Cryst. Res. Technol.	**35**	2000	3	315–319

E. HERNÁNDEZ, A. ROMERO

Laboratorio de Caracterización de Materiales, Departamento de Física, Facultad Experimental de Ciencias, La Universidad del Zulia, Maracaibo, Venezuela

Current Density-Voltage and Capacitance-Voltage Characteristics of Local p-n Junction Structures in $CuInSe_2$ Single Crystals

Local p-n junction were obtained under room temperature conditions in $CuInSe_2$ by applying strong electric field through small indium and copper contacts. The current density voltage (J-V) and the capacitance-voltage (C-V) of three different samples were measured at room temperature. The J-V method shows that the current is dominated by the drift component of the injected carriers. The C-V method gave a barrier height of 1.04 eV for all three samples which agrees with the reported energy gap of this material. Analysis of these results indicate that the p-n junction structures formed by strong electric fields are hihgly compensated and the current transport is dominated by the space charge limited current effect.

Keywords: $CuInSe_2$; ternary semiconductor ; p-n junction ; SCL current effect ; capacitance-voltage ; current density-voltage

(Received October 14, 1999; Accepted January 21, 2000)

1. Introduction

Copper indium diselenide (CIS) is a ternary chalcopyrite semiconductor widely investigated because of its application as an absorber in high efficiency solar cells. It has been reported that application of pulse of reverse bias voltages to electrical contacts can create doping profiles in this material, which correspond to p-n or even p-n-p structures (CAHEN et. al.; CHERNYAK et. al.). The junctions formed by this method, as observed by J-V curve, are sharp and the process occurs under room temperature conditions. However, such a characteristic is not always reproducible and important problems related to the devices made with ternary compounds in general and CIS in particular, must be solved before realiable p-n structures can be produced experimentally. One key area for the improvement is in the understanding of the physics involved in the formation of p-n junctions by these techniques and the characterization of the dominant transport mechanism. In this paper we report on the study of the dominant current transport mechanism in a p-n structure in CIS obtained by this technique.

2. Experimental Methods

$CuInSe_2$ single crystals were grown from the melt containing stoichiometric quantities of the elements of at least 5 N purity. p type conductivity was determined by the conventional thermal probe method. The as-grown crystal was cut into slices of 3.0 x 3.0 x 1.0 mm^3. The electrical contacts were made on samples C43 and C45 using indium pellets and electrodeposition of copper on C23, and were attached to copper leads. The local p-n junction around the contacts were formed by applying through the contacts a square pulse of 200 ms width, 30 V height, yielding a peak current of approximately 20 mA.

The current density-voltage characteristic were measured using a Keithley Programmable Voltage Source model 230 and a Keithley 485 picoammeter. The capacitance-voltage measurements were made with a Keithley high frecuency C-V meter at 100 KHz.

3. Experimental Results and Discussion

The forward and reverse current density-voltage characteristics of the three devices are shown in Fig. 1. Normally, the current density flowing through a forward and reverse biased p-n structure is given by the Shockley equation (Shockley),

$$J = \left(\frac{qD_p p_{no}}{L_p} + \frac{qD_n n_{po}}{L_n} \right) \left(e^{\frac{qV}{KT}} - 1 \right) \tag{1}$$

This is the ideal diode law, but when the injected minority-carrier is comparable to the majority concentration (space charge effect), the Shockley equation is no longer valid and the high injection condition is established. This situation is clearly observed at higher voltages in the semilogarithmic plot of the forward bias of the current density-voltage characteristics shown in Fig. 2, where the current becomes roughly proportional to exp(qV/2KT) (Sze).

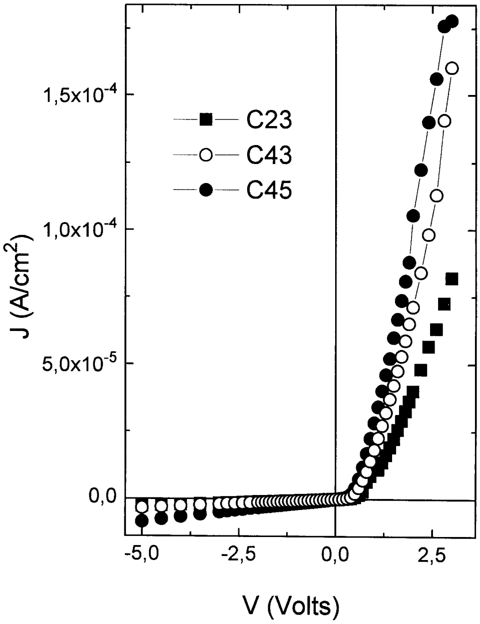

Fig. 1. : Forward and reverse bias portions of a typical den current-voltage characteristic for a p-n CIS junction structure.

In the high injection condition, the injected carriers control the space charge and the electric field profile. This leads to a feedback mechanism where the field drives the current which in turn sets up the field. Under this condition the total current is given by both the drift and the diffusion current components. If the current is dominated by the drift component of the injected carriers, the space charge limited (SCL) current effect is observed

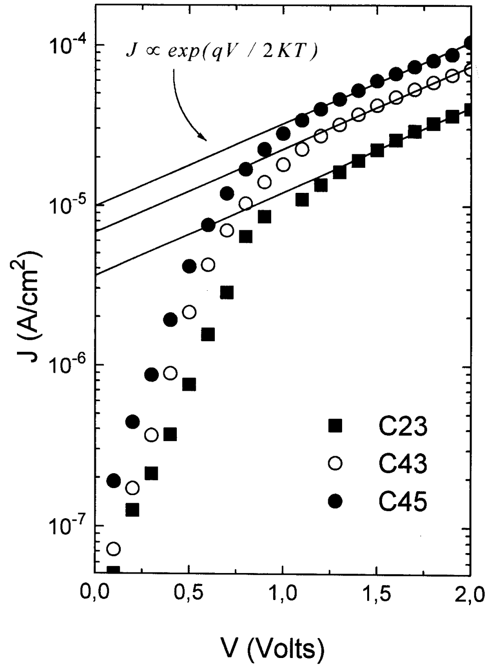

Fig. 2. : Semilogarithmic plot of the forward bias portion of the density current-voltage characteristic.

The SCL current in the mobility regime is given by the expression (KWOK),

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8L^3} \tag{2}$$

where ε is the dielectric constant, ε_o the free space permitivity, L the diode thickness and μ the mobility of holes.

A typical logarithmic plot of the current density-voltage of SCL current is shown in Fig. 3 for the devices. Square dependence in the region higher than 1 volt is found which confirm the SCL current effect in the mobility regime. This behaviour has also been observed previously in p-type CIGS/In Schottky diodes (HERNÁNDEZ). From the slope of the linear fit of the data using Eq. (2) in the region higher than 1 volt, the mobility of the holes was estimated to be 12 cm^2/Vs. This is a typical value for a p type CIS (WASIM) .

For a p-n abrupt junctions, the capacitance per unit area is given by (ROBERT et. al.)

$$C^{-2} = \frac{2}{q\varepsilon N_B}(V_o + V - \frac{2KT}{q}) \tag{3}$$

where ε is the dielectric constant of the semiconductor, q is the elemental charge, K the Boltzman constant, T is the absolute temperature and N_B the impurity concentration of the substrate.

Fig. 4 shows C^{-2} -V curves measured at a high frequency of 100 KHz for the C23, C43 and C45 samples. The C^{-2} value increase linearly with the reverse bias voltages for the three samples. However, at lower voltages the C^{-2} -V plot show a nonlinear behaviour. This is usually attibuted to the existence of deep levels (ROBERTS et. al.). From the slopes of the linear bias range shown in Fig. 4, the N_A values of the C23, C43 and C45 are estimated to be 2.0x10^{14}, 8.3x10^{14} and 1.2x10^{15} respectively. Vo, obtained from the interception with the xaxis is found to be 1.04 V for all the samples. This corresponds to the energy gap of CIS and could perhaps be associated with the fact that the discrete energy levels located below the energy gap has been filled.

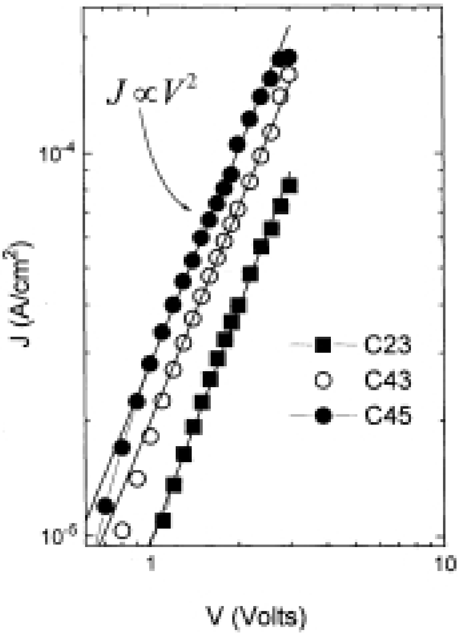

Fig. 3: Logarithmic density current-voltage plot of space charge limited current in p-n CIS junction structures.

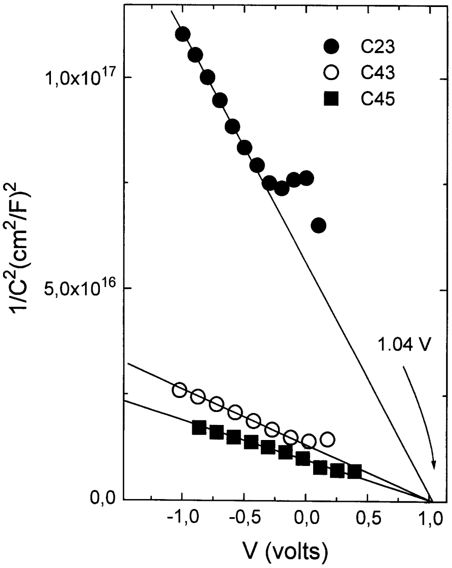

Fig. 4: $1/C^2$ versus voltage characteristic for the p-n CIS junction structures.

During the formation of p-n structure by the application of strong electric field, conversion of conductivity could take place by the increase of the concentration of donor levels over the acceptors. For this to occur, the local p-n structure should be expected to be highly compensated. This could perhaps explain the relatively low effective N_A values obtained by the C-V measurements and the fact that the current transport is dominated by SCL current effect.

Usually the quasi-Fermi level position is dominated by localized states situated in the forbiden gap. But, for the case of SCL current the quasi-Fermi level position changes with the injection of carriers (ZMESKAL et. al.; LAMPERT et. al.; SCHAUER et. al.). Under this condition, the quasi-Fermi level position is dominated by the weighted average of one set of localized states and the transport band. Increasing the space-charge density by injection, accompanied by the shift of the quasi-Fermi level, the first set of states is gradually filled and the transport band start to become occupied. Consequently there is a jump in the dominating energy from the set of states to the transport band. Hence, the conduction band goes below the quasi-Fermi level due to high carrier concentration. This argument could explain the results obtained by the C-V measurements.

4. Conclusions

The current transport mechanism of local p-n junction structures in CIS single crystals produced by applying strong electric field, is found to be influenced by the shift of the quasi-Fermi level due to the high concentration of injected carriers. The observed J-V and C-V measurements can be understood on the basis of space charge limited current effect in the mobility regime.

Acknowledgments

This work was supported by grants from the Consejo de Desarrollo Científico y Humanístico (CONDES) of La Universidad del Zulia under contract No. 01451-99 and the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) of Venezuela under contract F-97000965.

References

CAHEN D., GILET J. M., SCHMITZ C., CHERNYAK L., GARTSMAN K. and JAKUBOWICZ A. Science **258**, 271 (1992)
CHERNYAK L., CAHEN D., ZHAO S., HANEMAN D. Appl. Phys. Lett. **65** (4) 1994
HERNÁNDEZ E. Cryst. Res. Technol. **33** (1998) 2, 285-289
KWOK K. NG. Complete Guide to Semiconductor Devices (MCGRAW HILL 1995) PP 564-565
LAMPERT M. A. and MARK P., Current Injection in Solids (Academic New York) 1970
ROBERTS G. I. and C.R. CROWELL. J. Appl. Phys. **41**, 1767 (1970)
ROBERTS G. I. and C.R. CROWELL. Solid State Electron., **16**, 29 (1973)
SCHAUER F., NESPUREK S. and VALERIÁN K. J. Appl. Phys. **80,** 2 (1996) 880
SHOCKLEY W., Bell Syst. Techn. J. **28**, 435 (1949)
SZE S. M. Physics of Semiconductor Devices, 2nd Edition, John Wiley & Sons (1981) PP 74-96
WASIM S. M., Solar Cells **16** (1986) 289
ZMESKAL O., SCHAUER F., NESPUREK D. J., J. Phys. C : Solid State Phys. **18**, 1873 (1985)

Contact information:

E. HERNÁNDEZ, A. ROMERO
Laboratorio de Caracterización de Materiales
Departamento de Física, Facultad Experimental de Ciencias
La Universidad del Zulia
4011. Apdo 526
Maracaibo, Venezuela

e-mail: elvis@solidos.ciens.luz.ve