Optical band gap, photocatalysis, surface structures and depth profile properties of $\text{Cu}_2\text{Se}$ nanostructured thin films

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Keywords: $\text{Cu}_2\text{Se}$, nanostructure, optical band gap, Urbach energy, photocatalytic

Abstract

The optical behaviour, stoichiometry, surface configuration of $\text{Cu}_2\text{Se}$ nanostructured thin layers prepared at different reaction times by the chemical process has been considered. The optical band gap of the deposited thin films decreases from 2.92 eV to 2.08 eV for the first transition and from 2.18 to 1.2 eV for the second transition. In addition, it was shown that Urbach energy is independent from the film thickness, and tail values of the localized states has decreased from 1.15 to 0.33 eV. It was found that the concentration of Cu: Se remains approximately constant across the depth of the deposited film at higher deposition time. The degradation efficiency of 98% was achieved by Congo red for the prepared $\text{Cu}_2\text{Se}$ thin film at optimal condition which make it a good candidate for organic dye. From these measurements and by controlling the band gap energy, the $\text{Cu}_2\text{Se}$ can find application in solar cell application.

1. Introduction

Copper-based chalcogenides are becoming popular as electrode materials for electrochemical energy storage (Anjana et al 2021). Copper chalcogenide thin films have a number of applications in various devices, such as solar cells, photodetectors, superionic conductors, photoconductors, sensors, photothermal conversion, electro-conductive electrodes, narrow band filters, microwave shielding coating, flexible thermoelectric units, etc (Korzhuev 1998, Mane and Lokhande 2000, Lin et al 2017, Li et al 2021). Copper Selenide is found to exist in number of stoichiometry ($\text{CuSe}, \text{Cu}_2\text{Se}, \text{Cu}_3\text{Se}_2, \text{Cu}_5\text{Se}_4, \text{Cu}_7\text{Se}_4, \text{a-Cu}_2\text{Se}$) and non-stoichiometric ($\text{Cu}_2–\text{Se}$) (Zhou et al 2018). An interesting p-type $\text{Cu}_2\text{Se}$ film electrodes with a band gap range 2.1–2.3 eV and high absorptivity, are promising candidates for Photo-electrochemical purposes (Zyoud et al 2018). In addition, the photosensitivity of $\text{Cu}_2\text{Se}$ nanocrystal thin films could be enhanced for solar cells applications (Sudha et al 2018, Henry et al 2020a, 2020b). Copper selenide catalysts that can be activated with sunlight radiation have importance for practical application (Ghobadi et al 2020).

There exist a number of techniques to prepare $\text{Cu}_2\text{Se}$ thin films including thermal evaporation (Yadav et al 2020), Sputtering (Yang et al 2021b), Selenization (Gadjiev et al 2016), Solvothermal (Lin et al 2009), Galvanic synthesis (Yang and Hu, 2008) and chemical bath deposition (Soehabi and Ghobadi, 2019). When compared to the techniques mentioned, electrochemical deposition is rapidity, low cost, free from porosity, high purity, easy to control alloy composition and its industrial applications (Grozdanov, 1994). $\text{Cu}_2\text{Se}$ thin films synthesized by chemical methods strongly depend on the growth mechanism (Thirumavalavan et al 2015). By adjusting the initial conditions such as the concentration, the complex agent (pH), and thermal behavior of the solution during the deposition process it is possible to control the stoichiometry, optical transition and other main quantities related to semiconductors (Piryaee et al 2016). Here, besides to the constituent concentration, the role of deposition time in sample preparation on surface structures and crystallinity was also studied. The stoichiometry variations in the depth of the prepared thin film were determined at different deposition times. The significant photocatalytic behavior exhibited by $\text{Cu}_2\text{Se}$ nanostructured thin films were also investigated.
XRD and the three-dimensional (3-D) surface topography related to nanostructured thin films are helpful to characterize the quality of thin film surfaces. Determining surface structure is crucial to control the quality of thin films and engineering the surface behavior for improved optical and electrical properties. Surface topography study of thin films at nanoscale resolution by AFM showing better facilities rather than other microscopic methods (Nguyen-Tri et al 2020) and allows meticulous observations and evaluations of the morphological characteristics of the films. A comprehensive analysis using parameters such as the average roughness, maximum peak to valley height, root mean square roughness, surface skewness, and surface kurtosis was made to study the Cu$_2$Se thin films surface properties. These parameters give more insight into the surface quality and properties.

The accurate band gap energy determination method is important for predicting the photochemical and photophysical behaviors of semiconductors. Commonly, the Tauc model are used for determining the band gap energy of semiconductors (Tauc et al 1966). Misusing the optical absorption spectra in Tauc plot may lead to inaccurate band gap estimation (Makula et al 2018). The exponential part of the absorption coefficient curve on the photon energy, near the optical band edge, called Urbach tail, is used to estimate the energy gap width (Belahssen et al 2015, Fedyunin and Spassky 2020). Urbach energy characterizes the optical absorption in the material which leads to an extension of the density of states in the band tails (Kranjčec et al 2009, Tanaka, 2014).

In this study, the Urbach energy is used to indicate the degree of crystalline structure on the electronic transitions on Cu$_2$Se thin films and thus we introduced a new approach to calculate the Urbach energy avoiding any need to determine the film thickness.

Quantitative elemental depth profiling analysis of thin films has a great importance for functional materials, including the very large and active field of nanomaterials. RBS is the most frequently used ion beam analysis technique to determine the elemental depth profiles non-destructively from the surface of materials in the range of light ions penetration with few MeV energies. Basically, the energy of the elastic backscattered ions depends on the mass of the atomic target through the kinematic factor relation and on the depth of ion penetration where the scattering occurs through the energy loss (stopping power) before and after the scattering. This leads to the elemental depth profiling besides to the stoichiometry of the sample close to the surface (Jeynes and Colaux 2016).

### 2. Sample preparation

Thin films of Cu$_2$Se were deposited on the glass substrates by using simple and low-cost chemical bath deposition technique. At first, the glass substrates were immersed in water and methanol and then were cleaned. To provide the Cu$^{2+}$ ions for the chemical bath solution used in preparing the copper selenide thin films Copper acetate (Cu(NO$_3$)$_2$) with various concentrations (table 1) were poured in a beaker, then liquid NH$_3$ was added by drops to this solution. At this step, the solution is cloudy which specifies the formation of Cu(OH)$_2$ while by addition the more amount of ammonia the solution turns into bright color which indicated the formation of [Cu(NH$_3$)$_4$]$^{2+}$ complex. The Sodium selenosulfide (Na$_2$SeSO$_3$), the source of the Se$^{2-}$ ions, with different concentrations (table 1) was gradually added to the Cu complex solution. The reaction mechanism involved in the Cu$_2$Se deposition to provide Cu$^{+}$ and Se$^{2-}$ ions is as follows:

| Se (mol) | Cu (mol) | Deposition time (h) | The First transition (eV) | The Second transition (eV) | Urbach energy (eV) |
|---------|----------|---------------------|---------------------------|---------------------------|-------------------|
| 0.05    | 0.05     | 2                   | 2.92                      | 1.4                       | 0.740             |
| 0.05    | 0.05     | 3                   | 3.46                      | 1.53                      | 0.741             |
| 0.05    | 0.05     | 4                   | 3.32                      | 1.26                      | 1.31              |
| 0.05    | 0.05     | 5                   | 3.22                      | 1.2                       | 1.15              |
| 0.05    | 0.05     | 6                   | 3.12                      | 1.34                      | 0.65              |
| 0.07    | 0.07     | 2                   | 2.91                      | 2.15                      | 0.589             |
| 0.07    | 0.07     | 3                   | 2.86                      | 2.14                      | 0.376             |
| 0.07    | 0.07     | 4                   | 2.92                      | 2.17                      | 0.373             |
| 0.07    | 0.07     | 5                   | —                         | 2.18                      | 0.414             |
| 0.07    | 0.07     | 6                   | —                         | 2.15                      | 0.319             |
| 0.09    | 0.09     | 2                   | 2.76                      | 1.22                      | 0.62              |
| 0.09    | 0.09     | 3                   | 3.37                      | 2.06                      | 0.74              |
| 0.09    | 0.09     | 4                   | 2.08                      | 1.87                      | 0.552             |
| 0.09    | 0.09     | 5                   | —                         | 1.97                      | 0.417             |
| 0.09    | 0.09     | 6                   | —                         | 1.28                      | 0.334             |
The cleaned glass substrates were vertically bolstered to the rim of the solution backer to impose the required pH and the temperature for the sample deposition. Finally, the samples were removed at different time intervals and washed with deionized water. The mass difference before and after the deposition was used to obtain the thin film thicknesses (Ghobadi and Dousi 2014).

The properties of the thin films become size-dependent when the dimensions of the material reach the nanoscale. In this regime, and the process of thin films deposition plays its role to control the different properties including crystallites, band gap energy, structural composition, and morphology.

### 3. Results and discussion

#### 3.1. Crystallinity investigation

The prepared sample have crystallite structure in accordance to the cubic Cu2Se with space group Fm3m. The XRD pattern of the Cu2Se nanostructured thin films is depicted for different initial concentration in figure 1. Two prominent peaks were observed at 2θ values of 26.3° and 43.7° respectively corresponding to (hkl) plane of (111) and (220) are consistent with JCPDS 00-004-0839 reference. By increasing the molar concentration from 0.05 M to 0.07 M another peak is appeared at 2θ = 52° which corresponds to the plane of (311) indication that the thin film is well crystallized at this concentration. According to the Cu2Se reference code of JCPDS 00-004-0839 the other possible peaks have lower intensity which were not resolved in the measured peaks. The average particles size of the prepared samples was calculated from the Scherer equation (Williamson and Hall, 1953)

\[ d = \frac{K\lambda}{\beta \cos \theta} \]

Where \( \beta \) describes the structural broadening peak and is equal to the angular line width at the half-maximum intensity (FWHM) in radians, \( \theta \) is the observed peak angle, \( K \) is the constant shape factor and \( \lambda \) is the Cu-Kα line wavelength. The average particles size were 31.2 nm, 36.8 nm and 38.9 nm and respectively for the constituent concentration of 0.05 mol, 0.07 mol, and 0.09 mol. The increasing of the average particle size is consistent with decreasing in the optical bang gap energy determined from UV-visible measurements. The increase in nanoparticle size is mainly resulted from the quantum confinement effects in nanoparticles in such a way that

![Figure 1. X-Ray diffraction spectrums of Cu2Se thin films at different initial constituent concentration.](image-url)
for small particle sizes the band gap increases due to the additional energy from the degree of confinement and Coulomb correlations in the effective band gap energy term (Sahana et al 2008).

3.2. Surface topography analysis
The surface topography of the nanostructured thin layers (figure 2) was performed by an atomic force microscope using scan rates of 10–20 μm/s. Experimental data extracted from the surface description of the AFM images (according to ISO 25178-2: 2012) for the three samples with different ions concentration as the root-mean-square deviation ($S_q$), the skewness of topography height distribution ($S_{sk}$), the kurtosis of topography height distribution ($S_{ku}$), the maximum peak height ($S_p$), the maximum peak valley ($S_v$), differences between peak height and valley ($S_z$), and the arithmetic mean height ($S_{a}$) from the AFM images are reported in table 2. The $S_{sk} < 0$ is for all samples and shows the dominance of valleys on their surfaces. The highest value was associated with the sample of 0.09 mol concentration ($-0.588$). $S_q$ for sample with 0.09 mol has a highest value of 221 nm and the lowest value of 97 nm for sample 0.05 mol. It was observed that by increasing the initial concentration of the Cu$_2$Se thin films from 0.05 mol to 0.09 mol the roughness parameters except skewness were increased. The roughness parameters indicate that by increasing the molar concentration the larger particles are formed and this leads into the absence of nanostructures on the surface of the substrate. From the skewness parameter, it was deduced that by increasing the constituent concentration the surface histogram distribution became more symmetric around the mean value and can be represented by a Gaussian function. This asymmetry is attributed to the regular distribution of nanoparticles on the surface. Indeed, with increasing the precursor concentration, Cu(OH)$_2$ ions get closer to each other in the nucleation process in the bath and then more

Figure 2. 2D and 3D AFM images of Cu$_2$Se thin films prepared at different initial molar concentration.
Cu(OH)$_2$ ions merge into each other in staking process. In summary, the higher concentration causes higher viscosity and more agglomeration is formed.

### 3.3. Optical Bandgap energy determination

The optical band gap energy, $E_g$, is related to the absorption coefficient, $\alpha$, via this relation

$$\alpha = \frac{A (h\nu - E_g)^n}{\hbar \nu}$$

where $A$ is a constant, $h\nu$ is the photon energy and, $n$ is index transition, takes the value of $\frac{1}{2}$ for direct gap semiconductors, 2 for indirect gap semiconductors (Tauc et al 1966).

From the Tauc model, the optical band gap is determined by taking into account the natural transition of semiconductors. In this way, the data of $(A\alpha(EV))^2$ in terms of $E$ (eV) were plotted in figures 3, 4 and 5 for Cu$_2$Se samples for various concentrations of 0.05, 0.07 and 0.09 mol. The X-intercept gives the band gap energy was calculated with 95% of confidence level and 0.99 of coefficient determination. For all spectra, the transition index was set to $\frac{1}{2}$. The optical spectra of the prepared thin films were recorded by Perkin-Elmer, Lambda 25-USA UV/VIS spectrometer in a wavelength range of 300–1100 nm for different sample concentrations.

By increasing the initial concentration, the optical band gap was decreased from 2.92 eV to 2.08 eV for the first transition and from 2.18 to 1.2 eV for the second transition. The more number of the nucleus are found in the solution, the more tiny composed colloids are formed in the nucleation process (Thanh et al 2014). In fact, the large amount of Cu$^{2+}$ ions producing as an electron acceptor and Se$^{2-}$ ions releasing as an electron donor increases the particle growth probability in the Cu$_2$Se deposition mechanism.

### 3.4. Urbach energy estimation

There is a relation between the absorption coefficient with energy spectra and Urbach energy as (Tauc et al 1966)

$$\alpha(E, T) = \alpha_0 \exp\left(\frac{E - E_U}{E_U(T)}\right)$$

$E_U$, the Urbach energy, is an exponential part in the energy spectrum of the absorption coefficient which appears near the optical band edge in amorphous, disordered and crystalline materials. (Kranjič et al 2009). The purpose of this section is to prove that it is possible to determine the Urbach energy of the samples from the absorption spectrum without the need to determine the adsorption coefficient from the determination of thickness. The absorption coefficient is defined by Beer–Lambert’s law as (Tkachenko 2006),

$$\alpha = \frac{2.303 \times A}{t}$$

where $t$ and $A$ are the film thickness and film absorbance, respectively. By equivalating equations (3) and (4) we have

$$\frac{2.303 A(\lambda)}{t} = \alpha_0 \exp\left(\frac{E - E_0}{E_U(T)}\right)$$

The logarithm form of the above equation, by choosing $A_0 = -\frac{E_0}{E_U(T)}$, is

$$Ln[A(\lambda)] = \frac{E}{E_U(T)} + A_0$$

Thus, the Urbach energy is the inverse of the slope of the linear part of the Ln (A) versus E (eV). These data are separately plotted in figure 6 and the results of the Urbach energy calculations have been shown in table 1. We must consider the types of transitions in nanostructure semiconductors, transitions between extended and extended states, tail and extended states, and tail and tail states. Urbach energy for samples synthesized with 0.05 mol concentration was higher than other concentrations because the particle size is low in 0.05 mol concentration due to quantum confinement and surface effects of atoms.

| Table 2. Height parameters of AFM surface topography. |
|--------------------------------------------------------|
| Mol. | Sq (nm) | Skk | Sku | Sp (nm) | Sv (nm) | Sz (nm) | Sa (nm) |
|------|---------|-----|-----|---------|---------|---------|---------|
| 0.05 | 97      | -0.241 | 2.45 | 241     | 263     | 504     | 79.3    |
| 0.07 | 153      | -0.109 | 2.4  | 377     | 467     | 843     | 129     |
| 0.09 | 221      | -0.588 | 3.67 | 480     | 829     | 1310    | 172     |
3.5. Depth profiling and stoichiometry analysis by RBS

For measuring high-resolution Cu2Se thin film depth profiles, the non-destructive nuclear analysis technique RBS was performed at Van de Graaff accelerator at Tehran (Kakuee et al 2016). In the experiment, the ion beam energy was adjusted at 2 MeV to provide a high depth resolution at surface and a large depth of analysis of at least 1 μm. A silicon surface barrier detector was placed at the backscattering angle of 165°. An RBS spectrum can be fully calculated using known physical parameters such as ion type, ion energy, backscattering angle, collected charge, beam current and extra (Jose Chirayil et al 2017). Cu2Se depth profiles were extracted from the experimental spectra with SIMNRA software (Mayer, 2014) by unfolding by means of an iterative simulation process.

Figure 7 shows the experimental, simulated spectrum and the correspondence depth profiling of the areal density concentration of Cu2Se thin film deposited on the glass substrate for different deposition times of 3, 4, and 5 h. The deviation between experiment and simulated spectra at low energies is due to plural scattering.
where more than one scattering event occurs for backscattered particles at a large scattering angle. As it can be seen at the deposition time of 3 h, Cu and Se front interface signals appear respectively at backscattered energies of 1560 keV and 1640 keV and are well resolved from each other. A distinct region between the Cu rear interface with lower energies indicates that the deposited film is a homogeneous mixture of constituents. The depth profile at this deposition time reveals that the film thickness is low enough at areal density of $400 \times 10^{15}$ atom/cm² to be discriminated from the substrate. At deposition time of 4 h, Cu and Se peaks overlap with each other. The corresponding concentration varies with depth and the formed film is thicker than 3 h deposition time since by passing the deposition time the more content of Cu and Se are synthesized. By increasing the deposition time to 5 h, thicker Cu and Se layers would shift the Se peak to the left until there is no distinct region between their peaks. The stoichiometry of Cu and Se remains approximately constant in-depth (Cu = 2: Se = 1) of the synthesized film until the areal density of $1000 \times 10^{15}$ (atom/cm²).
3.6. Photo-catalytic activity measurement

The photocatalytic behavior of Cu$_2$Se nanostructured thin films was performed by aqueous Congo Red (CR) solution under the irradiation of sunlight. To this aim, Cu$_2$Se nanostructured thin film was dipped in aqueous CR solution. At given irradiation times of 60, 90, 120 and 150 min, thin films were taken out from the solution and they were measured by UV–visible spectrophotometer while DI water was used as the reference (Sohrabi and Ghobadi 2019). The mechanism of these reaction can be expressed as follows:

\[
\text{hv} + \text{Cu}_2\text{Se} \rightarrow \text{Cu}_2\text{Se}(h^+ + e^-) \tag{7}
\]

\[
\text{Cu}_2\text{Se}(e^-) + \text{O}_2 \rightarrow \text{O}_2^- \tag{8}
\]

\[
\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot\text{OH} \tag{9}
\]

\[
\text{CR}^* + \cdot\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{10}
\]

Figure 5. Absorbance and optical band gap determination for samples with 0.09 mol concentration and different deposition times.
In semiconductor photocatalytic reaction, sunlight is mainly used to generate electron ($e^-$) and hole ($h^+$) pairs. Electrons in the valence band (VB) are excited to the conduction band (CB) leaving holes in the valence band (equation (7)). The electrons in the conduction band release radical ions ($O_2^-$) (equation (8)) and the holes in the valence band produce (OH) radicals (equation (9)). The OH then reacted with the CR molecules to convert them into CO2 and H2O (equation (10)).

The intensity of the CR characteristic band at 500 nm (I500: the main absorption band of CR in the obtained UV–Vis spectrum was used to determine the absorption of CR in the solution ($A_t$). The degradation rate of CR, which indicates the photo-catalytic efficiency of the photocatalyst nanoparticles, was calculated through this relation (Koozegar Kaleji et al 2018).

$$\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100$$ (11)

Where $\eta$ is degradation rate, $A_t$ is absorption after radiation at time $t$, and $A_0$ is absorption before radiation. It was observed that the sample with 4 h deposition times deposited at 0.07 mol concentration degrade the dye pollutant in a short time rather than other samples with deposition times (figure 8). The three samples with different deposition times of 3, 4, and 5 h, the height of the characteristic absorption peak of CR is decreased with the increase of irradiation time, and the CR pollutant tends to colorless. After passing 150 min of irradiation, the
percentage of CR degradation efficiency for different deposition times reaches to 91.5%, for 3 h, 98.1% for 4 h and 88% for 5 h. Thus, CR degradation efficiency indicates that sample with 4 h deposition times has an optimal state for CR degradation. The same degradation efficiency is obtained for Cu$_2$Se synthesized by alkaline hydrothermal method at longer treating time of 6 h sample preparation (Yang et al 2021a). In this work the degradation efficiency of 98.1% was obtained after 1.5 h irradiation time for Cu$_2$Se compared with the photocatalytic activity of Cu-Se based photocatalysts, 74% for Cu$_2$Se after 1.36 h (Wang et al 2017), 76% for pure CuSe after 1.5 h (Kaviyarasu et al 2016), 96% for ZnSe after 1 h (Hsieh et al 2015) and 90.89% for ZnSe doping with ZnO after 3h (Ehsan et al 2018), it could be found that the as-prepared Cu$_2$Se had the highest photocatalytic activity for degradation.

**Figure 7.** The RBS spectra and depth profile concentration are plot at left and right of the for different deposition times at 0.07 M sample preparation.
4. Conclusions

Through this study, Cu$_2$Se nanostructured thin films were prepared using the chemical solution deposition method. We were able to control the initial condition of the composed material during the precipitation stage to improve the growth conditions of nanoparticles to a favorable optical band gap. The deposition conditions were optimized for Cu$_2$Se thin films to exhibit a good surface roughness. The Urbach energy of the samples was successfully determined from the absorption spectrum without prerequired the adsorption coefficient. From the analysis of Rutherford backscattering spectroscopy, it was identified that the concentration of Cu:Se approximately remains constant at higher deposition time across the depth of the deposited film. It was concluded that the extra constituent concentration, increases the Cu$^{2+}$ and Se$^{2-}$ ions, leads to control the growing process and the film thickness to enhance the photocatalytic activity. The degradation efficiency percentage of Congored for the Cu$_2$Se nanostructured thin films was attained 98.1% which can potentially be used as an effective photocatalyst for degradation of organic dyes.

Figure 8. Photo-catalytic decomposition profile of Congo Red (left) and Photo-catalytic degradation (right) after 150 min visible irradiation for 3, 4 and 5 h deposition times in (a), (b) and (c).
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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