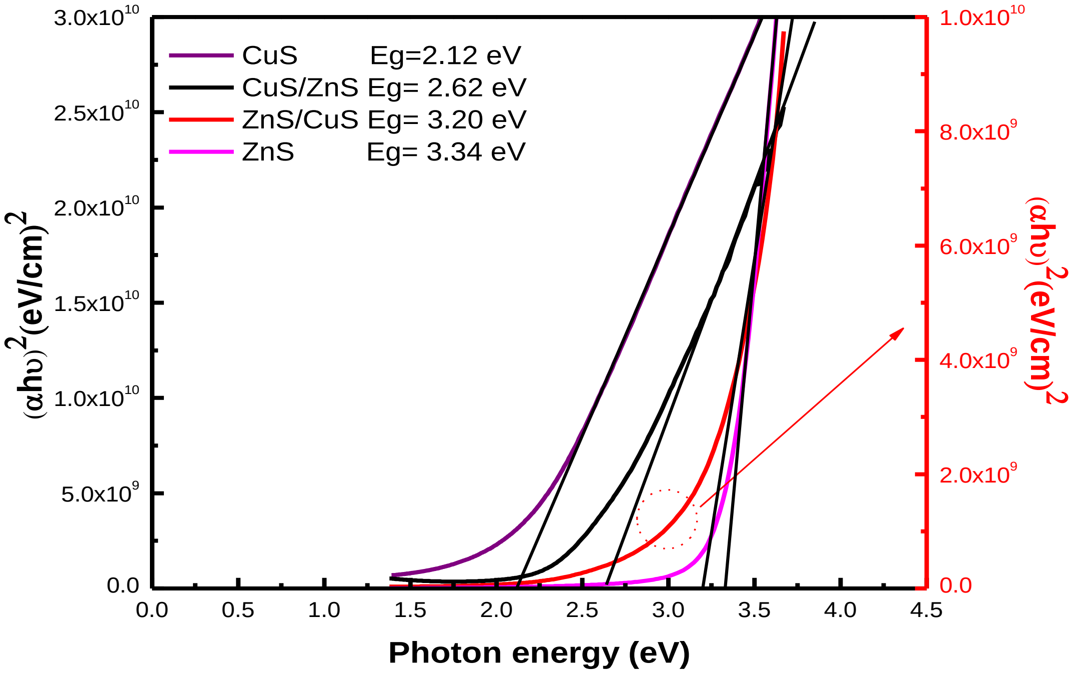


Fig. (7): The relation between $(\alpha h\upsilon)^2$ and (hυ) of (CuS), (ZnS) and their stacked layers (CuS/ZnS and ZnS/CuS) thin films.

the region of (300-900) nm. Figure (5) shows the transmittance spectra as a function of the wavelength of CuS, ZnS, and their stacked layers (CuS/ZnS and ZnS/CuS) thin films. From the figure, it is observed that the transmittance of ZnS film starts with a sharp and rapid increase within the wavelength range of (300-400) nm, then after this region, it increases slowly with the increase in wavelength. The fundamental absorption edge is sharp and starts at (440 nm) and the highest value of transmittance is (94 %).

We notice from figure that the transmittance of the ZnS/CuS film begins with quick increase among the wavelength range (300-500) nm and then increases slowly with increasing of wavelength and the fundamental absorbance edge is not sharp and starts at (540 nm) and the highest transmittance value is (87%), of CuS/ZnS film, the transmittance begins with a sharp and quick increase among the wavelength range (300-600) nm, then its decreasing after this region with increasing of wavelength and the fundamental absorption edge is not sharp and its starts at (620 nm), the highest transmittance value is (70%), as well as the transmittance of the CuS film begins with a quick increase within the wavelength range (300-600) nm, then begins slowly increases with increasing of wavelength and the fundamental absorption edge is not sharp starting at (750 nm) and the highest transmittance value is (55%).

The absorption coefficient (α cm^{-1}) can be estimated from the absorbance (A) using the formula [20]:

$$\alpha = (2.303\times A)/t \qquad \text{...... (5)}$$

Where (t) is the thickness of the film. Figure (6) shows the relationship between the absorption coefficient and the photon energy of (CuS), (ZnS) and their stacked layers (Cus/ZnS and ZnS/CuS) thin films. The figure shows that the absorption coefficient increases with increasing the photon energy for all prepared thin films in the visible spectrum region. The absorption coefficient value is >10^4 cm^{-1} for all prepared thin films, which indicates that the films have direct electronic transitions. The highest value of the absorption coefficient is for CuS thin film.

The optical energy gap values (Eg) can be calculated by using Tauc's relation [15]:

$$\alpha h\nu = B(h\nu - E_g)^r \qquad \text{...... (6)}$$

Where $h\nu$ is the photon energy, Eg is the optical band gap, B is a constant which does not depend on photon energy and r has four numeric values, (1/2) for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions". Figure (7) shows the plot of $(\alpha h\upsilon)^2$ versus hυ and the energy gap (Eg) value is calculated by using Tauc's equation by assuming allowed direct transition between valance and conduction bands. The energy band gap of CuS thin film is found to be (2.12 eV), this is in agreement with the value reported by Xin and Wang [14]. The value of ZnS thin film energy gap is (3.34 eV) which is in agreement with the result obtained by Priya et al. [18]. Moreover, the values of energy gap were (2.62 eV) and (3.20 eV) for stacked layers (Cus/ZnS and ZnS/CuS) thin films respectively.

4. CONCLUSIONS

In this study, the chemical spray pyrolysis method was used successfully for deposition of CuS, ZnS, and their stacked layers (Cus/ZnS and ZnS/CuS) thin films on glass substrates at temperature of (400°C). From X-ray diffraction results, it is concluded that the (CuS) thin film has polycrystalline structure (covellite-hexagonal) type with preferred orientation of (103), whereas the ZnS thin film has a polycrystalline structure and (wurtzite-hexagonal) type with preferred orientation of (0010). Furthermore, the stacked layers (CuS/ZnS) and (ZnS/CuS) thin films have polycrystalline structures with a mixture of the two phases. The AFM results show that all prepared films are homogeneous and smooth. Also FESEM results showed the formation of nanostructures with different forms, such as cauliflower, semi spherical, and in the form of plates and rods. The values of the optical energy gap were (2.12, 3.34, 2.62 and 3.20) eV for (CuS), (ZnS) and their stacked layers (CuS/ZnS and ZnS/CuS) thin films respectively. From the results of structural and optical studies of all prepared films, we conclude that the thin films can be used as effective materials in the manufacture of optical devices.

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