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Influence of hydrocarbon environment on electrical characteristics of Ge-As-Se-S chalcogenide glass system

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Abstract

The effect of propane-butane gas mixture on volt-Ampere characteristic (VAX) of thin–layer sandwich structure Al-$Ge_{33}As_{17}S_{35}Se_{15}$-Te obtained by thermal evaporation method in vacuum was investigated. It has been established that under the influence of gas atoms, the oscillations observed in VAX gradually decrease and disappear. This result is explained by the accumulation of neutral gas atoms into lower atomar pores. It has been shown that neutral gas atoms collected in pores lead to weakening of thermal-field ionization processes of U^--centers, and to increase the speed of periodic deflection of charge carriers by these centers, which leads to an increase in the resistance of the sample.

Keywords: chalcogenide, glass, amorphous, non-crystalline.

Introduction

A comparative analysis of the available scientific literature shows that sensors made on the basis of ceramics (Al_2O_3, TiO_2, SiO_2) and their spindle connections, along with advantages, have disadvantages. SiO2 porous material, manufactured by special technological methods with high financial cost, with low sensitivity to toxic gases such as SO_2, CO_2, CO, NH_3, CH_4, has an equivalent reverse reaction <10 sec [1]. Studies have shown that the sensitivity of sensors made of chalcogenide glasses ($As_2(Se_{0.9}Te_{0.1})_3$, As_2Se_3) in the form of thin amorphous sheets, depended on their composition, the inertia of which is extremely low. The main reason for this is that the change in bulk conductivity as an electronic process occurs quite quickly [2]. On the other hand, chalcogenide glass sensors (As_4S_3 and as-Ge-Te) have compact dimensions, low cost and energy consumption, as well as high sensitivity [3]. Resistive sensors based on glassy thin layers of chalcogenide As_4S_3 and As-Ge-Te were highly sensitive to the medium of propylamine ($C_3H_7NH_2$) and nitrogen dioxide (NO_2) and can be successfully used to monitor these media, since they have the characteristics of dynamic response to humidity, high recovery properties and reversibility [3]. Sulfide chalcogenide glasses (for example, As-S) have a wavelength mainly in the range of 0.6–7 microns, while chalcogenide glasses containing Germanium (Ge), selenium (Se), sulfur (S) and tellurium (Te) (Ge-S, Ge-Se, Ge-As-S, Ge-As-Se, Ge-As-Se) have wider wavelengths, it has high optical transparency (2-12 microns) and it can be applied as a more effective fiber optic material in a relatively wide temperature range (200-300 °C) [4.5].

The purpose of the article is to identify the physical mechanisms of susceptibility of sandwich structures obtained by thermal evaporation in vacuum (complex chalcogenide glass Al-$Ge_{33}As_{17}S_{35}Se_{15}$-Te) to propane-butane gas mixture and the possibilities of using these structures.

Experimental details

The syntheses of $Ge_{33}As_{17}S_{35}Se_{15}$ chalcogenide glass semiconductor were performed in a rotary furnace. To do this, samples of high purity (99.9999%) of these elements are weighed on electronic scales. The components of a proper composition were placed in a quartz ampoule (diametre 12÷17 mm) which was evacuated to a residual pressure of 10^{-3} Pa. The heating of the furnace was carried out using a nichrome spiral, and the temperature measurement was carried out using a chromel-alumel thermocouple. The synthesis of the composition selected for the study was carried out at 950°C temperature. For reaching homogenety the melting proces kept at this temperature for 11 hr. After finishing the synthesis, the ampoules were pulled out

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and were quenched in air. Measurement of the Volt-Ampere characteristic was carried out on thin amorphous sheets of sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te** (thickness d=2 mkm) obtained by thermal evaporation in vacuum on glass pallets. The amount of gas was determined by detector Mestek CGD02A.

Discussion

Fig.1 describes volt-ampere characteristic (VAX) of the sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te** in atmosphere and in a propane-butane gas mixture . In the atmosphere at different values of the voltage are observed transitions from low-resistance state to high-resistance state without oscillations or with partial oscillations. The study shows that in a sandwich-structured sample Al-$Ge_{33}As_{17}S_{35}Se_{15}$-Te (obtained by thermal evaporation in vacuum) with an increase amount of propane-butane gas mixture added to the closed experimental camera, charge transfer proceses and values of transition voltages in VAX from low-resistance to high-resistance (or vice versa) acquires sagnificiant changes.

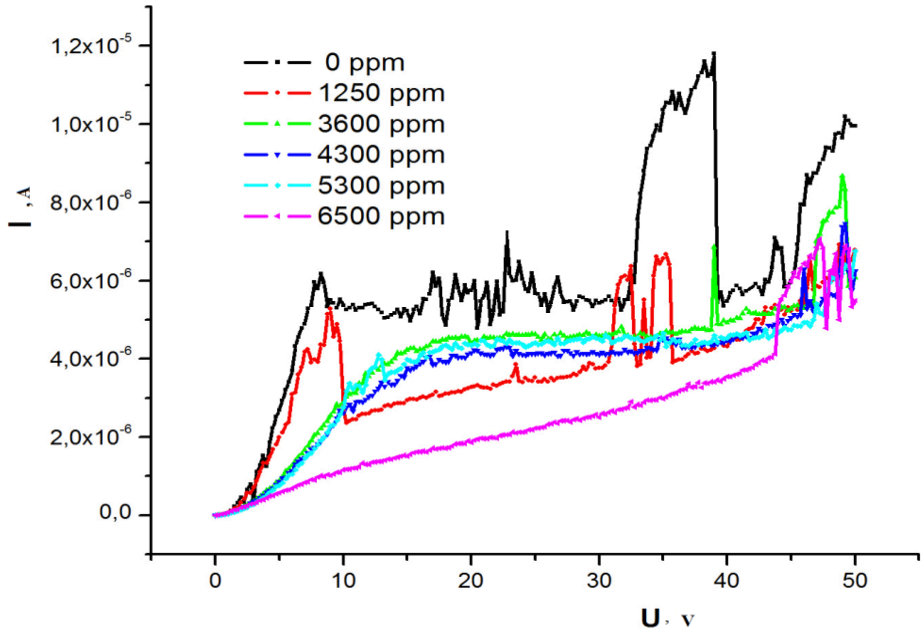

Fig.1. Volt-ampere characteristic (VAX) of the sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te** in atmosphere and in a propane-butane gas mixture.

As can be seen from VAX, only in the atmospheric environment, in the absence of a propane-butane gas mixture, at values of the voltage applied to the sample U-8.2 v; 17.6 v; 22.8 V; 39 V; 43.75 v, there is a partial decrease in current and a sharp decrease in current in different areas. The observation of transitions from low-resistance state to high-resistance state (or vice versa) in the Vax of the studied sample, i.e. limitation of current at certain values of voltage and at the same time observation partial oscillations explaine by the serious impact on the generation-recombination processes of U^--centers with negative correlational energy, which have decisive influence to manage charge transfering proces in chalcogenide glass[6].

When considering the effect of the propane-butane gas mixture on the VAX of the sample, it turns out that a relatively small amount of gas (1250 ppm) in the experimental chamber mainly affects the values of transient voltages from a state of low resistance to a state of high resistance (or vice versa), causing the complete disappearance of the transition noted at voltage values U = 39 V and 43.75 V. Analysis of VAX shows that under the influence of a relatively small amount of propane-butane gas mixture (1250 ppm), the transition voltage to a high-resistance state increases from U-8.2 V to U=9 V, the oscillations observed at voltage intervals U=17÷22 V and U=23.58÷28.8 V are mostly attenuated and lost (except for weak intensity peaks observed at U= 23.4 V and 29.2 V), the transition voltage to the high-resistance state observed at U=39 V is partially reduced, causing repeated oscillations to be observed in the range of U=32.5÷35.6 V.

At a value of U=43.75 V of the voltage applied to the sample, the low-amplitude maximum observed in the atmospheric medium (1250 ppm) shifts into relatively large voltages (U=46.4 V; U=49 v), being replaced by other low-amplitude maximums. An increase in the amount of gas in the experimental chamber leads to more

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serious changes in the VAX of the sample. Thus, the amount of gas in the chamber 3600 ppm leads to the complete disappearance of the transition areas to the high-resistance state observed at VAX up to U=39 V (excluding the presence of transitions to low and high-resistance States at U=39 V), as well as oscillations characterized by unsteady conduction states. A continuous increase in the amount of gas leads both to an increase in the overall resistance of the sample, and the occurrence of the above-mentioned unsteady switching cases results in a shift of the voltage to a greater value of U≥47 V.

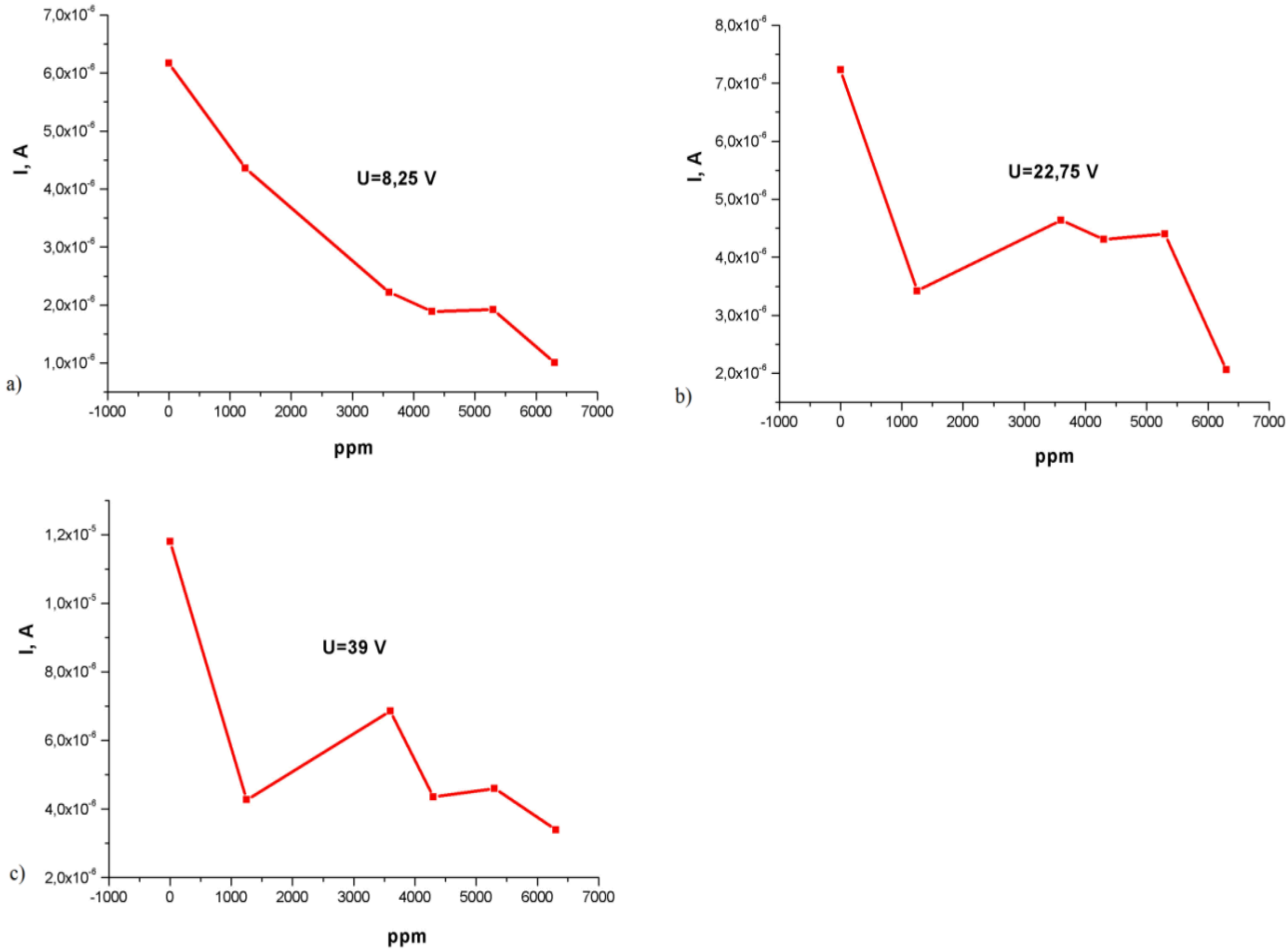

Fig.2. The effect of the amount of propane–butane gas mixture on the current values corresponding to different voltages in the volt-ampere characteristic of the sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te**

As can be seen in Fig.2, the effect of increasing the amount of gas in the experimental chamber on the current values corresponding to the switching voltages also proves the correctness of the above results. It has been found that at a relatively low switching voltage (U=8.25 v), an increase in the amount of gas leads to a monotonous decrease in current. However, an increase in the amount of gas from 1250 to 3600 ppm led to a partial increase in current at switching voltage values U=22.75 V; U=39 V. The subsequent increase in the amount of gas caused the current to decrease again. The analogous result is also reflected in the dependence of the resistance calculated from VAX on the amount of gas at the corresponding switching voltages.

In sensors whose resistance changes under the influence of gas, the way the relative resistance changes depending on the amount of gas is of particular importance from the point of view of their application. The relative resistance of the the investigated sample is determined depending on the amount of gas at various transition voltages, and the results obtained are shown in Fig.4 as a graphical dependence.

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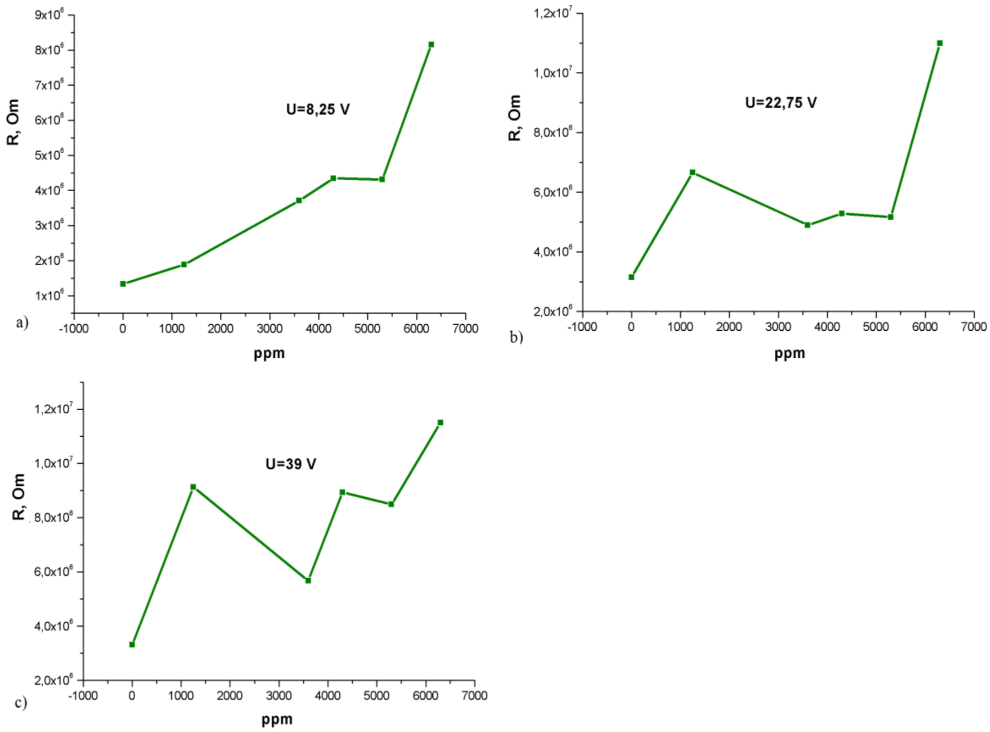

Fig.3. The effect of the amount of propane–butane gas mixture on the resistance values corresponding to different voltages in the volt-ampere characteristic of the sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te**

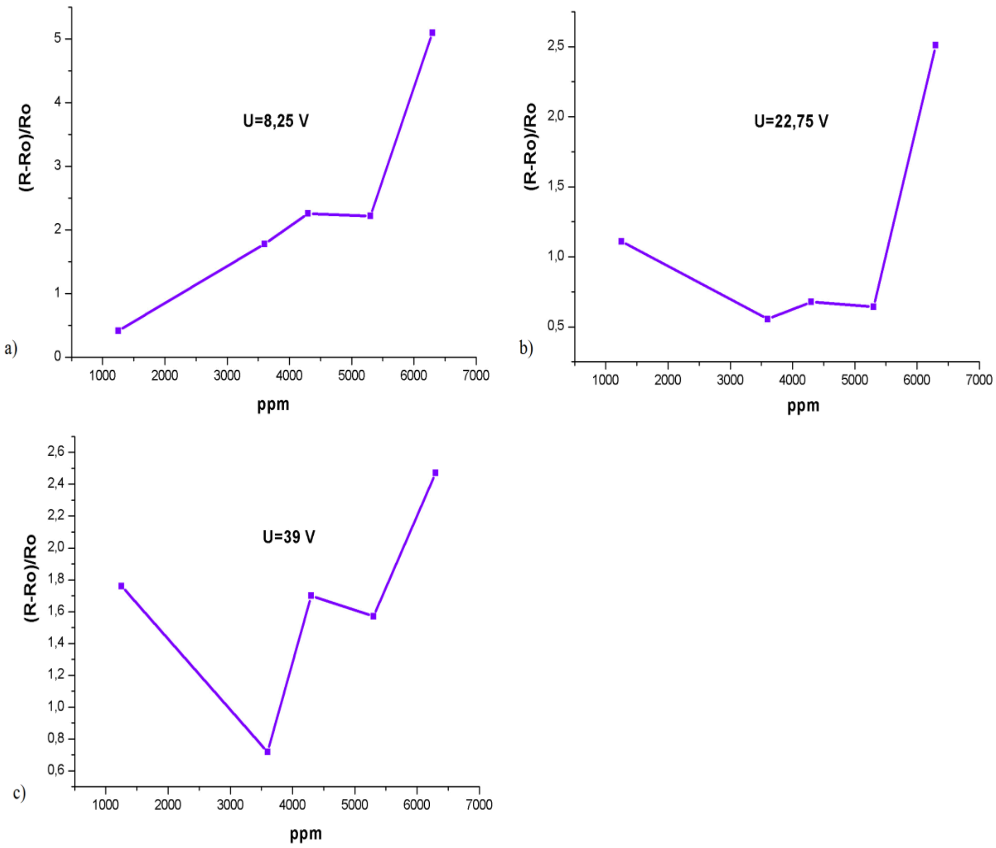

Fig.4 The effect of the amount of propane–butane gas mixture on the relative resistance values corresponding to different voltages in the volt-ampere characteristic of the sandwich structure **Al**-$Ge_{33}As_{17}S_{35}Se_{15}$-**Te**

An analysis of the results described in Figure 4 shows that at a relatively low voltage (U=8.25 V), the relative change in resistance, depending on the amount of propane-butane mixture, is an order of magnitude greater. This result shows that samples with the sandwich structure Al-$Ge_{33}As_{17}S_{35}Se_{15}$-Te, made on the basis of chalcogenide glasses, are more sensitive to the effects of propane-butane gas mixture in the range U=0÷10 V of applied voltage. In order to clearly describe the results obtained, the dependence of the resistance corresponding to the above-mentioned switching voltages on the amount of gas is described in the form of 2D and 3D-diagrams (Fig.5, Fig. 6).

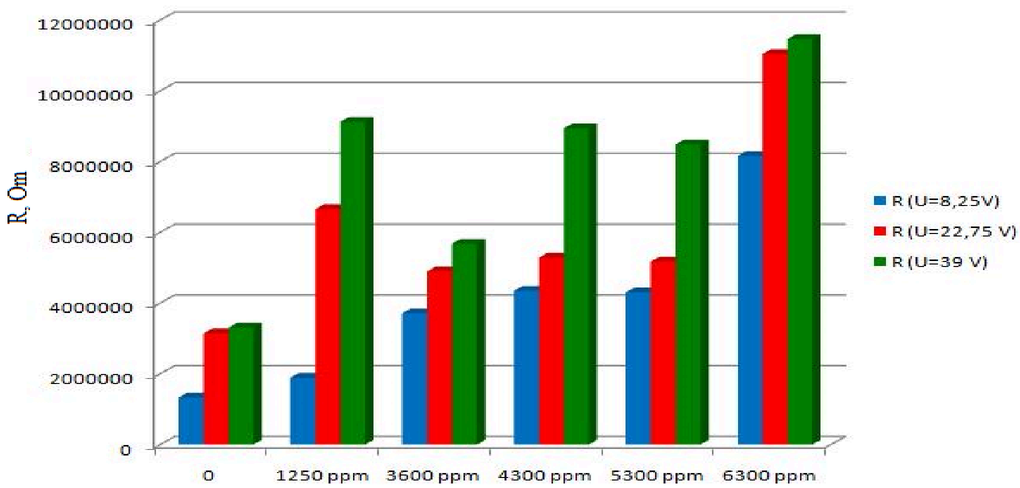

Fig.5. Description on a 2D diagram of the effect of the propane-butane gas mixture on the resistance of a sample of the composition Ge33As17S35Se15 with applied various voltages.

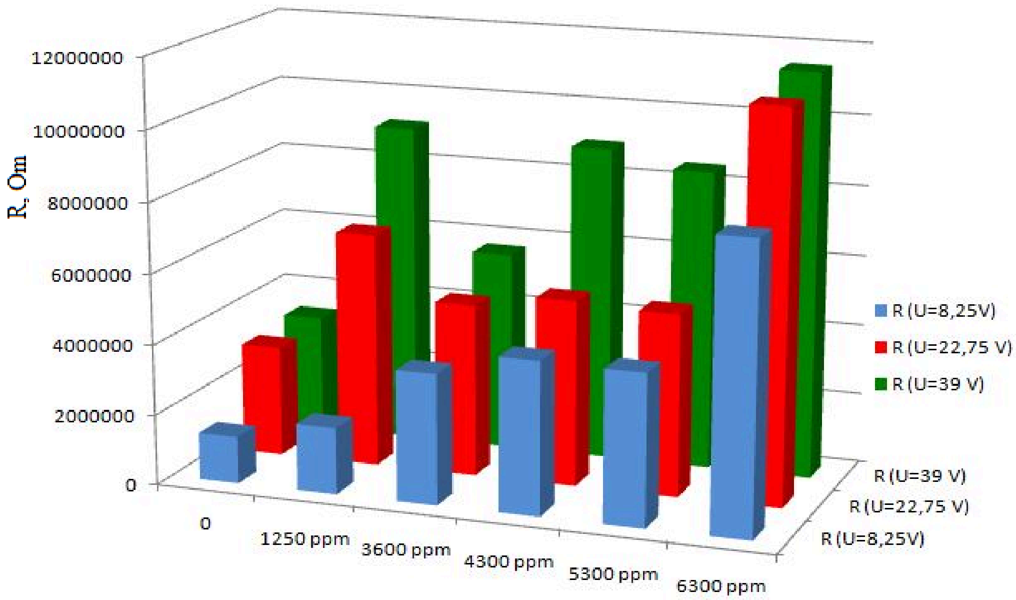

Fig.6. 3D-diagram representation of the effect of propane-butane gas mixture on the resistance of $Ge_{33}As_{17}S_{35}Se_{15}$ at different applied voltages.

As can be seen from the 2D and 3D diagrams described above, the increase in sample resistance as a result of an increase in the amount of gas is characterized by higher columns at a transition voltage U = 39 V. To explain the physical mechanisms of the effect of the propane-butane gas mixture on the volt–ampere characteristic of

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the sandwich structure of the sample Al-$Ge_{33}As_{17}S_{35}Se_{15}$-Te, Elliott's cluster-void model [6,7] or the concept of double electrons with negative correlation energy (Uef) proposed by Anderson (to determine the nature of defects in amorphous substances, especially in chalcogenide glass semiconductors) [8] or the polyaron model were used. According to this model, both the electron energy and local distortions of defects in the case of basic energy configurations should be taken into account, while atomic relaxations around defects are not taken into account. In this case, the relaxation of the system leads to the transition of the electron-phonon bond to a state of equilibrium with the lowest energy. According to the mentioned model, the addition of an electron to a broken bond leads to spin contestation and a change in the binding energy at the center of the defect. As a result, the energy of the electrons decreases by the amount of Ur [8]. According to the idea of Mat and Street [9], during the optical transition of electrons, the transition of U^-- centers from the state D^+ -with the main charge to the excited state D^o -is observed. According to the Elliott's model [6,7], the studied materials consist of regions with low atomic density or structural regions or clusters, one of which is separated from the other by voids.

In these substances, atomic contrast and, respectivily, the average electron density between clusters and voids lead to the formation of the first sharp diffraction peak (FSDP) in the spectral dependence of the final structure coefficient (S (Q)). Therefore, the occurrence of transitions to a low-intensity state in the VAX measured in the atmosphere and gas environment of the studied sample is due to the release of chargs from low energy levels, and instability of the N-shaped area in the form of irregular oscillations is due to the ionization processes of the U--centers and the periodic capture of chargs by these centers [10]. The gradual weakening and disappearance of oscillations in VAX under the influence of gas atoms in the experimental camera occurs as a result of the accumulation of neutral gas atoms into low atomic density domains or pores. It is considered that the neutral gas atoms collected in the pores lead to weakening of ionization processes of U-- centers and acceleration of periodic deflection of charge carriers by these centers. An increase in the amount of gas in the experimental camera due to the mentioned factors leads to an increase in the resistance of the sample (Fig.5, Fig. 6).

Conclusion

The effect of propane-butane gas mixture medium on the volt-Ampere characteristic (VAX) of the sandwich structure Al-Ge33As17S35Se15–Te has been studied and shown that the gradual weakening of oscillations in VAX under the influence of gas atoms occurs as a result of the accumulation of neutral gas atoms in low atomic density areas or pores. It is assumed that neutral gas atoms accumulated in the pores cause a weakening of the ionization processes of the U^--centers. The periodic retention of charges by these centers leads to acceleration . As a result, an increase in the amount of gas in the experimental camera leads to an increase in the resistance of the sample.

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