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.

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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\textsubscript{2}, SeCl\textsubscript{4} and (N\textsubscript{2}H\textsubscript{4}H\textsubscript{2}O)\textsubscript{5}, Hg(CH\textsubscript{3}COO)\textsubscript{2}∙SeCl\textsubscript{4} [5] in the presence of N\textsubscript{2}H\textsubscript{4}H\textsubscript{2}O, Hg(NO\textsubscript{3})\textsubscript{2} and Na\textsubscript{2}SeSO\textsubscript{4} [6]. 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 vapor pressure 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 (Sh, 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/m³.

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 Se₁₀₀₋₃₀₋₅₀ 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 Se₁₀₀₋₃₀₋₅₀, (3≤x≤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 (dSe), the surface area of the mercury drops (Smercury) and the temperature, at which we measured the dependency of the 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 mm².

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 Se₅ rings and the elements of the helical Se₅ 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
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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).

Fig. 2. The graph showing the dependence of the electrical resistance of planar samples such as the “Ni layer – Se amorphous film – Ni(Cr) layer” modified with mercury.

Fig. 3. 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\(_x\)Te rings and Se\(_x\) 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 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].

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
that with an increase in the content of Sb and As in the surface layer of chalcogenide film. It is seen from Fig. 3 that with an increase in the content of Sb and As in the 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_x 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.

![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.](image1)

Fig. 3. 

![Graph showing the dependence of the electrical resistance from planar samples such as the “GP-ACF-GP” from the time of exposure to mercury vapour.](image2)

Fig. 4. 

The graph showing the dependence of the electrical resistance from planar samples such as the “GP-Se_{100-x}Sb(As)_x” from the time of exposure to mercury vapour, 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 vapour.

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.

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Вплив парів ртуті на електричний опір халькогенідних аморфних плівок

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 введені 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, модифікуваних 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.