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## Optical Properties of CuSe Thin Films – Band Gap Determination

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### Abstract:

Copper selenide thin films of three different thicknesses have been prepared by vacuum evaporation method on a glass substrate at room temperature. The optical properties of the films were investigated by UV–VIS–NIR spectroscopy and photoluminescence spectroscopy. Surface morphology was investigated by field-emission scanning electron microscopy. Copper selenide exhibits both direct and indirect transitions. The band gap for direct transition is found to be  $\sim 2.7$  eV and that for indirect transition it is  $\sim 1.70$  eV. Photoluminescence spectra of copper selenide thin films have also been analyzed, which show emission peaks at 530, 550, and 760 nm. The latter corresponds to indirect transition in investigated material.

**Keywords:** Copper selenide; Thin films; Semiconductors; UV–VIS–NIR spectroscopy; Photoluminescence spectroscopy.

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## 1. Introduction

Copper selenides are interesting metal chalcogenide semiconductor materials. They exist in many phases and structural forms: different stoichiometry such as CuSe (klockmannite),  $\text{Cu}_2\text{Se}_x$ ,  $\text{CuSe}_2$  (marcasite),  $\alpha$  -  $\text{Cu}_2\text{Se}$  (bellidoite),  $\text{Cu}_3\text{Se}_2$  (umagnite),  $\text{Cu}_5\text{Se}_4$  (athabaskite),  $\text{Cu}_7\text{Se}_4$  etc., as well with non-stoichiometric form such as  $\text{Cu}_{2-x}\text{Se}$  (berzelianite), and can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc.). Their color ranges from blue black to bluish green depending on the type of stoichiometric composition. Special constitutions of these compositions make copper selenide an ideal candidate for scientific research.

Copper selenide is a semiconductor with p-type conductivity. It has both direct and indirect transitions so the presence of both band gaps, direct and indirect, is observed. The band gap of copper selenide is not well defined. Literature data are quite controversial: direct allowed transitions are reported to have corresponding band gap in the range of 2 to 3 eV, and indirect band gap between 1.1 and 1.5 eV [1-4]. The indirect band gap being near the optimum value for solar cell applications makes this material capable to potentially offer a high efficiency of conversion. However, copper selenide nanoparticles have been reported to

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possess a direct band gap of 4 eV [5] and indirect one of 1.87 eV. The reasons of such variation in band gaps could lie in the sharp cut off of the wavelength with the spectral transmittance instead of the slow increase, the presence of large number of dislocations, wide range of stoichiometric deviation and quantum confinement effect.

Copper chalcogenide thin films have numerous applications in various devices such as solar cells [6-8], photodetectors [9], optical filters [10], microwave shielding [11], thermoelectric converters [12]. Photovoltaic cells and Schottky diodes are associated with these metal chalcogenide compound [13, 14]. Copper selenide is a precursor material of  $\text{CuInSe}_2$ , used for highly efficient photovoltaic elements [15]. Also,  $\text{CuSe}_2$  is served as a typical anion conductor and significant Cu-Se alloys targets for the preparation of CIGS/CIS thin film solar cells in RF magnetic sputtering [16].

A number of methods have been reported for the deposition of thin films of different crystalline modifications and varying stoichiometries such as an electrodeposition [17], selenisation [18], vacuum evaporation [19], solid state reaction [20], and chemical bath deposition [21].

In this paper, we report the preparation of CuSe thin films deposited onto glass substrate using vacuum evaporation technique at room temperature and their characterization through FESEM, UV-VIS-NIR and photoluminescence spectroscopy.

## 2. Experimental

The vacuum evaporation technique was used to deposit thin films of copper selenide onto glass substrate. Copper selenide alloy of high purity (99.99 %) was purchased from Aldrich Company. With use of a Mo boat, the powder was deposited onto highly pre-cleaned glass substrates at vacuum  $\sim 3$  mPa at room temperature, with use of conventional coating unit-Edwards, E-306 A. During the evaporation of CuSe thin films, the rate of deposition was kept constant  $\sim 10$  nm/s. The film thickness was controlled with use of a quartz crystal thickness monitor - FTM4, Edwards. Films of three different thicknesses: 56 nm ( $\text{CuSe}_1$ ), 79 nm ( $\text{CuSe}_2$ ), and 172 nm ( $\text{CuSe}_3$ ) were obtained by deposition onto glass substrates.

Field-emission scanning electron microscopy (FESEM) images were obtained for CuSe thin films deposited on glass substrate in order to study the surface morphology of the thin films. A Jeol JSM-7600F with a Schottky-type emitter was used at an accelerating voltage of 1.5 kV.

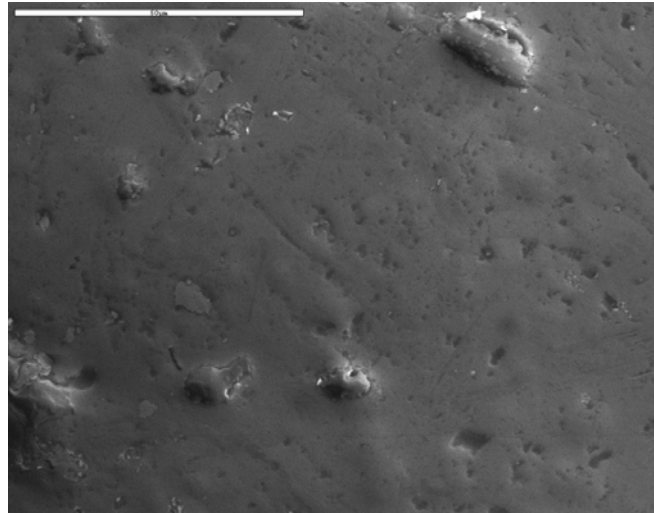
The UV-VIS-NIR diffuse reflectance and transmittance spectra were recorded in the wavelength range of 300 – 1000 nm on a Shimadzu UV-2600 spectrophotometer equipped with an integrated sphere. The diffuse reflectance and transmittance spectra were measured relative to a reference sample of  $\text{BaSO}_4$ .

Photoluminescence emission measurements were obtained using Jobin-Yvon U1000 spectrometer, equipped with RCA-C31034A photomultiplier with housing cooled by Peltier element, amplifiers and counters. As an excitation source we used the 488 nm laser line of Argon laser.

## 3. Results and discussion

### 3.1. FESEM

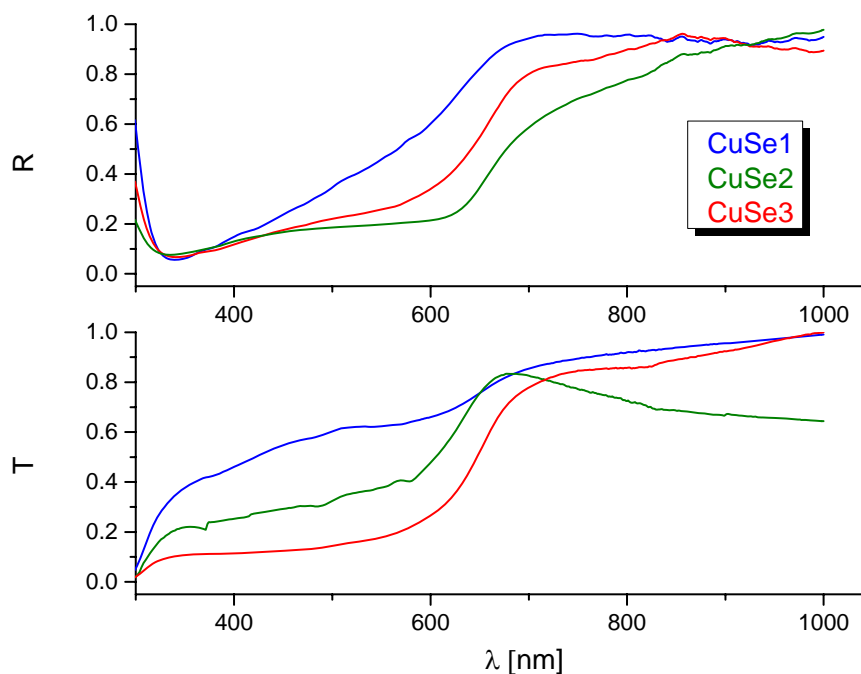
Fig. 1 shows representative FESEM image of sample  $\text{CuSe}_2$  at room temperature and images of two other films are similar. As we may observe, film is packed and continuous without the presence of porosity or voids. The surface is rather smooth with no cracking observed.



**Fig. 1.** Top view micrograph of CuSe<sub>2</sub> thin film at room temperature using SEM.

### 3.2. UV–VIS–NIR spectroscopy

In Fig. 2. diffuse reflectance (R) and transmittance (T) spectra of our thin films samples in the wavelength range 200–1000 nm are presented. As we can see, the transmittance increases with decrease in the film thickness, which is not the case for reflectance. This is typical for films with high electrical conductivity and implies a reflection coefficient nearing 1 for films of metallic conductivity.



**Fig. 2.** Diffuse reflectance and transmittance spectra.

In this study we used Tauc plot for the determination of optical band gap from diffuse reflectance measurements. The determination of band gap in semiconductors is significant for obtaining the basic solid state physics. The relation expression proposed by Tauc, Davis and

Mott [22-24] is following:

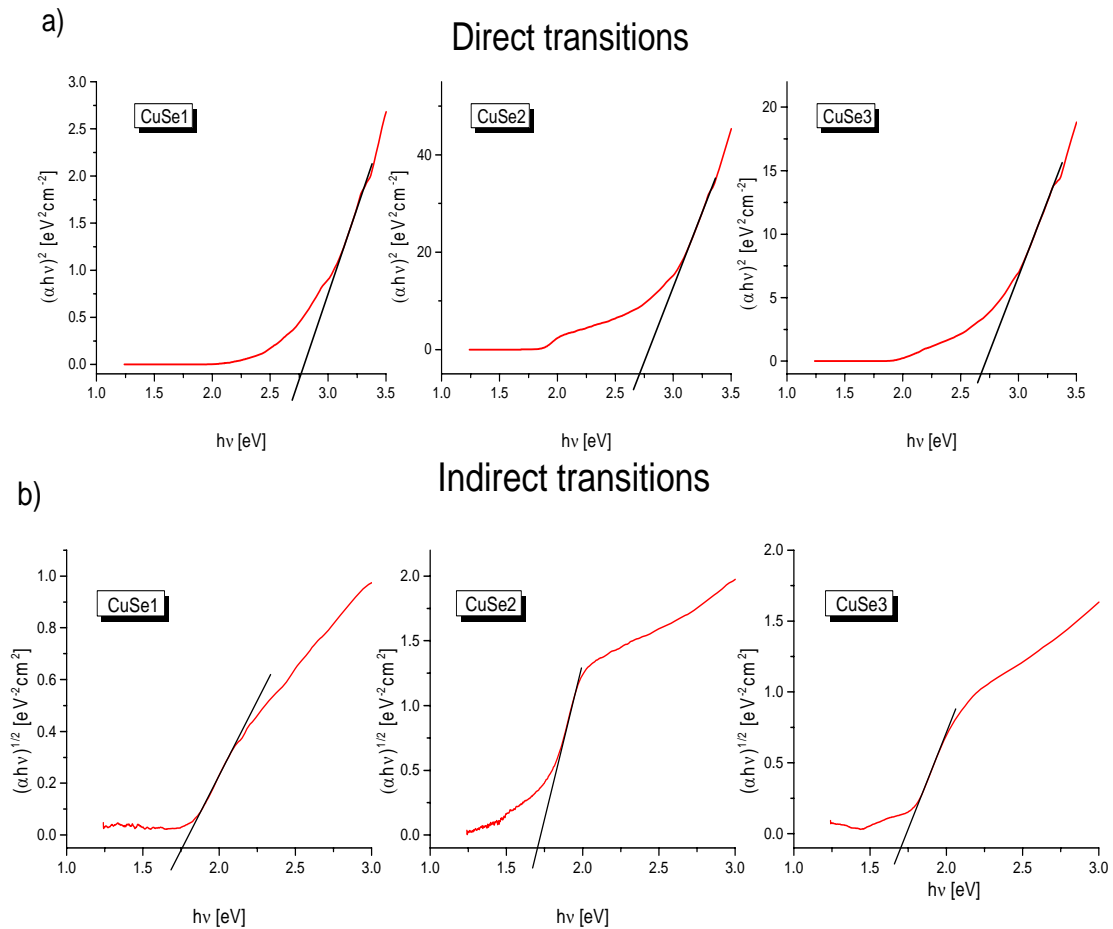
$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{n}} \quad (1)$$

where  $h$  is a Planck's constant,  $A$  is the transition probability constant depending on the effective mass of the charge carriers in the material,  $E_g$  is the band gap,  $h\nu$  is the photon energy and  $\alpha$  is absorption coefficient which is defined as the relative rate of decrease in light intensity along its propagation path, i.e. a property of a material that defines the amount of light absorbed by it. The value of  $n$  denotes the nature of the transition. In case of direct transitions  $n$  equals  $1/2$  and  $3/2$  for allowed and forbidden transitions, respectively. As for indirect transitions,  $n$  equals  $2$  and  $3$  for allowed and forbidden transitions, respectively. Since CuSe exhibits both direct and indirect allowed transitions,  $n = 1/2$  and  $n = 2$ .

Then, the acquired diffuse reflectance spectra are converted to Kubelka–Munk function [25]:

$$\alpha = \frac{(1-R)^2}{2R} \quad (2)$$

So using this function, a plot of  $(\alpha h\nu)^{1/n}$  against  $h\nu$  is obtained. The energy band gap is determined by extrapolating the linear portion of  $(\alpha h\nu)^{1/n}$  vs.  $h\nu$  to the energy axis at  $(\alpha h\nu)^{1/n} = 0$ . The intercept of these plots on the energy axis gives the energy band gap. Such plots are given in Fig. 3a) – direct transitions and Fig. 3b) – indirect transitions.



**Fig. 3.** a) Dependence of the  $(\alpha h\nu)^2$  of the photon energy ( $h\nu$ ), b) Dependence of the  $(\alpha h\nu)^{1/2}$  of the photon energy ( $h\nu$ ).

**Tab. I** The estimated band gap energies of CuSe thin films.

	CuSe1	CuSe2	CuSe3
Direct transition (eV)	2.77	2.71	2.69
Indirect transition (eV)	1.75	1.70	1.70

The experimentally determined values of energy gaps for CuSe thin films slightly differ from each other on second decimal place, their values range from 2.69 to 2.77 eV for direct transitions, and from 1.70 to 1.75 eV in the case of indirect transitions. The estimated band gap positions of each sample are given in Table I. It seems that despite the difference in film thicknesses, their optical properties such as band gap energies are quite similar.

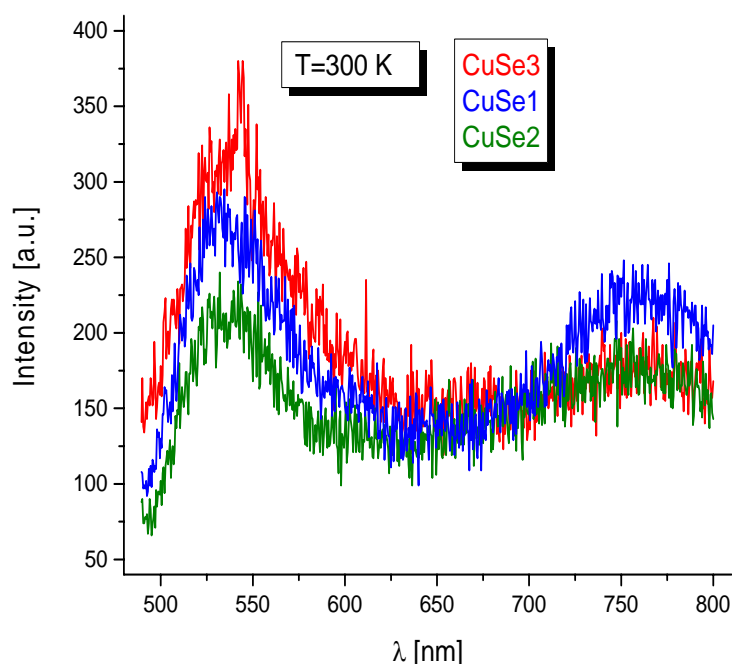
References report a large range of energy band gap values for CuSe. For direct transitions that values usually go between 2 and 3 eV. R. Bari et al. [26] obtained the value of 2.51 eV for the sample thickness of 150 nm, and with the increase of film thickness they reported the decrease of band gap width. I. Grozdanov [27], V. Garcia et al. [2] and G. B. Sakr et al. [28] obtained the value of 2.33, 2.13–2.38 and 2.74 eV, respectively. The latter is very similar to the results obtained in this paper. D. Rajesh et al. [29] got a diversity of band gaps ranging from 1.95 (the thickest film) to 3.70 eV (the thinnest film). As for indirect transitions, they received less attention. In [2] the obtained values are 1.22–1.34 eV, whereas in [12] the value is about 1.4 eV. The values we obtained, ~1.7 eV, are bigger than reported in literature. In our opinion, the larger indirect band gap values are due to quantum confinement effect [30, 31] whereby the electrons are localized in individual crystallites.

### 3.3. Photoluminescence spectroscopy

Photoluminescence emission spectra can be used for investigation of the possible outcomes of photoinduced electrons and holes in a semiconductor, since photoluminescence emission results from the recombination of free charge carriers. A semiconductor is characterized with the electronic band structure and its main features – the valence band or the highest occupied molecular orbital (HOMO) and the conduction band or the lowest unoccupied molecular orbital (LUMO). The difference between the valence band and the conduction band in the means of energy is called band gap ( $E_g$ ). We talk about two types of photoluminescence phenomenon according to its attributes and formation mechanism: the band-to-band photoluminescence and the excitonic photoluminescence [32-34]. The band-to-band PL spectrum regards the separation situation of photogenerated charge carriers. The excitonic PL spectrum, however, cannot directly reflect the separation situation of photoinduced carriers. If discrete energy levels are present in the band gap, these may dominate the optical spectrum. PL measurements then yield information about the energetic positions of the electronic states in the gap. Such localized states can originate from various types of imperfections like vacancies, interstitial atoms, atoms at surfaces and grain boundaries. However, it is often difficult to determine the exact position and origin of these states.

Photoluminescence spectra of CuSe thin films of three different thicknesses at room temperature are presented in Fig. 4. In all spectra, the band in the red spectral region, positioned at about 760 nm (1.63 eV), is clearly seen. According to the UV-VIS results (see previous chapter), we can attribute this PL peak to indirect band-to-band transition for indirect transition in CuSe. Since the excitation energy (488 nm = 2.54 eV) is lower than the energy for direct transitions (460 nm = 2.7 eV), peak that corresponds to direct transitions cannot be observed. In green area, a broad band is observed which consists of two peaks, at

about 530 nm and about 550 nm. These localized states must originate from native defects of Se or Cu.



**Fig. 4.** Photoluminescence emission spectra of CuSe thin films at room temperature.

#### 4. Conclusions

CuSe thin films of three different thicknesses, obtained by vacuum evaporation technique on glass substrate, underwent through photoluminescence investigation along with UV–VIS–NIR measurements and FESEM analysis. Reflectance measurements revealed values for both direct and indirect band gap:  $\sim 2.7$  and  $1.7$  eV, respectively. The existence of indirect band gap on this value, somehow wider than in literature, is confirmed by photoluminescence measurements. Presence of localized states between the direct and indirect band gap is discovered from luminescence measurements. In this paper we proved that simple and low cost technique as vacuum evaporation is capable of producing high quality thin films.

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**Садржај:** Танки филмови бакар селенида три различите дебљине добијени су техником вакуумског напаравања на супстрат од стакла на собној температури. Оптичке особине филмова испитиване су методама UV-VIS-NIR и фотолуминесцентне спектроскопије. Морфологија површине испитивана је методом

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скенирајуће електронске микроскопије са ефектом поља. У бакар селениду се догађају и директни и индиректни прелази. Измерена забрањена зона која одговара директним прелазима је  $\sim 2.7$  eV, док је забрањена зона која одговара индиректним прелазима  $\sim 1.70$  eV. Анализирани су и спектри фотолуминесценције танких филмова бакар селенида, и уочени су пикови на 530, 550 и 760 nm. Последњепоменути пик одговара индиректним прелазима у изучаваном материјалу.

**Кључне речи:** Бакар селенид; Танки филмови; Полупроводници; UV–VIS–NIR спектроскопија; Фотолуминесцентна спектроскопија.

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