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INFLUENCE OF PROTONS ON THE ANISOTROPY OF $TlInS_2$ CRYSTAL

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Abstract: The dielectric and electrical properties of the $TlInS_2$ crystal implanted with protons (protons with the energy of 150 keV) were investigated both in the tetragonal c axis and in the direction perpendicular to this axis. It is shown that the numerical values of the permittivity and electrical conductivity increase sharply in the direction of the c axis and decrease in the direction perpendicular to this axis. The decrease in the anisotropy in the $TlInS_2$ crystal under the influence of protons is associated with the amorphization of the crystal.

Key words: implantation, permittivity, anisotropy, amorphization, electrical conductivity

1. Introduction

At present, TlInS2 is one of the few semiconductor compounds in which a sequence of incommensurate and ferroelectric phase transitions (PT) is observed [1–4]. According to neutron diffraction and X-ray studies [2,5], the incommensurate phase existing in the temperature range Tc = 201K < T < Ti = 216 K is characterized by a wave vector ki = (δ, δ, 0.25), where δ = 0.012 is a disproportion parameter. In this case, in the temperature range of existence of the incommensurate phase, the dynamics of the process is very complex and very sensitive to the defectiveness of the structure.

It was shown in [6-8] that In in the $TlInS_2$ compound has a normal valence with the configuration of outer electrons 4dl0 and an oxidation state of (+3). Valence electrons in sulfides are characterized by the S^2P^4 configuration and the oxidation state - (-2), thallium has a $6S^2$ shell. Eight electrons of SP hybridization correspond to 3 electrons of the $5S^25P^1$ shell of indium, 6 electrons of the S^2P^4 shell of each of the two sulfur atoms, and 1 electron of thallium. This hybridization provides a polarized covalent bond between indium and sulfur and a tetrahedral orientation of the latter relative to indium. The ionic bond between Tl+ and $[TlS_2]$1+ is via sulfur.

In [9], the impedance spectra of $TlInS_2$ crystals in an alternating measuring field at temperatures of 100÷500K were studied. On the frequency dependence of the imaginary part of the Z″ impedance, a well-defined peak is observed at a temperature range of 215K-500K. With increasing temperature, it shifts to the high-frequency region. Under the influence of a constant electric field, the ionic conductivity contribution is estimated from the kinetic change in electrical conductivity (σ). In the frequency range of 10-106Hz, diagrams were measured in the complex plane (Z" - Z') and carried out using the method of equivalent circuits.

It is known that the $TlInS_2$ crystal has a layered structure and is anisotropic. The physical properties of this crystal above room temperature have not been studied in detail. Also, the influence of protons on the anisotropic properties of the $TlInS_2$ crystal has not been studied.

This work aims to study the influence of protons on the dielectric and electrical properties of $TlInS_2$ crystals at a temperature range of 300-600K and a frequency range of 25-10^6Hz both parallel and perpendicular to the tetragonal axis "c" of the crystal.

2. Experimental technique

$TlInS_2$ single crystals were grown by the modified Bridgman - Stockbarger method. For measurements, we used samples in size of 5×2×2 mm. The measurements were carried out in parallel and perpendicular to the tetragonal axis "c" of the crystal. The silver paste was used as contacts. The complex permittivity and electrical conductivity were measured using an E7-12 AC bridge in the frequency range of 25–10^6 Hz using a copper – constantan thermocouple at a step of 0.1 K/min.

3. Experimental results and their discussion

The most important task of semiconductor materials science is the creation of new materials with predetermined properties to meet the needs of instrumentation. In solving this problem in the field of materials with a layered structure, more attention is being paid to the technological method of implantation, i.e. introducing foreign ions and atoms into the space of layered crystals.

As is known, $TlInS_2$ ternary semiconductor crystals belong to the class of ferroelectric materials and are of particular interest in terms of studying their physical properties. They have a layered structure and are easily split along the soldering planes, forming plates with mirror surfaces, which are oriented in planes perpendicular to the *c* axis. The main structural unit of the compound is a two-dimensional periodic layer consisting of groups of In_4S_{10} tetrahedra. They represent a union of four elementary In_4S_{10} tetrahedra arranged according to the diamond law around the central empty S_6 octahedron. Such layers in the crystal are transferred parallel to the crystallographic plane (001) or perpendicular to the "c" axis. Each next tetrahedral layer is rotated concerning to the previous layer by 90º. Only with this method of alternating layers, it is possible to form trigonal-prismatic voids, which are convenient for filling with Tl^+ ions. Therefore, layers of the same parity will be identical and spontaneous polarization is observed only in the direction of the layers.

In this work, we considered the change in the anisotropy of the $TlInS_2$ crystal as a result of the influence of protons.

The temperature dependence of the permittivity ε(T) in the $TlInS_2$ compound is shown in Fig. 1. (b) - measurements were performed along the tetragonal axis of the crystal ε||(T) and (a) - perpendicular to it $\varepsilon\perp$(T).

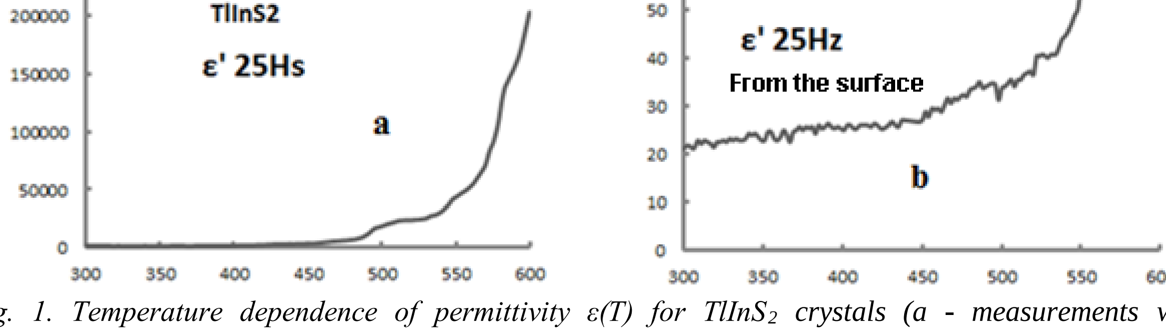

Fig. 1. Temperature dependence of permittivity ε(T) for $TlInS_2$ crystals (a - measurements were performed perpendicular to the tetragonal axis "c"; b - measurements were performed along the tetragonal axis "c".

As can be seen from Figure 1 (a, b), the maximum value of the permittivity in the direction of the tetragonal axis “c” is about 60 at the temperature of 570K, and in the direction perpendicular to this axis, it is 150000 at this temperature.

Figure 2 (a, b) shows the temperature dependence of permittivity ε(T) after implantation of a TlInS2 crystal with hydrogen ions H+ both along and perpendicular to the direction of the “c” axis (the proton energy is 150 keV). As can be seen from Fig. 2, after implantation of the TlInS2 crystal, the permittivity ε(T) increases along the direction of the “c” axis, decreases perpendicular to the direction of the “c” axis, and the anisotropy greatly decreases. That is, the maximum value of the permittivity in the direction of the tetragonal axis “c” reaches about 100000 at a temperature of 570 K, and in the direction perpendicular to this axis, it is 25000 at this temperature. As can be seen from a comparison of Fig. 1 and Fig. 2, after the implantation of the TlInS2 crystal, the numerical value of the permittivity in the direction of the c axis increased 1600 times, and in the direction perpendicular to the c axis, decreased 6 times.

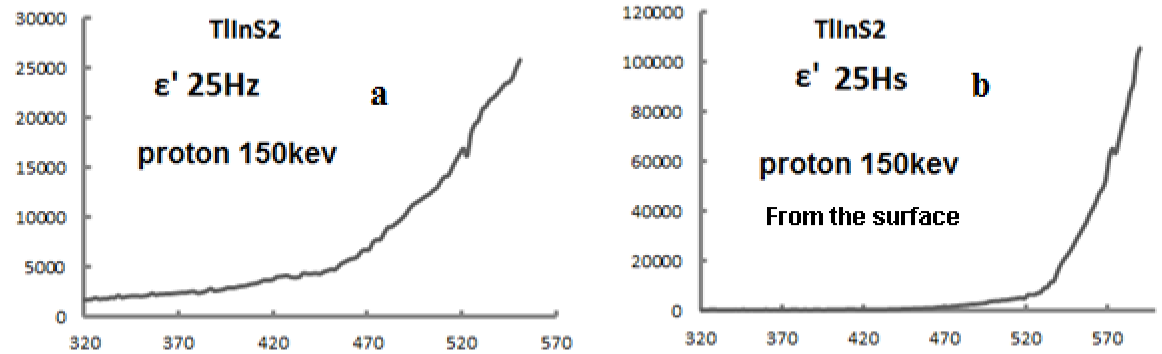

Fig. 2. Temperature dependence of permittivity ε(T) for $TlInS_2$ crystals (a - perpendicular to the tetragonal axis “c” of the crystal; b - along the tetragonal axis of the crystal)

We have studied the polarized Raman spectra of a $TlInS_2$ crystal at 300 K [10]. The experiment showed that the Raman spectra before and after implantation do not match. It was shown that, after implantation of the $TlInS_2$ crystal with H^+ ions, an increase in the spectra of In and Tl ions and a decrease in the Tl content in the surface layer of the crystal were observed. This is due to the amorphization of the crystal structure after implantation.

In fig. 3 (a, b) shows the temperature dependence of the electrical conductivity σ(T) in the direction of the tetrogonal axis c. As can be seen from Figure 3 (a, b), the electrical conductivity increases by 10^4 times after the influence of protons with an energy of 150 kV.

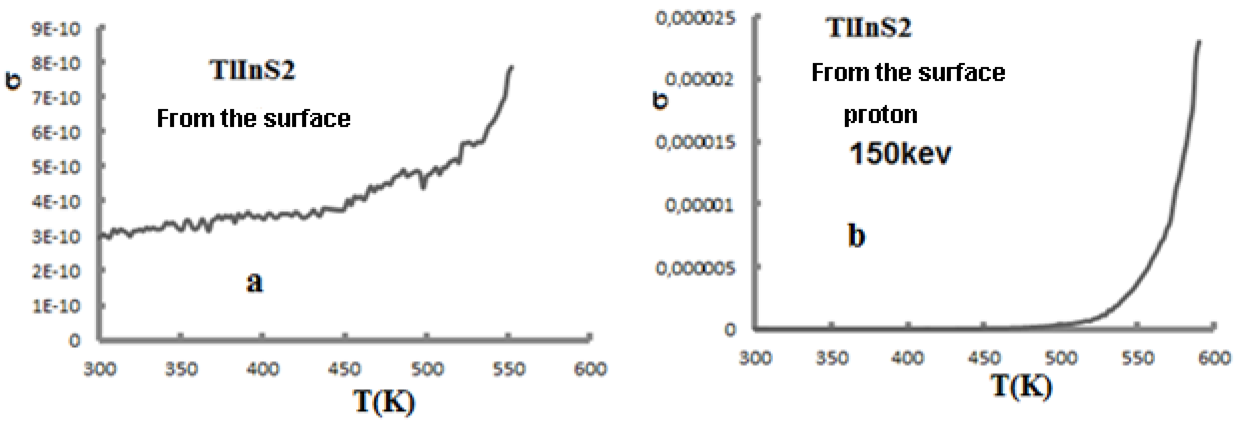

Fig. 3. Temperature dependence of electrical conductivity σ(T) for $TlInS_2$ crystals (measurements were performed along the tetragonal axis “c”. a - without irradiation; b - exposed to proton influence - 150 keV)

4. Conclusion

Thus, the dielectric and electrical properties of a $TlInS_2$ crystal implanted with H^+ ions (H^+ ions with an energy of 150 keV) were investigated both in the direction of the c axis and in the direction perpendicular to the c axis. An increase in the numerical values of the permittivity and electrical conductivity in the direction of the C axis and a decrease in the direction perpendicular to the c axis was observed. It is shown that the decrease in anisotropy as a result of implantation is associated with the amorphization of the crystal.

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ВЛИЯНИЕ ПРОТОНОВ НА АНИЗОТРОПИЮ КРИСТАЛЛА $TlInS_2$

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Резюме: Диэлектрические и электрические свойства кристалла $TlInS_2$, имплантированного протонами (протоны с энергией 150 кэВ), были исследованы как в тетрагональной оси С, так и в направлении, перпендикулярном этой оси. Показано, что численные значения диэлектрической проницаемости и электропроводности резко возрастают в направлении оси С и уменьшаются в направлении, перпендикулярном этой оси. Уменьшение анизотропии в кристалле $TlInS_2$ под действием протонов связано с аморфизацией кристалла.

Ключевые слова: имрлантация, диэлектрическая проницаемость, анизотропия, аморфизация, электропроводность

$TlInS_2$ KRİSTALININ ANİZOTROPİYASINA PROTONLARIN TƏSİRİ

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Xülasə: Protonlarla (enerjisi 150 keV olan protonlar) implantasiya olunmuş$TlInS_2$ kristalının dielektrik və elektrik xüsusiyyətləri həm tetragonal C oxu istiqamətində, həm də bu oxa perpendikulyar istiqamətdə araşdırılmışdır. Dielektrik nüfuzluğu və elektrik keçiriciliyinin ədədi qiymətlərinin C oxu istiqamətində kəskin şəkildə artdığı və bu oxa perpendikulyar olan istiqamətdə azaldığı göstərilir. Protonların təsiri altında $TlInS_2$ kristalındakı anizotropiyanın azalması kristalın amorflaşması ilə əlaqələndirilir.

Açar sözlər: implantasiya, dielektrik nüfuzluğu, anizotropiya, amorflaşma, elektrik keçiriciliyi