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IMPEDANCE SPECTRUM OF TlGaSe₂ CRYSTAL IMPLANTED WITH He⁺ IONS

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Abstract: The impedance spectrum of TlGaSe₂ crystal implanted with He⁺ ions (with 150keV-energy He⁺ ions) has been investigated at the temperatures of 275-550K and frequencies of 100-106 Hz. After the implantation, the numerical value of the permittivity and the relaxation period increased by 10 times. It has been shown that the main reason for the increase in the numerical value of permittivity as well as the relaxation period as a result of implantation is the increase in the concentration of mobile ions. It was found that the distribution of Tl in cavities is at the depth of 1000 nm.

Keywords: Dielectric properties; impedance; TlGaSe₂ crystals

1. Introduction

In recent years, materials with high-ion conductivity are in the focus of world researchers [1-3]. Currently, materials with high ion conductivity are used as functional electrodes on various devices. One of the prospects of applications of materials with high ion conductivity is the use of them in the devices that convert thermal energy, corresponding to chemical bond, into electrical energy. However, at present, there are many problems with the way to solve these problems. The solution of such problems requires the acquisition of stable materials with high ion conductivity. The development of modern microelectronics needs to acquire new semiconductor materials with both electronic and ionic conductivity. For this reason, A³B³C₂⁶ – type semiconductors are extensively studied in recent years [4 - 11].

TlGaSe₂ semiconductor compound belongs to the class of A³B³C₂⁶ group compounds and lattice periods become crystallized in monocline crystal system being $a = 10.772 \text{ \AA}$; $b = 10.771 \text{ \AA}$, $c = 15.636 \text{ \AA}$, $\beta = 100.6^\circ$. TlGaSe₂ crystal is included in the C2/c-C_{2h}⁶ space group. Ga₄Se₁₀ tetrahedrons constitute the basis of the structure of the TlGaSe₂ monocline structure layered crystal included in A³B³C₂⁶ group compounds. The results of X-ray studies of TlGaSe₂ and TlInS₂ layered compounds at room temperature were presented in the work [12]. The results of low-temperature X-ray diffraction studies for the TlGaSe₂ compound show that the crystal has an incommensurate phase with a modulation wave vector $(\delta; \delta; 1/4)$ and $\delta = 0.02$ in the temperature range 110-117K [13]. At 110K temperature δ drops sharply to zero and crystal passes to the commensurate phase. In this case, the spontaneous polarization line in the crystal increases and gets the value of $1.3 \cdot 10^{-7} \text{ C/cm}^2$ [14].

In the work [15], it has been reported for the first time, the observation of ion conductivity at the temperatures higher than 300K in the TlGaSe₂ crystal. It was found that the presence of ionic conductivity in TlGaSe₂ crystal at the temperatures above 300K is due to the diffusion of Tl⁺ ions in the thallium sublattice between nanorods (Ga³⁺Se²⁻₂) on vacancies. The obtained results show that the electron accumulation of electrical conductivity dominates at temperatures below 300K. A leaping increase in the conductivity is observed with the subsequent increase in temperature (above 300 K), and this is associated with an increase in ion accumulation due to the disorder of the Tl⁺ cation sublattice.

In this study, the dielectric and complex impedance spectra of the TlGaSe₂ crystal at the temperature range of 275-550K were studied comparatively before and after implantation with He²⁺ ions. The interest in studying the defects arising after the implantation with Helium ions is due to the study of both the nature of the defects themselves, their formation mechanisms, and the effect of the defects on the physical properties of the crystal [16].

The SRIM software (The Stopping and Range of Ions in Matter) is a program group that calculates the quantum mechanical process of ionic-atomic collisions and the braking and ion range in the matter, as with all target atoms. The SRIM software allows you to calculate the electron braking power of any ion in any material, based on a wide range of experimental data average parameters [17].

2. Experimental

TlGaSe₂ crystal, which is the subject of the study, was synthesized using the Bridgman–Stockbarger method. The geometric parameters of the crystal used in the experiments were in sizes of 5x2x2 mm³. During the study of the electrical and dielectric properties of TlGaSe₂ crystals, silver electrodes were used as electrical contacts. These studies were conducted in the direction of the samples perpendicular to the “c” axis. The study of the complex dielectric properties was performed on the MNIPI E7-25 impedance analyzer. Experiments were conducted at 25-10⁶ Hz frequencies and 275-550K temperatures. The ion implantation of the samples was carried out at the Department of Ion Physics and Implantation at the Physics Institute of Maria Curie-Skłodowska University in Lublin, Poland. The implantation was carried out at room temperature and under 10° angle in the UNIMMA79 accelerator. Samples were implanted with He²⁺ ions at 150 keV energy and $\Phi=10^{15}$ ion/cm²×sec doses. Ionic implantation was simulated with the help of SRIM software.

3. Results and Discussion

It is required the search for high-conductive ionic materials and the comprehensive study of the movement dynamics of ions in solids, along with the synthesis conditions. The best method for this is the impedance spectroscopy method. The study of the system's reaction to the low amplitude sinusoidal signals allows a detailed study of the processes of charge transfer in materials related to both ionic migration and polarization effects. Modern methods of modeling processes in disordered systems based on impedance spectroscopy greatly extend the understanding of the diffusion mechanism of ion in them.

Using the results of frequency dependence analysis of the impedance, it is possible to determine the alternating current frequency field, where the electrode impedance has little contribution to the experimental parameters. The results obtained from the temperature dependence of the electrical conductivity at the selected frequency in this region will characterize the real properties of the material. It should be noted that the specified frequency range may be change due to external influences (for example, frequency region boundary may shift to the high-frequency region with the increase in temperature).

The figures 1 and 2 show the dependence of the real and imaginary part of the $Z^*(f)$ complex impedance of TlGaSe₂ crystal on the measurement frequency at the different temperatures, respectively. As it is seen from the figures, the frequency dependence of the real part of $Z'(\omega)$ complex impedance changes like a stair at different temperatures, and the imaginary part $Z''(\omega)$ is accompanied by peaks. The frequency dependencies of the peaks of the imaginary part of $Z''(\omega)$ shift to the higher frequency region as the temperature increases. There

is a decrease in the numerical value of impedance with the increase in the electric field frequency in the frequency dependence of impedance. According to the peaks observed in the higher values of temperature.

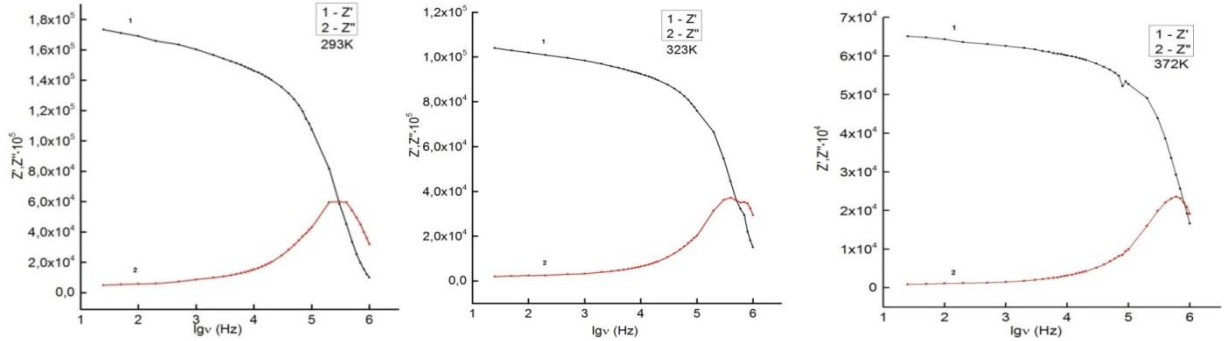


Fig. 1. Frequency dependence of the real and imaginary part of the complex impedance spectrum of the $TlGaSe_2$ crystal (293K, 323K, 372K).

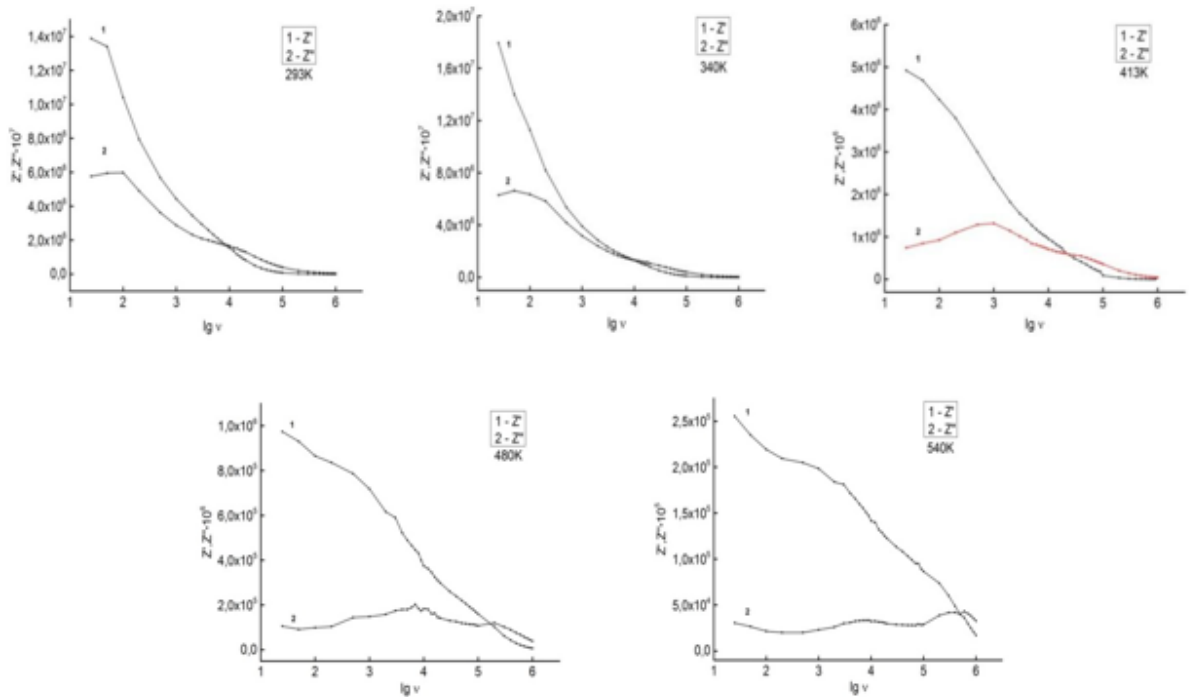


Fig. 2. Frequency dependence of the real and imaginary part of the complex impedance spectrum of $TlGaSe_2$ crystals implanted with He^{2+} ions (293K, 340K, 413K, 480K, 540K).

Figure 3 shows the frequency dependence of the real part of the impedance spectrum of the $TlGaSe_2$ crystal (a - before implantation, b - after implantation). Measurements were performed at 4 different temperature regions at different frequencies. As can be seen from the figure, the value of the real part of impedance increased by 10^2 after implantation.

The relaxation period can be calculated in $TlGaSe_2$ crystals. The shifts in the direction of frequency increase in peaks after the implant indicate an increase in the relaxation period.

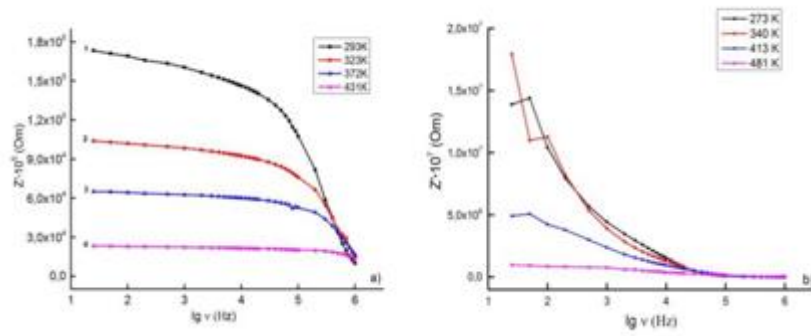


Fig. 3. Frequency dependence of the real part of the $Z^*(f)$ complex impedance of the $TlGaSe_2$ crystal. (before implantation (a) and after implantation with He^{2+} ion (b))

Using the SRIM software, the ion distribution at depth and the vacancies created by the implantation ions have been calculated in the $TlGaSe_2$ crystal implanted with 150 kV energy He^{2+} ions. Figure 4 shows the atomic density at the depth of the implantation ions (He^{2+}) in $TlGaSe_2$ crystal.

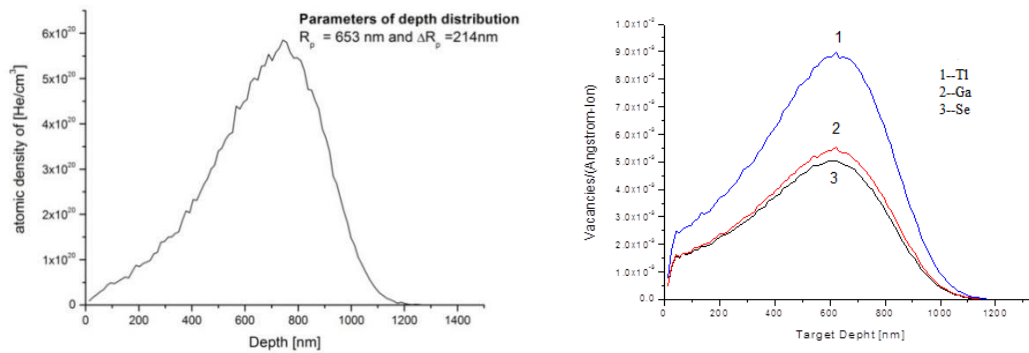


Fig. 4. a - distribution of ions at different depths, b - distribution of vacancies at different depths in $TlGaSe_2$ crystals implanted with He^{2+} ions

10^6 ions have been estimated during the calculation in the program. The distribution of vacancies at different depths in the $TlGaSe_2$ crystal, implanted with 150 keV He^{2+} ions has been shown in Figure 4 using the SRIM simulation. Here, the atoms that move in the substance have been shown. At the target atoms, as shown in Figure 4, He^{2+} ions can create vacancies up to 600nm depth. This is the maximum range observed in $TlGaSe_2$ crystals with 150kV energy He^{2+} ions. According to the SRIM simulations, the maximum Tl cavity distribution is at a depth of 1000 nm when implanted with He^+ ions.

4. Conclusions

The dielectric properties and impedance spectrum of $TlGaSe_2$ crystal implanted with He^+ ions (with 150kV energy He^+ ions) have been investigated. After the implantation, the numerical value of the dielectric permeability and the relaxation period have increased by 10 times. The increase in dielectric permeability depending on temperature is the result of increased mobility of Tl ions in $TlGaSe_2$ crystals. Changes in dielectric characteristics under the implantation effect lead to a change in ion mobility with the formation of radiation defects. It has been shown that the main reason for the increase in the numerical value of dielectric permeability and relaxation

period as a result of implantation is the increase in the concentration of mobile ions. The distribution of the Tl, Ga, and Se atoms in the implanted TlGaSe₂ crystal has been also given using the SRIM software. It was found that the distribution of Tl in cavities is at the depth of 1000 nm.

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СПЕКТР ИМПЕДАНСА КРИСТАЛЛА TlGaSe_2 ИМПЛАНТИРОВАННОГО ИОНАМИ He^+

С.Ф. Самадов

Резюме: Спектр импеданса кристалла TlGaSe_2 , имплантированного ионами He^+ (с ионами He^+ с энергией 150 кеВ), был исследован при температурах между 275-550К и частотой 100-10⁶ Гц. После имплантации численное значение проникновения диэлектрика и период релаксации были увеличены в 10 раз. Показано, что основной причиной численного значения проникновения диэлектрика, а также период релаксации в результате имплантации является увеличение концентрации подвижных ионов. Было обнаружено, что распределение Тl в полостях находится на глубине 1000 нм.

Ключевые слова: диэлектрические свойства, импеданс, TlGaSe_2 кристаллы

He^+ IONLARI İLƏ İMPLANTASIYA OLUNMUŞ TlGaSe_2 KRİSTALLININ İMPEDANS SPEKTRİ

S.F. Səmədov

Xülasə: He^+ ionları ilə implantasiya olunmuş (150keV enerjili He^+ ionları ilə) TlGaSe_2 kristallının impedans spektri 275-550K temperatur və 100-10⁶ Hz tezlik intervalında tədqiq edilmişdir. İmplantasiyadan sonra dielektrik nüfuzluğunun ədədi qiyməti və relaksasiya müddəti 10 dəfə artmışdır. Göstərilmişdir ki, implantasiya nəticəsində dielektrik nüfuzluğunun ədədi qiymətinin və relaksasiya müddətinin artmasının əsas səbəbi mobil ionların konsentrasiyasının artmasıdır. Müəyyən edilmişdir ki, Tl boşluqlarda paylanması 1000 nm dərinlikdədir.

Açar sözlər: dielektrik xassələri, impedans, TlGaSe_2 kristalları