Effect of Annealing on the Electrical Properties of Cu$_x$S Thin Films

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Abstract

Copper sulphide CuS was deposited on three substrates; glass, Indium Tin Oxide (ITO) and Ti by using spray pyrolysis deposition (SPD). After depositing CuS thin films on the substrates at 200°C, they were annealed at 50, 100, 150, and 200°C for 1 hour. Structural measurements revealed covellite CuS and chalcocite Cu$_2$S phases for thin films before and after annealing at 200°C with changes in intensities, and only covellite CuS phase for thin films after annealing at 50, 100, and 150°C. Morphological characteristics show hexagonal-cubic crystals for the CuS thin film deposited on glass substrate and plates structures for films deposited on ITO and Ti substrates before annealing, these crystals became bigger in size and there were be oxidation and some agglomerations in some regions with formation of plates for CuS on glass substrate after annealing at 200°C. For Hall Effect measurements, thin films sheet resistivity and mobility increased after annealing while the carrier concentration decreased. Generally, the thin film deposited on ITO substrate had the lowest resistivity and the highest carrier concentration before and after annealing. The thin film deposited on Ti substrate had the highest mobility before and after annealing, which makes it the best thin film for device performance. The objective of this research is to show the improvement of thin films electrical properties especially the mobility after annealing those thin films.

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1. Introduction

In the past few decades, there has been an increasing investigation in semiconducting chalcogenide thin films, which have been due to their wide applications in various fields of science and technology. Among them, copper sulfide is the most commonly used material. The copper sulfide thin film attracts the attention of many researchers mostly due to its semiconducting properties. Also, the constituent elements of this material (Cu and S) are non-toxic and abundant in nature.

The copper sulphide is an important material from the point of basic research because it is known to exist in several crystallographic and stoichiometric forms. They are copper-rich phases exist as chalcocite (Cu$_2$S), djurite (Cu$_{1.96}$S), digenite (Cu$_{1.8}$S) and anilite (Cu$_{1.75}$S). And sulphur rich phase exists as covellite (CuS). It is well known that Cu$_x$S (1<x<2) has a distinct composition because of the variation in x, with different stoichiometry and oxidation and temperature is responsible for a change from one composition to another.

Chemical methods have been used to grow CuS films. The shape, phase and the size of inorganic nano-crystals and micro-crystals are the determinant elements in varying their electrical, optical and other properties.

The chemical methods are economical and desirable structure can be obtained with them. Therefore, to grow CuS thin films with desirable shape and structure, the chemical method was employed. Several techniques have been used: Chemical Bath Deposition (CBD), Successful Ionic Layer Adsorption and Reaction (SILAR), and Spray Pyrolysis Deposition (SPD).

As an important semiconductor with unique electronic, optical and chemical properties, CuS thin films are of great concern due to its wide range of application in optical and electrical devices, such as photothermal conversion of solar energy, electro-conductive electrodes, microwave shielding coatings, solar control coatings, dye-sensitized solar cell, potential nanometer-scale switch, selective radiation filter on architectural windows, solar cells, cathode material in lithium rechargeable batteries and some chemical sensing applications, photoconductor, antireflection coatings, interference items, polarizers, narrow band filters, waveguide coatings, IR detectors, temperature control of satellites, light emitting diodes and other optoelectronics.

In this paper, CuS thin films were deposited on three different substrates by spray pyrolysis deposition. Then these thin films were annealed at 50, 100, 150 and 200 °C for 1 h. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Hall effect measurements were obtained for thin films before and after annealing to find which thin film and at which temperature has better contact and can perform as a device. To the best knowledge of the authors the results presented in this paper are not reported so far in the literature, only deposition CuS on different substrate or annealing for one substrate were reported. This search studies the effects of four different temperatures for thin films deposited on three different substrates to find which one will be more suitable as a device according to its electrical properties.

2. Experimental

Copper chloride and sodium thiosulfate were used to prepare the solution for depositing CuS thin film by spray pyrolysis deposition. The deposition by this method is simple, cover a large area, low cost and widely used. The solution was sprayed on glass, ITO and Ti substrates at 50, 100, 150 and 200 °C which is suitable for deposition CuS because at higher temperature the film will peel and the lower temperature is not enough for composition CuS thin film on the substrate as there is no catalyst in this work so the temperature will take place the catalyst. The best results of CuS thin films were obtained at 200-210 °C, this range of temperature was chosen because CuS is reported to decompose at ≈220 °C. The distance between the nozzle and the substrates was 30 cm, which is the best spray distance because more than this will cause spray flight out of the substrate, less than this will cause the combined solution drops in one spot. Then after completing the deposition, these thin films were annealed at 50, 100, 150 and 200 °C for 1 h. Annealing can be defined as heat treatment of materials at elevated temperatures aimed at investigating or improving their properties. Material annealing can lead to the phase transition, recrystallisation, homogenization and relaxation of internal stresses. Structural and electrical properties were measured for thin films before and after annealing using XRD, FESEM and Hall effect measurements.
3. Result

3.1. Structural characteristics

The structure of CuS thin films on a glass substrate before and after annealing is shown in Fig. 1. Figure (1-a) reveals three orientations, namely (103), (006) and (102) which indicate a covellite CuS phase with hexagonal structure, and two orientations, namely (110) and (002) attributed to the chalcocite Cu$_2$S phase with hexagonal structure. Cu$_2$S has large minority carrier diffusion length and low sheet resistivity$^3$. Structure characteristics of these thin films after annealing at 50, 100 and 150 °C refer to higher intensity and three orientations namely (103), (102) and (106) for covellite CuS phase only, the intensity decreased with increasing temperature as shown in Fig. (1b-1d). Comparing to thin film structure before annealing, there is a change in some orientations of the crystals after annealing at 200 °C with reducing the intensity for CuS phase and increasing intensity for Cu$_2$S phase as shown in Fig. (1-e), there are just two orientations for CuS covellite phase with weaker intensity, namely (103) and (102), and two orientations for Cu$_2$S chalcocite phase, namely (002) and (101) with stronger intensity. The orientation (006) of CuS covellite phase disappeared, and the orientation (110) replaced by (101) for Cu$_2$S chalcocite phase after annealing.

![Fig. 1. XRD for CuS thin films on a glass substrate, (a) before annealing, (b, c, d, and e) after annealing for 1 h at (50, 100, 150, and 200°C) respectively.](image)

3.2. Morphological characteristics

It is observed from Fig. (2) that as-deposited thin films are relatively good (because they have no cracks, compact, homogeneous and uniformly covered). The different shapes of crystals were attributed to the nucleation that happened when depositing CuS on different substrates. For a thin film deposited on glass substrate, the structure has the shape of hexagonal and cubic crystals. Thin films deposited on ITO substrate and Ti substrates have plate structures. No oxidation happened for CuS films before annealing. FESEM scale is 50kx (1 µm).
After annealing at 50 °C, 100 °C, 150 °C and 200 °C for 1h, the thin films had a lot of agglomerations, and the size of crystals was larger than that before annealing which leads to large surface-to-volume ratio and high grains barrier density and that is the cause of increasing resistance as shown in Fig. (3). Plate structures and a large amount of agglomerated crystals were seen for CuS thin film deposited on glass. Also for thin films deposited on ITO and Ti substrates, they had bigger plates with very large amounts of agglomerations. The heat treatment may lead to oxidation or agglomeration which are very clear in Fig. (3). Due to this phenomenon there is a possibility for the formation of Cu₂O, Cu₂SO₄ that results in the increase in resistance. FESEM scale is 50kx (1 µm).
3.3. Electrical characteristics

Annealing all thin films at 50, 100, 150 and 200 °C for 1 h caused the sheet resistivity and the mobility to increase and the carrier concentration (density) to decrease, as shown from Hall effect measurements in the table (1). The increase in sheet resistivity can be attributed to the oxidation of the CuS thin films that happened during annealing, then at a certain temperature (200 °C) when the oxidation finished the sheet resistivity decreased. The carrier mobility also increased at high temperature, for semiconductors, the behaviour of the devices can be very different depending on whether there are many electrons with low mobility or a few electrons with high mobility. Therefore, mobility is a very important parameter for semiconductor materials. Almost always, higher mobility leads to better device performance. Conductivity is proportional to the product of mobility and carrier concentration (density). For example, the same conductivity could come from a small number of electrons with high mobility for each or a large number of electrons with a small mobility for each. The thin film deposited on Ti substrate has the highest mobility before and after annealing, so it is the best thin film for device performance. After annealing, all CuS thin films may expose to oxidation, increase in carrier mobility, and agglomeration which leads to high surface-to-volume ratio and large crystals barriers density that make the sheet resistivity increases, but as illustrated in table (1) the sheet resistivity for CuS deposited on ITO is the lowest so when it increased after annealing at 200 °C, it still the lowest. All films have high electrical conductivity, but CuS deposited on Ti substrate being the most conductive. CuS thin film is more conducting than the Cu2S thin film11, so the better conductive characteristics for the thin film after annealing at 200 °C may be attributed to the higher Cu2S phase intensity.

Table 1. Comparison between three types of substrates before and after annealing at four different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Glass substrate</th>
<th>ITO substrate</th>
<th>Ti substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sheet Resistivity (Ω/Sq)</td>
<td>Mobility (cm²/V.s)</td>
<td>Density (/cm³)</td>
</tr>
<tr>
<td>Before annealing</td>
<td>165.6</td>
<td>22.7</td>
<td>8.31E+17</td>
</tr>
<tr>
<td>50</td>
<td>1.129E+6</td>
<td>967</td>
<td>2.49E+12</td>
</tr>
<tr>
<td>100</td>
<td>5.924E+5</td>
<td>967</td>
<td>2.54E+13</td>
</tr>
<tr>
<td>150</td>
<td>3.582E+6</td>
<td>21.5</td>
<td>3.53E+13</td>
</tr>
<tr>
<td>200</td>
<td>2.793E+5</td>
<td>1.3E+4</td>
<td>8.56E+11</td>
</tr>
</tbody>
</table>

4. Conclusion

The SPD was successfully applied to deposit nanocrystalline CuS thin films from CuCl₂ and Na₂S₂O₃ at relatively low temperature without any complexing agent. The films were characterized by XRD, FESEM and four probe Hall effect measurements.

The appropriate increase of the temperature will enhance the crystalline growth of Cu₂S phase. The intensity of the diffraction peaks before annealing was stronger than those after annealing at 200 °C for CuS phase. However, contrarily, to CuS, Cu₂S phase before annealing have a stronger intensity than those after annealing at 200 °C. While the intensity increased very sharply for thin film annealed at 50 °C, then it decreased with increasing temperature (100 and 150 °C), and the structure was only covellite CuS phase.

The purpose of using all these substrates is to find which one has the best electrical properties (most conductive), so can perform as a device. The structure of the thin films after annealing has many agglomerations with bigger crystals; plates appear clearly in the thin films especially for the thin film deposited on ITO substrate.
As concluded from this paper; the CuS thin film deposited on Ti substrate annealed at 200 °C is the best thin film because it has higher mobility. The annealing helped the mobility to increase while the density decreased, and the resistivity increased because of the oxidation, high surface-to-volume ratio and large grains barriers that happened during annealing which is good for many applications, like gas sensor for CuS thin films because of their good electrical properties and solar cell for Cu$_2$S thin films because of their good optical properties.

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References