

OPTICAL CHARACTERIZATION OF CHEMICALLY DEPOSITED Cu_xS LAYER FOR THIN FILM $\text{CdS}/\text{Cu}_x\text{S}$ SOLAR CELLS

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ABSTRACT

A chemical bath has been developed for the formation of Cu_xS thin film useful for low cost $\text{Cu}_2\text{S}/\text{CdS}$ solar cells. The coating, on glass substrates has been characterized by optical methods and reported.

Key words: Solar cells, $\text{Cu}_2\text{S}/\text{CdS}$ cells, optical absorption measurement

INTRODUCTION

Availability of sunlight in plenty makes conversion of solar energy into electricity a cheap alternative for the fast depleting natural energy resources. The costly fabrication methods in the $\text{Cu}_2\text{S}/\text{CdS}$ solar cell manufacturing make the cells uneconomical for terrestrial purposes. Hence there is the necessity for the evaluation of a simple and economical method at each and every step of solar cell fabrication. Amongst the different techniques, screen printing [1] is a very low cost method for the formation of thin film CdS on any desired substrate in a relatively simple manner. Though Cu_2S layers can be formed successfully by the dipping process [2] which is widely used in fabrication of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells, stoichiometric control is difficult. As an alternative, the chemical bath deposition technique has been used in this laboratory to coat Cu_xS , which makes use of cuprous chloride as the starting material instead of copper sulphate [3]. The bandgap, refractive index, absorption coefficient and stoichiometry of Cu_xS coating deposited by this technique have been studied by optical methods.

EXPERIMENTAL

The bath used for chemical deposition of Cu_xS consisted of 0.5% cuprous chloride solution to which 25 to 50 ml of glacial acetic acid was added to convert the sparingly soluble cuprous chloride to cuprous acetate. This solution appeared dark blue in colour indicating the presence of Cu^{2+} ions which would result in CuS rather than Cu_2S . So a controlled amount of a dilute solution of hydrazine hydrate (reducing agent) was added to reduce all the cupric ions to cuprous ions forming a colourless solution. When ammonia (pH 10.5-12) was added to this solution Cu^+ -ammonia complex was formed. The bath was heated to 45°C and magnetically stirred to obtain a clear and homogeneous solution. 0.1 N thiourea was slowly added and a brown tinge appeared after two minutes indicating the beginning point for formation of Cu_xS . During the reaction, the Cu^+ from the complex combines with the S^{2-} ions liberated from the decomposition of thiourea. The glass substrates used were first cleaned with running water, Teepol solution, followed by rinsing in distilled water, the substrates were then boiled in triple distilled water and finally cleaned with acetone. The cleaned glass substrates were kept horizontally inside the bath and 2 ml of thiourea was periodically added to obtain the required thickness.

Surface morphology and stoichiometry of the film were studied using scanning electron microscope (SEM). Optical absorption measurements were recorded with a spectronic 21 spectrophotometer placing an uncoated glass slide in the reference beam. Four-probe method was used for resistivity measurements and refractive index determined by ellipsometer.

RESULTS AND DISCUSSION

The colour of the as-grown films varies from brown to grey brown for thin

and thick films. Figure 1 depicts a micrograph of the chemically deposited film, which has a uniform dark background coating of Cu_xS over which white spots are observed. These spots are the copper rich nodules on the

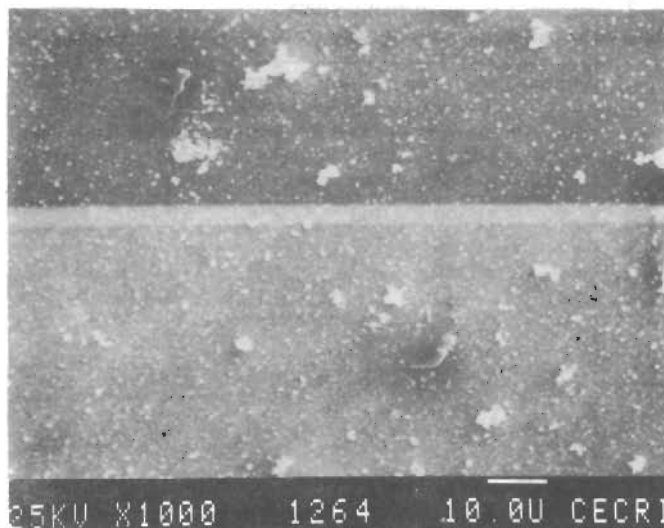


Fig. 1: Micrograph of Cu_xS chemically grown thin film

the surface. Similar results have been reported [4], which suggest that these nodules help in improving the stoichiometry upon heat treatment. X-ray microanalysis data on these films are shown in figure 2. Resistivity of the films was of the order of 7×10^{-2} ohm.cm. These are in agreement with results reported earlier [5]. In Table I the results on the stoichiometry 'x', sulphur content and resistivity values of the films are presented. The optical absorption spectrum of the films deposited under different conditions is shown in figure 3. It is observed that the absorption minimum shifts from 850 to 700 nm which could be attributed to the increase of sulphur content [6]. Also the total absorption in the long wavelength region is found to increase with sulphur content. The higher absorption associated with the $\text{Cu}_{1.86}\text{S}$ coating may be due to the combined formation of LT digenite and djurleite [2]. An analysis of the absorption spectrum (Figure 4) yielded direct bandgap values in the range 2.4-2.6 (cf. Table I). The bandgap values are found to decrease with increase of stoichiometry. Refractive index values measured by the ellipsometry technique yielded values cf. Table I which are comparable with the reported values [4].

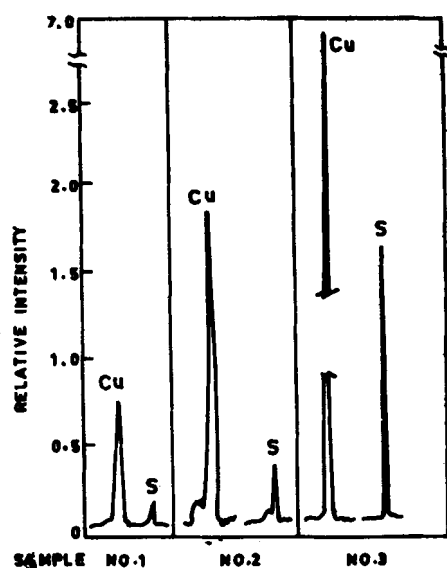


Fig. 2: Graphical X-ray micro analysis data

Table I: Optical and electrical parameters of Cu_xS films—chemically grown

Sample	Composition of Cu _x S (x)	Sulphur content (relative)	Absorbance minimum (nm)	Direct energy gap E _{g,d} (eV)	Resistivity (ohm-cm)	Refractive Index (n)
No. 1	1.45	0.409	700	2.58	5.9×10^{-2}	3.2
No. 2	1.75	0.364	750	2.48	6.6×10^{-2}	3.3
No. 3	1.86	0.349	850	2.38	7.4×10^{-2}	3.6
No. 4	1.86	—	—	2.58	3×10^{-2}	3.08

[3]

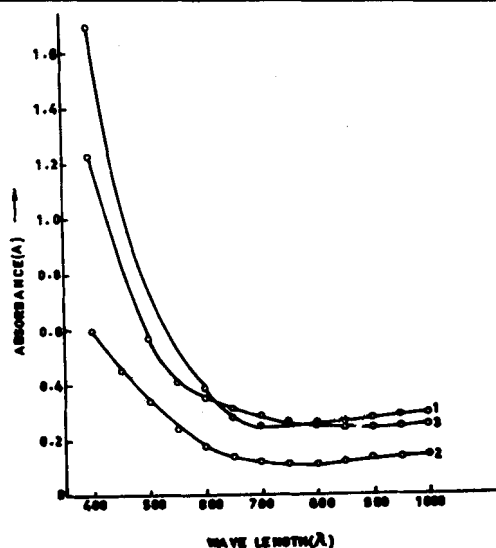
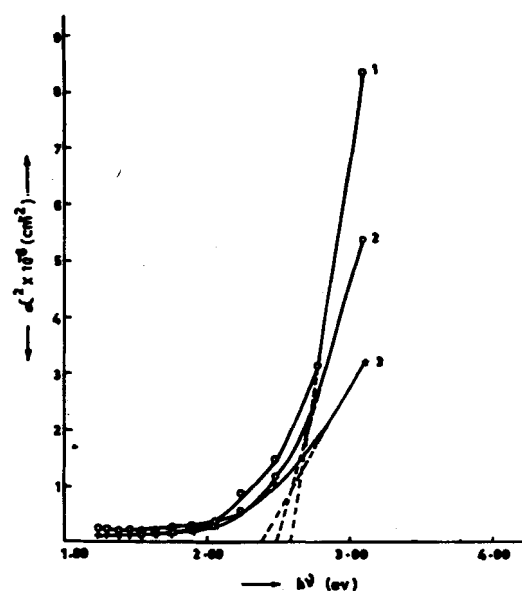
Fig. 3. Optical absorbance spectra for typical Cu_xS films (1) x=1.45 (2) x=1.75 (3) x=1.86

Fig. 4: Square of absorption coefficient as a function of the photon energy (1) x=1.45 (2) x=1.75 (3) x=1.86

CONCLUSION

In the chemical deposition technique the ion production is controlled by the addition of either ammonia or thiourea. Here even small traces of Cu²⁺ ions present in the starting material can be completely eliminated before formation of complex which is not the case when copper sulphate is used as the starting material where triethanolamine-Cu²⁺ complex is formed. Even though the stoichiometry attained is 1.86, further control of composition would yield layers with X=2. Thus this method appears to be a simple and economical process for the formation of Cu_xS films in CdS/Cu_xS solar cell applications.

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REFERENCES

1. M Jayachandran, Mary Juliana Chockalingam, K Nagaraja Rao, I Radhakrishna and N Rangarajan, Paper to be presented in the National Solar Energy Convention 1985, IIT, Kharagpur
2. B O Seraphin, "Solar Energy conversion", Springer-Verlag, Berlin (1979), p. 213
3. E Fatas, T Garcia, C Montemayor, A Medina, E Garcia-Camarero and F Arjona, *J Mat Chem Phys* 12 (1985) 121
4. F Arjona, E Garcia Camarero, R Duo and E Fatas, *J Power Sources*, 9 (1983) 41
5. S Couve, L Gousskov, L Szepessy, J Üedal and E Castel, *Thin Solid Films*, 15 (1973) 223
6. R D Engelken, H E McCloud, *J Electrochem Soc*, 132 (1985) 567