

## EFFECT OF THERMAL TREATMENTS ON THE PROPERTIES OF $\text{Cu}_x\text{S}$ FILMS OBTAINED BY EVAPORATION

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(Received May 7, 1982)

### Summary

It has been observed that  $\text{Cu}_x\text{S}$  films with a high sulphur content ( $x < 1.9$ ) transform into the chalcocite phase ( $x > 1.99$ ) after undergoing thermal treatment at 170 °C under vacuum, following evaporation of a thin copper film of 80 - 120 Å thickness. Similar treatments in an oxygen atmosphere, or in air (for longer than 5 min) do not result in such high stoichiometries.

It was also observed that the evaporation of a thin (~ 80 Å) copper film on  $\text{Cu}_x\text{S}$ , followed by the same thermal treatment under vacuum, noticeably improves the  $\text{Cu}_x\text{S}/\text{CdS}$  heterojunctions due to a rise in the fill factor.

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### Introduction

In spite of the fact that the evaporation method, described several years ago [1], cannot compete with the "Clevite" method [2] in the manufacture of solar cells, we still believe that it is a suitable method for the study of basic properties of materials and, in particular, of optical properties where a great variety of results are obtained.

The evaporation of a copper layer of 100 Å thickness onto the  $\text{Cu}_x\text{S}$  film, followed by air heat treatment, was investigated by Bogus [3] in order to optimise the efficiency of the heterojunctions. Bloss *et al.* [4] proposed a model to interpret the effects of this method. Their studies are based on the analysis of the variations in open-circuit voltage and in short-circuit current resulting from the application of the treatment.

In the present work, we have studied the variations in the optical and electrical properties of evaporated copper sulphides of several stoichiometries with thermal treatments applied after evaporation of a thin copper film.

Two types of samples were used: the first on a glass substrate in order to distinguish clearly the effect of the treatments and to study carrier diffusion mechanisms between  $\text{Cu}_2\text{O}$  and  $\text{Cu}_x\text{S}$  layers. The second samples were obtained by evaporating  $\text{Cu}_x\text{S}$  on  $\text{CdS}$  and were used to observe the effect of the treatments on the efficiency and on the characteristics of these heterojunctions.

## Experimental

Samples were prepared on glass substrates and the film was deposited under vacuum at  $10^{-6}$  Torr at thicknesses of 700, 1500 and 2000 Å.

Throughout the evaporation process, the substrate was kept at 120 °C as we have previously reported [5], since phases close to  $\text{Cu}_{1.99}\text{S}$  are obtained under these conditions.

Reflection and transmission measurements have been used to determine optical constants, although other methods could also be used (*e.g.*, reflectivity and phase at differing angles of incidence, transmittance of samples of differing thickness, etc.). The method of calculation accounts for multiple reflections [6] and uses Bennet's hypothesis [7] with the following formulae:

$$T_f = T_{ob} \frac{(1 - R'_s)(1 - R'_s R_{ob})}{(1 + R'_s)(1 - R'_s)^2}$$

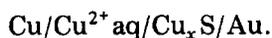
$$R_f = R_{ob} - T_f^2 \frac{R'_s}{1 - R_{ob} R'_s}$$

where  $R'_s$  is the reflectance at the substrate-glass interface and  $T_{ob}$  and  $R_{ob}$  are the transmittance and reflectance measured with a spectrophotometer. The absorption and reflection coefficients have been calculated from  $T_f$  and  $R_f$  by means of a computer program.

After determining the absorption coefficient, gaps and refraction index, a copper layer of between 80 and 120 Å was evaporated on the samples. Vacuum treatment at 170 °C for 30 min, or air treatment at 170 °C for a few minutes, was given to different samples.

Van der Pauw's method [8] was used to determine the carrier concentration of copper sulphide samples before and after the above thermal treatments. In each case, four gold points evaporated on the copper sulphide layers, providing good ohmic contact, served as electrodes. Measurements were carried out with the samples in magnetic fields of 14 kGauss, and currents ranged between 10  $\mu\text{A}$  and 1 mA.

The electrochemical determination of the stoichiometry of copper sulphide films was carried out using the method proposed by Castel and Vedel [9] based on e.m.f. measurement of the cell.



The  $\text{Cu}/\text{Cu}^{2+}$  system was shown to be suitable as a reference by measuring its potential vs. S.C.E. The resulting value equals the calculated theoretical value within a  $\text{Cu}^{2+}$  ion concentration of 0.001 to 0.1M. Oxygen was removed from the cell solution by means of purified nitrogen. The reference electrode was separated from the working electrode by means of a diaphragm in order to avoid contamination of the  $\text{Cu}_x\text{S}$  by  $\text{Cu}^+$  ions resulting from  $2\text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{2+}$ .

From an electrical point of view, the high resistivity of the films and the low values of the potentials to be measured have necessitated working conditions with a high degree of protection from noise and from both parasitic and static potentials. Likewise, it was necessary to construct a differential amplifier with a very high input impedance and common-mode rejection ratio. As a result, potential values could be achieved within a few seconds with a fluctuation equal to or less than 0.2%. The short time required to achieve a stable value decreases any risk of electrode contamination and of changes in the  $\text{Cu}_x\text{S}$  film.

## Results

The samples were divided into three groups: Q-1 (evaporated heterojunctions), Q-2 (the same heterojunctions after evaporation of copper followed by vacuum heat treatment) and Q-3 (samples with air heat treatment). Direct and indirect gaps (see Fig. 1), refraction index, composition,

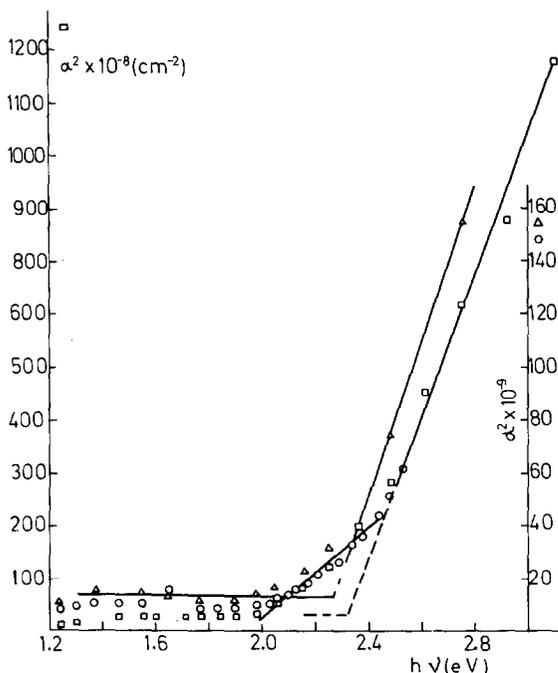


Fig. 1. Determination of direct gap for evaporated samples of  $\text{Cu}_x\text{S}$ .  $\square$ , Q-1;  $\circ$ , Q-2;  $\triangle$ , Q-3.

and carrier concentration are given in Table 1. Of the various films obtained, those of 2000 Å thickness were used.

The heterojunctions studied were obtained by evaporating 1500 and 2000 Å of copper sulphide on cadmium sulphide substrates supplied by Prof. Dr. H. Bloss (Stuttgart University) and similar treatments were given.

At an illumination intensity of 90 mW/cm<sup>2</sup> and for Q-1 heterojunctions we found an open-circuit voltage of 480 mV and short circuit currents of 8.4 mA/cm<sup>2</sup>. The FF was 45%. In Q-2 samples, the FF was observed to increase significantly to 69% and there was a slight increase in the short circuit current which resulted in 11.4 mA/cm<sup>2</sup> at the same illumination (Fig. 2). In Q-3 heterojunctions, the short circuit current increased sharply to about 14 mA/cm<sup>2</sup>, the FF was around 54% and there was a slight decrease in the open-circuit voltage.

These results show an improvement in the stoichiometry of the copper sulphide films with vacuum heat treatment. This can be interpreted as an

TABLE 1

Direct and indirect gaps, refraction index, composition, and carrier concentration of Cu<sub>x</sub>S.

	$E_{gd}$ (eV)	$E_{gL}$ (eV)	$n$	$x$	$p$ (cm <sup>-3</sup> )
Q-1	2.22	1.1	3.6	1.90	$1.5 \times 10^{19}$
Q-2	1.99	1.16	3.3	1.99	$1.04 \times 10^{19}$
Q-3	2.27	0.99	2.8	1.85	$8.1 \times 10^{21}$

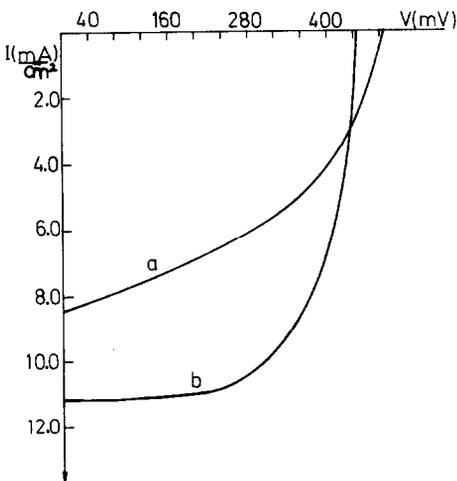


Fig. 2. I-V characteristics of CdS/Cu<sub>x</sub>S heterojunctions: (a) before heat treatment; (b) after vacuum heat treatment.

increase in the  $\text{Cu}_2\text{S}$  phase, due to diffusion of the surface copper to the bulk  $\text{Cu}_2\text{S}$ .

On the other hand, when the copper evaporation is followed by air heat treatment, the stoichiometry passes to phases of higher sulphur content. It is possible that, during the copper oxidation process, copper is extracted from the  $\text{Cu}_x\text{S}$  because there is a greater affinity between copper and oxygen than between copper and sulphur, which is in agreement with refs. 3 and 4. If this process predominates over the diffusion of copper in sulphur, the  $\text{Cu}_x\text{S}$  would gain a type  $p$ -conductivity which would explain the increase in efficiency of the heterojunction.

## Conclusions

The variations in optical and electrical properties of  $\text{Cu}_x\text{S}$  films obtained by evaporation and vacuum heat treatment, together with electrochemical diagnosis, confirm that although the diffusion of the surface copper in the  $\text{Cu}_x\text{S}$  improves the stoichiometry, the oxidation produced by air heat treatment creates copper vacancies in the bulk of the  $\text{Cu}_x\text{S}$  and, hence, reduces its stoichiometry.

Therefore, the observed improvement in the efficiencies of the  $\text{Cu}_2\text{S}/\text{CdS}$  heterojunctions brought about by these treatments corresponds to different mechanisms. The combined results show that the predominating mechanism in the cells treated in air is produced by the  $\text{Cu}_2\text{O}$  layer.

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