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Germanium coordination compounds – structure, properties, possible applications

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Abstract. Germanium coordination compounds (GCC) with oxiethilidendyphosphonic acid (Ge-Oedph) film structures electrophysical, optical, structural and adsorptive properties investigation results are represented. This structure concerns to a new perspective class of functional materials. The mechanism GCC films electric conductivity is investigated and explained. GCC possible application fields are specified.

1. Introduction

The achievements high metrological and operational characteristics of various purpose sensors depend mainly on application new functional materials with corresponding properties In this sense functional materials which have supramolecular architecture is of particular interest [1]. Generally they represent polymolecular ensembles which structure includes the molecular components which are carrying out the given function on the basis of photo, electro-, iono-, мagneto-, thermo-, mechano-and other effects, depending on the solve problem. Such synthetic polymolecular ensembles functional properties are intensively studied [2,3]. In the present work the GCC films structure, the conductivity mechanisms, optical and adsorptive properties are investigated.

2. Materials and investigation methods

Germanium coordination compounds are a new class of functional materials having successful combination physical and chemical properties and electrophysical parameters important in respect to their application in functional microelectronics and sensor engineering. Besides GCC differ high adaptability to manufacture and have ability to form films from water solutions.

The GCC films were deposited on dielectric substrates made of Al_2O_3, glassceramic, quartz and glass by different methods, including Langmuir-Blodgett (L-B) method. [4]. Films thickness was 1-$50{\cdot}10^{-6}$ m. The resistivity was less then $1{\cdot}10^{7}$ Om·m.

The water, ammonia, acetic acid, benzol, acetone molecules increased concentration in the air was created with the help of the appropriate stand.

Gas sensitive sensors were created on the basis of elements on surface acoustic waves (SAW). They had classical filter structure - two opposing-pin converters (OPC) with apodisation one of them or structure one-enter resonator on SAW. Each of these variants has the advantages and lacks. However the overall advantage of elements is the opportunity of more exact definition sensor target signal frequency or phase change appropriate to controllable analit concentration change. GCC film was deposited on a piezoelectric soundconductor working surface between OPC.

The film GCC surface investigations were carried out with the help of metallographic microscope MIM-8M, and optical characteristics with the help of Perkin Elmer firm spectrophotometer

3. Results and discussion

The Germanium coordination compound film with oxiethilidendyphosphonic acid (Oedph) structure investigation presented in figure 1, showed that it determines by hexadimentional cyclic complex anions [Ge$_6$ (μ-OH$_6$ (μ-Oedph)$_6$]$^{6-}$.

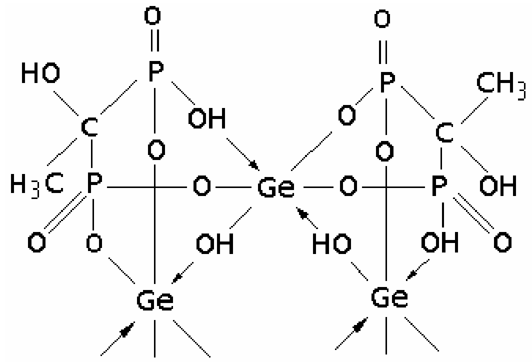

Figure 1. Ge-Oedph structure fragment.

Germanium atoms are in pairs incorporated by hydroxyl and oxiethilidendyphosphonic bridges. Thus each Ge atom is coordinated on tops of an octahedron to two oxygen hydroatoms and four oxygen atoms of four phosphon groups of two Oedph ligands. It is accompanied by short circuit of two six-membered GeO_2P_2C cycles and eight-membered bimetallic $Ge_2O_4P_2$. Each complex fragment form a part from 12 up to 40 hydrate water molecules. Water molecules oxygen atoms contact in short distances with several (from three up to six) "neighbours" – water and ligand molecules and hydroxgroops, i.e. take part both in donor, and acceptor H-links.

Such structure potentially corresponds to ability to bind and transfer cations, being in nonprotoning condition, and anions - in protoning condition and also to pass from bind to unbind condition or, on the contrary, dependening on PH values. Hence, such materials are perspective in respect to creation on their basis molecular and supramolecular proton devices.

The investigation GCC structure and properties experimental data analysis has shown, that functional materials various in their physical and chemical properties can be produced on their basis. So, for example, by introduction some additives the films were synthesized, having high transparency in the 310-1200 nm wave lengths range. In figure 2 the relative (relative to sodium glass) GCC transmission spectrum of two structures are given. It is visible, that in the range of 1000 - 1200 nm the increase of transmission factor on 1-7 % takes place. It is essential, that optical characteristics can be operated at a stage of synthesis by introduction into their structure some components.

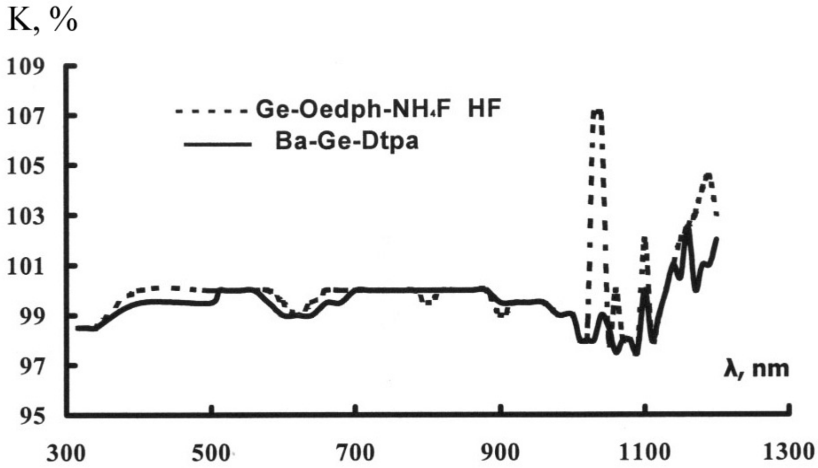

Figure 2. GCC transmission spectrum relative to sodium glass.

The investigation have shown, that GCC have adsorbed properties in respect to some gases.

It was revealed, that GCC conductivity changes under the water vapour, ammonia and some organic liquids influence. In the range of temperatures 25 – 120 ^{0}C, the GCC films conductivity increases with growth air relative humidity from 50 up to 95%, and also with increase air vapour, ammonia and an acetic acid concentration (figure 3). Presence of benzene and acetone molecules in the air results in GCC film conductivity decreasing.

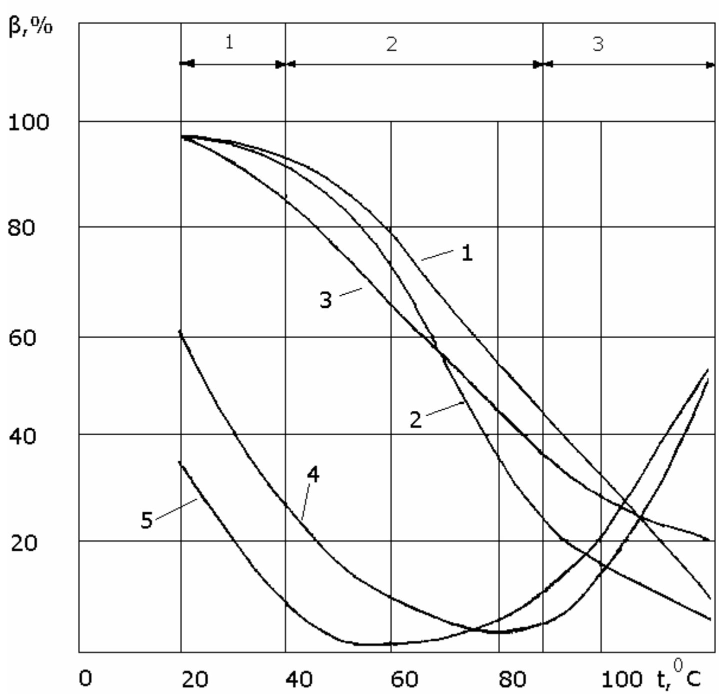

Figure 3. Dependence Ge-Oedph film sensitivity to the organic liquids vapours on temperature. 1 - H_2O; 2 - NH_3; 3 - acetic acid; 4 - benzol; 5 - acetone.

Adsorption-desorption processes and the film conductivity mechanism are considered in view of possible heterophase reactions occurring between molecules of the gas environment and complex Germanium ions.

At vapour water adsorption, in particular, the film electric conductivity increase, what is caused both by ionization of complex acid molecules, and by number bridge hydrate water molecules and ions H_3O^+ increase. Thus a proton – conducting channel is formed which stands as a proton wire. At benzene and acetone vapour adsorption the film conductivity reduction was observed what is most likely caused by hydrogen bond system break and by their molecules hydration.

With the temperature growth the GCC films sensitivity to various vapours (figure 3) changes and some peculiarities in adsorptive curves kinetics appears at temperature 120^0C.

In figure 4 Ammonia vapour adsorption – desorption kinetics for GCC L-B film is shown. It is essential, that the given dependence is received without heating – at room temperature.

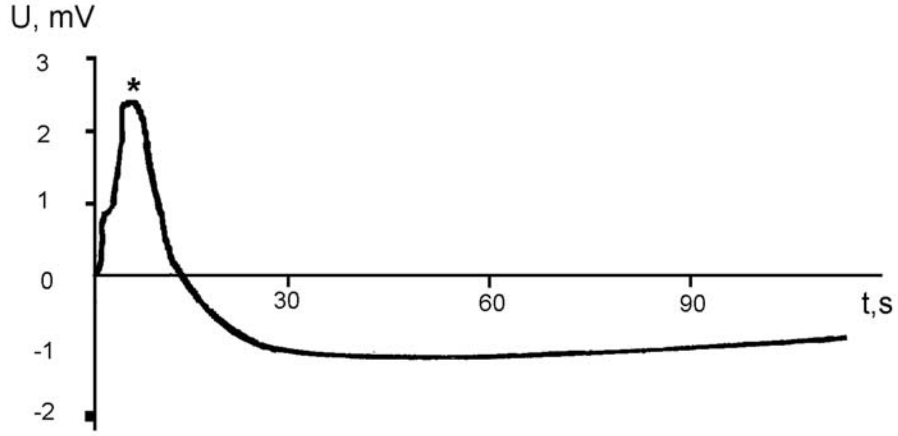

Figure 4. Ammonia vapour adsorption-desorption kinetics for GCC L-B film.

* – gas pumping-out beginning.

It was revealed also that at interaction GCC film with analit the essential change its dielectric permeability takes place. This also allows creating capacitive type gas sensors. Thus it is enough to use the same technology, as at formation OPC elements on SAW. However in the greater measure the GCC efficiency, having high sensitivity and selectivity to analits, small relaxation time (restoration of serviceability) etc., can be used at new generation sensors creation [5, 6].

Hence the investigations on intelligent gas sensors consisting of an element on SAW and GCC layered structure creation were carried out. Thus high sensor sensitivity and selectivity are provided by film material receptor properties, and intellectualization - by element on SAW. The frequency shape of a target signal and a sensitive film fast response if based on sensor and microprocessor engineering combination allow to trace up gas concentration changes in the controllable environment in a mode on-line.

It is important to notice that the adequacy sensor with an element on SAW reaction on gas adsorption - desorption processes essentially depend on geometrical parameters of a film deposited on element on SAW working surface. Therefore the geometry of a film should choose in view of requirements of ensuring distribution stability only Rayleigh type waves and exception its transformation in another type waves. In figure 5 the element on SAW with adsorbing film structure is shown. Here are shown also the possibilities under some conditions variants Rayleidh wave 1 transformation into Sezava 2 dispersing wave or volumetric shift Lyava 3 wave.

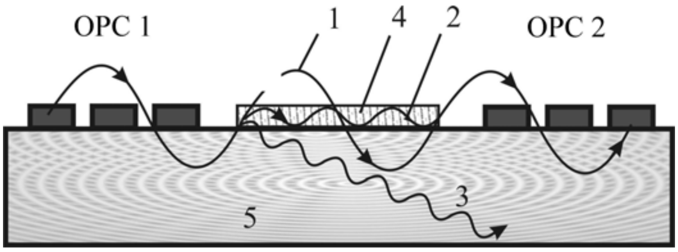

Figure 5. The element on SAW with adsorbing film structure.

Under certain conditions the situation of a "slow" wave on " fast" soundconductor or a "fast" wave on "slow" soundconductor can be created. Such situation does not allow adequately reflect the adsorption - desorption process on a soundconductor surface and will essentially complicate unique dependence the target signal changed frequency (phase) on change the controllable analit concentration.

Thus the investigations have shown that Ge-Oedph GCC is a supramolecular ensemble with branched system of hydrogen bonds. Electrophysical and adsorption Ge-Oedph properties make it perspective functional material for various purpose sensors creation, including gas sensors.

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