Synthesis and Electrical Transport Properties of CuInGaTe₂

Salem A*, Salwa AS, Hussein SA and Ezzeldien M
Solid State Lab., Physics Department, Faculty of Science, South Valley University, Qena, Egypt

Abstract

Copper Indium Gallium di-telluride (CIGT) single crystals were synthesized by a special modified Bridgman technique for crystal growth. Our XRD patterns clearly exhibited single phase. The temperature dependence of the electrical conductivity \(\sigma(T)\), Hall coefficient \(RH(T)\) in CuInGaTe₂ single crystals have been demonstrated over the temperature range 143-558 K for the first time. The Hall coefficient sign confirms the samples displays the p-type conducting. The temperature dependence of the conductivity, Hall coefficient, Hall mobility, and charge carriers concentration were investigated with a clear and effective pictures. CuInGaTe₂ single crystals revealed electrical band gaps (or "transport gaps") ranging from 0.64 eV to 0.85 eV. The results obtained from electrical conductivity and carrier concentration revealed the sample p-type with acceptor energy level equal to \(\approx 0.027\) eV. From the obtained experimental data, the main fundamental physical constants and others for crystals under consideration have been estimated.

Keywords: Single crystals; Electrical conductivity; Cu–III–VI₂ Chalcopyrite semiconductors

Introduction

I–III–VI₂ type chalcopyrite semiconductors where the group I element is Cu are feasible candidates for application as photo detectors [1], photo-voltaic cells [2] and light-emitting diodes [3]. CuInTe₂ and CuGaTe₂ ternary compounds are direct band gap semiconductors crystalizing in the chalcopyrite structure. Their band gaps are \(E_g=0.96\) eV (CuInTe₂) and \(E_g=1.35\) eV (CuGaTe₂) [4]. These values are well adapted to the solar spectrum and talking into consideration the high absorption coefficients of these materials they are very attractive for applications such as solar cells and optoelectronic device. Meanwhile to the best of our knowledge there have only been a few published reports on thin films of the quaternary compounds CuGaInTe₂.

CuInGaTe₂ films deposited for the first time at room temperature by using pulse electrode position method at a constant potential of \(-0.75\) V (SCE). The films exhibit one phase with optical band gap of range 0.9-1.5 eV for different work cycle [5]. The dependence of the optical, structural and morphological properties were studied of CuInₓGa₁₋ₓTe₂ thin films for two different compositions (for \(x=0.2\) and 0.8). The films exhibit high absorption coefficient when evaporated by the electron-beam method on soda lime glass substrates. The optical energy gaps calculated to be 1.17 eV to 1.06 eV for \(x=0\) at highest annealing temperature at 525°C and 1.12 eV to 1.02 eV for \(x=0.8\) and at highest annealed temperature at 600°C. I-III-VI, compounds have great interest semiconducting material which have energy gap lies between 0.9 and 3.5 eV, and also many possibilities so I-III-VI, compounds used for electro-optical devices [6]. In spite of all the correction of the measured Hall voltage according to calculated aspect ratio is useful to a void a Hall voltage drop. This aspect ratio is useful to a void a Hall voltage drop. The correction of the measured Hall voltage according to calculated correction factors [9] was applied. Silver paste was used for the ohmic



Crystal growth and sample preparation

Bulk CuInGaTe₂ was prepared by the melt growth technique based on Bridgman method [7]. The constituent elements of Cu, In, Ga, and Te of high purity (6N) were weighted according to their stoichiometric molar ratio and sealed in evacuated silica tube (10⁻⁵torr) and heated in a three zone tube furnace. The silica ampoule was internally coated with thin layer of carbon to prevent contamination of charge. The temperature of the furnace was raised gradually and kept constant for 12 h at 1100 K in the upper zone of the furnace at which the entire contents were completely melted. The lower portion of the growth tube was necked into a 2 mm diameter in order to promote the growth of single crystals. The ampoule was dragged slowly from the high temperature zone to the low temperature zone with a rate 2 mm/h. The ampoule was agitated to be mixing. As the ampoule drag into the low temperature zone, crystallization proceeds until the contents solidify. In the middle zone of the furnace the temperature was corresponds to the crystallization temperature of the compound. The ampoule drag into the third zone of the furnace slowly to cooled down, and then the furnace was switched off. The experimental equipment details for crystal growth are described elsewhere [8]. Crystal perfection was checked by means of XRD to ensure the presence of the crystalline phase with high quality in the prepared ingot. After finishing the growth, the samples prepared polishing and washing have good optical quality surfaces.

Measurement technique

Specimens of CuInGaTe₂ with plane-parallel mirror surfaces were prepared from a large ingot. For studying the electrical conductivity and Hall effect, the sample was prepared in a rectangular shape with dimension 7.5 x 3 x 1 mm³. The sample had a length is more than three times its width. This aspect ratio is useful to a void a Hall voltage drop. The correction of the measured Hall voltage according to calculated correction factors [9] was applied. Silver paste was used for the ohmic

*Corresponding author: Salem A, Solid Sate Lab, Physics Department, Faculty of Science, South Valley University, Qena, Egypt. Tel: +20 96 5211281; E-mail: aasalem@kku.edu.sa

Received April 11, 2018; Accepted April 18, 2018; Published April 25, 2018

Citation: Salem A, Salwa AS, Hussein SA, Ezzeldien M (2018) Synthesis and Electrical Transport Properties of CuInGaTe₂. J Laser Opt Photonics 5: 183. doi: 10.4172/2469-410X.1000183

Copyright: © 2018 Salem A, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
contact. Measurement of the current voltage characteristics showed that the contacts were ohmic.

A compensation method used to measure the electrical conductivity and Hall effect measurements in a special cryostat [10] with a conventional D.C type potentiometer (type UJ33E mark) in a magnetic field of 6000 G which supplied from GMW electromagnet model 5403. During the investigation the temperature was varied 143-558 K and the sample was placed in Pyrex cryostat under vacuum 10^-3 torr. The special cryostat used for low and high temperature measurements. Details of the experiments procedures and apparatus have been published [11].

Results and Discussion

Structural properties of CuInGaTe2 single crystals

Figure 1 depicts the X-ray diffraction and powder X-ray diffraction measurements of the CuInGaTe2 single crystal. All the major reflections are indexed as (hkl) peaks of CuInGaTe2 phase. The XRD patterns of CuInGaTe2 are well consistent with the literature data, so it can be said that the pure compounds with no impurities could be obtained.

Figure 2 shows the observed values of electrical conductivity σ plotted against the inverse of temperature for CuInGaTe2 single crystal over a wide temperature range extending from 143 K to 558 K. At low temperature the electrical conductivity is low and increased with the rise of temperature, i.e., the temperature coefficient of resistance is negative and this is a characteristic of a semiconductor [12-14]. To understand the conductivity mechanism in CuInGaTe2, the conductivity curve shown is divided into three regions, the curve shows the typical semiconductor behavior. A typical semiconductor behavior curve consists of three major parts, below the transition, the transition region, and above the transition. For these regions, the electrical conductivity of CuInGaTe2 can be analyzed by the Arrhenius equation which relates the electrical conductivity and the temperature [15]:

\[
\sigma = \sigma_0 \exp \left( -\frac{\Delta E_a}{2k_B T} \right)
\]

where \( \sigma_a \) is the pre-exponential factor and is the ideal conductivity of monocrystalline structure and \( \Delta E_a \) is the energy gap for the conductivity. The energy gap width \( \Delta E_g \) could be calculated. It was found to be 0.85 eV. The value of energy gap is consistent with the results of CuIn0.7Ga0.3(Se1−xTex)2 thin films for two different compositions (for \( x=0.2 \) and 0.8) [5], so that CuInGaTe2 single crystals can be potential candidates as absorbers in photovoltaic applications. The room-temperature electrical conductivity of a semiconductor specimen is equal to (0.35 Ω⁻¹m⁻¹).

The factor of (% in the exponent appears with intrinsic semiconductors due to the possibility of distributions of electrons in the conduction band are independent of the distributions of holes in the valence band. By assuming that the carrier mobility varies rather slowly with temperature, eqn. (1) becomes:

\[
\sigma = \sigma_0 \exp \left( -\frac{\Delta E_a}{k_B T} \right)
\]

where \( \Delta E_a \) refers to the activation energy. This energy is important factor for organic semiconductors studying [12].

The first activation energy (\( \Delta E_{a1} \)) occurs at low temperature while the second is at high temperature [16,17]. The second activation energy (\( \Delta E_{a2} \)) which occurred at high temperatures by the charge transfer is due to the thermal excitation of the carriers at the grain boundaries [17].

\( \Delta E_{a1} \) value (in temperature range 143 K–193 K) was calculated from the slope of best fit straight line of Figure 2, from this region the ionization energy was calculated, indicating that the acceptor level lies 0.041 eV above the top of the valance band. The \( \Delta E_{a2} \) value (in temperature range 193 K–313 K) was calculated from the slope of the Arrhenius plot as shown in Figure 2 and is 0.34 eV. There are two slopes indicate two conduction mechanisms are possible, observed two-stage temperature dependence of conductance (σ).

An intermediate region of the σ–T curve has been identified in temperature range 321 K–511 K, in which the carrier concentration is not actually constant, and in the third region, σ rises again. In the intermediate region where the carrier density (NA–ND=constant), until the intrinsic region is reached.

Since Hall measurements are an important tool to characterize the materials especially semiconductors, Hall coefficient (\( R_h \)) have been measured on CuInGaTe2 single crystals. Samples were investigated in the same temperature range along a direction perpendicular to the C-axis which shown in Figure 3. \( R_h \) was calculated from Hall voltage. The results showing p-type conduction indicate that the majority carriers are holes. The room temperature value of \( R_h \) obtained by d.c. Hall coefficient measurements, is positive and equal to 87 x 10⁻³m²/C. Hall coefficient (\( R_h \)) directly determines the density of charge carriers in a given sample. Compute the concentration of charge carriers \( P=1/e \) \( R_h \) and carrier concentration at room temperature are 7.18 x 10²⁰m⁻³.
T<248 K, it seems that the value of the exponent n in the relation $\mu \propto T^n$ is in good agreement with the 1.5 value predicted by theory with those obtained for impurity and lattice scattering in other semiconductors. In the high temperature range $T>248$ K, the mobility decreases according to the law $\mu \propto T^{-3.65}$. This usually assumed that contribution to thermal conductivity by phonon-electron scattering is dominated. The room temperature value of the mobility equals $285 \, m^2/Vs$.

Compute the concentration of charge carriers, $p = \frac{1}{eR_H}$. The temperature dependence of the carrier concentration is illustrated in Figure 6. At thermal equilibrium the formula:

$$P = c \exp \left( -\frac{\Delta E_g}{2k_B T} \right)$$  \hspace{1cm} (4)

Thus the energy gap ($\Delta E_g$) can be calculated from the slope of the curve in the intrinsic region, the energy gap is equal $0.64$ eV, which is in accordance with that obtained from the conductivity and Hall effect measurements. The presence of an ionized acceptor level at $0.019$ eV above the top of the valence band obtained is in accordance with that obtained from the conductivity measurements. At room temperature, the concentration can be estimated to be $7 \times 10^{20} \, m^{-3}$. By using the assumption that the effective mass for holes is equivalent to the rest mass, the diffusion coefficient of holes can be calculated from the equation:

$$D_p = \frac{K T}{e} \mu_n$$  \hspace{1cm} (5)

Determination of the energy gap and ionization energy from Hall data is possible by plotting the relation between $R_H T^{3/2}$ and $10^3/T$ as shown in Figure 4. According to the relation:

$$R_H T^{3/2} = c \exp \left( -\frac{\Delta E_g}{2k_B T} \right)$$  \hspace{1cm} (3)

By using the data presented in Figure 4, we can determine the band gap energy. It was found to be $0.71$ eV. The depth of the impurity level was also computed and it was found to be $0.019$ eV. These values closed to those obtained from the temperature dependence of electrical conductivity.

The relation of the conductivity and free carriers mobility as follows, $\sigma = \mu n$. The presented simultaneous measurements of the electrical conductivity and Hall effect will allow to systematically investigate the influence of temperature on the Hall mobility. Values of the temperature dependence of the natural logarithm of Hall mobility, $\ln \mu$ plotted against $\ln T$ in Figure 5, the result is a straight line.

The slope of this straight line plot is then used to calculate the exponent. From the curve (5), we can demonstrate the presence of two different kinds modes on mobility variation around the transition temperature i.e., $248$ K. At low temperature range $T<248$ K the mobility behavior increases with the increase of temperature obeying the law $\mu \propto T^{n}$.
The value of diffusion coefficient at room temperature estimated to be $7.37 \text{ m}^2\text{s}^{-1}$. The mean free time of holes computed to be $4.2 \times 10^{-15} \text{ sec}$ at room temperature from the following equation $\tau_p = \mu_p \frac{m_T}{e}$. The diffusion length of holes ($L_p$) in CuInGaTe$_2$ specimen at room temperature was estimated as $1.76 \times 10^{-7} \text{ m}$.

**Conclusion**

CuInGaTe$_2$ was prepared in single crystal form by Bridgman technique. XRD was used to identify the crystalline nature of the compound. D.C electrical conductivity and Hall Effect measurement were carried out in a wide range of temperature (143-558 K). The measurement revealed that the compound P-type conductivity with energy gap ranging from (0.64-0.85 eV). Important parameter such as conductivity, hole concentration, Hall mobility, diffusion coefficient, diffusion length and relaxation time at room temperature were estimated.

**References**

1. Devaney WE, Mickelson RA, Chen WS (1985) The conference record of the eighteenth IEEE Photovoltaic Specialists Conference—1985: Las Vegas, Nevada. New York: Institute of Electrical and Electronics Engineers.
2. Loferski J, Sewchun J, Roesler B, Beaulieu R, Plekoszeski J, et al. (1978) Chapman in: Proceedings of the 13th IEEE Photovoltaic Spec. Conference, pp: 190.
3. Kazmerski LL, Hallerdt M, Ireland PJ, Mickelson RA, Chen WS, (1983) J Vac Sci Technol, A1: pp: 395.
4. 4 Heinz A, Ossenbrink, Helm P, Ehmann H (1997) Proceedings of the 14th European Photovoltaic Solar Energy Conference, Barcelona, Spain, pp: 2161.
5. Vinothini C (2015) (ISSN (Print): 2279-0047 ISSN (Online): 2279-0055. IJETCAS 15-751.
6. Shay JL, Wernik JH (1975) ternary chalcopyrite semiconductors: Growth, Electrical Properties and Applications, Pergamon, New York.
7. Gamal GA, Nassary MM, Hussein SA, Nagat AT (1992) Single Crystal Growth and Electrical Properties of Gallium Monotelluride. Cryst Res Technol 27: 629-635.
8. Hussein SA, Nagat AT (1989) On the preparation and electrical properties of Thallium selenide monocrystals. Cryst Res Technol 24: 283-289.
9. Runyan WR (1975) Semiconductor measurements and instrumentation. McGRAW-HILL Book company.
10. Nagat AT (1989) Investigation of the electrical properties of Thallium monosulphide single crystal. J Phys Condens. Matter 1: 7821-7825.
11. Nagat AT, Hussein SA, Ganeel YH, Belal AA (1990) Anisotropy of electrical conductivity and Hall effect in gallium selenide crystals. Indian J Pure Ap Phy 28: 586-589.
12. Omar MA (1975) Elementary Solid State Physics, (2nd edn.), John Wiley and Sons Inc, New York.
13. Okamoto Y, Brenner W (1964) Organic Semiconductors. Chapman and Hall Ltd, London.
14. Mille M (1966) The Structure of Polymers. Reinhold Publishing Corporation, New York.
15. Blakemore JS (1974) Solid State Physics. (2nd edn.), by W.B. Saunders Company.
16. Orton J, Cold Smith BJ, Chapman JA, Powell MJ (1982) The mechanism of photoconductivity in polycrystalline cadmium sulphide layers J Appl Phy 53: 1602.
17. Nicodemo L, Nicolais L, Romeo G, Scafora E (1978) Temperature effect on the electrical resistivity of metal/polymer composites. Polym Eng Sci, Academic Press, New York.