Optical and Structural Study of CuSe and CuSe/In Thin Films

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Abstract. The preparation of (Cu,Se)(In,N) thin films by r.f magnetron sputtering technique opens an interesting research area with potential application in solar cells. In this work, we presented a systematic study of growth and characterization of CuSe thin films and layers of CuSe/In deposited on glass substrates by varying the power r.f source and substrate temperature. The effects of experimental parameters on morphology and the optical properties of the films were investigated by XRD, UV-Visible and SEM. The results show that the samples are polycrystalline with a hexagonal structure for the CuSe films, and tetragonal structure for the CuSe/In layers. SEM images took on the surface of the films, showed a change in their morphology, evidencing a strong dependence of the experimental parameters. From UV-Visible measurements determine the bandgap and the optical behaviour of the films.

1.   Introduction

The ability to deposit a wide variety of thin film alloys, in a homogeneous and uniform way, has enable the development semiconductor alloys applied in fields such as optoelectronics, photonics, fiber optics, data storage devices and energy conversion [1]. CuSe alloys has been one of the most studied in recent years, with stoichiometric compositions (α-Cu_2Se, Cu_3Se_2, CuSe and Cu_2Se) and non-stoichiometric ($Cu_{2-x}Se$) reporting a continuous change of physical properties. Moreover, different crystalline phases have been reported with orthorhombic structure [2], cubic, hexagonal, [3] and tetragonal [4], depending on the stoichiometry and the growth methods. These features make the electrical and optical properties are of interest for applications in solar cells [5], super ionic conductor [6], optical filters [7] and lasers. [8] The CuSe semiconductor could be a direct gap of 2.2 eV or 1.4 eV indirect [9]. On the other hand, it is worth to note that the semiconductor alloys $CuInSe_2$ (CIS) thin film, are one of the most material promising because of their high energy conversion efficiencies, high absorption coefficient, and its low toxicity (without post-selenization) and optical and electrical properties, which make it a good candidate for solar cells [10].

We report the preparation of CuSe films and In/CuSe layers, by systematic variation of deposition parameters such as rf source power. It was found that the crystallographic orientation and morphology show a strong dependence with the power growth. Furthermore, from optical absorption determined the band gap energy in UV/Vis range.

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2.   Experimental procedure

Films CuSe and CuSe/In were deposited on glass substrates by magnetron sputtering system rf (13.56 MHz). The substrates were cleaned with acetone in an ultrasound chamber. CuSe and In targets of high purity with diameters of 2 inches and 1 inch were used in the process. Vacuum chamber base pressure before deposition $\approx$ 1x 10^{-6} Torr. CuSe layers were deposited in Argon atmosphere at a working pressure of 5 x 10^{-3} Torr for 120 minutes, with a 150 °C substrate temperature and a power of 15 Watts (sample M1) and 35 Watts (sample M2). The target-substrate distance was set at 5 cm, tilted 35 ° with respect to the normal of the substrate.

CuSe/In bi-layers were deposited on glass substrates in order to study the influence of the In layer on their structural properties. Three samples were deposited at In target power source (P_{In}) of 5 Watt (sample M3), 15 Watt (sample M4), and 30 Watt (sample M5). The deposition time of each CuSe and In layer was of 20 min and 2 min, respectively. The residual pressure for all layers is holding in 1.2×10^{-3} Torr. The experimental conditions are show in the table 1.

Table 1. Experimental conditions for CuSe/In layers

Layer	r.f Power (Watts)		Ts (°C)	
	In	CuSe	In	CuSe
M3	5	20	300	150
M4	15	20	300	150
M5	30	20	300	150

The crystal structure was determined by X-ray diffraction (System XRD Cu Ka radiation, Rigaku = 1.5405 A). The surface morphology was analyzed by in-plane view scanning electron microscopy (SEM). Optical transmission spectra were measured with a UV-Visible spectrophotometer (LAMBDA PERKINELMER) in a wavelength range 400 - 900nm.

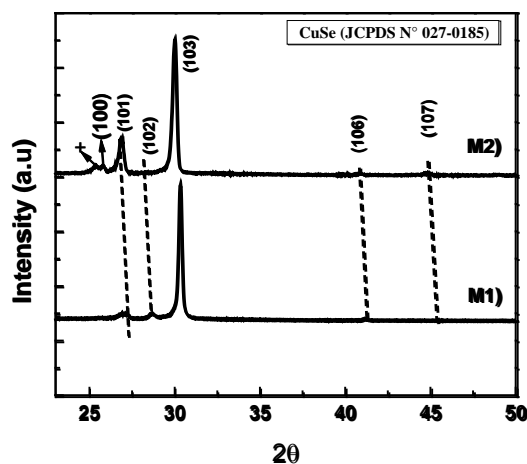## 3.   Results and discussion

Figure 1. XRD Difractograms for CuSe samples. M1) 15 Watt M2) 35 Watt

Figure 1 shows the X-diffraction patterns of CuSe films. The samples were found to be polycrystalline and all orientations of the planes correspond to a hexagonal crystal structure, according to the database (JCPDS N0 027-0185) for CuSe. XRD revealed the presence of three predominant planes corresponding to directions (101), (102), (103) and (106) at 2θ of 26.91 °, 28.66 °, 30.32 ° and 41.14 ° respectively, for the film prepared at a power of 15 Watts (sample M1). For sample deposited at 35 watts (M2), are observed six planes, which two of them present low intensities and correspond to the

crystallographic directions (101) and (107) at 25.81 ° and 44.76 °. One possible explanation for this behavior may refer to the presence of an impurity phase which could be increased with the sputtering power [11].

The shift observed in the position of the all plane can be due to the micro-tensions that gave line defects such as dislocations edge as a consequence of the difference of the lattice parameters. The plane labeled by (+) in Fig. 1, was not possible to identify. From these spectra the grain sizes were estimated using the Debye-Scherrer equation taking into account the instrumental width, obtaining values of 35 nm for M1 and 30 nm for M2, where can see a decrease of the crystallite size due to the increase of the sputtering power.

SEM images taking in-plane view of the M1 (P_{In} = 15 Watt) and M2 (P_{In} = 35 Watt) CuSe samples are shown in the Fig. 2, a) 50 kX, b) 100kX and c) 200kX magnification for sample M1, and Fig. 2, d) 10kX, e) 15kX and f) 30kX magnifications for sample M2, respectively. The images show crystals with different shapes and geometries, being visible laminar pentagons and hexagons. Hexagons have sizes up to 400 nanometers to larger crystals (Fig.2c), distributed over the surface. For M2 sample, the images reveal the formation of hexagonal crystals with average sizes between 0.5 μm and 1 μm, showing a clear increase in the size of the crystals with the sputtering power. It is worth to note, that SEM images confirm XRD results regarding the shape of the hexagonal crystal structure.
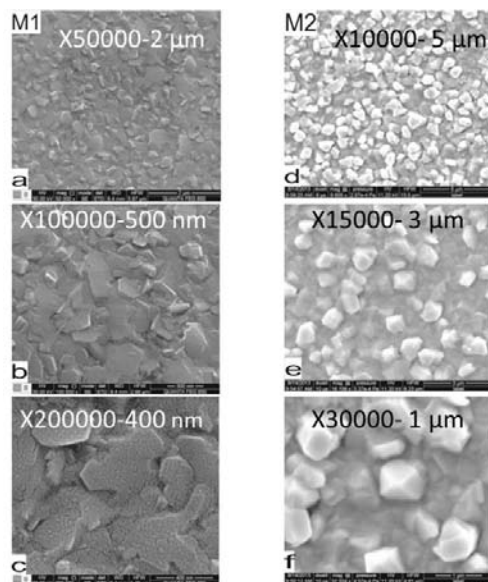

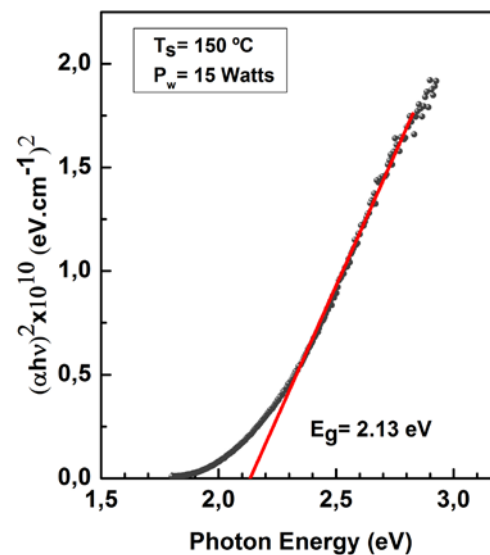**Figure 2.** SEM - Microgrhaps for M1 and M2 CuSe samples at different magnifycations.

Figure 3. Plot of $(\alpha h\nu)^2$ vs Photon Energy for M1 CuSe sample.

In order to analyze the optical behavior of the thin films, the energy band gap was determined from the absorption coefficient vs photon energy, as shown in Figure 3. For high absorbing region where α obey the equation $\alpha h\nu = cte(h\nu - E_g)^{1/2}$, by plotting $(\alpha h\nu)^2$ as a function of photon energy hν, as shown in the Figure 3, and extrapolating the linear region of this curve to $(\alpha h\nu)^2 = 0$ we obtain the value of $E_{g,}$ = 2,13 eV, in good agreement with the value of data reported [9,11].

Figure 4 shows the XRD results of the M3, M4 and M5 layers, where we can see a quasi-crystal growth. XRD spectra revealed the presence of two planes corresponding to (112), and (103) orientations at 2θ = 25.93 ° and 25.87 ° for M1-M3 samples, respectively. The crystallographic orientations of the planes correspond to tetragonal structure, according to the database for tetragonal CuInSe$_2$ (JCPDS No. 089-5646). It is clear that all samples present a preferred orientation in the [112] direction. The crystallite size estimated from the Debye-Scherrer equation for the samples M3, M4 and

M5 was of 28, 37 and 29 nm. The x-ray results have also showed the incorporation of In atoms in the CuSe matrix forming the InCuSe alloy. The CuInSe semiconductor alloy likely is formed by indium (In) diffusion into CuSe layers. As far as we know does not exist report of the quasi-crystalline growth of CuInSe by Magnetron sputtering.
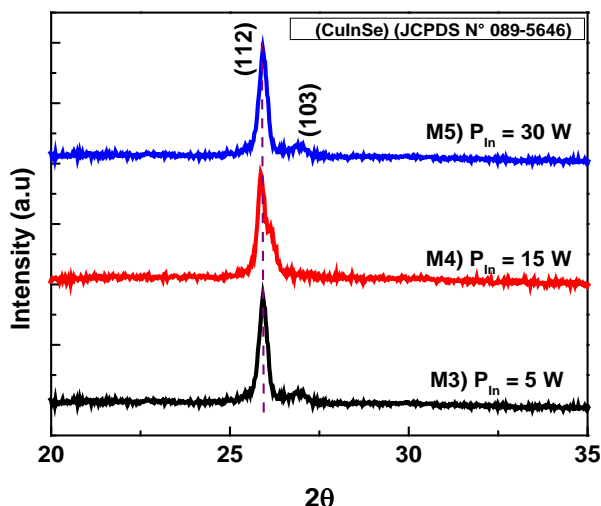

Figure 4. XRD spectra for CuSe/In layers at power source of 5 (M3), 15 (M4) and 30 (M5) Watt.

4. Conclusions

CuSe films and CuSe/In layers were deposited by rf magnetron sputtering technique. CuSe films have a high-crystalline quality, a hexagonal structure and crystallite sizes between 35 and 30 nm. The absorption measurements show that CuSe thin films present a direct band gap transition at 2.13 eV. From CuSe/In bilayers we obtain the CuInSe alloy, which is formed by indium (In) diffusion into CuSe layers.

5. References

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