PHYSICS

ELECTRICAL TRANSPORT PROPERTIES OF $Cu_2ZnSnSe_4$ THIN FILMS FOR SOLAR CELLS APPLICATIONS

PROPIEDADES DE TRANSPORTE ELÉCTRICO DE PELÍCULAS DELGADAS DE $Cu_2ZnSnSe_4$ PARA APLICACIONES EN CELDAS SOLARES

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ABSTRACT

Seña, N.J., A. Dussan Cuenca, G. Gordillo Guzmán. Electrical transport properties of $Cu_2ZnSnSe_4$ thin films for solar cells applications. Rev. Acad. Colomb. Cienc., 37 (1): 22-26, 2013. ISSN 0370-3908.

In this work we study the electrical transport properties of $Cu_2ZnSnSe_4$ (CZTse) thin films. CZTSe thin films were prepared by PVD method; the parameters of deposition as substrate temperature (T_s) and mass, (Mx), (Mx = ZnSe, Cu) were varied for a range wide. Conductivity and resistivity measurements as a function of temperature were obtained between 120 and 400 K. It was observed, that high-temperature range above room temperature (>300 K) the carrier transport is thermally activated, with a single activation energy that changes with the variation of T_s and Mx. In the low-temperature range (<300 K), variable range hopping (VRH) was established as a predominant electronic transport mechanism for all samples. Hopping parameters were obtained by Diffusinal model and percolation theory.

Key words: Semiconductors, Electrical properties, VRH

RESUMEN

En este trabajo presentamos un estudio de las propiedades de transporte eléctrico de películas delgadas de $Cu_2ZnSnSe_4$ (CZTSe). Las películas de CZTSe fueron preparadas a través del método PVD, variando en un amplio rango la temperaturas de sustrato (T_s) y la masa (Mx), (Mx = ZnSe, Cu). Las medidas de conductividad y resistividad en función de la temperatura fueron realizadas entre 120 y 400 K. Se evidenció que para la región de altas temperaturas (>300 K) los portadores son térmicamente activados con una única energía de activación que cambia con T_s y Mx. Para la región de bajas temperaturas (<300 K), se estableció, para todas las muestras, que el mecanismo de transporte es hopping de rango variable (VRH). Se obtuvieron los parámetros hopping a partir del modelo Difusional y la Teoría de Percolación.

Palabras clave: Semiconductores, Propiedades Eléctricas, VRH

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Introduction

Quaternary compounds Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have attracted increasing attention as potential absorber materials for thin film solar cells. [Lechner R., Jost S., Palm J., Gowtham M., Sorin F., Louis B., Yoo H., Wibowo R. A., Hock R., 2013; Guo Q. J., Ford G. M., Yang W. Ch., Charles J. H., Hugh W. H., Rakesh A., 2012] This is due to their cheap resource, n-type conductivity, high absorption coefficient (>10^4 cm^{-1}), and direct band gap close to the optimum value for solar energy conversion. [Lin S., Jun H., Hui K., Fangyu Y., Pingxiong Y., Junhao Ch., 2011; Lee S. M., Mohanty B. Ch., Jo Y. H., Yong S. Ch., 2013] There are some reports in which CZTS and CZTSe thin-film have been prepared by several typical techniques, such as sol gel [Fahrettin Y., 2011], electrodeposition [Ji L., Tuteng M., Ming W., Weifeng L., Guoshun J., Changfei Z., 2012], selenization of elemental precursor [Salomé P.M.P., Fernandes P.A., Da Cunha A.F., 2009], sputtering [Brammertz G., Ren Y., Buffière M., Mertens S., Hendrickx J., Marko H., Zaghi A., Lenaers N., Köble Ch., Vleugels J., Meuris M., Poortmans J., 2013], etc.

A thorough understanding of the physical properties of $Cu_2ZnSnSe_4$ thin films is quite essential for its ultimate use as absorber in thin film solar cells; however few studies are reported on electrical and transport properties for this compound semiconductor.

In this work we present a study on electrical and transport properties of $Cu_2ZnSnSe_4$ (CZTse) thin films prepared by thermal co-evaporating method. The influence of the initial composition of the films was studied for Cu-rich, stoichiometric and Cu-poor layers, as well as also on effect of the temperature. From dark conductivity measurements performed over a wide range of temperatures, showed that above room temperature the dominant mechanism is the thermal activation of carriers. In the low-temperature range, it is between 300 and 120 K, variable range hopping (VRH) was established as a predominant electronic transport mechanism for all samples. Using classical equations from the percolation theory and the diffusional model, the density of states near the Fermi level, as well as the hopping parameters, were calculated. A correlation between the hopping parameters for both models is presented.

Experimental details

Thin films $Cu_2ZnSnSe_4$ were prepared on Soda Lime-type glass substrates through physical vapor deposition (PVD) in the presence of Se. The substrates were washed with sulphochromic solution and after cleaned with neutral PH liquid soap and followed by cleaning with deionized water in ultrasonic bath. The masses of the precursors used were between 0.104 and 0.131 g for Cu, 0.097 g for Sn, and between 0,134 and 0.171 g for ZnSe; It compounds had a high degree of purity (99.95 ± 0.05%). The deposition process was conducted in three stages. During the first stage, Cu and Se_2 were simultaneously co-evaporated at a substrate temperature of T_s(Cu) varying between 573 and 773 K. This stage formed the Cu_2Se composite, as a result of the reaction of the two precursors. During the second stage (in situ), Sn and Se were simultaneously co-evaporated, maintaining T_s(Sn) = 523 K; this stage formed the $SnSe_2$ composite, which in turn reacted with Cu_2Se to give way to the formation of the Cu_2SnSe_3 ternary composite. During the third stage (in situ), ZnSe was evaporated varying T_s(ZnSe) between 573 and 773 K. The final reaction gave way to the formation of the $Cu_2ZnSnSe_4$ quaternary composite. The successive reactions during thin films deposition by PVD method allowed obtaining of the CZTSe compound with characteristic phase. [Seña N., 2013] These reactions occurring have been considered by other researchers in the fabrication of the composite. [Redinger A., Mousel M., Djemour R., Gütay L., Valle N., Siebentritt S., 2013]

Dark conductivity measurements were carried using four-probe method by Van der Pauw method in equipment PPMS resistivity. The electrical current was measured with a Keithley electrometer 617 connected to a computer. The samples were annealed at 400 K and then cooled down to 120 K at a constant rate of 2 K per min. The applied field was 5mV/cm. Conductivity n type for $Cu_2ZnSnSe_4$ thin films was identified from thermo power measurements.

Results and discussion

Figure 1 shows an Arrhenius plot of the dark conductivity of the quaternary $Cu_2ZnSnSe_4$ thin films varying the mass of ZnSe compound and substrate temperature T_s(Cu).

A linear behavior is only observed in the high-temperature region, as shown in the Figure 1 (300 K < T < 400 K). In this temperature region, it is over 300 K, the transport mechanism involves carriers activated directly from levels below the Fermi level to states at the bottom of the conduction band. Fit linear for both cases is showed in the inset of Figure 1. Region for higher temperature in the sample with open squares symbols (see Figure 1 a, b) can be associated to formation of structural disorder during the characteristic phase formation of CZTSe contributing to the improvement of ionic conductivity. [Dong-Hau Kuo D., Tsega M., 2014; Yilmaz S., Turkoglu O., Belenli I., 2007] Termopower measurements (TM) are used for conduction type identification.

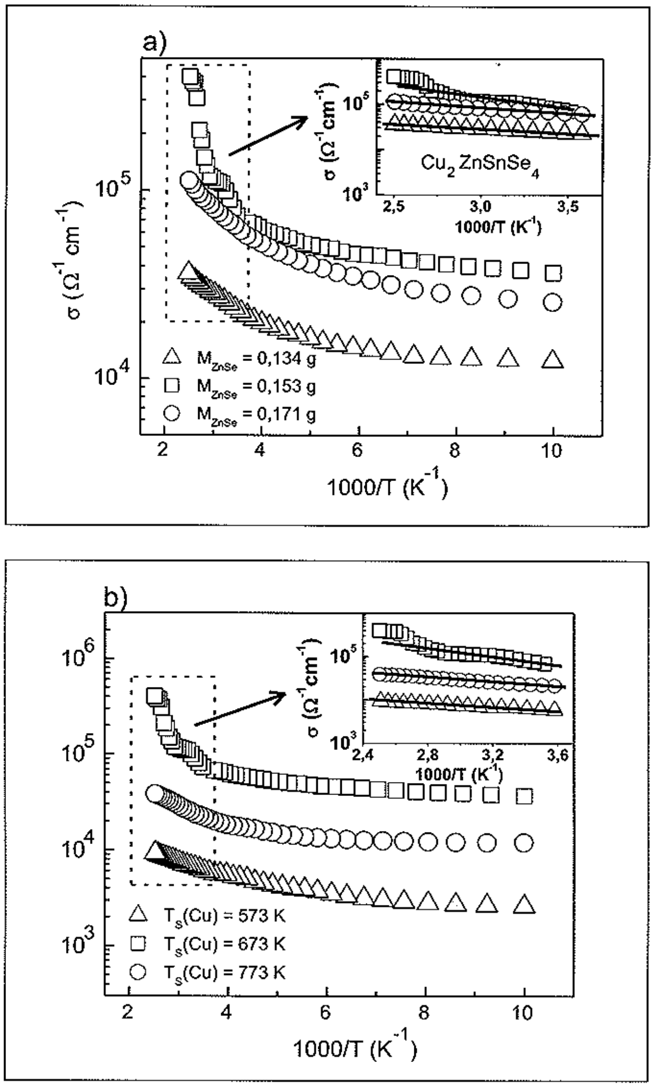

Figure. 1. Dark conductivity as a function of the inverse temperature for CZTSe samples varying a) M_{ZnSe} and b) T_s(Cu).The Figure inset shows a lineal fitting for all samples in the high-temperature range.

[Xie H., Tian C., Li W., Feng L., Zhang J., Wu L., Cai Y., Lei Z., Yang Y., 2010] In this case, TM were performed on all samples and it was observed, that conductivity is n-type. Being the conductivity an exponential function of the activation energy, small changes in the Fermi level will result in large variations of σ_{dk}, as it can be seen in Fig. 1. The activation energies, E_a, are reported in the table 1.

Table 1. Activation energies calculated from dark conductivity measurements for the CZTSe samples varying the M_{ZnSe} and T_s(Cu).

MZnSe (g)	TS(Cu) (K)	Ea (eV)
0.134		0.020
0.153	673	0.072
0.171		0.014
	573	0.021
0.117	673	0.072
	773	0.014

Quaternary phase, without binaries phases was obtained with 0.118 g for Cu, 0.097 g for Sn, and 0.151 g for ZnSe; temperatures for Cu, Sn and Se were 673, 523 and 673, respectively.

From Table 1 it´s observed that increasing the substrate temperature, T_s(Cu), from 573 K to 673 K evidence an increase in the activation energy of the material, therefore an increasing substrate temperature favors the formation copper bonds on surface, as thus the reducing on charge trapping centers, structural dislocations and the breaking bonds at crystal lattice. When the substrate temperature rises again from 673 K to 773 K is evidenced a drop in the value of the activation energy and the conductivity, this can be attributed to the fact that possibility, at these temperatures the copper was re evaporated showing thus a shortage of carriers.

On the other hand, in the case of the variation of M_{ZnSe}, the behavior observed in the curves is similar to that described above, except that the increase in conductivity is associated with increased presence of Cu atoms participating in the electric conduction.

Since the Arrhenius plot does not fit at low temperatures (See Figure 1) and then, other possible transport mechanisms were sought. In Figure 2, the variation of dark conductivity versus $1/T^{1/4}$ is shown.

It is observed, that at low temperatures, the lineal fitting is very good giving a correlation according to Mott's equation. [Mott N. F. (1969)] (See Figure 2)

$$\sigma = \sigma_0^* \, e^{(\frac{T}{T_0})^{1/4}} \qquad (1)$$

The percolation theory has been widely used to study transport phenomena in semiconductors, in particular to calculate the hopping parameters of Mott's equation for the case of VRH; however, these parameters are improved by Diffusional model. [Dussan A., Buitrago R. H., 2005] In this last model, is assumed that the density of states is constant in a range

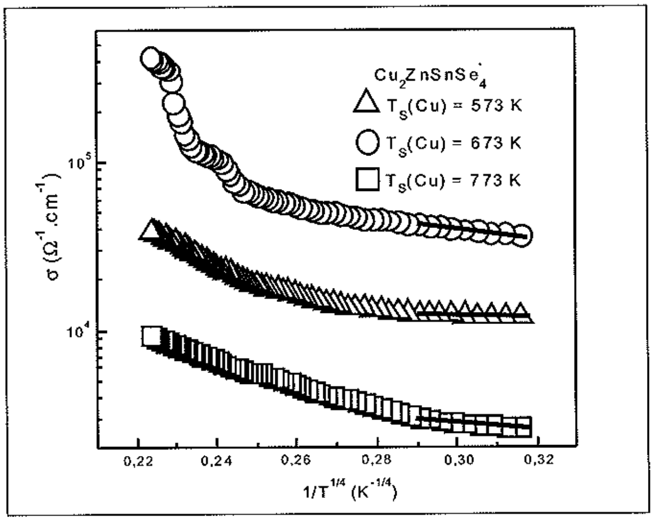

Figure 2. Dark conductivity as a function of $T^{1/4}$ for CZTSe samples varying T_s(Cu).

of some k_BT around the Fermi energy, and the latter is within the localized states, then for the three-dimensional case, the number of states per unit volume and energy (N_{Fermi}), separated by a hopping distance R_{hopp}, is related to the energy difference between hopping states as W_{hopp}.

Table 2 shows the results for the hopping parameters R_{hopp} and W_{hopp}, calculated from the diffusional model at a temperature of 150 K. The density of states at the Fermi level, N_{Fermi}, was calculated.

Table 2. Values of W_{hopp} and R_{hopp} for T = 150 K in samples CZTSe varying the substrate temperature during the evaporation of Cu. Calculating $N(E_{Fermi})$ we assumed c = 2.0, γ= 257 Å [Thamilselvan M., Premnazeer K., Mangalaraj D., Narayandass S. K., 2003]

$Cu_2ZnSnSe_4$ TS(Cu) (K)	$N(E_{Fermi})$ ($cm^{-3}\cdot eV^{-1}$)	Diffusional Model	
		R_{hopp} (cm)	W_{hopp} (eV)
573	7.11×10^{20}	6.22×10^{-7}	0.01
673	3.40×10^{18}	2.36×10^{-6}	0.05
773	$3.87\times10_{19}$	1.28×10^{-6}	0.02

Values of W_{hopp} and R_{hopp} are in agreements with the basic initial assumption that the density of states was constant around the Fermi level, and that the jumps of the carriers from one state to the other were only of the order of some k_BT.

Conclusion

Dark conductivity measurements performed over a wide range of temperatures for CZTSe samples were investigated. It was found that for temperatures higher than 300K the dominant mechanism is the thermal activation of carriers. The different activation energies found were obtained in terms of presence of Cu in the material. In the low-temperature ranges, the main transport mechanism is the VRH. From the diffusional model and using experimental data W_{hopp} and R_{hopp} were calculated.

Acknowledgments

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