Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 2. P. 201-204.
doi: 10.15407/spqeo19.02.201

PACS 71.20.Nr, 72.15.Rn, 72.20.Ee, 72.20.Jv, 72.30.+q, 73.20.At

Dielectric spectroscopy of CuInSe$_2$ single crystals

S.N. Mustafaeva[1], S.M. Asadov[2], D.T. Guseinov[1], I. Kasimoglu[1]
[1]Institute of Physics, Azerbaijan National Academy of Sciences,
G. Javid Pr. 131, AZ-1143 Baku, Azerbaijan
E-mail: solmust@gmail.com
[2]Institute of Catalysis and Inorganic Chemistry, Azerbaijan National Academy of Sciences,
G. Javid Pr. 113, AZ-1143 Baku, Azerbaijan
E-mail: mirasadov@gmail.com
Telephone: (99412)539-59-13; Fax: (99412)539-59-61

Abstract. The results of high-frequency dielectric measurements with obtained α-CuInSe$_2$ single crystals provided an opportunity to determine the mechanisms of dielectric losses and charge transport, and also to evaluate the density of states at the Fermi level; the average time of charge carrier hopping between localized states, average hopping distance, scattering of trap states near the Fermi level; concentration of deep traps responsible for hopping conductivity in alternate electric fields.

Keywords: single crystal, X-ray diffraction, frequency dispersion, dielectric permittivity, loss tangent, hopping conductivity.

Manuscript received 25.11.15; revised version received 12.04.16; accepted for publication 08.06.16; published online 06.07.16.

1. Introduction

There are two polymorphic forms of the compound CuInSe$_2$: low temperature α-CuInSe$_2$, crystallizes in the tetragonal system with a chalcopyrite structure, and high-temperature β-CuInSe$_2$ with sphalerite structure. Chalcopyrite phase α-CuInSe$_2$ has a high efficiency for conversion of solar energy into electricity. Below we shall consider the low-temperature modification.

The chalcopyrite structure of ternary CuInSe$_2$ compounds have a high absorption coefficient (10^4 cm^{-1} [1]) making them well-suited for light-emitting diodes, photovoltaic detectors and solar cells. The melting temperature of CuInSe$_2$ is 1260 K [2]. X-Ray diffraction analysis of CuInSe$_2$ samples indicated them to have lattice parameters of a = 5.782 Å, c = 11.620 Å [3]. According to [4] a = 5.781 Å; c = 11.552 Å. CuInSe$_2$ single crystals have the p-type of conductivity and bandgap 1.02 eV [2]. In [3], the dielectric permittivity ε_0 was calculated (13.6±0.8) for CuInSe$_2$. Capacitance measurements of CuInSe$_2$ in the low-frequency range (1…5 kHz) showed a slight frequency dependence of ε_0. In [2], the following values for dielectric permittivity of CuInSe$_2$ were given: $\varepsilon(0)$ = 15.2 (E||C), $\varepsilon(0)$ = 16.0 (E⊥C), $\varepsilon(\infty)$ = 8.5 (E||C), $\varepsilon(\infty)$ = 9.5 (E⊥C) at 300 K.

Reported here are the results of our high-frequency dielectric measurements performed with CuInSe$_2$ single crystals.

2. Experimental technique

Cu, In and Se elements of high purity were used to synthesize $CuInSe_2$ compound. The 1:1:2 molar ratio of Cu, In and Se with 0.1% excess of selenium as the precursor materials were taken in a silica ampoule. In order to prevent the component deviation from stoichiometry resulting from all possible volatile loss of sulfur during initial steps, it was found necessary to add some excess selenium. The starting materials were taken in a silica ampoule (15 mm in diameter and 150 mm in length) evacuated to 10^{-3} Pa and then sealed off. The ampoule was placed into the single zone horizontal electrical furnace. The furnace was controlled by a thermocouple with the accuracy close to ±0.1 K. During the first stage, the furnace was slowly heated up at the rate approximately 10 K/h. The temperatures of the growth zones were allowed to reach up to 1263 K. Heating duration was 20 h. After this, the temperature of zone synthesizing compound $CuInSe_2$ was maintained at 1263 K for the next 2 days. After these 2 days, the furnace was slowly cooled off at the rate close to 20 K/h down to room temperature. When the temperature of the ampoule reached the room temperature, it was opened to obtain black colored $CuInSe_2$ crystals. The crystals were then cleaned and subjected to physical and chemical analysis. The experiments confirmed the identity of the synthesized compound $CuInSe_2$. The melting temperature of $CuInSe_2$ is 1263 K.

After completion of the synthesis, homogeneity and phase purity of the samples were checked using X-ray diffraction. α-$CuInSe_2$ crystals were characterized using X-ray diffraction by using the D8-Advance powder X-ray automatic diffractometer within the angular range $2\theta = 0.5...80°$ (CuK_α radiation, $\lambda = 1.5418$ Å, 40 kV, 40 mA). The X-ray diffraction results were analyzed using the EVA and TOPAZ programs and ICDD Powder Difraction File data. The angular resolution of the record was 0.1°. The errors of determining the reflection angles were no higher than $\Delta\theta = \pm 0.02°$.

The single crystals of α-$CuInSe_2$ were grown using the Bridgman method in a two-zone furnace with top zone temperature close to 1263 K. The temperature differences within the limits 50 to 80 K were maintained between melt and growth zones so that the temperature of the growth zone was maintained at 973 K. The growth was carried out at a rate 3-5 mm/h. The obtained α-$CuInSe_2$ single crystals were black in color. Single crystals were thermally annealed for 150 hours to provide homogenization. The structure of the compound α-$CuInSe_2$ identified by X-ray diffraction and consistent stable under normal conditions is the tetragonal structure of chalcopyrite (Fig. 1).

A typical diffraction pattern of a powder $CuInSe_2$ sample at room temperature is shown in Fig. 2. X-ray diffraction characterization showed that the samples had a tetragonal crystal structure, $a = 5.781$ Å, $c = 11.642$ Å.

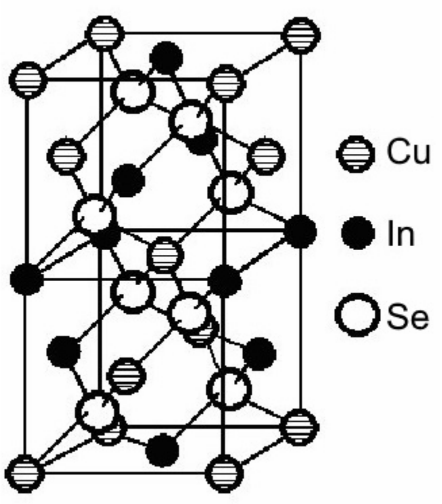

Fig. 1. Tetragonal structure of chalcopyrite α-$CuInSe_2$.

Investigated polished $CuInSe_2$ samples for dielectric measurements were formed as flat capacitors. Ohmic contacts of the samples were made using Ag paste. Measurements of the dielectric coefficients of the studied single crystals were performed at fixed frequencies within the range $5\times10^4\ldots3.5\times10^7$ Hz by the resonant method using TESLA BM 560 Qmeter. For electrical measurements, the samples were placed into a specially designed screened cell. An *ac*-electric field was applied along the C-axis of $CuInSe_2$ single crystals. The amplitude of the applied field corresponded to the Ohmic region of the current-voltage characteristics of the samples. All measurements were performed at $T = 300$ K. The accuracy in determining the resonance capacitance and the quality factor $Q = 1/\tan\delta$ of the measuring circuit were limited by errors related with resolution of the device readings. The accuracy of the capacitor graduation was ±0.1 pF. Reproducibility of the resonance position was ±0.2 pF in capacitance and ±(1.0…1.5) scale divisions in quality factor. The largest deviations from the average were 3…4% in ε and 7% in $\tan\delta$.

3. Results and discussion

The electrical properties (loss tangent, real ε' and imaginary ε'' parts of complex dielectric permittivity, and *ac*-conductivity of $CuInSe_2$ single crystals have been studied within the frequency range from 50 kHz to 35 MHz. The adduced results demonstrate that the dielectric dispersion in the studied crystals has a relaxation nature (Fig. 3). However, if the ε' value descended from 17.3 down to 13.5 within the mentioned frequency range with an increase in frequency, then the value of ε'' was subjected to stronger frequency dispersion decreasing by a factor of 10.

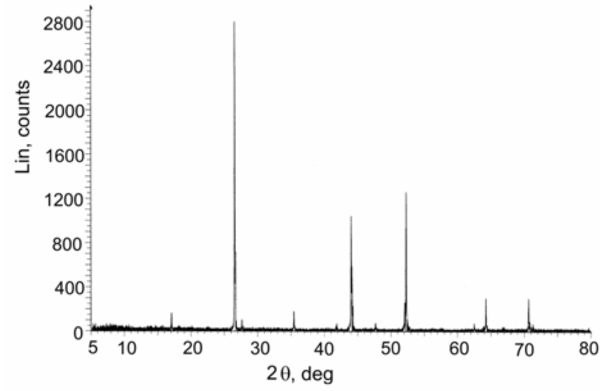

Fig. 2. X-ray diffraction pattern of the powder α-$CuInSe_2$ sample at room temperature.

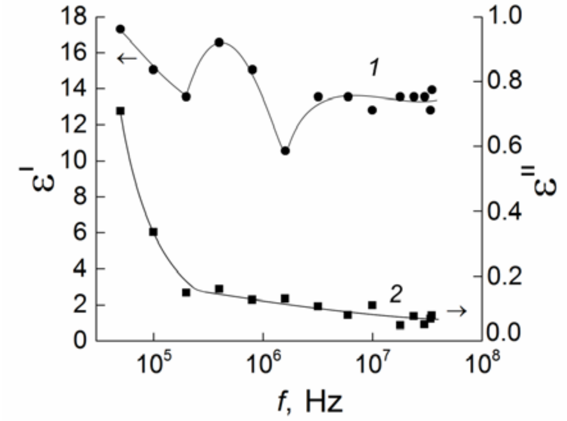

Fig. 3. Frequency dependences of real (*1*) and imaginary (*2*) parts of complex dielectric permittivity of α-$CuInSe_2$.

Fig. 4 shows the experimental frequency dependence of the dielectric loss tangent in the $CuInSe_2$. It is seen from Fig. 4 that tanδ descends with an increase in frequency, which indicates conductivity losses [5].

Fig. 5 presents the frequency dependence of the *ac*-conductivity of $CuInSe_2$ single crystal at T = 300 K. The value of σ_{ac} is increased from 2×10^{-8} up to 1.5×10^{6} $Ohm^{-1}cm^{-1}$ within the mentioned frequency range with increasing the frequency. It must be noted that *dc*-conductivity of $CuInSe_2$ single crystal was equal to 6.7×10^{-9} $Ohm^{-1}cm^{-1}$ at T = 300 K. The frequency dependence of conductivity is described by the power law $\sigma_{ac} \sim f^n$, where $n = 0.8$ at $f = 4\times10^5 \ldots 3.5\times10^7$ Hz. It is known that the band-type *ac*-conductivity is mainly frequency independent up to $10^{10} \ldots 10^{11}$ Hz. The experimental dependence $\sigma_{ac} \sim f^{0.8}$ that we observed indicates that it is conditioned by hops of charge carriers between the states localized in the forbidden band of $CuInSe_2$. These can be states localized near the edges of allowed bands or localized near the Fermi level [6]. However, since the conductivity over the states near the Fermi level always surpasses the conductivity over the states near the edges of allowed bands under experimental conditions, law $\sigma_{ac} \sim f^{0.8}$ that we found indicates the hopping mechanism of the charge transfer localized in the vicinity of the Fermi level:

$$\sigma_{ac}(f)=\frac{\pi^3}{96}\cdot e^2 kTN_F^2 a_L^5 f\left[\ln\frac{\nu_{ph}}{f}\right]^4 \tag{1}$$

where e is the elementary charge, k – Boltzmann constant, N_F – density of localized states near the Fermi level, $a_L = 1/\alpha$ – localization length, α – decay parameter of the wave function of a localized charge carrier, $\psi \sim e^{-\alpha r}$, and ν_{ph} – phonon frequency.

Using the expression (1), we can calculate the density of states at the Fermi level from the measured values of the conductivity $\sigma_{ac}(f)$. The calculated value of N_F for $CuInSe_2$ single crystals was equal to 7.8×10^{17} $eV^{-1}cm^{-3}$ (localization radius is chosen to be 30 Å, by analogy with that of the $CuInS_2$ single crystal [7]). In our case, ν_{ph} is generally of the order of 10^{12} Hz.

The theory of *ac* hopping conductivity provides an opportunity to determine the average time τ of charge carrier hopping from one localized state to another by using the formula [6]:

$$\tau^{-1}=\nu_{ph}\exp(-2R\alpha), \tag{2}$$

where R is the average hopping distance.

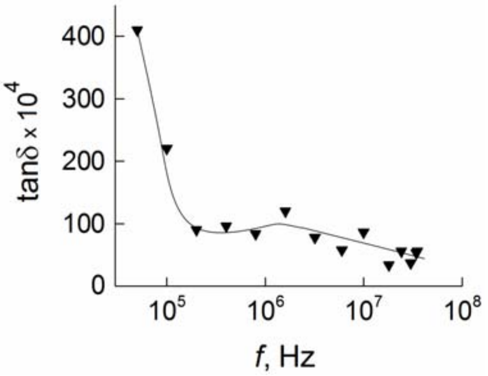

Fig. 4. Frequency dispersion of loss tangent in α-$CuInSe_2$.

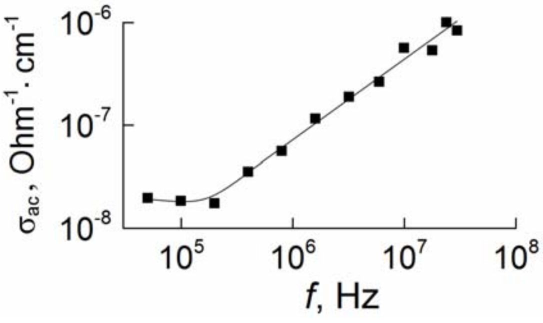

Fig. 5. Frequency-dependent *ac*-conductivity of α-$CuInSe_2$ single crystals at T = 300 K.

Experimentally, τ^{-1} has been determined as the average frequency in the $f^{0.8}$-region, *i.e.*, $\tau^{-1} = 1/f$.

It follows that

$$R = \frac{1}{2\alpha}\ln\frac{\nu_{ph}}{f}. \qquad (3)$$

The calculated values of τ and R for $CuInSe_2$ single crystals were equal to 5.6×10^{-2} μs and 166 Å, correspondingly.

Knowing N_F and R from [6]:

$$\frac{4\pi}{3}R^3 N_F \cdot \frac{\Delta E}{2} = 1, \qquad (4)$$

we estimate scattering of trap states near the Fermi level: $\Delta E = 0.13$ eV for $CuInSe_2$ crystals.

By formula:

$$N_t = N_F \cdot \Delta E \qquad (5)$$

we can determine the concentration of deep traps in $CuInSe_2$: $N_t = 10^{17}\,cm^{-3}$.

4. Conclusions

The electrical properties (loss tangent, real and imaginary parts of complex dielectric permittivity, and *ac*-conductivity) of α-$CuInSe_2$ single crystals have been studied within the frequency range from 50 kHz to 35 MHz. The results demonstrate that the dielectric dispersion in the studied crystals has a relaxation nature. The experimental frequency dependence of the dissipation factor for α-$CuInSe_2$ single crystals is characterized with a monotonic descending with frequency, which is evidence of the fact that conductivity loss becomes the main dielectric loss mechanism within the studied frequency range. At frequencies from the range of $f = 4\times10^5…3.5\times10^7$ Hz, the *ac*-conductivity of the crystals varies according to the law $\sigma_{ac} \sim f^{0.8}$, characteristic of hopping conduction through localized states near the Fermi level. The Fermi-level density of states, dispersion of their energies as well as the mean hop distance and time have been estimated.

References

1. S. Prabahar, V. Balasubramanian, N. Suryanarayanan, N. Muthukumarasamy, Optical properties of copper indium diselenide thin films // *Chalcogenide Lett.* **7**(1), p. 49-58 (2010).
2. O. Madelung, *Semiconductors*: *Data Handbook* (3-rd ed.). Springer, 2004.
3. P. W. Li, R.A. Anderson, R.H. Plovnick, Dielectric constant of $CuInSe_2$ by capacitance measurements // *J. Phys. Chem. Solids*. **40**, p. 333-334 (1979).
4. C. Rincon, F. J. Ramires, Lattice vibrations of $CuInSe_2$ and $CuGaSe_2$ by Raman microspectrometry // *J. Appl. Phys.* **72**(9), p. 4321-4324 (1992).
5. V. V. Pasynkov and V. S. Sorokin, *Materials of Electron Techniques*. St-Peterburg – Moscow, 2004 (in Russian).
6. N. Mott and E. Davis, *Electron Processes in Noncrystalline Materials*. Clarendon Press, Oxford, 1971.
7. S. N. Mustafaeva, M. M. Asadov, D. T. Guseinov, I. Kasimoglu, Dielectric properties of $CuInS_2$ single crystal at alternate electric fields of radio-frequency range // *Physics of Solid State*, **57**(6), p. 1079-1083 (2015).