Effect of laser fluence on structural and optical properties of CuₓS films grown by pulsed laser deposition at different wavelengths

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Abstract

CuₓS thin films were grown onto soda-lime glass substrates by pulsed laser deposition at two different wavelengths: 1064 and 532 nm. X-ray diffraction, Raman and UV–vis spectroscopies were used to characterize the CuₓS films. Results are presented as a function of laser fluence. XRD patterns indicate that covellite and chalcocite phases were obtained. Raman spectra showed that chalcocite is the predominant phase in the crystalline samples. Optical band gap values are between 2.29 and 2.74 eV for ablation with 1064 nm wavelength; meanwhile, for 532 nm band gap values varied from 2.24 to 2.66 eV; which are in the range of expected values for CuₓS films. At 1064 nm and 4.4 J cm⁻² sample presented the highest optical absorbance in the visible range, which corresponds to the highest thickness. These are the best growth parameters for CuₓS films in order to be used as absorber films for solar cells applications.

Introduction

Semiconductors have been considered promising materials with a wide application range in science and technology. Within them, copper sulfide is an interesting p-type semiconductor material which has near ideal solar control characteristics: transmittance in the infrared range and less than 10% reflectance in the visible range [1]. Variations in x (1 ≤ x ≤ 2) can provide different crystalline phases depending on the temperature, producing significant variation in the film’s properties [2]. At room temperature, CuₓS has five stable phases: (CuS) covellite, anilite (Cu₁₋ₓS), digenite (CuₓS), djuriteite (Cu₁₋ₓS) and chalcocite (Cu₂S) [1, 2]. It is a material which has applications in fields such as solar cells, electroconductive coatings, electrodes and it is also used in catalysis [3]. The optical band gap of CuₓS varies in the range of 1.2–2.5 eV. On the other hand, electrical conductivity can vary from 0.07 to 2400 Ω cm⁻¹ as x changes from 2 to 1.8 [1, 2].

Several methods have been used for growing CuₓS films, such as chemical bath deposition (CBD), spray pyrolysis, atomic layer deposition (ALD), chemical vapor deposition (CVD), vacuum evaporation, among others [3, 4]. In order to improve and control some stoichiometric phases, several physical techniques have been used. However, stoichiometry transfer from the target to the substrate is difficult to obtain with evaporation or magnetron sputtering using a single target. Pulsed laser deposition (PLD) is an alternative deposition technique to keep this property required for the growth of complex systems [5].

Some of the advantages that make PLD an important technique are: (a) it has been used to fabricate high quality thin films of materials with a complex stoichiometry, or multilayered structures from a target with similar composition [6, 7]; (b) some process parameters such as background pressure, type of background gas, type of substrate and substrate temperature can be separated from the laser–target interaction; (c) the number of particles arriving to the substrate can be controlled by the number of pulses and the fluence [7]. In addition, a lot of variables can be manipulated in order to improve the properties of the films in the PLD technique, such as...
background gas pressure, substrate temperature and laser incident energy. It is well-known that laser incident energy could change morphology, microstructure and promote formation of specific crystalline phases [8].

To the authors knowledge, copper sulfide films grown by pulsed laser deposition have not been reported. For that reason, the main objective in this work is to evaluate the effect of laser fluence on structural and optical properties of Cu$_2$S films grown onto soda-lime glass substrates by PLD, changing the wavelength and the distance between the target and lens. Results are discussed as a function of the laser fluence.

**Materials and methods**

**Growth of Cu$_2$S films**

Copper sulfide films were grown onto soda-lime glass substrates with a size of $1.5 \times 2.0 \text{ cm}^2$ by PLD in a vacuum chamber evacuated to a base pressure of $2.6 \times 10^{-4} \text{ Torr}$, using a CuS (covellite) solid target. The ablation was induced by a Nd:YAG laser beam with two different wavelengths 1064 and 532 nm, a pulse width and frequency of 5 ns and 10 Hz, respectively. The growth time was 300 s and the distance between substrate and target-material was 2 cm. The fluence varied from 0.7 to 13.6 J cm$^{-2}$ at 1064 nm. At 532 nm the laser fluence varied from 0.6 to 13.1 J cm$^{-2}$ by changing the spot size. To investigate the influence of the laser fluence on the properties of the films, the position of the target surface relative to the laser focus was adjusted by moving the lens. Spot size was changed because of the variation in the distance between lens and target, as shown in table 1.

As a result, laser fluence also has different values according with the equation $F = \frac{E}{A}$, where F is the laser fluence; E is the laser energy with values of 0.426 J at 1064 nm and 0.410 J at 532 nm. A is the spot area.

**Characterization**

X-ray Diffraction patterns were obtained in a Siemens D5000 Diffractometer, using the Cu-K$_\alpha$ line (1.5406 Å). Raman spectroscopy measurements were carried out in a Thermo Scientific Raman microscopy DXR2, employing a 532 nm laser line as excitation source. An UV–vis Perkin Elmer Lambda 25 spectrophotometer was used to obtain the optical transmittance spectra. Finally, film thicknesses were measured with a KLA Tencor D-100 profilometer. Energy laser fluence was measured with the Handheld Laser Power Meter—Nova II.

**Results and discussion**

**XRD analysis**

XRD patterns for Cu$_2$S films grown by PLD with wavelengths of 1064 and 532 nm are shown in figures 1 and 2, respectively. The diffractogram of the sample grown at 0.7 J cm$^{-2}$ showed in figure 1, presents two peaks centered at 26.49° and 21.87°. The highest intensity peak at 2θ = 26.49° corresponds to Cu$_2$S hexagonal phase (PDF 26–1116) and the diffraction plane is (002); the peak at 21.87° is related to S (PDF No. 08–0247) with (220) diffraction plane [9]. The diffractogram of the sample grown at 4.4 J cm$^{-2}$, shows eight peaks. The dominant peak at 2θ = 26.49° corresponds to the Chalcocite (Cu$_2$S) and the (002) diffraction plane, as well as the peak at 23.08°, is associated to S and the diffraction plane is (222); the peaks at 29.27, 31.78, 47.94, 52.71 and 59.34°, are related to covellite (CuS) hexagonal phase (PDF No. 06–0464) [10, 11]. The crystallinity for samples at 8.7 and 13.6 J cm$^{-2}$ is missed out, as diffraction patterns show. At 0.7 J cm$^{-2}$ fluence, sample is mostly Cu$_2$S phase with a small quantity of elemental sulfur. On the other hand, when laser fluence is increased, some peaks of covellite phase are present; however, the highest peak is still corresponding to chalcocite hexagonal phase. The increase in the laser fluence causes an increase in plasma density and kinetic energy. Mobility of deposited atoms are supposed to be improved with highest laser fluences; however, when this fluence is too high, the crystallinity is
degraded due to the bombardment of the surface with high kinetic energy species, this is a particular behavior that has been reported for other materials [8].

X-ray diffraction patterns of Cu_xS films grown with a wavelength of 532 nm show that they present lower crystallinity than the samples grown at 1064 nm as it is shown in figure 2. Moreover, when fluence is increased, a sulfur–impurity related signal appeared at 2θ = 21.87° (PDF No. 08-0247). At 0.6 J cm^{-2} the peak at 23.08° corresponds to S and the diffraction plane is (222); there are some small diffraction peaks at 32.85 and 47.94 degrees, which correspond to covellite phase. A mixture of amorphous and crystalline phases is favored by 532 nm wavelength ablation, as XRD patterns indicate [12]. A proper laser energy incident is acquired to vaporize the target and the kinetic energy in the plume can be enhanced, in this way the crystallinity could be improved, as well [8, 13].

**Raman spectroscopy analysis**
Raman spectra of Cu_xS films grown by PLD at different laser fluences are shown in figures 3 and 4, for 1064 and 532 nm, respectively. Two Raman modes at 264 cm^{-1} and 470 cm^{-1} can be observed for samples grown at 0.7 and 4.4 J cm^{-2}. The mode centered at 470 cm^{-1} can be attributed to an octasulfure of Cu_xS [12, 14]; some
authors have reported a smaller band around 267 cm$^{-1}$ attributed to lattice vibrations of covellite [14]. The intensity of the 470 cm$^{-1}$ Raman mode in the sample grown at 8.7 J cm$^{-2}$, is lower than the signal corresponding to the films grown at low fluence and the peak is not well defined, which could indicate a poor crystallinity. Finally, the 13.6 J cm$^{-2}$ sample does not present any signal, this means that an amorphous material was grown, which is in agreement with the data obtained from XRD measurements. According to XRD patterns and Raman spectra for samples grown using 1064 nm, lower laser fluence values favor the growth of crystalline materials, being chalcocite the predominant phase.

Raman spectra of Cu$_x$S films grown by PLD at different laser fluences for 532 nm are shown in figure 4. A Raman signal centered at 450 cm$^{-1}$ can be observed and attributed to a $\nu$ S–S vibration, which is different from octasulfur (471 cm$^{-1}$) or covellite at 474 cm$^{-1}$ signals [14]. As it was mentioned before the peak around 470 cm$^{-1}$ has been identified to chalcocite phase, more specifically to S–S stretching mode of S$_2$ ions at the 4e sites [10]. The vibrational mode observed at 482 cm$^{-1}$ in the Raman spectra is assigned to the S–S stretching vibrations in Cu$_x$S copper-deficient sulfides with $x = 1.12$ [15]. Raman spectra confirms XRD results, the ablation with 532 nm wavelength induces multiple phases of CuS.

Figure 3. Raman spectra of Cu$_x$S films grown by PLD with wavelength 1064 nm at different laser fluences.

Figure 4. Raman spectra of Cu$_x$S films grown by PLD with wavelength 532 nm at different laser fluences.
Optical properties

Figures 5 and 6 show the optical transmittance of Cu$_x$S films deposited using 1064 and 532 nm wavelengths, respectively, in the electromagnetic spectral region of 300–1000 nm. In the samples grown at 1064 nm, it can be noticed that optical transmittance increases for increasing laser fluence, however, sample grown at 4.4 J cm$^{-2}$ presents the highest absorbance in the visible range (400–700 nm) for Cu$_x$S films at 532 nm, sample at 0.6 J cm$^{-2}$ presents the highest light absorbance in the visible range. When laser fluence is increased, a shoulder in the blue region appear due to quantum confinement effects in CuS nanomaterial [16]; this effect is more evident at 4.3 and 13.1 J cm$^{-2}$ with a wavelength of 532 nm, in which there is a shoulder in the blue region and a slightly blue-shift due to quantum confinement effects of covellite or the free-carrier intra-band absorption [17–19].

The absorption coefficient ($\alpha$) was calculated from equation $\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$, where $d$ is the film thickness and $(1 - R) = A + T$ and considering that $A + T + R = 1$. The absorption coefficient was used to calculate the band gap ($E_g$) using the relation $\alpha h\nu = (h\nu - E_g)^{1/2}$ where $h\nu$ is the photon energy. The $E_g$ value was calculated by extrapolating the linear part of the Tauc plot to the energy axis as figures 7 and 8 indicate. The energy band gap values and thicknesses are shown in table 2. The direct band gap varies from 2.24 to 2.74 eV, which are similar to the values reported in literature [16, 18]. In fact, these values are similar to the reported for amorphous CuS thin films; most of the Cu$_x$S films grown in the present work, show the same behavior as XRD.

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**Figure 5.** Optical transmittance of Cu$_x$S films grown by PLD with wavelength 1064 nm at different laser fluences.

**Figure 6.** Optical transmittance of Cu$_x$S films grown by PLD with wavelength 532 nm at different laser fluences.
patterns indicate [20]. It is observed that the thickness does not follow a particular trend, the highest thickness is obtained at 1064 nm and 4.4 J cm$^{-2}$ in which the lowest transmittance was observed. It is known that the optical properties of a semiconductor depends on the crystallinity [16] and this sample has a highest crystallinity as XRD

Table 2. Band gap energy values, determined from Tauc plots and thickness of Cu$_2$S films by PLD at two wavelengths.

| Wavelength (nm) | Laser fluence (J cm$^{-2}$) | Thickness (nm) | Eg (eV) |
|-----------------|------------------------------|----------------|---------|
| 1064            | 0.7                          | 829            | 2.74    |
|                 | 4.4                          | 1094           | 2.29    |
|                 | 8.7                          | 124            | 2.62    |
|                 | 13.6                         | 64             | 2.44    |
|                 | 0.6                          | 257            | 2.51    |
| 532             | 4.3                          | 135            | 2.33    |
|                 | 8.4                          | 303            | 2.24    |
|                 | 13.1                         | 158            | 2.66    |

Figure 7. Optical band gap energy for Cu$_2$S films with wavelength 1064 nm at different laser fluences.

Figure 8. Optical band gap energy for Cu$_2$S films with wavelength 532 nm at different laser fluences.
and Raman results show. Moreover, the increase in the band gap could be related to a change in the composition [18]. However, the smallest band gap value (2.24 eV) corresponds to the sample grown at 532 nm and 8.4 J cm⁻². It is known that the optical properties of semiconductors depend on their crystallite size, moreover, a variation on the band gap may be related to a change in stoichiometry [18], as it can be seen in table 2, band gap values are variable. This could be explained by the existence of crystalline phases mixtures on the samples as show in Raman spectra.

Conclusions

Copper sulfide films were grown onto soda-lime glass substrates by pulsed laser deposition with incident wavelengths of 1064 and 532 nm and varying the laser fluence. According to XRD patterns, at 1064 nm and low fluence values, Cu₂S preferential phase films with high crystallinity and Cu₂S preferential phase are obtained. At 532 nm films, lower crystallinity was observed as compared for samples grown at 1064 nm. Furthermore, a mixture of amorphous and crystalline phases was obtained. Raman spectra showed the highest Raman mode corresponding to chalcocite phase at 0.7 and 4.4 J cm⁻² for 1064 nm. The 532 nm wavelength promotes multiple phases of Cu₅. As XRD and Raman analysis demonstrated, the crystallinity is decreased when laser fluence is increased for both wavelengths. A low laser energy beam causes a crystallinity improvement. Energy band gap values were between 2.22 to 2.49 eV. Sample grown at 1064 nm and 4.4 J cm⁻² presented the highest optical absorbance in the visible range, which corresponds to the highest thickness. At these growth parameters, Cu₅ films present the best conditions to be used as absorber films for solar cells applications.

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