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EFFECT OF TREATMENTS ON THERMALLY STIMULATED CURRENT AND PHOTOCONDUCTIVITY IN $CuInSe_2$ THIN FILMS

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Abstract

$CuInSe_2$ polycrystalline thin films (CIS) have been prepared by the coevaporation method from three boats (Cu, In, Se). "Thermally Stimulated Current" method (TSC) has been used to identify some defect states in the material. Photocurrent versus 1000/T characteristics have also been carried out. In this paper, we discuss the effects of O_2 and H_2 plasmas on (TSC) and photoconductivity in p and n type $CuInSe_2$ thin films. In fact, strong (TSC) has been exhibited for these films at temperatures from 80 to 500K using coplanar configuration with thermal evaporated Cr-Ag contacts while a stability of photocurrent has been observed. Exposure to O_2 and H_2 plasmas modified this behaviour leading to a change of (TSC) way and appearing of the thermal "Quenching" in photoconductivity spectra.

Keywords: *$CuInSe_2$, Thin films, Thermally Stimulated Current, Photoconductivity, Oxygen, Hydrogen.*

Résumé

Des couches minces polycristallines de $CuInSe_2$ ont été préparées en utilisant la méthode de coévaporation à partir de trois creusets de cuivre, indium et sélénium. Afin de déterminer les défauts présents dans le matériau, la méthode du "Courant Thermiquement Stimulé" (TSC) a été appliquée. Les caractéristiques du photocourant en fonction de la température ont aussi été mesurées. Dans ce travail, les effets du traitement aux plasmas de O_2 et de H_2 sur le (TSC) et la photoconductivité dans les couches minces de $CuInSe_2$ du type p et n sont étudiées. En effet, ces couches ont montré un fort (TSC) dans l'intervalle de température allant de 80K à 500K en utilisant la configuration coplanaire et des contacts en Cr-Ag. Cependant, une stabilité du photocourant été observée. L'exposition aux plasmas de O_2 et de H_2 a modifié ce comportement en changeant l'allure du (TSC) et en faisant apparaître un "Quenching" sur les courbes de photoconductivité.

Mots clés: *$CuInSe_2$, Couches minces, Courant Thermiquement Stimulé, Photoconductivité, Oxygène, Hydrogène.*

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ملخص

تم تحضير شرائح رقيقة من $CuInSe_2$ (CIS) متعدد البلورات باستعمال طريقة التبخير انطلاقا من ثلاث مصادر من النحاس، الانديوم والسيلينيوم. من اجل التعرف على العيوب الموجودة في المادة، استعملت طريقة التيار المنشط حراريا (thermally stimulated current) إضافة إلى تسجيل خاصية التيار الضوئي بدلالة 1000/T. في هذا العمل سوف نناقش أثر بلازما الأكسجين والهيدروجين على التيار المنشط حراريا والتيار الضوئي الناتجين عن شرائح رقيقة من $CuInSe_2$ من النوعين P و N. بالفعل قبل المعالجة بالبلازما ، أظهرت العينات المدروسة تيارا منشطا حراريا قويا عند درجات حرارة محصورة بين 80K-500K باستعمال تلامسات مستوية ناتجة عن تبخير Cr-Ag بينما لوحظ تيار ضوئي مستقر. المعالجة ببلازما الأكسجين والهيدروجين غيرت هذا السلوك مؤدية إلى تحول بيانات التيار المنشط حراريا وظهور "Thermal Quenching" في التيار الضوئي.

الكلمات المفتاحية: *شرائح رقيقة،التيار المنشط حراريا، التيار الضوئي، الأكسجين،الهيدروجين.*

The chalcopyrite semiconductors and particularly $CuInSe_2$, have been extensively studied due to their potential application in optoelectronic devices. Solar cells fabricated on $CuInSe_2$ and $Cu(In,Ga)_3Se_5$ by "Chemical Vapour Deposition" have shown conversion efficiencies exceeding 17% [1]. It is known that electrical and optical properties in the chalcopyrite structure are dominated by the defects. Many methods exist to test the presence of traps. Experimentally, we can vary bias, temperature or light flux as independent parameters and measure electrical current.

Thermally Stimulated Current is a well-known method for the determination of defects. It permits a rapid and an easy detection of these levels. This method has been applied to several semiconductors including Si-a [2] and CdS [3]. In this work, samples of CIS polycrystalline thin films were prepared by coevaporation and characterizied by the (TSC) before and after a short exposure at the room temperature to O_2 plasma during 20 min or H_2 plasma treatment of 10min. Photoconductivity measurements were also done.

1-EXPERIMENTAL

The CIS layers under investigation were coevaporated in a vacuum chamber at 10^{-6} torr from separated Cu, In, Se boats (Fig. 1). The rate deposition of each element was stabilized at 2Å/s, 2Å/s, and 6Å/s, respectively. The substrate temperature was measured by means of chromel-alumel thermocouple attached to the back side of the glass substrate and fixed at 200°C. TSC was measured from 80 to 500 K 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 80 K, and a rest time of 5 min. After release, only the carriers that survive retrapping and recombination processes contribute to the current. Current under illumination was also measured using the same lamp. All these measurements were carried out before and after a short exposure to O_2 plasma at the room temperature during 20 min under a pressure of 1.5×10^{-1} torr for p type samples and H_2 plasma treatment of 10min under 0.75 torr for n type ones.

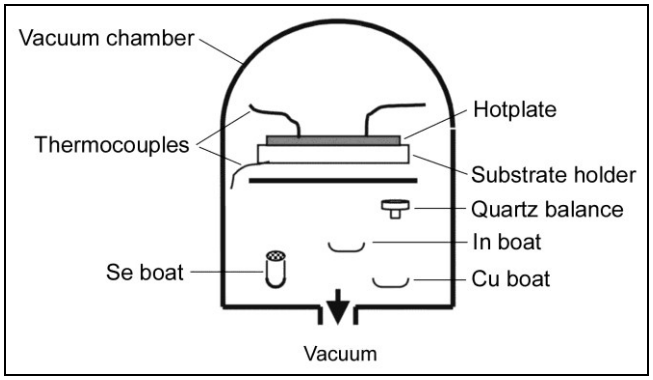

Figure 1: Experimental system used for the coevaporation.

2-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 [4]:

$$I = I_0 \exp(-EKT) - (\nu/\beta)\int_{T_0}^{T} \exp(-EkT)dT' \qquad (1)$$

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 [5] as:

$$E = 1.51\ k\ (T_m.T_1)/(T_m - T_1) \qquad (2)$$

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 (1) becomes insensitive to temperature and may be treated as constant, thus:

$$I(T) \approx \exp(-E/kT) \qquad (3)$$

E can therefore be obtained from the slope of the linear part of LnI 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.

(TSC) measurements have been done on p and n type films before and after exposure to O_2 and H_2 plasmas, respectively. Before the treatments, most of the samples exhibited a single or several peaks revealing the presence of defects. However, plasma treatments modified this behaviour and showed that these samples can be divided into two groups. In fact, some of the peaks changed while others disappeared totally.

2.1-Effect of treatments on the first group of films

Figures 2 and 3 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 first group 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 93K corresponding to 1.7meV. For the *n* type one, three distinct peaks of 1.7meV, 5meV and 13.5meV are visible. These peaks which correspond to defect energy levels appear at 85K, 113K and 306K, respectively. Comparing with defects detected by other authors [6], the energy level of 13,5meV can be associated to Cu vacancy. The exposure of the p type sample to O_2 and the n type one to H_2 made the peaks disappear totally probably due to a passivation effect. Many results confirm that the effect of oxygen and hydrogen depends on the material stoechiometry. The presence of these elements affects electrical properties of thin films. These authors suppose the creation of donor-O bonds in *p* type samples and acceptor-H bonds in n type ones. In fact, In-O bond was observed by Cahen *et al.*[7] using infrared measurements. The same result was reported by Noufi *et al.*[8].

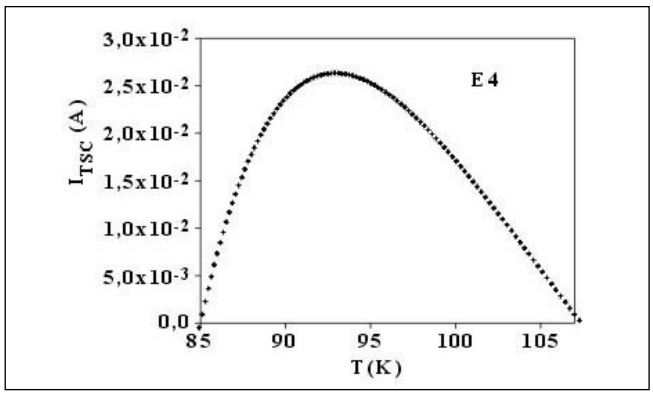

Figure 2: (TCS) spectrum for a first group *p* type film before O_2 treatment.

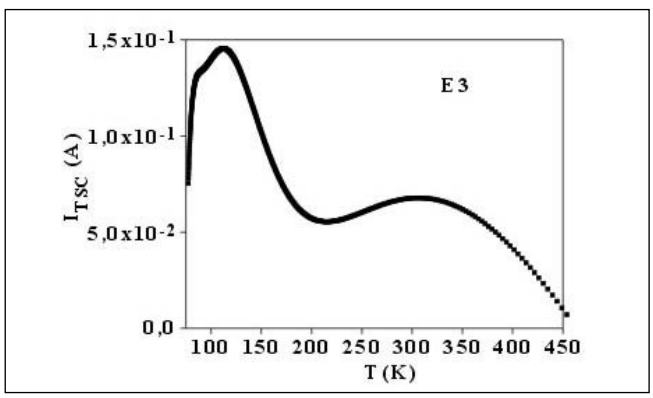

Figure 3: (TSC) spectrum for a first group *n* type film before H_2 treatment.

2.2-Effect of treatments on the second group of films

Figures 4 and 5 show (TSC) spectra obtained for a p type second group sample before and after O_2 plasma treatment, respectively. Before the treatment, the spectrum exhibits a single peak with energy of 11.5meV at 194K. This value can be associated with the anti site defect In_{Cu} (Indium atom in Copper site). This defect was reported by other authors [6]. However, after O_2 treatment, we can observe the shifting of the peak to 130K and an emergence of a new one at 85K. Supposing the existence of two defects, energies of 4meV and 15meV were calculated for 85K and 130K, respectively.

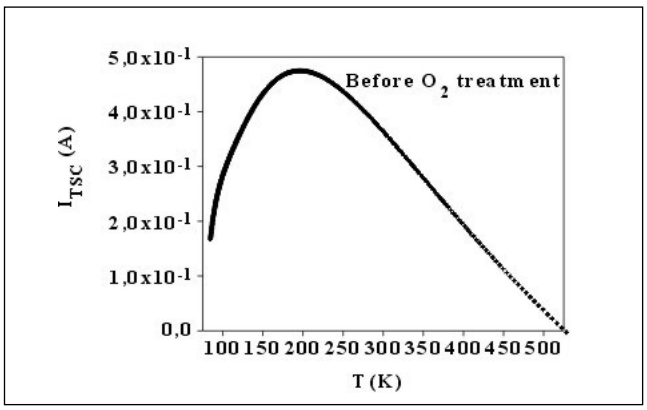

Figure 4: (TCS) spectrum for a second group p type film before O_2 treatment.

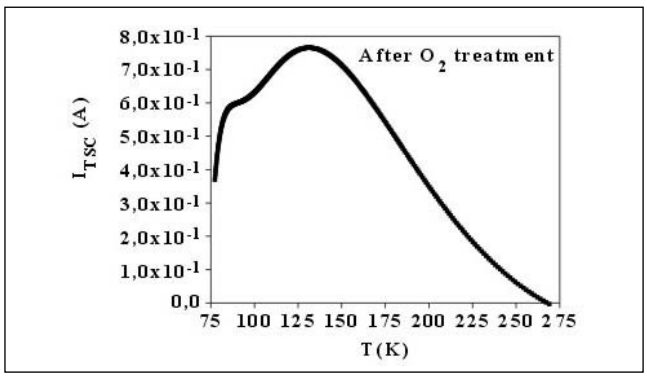

Figure 5: (TSC) spectrum for a second group p type film after O_2 treatment.

Figures 6 and 7 show (TSC) spectra obtained for a n type second group sample before and after H_2 plasma treatment. Before exposure to hydrogen, two peaks of 90meV and 130meV are clearly visible at 92K and 261K, respectively. Comparing with other results [6], the energy level of 90meV can be related to selenium vacancy. Hydrogen plasma modified (TSC) way leading to the disappearing of 130meV peak and the moving of the second one to a very low temperature of about 80K. The value of energy corresponding to this temperature cannot be calculated using the " Initial Rise Method ".

In summary, it is obvious that for this second group specimens exposure to oxygen and hydrogen of *p* and *n* type CIS films respectively changes the general way of (TSC) curves but does not affect all the centres uniformly. However, it appears that most of the peaks are displaced to lower temperatures preferentially. The results obtained for the two groups described above are gathered in table 1.

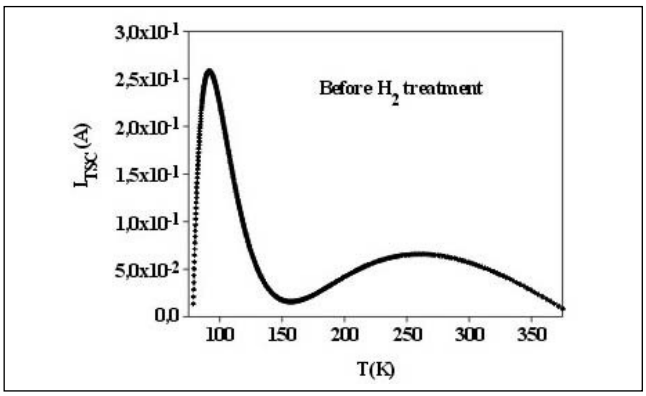

Figure 6: (TCS) spectrum for a second group n type film before H_2 treatment.

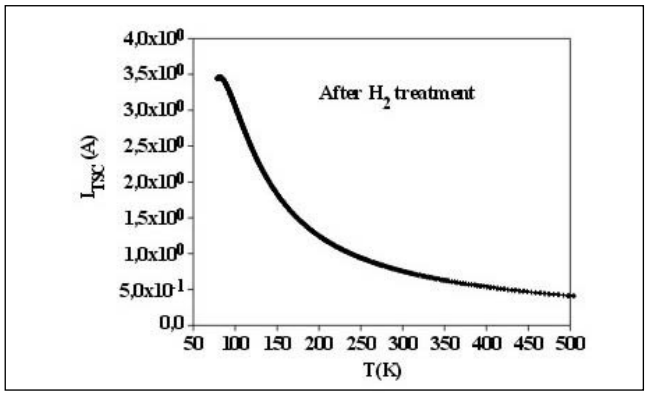

Figure 7: (TSC) spectrum for a second group n type film after H_2 treatment.

samples		First group of samples				Second group of samples			
		E3			E4	E5		E6	
Type		n			p	p		n	
Treatment		H_2			O_2	O_2		H_2	
E (meV)	Before	1.7	5	13.5	1.7	11.5		90	130
	After	-	-	-	-	4	15	Not calculated	
T_m (K)	Before	85	113	306	93	194		92	261
	After	-	-	-	-	85	130	80	

Table1: (TSC) results for CIS thin films before and after treatments.

3-PHOTOCONDUCTIVITY MEASUREMENTS

Figures 8 and 9 show photoconductivity variation spectra obtained from the current in excess of dark contribution versus $1000/T$ for *p* and *n* type samples before and after O_2 and H_2 treatments, respectively. Before the treatments, a stability of photocurrent is observed. However after exposure to O_2 and H_2 plasmas, the curves show "Quenching" features centred at approximately 380K and

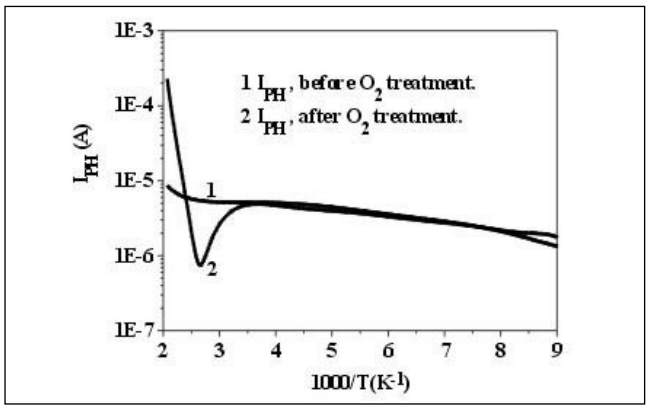

Figure 8: Photoconductivity spectra for a p type film before and after O_2 plasma treatment.

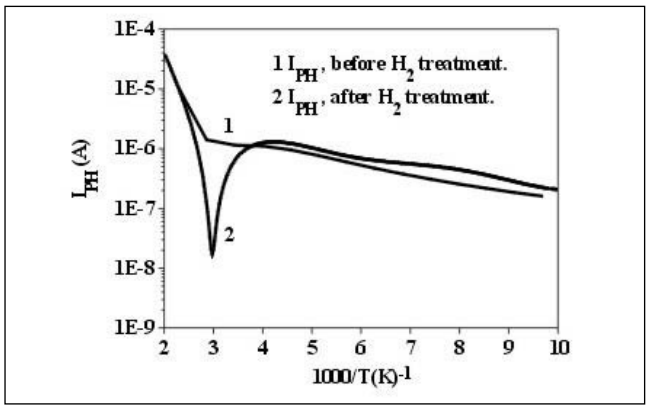

Figure 9: Photoconductivity spectra for a n type film before and after H_2 plasma treatment.

330K, respectively. If we consider that photocurrent is mainly due to electrons, "Quenching" in materials is caused by the optical excitation of an electron from the valence band into a defect centre, which has previously captured a photoexcited hole. The hole is then freed and is subsequently captured at a centre where a recombination with a free electron is possible. The concentration of free electrons, at the temperature where the photocurrent starts to decrease, has been done by Bube [9] as:

$$\mathrm{Ln}\,(n) = \mathrm{Ln}\,[\,N_v\,(\beta/\beta')\,] - (E/kT) \qquad (4)$$

where N_v is state concentration in the valence band, β and β' are the product of capture cross section by thermal velocity for electrons and holes, respectively.

Because the appearance of "Quenching" features is due to O_2 and H_2 treatment on p and n type films respectively, we suppose that the decrease of photocurrent could be attributed to active plasma atoms, which acted in this case as recombination centres.

CONCLUSION

The effects of O_2 on p type polycrystalline coevaporated CIS thin films and H_2 on *n* type ones have been studied using Thermally Stimulated Current and Photoconductivity measurements.

Before any treatment, all the samples exhibited (TSC) peaks revealing the presence of defects. Exposure to O_2 and H_2 plasmas modified this behaviour: for some samples, the peaks disappeared totally probably due to a passivation effect while for others shifting to lower temperatures was observed.

For photoconductivity measurements before the treatments, photocurrent was stable. However, interaction with O_2 and H_2 plasma active atoms showed "Quenching" features.

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