EFFECT OF UNIAXIAL STRESS ON LOW-FREQUENCY DISPERSION OF DIELECTRIC CONSTANT IN HIGH-RESISTIVITY GaSe CRYSTALS

J.M. STAKHIRA, O.YE. FL'UNT, YA.M. FIYALA

Ivan Franko National University of L'viv
(50, Dragomanov Str., L'viv 79005, Ukraine; e-mail: `flunt@electronics.wups.lviv.ua`*)*

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Low-frequency dielectric spectra of high-resistivity GaSe layered crystals have been studied on the samples clamped between two insulating parallel plates at frequencies up to 100 kHz. The measurements have been carried out at different uniaxial stresses up to 2.4×10^5 Pa applied along the c-axis normal to crystal layer's plane. It is revealed that the dielectric spectra of high-resistivity GaSe layered crystals with insulating plates obey a universal power law $\sim\omega^{n-1}$, where ω is the angular frequency and $n \approx 0.8$, earlier observed on high-resistivity GaSe crystals with indium-soldered contacts. The same type of spectra on the crystals with different types of contacts (insulating and ohmic) confirms the bulk character of the observed polarization caused by hopping charge carriers. It is shown that the frequency-dependent dielectric constant increases linearly with the uniaxial stress characterized by the coefficient $\Delta\epsilon/(\epsilon\Delta p) = 8{\times}10^{-7}$ Pa^{-1}. A slight increase of power $1-n$ with the stress is observed, that leads to a stronger dielectric dispersion. The strong stress dependence of the low-frequency dielectric constant in high-resistivity GaSe crystals may be referred to the presence of the formations of elementary dipoles, rotations of which correspond to hops of localized charge carriers.

1. Introduction

Gallium selenide is a layered semiconductor with a band gap of 2 eV at room temperature. Each layer of this crystal consists of four sheets of like atoms in the sequence Se–Ga–Ga–Se, within which the atoms are hold by strong covalent bonds [1, 2]. Weak crystalline bonds between atoms, belonging to different neighbor layers, and the possibility to stack the layers in different ways allow the formation of a few polytypes. But gallium selenide crystals, grown from a melt of the stoichiometric composition by the Bridgman–Stockbarger method, usually belong to the ϵ-polytype [3], the hexagonal unit cell of which contains 8 atoms and spans two layers in the direction normal to layer's plane. The disposal of atoms inside a unit cell corresponds to the space symmetry group P-6m2 (187). The large crystallographic anisotropy of GaSe crystals causes the singularities of mechanical, electrical, and optical properties [4–6]. The high electrical resistivity due to the wide band gap makes gallium selenide attractive for studying the low-frequency dielectric spectra and the effects appearing under condition of the domination of displacement currents. From earlier studies [7], it is known that the dielectric spectra of high-resistivity GaSe crystals with resistivity over 10^5 Ω·cm are characterized by the dispersion obeying the universal power law [11]

$$\epsilon_1(\omega) - j\epsilon_2(\omega) =$$

$$= B(j\omega)^{n-1} = B\left\{\sin\frac{n\pi}{2} - j\cos\frac{n\pi}{2}\right\}\omega^{n-1}, \qquad (1)$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are real (in-phase) and imaginary (phase shifted by $\pi/2$) frequency-dependent components of the complex relative dielectric constant, respectively, j is the imaginary unit, ω is the angular frequency, and the exponent $1 - n \approx 0.2$. A dispersion of this type, when the exponent $1 - n < 0.3$, but not too small, is usually connected with the hopping transport of quasilocalized electrical charge carriers [10,11]. The localization of charge carriers in GaSe crystals can be a result of the non-controlled intercalation and a deviation of the chemical composition from the stoichiometric one. In particular, according to [12, 13], the local stacking faults of layers lead to breaking down the translation symmetry of GaSe crystals along the axis normal to layer's plane, that, in turn, leads to the localization of charge carriers in the regions restricted by two consequently displaced faults. Therefore, in most cases, layered crystals and GaSe crystals, particularly, are characterized by a high density of localized levels in the forbidden gap and in the tails of bands of allowed energies. Recently, the low-frequency dielectric spectra of GaSe crystals have been measured on samples with nearly ohmic contacts fabricated by indium soldering on fresh cleaved surfaces of the crystal [7]. Studies of the dielectric spectra of GaSe crystals with the use of blocking contacts that do not allow the injection of excess charge carriers into the crystal volume, as well as studying the influence of external factors (particularly, a uniaxial pressure) on the frequency-dependent dielectric permittivity, are of importance to

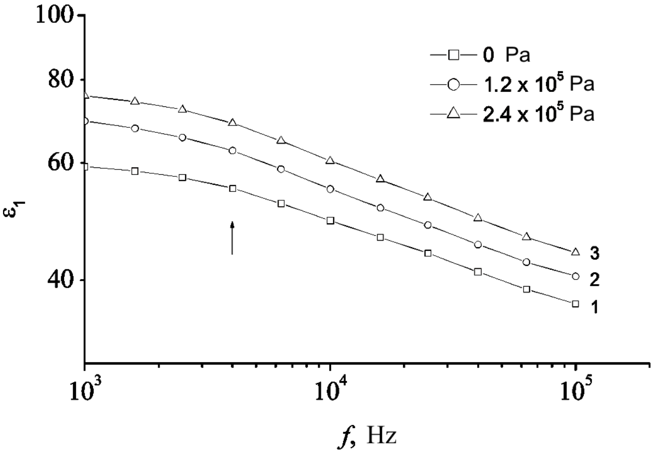

Fig. 1. Frequency dependencies of the relative dielectric constant of a high-resistivity GaSe layered crystal at different uniaxial stresses applied along the *c*-axis (*1* – 0 Pa, *2* – 1.2×10^5 Pa, *3* – 2.4×10^5 Pa)

confirm the bulk character of observed polarization processes and to obtain the information about singularities of the localization of electrical charge carriers and the character of interaction between them.

2. Experimental

This paper studies the low-frequency dielectric spectra of high-resistivity GaSe crystals measured with the use of the plates which are blocking (insulating) for the electrical charge carriers under a uniaxial stress applied along the *c*-axis normal to layer's plane. The disc-shaped ferroelectric capacitors with metal plates ground from one side were used as blocking contacts [8, 9]. The dielectric spectra of these plates itself do not show a noticeable dispersion within the investigated frequency range, and their capacity in the case of the squeezing of the measuring cell without a sample is enough large (more than 50 pF) to create the conditions for prevailing the impedance of the samples under study. Crystals for measurement were grown by the Bridgman–Stockbarger method; samples were cleaved along layers with a thickness of about 1 mm. The measurements of dielectric spectra at frequencies up to 100 kHz have been carried out, by transducing the complex capacity into a proportional ac voltage. The transducer of the complex capacity fabricated on the basis of an operational amplifier allows us to elucidate the effect of the capacity of connecting cables on the measurement results. In the process of measurement, the ac sinusoidal voltages were consequently applied to the sample with different frequencies with an approximately linear step on the log-scale in the set frequency range with an rms voltage of 100 mV. The rms voltage on the output of a transducer was measured with a digital voltmeter, and the phase shift between input and output (proportional to the current across the sample) signals with a digital phase-meter. The preceding correction of the measuring equipment using the standard elements allows us to avoid the constant bias. We note that the impedance of dielectric plates decreases with increase in the frequency according to the law $\sim 1/\omega$ (in the case of ideal capacity), and the impedance of high-resistivity GaSe crystals in the region, where the displacement current prevails, is proportional, as expected, to ω^{-s}, where $s \approx 0.2$. Therefore, at frequencies higher than some critical value, the dielectric response of the sample under study will dominate in the measuring spectra. We succeeded to observe this domination of the dielectric spectrum of the sample under study squeezed in a measuring cell with dielectric plates just on high-resistivity GaSe crystals.

3. Results and Discussion

The frequency dependencies of the relative dielectric constant of a high-resistivity GaSe layered crystal at various uniaxial stresses are shown in Fig. 1. It corresponds to the real part of polarization that changes in-phase with the applied sinusoidal electric field. It can be observed on the frequencies higher than $\sim 4 \times 10^3$ Hz, that is connected with the limiting effect toward low frequencies of the capacities of dielectric plates of a measuring cell which are connected schematically in-series. The linear dependence of the dielectric constant on the frequency on the log-log scale indicates that the spectra obey a universal power law $\sim \omega^{-(1-n)}$, where $1 - n \approx 0.2$. The presence of the dispersion in high-resistivity GaSe crystals, under condition of the impossibility of the across current via a sample, is one more confirmation of the bulk character of the polarization process under study.

As can be seen from Fig. 2, the dispersive dielectric constant of GaSe layered crystals linearly increases with the uniaxial stress with a sufficiently high coefficient that equals, for example, 3.5×10^{-5} Pa at a frequency of 63 kHz. Since the spectra obey the universal power law, it can be concluded, omitting a weak dependence of the exponent $1 - n$ on the pressure, that the ratio of a relative change of the dielectric constant to a change of the stress $\Delta\epsilon/(\epsilon\Delta p) = 8 \times 10^{-7}$ Pa^{-1} is independent of the frequency and can characterize the sensitivity of the frequency-dependent dielectric constant to a uniaxial stress in high-resistivity GaSe crystals. The exponent $1 - n$ can be obtained from the slope of the frequency dependence $\epsilon_1(\omega)$ on the log-log scale or from the ratio of the imaginary and real components of the dielectric constant which is frequency-independent for a specific polarization process according to the universal power law [11]:

$$\frac{\epsilon_2(\omega)}{\epsilon_1(\omega)} = \text{ctg}\left(\frac{n\pi}{2}\right). \qquad (2)$$

In Table, we give the values of exponent $1-n$ which are obtained from the ratios of the real and imaginary parts of the dielectric constant (column 3) and from the slopes of the frequency dependence of the dielectric constant on the frequency on the log-log scale (column 4). Close values of $1-n$ obtained by two different methods confirm that the response of a GaSe cystal under study prevails in the high-frequency part of the spectrum. The results shown in Table allow us to assert also that the exponent $1-n$ weakly increases with the uniaxial stress.

The measured ratios of a relative change of the frequency-dependent dielectric constant to a uniaxial stress in GaSe layered crystals significantly exceed the piezoconductivity coefficients for most known semiconducting materials, which is explained by a transformation of the energy band spectra of crystals and a change of the effective mass of charge carriers [14]. Further, let us estimate a possible change of the dielectric constant within the model of hops of localized charge carriers in rigid double potential wells which corresponds to the absence of interaction between charges. For example, the hopping frequency depending on the tunneling factor can be written as $f = f_0 \exp(-2\alpha R)$, where f_0 is the attempt frequency, α is the wave function decay constant, and R is the distance between localization centers. A change of the distance between two centers by ΔR leads to a relative change of the hopping frequency $\Delta f/f = -2\alpha\Delta R = ln(f/f_0)(\Delta p/B_3)$, where B_3 is the elasticity modulus of a GaSe crystal along the c-axis. The component of the elasticity modulus characterizing a change of interlayer distances in GaSe layered crystals [15], which is significantly less than that connected with a change of the distances between atoms inside layers, can be considered as B_3. But even in this case, the relative change of the hopping frequency at the applied stress 2.4×10^5 Pa is about 10^{-4}, which leads to an even less relative change of the dielectric constant. Therefore, the model of independent hops of charge carriers in rigid double potential wells, for which the distance between energy minima changes proportionally to a relative change of interlayer distances, is also incapable to explain the observed change of the frequency-dependent dielectric constant of crystals under the action of a uniaxial stress.

Dependence of dielectric loss tangent and exponent $1-n$ of a GaSe crystal on the uniaxial stress at a frequency of 40 kHz

p, Pa	tgδ, 40 kHz	$1-n$	$1-n$
0	0.21	0.132	0.129
1.2×10^5	0.223	0.139	0.139
2.4×10^5	0.237	0.148	0.144

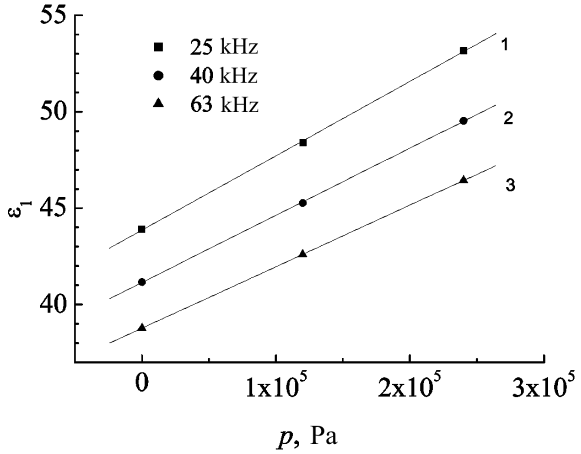

Fig. 2. Dependencies of the relative dielectric constant of a high-resistivity GaSe layered crystal on the uniaxial stress applied along the c-axis measured at various frequencies (*1* – 25 kHz, *2* – 40 kHz, *3* – 63 kHz)

But, according to the modern conceptions, the polarization in condensed matter cannot be considered as a rotation of independent dipoles, each of which changes the orientation in rigid double potential wells or wells with more minima [11, 16]. A change of the position of each localized charge carrier equivalent to the rotation of an elementary electric dipole leads to a change of the dispositions of many other neighbor localized charges within the region of a certain radius. So, the experimentally measured macroscopic parameters of polarized condensed media characterize not the individual dipoles, but some formations on the basis of elementary dipoles. At present, the behavior and dimensions of these formations are known very little. They are characterized by their own effective dipolar moments and relaxation times which differ from those of elementary dipoles and cause, in most cases, a distribution of relaxation times in a wide interval. A significant sensitivity of the dielectric constant of GaSe crystals to a mechanical stress can be explained by the presence of the formations of elementary dipoles, whose rotations are equivalent to localized charge carrier hops. As a result, each elementary localized charge does not stay not in some mean electric field, but undergoes the action of a local electric field formed by a certain arrangement of surrounding electric charges, which is established in the process of creation of dipole's formations at a certain time moment. The establishment of a distribution of local electric fields and the creation of formations of elementary dipoles are random processes strongly dependent on previous step-by-step changes in the dipolar system and thereby very sensitive to defects of the crystal structure and different external factors, particularly a uniaxial stress. An insignificant influence of some external factors can decline the preferred positions from one side to another one for some individual dipoles with close values of probabilities to be in two different directions. As a result of the subsequent processes of reorientation of the neighboring dipoles, this can cause a significant change of parameters of the formations of individual dipoles, which will reveal, in our case, in changes of the low-frequency dielectric constant under a uniaxial stress.

4. Conclusions

Our investigations of the low-frequency dielectric spectra of high-resistivity GaSe crystals clamped between dielectric plates of a flat capacitor demonstrated the dominance of the dielectric spectrum of the ω^{n-1} type, where ω is the angular frequency and the exponent $n \approx 0.8$, which is characteristic for the systems with hopping motion of charge carriers. It is established that the disperse permittivity of high-resistivity GaSe crystals linearly depends on the uniaxial stress and can be characterized by the frequency-independent coefficient $\Delta\epsilon/(\epsilon\Delta p) = 8\times10^{-7}$ Pa^{-1}. The exponent $1-n$ insignificantly grows with increase in the uniaxial stress. The revealed considerable dependence of the low-frequency permittivity of high-resistivity GaSe crystals on the uniaxial stress is related to the formation of ensembles of elementary dipoles in the crystal, whose rotations are equivalent to hops of localized charge carriers. The established regularities of the dependence of the dispersive permittivity on the uniaxial stress can be used for studying the peculiarities of the formation of dipole ensembles in solids, as well as for creating the uniaxial stress sensors based on new physical phenomena.

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ВПЛИВ ОДНОВІСНОГО ТИСКУ НА НИЗЬКОЧАСТОТНУ ДИСПЕРСІЮ ДІЕЛЕКТРИЧНОЇ ПРОНИКНОСТІ У ВИСОКООМНИХ КРИСТАЛАХ GaSe

Й.М. Стахіра, О.Є. Флюнт, Я.М. Фіяла

Резюме

Проведено дослідження низькочастотної діелектричної проникності високоомних кристалів GaSe на частотах до 100 кГц з використанням блокуючих для носіїв електричного заряду (ізолюючих) контактів. Вимірювання проводили при прикладанні до зразка невеликого одновісного тиску в межах до $2,4\cdot10^5$ Па вздовж осі c, нормальної до площини шарів кристала. Встановлено, що діелектричний спектр високоомних кристалів GaSe з блокуючими електродами підлягає універсальному степеневому закону $\sim\omega^{n-1}$, де ω – кутова частота, $n \approx 0,8$, який раніше спостерігали на високоомних зразках з контактами з наплавленого індію. Однакова форма діелектричного спектра на кристалах з різними типами контактів (омічними та блокуючими) підтверджує об'ємний характер спостережуваного явища поляризації, яке пов'язується зі стрибкоподібним переміщенням квазілокалізованих носіїв електричного заряду. Встановлено, що діелектрична проникність лінійно зростає з величиною прикладеного одновісного тиску з коефіцієнтом $\Delta\epsilon/(\epsilon\Delta p) = 8{\cdot}10^{-7}$ Па$^{-1}$. Спостерігається незначне збільшення показника степеня $1-n$ при збільшенні тиску, що приводить до посилення дисперсії діелектричної проникності. Значна залежність низькочастотної діелектричної проникності від одновісного тиску в високоомних кристалах GaSe пов'язується з формуванням утворень диполів, обертання яких еквівалентні стрибкам локалізованих носіїв електричного заряду.