The Impact of Cu Content on Some Physical Properties of Pb0.5S0.5 Films Prepared by Flash Evaporation

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ABSTRACT
A polycrystalline Pb0.5S0.5 alloy has been prepared successfully. Films of Pb0.5S0.5-Cu were prepared with various Cu content (0.10,0.15,0.20,0.25 and 0.30)wt% with thickness 2µm. These prepared film have been deposited on glass and Si substrates by flash thermal evaporation technique at room temperature (RT), under vacuum 10⁻⁶ Torr. The composition of prepared Pb0.5S0.5 alloy is determined by atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF). The optical measurement showed that Pb0.5S0.5-Cu films have a direct energy gap (Eg). The energy gap increased with increasing Cu content from 0.1-0.15 wt%, then decreased at higher value of Cu. The absorption coefficient, refractive index, extinction coefficient, dielectric constants, and the width of the tails have been studied also as a function of Cu contents.

INTRODUCTION

Narrow gap semiconductors are among the most suitable materials for infrared detectors due to their high quantum efficiency. Lead sulphide (PbS) has been a rapidly growing area of importance to study the quantum size effect in recent years (Zaman, S., 2013). A relatively less studied but equally interesting material is PbS a narrow gap semiconductor with a bulk band gap in the near infrared at 3200nm and can be used as photodiode and photovoltaic detector. (Alias, M. F. A, 2011) Its emission and absorption lines are consequently broader but by monitoring its crystallite size, tunable emission can be obtained in large spectrum ranges, ranging from visible to the near infrared. This spectral range is of great interest for fabricating light sources (including lasers IR detectors such as solar cells, field effect transistors or optical amplifiers or photo detectors) as heterogeneous detectors. Broad emission in the near infrared is especially interesting for optical telecommunication devices, also PbS quantum dots have been found to have exceptional third-order nonlinear optical properties that may be useful in optical devices such as optical switches. Also it has been found that the properties of chemically deposited PbS thin films depend strongly on the growth conditions (Oriaku, C.I., 2008, Carter, D. L., 1970).

Lead salts and their alloys have a number of interesting physical properties as well as numerous potential applications because it is a narrow energy band gap semiconductor of approximately 0.4 eV at 300K and Bohr radius of 18nm. (Carter, D. L., 1970, Ravich, Yu. I., 1970, Mosiori, 2014). Lead sulphide (PbS) is a semiconducting chalcogenide with a direct bandgap of 0.41 eV and has a cubic structure and a relatively large excitation Bohr radius of 18 nm. These properties make PbS very suitable for infrared detection application. This material has also been used in many fields such as photography, Pb²⁺ ion selective sensors and solar absorption. In addition, PbS has been utilized as photoreistance, and temperature sensors, decorative and solar control coatings (Sharma, B.L., 1974, Alessandro, Martucci, 2004).

Fabrication of doped films is especially necessary for application in the field of integrated optics and heterojunction (HJ) detectors. Copper is a very substance that occurs naturally in the environment and spreads through environment through natural phenomena. Coppers colors is unique softly reflective brown red to deep brick red (Mosiori, 2014). The nature and role of defects in PbS and the part played by copper have still not been well established as with most of the IV-VI compounds, accidental trace contamination with copper is quite common. This is particularly important in HJ device. The copper may diffuse...
readily across the junction. On the other hand, copper is widely used as a counter dopant in the preparation of photoconductive and photovoltaic detector. Flash evaporation technique involves instantaneous evaporation of the material with minimum possible time of contact with the evaporator, has been successfully used for growing precisely stochiometric films of compounds whose constitutes have widely different vapor pressures (Sharma, B.L., 1974, Pankove, J.I., 1971). The purpose of this work is to study the effect of Cu content on some properties of Pb$_{0.5}$S$_{0.5}$-Cu films

**Experimental procedure:**

The Pb$_{0.5}$S$_{0.5}$ alloy was prepared from pure lead and sulfur powders whose purity is about (99.9999%), the weighted lead and sulfur were loaded into a clean and baked quartz tube. These alloys were powdered to a fine grain powder. The powder of the compounds was as a source of the evaporation to prepare the films. Pb$_{0.5}$S$_{0.5}$ powder doped with copper by chemical diffusion by mixed with solution of CuCl(0.1, 0.15, 0.25, 0.3wt%) and dried at 373K for one hour and were taken as a source materials. The Pb$_{0.5}$S$_{0.5}$-Cu films have been prepared by vacuum flash evaporation technique using Edward E306A under lower pressure of about 10$^{-3}$mbar with 2µm thickness. To have high sensitive layers, heat treatments have been used in vacuum by electric furnace in the temperatures 600K for 1h. For composition analysis, the atomic absorption spectroscopy (AAS) and x-ray fluorescence (XRF) were used. The structure of the Pb$_{0.5}$S$_{0.5}$ alloys as bulks and films has been examined by x-ray diffraction (XRD) with CuKα wavelength (λ) (1.5405)A. The optical properties of these films have been studied by FTIR spectrophotometer.

**RESULTS and DISCUSSION**

Atomic absorption spectroscopy and X-ray fluorescence have been used to examine the concentration of the elements (Pb and S) in the alloy as bulk, by depending on the atomic absorption of the standard elements of these components. The experimental data results are coincide to the theoretical values as shown in Table 1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>N$_{Pb}$%</th>
<th>N$_{S}$% by AAS</th>
<th>N$_{Pb}$% by XRF</th>
<th>N$_{S}$% by XRF</th>
<th>Total %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$<em>{0.5}$S$</em>{0.5}$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>100</td>
</tr>
</tbody>
</table>

The structure of the Pb$_{0.5}$S$_{0.5}$ alloy and prepared films which doped with copper content (0.10, 0.15, 0.20, 0.25 and 0.30)wt% have been studied by X-ray diffraction. It is observed that the structure for prepared alloy and films were polycrystalline of FCC structure according to ASTM cards as shown in Fig.1. The reflection surfaces (111), (200), (220), (311), and (222) have been appeared as shown in Fig.1. It is similar to the ASTM cards data, and this agree with (Alessandro, Martucci, 2004, Alias, M. F. A., 2011) when he doped films with polymer. It is observed a preferred orientation growth along the (200) and (111) direction. Also the intensity of the peaks increases with increasing Cu content. This can be related to the increasing of Cu content which leads to fill all dangling bond and vacancy by doping with Cu, for this, the grain size increases. The grain size and lattice constant of the films as a function of Cu were determined by using Scherrer formula (Seghaier, S., 2006, Alias, M. F. A., 2011). This results are shown in Table 2. The lattice constant of the films are approximately 5.88Å, and it increase slightly with change of Cu content. This lattice constant value is very similar to the bulk PbS indicating that films grow on the glass substrate without stresses at the interface. However, the doped Cu produce an increase in the grain size of Pb$_{0.5}$S$_{0.5}$-Cu films, approximately 20.9-60.3nm for the doped Cu from (0.10-0.30wt%) respectively. This result is agree with observation of (Seghaier, S., 2006, Alias, M. F. A., 2011).

The optical properties of Pb$_{0.5}$S$_{0.5}$-Cu films of 2µm thickness of different Cu content (0.1, 0.15, 0.2, 0.25 and 0.3wt%) have been determined from FT-IR transmittance spectrum in the region (1-5)µm on silicon substrate. The absorbance, transmittance, and reflectance spectra have been studied, also the energy gap and optical constants have been determined.
From Fig. 2, in general, the Cu content increase shifts the peak of transmittance spectrum to the higher wavelength. Another noticeable remark is that the transmittance decreases with increasing Cu content. This may be attributed to the creating levels at the energy band by adding more Cu and this leads shift to smaller energies. This indicates that the adding of Cu leads to an increasing new states in the energy gap, we can visualize this as an increase in the width of valence or conduction tail leading to a shift of Fermi level towards the valence or conduction bands (Alias, M. F. A., 2011). The spectra of absorptance and reflectance are shown in the Fig. 2(b) and Fig. 2(c). It is obviously that its behavior is opposite to that of the transmittance spectrum.

![Graph showing the X-ray diffraction for Pb_{0.5}S_{0.5} alloy and doped films at different Cu content.](image)

**Table 2:** Values of d-space, grain size and lattice parameter for Pb_{0.5}S_{0.5} alloy and Cu doped films at (200).

<table>
<thead>
<tr>
<th>Cu content</th>
<th>d_{exp}(Å)</th>
<th>d_{calc}(Å)</th>
<th>D nm</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alloy</td>
<td>2.969</td>
<td>2.917</td>
<td>20.9</td>
<td>5.834</td>
</tr>
<tr>
<td>0.1</td>
<td>2.969</td>
<td>2.917</td>
<td>36.0</td>
<td>5.834</td>
</tr>
<tr>
<td>0.15</td>
<td>2.969</td>
<td>2.911</td>
<td>40.0</td>
<td>5.822</td>
</tr>
<tr>
<td>0.2</td>
<td>2.969</td>
<td>2.959</td>
<td>41.0</td>
<td>5.928</td>
</tr>
<tr>
<td>0.25</td>
<td>2.969</td>
<td>2.963</td>
<td>44.8</td>
<td>5.928</td>
</tr>
<tr>
<td>0.3</td>
<td>2.969</td>
<td>2.973</td>
<td>60.3</td>
<td>5.948</td>
</tr>
</tbody>
</table>

![Graph showing the transmittance, absorptance and reflectance spectrum of Pb_{x}S_{1-x}:Cu films with different Cu content.](image)

The absorption coefficient (α) increased with increasing Cu and its shifted to higher wavelength for all samples as shown in Table 3 and Fig. 3, and this is due to the decreasing value of energy gap with increasing Cu. Our value of α which varies between (0.317-0.62)×10^{-4} cm^{-1} for Cu(0.1 -0.3)
nearly agrees with other researcher (Choudhury, N., 2009. Also we can observe that the value of $\alpha$ increases two times with increasing Cu value for all samples, this is related to the increase in the metal concentration of Cu. This non stoichiometric in the films leads to increase the dangling bonds or the density of localized state which increases the absorption coefficient. This is an agreement with the researcher (Alias, M. F. A., 2011).

![Fig. 3: The absorption coefficient of PbS$_{1-x}$Cu films with different Cu content.](image)

To determine the type of optical transition, we have examined $(\alpha h \nu)^{1/2}$, $(\alpha h \nu)^{3/2}$, $(\alpha h \nu)^{2/3}$, $(\alpha h \nu)^{2}$, versus $h \nu$ and found that the last relation yielded a linear dependency, which describes allowed direct transitions (Carter, D. L., 1970). From Fig. 4 the energy gap is determined by plotting Tauc equation and taking the extrapolation of the linear portion, where $(\alpha h \nu)^{2}$ as a function of $h \nu$ curve to $\alpha = 0$. The direct energy gap value was found to be as shown in the Table 3, which nearly in agreement with the other literatures (Valenzuela, J.J., 2003, Rasha, A., 2010). The value of optical energy gap increases with increasing Cu value from 0.10 to 0.20 wt% and then decreased for the Cu value >0.2wt% as shown in Table 3. This is due to the improving of the structure by adding Cu by re-crystallizations the lattice by Cu and fill all dangling bond which lead to growth of grain size and the decrease in defect states near the bands and this is turn increased the value of $E_g$, and then the value of $E_g$ nearly decreasing at higher Cu which is due to create levels inside energy gap by Cu and then increased the defect state inside $E_g$. The value of $E_g$ is nearly agreement with other researcher (Alias, M. F. A., 2011, Valenzuela, J.J., 2003. The coefficient (B)(Tauc slope) in the Tauc equation has been obtained from the root square of the straight line slope in the Fig.4. From this figure the value of B is increased with increasing Cu value for (0.1 to 0.2 wt%) and then decreased for the Cu value >0.2wt% as shown in Table 3. We know that B is inversely proportional to amorphosity and the width of the band tails (Rasha, A., 2010). This mean that the amorphosity decreased at doped Cu(0.1-0.2) and then increased for Cu value >0.2wt% which is due to the same reason that mention before. This increased is due to increase the density of localize states in the $E_g$ (Alias, M. F. A., 2011).

![Fig. 4: $(\alpha h \nu)^2$ as a function of $h \nu$ for Pb$_{0.5}$S$_{0.5}$Cu films with different Cu content.](image)

The density of localize states in the band can be evaluated from the Urbach energy(Carter, D. L., 1970, Ravich, Yu. I., 1970) $(E_u)$ at $\alpha <10^4 \text{cm}^{-1}$ which is referred to absorption tails at energies smaller than
the optical energy gap, by plotting $\ln \alpha$ as a function of $h\nu$, and the reciprocal slope of the linear part give the value of $E_g$. We can see from Table 3 and Fig. 5 that $E_g$ decreases from 0.0833-0.07 eV for Cu value 0.1-0.2 wt% and then increased from 0.078 to 0.0819 eV for the Cu value 0.25 and 0.30 wt% respectively. This may be attributed to improvement in the structure by doping and decreasing the degree of amorphous films leading to decrease the localized states and fill all dangling bond, and then the value of $E_g$ increases with increasing Cu content. This increasing is due to create levels and localized states in $E_g$ which give the value of $E_u$.

![Fig. 5: Ln α as a function of hv for Pb$_{0.5}$S$_{0.5}$:Cu films with different Cu content.](image)

The optical behavior of materials is generally utilized to determine its optical constants for example the refractive index ($n$). Fig. 6 and Table 3 shows the variation of refractive index at different Cu content. It is interesting to see that $n$ decreases slightly with increasing Cu. This behavior is due to increase in energy gap which causes to expand the lattice and grow the grain size and decreases the defect which means increasing the absorption and decreasing the reflection which the refractive index depend on it. This is an agreement with the researchers (Barote, M. A., 2011). Also from Table 3 and Fig. 6 the values of $n$ increases with increasing Cu content. This is due to increase in packing density and decrease in degree of amorphousity. The increase in the reflectivity is due to the fact that the value of $n$ for Cu is greater than that for S and moreover the addition of Cu causes an increase in the density and changes the distribution of dangling bonds and thus leads to higher absorption and consequently increasing in the refractive index. Our values of $n$ are nearly in agreement with the researchers (Sushil, K., 2003). They found that the value of $n$ are equal to 4.8 and 4.22 respectively for PbS films grown by hot wall method, and the researcher (Alias, M. F. A., 2011) found that the value of $n$ equal to 4.2 for Pb$_x$S$_{1-x}$ films which prepared by thermal vacuum evaporation.

![Fig. 6: The refractive index as a function of wavelength for Pb$_{0.5}$S$_{0.5}$:Cu films with different Cu content.](image)

The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient at different Cu, it is observed from Table 3 and Fig. 7 that k increasing with Cu. This attributed to the same reason, which mention previously in absorption coefficient.

Fig. 8 and Table 3 shows the variation of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constant with different Cu content. The behavior of $\varepsilon_1$ is similar to
refractive index because the smaller value of $k^2$ comparison of $n^2$, while $\varepsilon_1$ is mainly depends on the $k$ values, which are related to the variation of absorption coefficient (Alias, M. F. A., 2011).

**Fig. 7:** The extinction coefficient as a function of wavelength for Pb$_{0.5}$S$_{0.5}$:Cu films with different Cu content.

**Fig. 8:** The variation of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constant as a function of wavelength for Pb$_{0.5}$S$_{0.5}$:Cu films with different Cu content.

**Table 3:** The optical constants for Pb$_{0.5}$S$_{0.5}$:Cu films with different Cu content.

<table>
<thead>
<tr>
<th>Cu content</th>
<th>$E_g$(eV)</th>
<th>$B^2 \times 10^9$ (eV/cm$^2$)</th>
<th>$n$</th>
<th>$k$</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>$\alpha$ (cm$^{-1}$) x $10^4$</th>
<th>$E_u$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.46</td>
<td>0.22</td>
<td>4.21</td>
<td>0.062</td>
<td>17.720</td>
<td>0.520</td>
<td>0.337</td>
<td>0.0813</td>
</tr>
<tr>
<td>0.15</td>
<td>0.47</td>
<td>0.69</td>
<td>4.21</td>
<td>0.065</td>
<td>17.722</td>
<td>0.551</td>
<td>0.380</td>
<td>0.075</td>
</tr>
<tr>
<td>0.20</td>
<td>0.48</td>
<td>0.48</td>
<td>4.26</td>
<td>0.086</td>
<td>18.260</td>
<td>0.730</td>
<td>0.464</td>
<td>0.070</td>
</tr>
<tr>
<td>0.25</td>
<td>0.475</td>
<td>0.48</td>
<td>3.97</td>
<td>0.107</td>
<td>15.820</td>
<td>0.850</td>
<td>0.579</td>
<td>0.078</td>
</tr>
<tr>
<td>0.30</td>
<td>0.46</td>
<td>0.46</td>
<td>3.81</td>
<td>0.115</td>
<td>14.400</td>
<td>0.880</td>
<td>0.620</td>
<td>0.082</td>
</tr>
</tbody>
</table>

**Conclusions:**

From the data of the present work, we can conclude that the Pb$_{0.5}$S$_{0.5}$:Cu alloy has successfully prepared which was used for films preparation with various Cu Content. From AAS and XRF studies, the experimental data results are coincide to the theoretical values. The crystalline orientation, relative intensity, and grain size of Pb$_{x}$S$_{1-x}$: Cu films were affected by Cu concentration. The preferred orientation are (200) and (111). The intensity of the peaks increases with increasing Cu content. The doped Cu produce an increase in the grain size of Pb$_{0.5}$S$_{0.5}$:Cu films. The increasing Cu content shifts the peak of transmittance spectrum to the higher wavelength. The absorption coefficient increase with increasing Cu and shifted to higher wavelength for all samples. The type of transitions is allowed direct and the value of energy gap varied with increases Cu content. The amorphosity and the width of tails decrease with increasing Cu and then increased. The refractive index and real dielectric constant was decreased slightly with increasing Cu. The behavior of extinction coefficient and imaginary dielectric
constant is nearly similar to the corresponding absorption coefficient at different Cu content.

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REFERENCES


