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FEATURES OF PHYSICOCHEMICAL INTERACTION IN THIN-FILM SYSTEM ON THE BASE OF ARSENIC TRISULPHIDE AND COPPER

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Physicochemical interactions in amorphous As_2S_3 - copper thin film systems were studied by the methods of resistometry, ellipsometry, microscopy and by the chemical dissolution. It was shown that considerable variation of chemical process activity observed in these systems is caused by an essential dependence of the physicochemical interaction rate on chalcogenide film stoichiometry and imperfection of its structure. Ellipsometric modeling results indicate that the thickness distribution of the dissolved copper is close to a rectangular shape. It confirms reactionary nature of interaction. Application of our thermochemical model for a probability estimation of quasi-molecular reactions of copper and oxygen with polymerized and non-polymerized fragments in arsenic trisulphide film enabled to give qualitative description of the interaction mechanism. Comparison with As_2S_3-Ag system is made. Results presented in this work indicate some new ways to control physicochemical interaction process in amorphous chalcogenide-metal thin-film systems.

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Keywords: As_2S_3 - Cu system, Amorphous chalcogenide, Thin film

1. Introduction

Thin-film photosensitive systems based on chalcogenide glassy semiconductors (CGS) and some metals (Ag, Cu) [1] have many unique properties. For example, they can be successfully applied in submicron lithography and are very promising in nanolithography as inorganic resists [2]. Among them, the systems containing silver and copper as metal component have the greatest light sensitivity [3].

Thin-film heterogeneous CGS-Me systems, in general, are thermodynamically nonequilibrium ones: there are physicochemical processes in them which cause their ageing. The systems containing silver and ChGS layers based on arsenic, germanium and sulfur are the only ones that are sufficiently sensitive and stable. Most of investigations concerning the nature of the phenomenon, technology of manufacturing, and practical applications have been carried out using above mentioned systems.

The use of ChGS-Cu non-silver systems is difficult due to their chemical instability: the physicochemical interactions (PCI) between CGS and copper are very intensive, what leads to their rapid ageing. Preparation of non-silver systems based on ChGS and copper with performances similar to those of CGS-Ag systems is an urgent problem. Its solution requires detailed investigations of physicochemical transformations in the CGS-Cu systems. Besides, the examination of physicochemical interactions of CGS and metal films is the important topic of research by itself. We have recently demonstrated that these effects can be applied to creation of blazed holographic diffraction gratings [4].

The problems mentioned above require a detailed study of specific features of the interaction in thin-film ChGS-Cu systems. Taking into account that the As_2S_3-Ag system is the most investigated among CGS-Ag systems, the As_2S_3-Cu system as model has been chosen for such examinations. It has allowed to carry out the most complete comparison of the processes of CGS interaction with silver and copper.

2. Experimental

Samples of sandwich-like thin-film CGS-Cu systems were prepared by deposition onto K-8 glass substrates vapours produced by the subsequent thermal vacuum evaporation of the copper load with initial weigh 0.5 g) and that of crashed powdered glassy As2S3 with initial weight 2g) from tantalum boats at residual pressure, P, of 5 * 10^{-3} Pa. The deposition rate and amount of deposited substance were measured by the KIT-1 quartz crystal oscillator monitoring system. Thicknesses of Cu and As_2S_3 films were also determined using the MII-4 interferential microscope.

The most universal physical property describing mass transport during solid-state reactions in such systems is the metal layer expenditure, Δh_{Cu}. It was observed by the electrical resistance measurements of the copper film. Specific implementation of this procedure and its metrological substantiation are given in [5].

The ellipsometrical angles of thin-film As_2S_3 -Cu samples and As_2S_3 and Cu control films, ψ and Δ, were measured using the LEF-3M-1 ellipsometer (λ = 632.8 nm) for angles of light incidence in the interval φ_0 = 45°...80°. In order to obtain information about the constitution of samples under investigation, we developed the Fortran-program which enabled to distinguish between various ellipsometrical models. Methodological and metrological aspects of the utilised ellipsometrical modeling method have been described in detail [6, 7].

3. Results

Thickness changes of the copper conductive film in As_2S_3 -Cu samples prepared in the same vacuum cycle began simultaneously with the start of the chalcogenide film deposition on it and continued after completion of the deposition at the same rate (see Fig. 1, chart 3). The change of copper film thickness over the 0...5 min. interval is approximated by the h =A*$t^{1/2}$ formula, where A is a constant. The rate of copper film expenditure, V_e reaches the values of 0.1...0.2 nm/s. When the $\Delta h_{Cu}/h_{As2S3}$ ratio reached the values of 0.25...0...30 (the average concentration of metal in As_2S_3< Cu > layer (interaction products (IP) layer) is 39...46 weight % or 33...37 at. %) the dissolution rate began to drop rapidly.

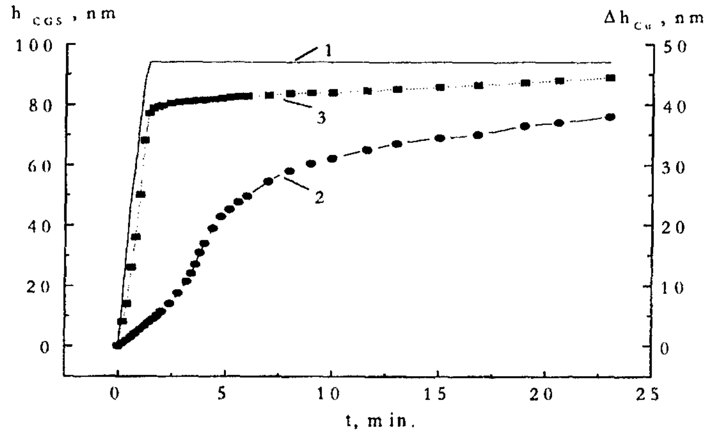

Fig. 1. Dependence of the thickness of the As_2S_3 film being deposited on the deposition time (1). Dependence of the copper film thickness change on the storage time in the vacuum chamber (2 and 3). (Starting from the moment when the CGS film deposition begins.) 3 - Cu film was not annealed on purpose before the As_2S_3 deposition. 2 - Cu film has been annealed before the As_2S_3 film deposition at 100 °C in the presence of glassy As_2S_3 in the chamber.

It has been determined that the physicochemical processes become more intensive when the copper film was deposited on the heated substrate before the formation of the CGS film, or when the copper film has been annealed after deposition at elevated temperatures in the presence of glassy As_2S_3 in the vacuum chamber. In this case the visually appreciable layer is formed on the copper film surface (apparently, due to the interaction of copper with components of rarefied gaseous medium of chamber).

The formation of such layer proves that the arsenic trisulphide is noticeably volatilized at $P < 10^{-2}$ Pa even at the ambient temperatures. This layer, most likely, consists of copper - sulfur compounds (Cu_xS), because the layer with similar optical and chemical properties is also formed on the surface of copper film annealed in the vacuum chamber in the presence of free sulphur.

During the deposition of As_2S_3 on Cu film covered by Cu_xS layer, V_e was proportional to chalcogenide deposition rate, and the rate of interaction of metal with ChGS reaches 0.8 nm/s. This rate drops sharply when the deposition of CGS film is completed (Fig. 1, curve 2). At this moment, the $\Delta h_{Cu}/h_{CGS}$ ratio for various samples is ~0,4...0,5. Thus, the average concentration of copper in As_2S_3<Cu> is 52...57 weight % or 45...50 at. %. These values are close to the maximum possible concentration of copper in interaction products of copper - amorphous As_2S_3 systems [8].

The results presented above show that for preparation of more stable As_2S_3-Cu systems, it is necessary to evaporate copper and arsenic trisulphide in separate vacuum chambers or in different "vacuum cycles". This should prevent the formation of the CuxS layer on the copper film surface, thus avoiding the facilitation of penetration of the copper atoms from the metal film into the As_2S_3 film through such layer. Subsequently, Cu and As_2S_3 films were deposited in different "vacuum cycles ", between which the copper film was exposed to variable duration free air cycles at temperatures from room and up to 150 °C. Under such conditions the Cu oxide layer is formed on the copper film surface [9, 10]. At the room temperature their thickness reached up to 7 nm [9]. Their thickness grows with rise of oxidation temperature [10].

As opposed to Cu_xS layers, the Cu_2O ones formed by this process have the barrier properties: there is an induction period of PCI in the systems which have intermediate Cu_2O layers. During this period the dissolution rate of the copper film is the lowest (Fig. 2). The general view of Δh_{Cu} (t) dependencies for samples with an oxide-coated Cu film is of the S-type: the induction period is followed by the period of PCI acceleration, then the period of PCI deceleration, and last stage is the saturation of the reaction. The concrete view of $\Delta h_{Cu}(t)$ diagram at various thicknesses of the oxide layer is presented at Fig. 2. The duration of the induction period, the Δh_{Cu} (t) curve inflection point position, the top metal dissolution rate can be used as quantitative parameters in describing the barrier properties of oxide layer. As the thickness of the oxide layer increases, both the duration of the induction period, and the time necessary to reach the inflection point on the Δh_{Cu} (t) curve increase. Thus, the period of reaction acceleration takes place over the wider range of Δh_{Cu} changes, and the maximum value of V_e decreases.

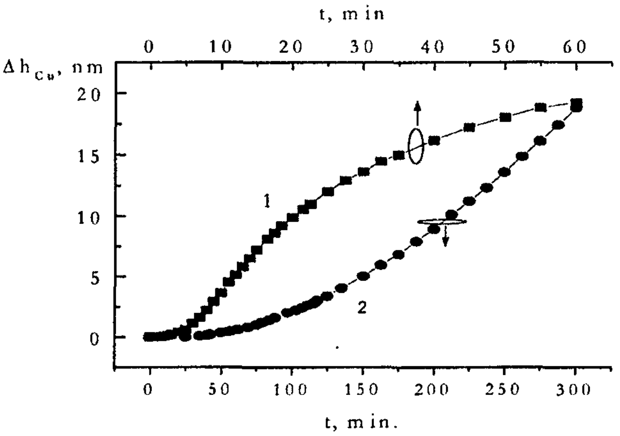

Fig. 2. Copper film thickness change depending on the duration of the As_2S_3-Cu systems storage in vacuum (h_{As2S3} = 150 nm). 1-intermediate Cu_2O layer, h_{Cu2O} = 4 nm; 2-h_{Cu2O} =7 nm.

The As_2S_3-Cu sampleageing rate depends not only on the condition of the interface between the Cu and As_2S_3 films but also on the conditions of preparation of the As_2S_3 film. During the sample storage in vacuum the PCI takes place most intensely when the CGS film obtained by evaporation of primary glassy As2S3, subsequent multiple using of the As_2S_3 load slows down PCI in systems obtained with their evaporation. For example, for samples with ~4 nm thick oxide layer the maximal value of V_e is 0.4 nm/min. However, as a result of multiple use of glassy As_2S_3 load the V_e gradually decreases down to 0.01 nm/min.

The films obtained by evaporating the previously used As_2S_3 shots have the refraction index that is several percents higher than the films obtained from the fresh load. This has been shown by the ellipsometrical measurements of the reference As_2S_3 films. The evaporator temperature, load mass, deposition rate, and the thickness of obtained As_2S_3 films were similar in all cases considered.

During the gradual heating of the evaporator containing the fresh load of 2 g of the glassy As_2S_3, deposition of small amounts of substance (up to 5 $\mu g/cm^2$) takes place on both the quartz oscillator and substrate. After that, the increase in the mass of deposited substance usually slows down considerably. With the further rise of the evaporator temperature, the deposition rate increases again. When the loads are used again, then the time progression of the mass of the deposited material becomes less obvious. More often, as the temperature rises, the sharp and monotonic increase of the mass of deposited substance is observed.

The stability of As_2S_3-Cu systems depends also on the storage conditions: in vacuum or in air. The character of atmospheric influence significantly depends on the conditions of CGS film production.

In As_2S_3-Cu systems with the films obtained from the fresh shots, the PCI in air is slower than in vacuum (Fig. 3, curves 1 and 2). From the comparison of these results, we can see that atmosphere has little influence on the duration of the induction period, and only slightly moves the inflection point position of the $\Delta h_{Cu}(t)$ dependence towards smaller times. However, V_e in air is much less than in vacuum. Also, $\Delta h_{Cu}(t)$ dependence for the air stored system is closer to linear than that for the vacuum stored one. Hence, the atmosphere has less influence on the barrier properties of copper oxide layer itself, but it slows down the velocity of transition of copper particles through copper/CGS interface area.

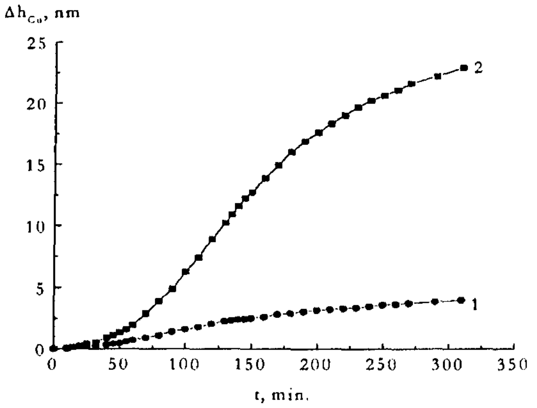

Fig. 3. Change of the Cu film thickness in the As_2S_3-Cu system. System was being stored in air (1) and in vacuum (2). (Thickness of the As_2S_3 film is 180 nm, thickness of the intermediate oxide layer is 5.5 nm.)

On the contrary, in As_2S_3 -Cu systems, in which ChGS films are obtained from earlier used material, the PCI rate in air is higher than in vacuum. Fig. 4 shows the $\Delta h_{Cu}(t)$ dependencies for the sample, in which CGS film was deposited from the glass sample whose weight was equal to approximately 30 % of initial mass. In vacuum the initial V_e is ~ 0.1 nm/min. and gradually decreases (close to square law, curve 2). In the sample taken from vacuum on air right after the deposition, the Vd is higher and is practically stationary (curve 1). Longer storage of the sample in vacuum (before placing it in air) gradually causes the low V_e initial period to occur (equal to the copper expenditure rate in vacuum at the moment of extraction). It also causes the decrease of the metal expenditure rate during the main (close to linear) stage of $\Delta h_{Cu}(t)$ dependence (curve 3).

An additional information about Cu-As_2S_3 thin-film interactions was obtained from their ellipsometrical investigations, and also from the investigations of their stability in etchtants as well as their mechanical properties.

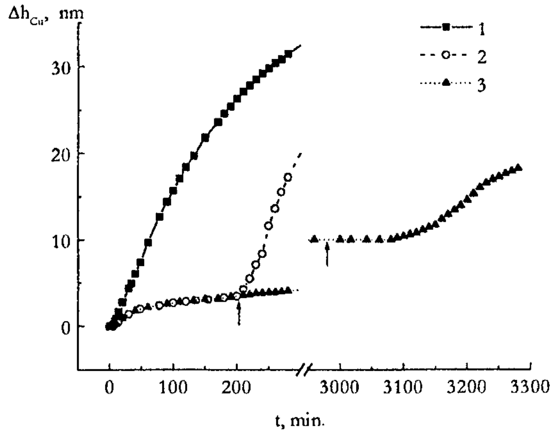

Fig. 4. Time dependencies of copper film thickness change for As_2S_3-Cu_2O-Cu system over the vacuum-and air-keeping. The As_2S_3 film has been obtained by the evaporation of load used earlier in four evaporations. The pre-evaporation weight was approximately ~30% of the initial weight. 1 - keeping in air. 2, 3 - keeping in vacuum (up to the time moment ↑) and in air (after the time moment ↑). (Thickness of the As_2S_3 film is 106 nm, thickness of the intermediate oxide layer is 5 nm.)

Ellipsometrical investigations were carried out immediately after the removal of the systems from vacuum chamber and also during their storage in air. The systems under investigation were modelled as multilayer structures with sharp layer interfaces. Such elipsometrical models have been successfully used for the description of interactions in CGS-Ag thin film systems [11].

Angular $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ dependencies for the systems stored in vacuum chamber depending on storage duration are described with good accuracy by the "copper substrate - homogenous layer of reaction products " or by the "copper substrate -homogenous layer of reaction products - homogenous ChGS layer" models. Transition from the former model to the latter one correlate with the stage of $\Delta h_{Cu}(t)$ kinetic dependence when the metal dissolution rate V_e rapidly decreases. This makes it possible to explain this rapid decrease by the fact that the outer surface of the semiconductor film was reached by the reaction front. Moreover, from the resistometrical and ellipsometrical data the next equation follows:

$$\Delta h_{Cu} + h_{As2S3} = h_{As2S3\,<Cu>}$$

Below we represent the details on ellipsimetrical investigations of the acceleration of PCI in air phenomenon. As an example, let us consider the system, kinetics of the copper layer expenditure of which is presented in Fig. 4 (curve 3). Calculations showed that the experimental angular $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ dependencies measured immediately after the system removal from vacuum (time moment ↑ on curve 3, Fig. 4) are described by the "copper substrate - two homogenous layer" model with 0.07 grad. accuracy. Calculated thicknesses, refraction (n) and absorption (k) indexes of these layers are: h = 50 nm, n = 2.57, k = 0.01 for the upper layer and h = 66 nm, n = 3.48, k = 0.43 for the lower one. This clearly demonstrates that the upper part is As_2S_3 layer, whereas the lower one is the As_2S_3 <Cu> reaction products layer. These ellipsometric modeling results indicate that the thickness distribution of the dissolved copper is close to rectangular shape. It confirms reactionary nature of interaction.

Dynamics of the thickness changes for these copper-doped and non-doped CGS layers during further storage in air is demonstrated in figure 5. From the modeling it is also obtained that, as the thickness of doped layer increases, the optical constants of this layer increase as well. This proves, obviously, the gradual change of a composition or/and a structure of the layer of reaction products. By the moment of the deceleration of dark interaction caused by the reaching of the doping front the external surface of As_2S_3 film the values of optical constants of Cu doped layer were: n = 3.6, k = 0.8. The accuracy of the description of $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ dependencies by "copper substrate - homogenous layer of interaction products" model was 0.3 grad.. This points out that the composition and/or structure of reaction products somewhat change(s) along the doped layer.

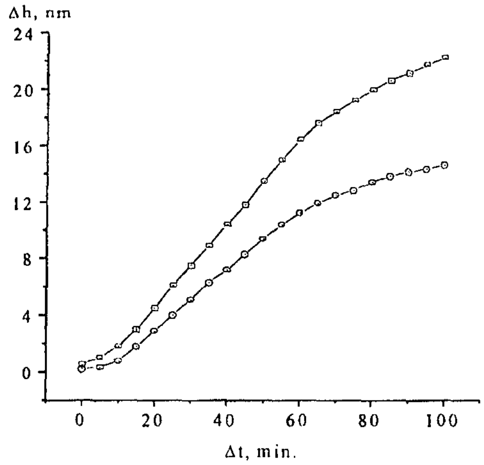

Fig. 5. Thickness change of non- doped (1) and copper-doped (2) parts of CGS film during the storage of the As_2S_3-Cu_2O-Cu system in air. The CGS film was obtained with the load of glassy As_2S_3 that had been previously used four times.

Further, in this system even slower changes take place. The gradual increase of values of optical constants of this layer has been observed. This points to the further increase of concentration of copper in doped layer. Thus, the precision of the description of system by the "copper substrate - homogeneous layer of interaction products" model also has gradually improved. After the dark reaction having reached the saturation point, the optical constants of As_2S_3 <Cu> layer were: $n = 4.0$, $k = 1.3$. The thickness of products layer was approximately 1.5 times more than the initial thickness of film. Accuracy of the description of system by the "copper substrate - homogeneous layer of interaction products" model slightly exceeded 0.1, which is 1.5 times worse than the accuracy of the description of system in which the interaction took place in vacuum.

Doping As_2S_3 films by copper is accompanied by a change of their dissolution rate in various alkaline etchants, in particular, in the aqueous solutions of NaOH and KOH. Their adhesion to the underlying Cu film also is reduced in comparison with the adhesion of the initially deposited non-doped As_2S_3 film. It enabled also to study changes occurring in Cu films during their interaction with As_2S_3 films. The mechanical or chemical removal of As_2S_3 <Cu> products layer from the surface of copper film and measuring the $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ dependencies on the remaining Cu film were done for this purpose upon the end of interaction.

It was ascertained that the $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ values after removal of As_2S_3 <Cu> layer in the majority of systems are close to $\Delta(\varphi_0)$, $\psi(\varphi_0)$ values for the reference Cu films. This proves that during the interaction of copper film with CGS one the state of the copper film surface and a volume structure of this film have not undergone essential changes.

As opposed to the previous cases, the copper films in systems stored in air, in which the As_2S_3 film is obtained from repeatedly utilised shots, had lower $\Delta(\varphi_0)$, values and especially the $\psi(\varphi_0)$ values, compared to the control copper films after removal of As_2S_3 <Cu> layer. This causes the growth in the effective refraction index values and reduction in the effective absorption index values of such copper films. For example, in the above described systems with a sulfur deficiency in the As_2S_3 film, the n grows from 0.15 to 0.44, and k drops from 3.20 to 3.03. The k/n ratio drops from 21.3 for the control Cu film to 6.9 for the residual Cu film after the reaction and mechanical removal of the As_2S_3 <Cu> layer. This should demonstrate the reduction of the film packing density [12].

The conclusion obtained with using ellipsometrical investigations is confirmed by observation of the surface of unreacted part of Cu film in reflective optical microscope. For Cu films with low $\Delta(\varphi_0)$ and $\psi(\varphi_0)$ values compared to the reference Cu films, the increase in the scattered light level and roughness are observed. The lower reflectivity spots are observed in the microscope' field of view. All this demonstrates that the dissolution of Cu films is non-uniform across the surface. As a consequence, the copper film becomes heterogeneous, with reduced volume content of metal.

Apparently, it is necessary to assume the presence of the spots too small to be visible in the optical microscope used in this study (x600). The presence of macroscopic as well as microscopic defects in the copper film also should result in the lower specular reflectivity and greater surface roughness. It affects the values of ellipsometrical parameters of copper film as well.

Thus, the results obtained show that the physicochemical processes during the interactions of the metal and ChGS films in As_2S_3-Cu systems have the complex dependency on such factors as the Me/CGS interface state, conditions of CGS film preparation, and composition of the environment.

4. Discussion

Comparison of interaction rates in As_2S_3 -Ag [13] and As_2S_3 -Cu (Fig. 1) thin-film specimens without intentionally formed intermediate layers shows that interaction rate of arsenic trisulphide film with the silver one is about four orders of magnitude lower than with the copper film. Thus, the difference in PCI kinetic shape is also observed in these systems.

For As_2S_3 -Ag the kinetics of metal thickness change may be described by square-root time dependence, $\Delta h(Cu) \sim t^{1/2}$ [13]. This points out that the dark interaction is being controlled by diffusion. On the other hand, for As_2S_3 -Cu the dependence is close to linear over the considerable part of the kinetics curve (Fig. 1, curve 2).

The explanation of such a substantial difference between chemical process rates can be based on heats of formation of silver, copper, and arsenic sulphides. Let us note that the similar approach has been used before by Phillips [14], when he proposed his thermochemical model of photodoping for ChGS-Ag systems. The relative heats of formation are given in Table 1 in kcal/mole chalcogen per formula unit in accordance with [14].

Table 1. Relative heats of formation for arsenic, silver and copper sulphides and arsenic, silver, copper and sulphur oxides.

Compound	ΔH_f, Kcal/[mole×{number of chalcogen or oxygen atoms per formula unit}]	Compound	ΔH_f, Kcal/[mole×{number of chalcogen or oxygen atoms per formula unit}]
As_2S_2	15.95 [16]	SO_2	35.48 [17]
As_2S_3	13.3 [15]; 10.0 [16]	SO_3	36.83 [17]
As_2S_5	7.0 [16]	S_3O_9	34.9 [17]
Ag_2S	7.837 [15]	S_2O_7	27.75 [17]
CuS	12.7 [15]; 12.1 [16]	Cu_2O	41.4 [17]
α-Cu_2S	19.0 [15]; 19.6 [16]	CuO	38.72 [17]
$Cu_{1.96}S$	17.83 [15]	As_2O_3	52.13 [17]
$Cu_{1.8}S$	17.24 [15]	As_4O_6	53.04 [17]
Ag_2O	7.44 [17]	AsO_2	43.9 [17]
Ag_2O_2	2.95 [17]	As_2O_4	47.77 [17]
S_2O	26.11 [17]	As_2O_5	44.28 [17]
SO	-0.098 [17]		

For arsenic trisulphide and silver sulphide the following is true: (see Table 1)

$$|\Delta H_f (As_2S_3)| > |\Delta H (Ag_2S)|.$$

In other words, chemical reaction between silver and arsenic trisulphide is endothermic (is not beneficial energetically). That is why for As_2S_3 -Ag compositions, most probably, one can expect only the diffusion intermixing of atoms of copper and ChGS layers, caused by an entropic component of Gibbs' free energy. This makes it possible to explain square-law dependence observed in [13] for As_2S_3 -Ag thin-film systems.

For arsenic trisulphide and cupric sulphides the following is true:

$$|\Delta H_f (As_2S_3)| = |\Delta H_f (CuS)|, \quad (1)$$

$$|\Delta H_f (As_2S_3)| < |\Delta H_f (Cu_2S)|, \quad (2)$$

$$|\Delta H_f (As_2S_3)| < |\Delta H_f (Cu_{2-\delta}S)| \quad (3)$$

From (2, 3) it follows, that, when copper and arsenic trisulphide contact, the fast exothermic exchange reactions should take place, producing the Cu_2S and $Cu_{2-\delta}S$ compounds. An interaction rate is determined by an enthalpy and entropy of reactions and by the kinetic factors. (Taking into account the propensity of silver and copper to form the triple compounds with arsenic and sulfur [18], strictly speaking, heat of dissolution of sulphides of these metals in arsenic trisulphide should be taken into account too, when the probability of reaction between silver and copper, on the one hand, and arsenic trisulphide, on the other hand, is estimated.)

Apparently, the almost-linear kinetics for the main stage of $\Delta h_{Cu}(t)$ dependence (Fig. 1, curve 3) means [19] that the surface reactions (at Cu/As_2S_3<Cu> or As_2S_3<Cu>/ As_2S_3 boundaries, in our case) control the interaction rate between CGS and copper as-deposited films. The slowdown of V_e begins at those concentrations of copper in the products layer, at which the electron diffraction pattern similar to that of pure a-As_2S_3 had already disappeared [8], and different amorphous diffraction pattern was observed. One can conclude that the above mentioned slowdown is caused by the As_2S_3<Cu> reaction product front reaching the external surface of As_2S_3 film. This conclusion is also confirmed by our ellipsometrical examinations.

The presence of Cu_xS layer on the surface of copper film considerably improves the interaction conditions at this surface. The interaction of copper particles diffused through the Cu_xS intermediate layer with As_nS_m (n, m = 0, 1, 2, 3 ...) molecular fragments being deposited from vapour phase [20, 21], most likely, controls the rate of Cu layer expenditure in this case.

When the copper oxide layer separates the metal and ChGS films, the interaction between them takes place in a different manner (Fig. 2). The decrease of the maximum value of V_e, and increase of linear-like part of the $\Delta h_{Cu}(t)$ dependence with increase of oxide layer thickness point out that this layer loses its barrier properties only partially. Hence, the copper oxide layer slows the PCI down from the beginning to the end.

The existence of the correlation between the refraction index of the as-deposited As_2S_3 film, and the state (fresh or already used) of the glassy sample of arsenic sulphide explains the influence of thermal history of glassy As_2S_3 on its interaction with copper. It is known from [22, 23] that the violation of stoichiometrical composition and structure of As_2S_3 being precipitated due to change of fragmentary composition of vapour phase causes changes of optical properties of the arsenic trisulphide films. In particular, this violation changes its refraction index.

Apparently, multiple evaporation of glassy As_2S_3 causes changes in composition of its vapour phase. As the evaporator temperature gradually increases from room temperature and up to melting temperature, the vapour phase composition appears to become enriched with sulfur from near-surface areas of the shots. At the melting point and above the intensive evaporation of other molecular fragments begins. Those fragments are produced by the decomposing As_2S_3. The dominant evaporation of more volatile sulfur-enriched fractions takes place, apparently, during the subsequent cooling of an evaporator loaded with the crashed As_2S_3. Hence, for these reasons one can assume that the near-surface layer of As_2S_3 shots gradually loses sulfur when taken through several heatings and coolings cycles (multiple partial evaporation). The average gross - composition of the obtained films gradually changes from sulfur-enriched to sulfur-deficient compared to the stoichiometrical composition. Since (see Table 1),

$$|\Delta H_f(As_2S_5)| < |\Delta H_f(As_2S_3)| < |\Delta H_f(As_2S_2)| \quad (4)$$

one should expect intensification of interaction between the copper and the sulfur-enriched films obtained during the first evaporation of arsenic trisulphide load. This has been confirmed experimentally.

There are reports on the influence of the environment on interaction of metal and CHGS [3, 24, 25]. It has been observed before [3] that for As_2S_3-Ag thin-film compositions the interaction between metal and ChGS slows down in air compared to vacuum. On the contrary, the [24] shows that the silver penetration into the arsenic sulphide plate for air annealed samples increases by several times compared to the vacuum annealed one.

The slowdown of physicochemical interaction in air is explained in [3] as follows: during the storage in vacuum the mobility of free sulfur in As_2S_3 film is higher. As a result, the sulfur diffuses into the Ag film and reacts with it, while in air the slow bi-directional diffusion of metal and As_2S_3 film material takes place. The results obtained by us do not contradict such explanation of this effect for As_2S_3-Ag(Cu) systems in case when As_2S_3 films are enriched with sulfur. Besides, it is necessary to take into account the penetration of atmospheric oxygen into the CGS film, and the possibility of its chemical interaction with sulfur. Such interaction is energy favourable (see Table 1).

On the contrary, in As_2S_3-Cu systems with lower free sulfur content, the amplification of the PCI processes (fig. 4) is observed in air, similarly to the effect of silver thermodiffusion increase in monolithic glassy arsenic trisuphide. The existence of a correlation between metal film expenditure rate in air and the duration of preliminary exposure to vacuum (Fig. 4) allows us to state that it is the activity of atmospheric gases that influences the rate of metal-CGS interaction. From data shown in Fig. 4, it is also possible to conclude that atmospheric oxygen causes acceleration of process activity taking place in the copper - IP interface, or in the IP layer. However, it does not accelerate the processes that undergo at the IP -ChGS interface. In the latter case, the duration of initial period of $\Delta h_{Cu}(t)$ dependence in air should have been decreased as the vacuum exposure is increased. This is due to the approach of IP -CGS boundary to the outer surface of CGS film. Besides, it is possible to make the conclusion that the IP layer formed during the vacuum storage of the system impedes the access of atmospheric gases to the Cu - CGS<Cu> interface.

Thus, close-to-square-root Δh_{Cu} (t) dependence for thin-film vacuum-kept specimens (Fig. 4, curves 2, 3 - up to the arrow mark) points to the dominant role of copper atoms diffusion processes through the gradually thickening product layer. At the same time, the slowest stage of interaction process in air is the reaction at the copper-IP boundary. This is the cause of the linear $\Delta h_{Cu}(t)$ dependence.

Ellipsometry and optical microscopy data show that the acceleration of interaction under influence of the atmospheric gases primarily occurs in those areas of the Cu/As_2S_3 interface where the access of atmosphere gases is facilitated. These areas are characterised by the presence of macrodefects due to the non-ideal technological conditions of preparation of structures, by the presence of pores, hollows, microdefects in as-deposited As_2S_3 films. These data support the conclusion that the Cu/IP interface performs the control function in the air-kept As_2S_3 -Cu systems without surplus of sulfur in As_2S_3 film.

The atmospheric influence effects can also be explained in the non-contradictory manner in terms of the thermochemical approach. In Table 1 the heats of formation for oxides of silver, sulfur, copper and arsenic are given. The analysis of these data shows that the exothermic effect of the 3-, 4-, 5-valence arsenic atoms reaction with oxygen is greater than the oxygen-copper and oxygen-sulfur reactions, and greater yet than the oxygen-silver reaction. This exothermic effect is also greater than that characteristic to silver, arsenic or copper atoms reactions with sulfur. This enables to assume that the overall PCI rate in air increases specifically due to the interaction of atmospheric oxygen with arsenic atoms. This interaction results in release of sulfur, which in turn interacts with atoms of copper or silver. Oxygen stimulated increase of Cu_x S compounds content in products layer should increase its n, k values. That explains the results of ellipsometrical studies.

The acceleration of the PCI interaction processes should be especially noticeable in samples without excess sulphur, such as monolithic samples of glassy As_2S_3 or thin-film samples without surplus of sulfur. According to [24], for glassy As_2S_3-Ag film systems stimulated by atmospheric oxygen, the silver expenditure rate from the film can be several times greater than that caused by the diffusion intermixing of components in such heterogeneous structure. Our experimental data show that for sulfur-deficient As_2S_3-Cu systems the sulfur expenditure rate can increase several times under the influence of the atmospheric oxygen. In this case we deal with the increase of the chemical process rate which, however, remains lower than rate of PCI processes in As_2S_3-Cu samples containing surplus of sulfur, and taking place in vacuum.

It is also possible to explain the results of work [25] by the chemical interaction of atmospheric oxygen with arsenic atoms. In [25] it was observed that there is considerable difference of properties of the photostimulated interaction products obtained by illumination of the As_2S_3--Ag composition in vacuum and in air. At the same time, there was small difference in properties for two such types of products inherent to the As_2S_5 - Ag system. There is clear correlation between the degree of an atmospheric influence and atomic concentration of arsenic in CGS film.

5. Conclusions

The results obtained in this work demonstrate the considerable range of chemical process activity that takes place in the As_2S_3-Cu system. It has been ascertained that the specific type of physicochemical interaction between copper and ChGS essentially depends on composition and structure of ChGS film, and also on the presence of intermediate layers between the film and the metal.

Based on the analysis of heats of formations of sulphides and oxides of silver, copper, and arsenic, the existing experimental data, as well as the data obtained in the present work can be explained. (on interaction of copper and silver with arsenic sulphide.)

The results of the present work pave the way to the precise control over stability of CGS-Me systems that is necessary for producing competitive silverless CGS-Me media.

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