Physica B 404 (2009) 1259-1263

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Electrical and thermoelectric power measurements of GaInSe₂ single crystals

M. Mobarak*

Physics Department, Faculty of Science, South Valley University, Qena, Egypt

ARTICLE INFO

Article history: Received 26 November 2008 Accepted 4 December 2008

Keywords: GalnSe₂ Electrical and thermoelectric power

ABSTRACT

A single crystal of GaInSe₂ was prepared from melt using a vertical Bridgman technique. The crystal was characterized by X-ray diffraction and Energy dispersive X-ray fluorescence spectrometer (EDXRF). Electrical conductivity, hall effect, and thermoelectric power (TEP) measurements were performed in the temperature range from 120 to 570 K. Throughout these measurements, various physical parameters such as carrier mobilities, effective masses of charge carriers, diffusion coefficient, relaxation time, and the diffusion length for both majority and minority carriers were estimated. In conjunction with the electrical conductivity and the charge carrier concentration, the TEP is discussed. All crystals were found to be of p-type conductivity.

© 2008 Published by Elsevier B.V.

1. Introduction

For many years, the properties of layered crystals have constituted a major research area in solid state physics. $GalnSe_2$ is a layered compound and the interest in this material is stimulated not only by its fundamental properties, but also by possible practical applications [1]. In addition, their quasi-two dimensional, structural anisotropy, as well as their peculiar optical and photoconductive properties have attracted investigators in an effort to acquire a better insight in the physics of these compounds [2,3].

The A^{III}B^{III}C^{VI} chalcogenide semiconductors belong among the A^{III}B^{VI}-type layered-structure semiconductors [4]. Although the ternary semiconducting chalcogenides have been investigated extensively in recent years [5–8], very few investigations have been performed on GaInSe₂. This material, just like other ternary semiconductor compounds, could have many possible applications, ranging from use in solar cells to nonlinear optical technologies. Furthermore, it could be easily intercalated with foreign ions, atoms and molecules, thus offering the realistic prerequisites for producing controllable superlattices based on it.

The present report deals with the preparation of GaInSe₂ in single crystal form by using a vertical Bridgman–Stockbarge method [9]. The chemical composition was analyzed by Energy dispersive X-ray fluorescence spectrometer (EDXRF). The crystal structures of GaInSe₂ compounds were characterized by X-ray diffraction. Also the physical properties of our samples were investigated by electrical conductivity, Hall effect and thermoelectric power (TEP) measurements.

E-mail address: moustafff@yahoo.com

2. Growth and characterization

Single crystals of GaInSe₂ were grown from a melt using a vertical Bridgman-Stockbarge technique [9]. Double-walled silica glass ampoules with the external part evacuated were used to minimize convection effects. The silica glass ampoules were cleaned using first a mixture of HF and distilled water (1:2 by volume) and then pure ethanol and hot distilled water. After chemical cleaning the evacuated tube was baked to 1000 °C for one day under vacuum (10⁻⁴ Torr) for out gassing. A carbon liner (thin film) was deposited by methane pyrolysis at 1000 °C and then the tube was cooled down and loaded with stoichiometrically weighted amounts of high-purity (six nine) elements: 5.359 g gallium (23.474%), 5.995 g indium (26.256%) and 11.477 g selenium (50.268%). The ampoule was re-evacuated to a pressure of less than 10^{-6} Torr and sealed off. In order to avoid the formation of holes in the crystal, 100 Torr argon was added before the reaction crucible was sealed. Care was taken when heating the ingot to control the high Se vapor pressure and the exothermic reaction between Se and In. The mixture was slowly heated (1.5 °C min⁻¹) over a temperature range of 200–250 °C to minimize the risk of cracking the ampoule. The temperature was kept at 950 °C for two days to homogenize the melt. The crucible was then lowered from the hot side to the cold side at 300 °C at a speed of 1.33 mm h^{-1} . The time required for this process was about 17 days. After the product had cooled to room temperature, the crystal was characterized by EDXRF and X-ray diffraction analysis.

The chemical composition analysis results were listed at central laboratory in South Valley University by the (JSX-3222) Element Analyzer with EDXRF (JEOL, Japan). The quantitative analysis is made by comparison with known standards, and clearly indicated that the produced crystal (29.224%) Ga, (22.748%) In and (47.969%) Se weight% concentration was of a





^{*} Tel.: +20965331761; fax: +20965213383.

^{0921-4526/\$ -} see front matter \circledcirc 2008 Published by Elsevier B.V. doi:10.1016/j.physb.2008.12.003



Fig. 1. The X-ray diffraction intensity as a function of the Bragg angle of GalnSe_2 powder.

stoichiometric compound corresponding to $GaInSe_2$, with a very small excess of Ga in agreement with literature data [10]. The crystal was identified by X-ray powder diffraction measurements as a single phase with lattice constants a = 8.002 Å and c = 6.537Å. These results are in good agreement with previous X-ray structure investigations for GaInSe₂ [11]. In Fig. 1, the peaks of the X-ray powder diffractogram as a function of 2θ (twice the Bragg angle) are reported, indicating the single-phase nature of the produced crystal.

3. Electrical conductivity and Hall effect measurements

Specimens for measurements were prepared by cleaving the initial single crystals in two mutually perpendicular natural cleavage planes, and were rectangular shaped with dimensions $6.7 \times 2.4 \times 1.2$ mm³. This sample, which has a length three times its width (to avoid Hall voltage drop), was used for electrical conductivity and Hall effect measurements simultaneously. Electrical load wires of copper were soldered to the sample with a small point of silver past which was used as an ohmic contact. The ohmic nature was checked by recording the I-V characteristics in both forward and reverse bias directions. A pyrex cryostat was used for adjusting the low temperature (with the aid of liquid nitrogen) and high temperature (via an electric heater). The cryostat (which contains the crystal) was evacuated $(10^{-4}$ Torr) for avoiding vapor condensation or oxidation. In this experiment we used a very sensitive potentiometer (2727 portable DC potentiometer) and an electromagnet (Oxford N 177 type) which generates 6000 G. If J, C and H are the current, the C-axis and the magnetic field, respectively, then the conditions of the measurements can be written as $(J//C \perp H)$. Both the direction of the current and the magnetic field were reversed, in order to avoid thermogalvanomagnetic effects. The electrical properties were determined using the four-point direct-current van der Pauw method [12].

4. Thermoelectric power measurements

For TEP measurements, we utilized the prepared crystal after removing it from the ampoule because it had a cylindrical shape. The investigated sample was adjusted to be 8 mm in diameter and 5 mm in length by a polishing process. The sample was washed by pure ethanol and hot distilled water and then left to dry without heat treatment. The measurement of the TEP (α) was made by establishing a temperature gradient between the two ends of the specimen (not more than 7K). The temperature was measured using two calibrated thermocouples. Silver paste was also used here as an ohmic contact. The sample with its holder (which contains an electric heater) was placed in a cylindrical container. It was closed at both ends to reduce convection currents and also to be evacuated. This was done to avoid the sample oxidation at high temperatures or water vapor condensation in low-temperature measurements. A temperature difference was controlled by energizing one of the two heaters. The temperature gradient direction was perpendicular to the c-axis. Two calibrated thermocouples were used as temperature-sensing elements between the two ends of the crystal. The measurements of the temperature and the developed thermovoltage were carried out simultaneously. For measuring either Hall voltage or thermovoltage, a high-sensitivity potentiometer was used (2727 portable DC potentiometer).

5. Analysis and discussion of the results

Measurements of the electrical conductivity (σ) were carried out in a direction parallel to the *c*-axis (i.e. in the plane of the layers). The measurements cover a temperature range extending from 120 up to 570 K. Fig. 2 shows electrical conductivity $\log \sigma$ vs. $10^3/T$ for a typical GaInSe₂ single crystal sample. As shown, in the investigated temperature range, the logarithm of the conductivity showed a linear dependence on temperature with two modes of conduction in addition to the transition region that appeared between them. Thus in this semiconductor, on the low-temperature side (extrinsic conduction) and at high-temperature side (intrinsic conduction), the conductivities are assumed to obey the following Arrhenius equations respectively:

$$\sigma = \sigma_0 \exp(-\Delta E_a/2 \text{ KT}), \quad 240 \text{ K}\langle T \rangle 120 \text{ K},$$

 $\sigma = \sigma_0 \exp(-\Delta E_g/2 \text{ KT}), 570 \text{ K}\langle T \rangle 350 \text{ K},$

where σ_0 is a constant, ΔE_a the impurity ionization energy, ΔE_g the energy gap width, *T* the absolute temperature and *K* the Boltzmann constant. From the above relationships the energy gap ΔE_g is deduced to be 1.8 eV while ΔE_a is 0.079 eV; these results are in quite good agreement with previous literature data [10]. The increase of σ in the intrinsic part (above 350 K) is regarded as a result of excitation of the carriers from the valence band to the conduction band. However, in the extrinsic part (below 240 K), σ increment is regarded as a result of ionization of impurity atoms.



Fig. 2. Electrical conductivity of GaInSe₂ as a function of temperature.



Fig. 3. Temperature dependence of Hall coefficient for GaInSe₂ single crystals.

The transition region (240–350K) is characterized by a slight increase as the temperature increases. For instance, the electrical conductivity at room temperature equals $2.2 \times 10^{-4} (\Omega \text{ cm})^{-1}$.

Fig. 3 shows the behavior of the Hall coefficient against temperature. The general shape of the figure is quite similar to that obtained usually in semiconductors. The Hall coefficients are positive all over the temperature interval investigated. This means that the major carriers are holes and hence GaInSe₂ is a p-type semiconductor. As illustrated in Fig. 3, three regions are observed. Starting from low temperatures (120–240 K), we can deduce the ionization energy of acceptor atoms (ΔE_a). It is 0.077 eV, i.e. close to that deduced from the conductivity curve (Fig. 2). The middle region is the transition range (240-350K) which corresponds to the transition from impurity to intrinsic conduction band. From the third region at high temperature (350-570 K) we deduced the forbidden gap width (ΔE_g). It has the same value as estimated from Fig. 2, i.e. 1.79 eV. The value of $R_{\rm H}$ at room temperature equals 7.5×10^5 cm³ C⁻¹. The variation of Hall mobility with temperature is shown in Fig. 4. The mobility is always seen to decrease with increasing temperature. In the temperature range of investigation it was found that the mobility decreases with increasing temperature according to the relation $\mu_p \sim T^{-n}$. At low temperature the average value of power *n* was found to be equal to 1.25. Such dependence leads to the assumption that the scattering mechanism is due to the impurities in the extrinsic region. At high temperature range (intrinsic), the average value of power *n* was found to be equal to 4.75. In this range we consider that the main reason for the scattering mechanism is due to the scattering optical phonons. At room temperature, the hole mobility equals $168 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The behavior of the carrier concentration as a function of temperature is shown in Fig. 5. It is observed from the curve that, as the temperature increases, the carrier concentration also increases. There are three regions of this curve, namely the extrinsic low-temperature range (120-240 K), the transition (240-350K) and the intrinsic region (350-570K). We calculated the energy gap width from the slope in the intrinsic region. It was found to be 1.81 eV. Also from the extrinsic region we calculated the ionization energy of acceptor atoms $(\Delta E_a = 0.079 \,\mathrm{eV})$. The carrier concentration at room temperature reaches $8.3 \times 10^{12} \, \text{cm}^{-3}$.

The TEP measurements were carried out as a complementary part to the electrical conductivity and Hall effect. The temperature gradient direction was perpendicular to the *c*-axis in the



Fig. 4. The behavior of hall mobility as a function of temperature for GaInSe₂.



Fig. 5. Dependence of carrier concentration of GaInSe₂ on temperature.

temperature range between 120 and 570 K. The results show that the conduction can be regarded as p-type with no polarity changes over whole temperature range, which is in agreement with our previous data of Hall coefficient. Fig. 6 shows the relation between the TEP and temperature. From this relation we observed that at low temperature (120–200 K) α increases with temperature. This is due to the thermal excitation of the impurity ionization in this extrinsic range. In the temperature region (200–340 K) α increases rapidly with temperature. Also above 340 K at high-temperature range α increases slowly with temperature; this is due to the thermal generation of the carriers with increasing temperature which occurs in the intrinsic conduction part. We consider a well-known relationship that governs the variation of (α) against temperature in the intrinsic part [13]:

$$\alpha = \frac{K}{e} \left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p} \left(\frac{\Delta E_g}{2 \, kT} + 2 \right) + \frac{3}{4} \ln \frac{m_n^*}{m_p^*} \right]$$



Fig. 6. Relation between α and Ln*T* for GaInSe₂ single crystals.

where μ_n , μ_p , m_n^* , and m_p^* are the electron mobility, the hole mobility, the electron effective mass, and the hole effective mass, respectively. If we plot the above equation we computed the ratios μ_n/μ_p and m_n^*/m_p^* from the slope and the intercept in the intrinsic part. They were 1.57 and 3.9×10 ,⁻³ respectively. Since the quantity of μ_p is known at room temperature as $168 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is deduced from the electrical conductivity and Hall effect data, μ_n becomes $263 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Another important formula was suggested to describe the relationship between α and $\ln T$ in the impurity region [14]:

$$\alpha = \frac{K}{e} \left(2 - \ln \frac{ph^3}{2(2\pi m_p^* kT)^{3/2}} \right)$$

If we plot the above equation we should get a linear relationship in the extrinsic region. From the plot, we calculated $m_n^* = 1.5 \times 10^{-33}$ kg, hence m_n^* was 5.9×10^{-36} kg. Determination of the effective mass values is important for finding the relaxation time of the charge carriers. The computed relaxation times for holes and electrons were 1.6×10^{-16} and 9.7×10^{-19} s, respectively. Also the diffusion constants for holes and electrons are calculated. They are $D_p = 4.2 \text{ cm}^2 \text{ s}^{-1}$ and $D_n = 6.6 \text{ cm}^2 \text{ s}^{-1}$, respectively. Another important physical parameter, which was estimated from both the relaxation time and the diffusion constant is the diffusion length. The diffusion lengths for holes and electrons were $L_p = 2.6 \times 10^{-8}$ cm and $L_n = 2.5 \times 10^{-9}$ cm, respectively. For more definite understanding of the behavior of TEP we used our electrical conductivity and Hall effect data. The behavior of the differential thermoelectric power α against the carrier concentration is presented graphically in Fig. 7. The general behavior is that in the impurity region the TEP is directly proportional to the concentration of carrier; this may be due to the impurity ionization in the extrinsic region. At high temperature α increases with the carrier concentration; this behavior of α in the intrinsic region may be due to the thermal generation of the carrier in the intrinsic region. Fig. 8 illustrates the relationship between TEP and the electrical conductivity σ . The relation between α and σ is similar to the general behavior of α against temperature. The similarity between the behaviors of these curves indicates that the mode of α variation against temperature is governed mainly by σ . But the conductivity is proportional to the carrier concentration and the mobility, so we can conclude that the mobility is the dominant factor that governs α [15].



Fig. 7. The relation between thermoelectric power and the carrier concentration for $GalnSe_2$.



Fig. 8. Dependence of TEP α on the natural logarithm of electrical conductivity for GalnSe₂ monocrystals.

6. Conclusions

High-quality GalnSe₂ single crystals were grown by the vertical Bridgman method and have been characterized by X-ray diffraction and energy dispersive X-ray fluorescence spectrometer (EDXRF). The electrical conductivity, Hall coefficient and thermoelectric power were measured as a function of temperature. Throughout joining the electrical with thermoelectric power (TEP) measurements many physical parameters were estimated. The energy gap was found to be 1.8 eV which confirms the possibility of utilizing such single crystal as a solar energy converter. The conductivity type throughout the entire temperature range was found to be p-type for our GalnSe₂ single crystal as concluded from the positive sign of both the Hall coefficient and the thermoelectric power.

References

 K.R. Allakhverdiev, S.S. Bahaev, N.A. Bakhyshov, T.G. Mamedov, T.G. Salaev, Sov. Phys. Semicond. 18 (1984) 817.

- [2] P.A. Lee, Optical and Electrical Properties of Layered Materials, Reidel, Dordrecht, 1976.
- [3] V. Capozzi, L. Pavesi, J.L. Staehli, Phys. Rev. B 47 (1993) 6340.
- [4] M.K. Rabinal, S.S.K. Titus, S. Asokan, E.S.R. Gopal, M.O. Godzaev, M.T. Mamedov, Phys. Status Solidi B 178 (1993) 403.
- [5] J.A. Kalomiros, A.N. Anagnoustopoulos, Phys. Rev. B 50 (1994) 7499.
- [6] M. Hanias, A.N. Anagnoustopoulos, K. Kambas, J. Spyridelis, Physica B 160 (1989) 154.
 [7] G.D. Guseinov, R.G. Guseinova, S.N. Mustafaeva, N.Z. Gasanov, S.G. Guseinov,
- Guseniov, R.G. Guseniova, S.N. Mustalaeva, N.Z. Guseniov, S.G. Guseniov, E.G. Abdullaev, Phys. Lett. 116A (1986) 281.
 W. Henkel, H.D. Hochheimer, C. Carlone, A. Werner, S. Ves, H.G. Von
- [8] W. Henkel, H.D. Hochneimer, C. Carlone, A. Werner, S. Ves, H.G. Von Schnering, Phys. Rev. B 26 (1982) 3211.
- [9] P. Hartman, Crystal Growth, An Introduction, North-Holland, Amsterdam, 1973.
- [10] M. Mobarak, H. Berger, G.F. Lorusso, V. Capozzi, G. Perna, M.M. Ibrahim, G. Margaritondo, J. Phys. D Appl. Phys. 30 (1997) 2509.
- [11] H.J. Deiseroth, D. Muller, H. Hahn, Z. Anorg. Allg. Chem. 525 (1985) 163.
- [12] R. Rymaszewski, J. Sci. Instrum. 2 (1969) 170.
- [13] V.A. Johnson, K. Lark Horowitz, Phys. Rev. 92 (1953) 226.
- [14] A.H. Wilson, Theory of Metals, second ed., Cambridge University Press, Cambridge, 1953.
- [15] G.A. Gamal, M. Abou Zied, M.K. Gerges, E.M. Galal, Jpn. J. Appl. Phys. 42 (1), (No. 9A) (2003) 548.