Chalcogenide Letters Vol. 12, No.11, November 2015, p. 547 - 554

TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY AND HALL EFFECT OF THALLIUM GALLIUM DISULPHIDE SINGLE CRYSTALS

A. T. NAGAT[a], S. A. HUSSEIN[b], S. E. AL GARNI[a], S.R. ALHARBI[a]

[a]*Physics Department, Faculty of Sciences-AL Faisaliah Campus, King Abdulaziz University, Jeddah, Saudi Arabia*
[b]*Physics Department, Faculty of Sciences, South Valley University –Qena, Egypt*

Single crystal of the layered compound $TlGaS_2$ were grown by direct synthesis of their constituents. Their electrical conductivity and the Hall effect was studied as a function of the temperature, both perpendicular and parallel to the layer planes, and their behaviour proved to be highly anisotropic. The Hall-effect measurements revealed extrinsic p-type conduction with an acceptor impurity level located at 0.586 eV for $\sigma_{\perp}$ and at 0.43 eV for $\sigma_{//}$ above the valence-band maximum. The variation of the Hall mobility and the carrier concentration with temperature were investigated. The scattering mechanism of the carriers throughout the entire temperature range of investigation was checked. The anisotropic factor was also estimated, and its temperature dependence was illustrated.

(Received July 12, 2015; Accepted November 2, 2015)

Keywords: $TlGaS_2$; Hall Effect; DC electrical conductivity; energy gap; acceptor level

1. Introduction

Over the past three decades, significant interest has arisen in chalcogenide semiconductors because of their interesting physical properties as well as their wide-ranging technological applications [1]. The semiconductor has attracted much attention because of its potential application in photovoltaic and optoelectronic devices, such as light sources and infrared detectors [2].

For many years, the properties of layered crystal have constituted a major research area in solid-state physics. Layered crystal has often been used to test some of the most advanced techniques in modern photoemission [3]. However, such studies have not been applied on a large scale to ternary chalcogenides containing thallium. The interest in these materials is stimulated not only by their fundamental properties but also by their possible practical applications. $TlInS_2$ and $TlGaS_2$ crystals are ternary thallium chalcogenides belonging to the III-III-VI2 family of crystals having layered crystalline structures. [4]

The ternary semiconducting $TlGaS_2$ single crystal, which is a wide-gap material, has a layered monoclinic structure [5]. Various studies concerning this material have been conducted throughout the past few decades. The optical properties of $TlGaS_2$ have been reported [6-10]. The photoluminescence spectra of $TlGaS_2$ layered crystal have been studied [11]. Thermally stimulated current analysis of $TlGaS_2$ single crystal has been performed [12,13]. The thermal expansion of $TlGaS_2$ has been investigated [14,15]. The crystal structure of the ternary semiconductor compound $TlGaS_2$ has been determined [16]. Raman scattering measurements under pressure have been performed on a single crystal of $TlGaS_2$ [17-18].

The photoconductivity of $TlGaS_2$ single crystal has been investigated [19-21]. A $TlGaS_2$ single crystal doped with paramagnetic Fe^{3+} ions has been studied with the electron paramagnetic resonance (EPR) technique [22]. The deformation effects in the electronic spectra of $TlGaS_2$ have been studied [23].

*Corresponding author: seef73@gmail.com

A low-temperature phase transition in $TlGaS_2$ layered crystals has been observed [24]. Infrared reflectivity spectra of $TlGaS_2$ have been reported [25].

The phenomenon of DC hopping conduction in $TlGaS_2$ has been established [26]. Recently, a further collection of crystal data for $TlGaS_2$ has been published [27].

In spite of all the above-reported studies, the literature still lacks information regarding the Hall properties, the impurity level and concentration, and the dominant scattering mechanisms in $TlGaS_2$ crystals. Therefore, the aim of this work is to report these properties through the measurement and analysis of the electrical conductivity and the Hall effect.

In the present work, I describe the electrical conductivity and the Hall effect in two crystallographic directions for $TlGaS_2$.

2. Experimental procedure

$TlGaSe_2$ monocrystals were grown with a modified Bridgman method from a stoichiometric melt of starting materials sealed in evacuated ($\approx 10^{-6}$ mbar) and carbon-coated quartz ampoules, each with a tip at the bottom, in our crystal-growth laboratory. The growth and the experimental apparatus have been described in detail elsewhere [28]. The grown single crystals exhibit good optical quality and have a light yellow colour.

The X-ray diffraction patterns show that these crystals have a monoclinic structure with the lattice parameters a=10.35 ºA, b=10.34 ºA, c=15.10 ºA and β=100º.

These single crystals can rather easily be cleaved into plates perpendicular to the c-axis. The samples that were suitable for the measurements performed in this work were freshly and gently cleaved from the ingot along the cleavage plane with a razor blade, and no further polishing or cleaving treatments were required because of the natural mirror-like cleaved faces. To study the electrical conductivity and the Hall effect, the samples were prepared in a rectangular parallelepiped shape with the required dimensions. Silver paste contacts were used as ohmic contacts. The ohmic nature of the contacts was verified by recording the current-voltage characteristics. The conductivity and the Hall coefficient were measured via a compensation method in a special cryostat with a conventional DC-type measurement system.

The measurements were performed under vacuum conditions in a cryostat that was especially designed for mounting between the polar expansions of an electromagnet. The designed cryostat allowed the collection of measurements in a wide range of temperatures.

To avoid the Hall voltage drop when the length-to-width ratio of the sample is less than three, as discussed by Isenberg [29], the specimen dimensions were chosen to be 5x1.5xmm^3. Each mirror-surfaced specimen was placed in its holder to avoid mechanical stresses from clamping or from differential expansion, in the case that measurements were to be made at a temperature different from room temperature. The Hall contacts were, effectively, infinitely small so that they did not distort the current flow. The temperature of each specimen was measured with the aid of a copper-constantan thermocouple.

The electrical conductivity $\sigma_\perp$ was measured when the current was oriented at right angles to the c-axis, and $\sigma_{//}$ was measured when the current was parallel to the c-axis. Additionally, the Hall coefficient that was measured with the magnetic field oriented along the c-axis and the current flowing at right angles to the c-axis ($J \perp C // H$) is denoted by $R_{H//}$. In the case of a parallel current and a perpendicular magnetic field ($J // C \perp H$), $R_{H\perp}$ was obtained.

3. Results and discussion

To investigate anisotropic phenomena in layered $TlGaS_2$ crystals, the temperature dependence of the electrical conductivity was studied in two crystallographic directions. The investigated temperature range was 388 K - 663 K. Fig. 1 shows the typical behaviour of the electrical conductivity as a function of temperature for a particular sample. The curves demonstrate typical semiconductor behaviour.

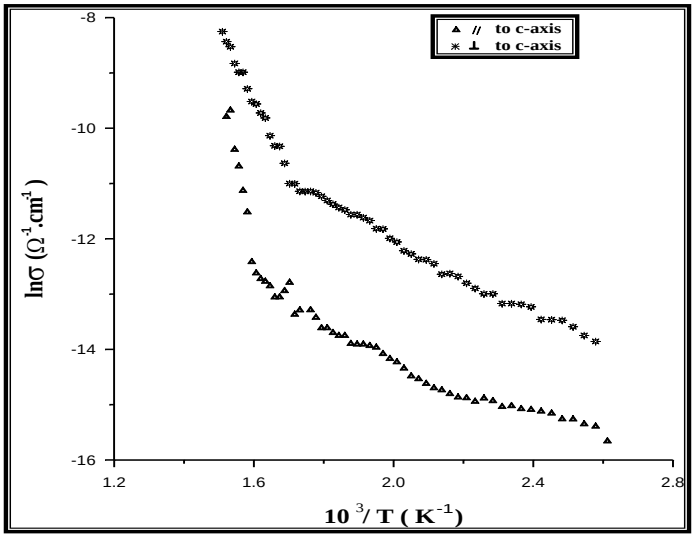

Fig. 1. The behaviour of the electrical conductivity (σ) of $TlGaS_2$ with temperature

In general, $\sigma_{\perp}$ is much higher than $\sigma_{//}$. For instance, at room temperature, $\sigma_{//} = 1.244 \times 10^{-7}$ $Ohm^{-1}cm^{-1}$ and $\sigma_{\perp} = 1.855 \times 10^{-7}$ $Ohm^{-1}cm^{-1}$. At low temperature (the extrinsic region), the carrier concentration may be determined by the number of ionised acceptors, as the main contribution to the concentration is from free-carrier transition from the impurity level, and consequently, the conductivity increases slowly.

The impurity ionisation energy ΔE_a was calculated and found to be 0.586 eV for $\sigma_{\perp}$ and 0.43 eV for $\sigma_{//}$. When the temperature rises, the conductivity increases very rapidly because of the rapid increase in total carrier density (electrons plus holes). This means that the intrinsic conduction becomes more favourable at high temperatures. The energy-gap width was determined to be 2.24 eV for $\sigma_{\perp}$ and 3.62 eV for $\sigma_{//}$.

As shown in fig. 1, an intermediate region is present between 438 K and 593 K for $\sigma_{\perp}$, while for $\sigma_{//}$, this region lies between 498 and 588 K. The conductivity within this region falls off because the mobility decreases with temperature because of lattice thermal vibrations.

The transition temperature from impurity to intrinsic conductivity depends on the impurity concentration in the specific semiconductor and on the forbidden bandwidth for a fixed impurity concentration.

The electrical conductivity is highly anisotropic; the value in the direction perpendicular to the c-axis exceeds that in the direction parallel to it by almost an order of magnitude in the low-temperature region, while in the high-temperature region, $\sigma_{\perp}$ is higher than $\sigma_{//}$ by several orders of magnitude.

Fig. 2 represents the variation of the anisotropy factor with temperature. The high value of the electrical conductivity across the layers may be attributable to the presence of "two-dimensional" defects that are located between the layers in a real semiconductor and are responsible for the carrier motion across the layers. Such faults can easily appear between layers because of weak interlayer bonding. Fig. 2 shows the ratio of the electrical conductivity $\sigma_{//}/\sigma_{\perp}$ as a function of the reciprocal of the temperature in the same investigated temperature range, following the Maschke and Shmid equation [30]

$$\sigma_{//}/\sigma_{\perp} = Ae^{-\Delta E/KT}$$

the data verify this relation.

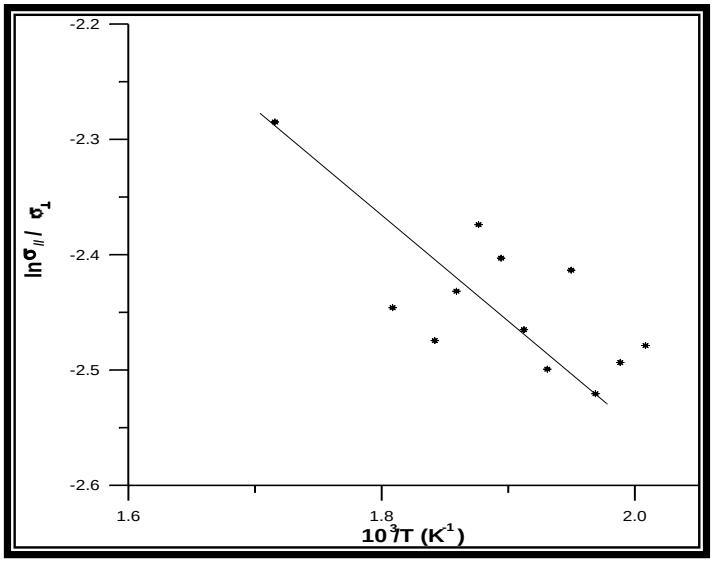

Fig. 2. Variation of the anisotropy factor of $TlGaS_2$ with temperature

The temperature dependence of the Hall coefficient was measured for two magnetic-field directions, one with the magnetic field parallel to the c-axis and the current flowing at right angles to the c-axis (J ⊥ C // H), denoted by $R_{H//}$, and the other corresponding to a perpendicular magnetic field and a parallel current (J // C ⊥ H), denoted by $R_{H\perp}$.

From the results of the experimental measurements, we can see that the Hall coefficient of $TlGaS_2$ has a positive sign, which indicates p-type conductivity for our investigated $TlGaS_2$ sample[31].

Fig. 3 represents the relation between the Hall coefficient and temperature, in which one can distinguish three regions. In the intrinsic region, the Hall coefficient varies linearly and rapidly with temperature, while in the impurity region, it varies slowly with temperature. An intermediate region is observed between these two regions. At room temperature, the measured values are $R_{H//}$ =1.187x10^{11} cm^3/c and $R_{H\perp}$=1.074x10^{11} cm^3/c. The Hall-effect results provide evidence for the values of the ionisation energy of the acceptor atoms and the energy-gap width obtained from the electrical-conductivity curves; these values can also be calculated from the relation between $\ln R_H T^{3/2}$ and $10^3/T$, which is shown in fig. 4.

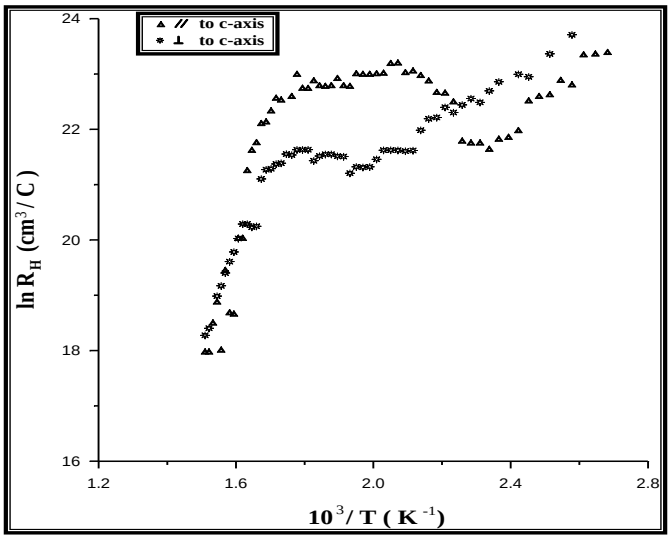

Fig. 3. The relation between the Hall coefficient and the temperature for $TlGaS_2$

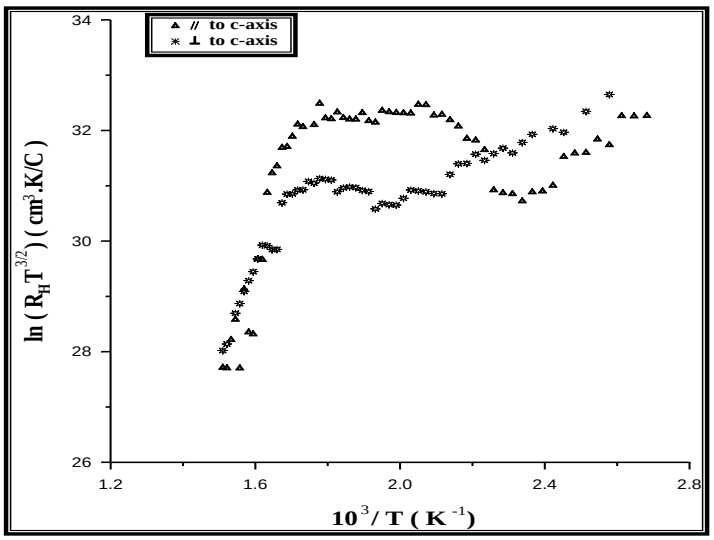

Fig. 4. The relation between $lnR_HT^{3/}2$ and $10^3/T$ for $TlGaS_2$

The mobilities of the charge carriers moving in the large plane and perpendicular to it depend on temperature. This dependence is shown in fig. 5. Two regions can be distinguished. In the low-temperature region, the mobility seems to increase slowly with increasing temperature. In this temperature range, all the mobilities exhibit a temperature dependence that is approximately proportional to $T^{1.6}$, which can be attributed to impurity scattering.

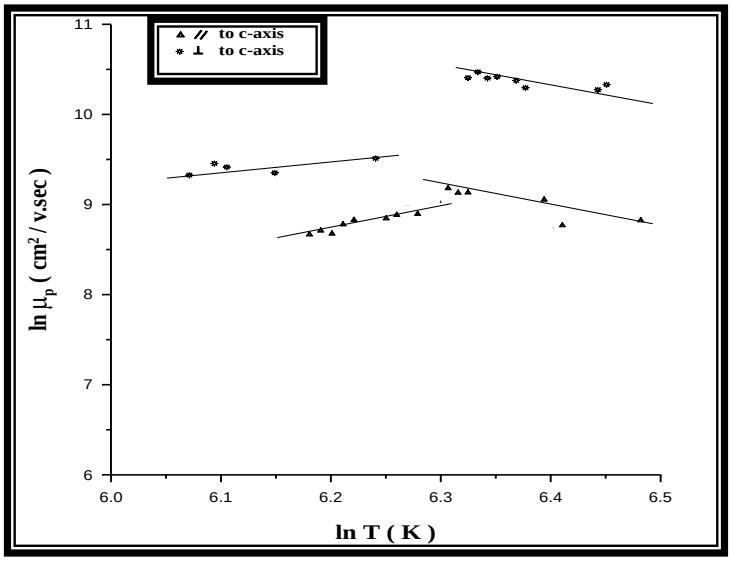

Fig. 5. Dependence of the charge-carrier mobilities on temperature for $TlGaS_2$

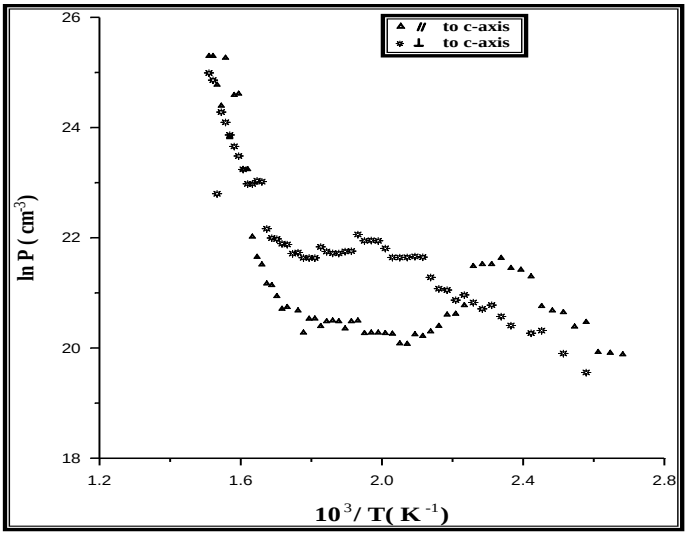

Fig. 6. The relation between the carrier concentration and the temperature for $TlGaS_2$

At high temperatures, both $\mu_{\perp}$ and $\mu_{//}$ are proportional to $T^{-1.3}$. This leads to the assumption that lattice scattering dominates, and the impurity concentration has little effect on the mobility. In this region, the mobility seems to decrease with increasing temperature; lattice scattering, which is arises from the thermal vibration of the atoms in the crystal, disrupts the periodicity of the lattice and thereby impedes the motion of free carriers. The difference in the values of $\mu_{//}$ and $\mu_{\perp}$ can be attributed to the strong anisotropy of the carrier motion along and normal to the layer plane as well as to the positions of macroscopic defects, which are responsible for the carrier motion. At room temperature, $\mu_{//}$ and $\mu_{\perp}$ are estimated to be 1.079×10^3 and 1.2×10^4 cm/V·s, respectively.

The relation between the carrier concentration and the temperature is illustrated in fig. 6. In the intrinsic region, the following relation is used:

$$P_i = (N_C N_V)^{1/2}\, e^{-(\Delta E_g/2KT)}$$

From this relation, the forbidden-gap width and the ionisation energy can be calculated, and these values show good agreement with our obtained values.

From fig. 6, one can notice that the carrier concentration in the intrinsic region increases rapidly with increasing temperature, while it increases slowly with increasing temperature in the impurity region. At room temperature, the free-carrier concentration lies between 1.30×10^7 cm^{-3} and 6.57×10^7 cm^{-3}.

4. Conclusion

High-purity starting materials were used for the preparation of $TlGaS_2$ crystals with a Bridgman technique. The resulting ingots were investigated by X-ray analysis. All measurements were taken under vacuum conditions in a special crystal designed for this purpose. The measurements were made over a wide range of temperatures. The results of the measurements of the Hall coefficient indicate a p-type conductivity for our investigated samples. The difference in the mobilities parallel and perpendicular to the c-axis was attributed to the strong anisotropy of the carrier motion along and normal to the layer plane and to the positions of macroscopic defects, which are responsible for the carrier motion. The scattering mechanism and the anisotropy factor were investigated. The electrical conductivity and the carrier concentration were observed to

decrease with decreasing temperature, while the Hall coefficient was found to simultaneously increase.

Acknowledgement

We would like to thank Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, for their kind help and providing the necessary facilities for the preparation of the paper. This work would not have been possible without the generous assistance of DSR.

References

[1] A.T. Nagat, I.Z. Mohammed, S.A. Hussein, E.M. Saed, F.S. Bahabri, Australian J. Basic and Applied Science **5,** 889 (2011).
[2] H.B. Abdallah, and R. Bennaceur, physica B **404**, 194 (2009).
[3] I. M. Ashraf, M. M. Abdel-Rahman, and A. M. Badr, J. Phy. D. Appl. Phys. **36**, 109 (2003).
[4] M. Acikgöz, Turk J Phys **32**, 145 (2008).
[5] Song, Ho-jun, Yun, Sang-Hyun, and Kim, J. Phys. Chem.. Sol. **56**, 787 (1995).
[6] B. G. Guseinov, G. D. Guseinov, N. Z. Guseinov, and S. B. Kyazinov, Phys. Stat. Sol. (b) **133**, 25 (1986).
[7] M. P. Hanis, A. N. Anagnostopuls, K. Kambasand, J. Spyridelis, Mat. Res. Bull., **27**, 25 (1992).
[8] B. Gürbulak, Phys. Stat. Sol. (a) **184**, 349 (2001).
[9] B. Abay, Güder, H. Efeoglu, and Y. K. Yogurtcu, Phys. Stat. Sol. (b) **227**, 469 (2001).
[10] A. Kato, M. Nishigaki, N. Mamedov, M. Yamazaki, S. Abdullayeva, E. Kerimova, H. A. Kato, and S. lida, J. Phys.Chem. Sol. **64**, 1713 (2003).
[11] N. S. Yuksek, N. M. Gasanly, A. Aydinli, H. Ozkan, and M. Acikgoz, Cryst. Res. Technol. **39,** 800 (2004).
[12] F. A. Mikailov, S. Kuzan, B. Z. Rameev, A. M. Kulibekov, E. Keaimova, B. Aktas, Sol. Stat. Commum. **138**, 239 (2006).
[13] N. S. Yuksek, N. M. Gasanly, and H. Ozkan, Semicond. Scien. Technol. 18 (2003) 834.
[14] G. L. Belenkü, S. G. Abdullayeva, A. V. Solodukhin, and R. A. Suleymanov, Sol. State. Commun. **44,** 1613 (1982).
[15] M. M. Kurbanov, Inorganic Material **39**, 916 (2003).
[16] G. E. Delgado, A. J. Mora, F. V. Perez, J. Gonzalez, Physica B:Cond. Matter **391**, 385 (2007).
[17] W. Henkel, H. D. Hochheimer, C. Carlone, A. Wener, S. Ves and H. G. Schering, Phys. Rev. B.**26,** 3211 (1982).
[18] F. V. Perez, R. Cadenas, C. Power, J. Gonzalez, and C. J. Chervin, Applied, J., Phys. **101,** 63534 (2007).
[19] N. Kalkan, J. A. Kalomiros, M. Hanias, , and A. N. Anagnostopoulos, Sol. Stat. Commum. **99,** 375 (1996).
[20] I. M. Ashraf, J. Phys. Chem. B., **108** 10765 (2004).
[21] A. F. Qasrawi, and N. M. Gasanly, Semicond. Scien. and Technol. **20**, 446 (2005).
[22] F. A. Mikailov, S. Kazan, B. Z. Rameev, Kulibekov, E. Kerimova, and B. Aktas, Sol. Stat. Commum. **138,** 239 (2006).
[23] K. R. Allakherdiev, T. G. Mammedov, R. A. Syleymanov, and N.Z. Gassanov, J. Phys. Condens. Matter **15**, 1291 (2003).
[24] A. Aydinli, R. Elliatiogluk, R. Allakhverdiev, S. Ellialtioglu, and N. M. Gasanly, Sol. Stat. Commun. **88**, 387 (1993).
[25] N. M Gasanly, B. M. Dzhavadov, A. S. Ragimov, V. I. Tagirov, and R.E. Guseinov, Physica B+C,**112**, 78 (1982).
[26] S. N. Mustafaeva, V. A. Aliev, and M. M. Asadov, Phys. Semicond. **40**, 561 (1998).
[27] A. M. Panich, S. Kashida, J. Phys. Cond. Matter **20,** 39521 (2008).

[28] S. A. Hussein, and A. T. Nagat, Ctyst. Res. Technol. **24**, 283 (1989).
[29] J. Isenberg, B. R. Russel, and R. F. Green, Phys. Rev. **79**, 286 (1950).
[30] K. Maschke, and P. Shmid, Phys. Rev. (B)**12**, 4312 (1975).
[31] A. F. Qasrawi and N. M. Gasanly Semicond. Sci. Technol. **20**, 446 (2005).