

ELECTROPHYSICAL PROPERTIES OF SUPRAMOLECULAR FILMS OF THE GERMANIUM— OXYETHYLIDENEDIPHOSPHONIC ACID COMPLEX

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UDC 537.31:539.21

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The results of researches of the structural, electrophysical, and adsorptive properties of the films made up of a new functional material, the germanium complex compound (GCC) with oxyethylidenediphosphonic acid, have been presented and discussed. The electrical conductivity has been investigated, and its mechanism has been explained. Possible applications of the GCC as a sensitive gas sensor have been considered.

1. Introduction

The need for new materials for micro- and nanoelectronics continuously grows. From this point of view, functional materials with supramolecular architecture are of special interest [1]. In the general case, they are polymolecular ensembles composed of molecular components which fulfill a required function owing to photoelectric, electric, ionic, magnetic, thermal, mechanical, and other effects, depending on a problem to be solved. The functional properties of such synthetic polymolecular ensembles, especially of those which are based on the coordination compounds of various metals, have been studied intensively [2,3]. For example, it was established [2] that the insertion of certain functional groups into molecules can result in the formation of ensembles which are capable to transfer charge carriers, electrons and ions. However, the mechanisms of conductivity in such polymolecular ensembles have not yet been studied sufficiently well.

In this work, the structure of a fragment of the GCC with oxyethylidenediphosphonic acid and the adsorption properties of GCC films with respect to the vapors of water and some other organic liquids have been studied. The electric conductivity of GCC films has been investigated, and its mechanism has been explained.

2. Materials and Methods of Researches

GCC films were grown on dielectric substrates by isothermal evaporation (20–25 °C) of the aqueous

solution of oxyethylidenediphosphonatohydroxygermanium acid [4,5]. The films were 1–50 μm in thickness, and their specific resistance at room temperature exceeded $1 \times 10^{10} \Omega \cdot \text{m}$. Ammonium hydrofluoride $\text{NH}_4\text{F} \cdot \text{HF}$ was added to the solution with the purpose to diminish the film resistance, and polyvinyl alcohol $(\text{C}_2\text{H}_3\text{OH})_n$ to enhance the mechanical strength of the films and their adhesion to dielectric substrates. In this case, the film was a polymeric composite with a specific resistance smaller than $1 \times 10^7 \Omega \cdot \text{m}$. Conducting layers made up of SnO_2 , Al, or Ag and deposited by various standard routines on substrates made up of Al_2O_3 , pyroceramics, or glass served as electrodes to GCC films. The distance between electrodes was 2 mm. The current through the film was registered by a measuring IMT-05 device for small currents. The output signal from it was recorded by a two-coordinate LKD4-003 potentiometer. The average strength of the electric field in specimens did not exceed 5 V/mm. The enhanced concentrations of water, ammonia, acetic acid, benzene, or acetone molecules in the air were created with the help of a local source situated above the GCC film surface. The relative humidity of air was 50% at $T = 25 \text{ }^\circ\text{C}$. The surface relief studies of the GCC films were carried out with the help of a metallographic MIM-8M microscope.

3. Results and Discussion

The analysis of the experimental data concerning the structure and properties of germanium complexes with polybasic organic acids, including the complex compounds that contained carboxyl and phosphorus, showed [6–8] that these complexes can serve as a basis for the production of functional materials diverse in their physical and chemical properties [9]. For example, by evaporating the GCC aqueous solutions with some admixtures, the films revealing high transparency in the wavelength range of 310–1150 nm were synthesized [4].

GCC films are composed of crystallites with a rather regular arrangement over the surface. The average

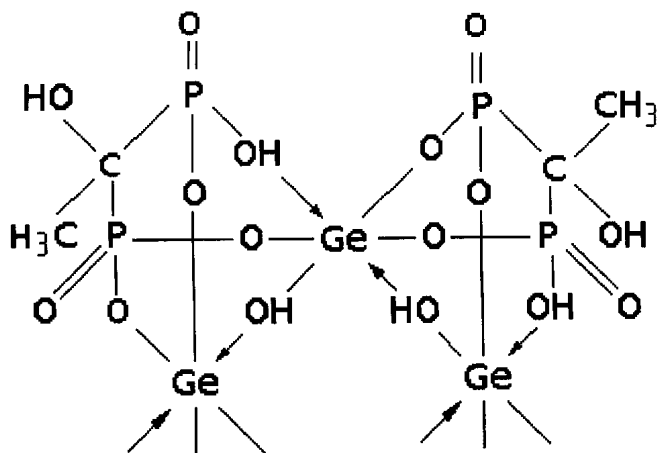


Fig. 1. Structure of the GCC fragment with oxyethylidenediphosphonic acid (H_4Oedph)

dimension of crystallites depends on the film thickness and amounts to 0.1–20 μm .

The structure of a fragment of the film-forming material on the basis of the GCC with oxyethylidenediphosphonic acid (see Fig. 1) is defined by hexameric cyclic complex anions $[Ge_6(\mu-OH)_6(\mu-Oedph)_6]_6$ [10, 11]. Ge atoms are linked in pairs by hydroxyl and oxyethylidenediphosphonate bridges. In so doing, each Ge atom is coordinated to the octahedron vertices by two oxygens of the Oedph hydroxygroups. All that is accompanied by closing two six-member cycles GeO_2P_2C and one eight-member bimetallic cycle $Ge_2O_4P_2$ [9]. Every complex fragment includes from 12 to 40 molecules of hydration water. The oxygens of water molecules contact at short distances with several (from three to six) "neighbors", namely, water and ligand molecules and hydroxygroups, i.e. they participate in both donor and acceptor H-bonds.

As a whole, the GCC film is a supramolecular ensemble, the structural units of which are linked by the ramified system of hydrogen bonds. Germanium is a member of a hexanuclear complex anion, hydrogen ions are situated in an external region of the complex, and water molecules fulfill the bridge function: they link the complex molecules into layers, and the latter with one another. Such a structure is capable to combine with and to transfer cations, when being in the nonprotonized state, and anions in the protonized one, as well as to change from the bound to unbound state or vice versa, depending on the pH values. Therefore, such materials are perspective from the viewpoint of being the basis for developing molecular and supramolecular proton-based devices, which are a special kind of ionic devices. They served as a basis for creating and studying the sensor

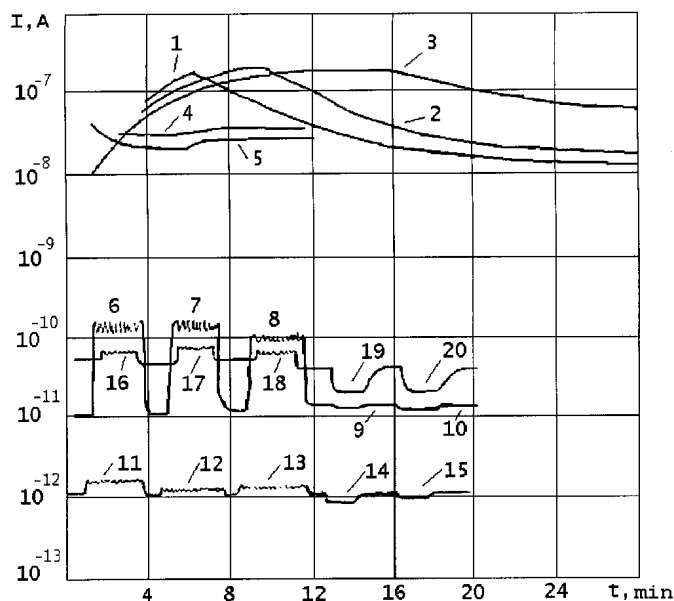


Fig. 2. Adsorption-desorption curves of the GCC films at various temperatures. $T=25\text{ }^\circ C$: 1 – H_2O , 2 – acetic acid, 3 – NH_3 , 4 – benzene, 5 – acetone; $T=40\text{ }^\circ C$: 6 – H_2O , 7 – NH_3 , 8 – acetic acid, 9 – benzene, 10 – acetone; $T=90\text{ }^\circ C$: 11 – H_2O , 12 – NH_3 , 13 – acetic acid, 14 – benzene, 15 – acetone; $T=120\text{ }^\circ C$: 16 – H_2O , 17 – NH_3 , 18 – acetic acid, 19 – benzene, 20 – acetone

structures for the detection of gases. The structures themselves were the GCC films of various controllable thicknesses deposited in that or other way onto dielectric substrates.

The conductance of polymeric composites on the basis of the $Ge-H_4Oedph$ complex was revealed to change under the influence of the vapors of water, ammonia, and a number of organic liquids (Fig. 2). In the temperature range of 25–120 $^\circ C$, the conductance of the GCC films increased as the relative humidity of the air grew from 50 to 95% or the concentration of the ammonia or the acetic acid vapor in the air rose. After having stopped the action of the ammonia and acetic acid vapors and reducing the air humidity, the conductance of the films decreased. The availability of benzene and acetone molecules in air results in the reduction of the GCC film conductance.

In Fig. 2, the adsorption-desorption curves measured for the vapors of water and a number of organic liquids in air at several temperatures are depicted. For curves 1–3, 6–8, 11–13, and 11–14, the intervals of the growing relaxation of the current correspond to the increased concentrations of the water, ammonia, and acetic acid vapors in the atmosphere, while for curves 4, 5, 9, 10,

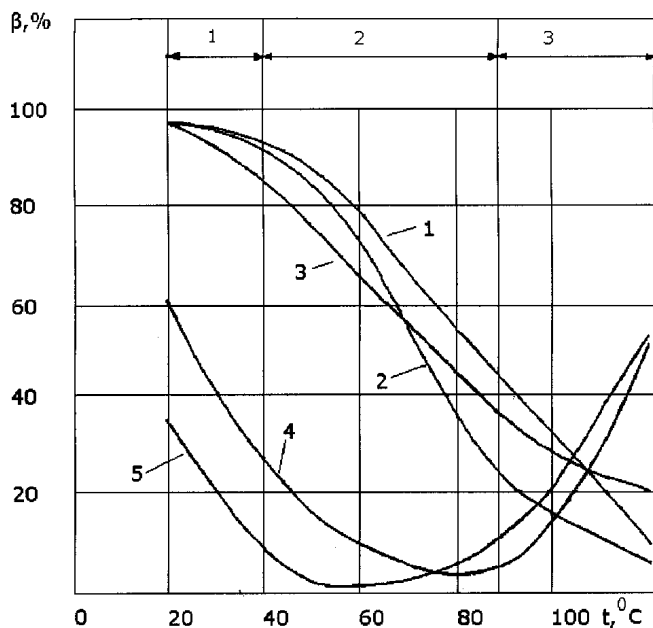


Fig. 3. Temperature dependences of the GCC film sensitivity to the vapors of organic liquids: 1 — H₂O, 2 — NH₃, 3 — acetic acid, 4 — benzene, 5 — acetone

14, 15, 19, and 20, the intervals of the decreasing relaxation of the current correspond to the increased concentrations of the benzene and acetone vapors.

Let us consider the features of the adsorption-desorption processes and the mechanisms of electric conductivity of the film, taking into account the probable heterophase reactions which occur between gas environment molecules and Ge complex ions. The high electric resistance of the GCC films prepared from oxyethylidenediphosphonatoxygermanium acid in the absence of NH₄F·HF is caused by the fact that, both on the surface and in the bulk of the film, it is an associate with a disordered system of hydrogen bonds. When the complex acid of ammonium hydrofluoride is added to the initial solution, ammonium hydrofluoride dissociates $\text{NH}_4\text{F} \cdot \text{HF} \rightarrow \text{NH}_4^+ + \text{HF}_2^-$. The ions which are formed, when building themselves into a polymeric composite of the film, raise ionic conductivity. The enhancement of this effect also occurs through the engagement of hydrofluoride ions HF_2^- into the hydrogen bond system, which favors its ordering.

When water vapor is adsorbed, there is an increase of the electric conductance of the film caused by both the ionization of complex acid molecules and the increase of the number of bridge hydration water molecules and H₃O⁺ ions, with a proton-conducting channel being formed which acts as a proton conductor. A similar

phenomenon is observed if acetic acid vapor is adsorbed, owing to the participation of the acid carboxyl groups in the hydrogen bond system. The enhancement of electric conductance of the film upon the adsorption of ammonia can be explained, on the one hand, by the acid-base interaction with a complex acid, resulted in the formation of ionized forms, and, on the other hand, by the ordering of hydrogen bonds. A reduction of the electric conductance of the film was observed provided the adsorption of benzene and acetone vapors, which was quite probably caused by breaks in the hydrogen bond system and the hydration of those molecules.

Relaxation phenomena, which occur in the films at a temperature of 25 °C owing to the variation of air humidity or the content of organic liquid vapor, are characterized by a large time of the transition of the system into a stationary state, amounting to tens and hundreds of minutes (curves 1–5 in Fig. 2). A relatively small growth of the air temperature up to 40 °C results in a significant enhancement of adsorption-desorption processes at the surface and in the bulk of the GCC film (curves 6–10 in Fig. 2), with both the adsorption and desorption relaxation times of the system being several seconds. The further increase of the air temperature up to 120 °C brings about the acceleration of relaxation processes (curves 11–20 in Fig. 2).

As the temperature grows, the sensitivity of the GCC films to various vapors changes (Fig. 3) and, at $T = 120$ °C, some features in the kinetics of adsorption curves appear. For example, the adsorption sensitivity of the GCC films to the water, ammonia, and acetic acid vapors monotonously decreases with the temperature increase (curves 1–3 in Fig. 3). On the contrary, the film sensitivities to the benzene and acetone vapors have a minimum in the temperature range of 40–90 °C and large values at low and high temperatures (curves 4 and 5 in Fig. 3).

The temperature dependence of the current which runs through the GCC film has a number of peculiarities (Fig. 4). Provided that the specimen is heated with a constant rate of 2 °C/min in air with the relative humidity of 50%, there is a reduction of the film conductance up to a temperature of 60 °C (curve 1 in Fig. 4). Then, the conductance of the film remains practically constant up to a temperature of 90 °C, and, in the range of 90–120 °C, the increase of the conductance is observed. If the film is cooled, a hysteresis in the current vs temperature arises, which manifests itself in a monotonous decrease of the film conductance while the temperature diminishes (curve 3 in Fig. 4), so that curve 1 is not reproduced. The phenomena observed

are obviously caused by the fact that the desorption of water molecules occurs from the bulk of the GCC film at elevated temperatures. As a result, ionic conductivity is reduced. After holding the film in air with a relative humidity of 50% and at a temperature of 25 °C for several hours, its conductance grows by 3–4 orders of magnitude (curve 4 in Fig. 4). The following heating of the film results in the variation of the current value that is shown in Fig. 4 by curve 2.

Provided that the GCC film was first heated up to 120 °C, the film resistance grows in the process of its further cooling according to the exponential law, which is characteristic of semiconductors.

High rates of variation of the GCC film conductance can be stimulated by several mechanisms. At low temperatures, the mechanism related to the presence of the proton bridges formed by hydration water [12] probably prevails. The removal of a certain amount of hydration water, which determines the proton conductivity of the complex, results in a decrease of the influence of this kind of proton motion on conductivity.

As the temperature grows up to 125 °C, the hydration of the GCC takes place, resulting in breaking the hydrogen bridges and forming the charge carriers with another nature of molecular bonds in the complex and with the presence of the system of acceptor H-bonds.

The responses of the GCC system in units of the adsorption sensitivity of the GCC film are listed in the table for different adsorption variants.

While the temperature grows up to 120 °C, a monotonous reduction of the GCC sensitivity to the water, ammonia, and acetic acid vapors is observed, which is caused by both the evaporation of water molecules from the film bulk and a decrease of the film ionic conductance.

A reduction of the GCC film sensitivity to the benzene and acetone vapors in the range of 25–75 °C is connected to a decrease of the hydration degree of these molecules, when the temperature grows. The enhancement of the adsorption sensitivity to the benzene and acetone vapors at temperatures higher than 75 °C may be connected to the processes of thermal ionization of the charge carrier capture centers with an energy level

Response $\beta = (I_2 - I_1)/I_2$, in percent, of the GCC system to various adsorption variants

$T, ^\circ\text{C}$	20	40	60	80	100	120
water	98	94	79	53	33	10
ammonium	98	92	73	35	16	6
acetic acid	98	85	66	44	28	20
benzene	61	28	10	4	16	50
acetone	34	9	2	7	20	52

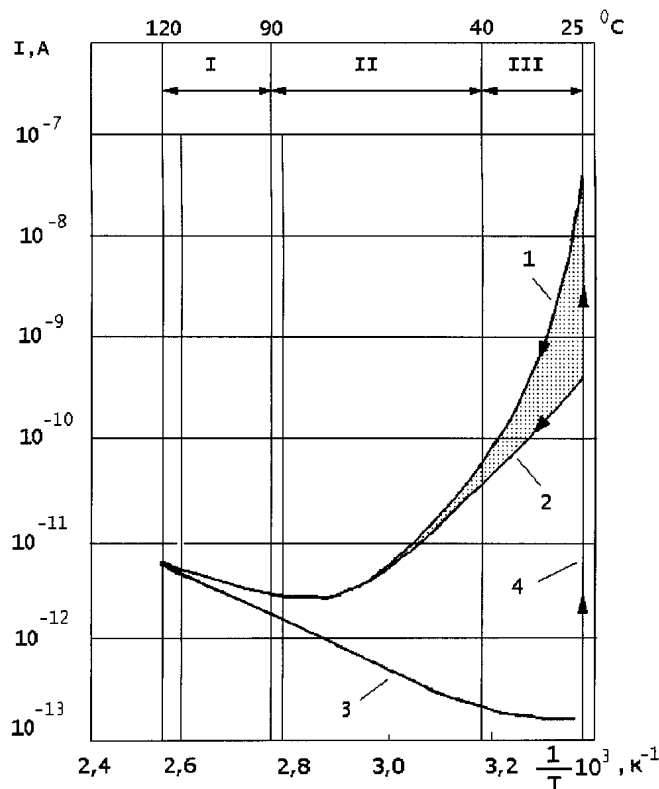


Fig. 4. Temperature dependences of the current through GCC films: 1 and 2 — heating up the films provided different initial film conductances, 3 — film cooling, 4 — current variation after the film cooling at $T=25$ °C. The heating and cooling rates of the GCC films were 2 °C/min

depth of 0.14 eV. This value was inferred from the temperature dependence of the current measured upon the GCC film cooling.

4. Conclusions

The researches have shown that the GCC Ge-Oedph is a supramolecular ensemble with a ramified system of hydrogen bonds. Such a structure is capable to combine with and to transfer cations in a nonprotonized state, and anions in a protonized one. The electrophysical properties of the Ge-Oedph complex make it a perspective material for the design of proton devices, in particular, gas sensors.

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Received 28.04.04.

Translated from Ukrainian by O.I.Voitenko

ЕЛЕКТРОФІЗИЧНІ
ВЛАСТИВОСТІ СУПРАМОЛЕКУЛЯРНИХ
ПЛІВОК КОМПЛЕКСУ ГЕРМАНІЮ
З ОКСИЕТИЛІДЕНДИФОСФОНОВОЮ КИСЛОТОЮ

Я.І. Лепіх, В.Д. Пронічкін, І.Й. Сейфуліна, О.Е. Марцінко

Резюме

Наведено і проаналізовано результати досліджень структурних, електрофізичних і адсорбційних властивостей плівок нового функціонального матеріалу — комплексної сполуки германію (КСГ) з оксиетилідендифосфоновою кислотою. Вивчено електричну провідність і дано пояснення її механізму. Розглянуто можливі застосування КСГ у ролі чутливих сенсорів газу.