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Effect of Interaction in System ZnS(ZnO)-Sb₂S₃-Ge on Parameters of the Produced thin Films

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Exchange reactions of ZnO impurity in zinc sulfide with Sb₂S₃ and Ge additives are investigated by XRDA, IR spectroscopy and electronic spectroscopy of diffuse reflectance. Possibility of entire sulfidizing of ZnO with antimony sulfide and production of a single-phase product – ZnS sfalerite is established. Interaction in subsystem Sb₂S₃-Ge results in formation of a glass-crystalline composite. Test of ZnS cleaned from oxide impurity, and also composites ZnS-Ge and Sb₂S₃-Ge by thermal evaporation in vacuum has made possible receiving thin-film coatings with high optical and operational parameters.

Key words: zinc sulfide, zinc oxide, admixture, alloying additive, antimony sulfide, Germanium, structure, optical properties, thin-film coating.

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Introduction

Zinc sulfide (ZnS) is one of the major substances as base of materials for infra-red (IR) optics, optoelectronics and other advanced branches of modern techniques [1, 2]. Now some ways of synthesis of ZnS among which one of the most effective is the method of self-propagating high-temperature synthesis (SHS) [3] are applied.

Samples of ZnS produced by high-temperature way possess, besides advantages (high degree of perfection of crystals, cleanliness on impurity of heavy metals), also a number of lacks which, undoubtedly, interfere with expansion of their application, in particular for manufacturing of base elements for IR-optics. These factors are the following:

a) poly-phase composition of samples, i.e. simultaneous presence of phases both of low-temperature one (α -ZnS, sfalerite), and high-temperature phase (β -ZnS, wurtzite), and in enough notable amounts - polytypic phases with transitive structure from sfalerite to wurtzite [4];

b) presence in polycrystalline samples - both in a powder, and in ceramics – of oxygen-containing impurity either in the form of separate phase ZnO (wurtzite) or as a part of solid solutions on the basis of ZnS, mainly, in phase of ZnS of wurtzite modification [5].

Effect of oxygen containing impurity on properties of materials on the basis of ZnS is considerable. So, habitual for technologists - optics value of long-wave

border of area of an optical transparency - 14,5-15,0 microns [6] is limited not by lattice oscillations of ZnS, but by valence oscillations of Zn-O (Zn-OH) bonds of oxide impurity. It worth noticing that the oxygen content (oxygen - containing impurity) is not normalized in let out products on a base of zinc sulfide (a powder, sintered pellet, ceramics), and also in thin-film coatings of interference optics.

At thermal evaporation (as a rule, with resistive heating) of a material in vacuum oxide impurity in ZnS cause deterioration of adaptability to manufacture of process (splashing of a material). Besides, ZnO impurity, unlike base substance, actively reacts with an evaporator material (Mo, Ta) forming defective structures that should result (and really results) in appreciable deterioration of optical and operational properties of a coating.

Recently the approach is developed, allowing minimizing influence of oxide impurity in zinc sulfide due to exchange reactions with special additives lanthanide sulfides Ln₂S₃ (Ln – Sm, Gd, Dy) [4]. It makes possible improving considerably properties of coatings from a base material, ZnS.

It was interesting to predict and pick up a sulfidizing additive, which itself would possess enough high volatility and at the same time would form even more volatile oxide as a product of sulfidizing. Antimony sulfide, Sb₂S₃ is easily enough synthesized from components and practically does not contain oxide impurity, represents itself such kind of an additive [7].

I. Experimental part

As initial reagents are used: high-purity zinc oxide (ZnO), produced by calcination of zinc hydroxycarbonate of composition $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ of qualification "os.ch." at 1250°C with the subsequent cooling in exsiccator, over CaCl_2 ; zinc sulfide (ZnS) and antimony (III) sulfide (Sb_2S_3) manufactured by JV „New materials and technologies”, Odessa (TU B3-639-88 and TU B3-613-84, accordingly). Zinc sulfide is received by SHS method, and antimony (III) sulfide – by melting of components in the evacuated ampoule. Single-crystalline germanium of semi-conductor cleanliness, trade mark GE, is used.

The materials taken in necessary for a stoichiometry parity were ground in an agate mortar to a thin powder, mixed, pressed in tablets and subjected to thermal processing in corresponding modes. Heat treatment of samples was made in the medium of additionally cleaned argon in the high-temperature tubular (horizontal) furnace RHTC 80-450 manufactured by Nabertherm (Germany) with automatic control of temperature with accuracy $\pm 1^\circ\text{C}$. A mode of heat treatment is chosen individually for each of systems.

Samples of systems with a stoichiometric parity of components $\text{Sb}_2\text{S}_3\text{-Ge}$, ZnS-Ge and ZnO-Ge were subjected to heat treatment at temperatures a little below temperatures at which it is observed appreciable volatility of the samples (about what there was judged on occurrence of a touch of certain coloring in cold parts of the reactor); they were, accordingly, 400 , 750 and 800°C for specified above systems. In case of need distillation of volatile components from low-volatile admixture at raised in comparison with above mentioned temperatures was carried out.

Identification of compounds and composites is carried out by a method of the quantitative X-ray diffraction analysis (XRDA) on automated installation DRON-3M (CuK_α radiation).

Test of the samples of investigated systems was carried out by thermal evaporation in vacuum (a resistive variant) on installation VU-1A from molybdenum evaporators (boats) at a current of heating up to 100A at residual pressure of gases to 10^{-3} Pa with speed of drawing of a coating of $25 - 30$ nm/min. Thin-film coatings from evaporated materials were drawn on substrates made of various materials (optical glass K8, quartz, germanium) and forms (plane-parallel and wedge-like plates). Definition of optical (a refractive index, a scattering factor) and operational (mechanical durability, climatic firmness) parameters of the coatings put on substrates were carried out as well.

Values of optical thickness nd , where n - a refractive index, d - the physical thickness of a coating comprised $1.5\text{-}2.5$ microns. Determination of n of coatings was carried out on microspectrophotometer MSFU by reflectance studying from wedge-like plates with the coating put on it. The scattering factor of a coating (σ) was measured at the laser stand with application of the He-Ne laser ($\lambda = 682$ nm). Mechanical durability was defined on the installation SM55 on number of turns of a

disk before scratch occurrence on the thin-film coating adjoining to a disk.

II. Results and their discussion

Data on IR-spectroscopy (not shown) in the range of $400\text{-}500$ cm^{-1} have revealed hidden and obvious peaks of the absorption corresponding to valence oscillations of Zn-O bonds in lattice of ZnS. The last follows from comparison of position and intensity of the specified peaks with the analogous values of a band of lattice oscillations in zinc oxide, and also presence of reflexes of ZnO phase in zinc sulfide on X-ray diffractogram of the last. On the IR-spectrum of antimony sulfide the bands of absorption in the interval of $500\text{-}800$ cm^{-1} , corresponding to valence oscillations of Sb-O bonds, did not reveal. The XRDA has confirmed presence of ZnO (hex.) and Sb_2S_3 (rhomb.) phases. At the same time sample of ZnS contained both sfalerite (cub.), and wurtzite (hex.) modifications.

The estimation of the content of ZnO in ZnS received by SHS method, by results of introduction of alloying additive Dy_2S_3 [4], specifies in value of an order of a 5 % mol. (or about 4 wt. %) of ZnO. Most part of ZnO occurs in a form of solid solution on the basis of both modifications of zinc sulfide. At first sight it is not clear, why so large content of ZnO as a part of phases of ZnS practically does not affect parameters of their lattices: they are $a = 5,406$ (7) \AA for a cubic phase, and $a = 3,820$ (1), $c = 6,251$ (2) \AA for hexagonal phase; at the same time under the literary data they are, accordingly, $a = 5,410$ (9) \AA and $a = 3,820\text{\AA}$, $c = 6,260\text{\AA}$ for sfalerite and wurtzite [10]. The possible solution concludes in availability (and, in notable quantities) in a SHS - product of the third phase - a hybrid of two phases (so-called 4H-structures [4]). Possibly, it represents itself a solid solution of zinc oxide and zinc disulfide, ZnS_2 in matrix of ZnS which exactly in the opposite manner affects parameters of lattices of ZnS phases and, thus, promote each other to intercalate in structure of zinc sulfide and to stabilize it as a whole. Yellowish coloring of SHS - product indirectly suggests it (tab. 1). An additional weak peak at $\tilde{\nu} = 210$ cm^{-1} in an IR-spectrum confirms presence of Zn-S₂ bonds in the product of SHS process.

Exchange processes occur between impurity of ZnO in ZnS (a SHS product) and Sb_2S_3 additive in system $\text{ZnS}(\text{ZnO})\text{-Sb}_2\text{S}_3$ [7]. Almost entire phase transformation of a mix of wurtzite + 4H-phase into sfalerite (tab. 1), essential change of coloring (from yellowish to light grey) and, accordingly, of spectra of diffuse reflectance is thus observed. It is especially remarkable; that is a total disappearance of „oxide” peak on IR-spectrum of a SHS product is observed. However, completely to get rid from sulfidizing additive (residual Sb_2S_3) is rather hard: for this purpose the raised temperatures (at which sublimation of the basic substance ZnS begins), and also long calcinations are required. Thus, as it will be shown further, Sb_2S_3 impurity even in insignificant quantities, extremely negatively affects properties of coatings

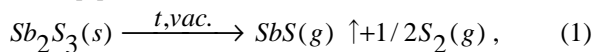
Table 1

Results of XRDA of specimens of ZnS(ZnO) – Sb₂S₃ – Ge system

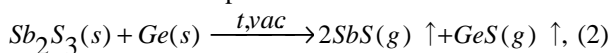
No of specimen	Chemical composition	Phase composition, coloring	
		Sintered (a)	Residue after evaporation (b)
1	ZnS(ZnO) (SHS product)	ZnS (sfalerite) ZnS (wurtzite), <i>yellowish</i>	–
2	ZnO - Sb ₂ S ₃ (3:1)	ZnS (sfalerite), <i>grey</i>	–
3	ZnS (ZnO-Sb ₂ S ₃ , 3:1) 1 mol. %	ZnS (sfalerite), <i>light–grey</i>	–
4	The same after prolonged distillation of the residues of Sb ₂ S ₃ at 800°C	ZnS (sfalerite) ZnS (wurtzite)-traces, <i>white with light greyish tint</i>	ZnS (sfalerite) ZnS (wurtzite)-small amount, <i>white with light greyish tint</i>
5	Sb ₂ S ₃ – Ge (1:1)	X-ray amorphous, <i>black</i>	
6	ZnS(ZnO) – (Sb ₂ S ₃ – Ge, 1:1)	ZnS (sfalerite) ZnS (wurtzite)- traces, <i>white with light greyish tint</i>	ZnS (sfalerite) ZnS (wurtzite)- small amount, <i>white with light greyish tint</i>
7*	ZnO – Ge	ZnO (wurtzite) Ge (cub.) Zn ₂ GeO ₄ (small amount – 1-2%), <i>dark-grey</i>	ZnO (wurtzite) Ge (cub.) Zn ₂ GeO ₄ (large amount up to –50%), <i>grey with black inclusions</i>
8	ZnS (specimen No3) – Ge	ZnS (sfalerite) ZnS (wurtzite)-traces, <i>white with light greyish tint</i>	ZnS (sfalerite) Ge (cub.), <i>grey with black inclusions</i>

*evaporator is destroyed during the test

produced from ZnS (owing to considerably high volatility of Sb₂S₃ compared to ZnS in vacuum). Ways of the solution of a problem, connected with necessity of removal of the rests of sulfidizing additives, study of systems ZnS-Ge [9] and ZnSe-Ge [10] has prompted. It has been established that evaporation process in vacuum of composites of the resulted composition is carried out at lower temperatures than each of its components separately, owing to the CVD ("Chemical Vapor Deposition")-mechanism. It consists in interaction between components with formation of volatile products with the subsequent condensation and a recombination of components, but already in the nano-sized form. This concept is applicable only in the case, when volatility of products is higher, compared to volatilities of initial components. Actually, process of evaporation of Sb₂S₃, is accompanied by thermal decomposition under the scheme [8]:



Subsulfide of SbS composition is stable only in a gaseous phase, but its volatility is higher, than of initial compound. Therefore, at addition of Ge to Sb₂S₃, process of their common evaporation under the scheme:



should be energetically more favorable. Actually, it is experimentally established that composite Sb₂S₃-Ge

evaporates at much lower temperature (approximately at 400°C), than Sb₂S₃ (about 600°C). Preliminary study of interaction between components of composite has made possible establishing the fact of its course just in a solid state: formation of an X-ray amorphous composite in this case, obviously, is caused by propensity of investigated system to vitrification [11].

So, addition of small amounts of Ge to zinc sulfide cleaned from an oxide impurity by means of additive of Sb₂S₃ has made possible to solve a problem of removal of excess amount of last at much lower temperatures and for not so long period of time. The product of almost clear white color, phase homogeneous (cubic phase) and practically without impurity (tab. 1) is as a result received. Small traces of residual germanium in sample of ZnS, as show earlier researches, should not affect properties of coatings produced from it negatively.

For influence check of oxide impurity in ZnS on behavior of additives of Germanium, study of properties of composites ZnO-Ge and ZnS(cleaned)-Ge, where as ZnS(cleaned), the material cleaned of an oxide impurity and of an sulfidizing additive is meant, is carried out. In case of the first of the specified systems presence in a composite, in addition to initial components, also of traces of compound Zn₂GeO₄ (tab. 1) is established; the last, most likely, is formed at the interaction of Germanium dioxide present on a surface of grains of Germanium powder with ZnO.

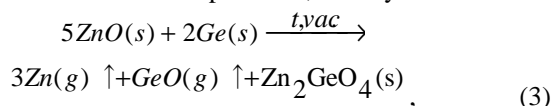
Table 2

Optical and operational properties of the thin-film coatings, produced by the thermal evaporation in vacuum of the specimens of ZnS(ZnO) – Sb₂S₃ – Ge system

No of the specimen (see tab.1)	Physical thickness, d, nm	Refractive index, n / λ, nm	Scattering factor, σ, %	Mechanical durability, rotations / group
1	667		0.26	6500/0
2	975	2.43/550		2000/2
3	1198	2.36/550	0.10	1500/3
5	631	2.78/550	0.026	4500/0
6	712	2.32/551	0.03	30000/0
7**	651		0.55	5500/0
8	527	3.17/750	0.68	15000/0
ZnS(ZnO) (SHS product) – Ge	726		0.10	2000/2 (10000/0*)

*a single case, **evaporator is destroyed during the test

In most cases the phase composition of the residues after evaporation changes a little in comparison with initial samples, unless parities between phases. The most essential change of phase composition is observed in case of the sample No 7 (ZnO-Ge system): after test by thermal evaporation in vacuum the content of phase Zn₂GeO₄ sharply increases. Probably, it is revelation of features of evaporation of a composite which occurs under the scheme, essentially distinct from that for composites of other compositions, namely:



Thus, process of evaporation of the sample of ZnO-Ge system should be far from congruent one that leads to accumulation of Ge and reduction of the content of ZnO in the residue after evaporation.

A product of sulfidizing of ZnO by means of Sb₂S₃ (the sample No 2), and ZnS cleaned from ZnO impurity in the same way (the sample No3), show the lowest mechanical durability. Fault to it, most likely, is because of residual presence of sulfidizing agent Sb₂S₃ which forms mechanically "weak" layer between ZnS coating and a substrate. Thus worth noticing that the coating produced from composite Sb₂S₃-Ge (the sample No 5) possesses a rather high (in comparison with that of Sb₂S₃) mechanical durability and an optical transparency; probably, it is provided with nano-sized Germanium in a coating which is formed as a result of reaction, return to scheme (2).

The coatings produced from carefully cleaned both from impurity ZnO, and sulfidizing additive Sb₂S₃ (samples Nos 4, 6), show an extremely high mechanical

durability (especially from the sample No 6) and low factor of scattering. Though mechanical durability and an optical transparency a little decreases under the influence of a Germanium additive to cleaned ZnS (the sample No 8), they are high enough even in comparison to a similar composite on the basis of ZnS (a SHS product). Even a coating produced from ZnO-Ge composite (the sample No 7) shows rather high optical and operational properties though adaptability to manufacture of the sample for resistive evaporation is rather doubtful (the evaporator has been destroyed during the process). Values of refractive indices of coatings (tab. 2), as a whole, depend on degree of cleaning of initial components of composites a little, and rather - on gross-composition of the composite.

Conclusions

1. Product of self-propagating high-temperature synthesis of zinc sulfide contains a rather sufficient amount of oxide admixture affecting negatively the properties of the material.
2. Interaction of ZnO with the alloying additive of Sb₂S₃ makes possible to eliminate undesirable oxide admixture. Residual traces of the alloying additive can be eliminated by CVD-reaction with germanium.
3. Zinc sulfide cleaned consecutively from oxide admixture with the additives of antimony sulfide and germanium exhibits very high operational and optical properties in thin-film coatings produced and is prospective for IR interference optics.

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Вплив взаємодії у системі ZnS (ZnO)-Sb₂S₃-Ge на параметри отримуваних тонких плівок

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Досліджено обмінні реакції домішки ZnO у сульфіді цинку з добавками Sb₂S₃ і Ge методами РФА, ІЧ спектроскопії й електронної спектроскопії дифузного відбиття. Установлена можливість повного сульфідуювання ZnO сульфідом стибію з одержанням однофазного продукту – сфалериту ZnS. Взаємодія в підсистемі Sb₂S₃ – Ge призводить до утворення склокристалічного композиту. Випробування очищеного від оксидної домішки ZnS, а також композитів ZnS – Ge та Sb₂S₃ – Ge термічним випаровуванням у вакуумі дозволило одержати тонкоплівкові покриття з високими оптичними й експлуатаційними параметрами.

Ключові слова: сульфід цинку, оксид цинку, домішка, легуюча добавка, сульфід стибію, германій, структура, оптичні властивості, тонкоплівкове покриття.