Space-Charge–Limited Currents in Evaporated GaS Thin Films

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Space-charge–limited–current (SCLC) measurements have been performed at room temperature on n-GaS thin films. Ohmic conduction was predominant at low applied fields, with the free electron concentration $n_0 \approx 3.25 \times 10^{14} \text{ m}^{-3}$. Two deep electron traps have been found at 0.51 and 0.56 eV below the conduction band with concentrations ranging between $10^{21}$ and $10^{22} \text{ m}^{-3}$. Two distinct activation energies $\Delta E_1$ and $\Delta E_2$ have been detected in the temperature range between 250 K and 400 K. The former represents a shallow level with $\Delta E_1 = 0.32 \text{ eV}$. The latter one, $\Delta E_2 = 0.63 \text{ eV}$, shows a deeper level located in the band gap. A comparison was made between the results of this work and data quoted by various authors with different techniques. The expected chemical defects are considered in data analysis.
Introduction:

Gallium sulphide is one of the layer-type semiconductors which belongs to the III–VI family. In these materials, the inter-layer bonding is very weak, since it is of Van der Waals type. On the other hand, the bonding inside layers is strong covalent.

The electrical and optical properties of III–VI compounds are strongly influenced by the presence of carrier trapping centers in the forbidden gap, arising from the native defect states. Lampert [1] showed that space–charge–limited currents (SCLC) measurements are an invaluable tool for determining low concentrations and energy distributions of carrier trapping states in insulators. The energy “width” of the traps can be measured from the “superquadratic” slope in the current–voltage (I-V) curve. A more refined model, which assumes a distribution function of exponential type for the trap density, has been developed by Sworakowski and Pigon [2]. This model has been tested extensively, especially in organic crystals and thin films [3, 4].

Several studies were carried out on n-GaS single crystals to detect the parameters of trapping centers using different methods [5-11]. However, very few data are available in literature on the electrical transport properties of GaS thin films, of which the study on GaS thin films prepared by vacuum evaporation [12].

The aim of this paper is to report a systematic investigation on the electron trapping states in n-GaS thin films, based on SCLC measurements, in order to determine the parameters of these traps.

Experimental:

GaS thin films were prepared on ordinary glass substrate held at room temperature (~300 K) during the deposition process. In–GaS-In sandwich structures of active area 4×10^{-6} m^2 were thermally deposited in vacuum of 10^{-4} Pa. The deposition rate was about 2 nm s^{-1} for GaS films. The thickness of the sample was controlled by means of a quartz crystal monitor (FTM6-type) and then measured by Tolansky’s method [13]. The thickness of the used films ranged from 500 to 1400 nm.

All films prepared under the conditions given above exhibit amorphous structure as indicated by X-ray diffraction examination. The EDX analysis (Fig.1) revealed that the GaS thin films obtained by the thermal evaporation technique are nearly stoichiometric (Ga_{0.482} S_{0.518}). The slightly excess of sulfur predicts that the GaS films are most likely n-type.
Fig. (1): Typical EDS spectrum of GaS thin film.

The conductivity type was determined by the hot point probe method. Contacts were checked to be ohmic at low voltages and to show a symmetrical behaviour with respect to the voltage polarity.

The electrical resistivity of GaS thin films were measured in a liquid nitrogen cryostat, in the temperature range of 250–400 K, using a Keithley 617 electrometer. The temperature was monitored via a chromel-alumel thermocouple. Current-voltage measurements were made at room temperature using a Keithley 617 programmable electrometer with integral power supply.

Results and Discussion:

Two typical examples of I-V characteristics are shown in Fig. (2). Figure (2a) clearly corresponds to a discrete trapping level [1], because of the long quadratic region following the ohmic one. Figure (2b) shows a clear example of a diffuse trapping level [2], because of the superquadratic region is long (Slope ~3), compared to the quadratic one. Figure (2b) represents the only example of a diffuse level which has been found.
Fig. (2): Room temperature I-V characteristics for GaS films showing (a) a discrete trapping level, (b) a trapping level diffused in energy.

The conductivity of the measured GaS films was found to be n-type. Then, the following relation describes the conductivity in the ohmic region:

\[ J = n_0 e \mu \frac{V}{d}, \]

where \( J \) is the current density, \( n_0 \) the concentration of thermally–generated electrons in the conduction band, \( e \) the electronic charge, \( \mu \) the electron mobility, \( V \) the applied voltage and \( d \) is the distance between the electrodes, i.e. the sample thickness. The electron mobility \( \mu \) obtained from the relation:

\[ \mu = 2.2[\exp(633/T) - 1] \text{ cm}^2\text{v}^{-1}\text{s}^{-1}, \]

where \( T \) is the temperature in Kelvin, assumed the value 15.95×10^{-4} m^2v^{-1}s^{-1}. Using the obtained value of \( \mu \), which is consistent with all literature under consideration, the value of \( n_0 = 3.25 \times 10^{14} \text{ m}^{-3} \) was obtained; this value represents the average for all the samples having the same order \( 10^{14} \), including the diffused trap level sample.

At a higher applied voltage, a square–law dependence of \( J \) on \( V \) is shown in Figure 2 and the current density obeys the relationship (Lampert theory [1]):

\[ J = \frac{9}{8} \varepsilon \mu \theta \frac{V^2}{d^3}, \]

where \( \varepsilon \) is the permittivity of the material. \( \theta \) represents the ratio of free electron concentration \( n \) to trapped electron concentration \( n_t \) and is given by [1]:
\[ \theta = \frac{n}{n_i} = \frac{(N_c / gN_t)}{\exp \left( \frac{E_t}{kT} \right)}, \]  
\hspace{1cm} (3)

where \( N_c \) is the effective density of states in the conduction band, \( g \) is the degeneracy factor for the traps, \( N_i \) is the concentration of traps situated at an energy \( E_t \) below the conduction band edge, and \( k \) is the Boltzmann’s constant.

The crossover from ohm’s law to square law, takes place at the voltage \( V_x \) given by [1]:

\[ V_x = \frac{e n_0 d^2}{\theta \epsilon} \]  
\hspace{1cm} (4)

The cross-over voltage \( V_x \) was determined for all samples and the slope of \( (V_x \) vs. \( d^2 \)) was found to be \( 3.33 \times 10^{12} \text{ Vm}^2 \) (Fig.3). The nearly vertical rise in current accompanying the filling of traps starts from the voltage value \( V_{TFL} \) (trap filled limit). According to the theory:

\[ V_{TFL} = \frac{e N_t d^2}{2 \epsilon} . \]  
\hspace{1cm} (5)

The trap-filled limit voltage \( V_{TFL} \) is shown in Figure 2(b). Assuming \( \epsilon = 5.58 \times 10^{-11} \text{ F m}^{-1} \) as reported for GaS thin films prepared under similar conditions [15], the values of \( \theta = 2.8 \times 10^{-7} \) and \( N_t = 2.76 \times 10^{22} \text{ m}^{-3} \) were obtained using Eqns. (4 and 5), respectively. An energy \( E_t \) is extracted from Eqn. (3). In this equation, \( N_c \) is obtained from the relation; \( N_c = 2.5 \times 10^{19} (m*/m)^{3/2}(T/300)^{3/2} \) [17], with the electron effective mass \( m* = 1.3 \) m [9], and \( g \) is taken equal to 2, which is typical for electron traps. Accordingly, the value of \( E_t \) was found to be 0.56 eV.

Fig.(3): Dependence of the cross-over voltage \( V_x \) on \( d^2 \) for GaS thin films.
Significantly different types of I-V relations can exist when an energy distribution of traps is present in an insulator. Sworakowski and Pigon [2] worked out a simple and interesting model for the case in which trapping states with uniform spatial distribution occur within the energy range \((E_U, E_L)\). The distribution function for the trap density \(h(E)\) has been approximated by the relation

\[
h(E) = \frac{H}{2kT_c} \exp \left( \frac{|E - E_T|}{kT_c} \right),
\]

where \(H\) is the total space density of trapping states, \(E_U, E_T, \) and \(E_L\) are the energies corresponding, respectively, to the upper, the maximum, and the lower edges of the distribution, and \(T_c\) is the characteristic temperature of the trapping states distribution. The trapping levels band is assumed to be sufficiently wide, i.e., \(E_T - E_U > 2kT_c\). According to this model, the I-V characteristic of a sample consists of an ohmic region followed by a quadratic region expressed by Eqn. (2). Taking into account Eqn. (6), with the assumptions \(E_L < E_T - 2kT_c\) and \(T_c > T\), \(\theta\) is defined, in this case, as

\[
\theta = n \frac{n}{n_T} = 2N_e (l - 1) \exp \left( \frac{E_U - E_L}{kT_c} \right) \exp \left( \frac{E_L}{kT} \right)
\]

with \(l = T_c / T\). At sufficiently high voltage, some traps would be located below the Fermi level, i.e., they would behave as deep traps and can be considered as completely and irreversibly filled. When the condition \(E_L + kT_c < F_n < E_T - kT_c\) is fulfilled, \(F_n\) being the quasi – Fermi level, the current density expression is given by

\[
J = N_e \mu \exp(1 - l) \exp \left( \frac{E_T}{kT} \right) \left( \frac{2e}{H} \right) \left( \frac{l}{l + 1} \right)^{2l + 1} \frac{V^{l+1}}{d^{2l+1}}
\]

The transition voltage at which the current converts from the square to the superquadratic law is given by

\[
V_{TR} = \frac{eHD^2}{2e} \exp \left( \frac{E_L - E_T}{kT_c} \right) \left[ \frac{9}{8} (l - 1) \right] \left( \frac{l + 1}{2l + 1} \right)^{l+1} \left( \frac{l+1}{l} \right)^{l+1}
\]

The I-V characteristic of the sample, shown in Fig. (2b), fits this theory quite well. From the experimental data, one can determine the lower energy limit \(E_L\).
of the trap distribution and the total trap density \( H \) for the extreme cases \( E_T = 0 \), maximum trap density, and \( E_T = E_L + 2kT_c \), minimum trap density. Finally, one can also obtain an estimate of \( E_T \). From Eqn. (8) a slope of 3 in superquadratic region shown in Fig. (2b), implies a value of \( l = 2 \) and, thus, a temperature parameter \( T_C = 600 \text{ K} \) for \( T = 300 \text{ K} \). Using the value of \( V_{TR} \) shown in Fig. (2b), one can deduce, the existence of a trapping level, only slightly diffused in energy (energy width 0.10 eV) at a depth of 0.51 eV and with a density of \( 2.16 \times 10^{21} \text{ m}^{-3} \). The main results obtained from the I-V measurements carried out at room temperature are reported in Table (1).

### Table (1): Results of the I-V characteristics.

| \( E_L \) | \( 2kT_C \) | \( E_T \) | \( E_I \) | \( N_t \) | \( H_{\text{min}} \) | \( H_{\text{max}} \) |
| (eV) | (eV) | (eV) | (10^{22}\text{m}^{-3}) | (10^{21}\text{m}^{-3}) | (10^{27}\text{m}^{-3}) |
| 0.61 | 0.10 | 0.51 | 0.56 | 2.76 | 2.16 | 2.13 |

*Note:* \( E_L \) is the lower edge of the distribution, \( 2kT_C \) is its width, \( E_T \) is an estimate of the maximum of the distribution, \( H_{\text{min}} \) and \( H_{\text{max}} \) are the minimum and the maximum values of the total trap density, for the case of diffused level, while \( E_t \) and \( N_t \) are the trap depth and concentration, respectively, in case of discrete level.

Checks with SCLC theory were carried out as follows:

1. The electron quasi-Fermi level was calculated at the end of quadratic region by the relation: \( F_n = kT \ln(N_C/n) \). The obtained value should be equal to \( E_t + kT \) for the discrete trap level, as expected from the SCLC theory [1]. Assuming \( n_t \approx N_t \) in case of deep trapping [1], a value of \( F_n = 0.575 \text{ eV} \) is obtained. This value is in very good agreement with \( E_t + kT = 0.582 \text{ eV} \).

2. According to the diffused level SCLC theory [2], in the superquadratic region \( F_n \) should vary between \( E_L + kT_C \) and \( E_T - kT_C \). Curve shown in Fig. (2b), fulfilled the above criterion.

The resistivity behavior, as a function of the temperature shown in Fig. (4), was measured in the ohmic region of the I-V curves. Two activation energies of 0.32 and 0.63 eV were obtained. The latter shows the deeper trapping level located in the band gap, obtained in the temperature range 350 - 400 K. The value of 0.32 eV obtained in the temperature range 270 – 345 K, refers to a shallow level. Both of these values are in a good agreement with previous results obtained using different techniques shown in Table (2).
Finally, as shown in Table (2), the two levels obtained at 0.56 eV and 0.51 eV according to the two methods of analysis (Lampert and Sworakowski–Pigon, respectively) are in a good agreement with data quoted by other authors [5–11, 16].
In the present work, some possible intrinsic defects in GaS thin films could be produced as a result of the slightly excess of sulfur. These defects are, Ga vacancy, $S_{Ga}$ antisite defects, or $S$, interstitial defects. Both $S_{Ga}$ and $S$, defects result in electrical activity as donor levels, while the Ga vacancies are like-acceptors. As the GaS films were proved here to be of the n-type conductivity, both $S_{Ga}$ and $S$, defects should dominate. The donor levels due to these defects are compensated by the electron trapping centers detected here. These traps can strongly influence the performance of n-GaS as a possible device. However, a noticeable increase in the values of total trap concentrations obtained here for n-GaS thin films compared with the values for n-GaS single crystals ($N_t = 2.3 \times 10^{19} \text{m}^{-3}$ [10]) obtained using the same technique of analysis. This increase is thought to result from an increase in the defect density in thin films.

Conclusions:

Room – temperature measurements on evaporated GaS thin films with In electrodes showed ohmic conduction at lower voltages and space-charge–limited conductivity at higher voltages. Two deep-lying electron traps have been found in n-GaS, at 0.56 eV and 0.51 eV below the conduction band. The former is a single level with a $2.76 \times 10^{22} \text{m}^{-3}$ density. The latter is a “diffuse” level with an energy width 0.10 eV and a total density of $2.16 \times 10^{21} \text{m}^{-3}$. These traps are probably correlated with compensated donors. The SCLC model has been extensively tested in GaS, both in its discrete and diffuse level formulation. A shallow level has been detected at 0.32 eV using resistivity measurements as well as a deeper one at 0.63 eV.

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