Effects of Annealing Temperature on Structural and Optical Properties Of CIGS Thin Films for Using in Solar Cell Applications

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Abstract. A copper indium0.5gallium0.5selenide2 thin films (CIGS) were deposited at room temperature on glass substrate by thermal evaporation technique. The deposited film were annealed at different annealing temperature (293, 100, 200 and 300)°C. The effect of annealing temperature on structural, optical and electrical properties CIGS films were studied by XRD, UV-Visible absorbance and Hall effect measurements. It is found that the crystallinety enhanced, optical energy gap increases and electrical conductivity decrease with increasing annealing temperature. Three design of solar cells, based on CIGS, were examined to reach the suitable solar cell with higher efficiency.

1. Introduction
CIGS is a I-III-VI2 compound semiconductor material composed of copper, indium, gallium, and selenium, with a chemical formula of CuInxGa1-xSe2, where the value of x can vary from 1 to 0.3. It is a tetrahedral bonded semiconductor, with the chalcopyrite crystal structure. The bandgap varies continuously with x from about 1.0 eV (for copper indium selenide) to about 1.7 eV (for copper gallium selenide)[1].

A copper indium gallium selenide solar cell (or CIGS cell) is a thin film solar cell. It is fabricated by depositing a thin layer of copper, indium, gallium and selenide on substrates, along with electrodes on the front and back to collect current. Because the material has a high absorption coefficient and strongly absorbs sunlight, a much thinner film is required than of other semiconductor materials. CIGS layers are thin enough to be flexible, allowing them to be deposited on flexible substrates.

CIGS cells being developed to reach silicon-like efficiencies, while maintaining their low costs, as is thin-film technology[2].

A p-type CIGS absorber layer is deposit in many techniques varied from high-temperature deposition like thermal evaporation [3] sputtering deposition [4] and low-temperature deposition techniques, screen print deposition [5] combined with a thin n-type like cadmium sulfide (CdS) to make heterojunction for photo-voltaic applications.

CIGS has an exceptionally high absorption coefficient of more than 10⁵ cm⁻¹ at higher energy photons[6]. Soda-lime glass [7] or flexible substrates such as polyimide or metal foils[8].

2. Experimental
A copper, indium, gallium, and selenium is made of Germany films were prepared onto different substrates by thermal evaporation technique in a high vacuum system of (10⁻⁵) torr using Edward coating unit model (E 306). The deposited films, on glass substrates, were examined by X-ray diffraction (XRD) measurements using (SHIMADZU diffractometer system (XRD-6000) in the range of 2θ from 20° to 60°, UV visible spectroscopy, The and atomic force microscopy type AA3000 Angstrom advanced and I-V characteristic MSIV.
3. Results and discussions

The X-Ray diffraction spectra for CIGS powder material, were recorded as illustrated in Fig (1). The inter planer distance \( (d_{hkl}) \) were calculated and compared with the standard valued in JCPDF as shown in Table (1). XRD pattern show a polycrystalline structure with monoclinic phase with high intensity for (112), (220), (312) and (332) directions and lower intensity for others. The crystalline size was calculated using Scherrer equation \([9]\) as shown in Table (1).

![Figure 1: X-ray diffraction of CIGS powder.](image-url)

### Table 1: X-ray diffraction parameters and crystalline size of CIGS powder.

| 2θ (Deg.) | FWHM (Deg.) | \( d_{hkl} \) Exp.(Å) | G.S (nm) | \( d_{hkl} \) Std.(Å) | hkl | card No. |
|-----------|-------------|------------------------|----------|-----------------------|-----|---------|
| 26.9130   | 0.1522      | 3.3102                 | 53.7     | 3.3121                | (112)| 35-1102 |
| 28.0217   | 0.1739      | 3.1817                 | 47.1     | 3.1801                | (103)| 35-1103 |
| 35.8478   | 0.1957      | 2.5030                 | 42.7     | 2.5021                | (211)| 35-1104 |
| 42.4348   | 0.3044      | 2.1284                 | 28.0     | 2.1291                | (105)| 35-1105 |
| 44.6739   | 0.2173      | 2.0268                 | 39.5     | 2.0281                | (220)| 35-1106 |
| 52.9565   | 0.3261      | 1.7277                 | 27.2     | 1.7281                | (312)| 35-1107 |
| 64.9565   | 0.3044      | 1.4345                 | 30.9     | 1.4340                | (400)| 35-1108 |
| 71.6957   | 0.3695      | 1.3153                 | 26.5     | 1.3150                | (332)| 35-1109 |

Fig. (2) shows the XRD patterns for (CIGS) thin films prepared by thermal evaporation and annealed at different annealing temperatures. Polycrystalline structure were observed in all samples with two phases tetragonal structure in nature of CIGS and with peaks diffraction at \( 2\theta = 26.98^\circ \), and \( 27.96^\circ \) with orientation (112) and (103) respectively, and CuSe hexagonal structure with peak located at \( 2\theta = 45.89^\circ \) belong (110) direction for 293K samples. Annealing at 200°C cause to appearance of another peaks corresponding to hexagonal structure at \( 31.19^\circ \) for (006) direction. While, at 300°C annealing temperature only CIGS peaks appeared at \( 2\theta = 26.73^\circ , 44.45^\circ \) with orientation (112) and
(220) with tetragonal structure. It can be concluded that the crystallinity of films is improved at 300°C with pure CIGS structure. The crystallize size (D) of CIGS thin film is estimated using Debye–Scherer’s formula

Summary of X-Ray characterization shown in Tables (2) with comparison between the experimental and the standard \( d_{hkl} \) values from International Centre for Diffraction Data (JCPDS). It can be concluded that by increasing annealing temperature the crystalline size increases. This means that the crystallinity of the films has improved due to defects reduction.

![Figure 2. X-ray diffraction of the CIGS thin films with deferent annealing temperature.](image)

**Table 2.** X-ray diffraction data for CIGS thin films with deferent annealing temperature

| 2θ (Deg.) | FWHM (Deg.) | \( d_{hkl} \)  | G.S (nm) | \( d_{hkl} \) Std.(Å) | hkl | card No. |
|-----------|-------------|----------------|----------|-----------------------|-----|----------|
| 26.9130   | 0.1522      | 3.3102         | 53.7     | 3.3121                | (112)| 35-1102  |
| 28.0217   | 0.1739      | 3.1817         | 47.1     | 3.1801                | (103)| 35-1103  |
| 35.8478   | 0.1957      | 2.5030         | 42.7     | 2.5021                | (211)| 35-1104  |
| 42.4348   | 0.3044      | 2.1284         | 28.0     | 2.1291                | (105)| 35-1105  |
| 44.6739   | 0.2173      | 2.0268         | 39.5     | 2.0281                | (220)| 35-1106  |
| 52.9565   | 0.3261      | 1.7277         | 27.2     | 1.7281                | (312)| 35-1107  |
| 64.9565   | 0.3044      | 1.4345         | 30.9     | 1.4340                | (400)| 35-1108  |
| 71.6957   | 0.3695      | 1.3153         | 26.5     | 1.3150                | (332)| 35-1109  |
The 2D AFM images and granularity accumulation distribution chart of CIGS structures synthesized by thermal evaporation technique annealed at different temperatures (Ta=100,200 and 300 °C) are shown in Fig. (3). The CIGS structures have balls or semi-balls -shaped. The grains are homogenous. By using special software the estimated values of root mean square RMS of surface roughness average and average grain size are listed in Table(3). The CIGS structures thin films agglomerate increases as annealing temperatures. The results of average grain size have agreed with those estimated from XRD and it is clearly seen that the surface was very smooth. It was found that the size of grain and the RMS of surface roughness increases as annealing temperatures increase, but with cracks at high temperature.

Figure 3. AFM images and granularity accumulation chart for CIGS thin films annealed at different temperature
Table 3: Particle size, average roughness and root mean square for CIGS thin films annealed at different temperature

| Ta (°C) | Root mean square (nm) | Average Grain Size (nm) |
|---------|-----------------------|-------------------------|
| 293     | 6.154                 | 87.2                    |
| 100     | 8.194                 | 110                     |
| 200     | 9.157                 | 112                     |
| 300     | 18.847                | 116                     |

Fig. (4) shows the optical transmission for CIGS films, deposited on glass substrate by thermal evaporation deposition and annealed with different annealing temperature, was carried out in the wavelength range 500–1100 nm. The transmittance of all deposited thin films increases with increasing of wavelength (λ) and increases with the increase of annealing temperature in the visible region. There are a Swanapol shape due to high film homogeneity[10]

![Figure 4](image4.png)

Figure 4. The transmission curves for CIGS thin films annealed at different temperature

The optical energy gap values were determined by Tauc equation. Fig. (5) shows the relation between $(\alpha h\nu)^2$ with photon energy ($h\nu$). It can be seen from this figure that the energy gap increase from 2.35 eV to 2.6 eV with increasing annealing temperature from RT to 300 °C maybe due to phase transition.

![Figure 5](image5.png)

Figure 5. Tauc plot for CIGS thin films annealed at different temperature
Fig. (6) shows the I-V characteristics for solar cells with different configurations Al grid/CdS/CIGS/AL, ITO/CdS/CIGS/AL and Algrid/CdS/CIGS/Si/AL using CIGS films annealed at 300°C. It can be seen from this figure that the first is the best one with highest $V_m$, $I_m$ and solar cell efficiency, as shown in Table (4).

**Figure 6.** The I-V characteristics for CIGS solar cells with different configurations (a) Al grid/CdS/CIGS/AL (b) ITO/CdS/CIGS/AL and (c) Al grid/CdS/CIGS/Si/AL.
### Table 4: Solar cells parameters for CIGS solar cells with different configurations

| Thickness | Al grid/CdS/CIGS/AL | ITO electrode base (ITO/CdS/CIGS/AL) | AL/Si electrode base (Al grid/CdS/CIGS/Si/AL) |
|-----------|----------------------|--------------------------------------|-----------------------------------------------|
| T=1000nm  | 1                    | 0.502                                | 0.148                                         |
| T=1000nm  | 1                    | 0.470                                | 0.002                                         |

4. Conclusions

Structural properties and optical for as deposited and annealed CIGS thin films at (100, 200 and 300) °C prepared by thermal evaporation I-V characteristics for solar cell can be summarized as follows:

- The XRD tests of CIGS powder and thin films indicates polycrystalline structure. Two phases tetragonal CIGS and hexagonal CuSe structure were observed at RT samples. Annealing at 300°C cause to convert to pure CIGS structure and enhance films crystallinity. The crystalline size increase with annealing temperature.
- The AFM topographic images, founded that the agglomerate increases as annealing temperatures, but with cracks at high temperature. The surface roughness increased by increasing annealing temperature
- The optical energy gap increase from 2.35 eV to 2.6 eV with increasing annealing temperature.
- I-V characteristics for solar cells with different shapes show that the best solar configuration is Al/CdS/CIGS/AL than the others examined.

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