

## Effect of thermal processing on optical and electrical properties of copper selenide thin films

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We report on the structural, optical and electrical properties of thin films of copper selenide obtained from chemical bath deposition and the changes brought about in these properties during thermal treatment at 200°C – 400°C in air and vacuum. CuSe thin films deposited using N,N-dimethylselenourea transform to Cu<sub>2-x</sub>Se during vacuum annealing at 400°C, whereas, the composition of chemically deposited Cu<sub>1.85</sub>Se films obtained using sodium selenosulfate remains practically stable during such annealing. The high near infrared reflectance (30-80%) and low transmittance of the films are related to a high p-type electrical conductivity ~ (1.5) × 10<sup>3</sup> W<sup>-1</sup>cm<sup>-1</sup> of these films. A theoretical analysis of experimental transmittance and reflectance curves is made, based on free carrier optical absorption. Thermal processing of Cu<sub>2-x</sub>Se-In and CuSe-In films, with vacuum evaporated In film (20 – 40 nm) results in partial conversion of the films to Cu<sub>x</sub>In<sub>y</sub>Se<sub>z</sub>. Applications of the films in automotive window coatings and photovoltaic conversion are suggested.

*Keywords:* Chemical bath deposition, copper selenide films

### 1. Introduction

Copper selenide has been studied with great interest during the past decades because of its potential application in the fabrication of photovoltaic devices. It has many phases and structural forms: stoichiometric  $\alpha$ -Cu<sub>2</sub>Se, Cu<sub>3</sub>Se<sub>2</sub>, CuSe, and CuSe<sub>2</sub>, as well as non-stoichiometric, Cu<sub>2-x</sub>Se. The thermal stability of these compounds varies depending on the composition. CuSe is reported as hexagonal at room temperature and undergoes transition to orthorhombic at 48°C and back to hexagonal at 120°C [1]. At still higher temperatures, CuSe decomposes into Cu<sub>2-x</sub>Se and selenium. A face centered cubic structure is reported for Cu<sub>2-x</sub>Se with 0.15 ≤ x ≤ 0.2 at room temperature, and eventually it will reach the tetragonal structure of Cu<sub>2</sub>Se phase. Copper selenide is a semiconductor with p-type conductivity, property useful in the solar cell production. Cu<sub>2-x</sub>Se is reported to possess a direct band gap of 2.2 eV and an indirect band gap of 1.4 eV for x = 0.2 [2]. The indirect band gap being near the optimum value for solar cell applications [3], the material could offer a high efficiency of conversion. The use of these films to form a junction with n-type semiconductors either as absorber in heterojunction with CdS or as window material in heterojunction with n-Si has been demonstrated [2,4-6], showing conversion efficiencies of up to 8.8%. This is the main motivation to study copper selenide thin films.

Thin films of copper selenide can be obtained by a variety of techniques like vacuum evaporation [2,4-6], melting of Cu and Se [7-10], electrodeposition [11,12] and chemical bath deposition (CBD) [13-19]. The perspectives of the CBD technique to obtain thin films of metal sulfides and selenides for solar energy applications developed at the Department of Solar Energy Materials has been reviewed in a previous paper [20]. The composition of the chemically deposited thin films using selenosulfate as the source of

selenide ions has been reported as CuSe in [14,15], and as Cu<sub>2-x</sub>Se in [16]. The films obtained using N,N-dimethylselenourea as the source of selenide ions are reported to be of CuSe composition [17]. There has also been a report that depending on the selenosulfate to copper ratio in the bath either Cu<sub>2</sub>Se or CuSe may be obtained [18].

In this work we used sodium selenosulfate and N,N-dimethylselenourea (DMSU) as sources of Se<sup>2-</sup> ions, to prepare copper selenide thin films by CBD. The results of structural, optical and electrical studies on these films are discussed. X-ray diffraction studies confirm that films produced from the selenosulfate bath are of Cu<sub>2-x</sub>Se composition, even though the precipitate may have a mixed composition Cu<sub>3</sub>Se<sub>2</sub>/Cu<sub>2-x</sub>Se. The films produced from dimethylselenourea bath are CuSe. Upon annealing at 400°C, they become Cu<sub>2-x</sub>Se. The optical absorption in the films is interpreted in terms of free carrier absorption in the near infrared and band-to-band transitions in the visible-ultraviolet region.

The clarification of the structure, composition, optical and electrical properties and thermal stability of chemically deposited Cu<sub>x</sub>Se thin films is important in the context of its use as a precursor material for forming CuInSe<sub>2</sub> thin films, and other multinary materials for thin film solar cell application.

Current research efforts are directed towards identifying a low-cost deposition technique for a precursor material from which solar cell grade CuInSe<sub>2</sub> can be produced. In recent results, Cu-In-Ga-Se mixture produced by electrodeposition has been subjected to chemical and thermal processing at 550°C in a four-source physical vapor deposition chamber to produce solar cells with conversion efficiencies of 13.7% [21]. Here it has been considered that the CuSe phase melts at temperature above 500°C, which along with the elements made available would lead to the

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formation of ternary and quaternary compounds with improved grain size due to re-crystallization at the elevated temperature. It is therefore apparent that CuSe/Cu<sub>x</sub>Se/CuSe(S) obtained by multiple dip chemical bath deposition technique along with physical vapor deposition technique and simultaneous or subsequent thermal processing could result in alternative solar cell absorber materials as suggested by us recently [20].

## 2. Experimental details

### a) Materials Employed

The Se<sup>2-</sup> sources, sodium selenosulfate and N,N-dimethylselenourea were prepared in our laboratory. Sodium selenosulfate solution was prepared by refluxing 100 ml of 1 M sodium sulfite and 4 g of selenium powder (from Aldrich chemicals) for about 2 h. The N,N-dimethylselenourea preparation was made following the reported method [17]. We also used copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and 30% NH<sub>3</sub>(aq.) of Baker Analyzed Reagent grade, copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), sodium tartrate (Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·2H<sub>2</sub>O), and anhydrous sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) of analytical reagent quality from Productos Químicos Monterrey. As substrates, Corning glass microscope glass slides of 76 mm x 26 mm x 1 mm were used, which were previously cleaned well using detergent and water and dried prior to the film deposition process.

### b) Chemical Bath Composition

Three different bath compositions were used to deposit the copper selenide thin films, by mixing the chemical solution specified for each bath.

*Bath S:* 10 ml of 0.5 M CuSO<sub>4</sub>·5H<sub>2</sub>O, 1.5 ml of 30% NH<sub>3</sub>(aq.) (~15 M), 30 ml of a freshly prepared solution of ~0.18 M Na<sub>2</sub>SeSO<sub>3</sub> and the rest distilled water to take the volume to 100 ml.

*Bath M:* 3.5 ml of 0.5 M CuCl<sub>2</sub>·2H<sub>2</sub>O, 20 ml of 0.8 M of sodium tartrate (Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·2H<sub>2</sub>O), 20 ml of 0.07 M N,N-dimethylselenourea (freshly prepared), and distilled water to take the volume to 100 ml.

### c) Film deposition

The glass substrates were placed vertically immersed in the deposition baths, supported against the wall of the beaker. The film deposition was carried out at room temperature for the bath S, and at 50°C for the bath M, for different durations, 1 to 12 h. At the end of each deposition, the substrates with copper selenide films were taken out of the bath, washed with distilled water and dried. The films obtained were specularly reflecting and compact, free from powdery deposit.

### d) Characterization of the films

Thickness of the films was obtained using an Alpha Step 100 (Tencor Instruments, CA). X-ray diffraction patterns were recorded on a Siemens D500 diffractometer with Cu-K $\alpha$  radiation. The optical transmittance and near normal specular reflectance of the films were recorded using a UV-VIS-NIR Shimadzu UV-3101 PC spectrophotometer, for film side incidence, with air and a

front aluminized mirror as references, respectively. To study the electrical properties, pairs of silver-paint electrodes of 5 mm length at 5 mm separation were printed on the surface of the film. A Keithley 230 programmable voltage source and a Keithley 619 electrometer were used for the measurement. The bias applied was 0.01 V.

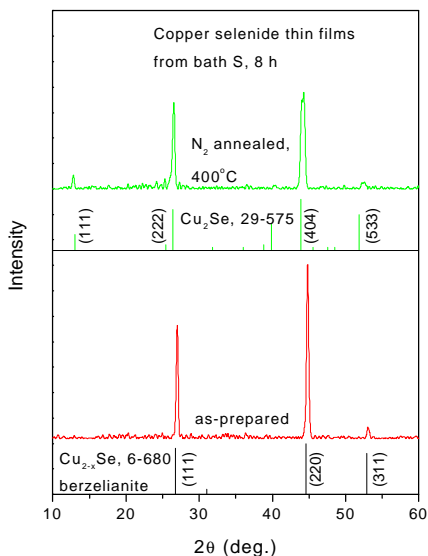
## 3. Results and discussion

Thin film formation in chemical bath deposition is well known; it is described by means of ion-by-ion condensation process at the surface of the substrate [22]. The specific case of deposition process of Cu<sub>x</sub>Se thin films was described in a previously paper [19]. The thickness of the films deposited from the bath S was 0.08  $\mu$ m, 0.10  $\mu$ m and 0.13  $\mu$ m, obtained after 4 h, 6 h and 8 h, respectively. For films obtained from bath M, the thickness varied from 0.09  $\mu$ m to 0.14  $\mu$ m for duration of deposition varying from 2 h to 12 h.

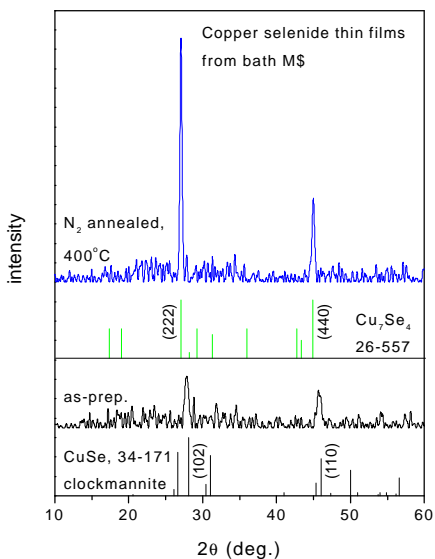
### a). Structural characterization of the films

Fig. 1 shows typical XRD patterns of the as-prepared (0.13  $\mu$ m) and N<sub>2</sub> annealed (50 mtorr, 1 h, 400°C) samples obtained from bath S. The patterns show well-defined peaks suggesting that the films are crystalline. A comparison of the observed peaks with the standard JCPDS cards show that the as prepared samples possess a structure matching the mineral berzelianite (JCPDS 6-680), Cu<sub>2-x</sub>Se with x = 0.15 which belongs to the cubic system with a = 0.5739 nm. The observed peak positions are in agreement with those due to reflections from (111), (220) and (311) planes of the reported structure. As the annealing temperature increases the orientation of the crystallites is more randomized than in the as prepared film. The composition or structure does not change due to annealing at temperatures up to 300°C [19]. In the pattern of the film annealed in nitrogen at 400°C, we observe a new peak at  $2\theta = 13.036^\circ$  ( $d = 6.89 \text{ \AA}$ ) along with broadening of peaks near  $2\theta = 26^\circ, 45^\circ,$  and  $54^\circ$ . With the presence of the additional peak at  $2\theta = 13.036^\circ$ , this pattern matches the standard pattern of stoichiometric Cu<sub>2</sub>Se called bellidoite (JCPDS 29-575). However, the presence of Cu<sub>2-x</sub>Se cannot be ruled out since the last three peaks of bellidoite are in common with those reported in the standard pattern of berzelianite. This leads to the conclusion that upon annealing in nitrogen at 400°C, a part of Cu<sub>2-x</sub>Se film loses Se and becomes stoichiometric Cu<sub>2</sub>Se. The crystallite grain size in the films was calculated using the Scherrer formula [19, 23] and information from the peaks at  $2\theta = 26.77^\circ$  (111) and  $2\theta = 44.7^\circ$  (220) for the Cu<sub>2-x</sub>Se thin films of Fig. 1 (as prepared, and nitrogen annealed at 400°C). The calculation indicates an average grain diameter of 20 nm in the as prepared film, which remains around this value in the annealed sample, due to Cu<sub>2-x</sub>Se to Cu<sub>2</sub>Se partial transformation, although the analysis of the peak at  $13.036^\circ$  indicates a grain size of 25 nm for Cu<sub>2</sub>Se.

Fig. 2 gives the typical XRD pattern of the as prepared (0.12  $\mu$ m) sample of copper selenide obtained from Bath M and that obtained after nitrogen annealed at



**Fig. 1.** XRD patterns of samples of 0.13 μm film from *Bath S*, as-prepared and after annealing in N<sub>2</sub> (50 mtorr) for 1 h at 400°C.



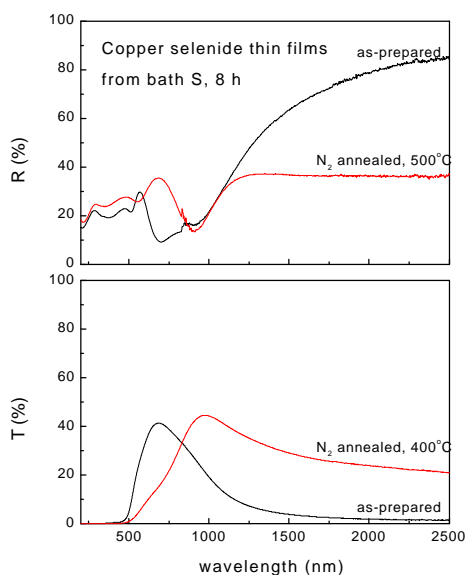
**Fig. 2.** XRD patterns of samples of 0.12 μm film from *Bath M*, as-prepared and after annealing in N<sub>2</sub> (50 mtorr) for 1 h at 400°C.

400°C. The as prepared film is of low crystallinity. The observed peaks match those (of intensity 100% and 64%, respectively) due to reflections from (102) and (110) planes of mineral klockmannite (JCPDS 34-171) which is hexagonal with composition CuSe. The absence of other peaks with significant relative intensities as in the JCPDS pattern is due to crystallite orientation in the thin film. Annealing the film in nitrogen enhances the crystallinity as evidenced from the increase in peak heights in the patterns of the annealed samples, up to 300°C (not shown in the Figure 1). The XRD pattern of the film annealed in nitrogen at 400°C show that the annealing changes the composition and crystallinity of the films. The patterns

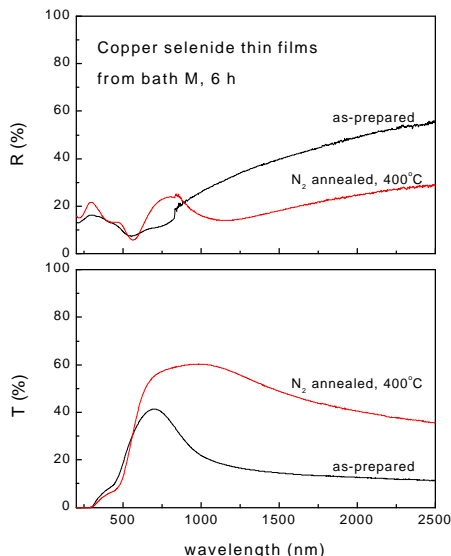
match the standard pattern reported for Cu<sub>7</sub>Se<sub>4</sub> (JCPDS 26-557) with an absence of certain peaks due to crystallite orientation. We consider that the match to Cu<sub>2-x</sub>Se is inferior, even though we are not ruling out a mixed composition. The grain diameter increases with the annealing temperature, it is 23 nm for the annealed sample. The change in composition to copper-rich phase of the CuSe films is due to the loss of selenium upon heating. This loss has been detected in XRF studies (not reported here): the Cu:Se ratio reduces from 1:1 (assigned to as prepared film) to 1.7:1 in the annealed film. In both cases the grain size is not enough for thin film solar cells application; it needs to increase up to 100 nm or higher.

**b). Optical and electrical characterization of the films**

The typical optical transmittance, T (%), and near normal reflectance, R (%), spectra of the films prepared using *Bath S* and *Bath M* are presented in Figures 3 and 4, respectively, for the as prepared and N<sub>2</sub> annealed samples (50 mtorr, for 1 h at 400°C). Annealing the Cu<sub>2-x</sub>Se film of 0.13 μm thickness in nitrogen at 400°C results in change in the optical transmittance and reflectance spectra of the films. Similarly changes in the optical spectra are also observed in a film of thickness 0.12 μm deposited from *Bath M*. These changes are attributed to structural, compositional and crystallinity changes in the film, taking place during the annealing process as discussed before. The near infrared reflectance has been found to decrease with annealing temperature causing a corresponding increase in the near infrared transmittance in both cases. This is associated with a decrease in the electrical conductivity with annealing temperature observed in all the films, according to the results reported earlier [19].



**Fig. 3.** Optical transmittance T (%) and near normal specular reflectance R (%) spectra of Cu<sub>2-x</sub>Se thin films obtained from *Bath S*, as-prepared (0.13 μm) and N<sub>2</sub> (50 mtorr) for 1 h at 400°C.



**Fig. 4.** Optical transmittance T (%) and near normal specular reflectance R (%) spectra of Cu<sub>2-x</sub>Se thin films obtained from Bath M, as-prepared (0.12 μm) and N<sub>2</sub> (50 mtorr) for 1 h at 400°C.

For example, the sample from bath S when annealed has a near infrared reflectance of around 35%, and an electrical conductivity of 4500 (Ω cm<sup>-1</sup>), and the sample from bath M when annealed has a near infrared reflectance of around 20 % has an electrical conductivity of 1500 (Ω cm<sup>-1</sup>). This behavior is associated with the theory of free carrier absorption of electromagnetic radiation [24, 19].

The band gap values for the films were estimated using the optical spectra given in figures 3 and 4. For this, the transmittance spectra have been corrected for the loss due to reflections:  $T_{corr.} = \{T(\%)/(100 - R(\%))\} \times 100$ . We assume that the predominant component in the reflected intensity is due to the air-film interface. The absorption coefficients ( $\alpha_g$ ) for band-to-band transition across the gap at different wavelengths are calculated using the corrected transmittance values:  $\alpha_g = (1/t)\ln(100/T_{corr.})$ , where  $t$  is the film thickness. The direct and indirect band gap values are obtained from plots of  $\alpha_g^2$  and  $\alpha_g^{1/2}$ , respectively, against the corresponding values of photon energy (hv).

The as-prepared sample has a  $E_{g,dir}$  value of 2.32 eV and for the annealed (400°C) sample it drops to 2.17 eV. The  $E_{g,ind}$  values are 1.87 eV for the as prepared and 1.16 eV for the annealed film obtained form bath S. For the samples obtained form bath M, the  $E_{g,dir}$  values are 2.15 eV (as prepared) and 2.14 eV (N<sub>2</sub> annealed at 400°C).

The  $E_{g,ind}$  is 1.32 eV for the annealed film. In both cases the optical absorption coefficient does not drop to zero because of the setting in of free carrier absorption before the band-to-band transitions disappear. Hence it is not possible to analyze the low energy region in the band-to-band absorption corresponding to indirect gaps. The values indicated above for the indirect band gap, are considered to be the upper limit. The larger band gap values

in the as prepared samples compared with that of the annealed samples are due to the quantum confinement effect [25,26] arising from smaller grain size in the former. All these optical band gap values are close to that reported earlier [2, 5] for the materials used for solar cells, which means that these materials have good chance to be used for this purpose.

All the analyzed samples, Cu<sub>2-x</sub>Se, Cu<sub>2</sub>Se, CuSe and Cu<sub>7</sub>Se<sub>4</sub>, have shown p-type conductivity which is known to arise from copper deficiency at any given composition. High electrical conductivity,  $\sigma = 5000$  (Ω cm)<sup>-1</sup> has been reported previously in evaporated films of Cu<sub>2-x</sub>Se [4], which matches values reported in this paper. Hole mobilities  $\mu_h \approx 2.5$  cm<sup>2</sup>/Vs and carrier concentrations  $p \approx 1.2 \times 10^{22}$  cm<sup>-3</sup> have been reported for such films. By analogy, we assume that the present films may possess similar carrier concentration and mobility.

The low conductivity observed in the films obtained from bath M compared with that of the annealed samples form bath S, is attributed to changes in composition through loss of selenium, confirmed in XRF (not reported in this paper).

**c). Analysis of the optical absorption**

The optical transmittance spectra presented in Figs. 3 and 4 suggest that a high electrical conductivity of the films gives rise to very high near-infrared reflectance. In Fig. 3, when the transmittance has been corrected for the reflection losses, the transmittance values still remain below 100% indicating absorption losses due to free carriers. Such characteristics of wide-gap degenerate semiconductors, such as SnO<sub>2</sub>:F and SnO<sub>2</sub>:Sb, In<sub>2</sub>O<sub>3</sub>:Sn are made use in heat-mirror coatings [27] and in Cu<sub>x</sub>S and Cu<sub>x</sub>Se have been used as solar control coatings [28, 29].

In the present case the electrical conductivity of Cu<sub>2-x</sub>Se films reported here is about  $5 \times 10^3$  (Ω cm)<sup>-1</sup>. For a partially conducting medium, the optical reflectance at the air-medium interface is given by the relation [24]

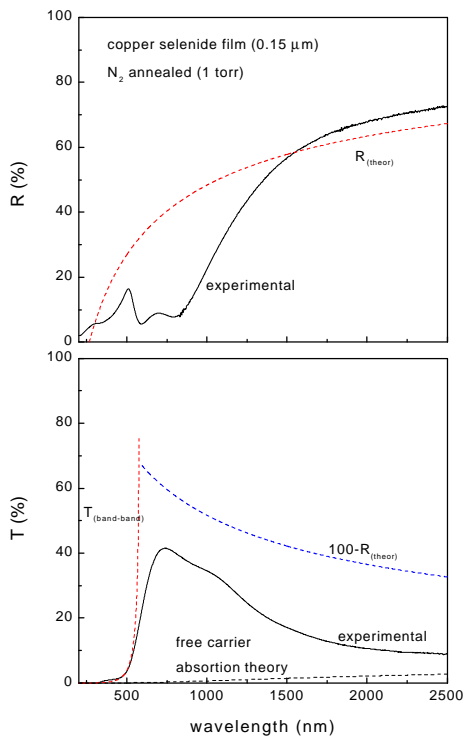
$$R = 1 - 4 \left( \frac{p c \epsilon_o}{s l} \right)^{1/2}, \tag{1}$$

where,  $c$  is velocity of light,  $\epsilon_o$  is the permittivity of free space,  $\sigma$  is the conductivity of the material, and  $\lambda$  is the wavelength of the incident radiation. Fig. 5 shows the comparison of the experimental reflectance curve and that calculated using equation (1) for electrical conductivity of the film,  $5 \times 10^3$  Ω<sup>-1</sup> cm<sup>-1</sup>. The correspondence is good in the near infrared region, away from the region of optical interference peaks.

The presence of a high carrier concentration also leads to free carrier absorption, governed by a wavelength dependent absorption coefficient [24]

$$a_f = 2 \left( \frac{p c m s}{l} \right)^{1/2}, \tag{2}$$

where  $\mu$  is the permeability of the material, taken equal to the permeability of free space,  $\mu_o$ . Thus, in the near infrared



**Fig. 5.** Analysis of the optical transmittance spectra of  $\text{Cu}_{2-x}\text{Se}$  film annealed (0.15  $\mu\text{m}$ ) at 300°C.

region where the approximation which leads to equation (2) is valid, the intensity of electromagnetic radiation transmitted into the medium would vary as

$$I = I_0 e^{-\alpha_f d} \quad (3)$$

where  $d$  is the depth into the film. The value of  $\alpha_f$  evaluated based on equation (2) for  $\text{Cu}_{2-x}\text{Se}$  films is  $3.3 \times 10^5 \text{ cm}^{-1}$  for  $\lambda = 2500 \text{ nm}$ . The value of  $\alpha_f$  is also obtained from  $T_{\text{corr}}(\%)$  in the near infrared region in the same way as done for band-to-band absorption region. The values are  $1.5 \times 10^5 \text{ cm}^{-1}$ , comparable to the theoretical value of  $3.3 \times 10^5 \text{ cm}^{-1}$ . The difference is due to the thickness effect.

For a semiconductor, the direct gap allowed transition is given by the equation [30]:

$$(\mathbf{a}_g)_{\text{direct}} = B(h\nu - E_g)^{1/2}, \quad (4)$$

where  $h\nu$  is the photon energy,  $E_g$  is the energy gap of the semiconductor and  $B = \frac{2n(2m_r^*)^{3/2}}{cph^2} P(\mathbf{n})$  is a constant.

For the wave vector  $k = 0$  the transition probability  $P(\mathbf{v})$  is practically constant. Here  $n$  is the refraction index,  $m_r^*$  is the effective mass,  $c$  is the velocity of light and  $\hbar$  is the Planck's constant. The value of  $B$  is obtained as the square root of  $\mathbf{a}_g^2$  vs  $h\nu$  plot. Thus for the visible region we reproduce the transmittance curve based on the absorption across the direct gap. The curve of  $100 - R(\%)_{\text{theor}}$  calculated from equation (1) is also shown. Thus, the

typical shape of the optical transmittance curve of chemically deposited  $\text{Cu}_{2-x}\text{Se}$  or  $\text{CuSe}$  may be explained as due to the band-to-band and free carrier absorption processes. The transmittance curve resulting from reflection losses is further multiplied by  $e^{-(\mathbf{a}_f)_d}$  to obtain the curve labeled free carrier absorption. The theoretical curve is much below the experimental curve, because the theoretical prediction is for a material with thickness  $\gg$  skin depth, which is not satisfied in the present case.

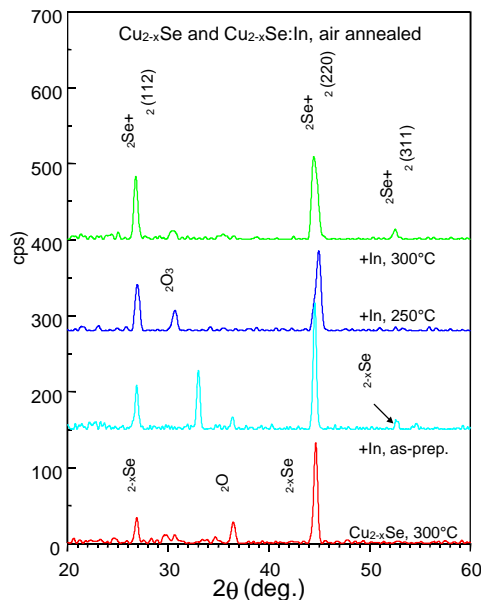
#### 4. Application of the films

##### a). $\text{CuInSe}_2$ films

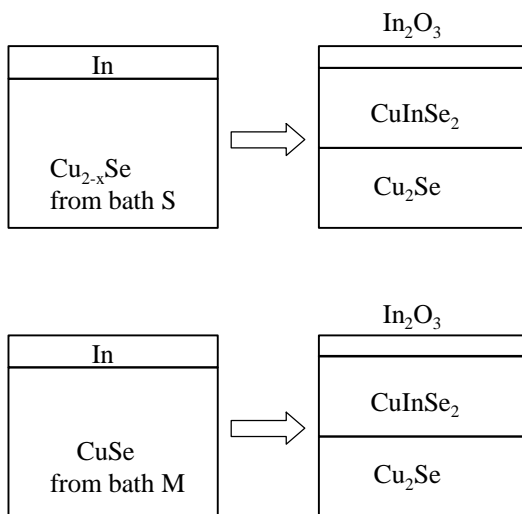
There is interest in development of  $\text{Cu(II)(S/Se)}_2$ ,  $\text{Cu}_2(\text{IV})(\text{S/Se})_3$  and  $\text{Cu}_x(\text{V})(\text{S/Se})_y$  absorber films for solar cells, based on the demonstrated capability of the Group-II ions to inhibit the movement of the copper ions towards the n-side of the photovoltaic junction. The formation of a mixture of  $\text{Cu}_2\text{Se} + \text{CuInSe}_2$  has been observed when  $\text{Cu}_{2-x}\text{Se}$  (S-bath) and thermally evaporated indium film has been annealed at 400°C in air. Here, initially an  $\text{In}_2\text{O}_3$  film is formed on the surface, which prevents the conversion of  $\text{Cu}_{2-x}\text{Se}$  to  $\text{Cu}_2\text{O}$ . XRD patterns in fig. 6 suggest a scheme of formation as shown if fig. 7. Alternatively, another scheme could be implemented, using film deposited from M-bath, according to the reaction  $3\text{CuSe} + \text{In} \rightarrow \text{CuInSe}_2 + \text{Cu}_2\text{Se}$ .

##### b). Solar control coatings.

The copper selenide thin films, from baths S and M) have low transmittance,  $\sim 10\%$ , in the infrared region, and moderate transmittance,  $\sim 40\%$  in the visible region, as well as a high infrared reflectance,  $\sim 60\%$  and low reflectance, 20%–30%, in the visible region. This properties are close to those desired for an ideal solar control coating. The specific



**Fig. 6.** XRD patterns of  $\text{Cu}_{2-x}\text{Se-In}$  and  $\text{Cu}_{2-x}\text{Se}$  samples, as-prepared and air annealed for 1 h at 250°C and 300°C.



**Fig. 7.** Scheme of formation for CuInSe<sub>2</sub> from Cu<sub>2-x</sub>Se and CuSe obtained from baths S and M, respectively.

application could be in architectonic and automotive glassing.

## 5. Conclusions

Good quality thin films of copper selenide of composition Cu<sub>2-x</sub>Se and CuSe with structures of berzelianite (cubic) and Klockmannite (hexagonal), respectively, are deposited from chemical baths of different compositions, using sodium selenosulfate and N,N-dimethylselenourea. The chemical bath F, using sodium thiosulfate leads films of mainly copper sulfide with a small copper selenide component. When annealed at 400°C in 50 mtorr of nitrogen, the Cu<sub>2-x</sub>Se films tend to become Cu<sub>2</sub>Se, and the CuSe films become to Cu<sub>7</sub>Se<sub>4</sub>. The copper selenide thin films reported in this paper have a high p-type electrical conductivity, which may be used as radiation filters. The application of these films as absorber materials in solar devices requires further work, to increase the thickness of the films and to improve also the grain size. The possibility of creating new ternary compounds using the chemically deposited CuSe film as a precursor, as mentioned in the introduction, may be by far the most prospective application of this deposition technique.

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