Hopping conductivity in p-$CuGaSe_2$ films

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The results of resistivity measurements on p-type $CuGaSe_2$ films are presented and analyzed within the framework of different hopping conductivity models. Both the Mott [N. Mott and E. A. Davies, *Electron Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979); N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1990)] and the Shklovski-Efros [*Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984)] regimes of variable-range hopping are observed. The values of the characteristic and transition temperatures as well as the complete set of parameters describing the properties of the localized holes (the localization radius, the dielectric permeability, the width of the Coulomb gap, and the values of density of states at the Fermi level) are determined. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338600]

I. INTRODUCTION

$CuGaSe_2$ is promising for use in red-light-emitting devices, light detectors, and as a material for solar cells. So far, $CuGaSe_2$ solar cells with a CdS buffer have achieved efficiencies of 9.5% and 9.7% as thin film[1] and single crystal solar cells, respectively.[2] This is about half of the efficiency achieved for Cu(In,Ga)Se_2 solar cells. However, $CuGaSe_2$ exhibits some advantages with respect to module integration due to its higher band gap.[3] Furthermore, a tandem arrangement of $CuInSe_2$ and $CuGaSe_2$ could increase efficiency above 33%.[4]

Transport phenomenon measurements were carried out on p-$CuGaSe_2$ films[5–10] and single crystals,[11–15] and the values of Hall mobility, the activation energies of the shallow and the deep acceptors, and their concentration were determined as well as the dominant scattering mechanisms.

In the present study we report on the measurements of the resistivity of p-$CuGaSe_2$ epitaxial films at low temperatures. The purpose of the work is to investigate variable-range hopping conductivity of this compound. Analysis of the experimental data is performed to determine parameters of the localized carriers such as the localization radius, the dielectric permeability, the density of states at the Fermi level, and the width of the Coulomb quasigap.

II. FILM GROWTH AND RESISTIVITY MEASUREMENTS

The epitaxial films are prepared by metal organic vapor phase epitaxy (MOVPE) on semi-insulating GaAs(001) at substrate temperatures of 570 °C, using cyclopentadienyl copper tertiarybutylisocyanide, ditertiarybutyl selenium, and triethyl gallium as Cu, Se, and Ga sources, respectively. Typical thickness of these films is 0.4 μm. Epitaxial quality has been shown by x-ray diffraction, electron channelling pattern, and scanning electron microscopy. Further details of the film growth can be found in Refs. 17 and 18. Growth rates are low at about 100 nm/h. In the growth process of the samples discussed here the rotation of the substrate was switched off to make use of the Cu gradient occurring along the flow direction. This allowed the growth of samples, while varying the Cu excess, in one process. The wafer was cut after the processing into small pieces, which were contacted for Hall measurements. Both of the samples discussed in this paper were cut from a position very close to the position where [Cu]/[Ga]=1 with sample A closer to [Cu]/[Ga]=1 then sample B, i.e., both were grown under a slight Cu excess but with a lower Cu excess in sample A than sample B.

The resistivity ρ was measured in the temperature range of 15–300 K. The contact arrangement used was a four-point probe in a van der Pauw geometry. Current reversal was applied. The films were p-type and their parameters (the values of the concentration of acceptor levels N_a, the concentration of donor levels N_d, and the degree of compensation $K=N_d/N_a$) determined in Ref. 16 are given in Table I.

III. RESULTS AND DISCUSSION

The temperature dependence of the resistivity ρ of the investigated films is shown in Fig. 1. The conductivity of our samples has an activated character, including two regions with different slopes for the $(1/T)$ dependence of ρ. The first one, at high temperatures, is connected with the band conduction (activation of carriers from acceptor levels to the valence band). The second slope, on the low-temperature side, is determined by the hopping conductivity or transition between the impurity centers or localized states inside the impurity band. The low-temperature slope is not constant but varies with temperature, suggesting variable-range hopping (VRH) conduction. Two different types of VRH could be distinguished. Mott (M)-type VRH takes place when the electron density of states (DOS) $g(\mu)$ at the Fermi level μ is constant,[19] and Shklovskii-Efros (SE) VRH is found when the DOS has a parabolic quasigap due to the long-range Cou-

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TABLE I. Parameters N_a, N_d, K, T_{0M}, T_{VM}, A_M, T_{0SE}, T_{VSE}, A_{SE}, and Δ for $CuGaSe_2$ films..

Samples	N_a (10^{18} cm^{-3})	N_d (10^{18} cm^{-3})	K	T_{0M} (K)	T_{VM} (K)	A_M (Ω cm K$^{-1/4}$)	T_{0SE}	T_{VSE} (K)	A_{SE} (Ω cm K$^{-1/2}$)	Δ (meV)
A	12	8.42	0.70	2 633	71	0.0188	66	22	0.0419	1.6
B	9.3	8.5	0.91	101 816	75	0.0108	250	24	0.6136	3.3

lomb correlations of the localized carriers in the energy range between $\mu-\Delta$ and $\mu+\Delta$.[20] The resistivity in the range of VRH conduction can be expressed as

$$\rho(T)=\rho_0\exp[(T_0/T)^p], \tag{1}$$

where $\rho=\frac{1}{4}$ (M-VRH) or $\frac{1}{2}$ (SE-VRH), $\rho_{0M}=A_M T^{1/4}$ and $\rho_{0SE}=A_{SE}T^{1/2}$ are the prefactors (A_M and A_{SE} are independent of T), and T_{0M} and T_{0SE} are the characteristic M-VRH and the SE-VRH regime hopping temperatures, respectively. T_{0M} and T_{OSE} can be expressed as[20]

$$T_{0M}=\frac{\beta_M}{k_B g_n(\mu)\alpha^3}, \quad T_{0SE}=\frac{\beta_{SE}e^2}{\kappa k_B\alpha}, \tag{2}$$

where $\beta_M=21$ and $\beta_{SE}=2.8$ are the numerical constants, κ is the dielectric permeability, $g(\mu)$ is the density of the localized states, and α is the localization radius of charge carriers.

The value of the width of the quasigap Δ and the density of states (DOS) outside the gap g_0 are given by[20]

$$\Delta=\frac{\kappa_B}{2}\sqrt{T_{0SE}T_{VSE}}, \tag{3}$$

$$g_0=\frac{k_B^2\kappa^3 T_{0SE}T_{VSE}}{16e^6}, \tag{4}$$

where T_{VSE} is the temperature of the transition to VRH conduction over states of the Coulomb gap (SE regime), or the opening of the Coulomb gap.

A simple estimation of the DOS at the Fermi level μ can be obtained using the following approximation.[20]

$$g^{calc}=\frac{KN_a}{E_0}, \tag{5}$$

where $E_0=e^2/\kappa_0 r_d$ is the energy of the Coulomb repulsion, $r_d=(4\pi N_d/3)^{-1/3}$ is the half of the mean distance between the acceptors, K is the degree of the compensation, and κ_0 is the dielectric permeability far from the metal-insulator transition (MIT).

The regime of the VRH conduction can be determined using presentation of the temperature dependence of the resistivity in different coordinates in accordance with Eq. (1). As can be seen from Figs. 2 and 3 the resistivity behavior of our films can be fitted to both M- and SE-VRH in the low and the lowest studied temperature intervals, respectively. As usual in low-temperature resistivity measurements the curves do not show a clear behavior according to Eq. (1).[21] This is due to the simultaneous presence of both mechanisms (and potentially other transport mechanisms) throughout the investigated temperature range, with M-VRH dominating the range between 70 and 20 K and SE-VRH dominating at lower temperatures.

The values of the temperatures T_{VM} (the temperature of the onset of M-VRH) and T_{VSE} (the temperature to the transition to SE-VRH conduction), and those of the characteristic temperatures T_{0M} and T_{0SE} are determined from the slope of the plots $\ln(\rho/T^p)$ vs $1/T^p$ (see Figs. 2 and 3). Using obtained parameters and Eqs. (6)–(9),[22]

$$g(\mu)=\frac{N_a}{2k_B(T_{VM}^3T_{0M})^{1/4}}, \tag{6}$$

$$\alpha_M=\frac{\beta_M^{1/3}}{[k_BT_{0M}g(\mu)]^{1/3}}, \tag{7}$$

$$\kappa=\frac{e^2\beta_{SE}^{1/2}}{k_B(2T_{0SE}T_{VSE})^{1/2}}, \tag{8}$$

$$\alpha_{SE}=\frac{\beta_{SE}e^2}{T_{0SE}\kappa k_B}, \tag{9}$$

the values of the localization radii α_M and α_{SE} (where the subscript M and SE refer to the VRH regimes in which the values of the localization radius are obtained), the DOS at the Fermi level $g(\mu)$, and the dielectric permeability κ were estimated (Table II). It worth mentioning that κ is a material constant depending on properties of a material. In doped

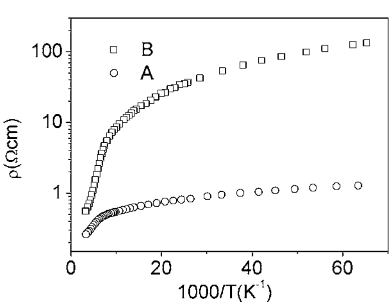

FIG. 1. Showing the temperature dependence of the resistivity of samples A and B.

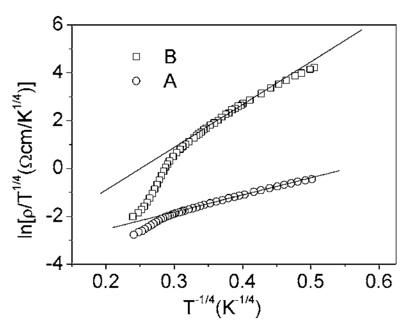

FIG. 2. The dependence of $\ln(\rho/T^{1/4})$ on $T^{-1/4}$.

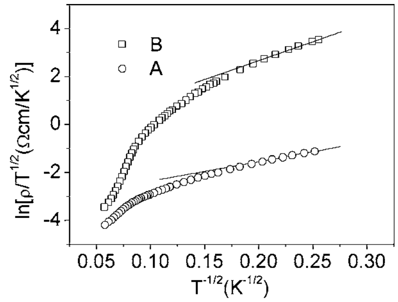

FIG. 3. The dependence of $\ln(\rho/T^{1/2})$ on $T^{-1/2}$.

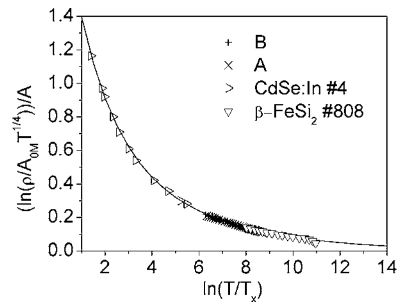

FIG. 4. $\ln(\rho/A_M T^{1/4})/A$ vs $\ln(T/T_x)$ for two $CuGaSe_2$ films, CdSe (Ref. 28) and β-$FeSi_2$ crystals (Ref. 27) with different parameters A and T_x. The solid line is the function $f(x)$ of Eq. (11).

semiconductors it depends on proximity to the MIT, increasing for $N \to N_c - 0$, as well as α increases, according to Eq. (10) (see below) where α_0 and κ_0 are the corresponding values far from the MIT (i.e., for $N \ll N_c$). Both α and κ exhibit a divergency at $N = N_c$, where N_c is the critical concentration of the MIT, whereas for $N > N_c$, i.e., in the metallic region, neither of these parameters could exist.

From Eqs. (3)–(5) we find a Δ (of about 2–3 meV) in the samples studied (Table I), g_0, and $g(\mu)^{\text{calc}}$ (Table II), respectively. It is worth mentioning the good agreement between α_M and α_{SE}. The obtained values of the DOS [g_0 and $g(\mu)$] are consistent and agree with the calculated data (g^{cal}).

The mean hopping length of the M-VRH and SE-VRH conductivities can be presented as[22]

$$R_{hM} = C_M \alpha_M \left(\frac{T_{0M}}{T} \right)^{1/4}, \quad R_{h\text{SE}} = C_{\text{SE}} \alpha_{\text{SE}} \left(\frac{T_{0\text{SE}}}{T} \right)^{1/2},$$

where $C_M \approx 0.357$ and $C_{\text{SE}} = 0.5$. In the temperature range where Mott's (SE's) VRH is observed the values of $R_{hM}/\alpha_M (R_{h\text{SE}}/\alpha_{\text{SE}})$ are more than 1 [2.1(1.6)] for sample B with the lower acceptor concentration and less than 1 [0.88(0.87)] for sample A with the higher acceptor concentration. The latter indicates the variable-range hopping near MIT.[23] Data on the other parameter, describing the properties of the localized holes, and their variation, with acceptor concentration, are in reasonable agreement with R_{hM}/α data (Table II).

As a system approaches a MIT, the scaling law,

$$\alpha = \alpha_0 (1 - N_a/N_c)^{-\nu}, \quad \kappa = \kappa_0 (1 - N_a/N_c)^{-\nu'}, \tag{10}$$

sets in and governs the dependence of α and κ on N where the critical exponents $\nu \approx 1$ and $\nu' \approx 2\nu$.[19,23] With $\alpha = \alpha_M$ and $\nu = 1$, we obtained $N_c \approx 14 \times 10^{18}$ and $\alpha_0 \approx 9$ Å. Also with the values of κ from the scaling relations with $\nu' \sim 2$, it follows that $\kappa_0 \approx 11$ and $N_c \approx 17 \times 10^{18}$. With $N_c = (16 \pm 2) \times 10^{18}$ obtained from the equations above and $\alpha_0 \approx 9$ Å, we obtain $N_c^{1/3} \alpha_0 \approx 0.22$–$0.23$, which is close to the value of ≈ 0.25 in agreement with the Mott criterion of the MIT.

Recently, Aharony *et al.*[24] have proposed that the temperature dependence of the hopping resistivity can be expressed by a scaling expression of the form $\ln(\rho/\rho_0) = A f(T/T_x)$, where $f(T/T_x)$ is a universal function and A, T_x, and ρ_0 are sample-dependent constants. The crossover universal function, where $x = T/T_x$, is written as

$$f(x) = \frac{1 + \{[(1+x)^{1/2} - 1]/x\}}{[(1+x)^{1/2} - 1]^{1/2}}. \tag{11}$$

Under this condition, in the asymptotic resistivity limits, one can get

$$T_{0M} = A^4 T_x, \quad T_{0\text{SE}} = 4.5 A^2 T_x, \tag{12}$$

where T_0 is replaced by T_{0M} and $T_{0\text{SE}}$ for Mott ($s = 1/4$) and SE ($s = 1/2$ type of conduction, respectively, in the expression $\ln(\rho/\rho_0) = (T_0/T)^s$.

Thus, knowing A and T_x one can get an estimation of T_{0M} and $T_{0\text{SE}}$ even if the experimental resistivity shows only one type of conduction. On the other hand, the model proposed by Aharony *et al.*[24] allows us to establish the range of critical temperature where the crossover from Mott- to SE-type conduction occurs. This temperature, T_c, lies between $4T_x$ and $200T_x$. The value of T_c can be also be estimated, using the criterion of Rosenbaum,[25] who obtained $T_c = 16 T_{0\text{SE}}^2 / T_{0M}$ by equating the average hopping energy in the two regimes when crossover occurs. Shlimak *et al.* used another criterion;[26] at the temperature T_c, when the width of the "optimal band" of localized levels, which are involved in the hopping conduction, becomes equal to the half width of the Coulomb gap. This leads to $T_c = 2.7 T_{0\text{SE}}^2 / T_{0M}$. The approach of Shlimak means that the Coulomb gap, effective only for temperatures lower than this, comes from what he calls "temperature induced smearing of the Coulomb gap."[26]

In our samples the prefactor ρ_0 is a temperature dependent value. That is why we plot $\ln(\rho/A_M T^{1/4})/A$ against $\ln(T/T_x)$ for the data of studied samples as well as $FeSi_2$ single crystals[27] (Fig. 4). The value of A_M was earlier deter-

TABLE II. Parameters N_a, α_M, α_{SE}, g_0, $g(\mu)$, g^{calc}, κ, T_{cR}, T_{cS}, A, T_x for $CuGaSe_2$ films.

Samples	N_a (10^{18} cm^{-3})	α_M (Å)	α_{SE} (Å)	g_0 (cm^{-3} meV^{-1})	$g(\mu)$ (cm^{-3} meV^{-1})	g^{calc} (cm^3 meV^{-1})	κ	T_{cR} (K)	T_{cS} (K)	A	T_x
A	12	61	60	3.8×10^{17}	4.0×10^{17}	1.7×10^{17}	122	26	5.6	16.9	0.028
B	9.3	27	35	1.4×10^{17}	1.2×10^{17}	1.9×10^{17}	54	9.8	1.7	36.6	0.049

mined from the slope of the plots $\ln(\rho/T^p)$ vs $1/T^p$ (Table I), and values of A and T_x were estimated for each sample as fitting parameters from nonlinear least-squares fit of the $\rho(T)$ dependence. We find, as expected from the scaling model of Aharony *et al.*,[24] that the temperature dependence of the electrical resistivity in the VRH regime can be represented by a universal curve (Fig. 4). Earlier it was shown that data on n-CdSe,[24] n-$CuInSe_2$, and p-$CuInTe_2$,[28] fall on a universal curve too. At higher temperatures where M-VRH regime is not valid, the deviation of the experimental data from the universal function $f(x)$ is observed.

Values of T_{0M} and T_{0SM} estimated using Eqs. (12) are in a satisfactory agreement with that determined from the $\rho(T)$ dependences. The value of T_c, the critical temperature where the crossover from Mott- to SE-type conduction occurs, was estimated using different models, namely, Aharony *et al.* (T_{cA}),[24] Rosenbaum (T_{cR}),[25] and Shlimak *et al.* (T_{cS}).[26] It was found that $T_{\mathrm{VSE}} \geqslant T_{cR}$ and $T_{\mathrm{VSE}} \geqslant T_{cA}$ (T_{cS}), where T_{VSE} is the temperature to the transition to SE-VRH conduction.

It should be mentioned that the Mott-type VRH was earlier observed in n-$CuInSe_2$ and p-$CuInTe_2$,[28] and a crossover to ES-type VRH was reported for p-$CuInTe_2$,[29] however, a detailed analysis was not performed and the set of parameters describing the properties of the localized carriers was not determined.

IV. SUMMARY

In conclusion, the low-temperature resistivity of the p-$CuGaSe_2$ films was investigated. Both Mott- and SE-variable-range hopping conductivities are observed, and the values of the characteristic and transition temperatures as well as the complete set of parameters describing the properties of the localized carriers have been determined. It has been established that the temperature dependence of the electrical resistivity of p-$CuGaSe_2$ that follows a variable-range hopping conduction mechanism can be expressed by a universal scaling expression of the form $\ln(\rho/\rho_0)=Af(T/T_x)$ according to the model of Aharony *et al.* The ρ vs T data of the studied samples, when plotted as $\ln(\rho/A_M T^{1/4})/A$ against $\ln(T/T_x)$, fall on the same curve.

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