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Optical properties of amorphous CuS thin films deposited chemically at different pH values

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ABSTRACT

Amorphous copper sulfide thin films were deposited on commercial glass substrates at room temperature by chemical bath deposition. The effect of the pH value of the chemical bath on the optical properties of the amorphous thin films is investigated and discussed. The influence of the pH value of the chemical bath was examined by means of the optical transmission of the thin films in the wavelength range of 300–1100 nm taken at room temperature. Next, using these data, the absorption coefficient, the optical band gap value, the extinction coefficient, the refractive index, and the real and imaginary parts of the dielectric constant were calculated. The dispersion of the refractive index of the thin films was also investigated in terms of the single-oscillator Wemple and DiDomenico method. The value of the optical band gap determined by Tauc's extrapolation was found to be equal to one and half times the oscillator energy values of all deposited films.

1. Introduction

The optical properties of thin films have been extensively studied over the past few years because their optical behavior is important to define their potential use in technological areas. Among thin film materials, chalcogenide thin films have attracted much attention due to their large area deposition capabilities and the possibility of depositing them on a variety of surfaces. They consist of sulfur, selenium or tellurium, which are amorphous thin films deposited at ambient temperature. These amorphous thin films are important in various technological areas because they exhibit some of the optical properties of their crystalline counterparts. Similar to other deposited thin films, the properties of amorphous chalcogenide thin films also dramatically depend on their deposition conditions [1–7]. The deposition of chalcogenide thin films is achieved by vacuum thermal evaporation [8], thermal evaporation [9], the flash evaporation method [10] and chemical bath deposition (CBD) [11]. Of all these techniques the CBD method, which is used for large area deposition without the need for sophisticated instrumentation, is a promising process for the fabrication of opto-electronic devices; it also offers a wide variety of applications, including ferroelectric thin films, high-density optical data storage or semiconductors [12].

In the literature, most studies have concentrated on the effect of different factors such as the molar ratio, solution and substrate temperature, ambient atmosphere, annealing temperature, deposition time and the influence of the substrate on the properties of the chalcogenide thin films [13–17]. Therefore, in this work, we are interested in the preparation and investigation of CuS thin films deposited by CBD from chalcogenide thin films and in studying the effect of the solution's pH value on its structural and optical properties. Moreover, it should be noted that this is the first study in which the extinction coefficient, the refractive index and the dielectric coefficients of deposited amorphous CuS thin films were determined via transmission data and the dispersion of the refractive index of the thin films was investigated by using the single-oscillator Wemple and DiDomenico method.

2. Experimental details

In this work, commercial glass slides (75 mm × 25 mm × 1 mm) were used as substrates. Prior to the deposition of the films, these substrates were cleaned using detergent, nitric acid 1% (v/v), and deionized water, and then dried in the oven. The amorphous CuS thin films used in this study were deposited by the CBD method. The films were prepared for different pH (1.7, 1.8, 1.9, 2.01 and 2.19) values of the chemical bath while keeping all other bath parameters the same. The bath used was a mixture of 10 ml of 0.1 M $Cu(NO_3)_2{\cdot}5H_2O$, 2 ml of concentrated ethylene glycole ($C_2H_6O_2$), 10 ml of 0.1 M thioacetamide (CH_3CSNH_2), and 20 ml of deionized water. In order to adjust the pH value of the solution to 1.7, 1.8, 1.9, 2.01 and 2.09, 10 µl, 500 µl, 750 µl, 1000 µl and 1100 µl of potassium hydroxide (KOH), respectively, were added to the solutions. The pH values of the chemical baths were determined using a pH meter (Lenko mark 6230 N). The clean substrates were placed vertically in the solution at 40 °C for 24 h without stirring. At the end of the deposition, the coated substrates were taken out of the bath, washed well with deionized water and then dried in air. The film on one side of the substrate was removed using cotton swabs moistened with diluted acid because both sides of the substrates were coated with thin films.

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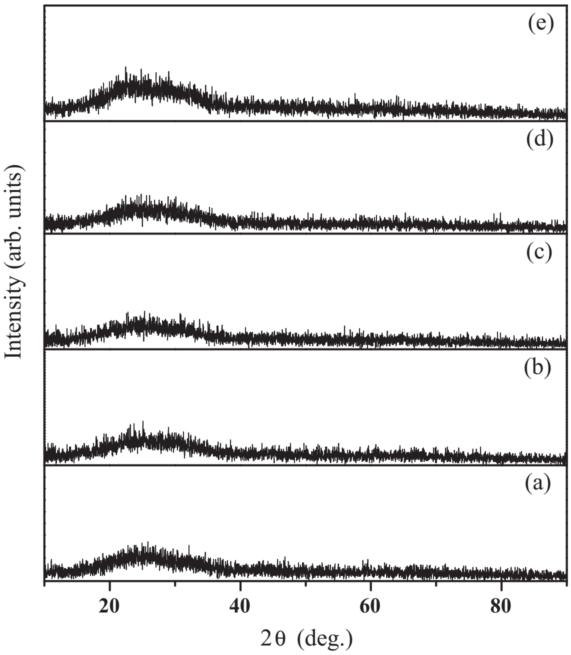

Fig. 1. X-ray diffraction pattern of CuS thin films deposited at 40 °C for 24 h at different pH values of chemical bath: (a) pH 1.7, (b) pH 1.8, (c) pH 1.9 (d) pH 2.01 and (e) pH 2.09.

The amorphous nature of the studied films was verified using a computer controlled X-ray diffractometer (Bruker AXS D8 advance model) with CuKα (1.54 Å) radiation operated at 40 mA and 40 kV. X-ray diffraction (XRD) patterns were recorded from 10° to 90° (2θ). The elemental composition of the thin films was determined using X-ray photoelectron spectroscopy (XPS). XPS images were acquired on a PHI 5000. During the process, an Al Kα anode was used, operated at 24.7 W and 15 kV. The binding energy (BE) scale of the instrument was calibrated using the surface carbon peak at 284.6 eV. To determine the surface morphology and film thickness of the amorphous CuS thin films, the sample surfaces were monitored using atomic force microscopy (AFM). AFM images were obtained using a VEECO Multimode 8 model atomic force microscopy. The optical transmission of the films was measured at room temperature with unpolarized light at normal incidence wavelength in the range of 300–1100 nm using a double beam spectrometer (PerkinElmer UV/vis Lambda 2S spectrophotometer). An uncoated commercial glass substrate was used as a reference during measurements to eliminate any possible influence of the substrate. Film thickness was measured using a profilometer (Filmetrics F30).

3. Results and discussions

3.1. Structural properties

The amorphous nature of CuS thin films was determined by the X-ray diffraction patterns (Fig. 1). As is shown in Fig. 1, the structural properties of the thin films deposited were not affected by the pH value of the chemical bath. From the XRD results, we saw that all the deposited films exhibited an amorphous structure because they were obtained at a low temperature. However, we believe that if these films are annealed in a nitrogen environment at different temperatures, the amorphous structure could be turned into a crystal structure because of low defects at high temperature. Studies on the effect of annealing temperature on the structural and optical properties of amorphous CuS thin films are on going and this will be the subject of another study.

In order to perform of the compositional analysis of CuS thin films, XPS analysis was used; this is a technique used to identify the chemical state of elements in thin films. The XPS analysis revealed that the atomic ratio of the element Cu, S in the deposited thin films was about 1.09:1.10, respectively, which is close to that of the CuS target. Fig. 2a and b shows the XPS spectra of a CuS thin film for the analysis of its copper and sulfur binding states, respectively. Fingerprints of both Cu and S atoms are clearly observed from the XPS spectra of the thin film. The bonding energies of Cu 2p at 932.30 eV and 952.01 eV were observed in the CuS thin films. The spectrum of S 2p shows two peaks (Fig. 2b). The first peak corresponded to 162.35 eV, which is in good agreement with that of the CuS compound. The second peak observed at 168.80 eV can be assigned to the SO_2 form on the surface [18]. From both the XRD and XPS analysis, we can confirm that CuS exists in amorphous thin films.

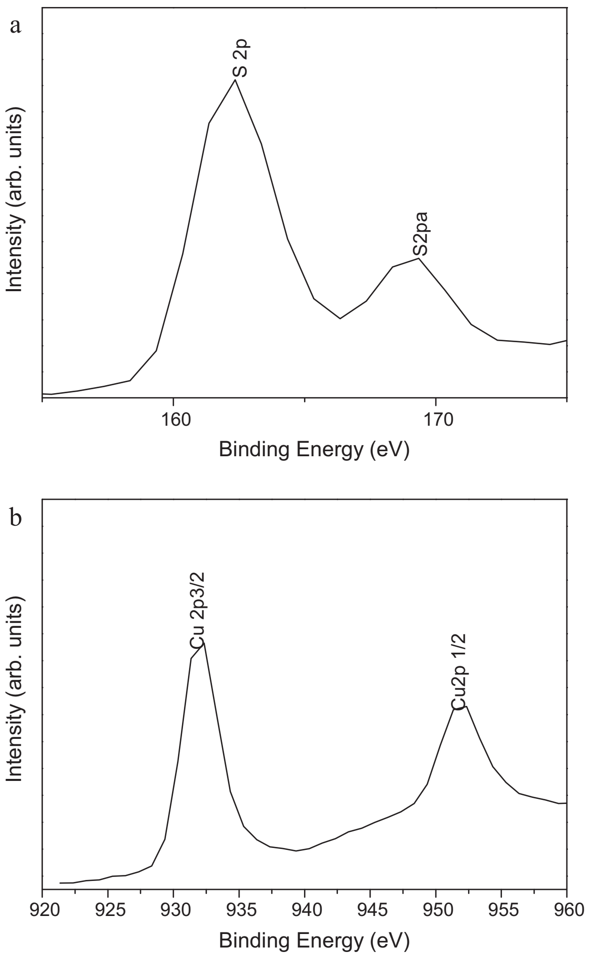

Fig. 2. XPS spectra of (a) Cu 2p and (b) S 2p regions of the peaks.

According to the AFM images of the thin films (Fig. 3), the surface roughness of the thin films increased as the thickness of the thin films increased.

3.2. Optical properties

The optical behavior of a material is determined by its optical constant, i.e. the band gap values (E_g), the extinction coefficient (k), the refractive index (n), and real (ε_1) and imaginary parts (ε_2) of the dielectric constant. These constants are calculated using transmission spectrum data. The transmission spectrum was recorded in the wavelength region ranging from 300 to 1100 nm. If multiple reflections are omitted, the transmittance (T) of the thin film is given by

$$T = (1 - R)^2 \exp(-A) \qquad (1)$$

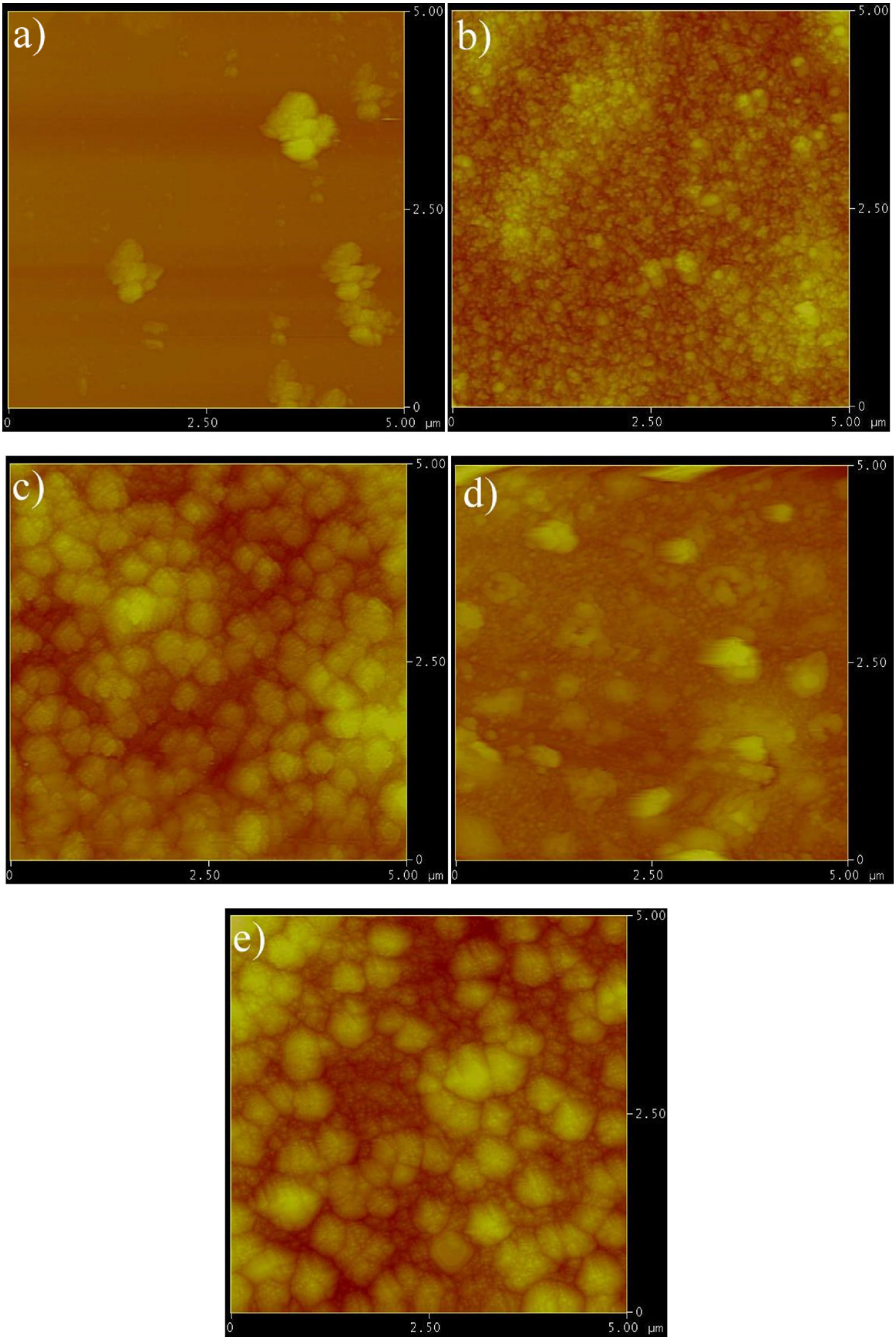

Fig. 3. AFM images of CuS thin films deposited at different pH solution, (a): 1.7, (b): 1.8, (c): 1.9, (d) 2.01 and (e) 2.09.

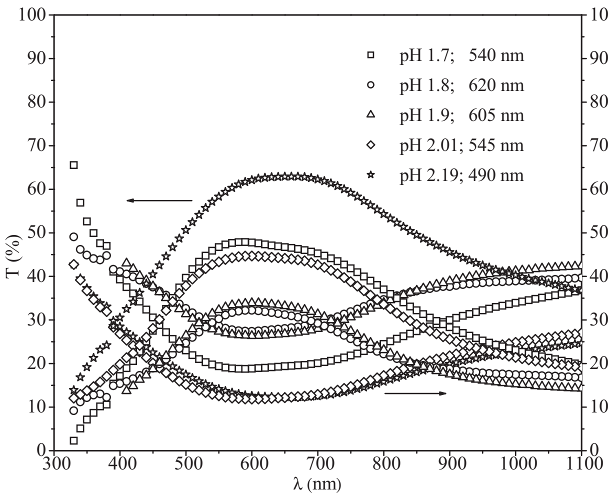

Fig. 4. Transmittance and reflectance spectra of amorphous CuS thin films.

where R is the reflectance, and A is the absorbance [19]. R can be determined from the data of both T and A using Eq. (1), which can be rearranged in the following form:

$$R = 1 - [T\exp(A)]^{1/2}. \tag{2}$$

Fig. 4 shows both the T and R spectra of the amorphous CuS thin films deposited at different pH values of the chemical bath as a function of wavelength.

From the data presented in Fig. 4, it is seen that the average transmission in the visible region is about 30–60% which is comparable to the values reported in the literature [20,21]. Another observation seen in Fig. 4, in the near infrared region, is that the transmittance T decreases, whereas reflectance R increases with increasing wavelength as observed in previous studies [22,23]. Fig. 5 shows that as the pH value of the solution increases from 1.8 to 2.19, and that the film transmission increases from 32% to 60% at the wavelength of 570 nm. Moreover, according to the same figure, it can be clearly seen that the deposition rate of the films is affected by the solution's pH value; also, the reaction rate decreases from 26 nm/h to 20 nm/h with increased pH value from 1.8 to 2.19, which may be the reason that the thin films deposited at the same time are thin.

The absorption spectrums of the deposited films are illustrated in Fig. 6. An absorption edge corresponds to an electron excited by a photon of known energy, whereby the electron can jump from a lower to a higher energy state. As shown in Fig. 6, the absorption edge is between 450 nm and 550 nm for all of the films deposited. It was observed that the absorption edge of the films shifts to a longer wavelength when the pH value increases to 1.8 and then, the absorption edge shifts towards the shorter wavelength side as the pH value of the chemical bath increases, which suggests an increase in the band gap value. Other authors also report this effect [24].

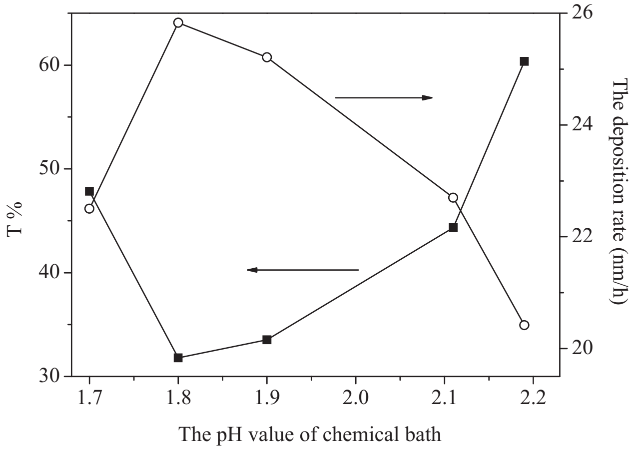

Fig. 5. Variation of transmittance at 570 nm and the deposition rate with the pH values of the chemical bath for amorphous CuS thin films.

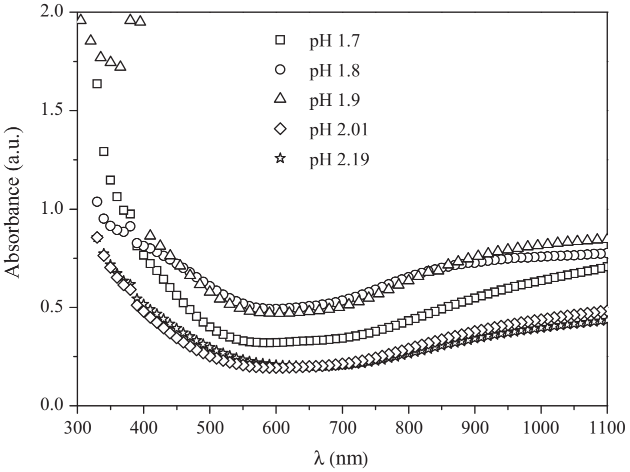

Fig. 6. Absorbance spectra of amorphous CuS thin films.

The spectral contribution of the absorption coefficient α was determined by using the following simple relation given by Beer–Lambert's law in the high absorption region:

$$\alpha = \frac{A \times \ln 10}{d} \tag{3}$$

where A is the absorption value of films, and d is the film thickness [25]. It is well known that α is related to the photon energy which is used to measure the optical band gap (E_g) and to determine the nature of the optical transitions. The optical band gap can be found in the high absorption and is characterized by the following expression [20]:

$$\alpha h\nu = C_\alpha (h\nu - E_g)^\gamma \tag{4}$$

where C_α is the constant, h is the Planck's constant, ν is the frequency, E_g is the optical band gap and γ is a number which relates the mechanism of the transmission process. $\gamma = 1/2$ or $3/2$ are directly allowed or directly forbidden while $\gamma = 2$ or 3 are indirectly allowed or indirectly forbidden transitions, respectively. The band gap of the amorphous thin films was obtained with $\gamma = 1/2$ meaning a directly allowed transition between the valence and the conduction band. The linear nature of the graphs supports the direct band gap nature of the semiconductor. It is well known that direct transitions across the band gaps are feasible between the valence and the conduction band edges in the k-space. In this process, the total energy and momentum of the electron-photon system must be conserved. The functional dependence of $(\alpha h\nu)^2$ vs. $(h\nu)$ is shown in Fig. 7. Here, the slope of the straight line fitting gives the value of C_α while the intercept of the straight line to the $h\nu$ axis gives the value of the direct optical band gap.

As shown in Fig. 7, the obtained amorphous thin films exhibited a linear dependence of $(\alpha h\nu)^2$ on $(h\nu)$ in the band gap range of 2.13–2.75 eV. The band gap values are summarized in Table 1, and are also shown in Fig. 8. As shown in Table 1 and Fig. 8, the optical band gap value of the amorphous thin films increased from 2.13 eV to 2.30 eV with increasing pH from 1.8 to 2.19 except for the amorphous film deposited at a pH of 1.70 where the band gap value was 2.35 eV. Furthermore, from these results it can be said

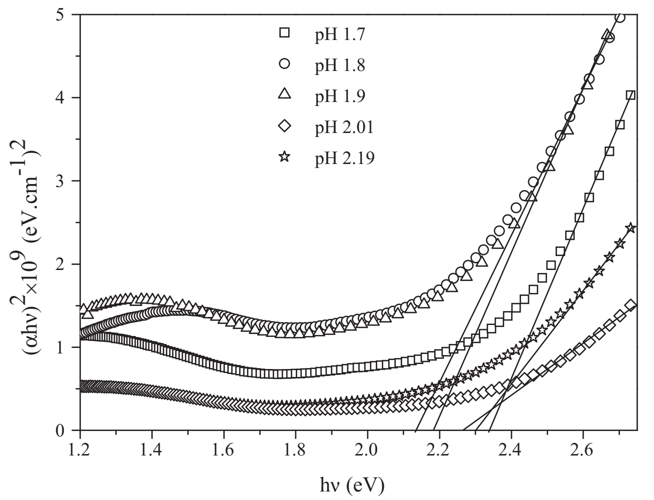

Fig. 7. Variation $(\alpha h\nu)^2$ with the photon energy $(h\nu)$ for amorphous CuS thin films.

Table 1
The pH value of the bath, independent photon energy (C_α), the band gap values (E_g) values obtained from Wemple–Didomenico model, single-oscillator energy (E_p) and dispersion energy (E_d).

pH	C_α (eV cm^{-2})	E_g (eV)	E_p (eV)	E_d (eV)
1.70	103.87	2.35	3.53	19.02
1.80	88.14	2.13	3.20	26.22
1.90	100.13	2.18	3.29	25.70
2.01	31.06	2.26	3.36	10.90
2.19	56.93	2.30	3.43	12.60

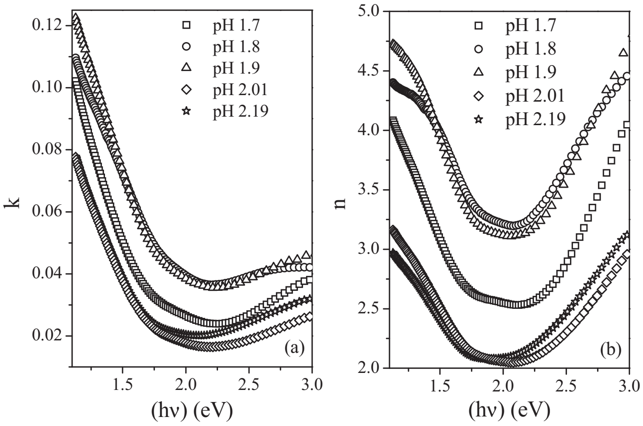

Fig. 9. Variation of (a) extinction coefficient (k) and (b) refractive index (n) and the photon energy $(h\nu)$ for amorphous CuS thin films.

that we observed a blue shift of the energy band gap as the pH value of the chemical bath increased from 1.8 to 2.19. The reason for this may be the arising of structural defects in the CuS thin films. As the incidence of the amorphous CuS phase increases in the films grown at high pH values, the extended localization in the conduction and valence bands increases so the absorption edge shifts towards blueshifted. In conclusion, the depositing of thin films at high pH values can be shown to be the main reason for the blueshift of the optical band gap. This may be due to the amorphous structure of CuS thin films. In this work, we found that the optical band gap values for the amorphous thin films were higher than the results obtained in a previous study [26]. In accordance with research on thin films, the band gap energies of highly crystalline films are similar to those of crystalline bulk materials, while poor crystallized or amorphous films illustrate band gap energies higher than those of the corresponding bulk materials [27].

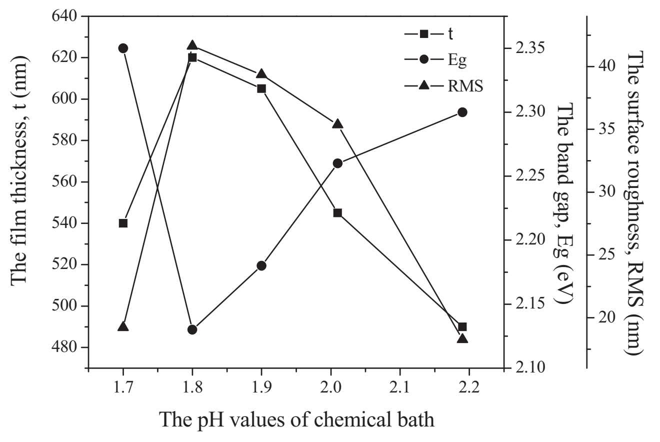

Fig. 8. Variation of the film thickness, the direct band gap and the surface roughness with the pH values of the chemical bath for amorphous CuS thin films.

Fig. 8 also depicts the variation in the film thickness of the amorphous CuS thin films as a function of the pH value of the chemical bath. It can be seen that as the thickness of the film increases the band gap value decreases, and vice versa. With the increase of film thickness, the changing of E_g values can be attributed to an increase in surface roughness (Fig. 8).

The optical band gap is an important parameter in understanding the band structure of a material while C_α represents the measure of disorder or randomness in the atomic configuration of the amorphous material [28]. A higher C_α indicates lower disorder. The values of C_α for different pH values of the bath are also presented in Table 1.

α is also related to the extinction coefficient (k) by

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

The dependence of the extinction coefficient obtained in Eq. (6) on the photon energy is displayed in Fig. 9(a). According to Fig. 9(a), k is slightly affected by the change of bath pH at lower energy values, while the change is observed more at higher energy values.

The refractive index (n) of thin films can be calculated from their reflectance and transmittance spectra using simple approximations [29]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1+R)^2} - k^2}. \tag{6}$$

The calculated n values of amorphous CuS thin films are shown in Fig. 9(b). It can be seen that n decreases linearly as photon energy increases followed by an increase at energies greater than 2 eV.

The spectral dependence of the refractive index was analyzed using the single effective oscillator model proposed by Wemple and DiDomenico [30], according to which

$$n^2(h\nu) = 1 + \frac{E_pE_d}{E_p^2 - (h\nu)^2} \tag{7}$$

where E_p is the single-oscillator energy and the lowest direct band gap value of the films is related to the following equation:

$$E_p = CE_g(D) \tag{8}$$

where C is a constant, typically ≈1.5. Also in Eq. (7), E_d is also the so-called dispersion energy. The E_p and E_d parameters are determined using the plot of $(n^2–1)^{-1}$ vs. $(h\nu)^2$ illustrated in Fig. 10, where E_p/E_d is the intercept of the vertical axis and $(E_pE_d)^{-1}$ is the slope [31]. In this work, the (E_p) value of the films was found as $E_p \approx 1.5E_g$. This

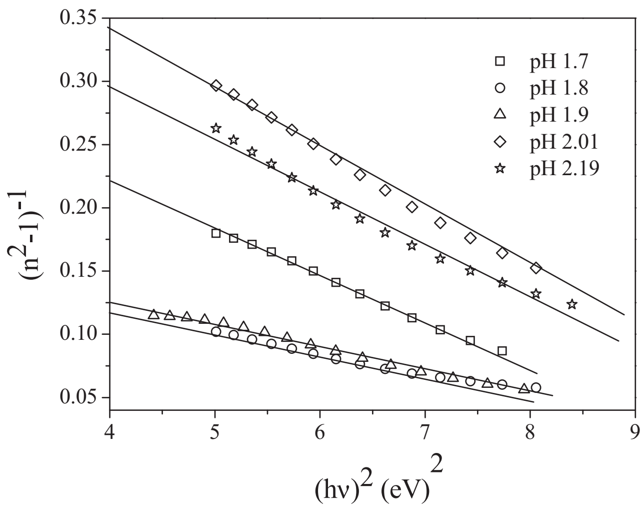

Fig. 10. Variation of $(n^2-1)^{-1}$ with $(h\nu)^2$ for amorphous CuS thin films.

relation is in agreement with another relation obtained from the single oscillator model [32]. The single-oscillator (E_p) and dispersion energy (E_d) values are listed in Table 1.

Considering dispersion, an electromagnetic wave loses its energy due to various loss mechanisms such as the generation of phonon, photogeneration, free carrier absorption and scattering while it passes through deformed materials. In such materials, the refractive index is a complex function of the frequency of light. The complex refractive index (N) with real part n and imaginary part k parts is given by

$$N = n - ik. \quad (9)$$

For further analysis of the optical data of amorphous CuS thin films, the following relations have been used:

$$\varepsilon = (n - ik)^2 = \varepsilon_1 - i\varepsilon_2 \quad (10)$$

$$\varepsilon_1 = n^2 - k^2 \quad (11)$$

$$\varepsilon_2 = 2nk \quad (12)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric constant, respectively [31]. The ε_1 and ε_2 of the dielectric constants for amorphous CuS thin films deposited at different pH values are shown in Fig. 11 as a function of photon energy. It is clearly shown that for deposited CuS thin films, the values of ε_1 first decreased with the photon energy until 2.08 eV, and then increased with the same form (Fig. 11a). Likewise, the ε_2 values decreased with the photon energy values up to 2.12 eV and then increased slowly (Fig. 11b). The ε_1 values changed in the range of 4.19–10.21 at the photon energy of 2.08 eV in Fig. 11a, while for the same samples the ε_2 values also varied in the range of 0.07–0.23 at the photon energy of 2.12 eV in Fig. 11b.

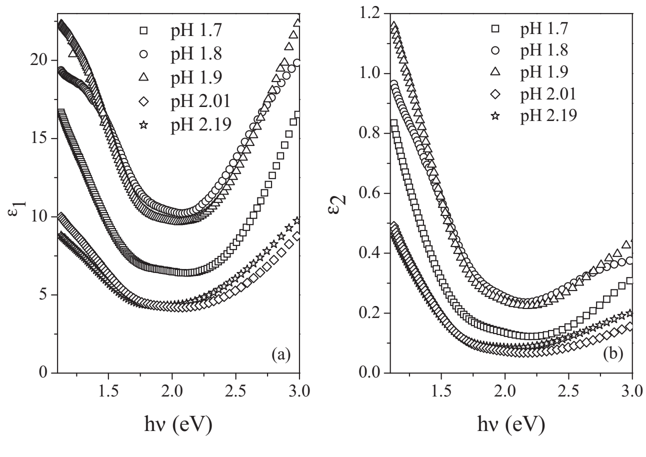

Fig. 11. Variation of the values of the real part (ε_1) and imaginary part (ε_2) of the dielectric constant with the photon energy ($h\nu$) for amorphous CuS thin films.

4. Conclusions

CuS amorphous thin films were successfully deposited on commercial glass by CBD. The effect of the pH value of the chemical bath on the optical properties of the obtained films was studied. While XPS studies confirmed that the CuS thin film was deposited on the substrate from the chemical bath, the XRD patterns did not show any evidence of the presence of the CuS thin film. According to what XRD patterns becoming an amorphous structure showed, the pH does not affect the film structure much; however, the characteristic UV–vis spectrum data of the film demonstrated that the pH value of the chemical bath may affect the optical properties. Optical transmission was found to increase when the pH increased from 1.8 to 2.19; the optical refraction decreased. Additionally, the optical transition and reflection of the film varied from about 30 to 60% and 2 to 10% in the visible range, respectively. It was found that the optical band gap increased with an increase in the pH value of the chemical bath from 2.13 to 2.3 eV. Moreover, the optical energy gap was found to be approximately equal to 1.5 times the oscillator energy for all amorphous films. The refractive index and extinction coefficient of all the films were calculated in the range $n = 4.72$–3.16 and $k = 0.122$–0.04, respectively. According to this study, it could be said that the obtained amorphous CuS thin films may be good candidates for use as solar filters to control solar radiation.

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