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The influence of mercury vapor on the electrical resistance of chalcogenide amorphous films

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Using the planar structures "Ni layer - chalcogenide amorphous film - Ni layer" and "graphite probe - chalcogenide amorphous film graphite probe" samples, the influence of mercury vapor on the electrical resistance of amorphous films of the Se-Te, Se-Sb and Se-As systems was investigated. It was established that exposure of samples in mercury vapor leads to a decrease in their electrical resistance by 4-7 orders of magnitude. As the temperature and mercury concentration increase, the transition time from a high-resistance state to a low-resistance state decreases. When introducing Te, Sb, and As into amorphous selenium and increasing their concentration in the composition of the films, the transition time increases, and the value of the change in resistance decreases. It was established that the change in resistance is mainly determined by the change in surface conductivity of chalcogenide films. A decrease in the electrical resistance of selenium-containing amorphous films modified with mercury is caused by the formation of HgSe crystalline inclusions in their matrix.

Keywords: chalcogenide amorphous films, electrical resistance, mercury film modification, mercury selenide, mercury vapor sensors.

Introduction

While studying the electrical and optical properties of semiconductor materials, it was found that the exposure of amorphous selenium films in mercury vapor leads to an increase in their electrical conductivity in 5–6 orders of magnitude [1]. The revealed impact is evidence of the possibility of using this material as an active element of sensitive sensors for detecting mercury vapor. The author of this academic study considers that the reason for the significant increase in the electric conductivity is most likely stipulated by the formation of crystalline inclusions of mercury selenide (HgSe) in the Se amorphous matrix. At the same time, it is assumed mercury selenide that appears because of the interaction of mercury with amorphous selenium is a non-stoichiometric compound (Se atoms predominate). A similar conclusion suggests itself upon the results of the study we have conducted with the structure and morphology of the surface of amorphous selenium films, which are modified with mercury by methods of the X-ray diffraction analysis, Raman spectroscopy and scanning electronic microscopy (SEM) [2-4]. On diffraction patterns of the Se amorphous films exposed to mercury vapor, we have found the reflections whose intensity is growing with increasing exposure time [2, 4]. The position of these reflections well agrees with the position of reflections on diffraction patterns of HgSe crystal received via the hydrochemical method using aqueous solutions of various substances such as $HgCl_2$, $SeCl_4$ and $(N_2H_4 \cdot H_2O)$ [5], $Hg(CH_3COO)_2$ i $SeCl_4$ [6] in the presence of $N_2H_4 \cdot H_2O$, $Hg(NO_3)_2$ and Na_2SeSO_3 [7]. In Raman spectra of the Se amorphous films modified with mercury, we have found weak bands [3] typical of similar spectra of HgSe Nanocrystals that were obtained by chemical deposition of Hg and Se vapors in zeolite matrix with the mostly spherical pores of Nd-Y [8]. Inclusions of

another phase also clearly appear on SEM images of surfaces that are modified with mercury from the selenium amorphous films [2]. The research results presented in scientific papers [2-4], with considerable reliability, allow us to state that the structure of the phase, which is forming in the matrix of Se amorphous films upon their modification with mercury, corresponds to the HgSe structure in cubic modification.

The Se-Te, Se-Sb and Se-As amorphous films, with a low content of Te, Sb and As (up to 15 at. %), may be used as promising materials for creating sensors for detecting mercury vapor in the environment. In comparison with the Se films, the films of these systems have higher softening and crystallization temperatures and, respectively, they are more stable and resistant to spontaneous crystallization [9-11].

We should note that the results of the studies presented in [1-4] concern the static mode of mercury modification of the selenium amorphous films. The measurements were done in a certain period, after exposure to the amorphous films in the mercury vapor. In terms of the practical application of selenium-containing amorphous films, the study of their electrical properties in the process of modification with mercury is of the most interest. In addition, we should specify that the rate of mercury evaporation and, respectively, mercury concentration and saturated vapor pressure in a certain volume shall be determined by the size of the open surface of a mercury drop and temperature [12]. Respectively, these parameters will significantly affect the formation rate of HgSe inclusions and the electrical resistance of the films.

In connection with the above, the study of the impact of temperature, mercury concentration, and chemical composition on the electrical characteristics of the amorphous Se-Te (Sb, As) system is of certain interest. We devote this scientific paper to solving these precise issues.

I. Experimental Methodology

We have conducted the studies of the graphs of dependency of the electrical resistance (R) of the amorphous films of the Se-Te, Se-Sb and Se-As systems (with low content of Te, Sb and As) on the time (t) of exposure in mercury vapors, using special hermetic containers, in the temperature range of 287-296 K, on planar structures such as the "Ni layer - amorphous chalcogenide film (ACF) – Ni layer" and structures such as the "graphite probe (GP) - amorphous chalcogenide film (ACF) –graphite probe (GP)". The pressure of saturated mercury vapor at such temperatures is 0.066-0.152 Pa, while the concentration is 5.6-13.3 mg/m^3.

To study the electrical properties of structures such as the "Ni layer-ACF-Ni layer", we have used a combined method [13], which makes it possible to measure the $R(t)$ dependency of films at changing the time of their modification with mercury. The sequence of operations for making planar samples such as the "Ni layer-ACF-Ni layer" is as follows. On the glass substrate, we applied the semi-transparent Ni layer, which is 50-150 nm thick. The 0.3-0.4 mm gap was forming on the layer by scribing. For this, an elliptical scriber was applied. Amorphous Se and Se$_{100-x}$Te$_x$ films, which are 150-300 nm thick, were applied to the gap area via a mask. We obtained the amorphous films of these compositions by a method of vacuum evaporation of vitreous Se and polycrystalline alloys such as Se$_{100-x}$Te$_x$ ($3 \leq x \leq 15$) from quasi-closed effusive cells on glass substrates with a nickel layer.

In several experiments to study the impact of mercury vapor on the electrical resistance of amorphous films of systems such as Se-Sb and Se-As we applied such structures as "GP-ACF-GP". The probes' diameters were 0.5 mm while the distance between them could be variable from 2 to 5 mm. Such structures have the advantages of the simplicity of high-quality cleaning of contact surfaces in the measuring system and constructively built-in stability of the distance between probes. It is important to simplify the structure of samples such as "GP-ACF-GP" because of the absence of the stage of sputtering of metal cords. In this structure of the measuring cell, the thickness of the chalcogenide film was approximately 1 mcm.

II. Experimental Results

Fig. 1. shows the graphs of dependence of the electrical resistance of planar samples such as the "Ni layer-Se film-Ni layer" from the time of their modification with mercury at various ambient temperatures and mercury concentration (the beginning of activating the amorphous selenium by mercury is marked on figures with an up arrow (↑)). The thickness of the selenium film (d_{Se}), the surface area of the mercury drops (S_{Hg}) and the temperature, at which we measured the dependency of samples' resistance at the time of their modification with mercury, are specified directly in the figures. The thickness of the Ni layer was 60-70 nm. In the experiments, we applied the vessels in which the surface drop area was 7 and 70 mm^2.

As you can see from Fig. 1., there is a latent period during which the resistance of the planar sample remains almost unchangeable. The period duration depends on mercury concentration and temperature and ranges from several minutes to one hour. Later, the resistance of the planar samples reduces sharply (by 4–6 orders of magnitude). For some structures of samples, we found a reduction in resistance by almost 7 orders of magnitude [14]. With the temperature rise, the duration of the latent period reduces and the rate of resistance increases. The same picture is also observed with an increase in mercury concentration. We got similar results (a sharp reduction in resistance by 4–6 orders of magnitude) while using samples such as "Cr layer - Se film - Cr layer" [15]. Such a course of dependency $R(t)$ may be explained from the point of structural changes, which occur in the Se amorphous films at their modification with mercury. In [16, 17], based on Raman studies, we concluded that the matrix of the Se amorphous film is built both by elements of the Se$_8$ rings and the elements of the helical Se$_n$ chains. During the latent period, the interaction of the Se and Hg atoms occurs. Such interaction ends with the formation of the HgSe 'island-bridge' structure in the Se subsurface layer. The studies' results of the Se amorphous films, which are modified with mercury, [2-4] do not negate this
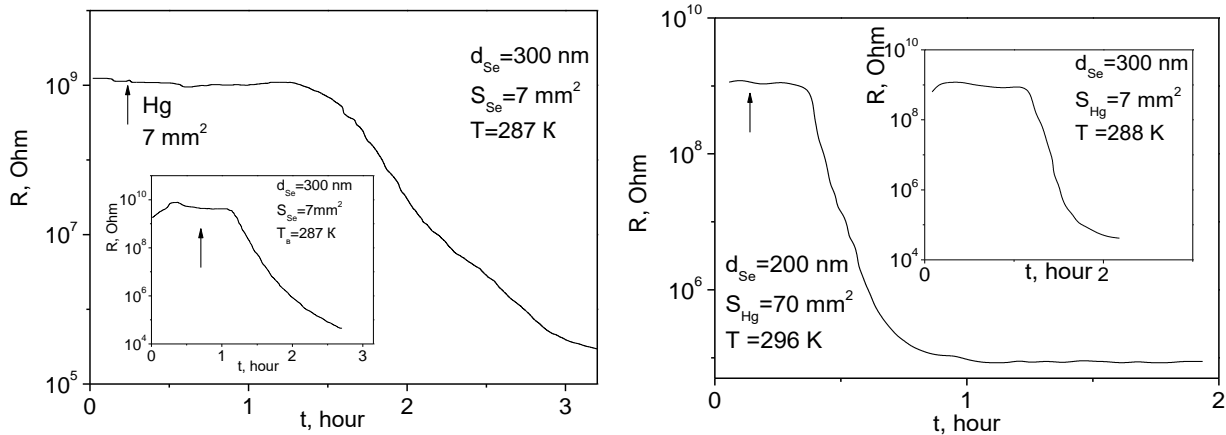
Fig. 1. The graph showing the dependence of the electrical resistance of planar samples such as the "Ni layer – Se amorphous film - Ni layer" from the time of exposure to the mercury vapour (there are explanations in the figure and in the text).

conclusion. Subsequently, the increase in the time of exposure of films in the mercury vapor leads to a significant increase in the islands' sizes and strengthening of the bridge connection between them. By this, we can explain the impact of a sharp reduction in the electrical resistance in samples such as the "Ni(Cr)layer - Se amorphous film - Ni(Cr)layer" modified with mercury.

Fig. 2. shows the graph showing the dependence of the sample resistance from the time of activation by mercury, for the case when the mercury concentration changed within the measuring (vessels with different S_{Hg} were alternately introduced in and removed from the measuring container). The moment of the vessel's removal in Fig. 2. is marked by an arrow down ($\downarrow$). We can see that when the vessels with mercury are introduced into the measuring container, the graph showing dependence $R(t)$ shows the sections where the resistance of the sample reduces sharply. The rate of changing the resistance of the sample decreases significantly at a reduction in the dynamic concentration of mercury, i.e. when we change the vessel with the Hg surface area of 70 mm^2 for the vessel with $S_{Hg}=7$ mm^2. On the graph showing the dependence of the electrical resistance of the sample such as the "Ni layer - Se film - Ni layer" from the time of its exposure to mercury vapor, some sectors are available where the resistance practically does not change (after removing the vessels with Hg), allows us to assert about the ability to keep in "memory" the mercury concentration, which the sample has absorbed before removing the vessels with mercury from measuring container.

Fig. 3. depicts the graph showing dependence R(t) for the samples such as the "Ni layer - Se$_{100-x}$Te$_x$ film - Ni layer". Just like for the Se amorphous films, modification with mercury of the amorphous films such as the Se$_{100-x}$Te$_x$ (x=3, 5, 10 and 15) leads to a reduction in their electrical resistance by 4-6 orders of magnitude. We can see that with an increase in the Te concentration in the composition of films of the Se-Te system, the resistance variation value reduces during the transition from a high-resistance state to a low-resistance state while the transition time and latent period increase. This may show a reduction in the instability of the structural network of

films in the Se-Te system when the Se atoms are replaced by the Te atoms. As we have noted above, the structural network of the selenium amorphous film is built up by elements of Se$_8$ rings and S$_{en}$ chains. When the Se atoms replace the Te atoms in Se$_{100-x}$Te$_x$ films, the tellurium atoms statically and uniformly replace the Se atoms in these chain groups. This, in turn, leads to a reduction in the Se$_n$ length and, consequently, to a reduction in the quantity of Se atoms, which can interact with mercury. As in the case of the selenium amorphous films, HgSe [17] inclusions are formed in the amorphous matrix if the Se$_{100-x}$Te$_x$ films are exposed to the mercury vapor. Such formation leads to a sharp decrease in the electrical resistance of planar structures such as the "Ni layer - Se$_{100-x}$Te$_x$ film - Ni layer". According to Raman studies, we did not find the HgTe inclusions in the Se$_{100-x}$Te$_x$ films modified with mercury [17].
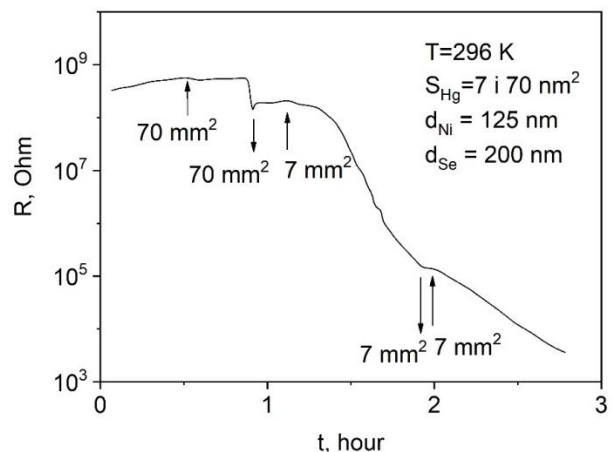

Fig. 2. The graph showing the dependence of the electrical resistance of planar samples such as the "Ni layer-Se film-Ni layer" for the case when the concentration of mercury changed within the resistance measuring (there are explanations in the figure and in the text).

Experiments proved that the course of the graph showing the dependence of planar structures such as the "Ni(Cr) layer-ACF-Ni(Cr) layer" practically does not depend on the thickness of the chalcogenide film. We
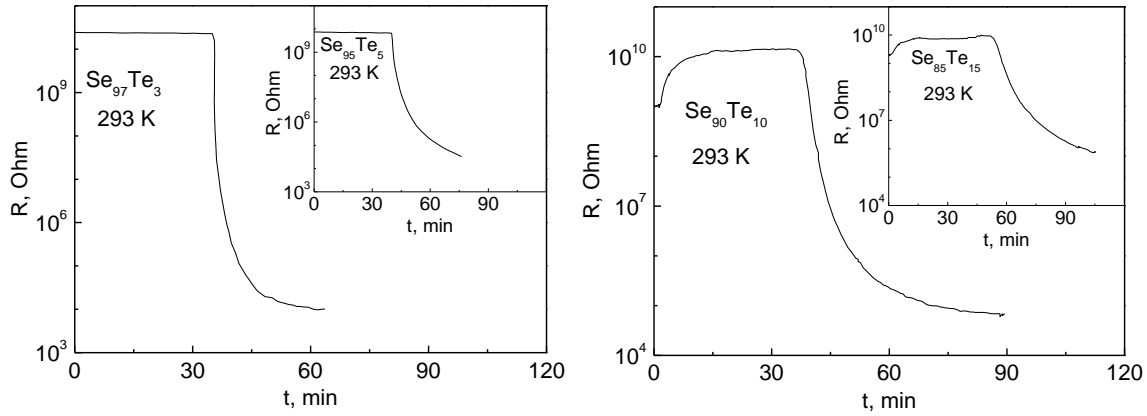
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Fig. 3. The graph showing the dependence of the electrical resistance from planar samples such as the "Ni layer –Se$_{100-x}$Te$_x$ film – Ni layer" from the time of exposure to mercury vapour.

remind that the thickness of chalcogenide films such as Se$_{100-x}$Te$_x$ ($0 \leq x \leq 15$) in these experiments was 150-300 nm. This allows us to conclude that the change in the electrical resistance of such planar structures is mainly determined by changes in the surface electrical conductivity of chalcogenide films. This conclusion is confirmed by the results of studies of the impact of mercury vapor on the electrical resistance of chalcogenide films while using the samples such as "GP- ACF-GP". The thickness of chalcogenide films such as the Se$_{100-x}$Sb(As)$_x$ (x=0, 3, 7) was 1 mcm in these experiments.

composition of films, the latent period, during which the resistance practically does not change, increases. In this case, the time of transition from the high-resistance state to the low-resistance state also increases. As for the Se$_{100-x}$Te$_x$ films, this fact is stipulated by the reduction in the length of the Se$_n$ chains due to the formation of such structural elements as Sb(As)Se$_{3/2}$ [10], in which the heteropolar Sb-Se bonds and As-Se bonds have more stability than homopolar Se-Se bonds of. Respectively, the quantity of the Se atoms, which may interact with Hg atoms to form HgSe, is much fewer.
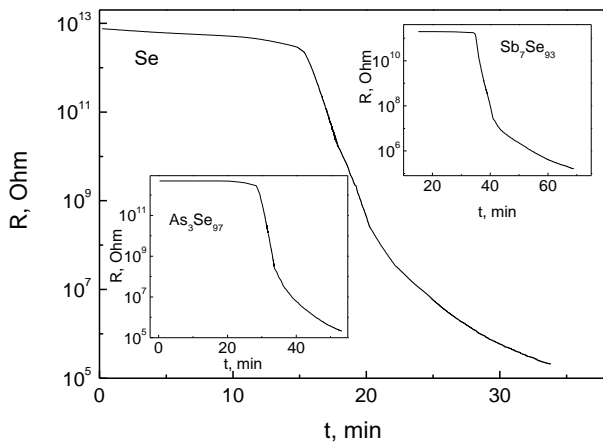
Conclusions

Having studied the graphs of dependence of electric resistance of amorphous films such as the Se, Se$_{100-x}$Te$_x$, Se$_{100-x}$Sb$_x$ and Se$_{100-x}$As$_x$ from the time of exposure to mercury vapor, we have found as follows.

There is a latent period during which the resistance of the samples is practically unchanged. Depending on the mercury concentration, the temperature and the chemical composition of the films, the above duration period may range from several minutes to one hour.

A further increase in exposure time of chalcogenide films in mercury vapor leads to a reduction in their electrical resistance by 4–7 orders of magnitude. Reduction in electrical resistance is mainly determined by an increase in the electrical conductivity of the films because of forming crystalline inclusions of mercury selenide in their surface layers.

The time of the film's transition from a high-resistance state to a low-resistance state reduces with increasing the temperature and mercury concentration. When the content of Te, Se and As increases in the films, the time of transition increases while the value of the variable resistance reduces.

The obtained results show the possibility of using amorphous films of the Se-Te, Se-Sb and Se-As systems as sensitive elements of the electric sensors for detecting the mercury vapor.

Fig. 4. The graph showing the dependence of the electrical resistance from planar samples such as "GP- ACF-GP" from the time of exposure to mercury vapor.

The graph showing the dependence of the electric resistance of some samples such as the "GP-Se$_{100-x}$Sb(As)$_x$ film- GP" from the time of their exposure to the mercury vapor at the temperature of 283-287 K are shown in Fig. 4. We can see that the graph showing dependency $R(t)$ of samples such as the "GP-Se$_{100-x}$Sb(As)$_x$ films-GP" are similar to the same graphs of the dependency shown in Fig. 1 and Fig. 3. Given the results of above studies, we may assume that the reduction in the electrical resistance of such samples as the "GP-ACF- GP", which are modified with mercury, is stipulated by the formation of the HgSe crystalline inclusions at the surface layer of chalcogenide film. It is seen from Fig. 4, that with an increase in the content of Sb and As in the

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Вплив парів ртуті на електричний опір халькогенідних аморфних плівок

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З використанням планарних структур «шар Ni-халькогенідна аморфна плівка-шар Ni» та зразків «графітовий зонд-халькогенідна аморфна плівка-графітовий зонд» досліджено вплив парів ртуті на електричний опір аморфних плівок систем Se-Te, Se-Sb і Se-As. Встановлено, що витримка зразків в парах ртуті призводить до зменшення їх електричного опору на 4-7 порядків. З підвищенням температури і концентрації ртуті час переходу з високоомного стану в низькоомний зменшується. При введенні в аморфний селен Te, Sb та As і збільшенні їх концентрації у складі плівок час переходу зростає, а величина зміни опору зменшується. Встановлено, що зміна опору визначається в основному зміною поверхневої електропровідності халькогенідних плівок. Зменшення електричного опору селеновмісних аморфних плівок, модифікованих ртуттю, викликане формуванням в їх матриці кристалічних включень HgSe.

Ключові слова: халькогенідні аморфні плівки, електричний опір, модифікування плівок ртуттю, селенід ртуті, сенсори наявності ртутних парів.