

# Physical properties of the thin films based on germanium compounds with a supramolecular structure



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## Introduction

One of the most important areas of modern science and technology is the creation of functional materials with specified properties.

Complex compounds of semiconductors, including complex compounds of germanium (CCG) are of special interest in this regard [1]. One of the main advantages of such compounds having a supramolecular structure [2] is that they have a successful combination of physicochemical properties and electrophysical

## Methods

The structure of the CCG film fragment of the material based on the complex of germanium with oxyethylenediphosphonic acid (OEDP) is presented in Fig. 1. It is determined by the hexameric cyclic complex anions  $[\text{Ge}_6(\mu\text{-OH})_6(\mu\text{-O})_6]^{6-}$ . At the same time, germanium atoms are united in pairs by hydroxyl and oxyethylenediphosphonate bridges.

CCG are a supramolecular ensemble, the structural units of which are united by a branched system of hydrogen bonds. Germanium is part of the hexanuclear complex anion, hydrogen ions are in the outer sphere of the complex, and water molecules bind the complexes together, which leads to the formation of layers.

The volt-ampere characteristics (VAC) of a pure CCG film with OEDP acid and a film of the same substance to which ammonium hydrofluoride  $\text{NH}_4\text{F}\cdot\text{HF}$  was added were

parameters (EPP) important for micro- and nanoelectronics. At the same time, the properties of CCG can be relatively easily modified by introducing impurities into their composition.

In this work, the task was to investigate the electrophysical properties of CCG and the physical mechanisms of current transfer in them.

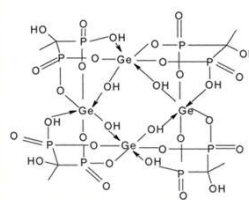


Fig. 1. The structure of the CCG fragment from the OEDP

measured. The temperature dependence of the current flowing through the CCG films with the addition of ammonium hydrofluoride in the heating and cooling modes was also investigated.

## Results and discussion

The results of the research are presented in fig. 2, 3. It was established that the physicochemical properties of CCG can be modified due to the introduction of ions of other metals and organic cations. The reduction of material resistance by three orders of magnitude recorded as a result of the experiment by introducing  $\text{NH}_4\text{F}\cdot\text{HF}$  into the complex confirms this fact.

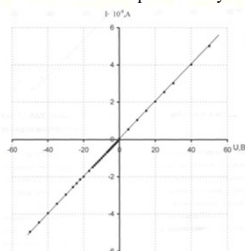


Fig. 2. VAC of CCG films with OEDP acid

The temperature dependence of the current flowing through the sample is presented in (Fig. 3).

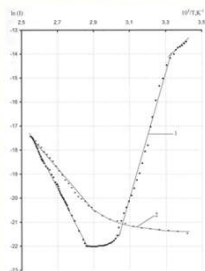


Fig. 3. Graph of temperature dependence of CCG conductivity with OEDP acid. Curve 1 - heating, curve 2 - cooling.

Sections of curve 1 in the ranges of 20-35°C and 35-65°C are characterized by a decrease in conductivity with increasing temperature. However, the pace of change is different. At temperatures up to 35°C, the rate of decrease in conductivity is lower than at subsequent heating to 65°C. This may occur due to a decrease in conductivity during the removal of water of crystallization during the heating process. Thus, up to 35°C, we observe the beginning of the process - the energy is not enough to remove such a quantity of water of crystallization, which would significantly affect the value of conductivity. Starting from 35°C, the system obviously receives sufficient energy to start the dehydration of CCG. When water molecules interact with structural components, not only five-, six-, etc. can be formed. component structures, but also three-dimensional formations:

## Conclusion

The physical properties of CCG are determined by their supramolecular structure and the impurity ions introduced into their composition at the synthesis stage. At the same time, various current transfer mechanisms can be implemented.

The magnitude of proton conductivity and its very presence in a substance with a supramolecular structure primarily depend on its structural features. A necessary condition is the realization of a continuous network of hydrogen bonds or the possibility of its formation during the rotation of proton-containing groups.

Physicochemical properties of CCG can be modified by introducing metal ions or organic cations.

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dodecahedral forms that can have the ability to form chain structures connected by common pentagonal sides.

Thus, the removal of some links of such a current conductor will lead to a decrease in conductivity due to an increase in the distance that must be overcome by the charge carrier, in particular, the proton. With a further increase in temperature, a decrease in the rate of decrease in conductivity was observed up to a certain steady state, in which the conductivity did not change with increasing temperature (in the range of 65-80°C). This fact can be explained by the presence of several charge carrier formation mechanisms in the CCG film. At low temperatures, the mechanism of proton bridges formed by hydrated water, the so-called relay mechanism, obviously prevails.

An increase in temperature (80-125°C) causes an increase in conductivity, which is described by an exponential dependence on temperature. This may indicate a qualitatively different mechanism of formation of charge carriers. The calculated activation energy for this site is 1.43 eV.

To understand the essence of the process of proton conduction in the supramolecular structure of CCG, it is important to find out the mechanisms of the formation of defects and their transfer in the structure of the substance. The process of formation of current carriers, as a rule, is reduced to the transfer of a proton from the ground state to an excited state characterized by higher energy. Proton defects can be formed due to the interaction of a substance with hydrated water molecules. In addition, the concentration of defects is significantly affected by the presence of various kinds of impurities, which for one reason or another can be included in the composition of solid proton-conducting electrolytes. At present, the most common idea is that a proton in a solid body can move either "relay", that is, due to transfer from one electronegative atom to another, or by the so-called "crew" mechanism. In the mechanism of relay transfer, a proton is transferred as if along a chain in the direction of the electric field from an oxonium ion to a water molecule, which is transformed into an oxonium ion, from it to the next molecule, etc.

The "crew" mechanism is proposed on the basis of the fact that compounds that contain water or ammonia molecules along with protons have the maximum proton conductivity at low temperatures. At the same time, the formation of  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$  etc. ions, which can move in the structure as a whole, becomes possible.

From what has been said, it follows that the requirement for the presence of large-sized channels in the structure of proton conduction is unprincipled. For ordinary structures with ionic conductivity, the activation energy of the transfer of charged particles has a minimum value for cations with a radius of about 1 Å. According to the tangents of the angles of inclination of the straight lines in fig. 3 (curve 1) the activation energies were calculated. In the range of 20-35°C, this value was 0.65 eV. In the range of 35-65°C - 2.1 eV. Such energy corresponds to the reorientation of polyatomic ions. However, it can be assumed that the given activation energy is the resulting value of several competing processes described above.

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