Rev. Energ. Ren. Vol.6. (2003) 15-24

Effect of O_2 and H_2 Plasma Treatments on the Properties of $CuInSe_2$ Polycrystalline Thin Films

S. Merdès, N. Benslim, L. Bechiri and L. Mahdjoubi.

Laboratoire de Cristaux et Couches Minces, Faculté des Sciences,
Département de Physique, Université de Annaba, BP 12, 23000.

Abstract – *In this work, the effects of O_2 and H_2 plasmas on the properties of grain bulk and the grain boundaries in polycrystalline $CuInSe_2$ (CIS) thin films are investigated. The electrical behaviour of such material is dominated by the defects; in particular grain boundaries, which control charge transport and carrier recombination. $CuInSe_2$ thin films obey to two mechanisms of carrier transport, which operate simultaneously: The thermoionic emission through the intergrain barrier at high temperatures, and the "Variable Range Hopping" (VRH) in the forbidden band at low temperatures. Characterization including Conductivity, Impedance and Thermally Stimulated Current (TSC) measurements was done before and after O_2 and H_2 treatments. Conductivity versus temperature characteristics were studied in the range of 80-400K while Impedance measurements for different frequencies were realized at high temperature. These measurements showed that O_2 and H_2 plasmas passivate grain boundary defects in p and n type samples, respectively and have doping effects on the bulk grain: p type films are doped p^+ by oxygen while n type ones are n^+ doped by hydrogen.*

Résumé – *Dans ce travail, les effets du traitement aux plasmas d'O_2 et d'H_2 sur les propriétés des grains et des joints de grains dans les couches minces polycristallines de $CuInSe_2$ (CIS) sont étudiés. Le comportement électrique de ces matériaux est dominé par les défauts notamment les joints de grains qui contrôlent le transport de charges et la recombinaison des porteurs. Les couches minces de $CuInSe_2$ obéissent à deux mécanismes de transport de charges qui opèrent simultanément : l'émission thermoionique à travers la barrière des joints de grains à haute température et l'effet tunnel " Variable Range Hopping " (VRH) dans la bande interdite à basse température. Une caractérisation incluant des mesures de Conductivité, d'Impédance et de Courant Thermiquement Stimulé (TSC) a été réalisée avant et après des traitements aux plasmas d'O_2 et d'H_2. Les caractéristiques de Conductivité en fonction de la température ont été étudiées dans l'intervalle de 80-400K alors que des mesures d'Impédance ont été réalisées à haute température pour différentes fréquences. Ces mesures ont montré que les plasmas d'O_2 et d'H_2 passivent les défauts des joints de grains dans les échantillons de type p et n, respectivement et ont un effet dopant sur le volume du grain : les couches de type p sont dopées p^+ par l'oxygène alors que celles de type n sont dopées n^- par l'hydrogène.*

Keywords: $CuInSe_2$ – Thin Films – Characterization – Oxygen – Hydrogen – Thermally stimulated current.

1. INTRODUCTION

Polycrystalline semiconductors with chalcopyrite structure and particularly $CuInSe_2$ have been extensively studied due to their potential importance in optoelectronic applications. Solar cells fabricated on $CuInSe_2$ achieved efficiencies exceeding 17%[1].

Electrical properties of such materials are dominated by the defects in particular grain boundaries, which control charge transport and carrier recombination limiting by the way the cells efficiencies. In order to improve the films quality, during the last decades many investigations have been done on the material growth. As a result, $CuInSe_2$ thin films can be obtained by different methods among them Selenisation [2], alternate-feeding Physical

Vapor Deposition [3], Electrodeposition [4], Close-Spaced Vapor Transport [5] and coevaporation [6].

In a previous work [7,8], we have shown that at high temperature the cross grain conductivity of CIS films is controlled by the grain boundaries, the contribution of the grain bulk being negligible. Electrical resistivity of the films determined so far by coplanar electrical resistivity or by the "fourth probe" method is attributed to the material while it is that of grain boundaries. Knowing that the grain bulk is the home of photovoltaic phenomenon, an electrical model which permits to separate the grain and the grain boundary resistivities by combining resistivity and impedance measurements at high temperature and high frequencies is proposed.

For the determination of the defects, many methods can be used. One of the most important ones is the Thermally Stimulated Conductivity. This method which has been applied to several materials [9, 10] permits a rapid and an easy detection of these levels.

In this paper, we will study the effects of O_2 and H_2 plasmas on electrical properties of polycrystalline $CuInSe_2$ thin films. We will investigate their role in the grain boundaries, their contribution to the grain conductivity, and their possible interaction with the defects in the material.

2. EXPERIMENTAL PROCEDURE

p and n polycrystalline CIS thin films were prepared by the coevaporation method in a vacuum chamber of 10^{-6} torr from three boats of Cu, In and Se. The rate deposition of each element was stabilized at 2Å/s, 2Å/s and 6Å/s, respectively. The type of the obtained samples was controlled after the deposition by the "Hot Probe Method". The substrate temperature was measured by means of chromel-alumel thermocouple attached to the backside of the glass substrate and fixed at 200°C. The details of this technique were described in a previous work [11]. Curves of electrical conductivity versus temperature were realized in a LN2 cryostat from 80 to 400K. Impedance measurements were done using an impedance analyzer (HP4192A) between 1 KHz and 1 MHz at the room temperature. For the TSC measurements, current was picked up from 80 to 300K along the films under a bias of 1V in a vacuum cryostat after an exposure to halogen lamp of $100mW/cm^2$ during 1min at 80K and a rest time of 5min. These experiences were realized before and after a short exposure at the room temperature to O_2 plasma during 20min under a pressure of 10^{-1} torr or H_2 plasma treatment under 0.75 torr of 10min.

3. RESULTS AND DISCUSSION

3.1. Conductivity measurements

Figures 1 and 2 show the variation of the conductivity versus the temperature for p and n type films respectively in the temperature range [80-400K] before and after the O_2 treatments. Figures 3 and 4 represent conductivity characteristics for n and p type samples before and after exposure to H_2 plasma. All these curves show two temperature domains where a linear variation of the conductivity is observed. In the first domain ($T<250K$), the carrier transport obeys to the "Variable Range Hopping" described by Mott [12] in the forbidden band with activation energies that vary for the different samples between 1.1meV and 7.5meV. However, in the high temperature domain the conduction is governed by the thermoionic emission through the potential barrier introduced by the grain boundaries according to $\sigma = CT \exp(-q\,\phi/kT)$ where C is a constant, q the elementary charge, ϕ the height of the potential barrier and k Boltzman constant. In that field of temperatures, the activation energies calculated vary from 0.01eV to 0.12eV.

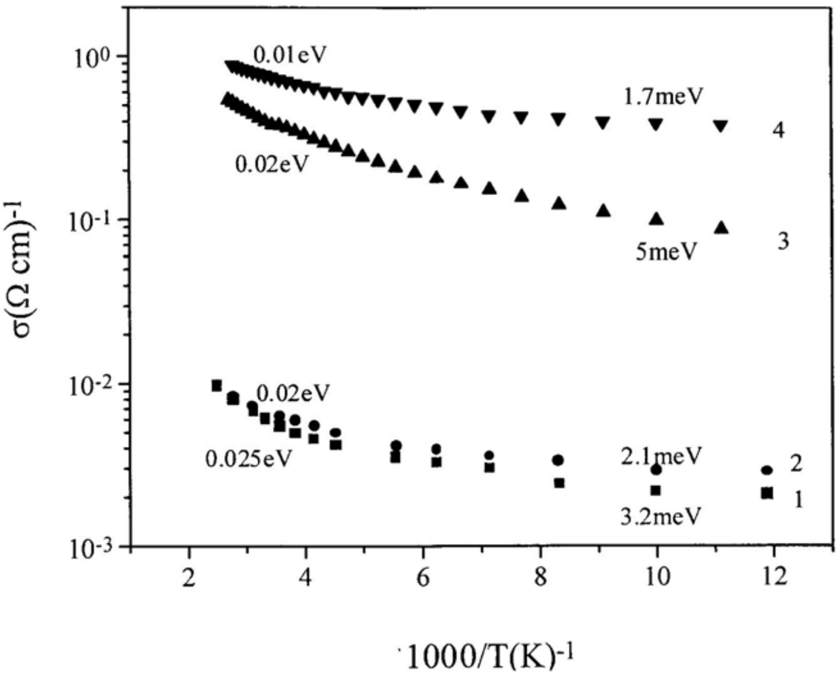


Fig. 1: σ = f (1000/T) for p type CIS thin films before and after O_2 treatment. 1. E1 before O_2 , 2. E1 after O_2 , 3. E24 before O_2 , 4. E24 after O_2

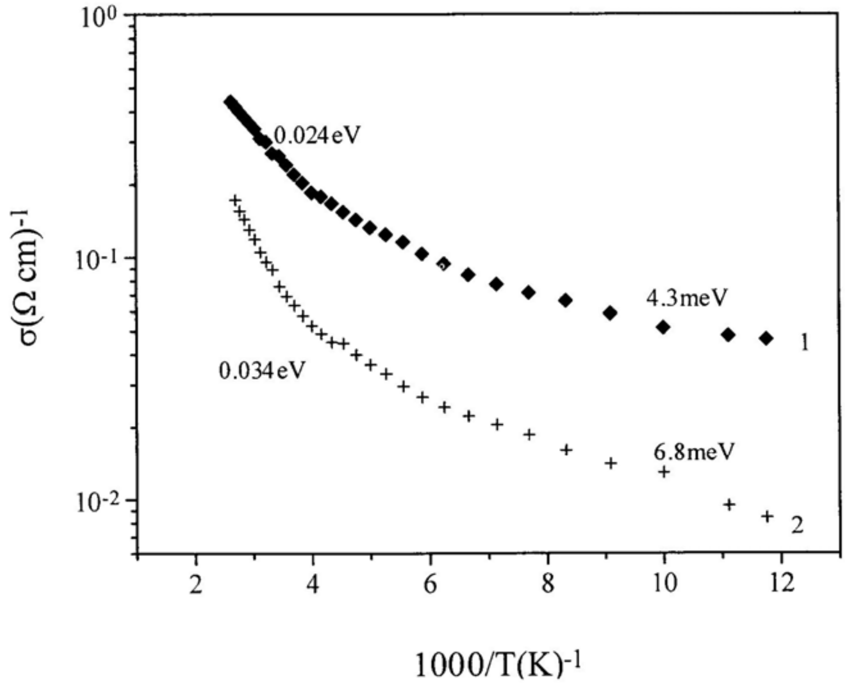


Fig. 2: σ = f (1000/T) for a n type CIS thin film before and after O_2 treatment. 1. E22 before O_2 , 2. E22 after O_2

These experimental facts allowed us to conceive the model of electrical scheme describing CIS polycrystalline films (Fig. 5). Considering the facts that both mechanisms operate simultaneously, this impedance is composed of two parallel branches. The first one which corresponds to the conduction at high temperature is constituted of a resistance Rvg attributed to grains and an impedance (Rgb//Cgb) introduced by the grain boundaries.

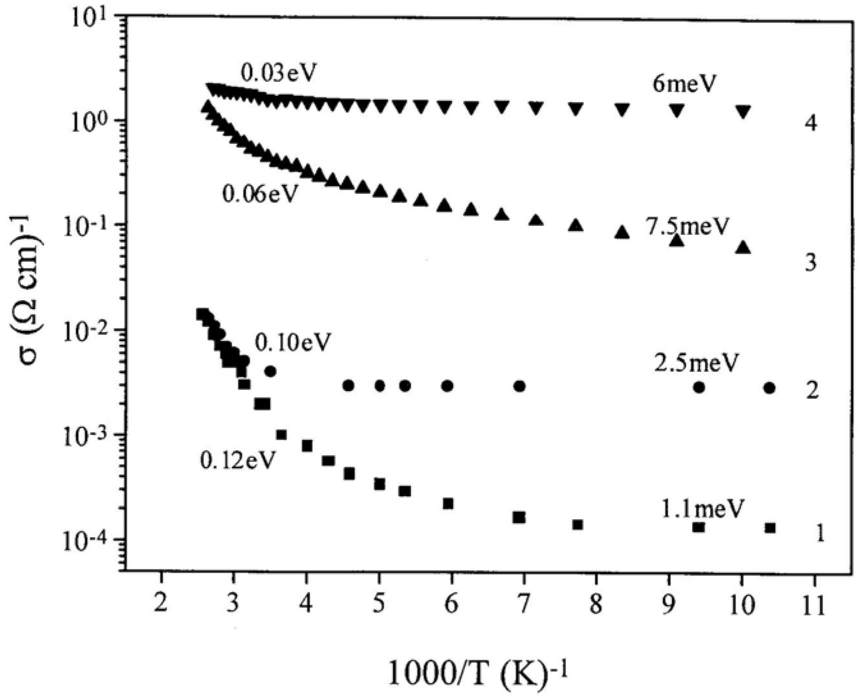


Fig. 3: $\sigma = f\,(1000/T)$ for n type CIS thin films before and after H_2 treatment. 1. E2 before H_2 , 2. E2 after H_2, 3. E21 before H_2 , 4. E21 after H_2

The resistance Rgb is dominant. The second branch which represents the conduction in the forbidden band by "Hopping" is constituted of a simple resistance Rfb. Thus, an important conclusion emerges: the bulk grain resistivity is unattainable with resistivity measurements because Rvg is negligible compared with Rgb. More details about this scheme can be found elsewhere [7].

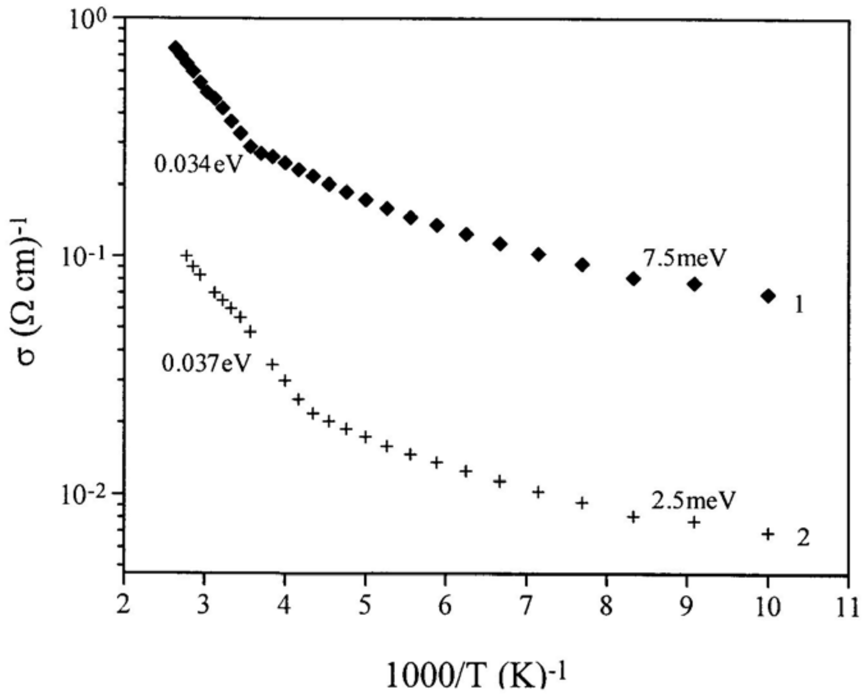


Fig. 4: $\sigma = f\,(1000/T)$ for a p type CIS thin film before and after H_2 treatment. 1. E28 before H_2 , 2. E28 after H_2

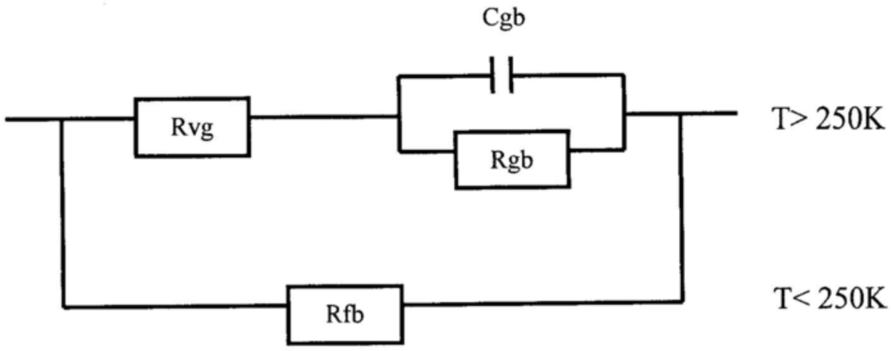


Fig. 5: Electrical model for polycrystalline CIS thin films.

Moreover, O_2 and H_2 plasma treatments allowed us to give a good support to our model in the first hand, and in the second one, they improve electrical properties of the films by passivating defects (native and grain boundaries). In fact, in the temperature range considered an increase of the conductivity is observed for the p type films exposed to oxygen (Fig. 1) and n type ones treated by hydrogen (Fig. 3) while a decrease of these characteristics is noticed after exposure of n type samples to O_2 (Fig. 2) and p type ones to H_2 (Fig. 4). In the high temperature domain, the increase of conductivity could be essentially caused by a reduction of activation energies indicating the passivation of grain boundaries. At low temperatures, the increase could be due to a p^+ doping with oxygen ions for the p type samples and n^+ doping with hydrogen for n type films. However, a possible decrease of compensating native defects by their passivation with the active atoms of oxygen and hydrogen is also probable.

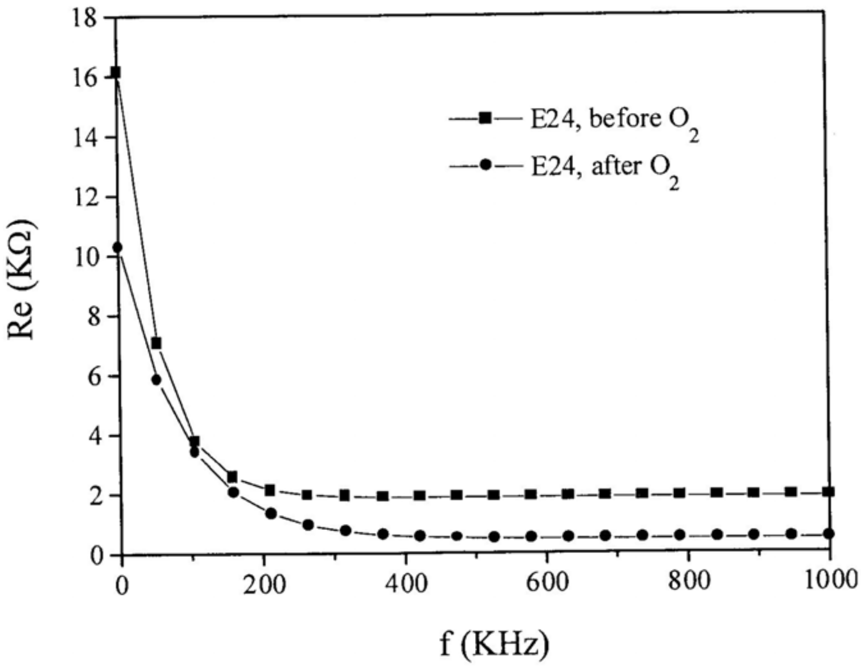


Fig. 6: Re_{HT} measurements for a p type sample before and after O_2 treatment.

3.2. Impedance measurements

Figures 6 and 7 show impedance measurements on p and n type samples before and after O_2 and H_2 treatments for frequency values from 1KHz to 1MHz. The importance of these measurements appears if we consider high temperature branch (T> 250K) in the electrical scheme proposed in figure 5.

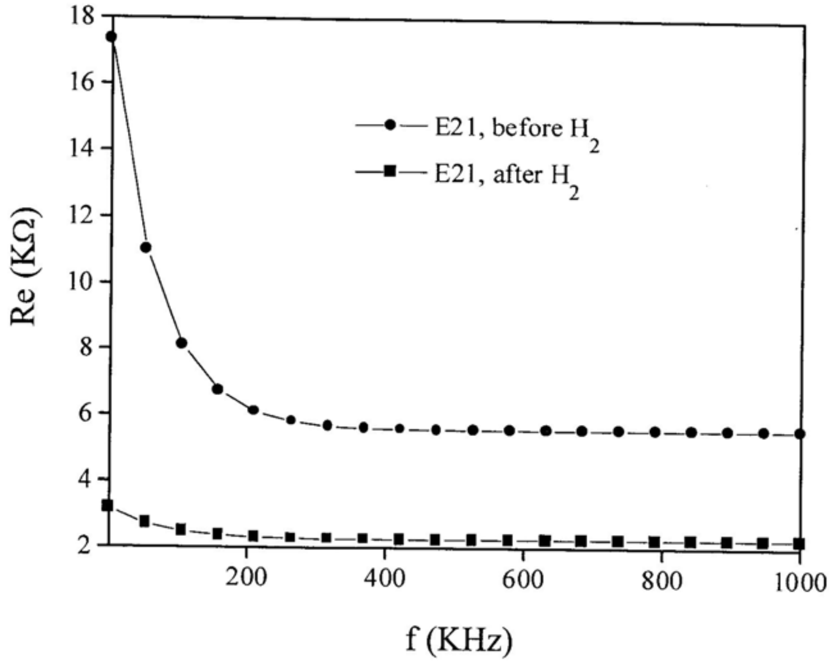
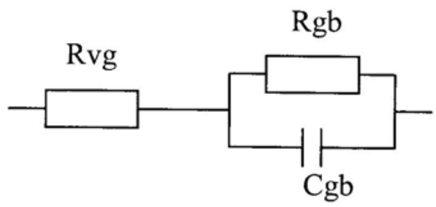
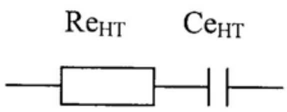


Fig. 7: Re_{HT} measurements for a n type sample before and after H_2 treatment.

The impedance analyzer can work in two modes: parallel and series. Because the measurements were more stable in the series mode, it was chosen. Impedance relations in this case given in table 1 are:

$$Re_{HT} = Rvg + [\ Rgb / (\ 1+ Rgb^2.Cgb^2.\omega^2)\ ] \quad (1)$$

Table 1: Electrical scheme of measurement and impedance relations at high temperature for CIS polycrystalline thin films.

	T>250K
Impedance electrical Scheme of polycrystalline CIS thin films	
Equivalent circuit of measure	
Impedance relations	$Re_{HT} = Rvg + [\ Rgb / (\ 1+ Rgb^2.Cgb^2.\omega^2)\ ]$ $Ce_{HT} = [\ Cgb\ (1 + Rgb^2.Cgb^2.\omega^2)\ ] / [\ Rgb^2.Cgb^2.\omega^2\ ]$

When frequency increases as far as Rgb. Cgb. ω >>1, Re_{HT} decreases gradually following the relation:

$$Re_{HT} = Rvg + [\ 1 / (Rgb.Cgb^2.\omega^2) \quad (2)$$

When the frequency is enough high at about 1MHz the term $[1 / (Rgb.Cgb^2.\omega^2)]$ becomes negligible indicating that the capacitance Cgb is short-circuited and the effect of grain boundary impedance is cancelled.

$$Re_{HT} \approx Rvg \quad (3)$$

So, we achieve the resistance Rvg of the grain, which is fundamental, if we want to determine grain resistivity, the active part of the photoconductivity.

In summary, Rvg values are given by Re_{HT} measured at the room temperature and at high frequencies while Rgb and Rfb are achieved by resistivity measurements at high and low temperatures, respectively. Rvg, Rfb and Rgb values before and after O_2 and H_2 treatments are gathered in table 2. For p type samples exposed to O_2 and n type ones treated by H_2, a decrease of the grain resistivity is observed. This decrease could be explained by a doping effect with O_2 or H_2 atoms for p or n type samples, respectively. However, a passivation of compensating native defects can also be supposed.

Table 2: Electrical parameters of CIS thin films before and after treatments.

Samples		E21	E22	E24	E28
Type		n	n	p	p
Treatment		H_2	O_2	O_2	H_2
ΔE (eV)	before	0.06	0.024	0.02	0.034
	after	0.03	0.034	0.01	0.037
Rgb (KΩ) (300K)	before	16	27.72	19.28	25.11
	after	4.65	89.70	10.69	97.5
Rvg (KΩ) (300K)	before	5.55	0.21	1.86	0.5
	after	2.25	2.89	0.40	0.80
Rfb (KΩ) (80K)	before	180	173.40	101.37	80
	after	5.60	950	26.69	138.75

3.3. Thermally Stimulated Current measurements

Experimentally, at a temperature low enough to make the probability of thermal release negligible, carriers were photoexcited and trapped in the gap states. As the sample was warmed up, the carriers trapped were released to produce a current in the presence of the applied field.

The thermally stimulated current I due to a single trap of depth E with negligible retrapping is given by [13]:

$$I = I_0 \exp(-E/kT) - (\nu/\beta) \int_{T_0}^{T} \exp(-E/kT)\, dT' \quad (4)$$

Where T_0 is the initial temperature, ν the attempt to escape frequency, and β the warm up rate. I_0 is often a weak function of temperature. The previous equation shows that I exhibits a maximum as a function of temperature at T_m. This maximum characterizes the trap of depth E. E is given by the Grossweiner model [14] as:

$$E = 1.51\ k\ (T_m.T_1)/(T_m - T_1) \tag{5}$$

Where T_1 is the temperature at half of the maximum current value on the low shoulder of the current peak. If we consider the data on the low temperature side of the peak, the integral in eq (4) becomes insensitive to temperature and may be treated as constant, thus:

$$I(T) \approx \exp\ (-E/kT) \tag{6}$$

E can therefore be obtained from the slope of the linear part of Ln (I) vs. T^{-1} plot. This method, which is called "Initial Rise Method", is very attractive because it is indifferent to the recombination kinetics and independent of the sample-heating rate.

Figures 8 and 9 show Thermally Stimulated Current spectra obtained from the current in excess of dark contribution before O_2 and H_2 plasma treatments on p and n type samples, respectively. Considering the "Initial Rise Method" and on the basis of the explanations given before, we can easily observe for the p type film a single peak at 93 K corresponding to 1.7 meV. For the n type one, three distinct peaks of 1.7 meV, 5 meV and 13.5 meV are visible. These peaks which correspond to defect energy levels appear at 85K, 113K and 306 K, respectively. Comparing with the defects detected by other authors [15], the energy level of 5 meV can be associated to anti-site defect In_{Cu} (Indium atom in Copper site).

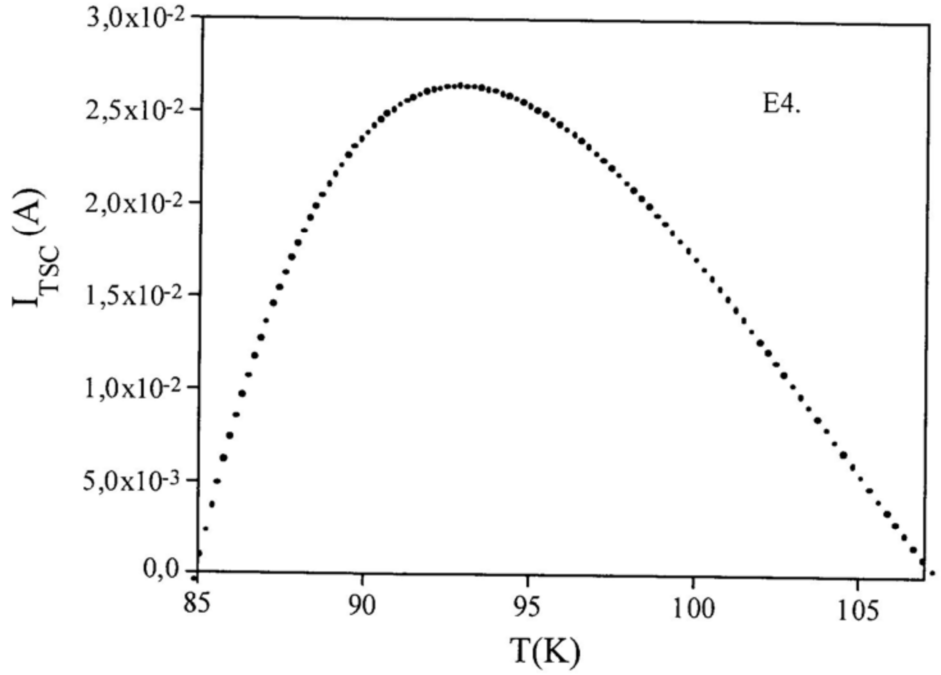


Fig. 8: TCS measurement for a p type sample before O_2 treatment.

The exposure of p type sample to O_2 and n type one to H_2 made the peaks disappear totally probably due to a passivation effect. A similar result was reported by Yakushev and al using photoluminescence measurements [16]. Other authors confirm that the effect of oxygen and hydrogen depends on the material stoechiometry. The presence of these elements affects electrical properties of thin films and the creation of donor-O bonds in p type samples and acceptor-H bonds in n type ones is supposed. Indeed, Tomlinson and al [17] suggest that oxygen atoms preferentially locate on selenium vacancy sites.

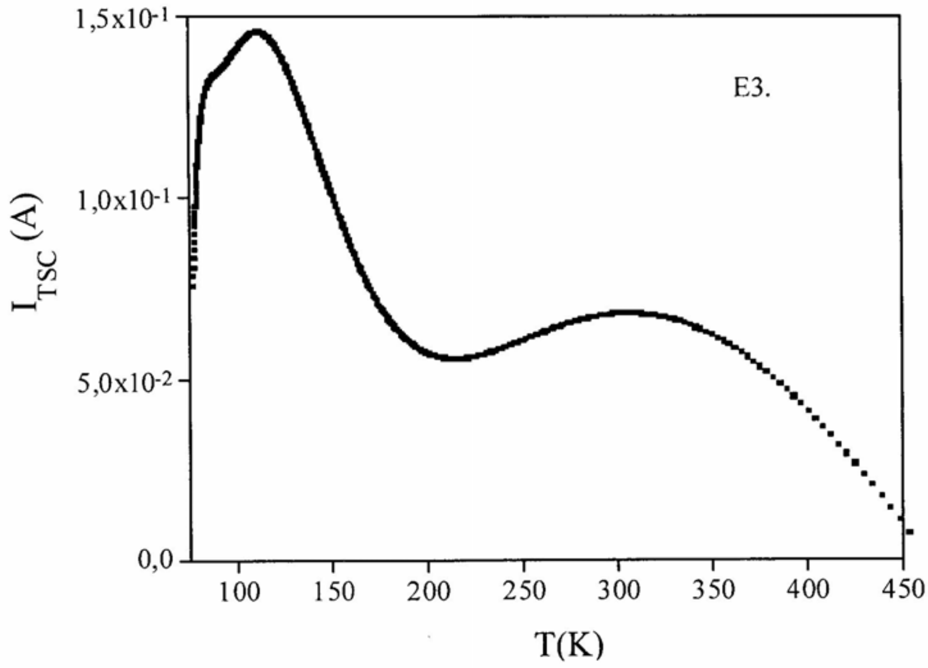


Fig. 9: TSC measurement for a n type sample before H_2 treatment.

4. CONCLUSION

The results presented in this work show clearly that oxygen and hydrogen have a visible effect on CIS coevaporated polycrystalline thin films. Thermally Stimulated Current measurements (TSC) enabled the identification of the defect levels. Combining resistivity and impedance measurements permitted to separate grain bulk and grain boundary resistivities and allowed us to study the impact of active plasma atoms on each of them separately. Oxygen and hydrogen plasmas passivate grain boundaries in p and n type films, respectively. This behaviour is observed by a decrease of the potential barrier and the disappearing of (TSC) peaks.

NOMENCLATURE

σ: Electrical conduction $[(\Omega\ \mathrm{cm})^{-1}]$
ϕ: Height of the potential barrier [eV]
Rgb: Grain boundary resistance [Ω]
Rfb: Forbidden band resistance [Ω]
Cgb: Grain boundary capacity [F]
I: Thermally Stimulated Current [A]
ν : The attempt to escape frequency
k: Boltzman constant $[\mathrm{J\ K}^{-1}]$
C: Constant
q: Elementary charge [C]
β : Warm up rate
Re_{HT}: Film impedance
Rvg: Grain resistance [Ω]
ω: The pulse
E: Trap energy [eV]
T_0: Initial temperature [K]

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