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Electrical and Optical Properties of $CuInSe_2$ Thin Films

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Abstract: *In this study, $CuInSe_2$ (CIS) thin films were prepared with various spray parameters. Their optical and electrical properties were investigated. It was observed that optical transmittance of CIS thin films prepared at 190±10 ºC substrate temperature is between 0.2–5.1 percent in visible region. Values of resistivity, resistance and sheet resistance were measured in the intervals of 0.01–72.0 Ω.cm, $0.96–9.7\times10^3$ Ω and $0.04\times10^2–438.4\times10^2$ $\Omega\cdot cm^{-2}$ respectively. Type of conductivity was detected as p-type. Resistivity was also measured by Van der Pauw method and found to be between 0.76×10^{-3} - 2.02×10^{-3} Ω.cm.*
Keywords: *Thin film, thickness, resistivity, optical transmittance.*

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I. Introduction

There are various fabrication methods as thin film making techniques. In addition to methods such as crystal growth, chemical deposition, evaporation, vacuum technique; chemical spray pyrolysis (CSP) is also used. Spray pyrolysis process is one of the most preferred film preparation technique by researchers because it has a cheaper cost than other methods. This method has been in use since the 1960s. It was first used in 1966 for the preparation of sulphide and selenite thin films [1].

Heterojunction thin film solar cells are made from a p-type semiconductor thin film and a n-type semiconductor thin film with this method.

Various materials have been used to obtain high-efficiency solar cells until now. One of them is CIS thin films, which exhibit a p-type semiconductor property and are a very good absorber. Studies on solar cell applications of these thin films, which have a good semiconducting property due to high absorption coefficient (10^4-10^5 cm^{-1}) and proper band gap (~ 1 eV), are underway [2, 3, 4].

In this work, optical and electrical properties of CIS thin films, which are preferred due to their appropriate properties, will be examined in the construction of $SnO_2/CuInSe_2$ thin film solar cells [5].

II. Material And Method

In this study, CIS thin films were prepared by CSP. The CSP is simply the process of spraying a finely atomized aqueous solution of a certain concentration onto a suitable hot substrate. The chemical substances present in the solution to be sprayed must satisfy these conditions: (a) The heat-insoluble chemical substances in the solution must have complexes that can form the desired thin film material, which can enter into active chemical reactions. (b) The other components in the solution containing the carrier fluid should readily evaporate at the substrate temperature.

Substrate temperature is very important for the precipitation process in this method, and the structure of the deposited film is very effective on its properties. Below the optimum temperature required, the thin film on the substrate surface does not form the desired properties, whereas the solution evaporates and no film is formed.

In the film preparation, 2.5 × 7.5 cm size glasses were used as substrate. The film character and quality are strictly related to the cleanliness of the glass substrates, and the cleaning of these glasses was meticulously carried out in the following stages. It was first washed in detergent water, then in purified water. Then it was left to stand for 3 minutes in methyl alcohol and dried to remove the oil stains and organic substances which may be on it. Finally, it was dried in isopropyl alcohol for 3 minutes.

2.1. Preparation Thin Films of $CuInSe_2$ by Chemical Spray Pyrolysis

The following materials are required to form of CIS thin film. (a) Copper chloride dihydrate ($CuCl_2$•$2H_2O$), (b) Indium chloride ($InCl_3$) and (c) N,N-dimethylselenourea ($NH_2(CH_3)_2NCSe$). When these three substances are mixed in the same container simulataneously, the formed solution loses its characteristic in a very short time due to chemical reaction between the air and the environment. Thus, items (a) and (b) were prepared in a container, and item (c) was prepared in another container. The solution prepared at the same molarity in both vessels was sprayed at the moment of spraying and then sprayed on the submerged plate at a certain temperature without waiting to obtain CIS thin films.

$(NH_2(CH_3)_2NCSe)$ substance in the formation of CIS thin film is a substance sensitive to heat, light, moisture and air. Since the d orbital of selenium (Se) atom is not full, it fills this gap with oxygen in the air and reaches saturation. That is, Se atom is oxidized to form SeO. In addition, when water vapor is present in the air, Se can also oxidize by grabbing moisture. Therefore, weighing the dimethylselenourea, the preparation of the solution was carried out in a nitrogen-enclosed environment. Thus, the interaction between air and moisture was prevented. In this study, CIS thin films were prepared with the spray parameters given in Table 1.

Table 1. Spray parameters used in the preparation of CIS thin films

Chemicals	$CuCl_2 \cdot 2H_2O$, $InCl_3$, $NH_2(CH_3)_2NCSe$
Spray solution	$CuCl_2 \cdot 2H_2O+InCl_3+NH_2(CH_3)_2NCSe+CH_3CH_2OH$(ethyl alcohol)
Spray concentration	0.02 M
Substrate temperature	190 ± 10 ºC
Heading distance	30 cm
Spray diameter	0.2 mm
Spray rate	15 mL/min.

Since CIS thin film contains three elements, three chemicals are required to form it. $CuCl_2 \cdot 2H_2O$ (copper chloride dihydrate) for Cu, $InCl_3$ (indium chloride) for In and $NH_2(CH_3)_2NCSe$ (N.N-dimethylselenourea) for Se. The chemical reaction of $CuInSe_2$, CO_2, $(CH_3)_2NH$, NH_3, HCl and CH_3CH_2OH occurs when the solution of these three substances in which ethyl alcohol (CH_3CH_2OH) is used as the solvent is sprayed on the substrate at the required temperature [6,7,8]. $CuInSe_2$ is solid state, and the others are in gaseous state. It is necessary to be careful and to take precautions when working with these substances since they are harmful substances for the body. These harmful materials include CO_2 (carbon dioxide), $(CH_3)_2NH$ (dimethylamine), NH_3 (ammonia), HCl (hydrochloric acid) and CH_3CH_2OH (ethanol).

2.2. Calculation of Thickness

By weighing using the precision scale, the thicknesses were calculated as follows: The glass bottom mass is subtracted from the total mass after the film is formed, and the film mass is found. Film thickness d, dimensions a and b, mass m, density ρ, and volume V = d · a · b

$$d = {}^{m}/_{\rho ab}$$

Thicknesses were calculated with this equation.

2.3. Resistivity Measurement

The resistivities of CIS thin films prepared in this study were measured by four point probe and Van der Pauw methods [9].

2.4. Optical Transmittance Measurement

Optical transmittances of prepared CIS thin films were measured by LKB BIOCHROMULTROSPEC 4050 Spectrophotometer. The wavelength range is between 200 nm and 900 nm. Optical permeability of glass + thin film was measured after optical transmittance of glass used as underlayer was taken as 100% when permeability was taken.

III. Results And Discussion

The CIS thin film is a semiconductor with direct band gap, forbidden energy range (E_g) of 0.96 to 1.04 eV, and absorption coefficient of α, exceeding 10^5 cm^{-1}. The conductivity type of CIS thin films grown by spraying is p [3].

3.1. Electrical Properties

In this study, the electrical properties of CIS thin films prepared by spraying method were examined by using a Four Point Meter (FPP5000 FOUR POINT PROBE Veeco Instruments Inc.). Resistance, layer resistance, resistivity, as well as the conductivity type can be determined with this tool. Conductivity type p of CIS thin film samples prepared was observed. In the measurements made with different samples, the resistance was $0.96\text{-}9.7\times10^3$ Ω and the layer resistance was $0.04\times10^2\text{-}438.4\times10^2$ $\Omega\cdot cm^{-2}$.

The resistivity was also measured by the Van der Pauw method [9]. The resistivities were calculated on the basis of the thickness values obtained by the weighing method according to this method. Table 2 shows the measured values of resistivity measured by four point probe (ρ_d) and Van der Pauw method (ρ_v) for some CIS thin films prepared at 190 °C ± 10 °C subcritical temperature.

Table 2. Resistivity and thickness values of some CIS thin films

Sample No	Resistivity, ρ_d ($\times 10^{-2}$ $\Omega\cdot$cm)	Resistivity ρ_v ($\times 10^{-3}$ $\Omega\cdot$cm)	Thickness (μm)
CIS-17	6.8	1.28	0.32
CIS-19	3.3	0.76	0.53
CIS-20	2.7	0.77	0.77
CIS-22	2.9	1.38	0.73

The graph showing the variation of the resistivities of some CIS thin film samples with respect to their thickness is shown in Fig. 1. As can be seen in the figure, the resistivity decreases with thickness.

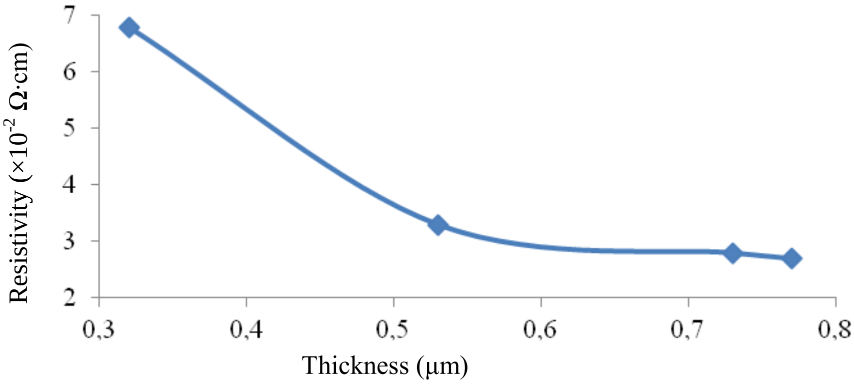

Figure 1. Variation of resistivities of some CIS thin films with respect to thickness

3.2. Optical Properties

Optical properties, such as electrical properties of CIS thin films, also vary with various parameters. α to the optical absorption coefficient, Eg band gap, subatomic temperature, solution concentration.
Fig. 2 shows a graph of the optical transmittance of some CIS thin films relative to the wavelength. In the visible region, the optical transmittance of these thin films ranges from 0.2 to 5.1%.

Table 3. Variation of the optical transmittances of some CIS thin films according to wavelength

Wavelength(nm)	**350**	**400**	**450**	**500**	**550**	**600**	**650**	**700**	**750**	**800**	**850**	**900**
CIS-3	0.2	0.2	0.2	0.4	0.8	1.7	2.7	2.8	2.2	1.5	1.1	0.7
CIS-6	0.2	0.3	0.3	0.7	1.5	2.9	4.2	4.5	3.9	3.0	2.2	1.6
CIS-15	1.2	1.4	1.3	1.4	1.6	2.1	2.4	2.5	2.2	1.8	1.5	1.3
CIS-16	0.3	0.4	0.5	0.8	1.2	1.9	2.8	3.6	2.4	2.2	1.7	1.4

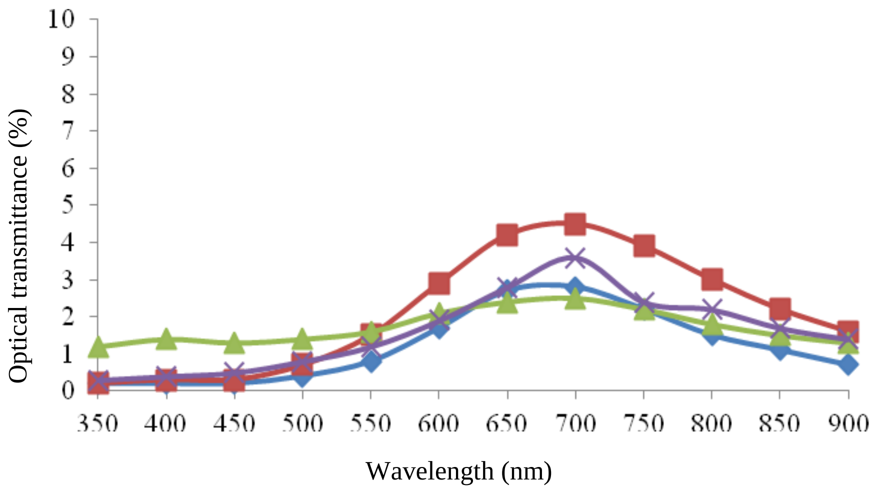

Figure 2. Variation of optical transmittance of some CIS thin films according to wavelength

IV. Conclusion

The electrical properties and optical transmittance of CIS thin films prepared by CSP were investigated. The thickness of CIS thin films prepared at different spraying times varied between 0.32-0.77 μm.

Electrical properties were measured with four point probe. The resistivity was 0.02-0.34 Ω·cm, the resistance was $0.964\text{-}9.7\times10^3$ Ω and the sheet resistance was $(0.04\text{-}438.4)\times10^2$ $\Omega\cdot cm^{-2}$. The resistivity was also measured by the Van der Pauw method and was found to be $(0.76\text{-}2.02)\times10^{-3}$ Ω·cm. It was seen that the conductivity type was p in the measurements made. The literatures of autocorrelation range from 10^{-3} to 10^3 Ω·cm. The type of conductivity encountered in the literature is also usually p. Therefore, the data obtained is in agreement with the literature values.

As can be seen from Fig. 2, the optical transmittance of CIS thin films was found to be between 0.2 and 5.1% at wavelengths of 350-900 nm. From these values, it is understood that these thin films behave as a very good absorber in the visible region.

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