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# Correlation of the near-infrared optical absorption with Cu concentration in coevaporated Cu–In–S films

J.F. Trigo *, A. Bollero, J. Herrero, M.T. Gutiérrez

*Dep. of Energy, CIEMAT, Avda. Complutense 22, 28040 Madrid, Spain*

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ABSTRACT

We have deposited Cu–In–S films by an innovative modulated flux deposition (MFD) procedure performed in a static physical evaporation chamber in compositional ranges as diverse as: [In] ranging 10–70%, [Cu]=2–43% and [S]=20–50%. We propose optical absorption ($A\%=100-R\%-T\%$) in the near-IR (about 0.5 eV or 2500 nm) as a non-contact measurement which could be indirectly correlated with chemical composition.
The films, characterized by spectrophotometry ($A\%$) and sheet resistance ($R$) by four-terminal sensing measurement, were classified in compositional groups by the use of the two-dimensional parameter ($R$, $A\%$). Interestingly, the optical absorption $A\%$ was linearly correlated with Cu content in our compositional range while $R$ presents a jump back related with the variation of S concentration. The independence of $R$ and $A\%$ in this case is discussed in terms of different conduction mechanisms.



## 1. Introduction

Elemental coevaporation of copper indium and sulfur ($CuInS_2$) for photovoltaic application is an increasingly used technique where the stoichiometry control is the main challenge [1,2]. Several control methods have been demonstrated but much of them result in expensive and complex setups. There is a long list of real time monitoring and in-situ diagnostic methods for thin film fabrication that has been applied for fabrication of $CuInS_2$/CIGS films (EDXRD, in-situ XPS, UPS, Raman, ellipsometry, light scattering, pyrometry…) [3–5]. The last one is now a routine instrumentation in CIGS coevaporation and its introduction represented an important advance in cell efficiencies [4]. Sheet resistance (Rs in Ω/□ or simply $R$ in Ω) is an easy to implement in-situ measurement, but it is not univocally related with $CuInS_2$ composition. As a ternary compound, $CuInS_2$ composition is a two-dimensional space and at least another independent measurement should be used. Additionally, no need to optical models, calculation or thickness knowledge, could make it useful for in-situ control.

Drude's free electron theory has been extensively utilized to understand the relationship between the optical and electrical properties of thin films. Its use has been very successful in the field of transparent contact oxides (TCO) where this relation is the key of the application [6,7]. In the last work, the density of free carriers and their mobility were independently estimated from optical free carrier absorption and compared with that obtained by Hall measurements. The agreement was notable for the concentration of free carriers and the discrepancies in carriers mobility was satisfactory explained due to different spatial range that the optical excitation and DC conductivity are probing. The grain boundaries hinder the carrier transport if the carrier density is not too high. It looks like IR optical absorption (or pyrometry) and DC conductivity are strongly related but could be complementary measurements in some manner because DC conductivity would be more sensitive to the morphology. In the present work we have tried to explore this complementarity in a phenomenological procedure that correlates these measurements with averaged composition of $CuInS_2$ films grown by coevaporation. We have not paid attention to the deposition conditions as no relation with fabrication parameters will be drawn and we needed the wider compositional space possible. Although we have used ex-situ measurements of $A\%$ and $R$, we realize that many technical problems would arise for the measurements to become compatible with the deposition process, especially if non transparent conductive layers are added to the substrate. We have not tried to solve this questions but a suggestion would be the use of removable glassy test samples.

## 2. Experimental

Several $CuInS_2$ films have been prepared onto 10×10 cm soda-lime glass substrates by the MFD procedure in a static physical evaporation chamber [8,9]. They have been grown in very different conditions (simultaneous or sequential fluxes, constant and ramping temperature of the sources, and substrates temperature ranging 250–500 °C) and with final thickness varying from 125 to 890 nm. The flashing of the sulfur source produced oscillations of the chamber pressure from $9\cdot10^{-3}$ to $3\cdot10^{-2}$ Pa. A 2×2 cm central part of the samples were ex-situ optically, electrically and chemically characterized.

* Corresponding author. Tel.: +34 913466669; fax: +34 913466037.
*E-mail address:* juanfrancisco.trigo@ciemat.es (J.F. Trigo).

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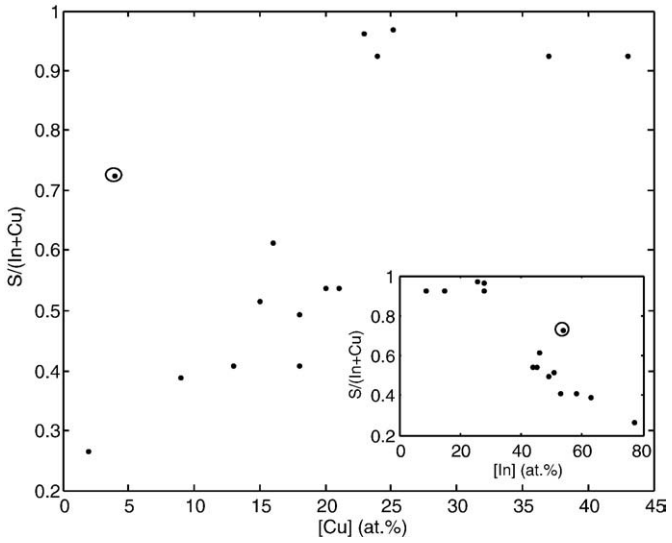


**Fig. 1.** Sulfur composition related with Cu (In on the inset) content from EDX (at.%). Marked point corresponds to a sample after thermal annealing in sulfur atmosphere.

The optical properties were carried out with a Perkin-Elmer Lambda 9 spectrophotometer operating at room temperature. The near normal Reflectance and Transmittance were measured in the dual channel configuration and by means of an integrator sphere in the 250–2500 nm range. The static electrical sheet resistance was measured using a four-point probe Veeco FPP5000 device. For simplicity we have used direct $R=V/I$ values in Ohms and no geometrical constant and thickness information has been operated. For a more precise study of some samples, a thickness value $d$ measured by profilometry has been operated to obtain resistivity and absorption coefficient following:

$$\rho_{(\Omega\,\mathrm{cm})} = R_{(\Omega)} \cdot d_{(\mathrm{cm})} \cdot \frac{\pi 0,94}{\ln(2)} \qquad \alpha_{(\mathrm{cm}^{-1})} = \frac{\ln\left(\frac{100-\overline{R\%_{0.5\mathrm{eV}}}}{\overline{T\%_{0.5\mathrm{eV}}}}\right)}{d_{(\mathrm{cm})}}$$

The last equation is an approximation where the absorption of the substrate has not been separated.

Finally their chemical composition was determined by energy dispersive X-ray (EDX) analysis in a scanning electron microscope Hitachi S-2500.

## 3. Results and discussion

As our initial goal was to define the general working ranges of our deposition system we have studied our compositional map for all the films in Fig. 1 where we observed a strong correlation between S and Cu contents, increasing together probably due to our simultaneous efforts introducing improvements of the process toward the stoichiometric $CuInS_2$. To check if it was possible to unlink these two parameters we tried a thermal treatment to a sample with low (4 at.%) Cu content. 35 min at 300 °C in sulfur atmosphere at a deposition process pressure were enough to have the S content rising in the marked sample on Fig. 1.

Another goal was to look for a fast mechanism to control the basic stoichiometric parameters (average content of Cu and S related to In). In this order we have tried with optical absorption in its more primitive expression: the energy conservation for the whole sample (including the substrate) $A\%=100-R\%-T\%$. There are other formulations intended to calculate the absorption coefficient of the material, but the thickness of the film and several data from the substrate are needed. If the substrate is transparent enough and the film is highly absorbent and with a low refractive index, as is the case with $CuInS_2$, the effect of film interferences

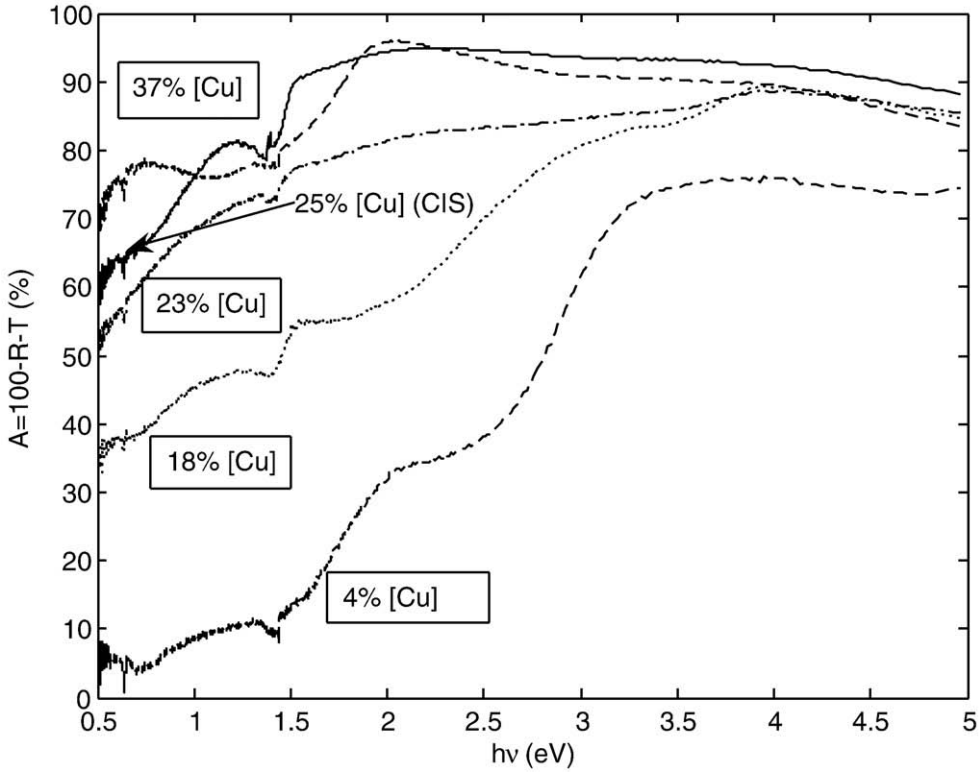


**Fig. 2.** Optical absorption defined as $A\%=100-R\%-T\%$ for selected samples with increasing Cu content (at.%) as determined by EDX.