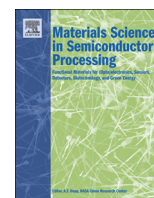




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# Materials Science in Semiconductor Processing

journal homepage: [www.elsevier.com/locate/mssp](http://www.elsevier.com/locate/mssp)

## Gap states density measurement in copper oxide thin films



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### ARTICLE INFO

#### Article history:

Received 31 October 2015

Received in revised form

26 December 2015

Accepted 14 January 2016

Available online 28 January 2016

#### Keywords:

Density of states

Thin films

Spray pyrolysis

Solar cells

### ABSTRACT

The density of gap states near the Fermi level have been measured in copper oxide (CuO) thin films deposited by spray pyrolysis technique. The measurement method is based on the exploitation of the current–voltage characteristics of the space charge limited current (SCLC) measured in a sandwich Au/CuO/Au structure. The measured gap states density is equal to  $1.5 \times 10^{14} \text{ cm}^{-3}$  and  $2.0 \times 10^{14} \text{ eV}^{-1}$  respectively in films prepared at 300 and 400 °C substrate temperature, while the defect position are located at 16 and 20 meV above Fermi level. The carriers mobility and concentration are also determined from SCLC, the obtained results are in good agreement with Hall effect measurement ones.

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### 1. Introduction

A large research activity have been devoted to new materials investigation for low cost thin films solar cells. Generally solar cell device is based on pn homo-junction or an heterojunction between two semiconductors with different gaps. Thin films based heterojunction solar cells is formed with a stack of buffer layer (such as CdS or ZnS) and an absorber layer. The commonly used absorber layers are CuIn(Ga)Se,  $\text{Cu}_2\text{ZnSnS}_4$ , CuO and SnS films. The incident photons are wholly absorbed and converted to free carriers in this layer. Thereafter solar cells performance i.e photocurrent, open circuit voltage and efficiency are close related to the electronic properties of the absorber layer. The presence of electronic defects in the band gap is crucial and may be a serious drawback of cells conversion, they hinder photo-generated charges collection through their recombination. Therefore, determination of the density of states (DOS) localized in the material band gap is an ambitious task and their diagnostic is important for the study of material dedicated to photovoltaic conversion. Several techniques have been used for DOS measurement in semiconductors such as: field-effect measurements [1], capacitance measurements [2], space charge limited current (SCLC) [3], deep-level transient spectroscopy (DLTS) [4] and photoluminescence (PL) measurements [5]. Among these techniques the space charge limited conduction (SCLC) technique has been extensively used for measurement of the DOS for amorphous hydrogenated silicon ( $\alpha\text{-Si:H}$ ) [6], organic semiconductors [7] and nano-cluster carbon [8]. The experimental measurement requested by this technique is

simple and easy, it needs less equipments by comparison to the other techniques. It is based only on the exploitation of the current–voltage characteristics. Copper oxide (CuO) has emerged as a promising material as absorber layer in solar cell [9,10]. CuO is a monoclinic semiconductor with an optical band gap ranged from 1.21 to 1.55 eV [11] which matches well with the solar spectrum and enjoys a high absorption coefficient in visible region which is suitable for solar energy conversion. Moreover, it is a p type semiconductor and is considered as a good partner to CdS or ZnS to form with an heterojunction necessary for thin films solar cells production [12]. On the other hand it is composed of inexpensive, no-toxic and available elements. To our knowledge no studies have been devoted to investigation of gap state density in CuO. The present work deals with the estimation of the density of localized state near the Fermi level and the carrier mobility in CuO thin films deposited by ultrasonic spray pyrolysis, using the space charge limited conduction (SCLC) measurements.

### 2. Experimental details

Copper oxide thin films have been prepared by ultrasonic spray pyrolysis. The precursor solution was prepared by dissolving 0.05 M copper chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) in distilled water. The precursor solution is sprayed, using an ultrasonic generator with a frequency of 40 KHz, in fine droplets of 40  $\mu\text{m}$  diameter on heated glass substrate in ambient air. Films are formed by pyrolytic reactions. During deposition, the substrate temperature is kept at 300 and 400 °C. This temperature range is chosen to ensure a complete precursor decomposition and to avoid the presence of chloride in films network. Deposition time was fixed equal to 30 minutes.

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Films thicknesses were determined by ellipsometry measurements. Films structural properties were determined by XRD using Philips X'Pert system with Cu  $K_{\alpha}$  radiation ( $\lambda_{Cu}=0.154$  nm). The space charge limited conduction (SCLC) measurements was carried using sandwich structure (Au/CuO/Au). The bottom contact layer, with a thickness of 200 nm, was deposited by DC sputtering of a high purity gold target, using 2.5 KV DC bias, on glass substrate surface prior to CuO deposition. The top contact, formed with 2 mm<sup>2</sup> area Au dots, were deposited on CuO film surface by the same sputtering system. The contacts were ohmic in nature. Current-voltage (I-V) characteristic were measured by Keithley electrometer 610 in dark and ambient temperature. The applied voltage is varied from 0 to 40 V.

Space charge limited current (SCLC) phenomenon occurs in semiconductors and insulator once the number of carriers injected into the sample exceeds the traps concentration in the sample. In this situation, the electric field in the sample becomes non-uniform, and the current no longer follows Ohm's law. Therefore, at voltages below traps filling limit, the semiconductor exhibits an ohmic behavior. However, at voltages where the injected charges are comparable to the thermal ones, the semiconductor current-voltage characteristic changes from ohmic to SCLC and its behavior obeys to the called the Mott-Gurney law given by [13]:

$$J = 9\epsilon_s \mu V^2 / 8d^3 \quad (1)$$

where  $\epsilon_s$  and  $\mu$  are the permittivity and the mobility of the material respectively,  $d$  is the sample thickness and  $V$  is the applied voltage.

Assuming a uniform distribution, the density of state near the Fermi level is calculated from sample J-V characteristic in the SCLC regime using de Boer method [14]. Taking two points ( $J_1, V_1$ ) and ( $J_2, V_2$ ) on the measured J-V-curve in the SCLC regime, the Fermi level shift (due to the applied bias)  $\Delta E_F = E_{F2} - E_{F1}$  corresponding to voltage change  $\Delta V = V_1 - V_2$  is calculated according to the following relation [14]

$$\Delta E_F = KT \ln (J_2 \cdot V_1 / J_1 \cdot V_2) \quad (2)$$

Where  $J_1$ , and  $J_2$  are the current densities measured at the bias  $V_1$  and  $V_2$  respectively

The defect density average  $N_s$  in the band gap between  $E_{F1}$  and  $E_{F2}$  is given by [14] :

$$N_s = 2\epsilon_s \Delta V / ed^2 \Delta E_F \quad (3)$$

where  $\epsilon_s$  is the permittivity of the material,  $d$  is the sample thickness,  $\Delta V$  and  $\Delta E_F$

the bias increment and the corresponding Fermi level respectively and  $e$  is the elementary electrical charge.

The trap density was calculated using Eqs. 2 and 3. Films should be thick enough (higher than 1  $\mu\text{m}$ ) to have an accurate measurement of the gap density [14].

Hall effect measurements were carried in a dark and at ambient temperature using Van der Paw structure.

### 3. Results and discussion

In Fig. 1 we have reported a typical XRD spectrum of CuO thin film prepared by spray pyrolysis with substrate temperatures 300 and 400 °C. As can be seen, two peaks assigned respectively to the planes (111) and (002) of CuO tetragonal structure are present (PDF card #45-0937). No peaks related to Cu<sub>2</sub>O phase are seen. Dominant CuO phase has been also reported in several studies [15–17] where (002) preferential orientation is observed.

Increasing substrate temperature reduces the diffraction peaks intensities, this is due to film thickness reduction . As shown in

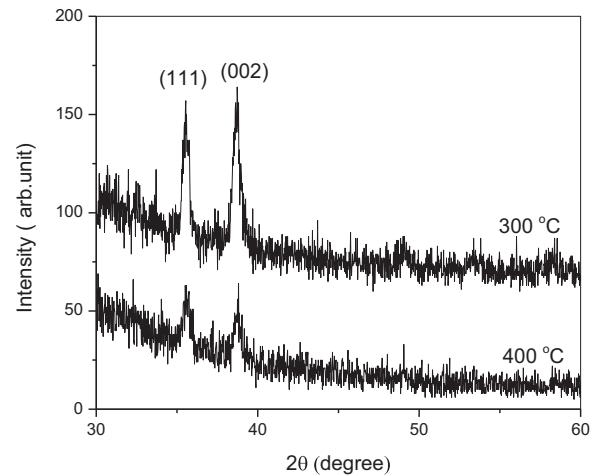


Fig. 1. XRD pattern of CuO thin film deposited by spray pyrolysis with substrate temperatures of 300 and 400 °C .

Table 1

Optical band gap, conductivity, defect density and position in films deposited at 300 and 400 °C substrate temperature.

Substrat Temperature (°C)	Eg (eV)	Conductivity ( $\Omega \text{ cm}^{-1}$ )	DOS ( $\text{cm}^{-3} \text{ eV}^{-1}$ )	Position $\Delta E_F$ (meV)
300 °C	1.37	$6.64 \times 10^{-4}$	$1.5 \times 10^{14}$	16
400 °C	1.41	$6.90 \times 10^{-2}$	$2.2 \times 10^{14}$	20

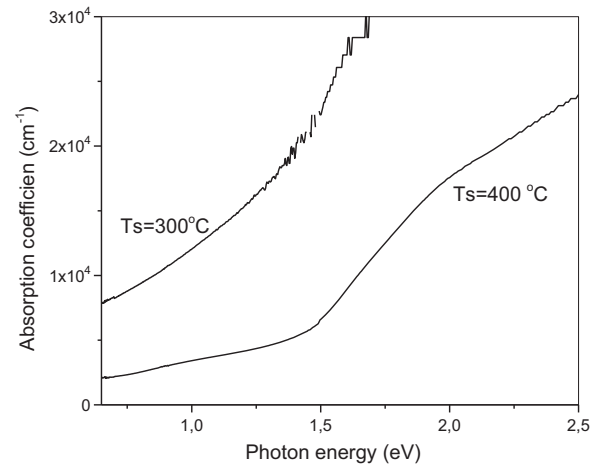


Fig. 2. Absorption coefficient as a function of photon energy of CuO films prepared with 300 and 400 °C substrate temperatures.

Table 1, the thickness of CuO film deposited at 300 °C substrate temperature is equal to 2800 nm, however the film prepared at 400 °C is thinner with 1800 nm. The reduction of films thickness with increasing substrate temperature is due to air convection around the substrate that may carry droplet away from the substrate. The same conclusion has been reported in ZnO thin films prepared by spray pyrolysis [18].

In Fig. 2 we have reported the variation of the optical absorption coefficient, of different CuO films, calculated from films transmittance in the visible range. As can be seen, the film deposited at 300 °C exhibits a larger absorption coefficient than the film prepared at 400 °C substrate temperature. This is consistent, as shown in Table 1, with the narrower band gap measured in this film. This suggests that 300 °C substrate temperature is suitable to produce CuO thin films candidate as absorber layer in thin films solar cell.

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