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AMORPHOUS NANO-STRUCTURED COATINGS PREPARED FROM CVD-COMPOSITES

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The main idea of the work is the development of a cheap and easy method for the manufacture of nanostructured systems based on the Chemical Vapor Deposition (CVD). Beginning with a new class of materials for interference optics in the infrared (IR) range of the spectrum, the evaporation of composites of systems germanium-metal chalcogenide (oxide), in particular, of the Ge-ZnS and Ge-Sb₂Se₃ systems was studied. They evaporate in vacuum congruently, and upon condensation on substrates form nano-structured thin-film coatings. In the first of these systems, the coating has an X-ray amorphous nature: the formation of a nano-dispersed composite in a Ge-ZnS film is confirmed by the absence of characteristic peaks of Ge and ZnS in X-ray diffraction patterns, but the formation of a characteristic halo takes place. At the same time, upon evaporation and condensation of a sample of the Ge-Sb₂Se₃ system, a glassy structure is formed; this is confirmed by high-resolution transmission electron microscopy (TEM), where no crystalline regions were found. The energy-dispersive X-ray (EDX) spectroscopy measurements of the coating (about 10 at.% of Ge, 40 at.% of Sb and Se, respectively) indicate a certain deviation from the stoichiometry compared to the initial sample of the system. This may indicate a slightly lower volatility of germanium selenides compared to antimony selenides. The EDX line scans along the cross-section of the coating exhibited strong fluctuations in the concentration of elements, and, consequently, the heterogeneity of the coating in terms of composition. Both coatings have high mechanical strength (group 0). At the same time, their optical properties differ significantly: the refractive indices are 3.00 and 3.66 for the Ge-ZnS and Ge-Sb₂Se₃ systems, respectively. It is believed that nano-structuring in the above systems is due to the high capability of germanium to amorphize upon condensation on a glass substrate.

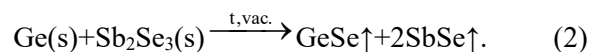
Keywords: CVD-mechanism, composite, amorphous nano-structured coating, optical properties, mechanical durability

INTRODUCTION

The main idea is to invent a cheap and simple way to manufacture nanostructured composite materials based on the germanium-metal chalcogenide (oxide) system, which will contribute to the creation of a new class of materials for interference optics in the infrared (IR) spectral range.

CVD-composites are a new class of materials based on germanium-metal chalcogenide (oxide) systems, such as Ge-ZnS, Ge-Sb₂Se₃, Ge-GeO₂, etc. They are named so due to the peculiarities of the evaporation mechanism: their characteristic feature is the almost congruent nature of evaporation in

vacuum, i.e. they behave as compounds, for example:



Thus, CVD-composites have higher volatility compared to individual components. At a sufficiently high temperature (900 K and 600 K for the above-mentioned systems, respectively), the starting components react with each other with the formation of more volatile compounds and substances. During the condensation on a substrate, there is the regeneration of the starting components, for example, in reaction (1) in the form of a nanostructured composite (completely

or partially). Alternatively, in some cases, for example in reaction (2), the amorphization of the components occurs at the stage of preparation of the CVD-composite. Therefore, volatile components in such systems can store themselves for a long time. One of the reasons for this behavior is the extremely high capability of germanium to amorphize in the thin-film state: in fact, the germanium coating exhibits a pronounced “blue” (hypsochromic) shift of the transmission region in the short-wavelength range. Based on this, the average size of germanium nanoparticles in the coating was estimated as 5.7 nm [1].

EXPERIMENTAL

Experimental methods such as thermal evaporation in vacuum with measurement of optical and operational properties of the films, XRPD (X-Ray Powder Diffraction), TEM (Transmission Electron Microscopy), EDX (Energy-Dispersive X-Ray) spectroscopy were used in this work. Tests of samples of the systems studied were performed by thermal evaporation in vacuum (resistive version) on the installation VU-1A from molybdenum evaporators (shuttles) at a heating current up to 130 A at a residual gas pressure up to 10^{-3} Pa with a coating rate of 40–250 nm/min. Thin-film

coatings of evaporating materials were applied to substrates of different materials (optical glass K8, quartz, germanium) and shapes (plane-parallel and wedge-shaped plates). The optical (refractive index) and operational (mechanical durability, climatic stability) parameters of the coatings applied to the substrate were also determined. The value of the optical thickness nd , where n is the refractive index, d is the physical thickness of the coating was 1.5–2.5 μm . The determination of n of the coatings was performed on a micro-spectrophotometer MFSU by studying the reflection on wedge-shaped plates coated with it. The mechanical durability was determined on an SM55 installation by the number of rotations of the disk before scratches on the thin-film coating appear. The X-ray diffraction was performed on an automated DRON-3M installation with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) by the powder method.

The nano-structuring of the composite Ge-ZnS during the evaporation and subsequent condensation on the substrate is confirmed by X-ray diffraction (Fig. 1 *a*): the diffraction pattern of sintered composite Ge-ZnS clearly shows peaks corresponding to its original components.

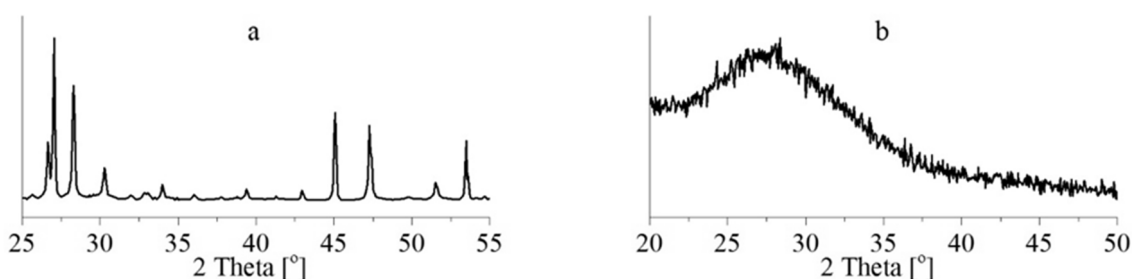


Fig. 1. Patterns of diffraction spectra of a CVD-composite Ge-ZnS (*a*) and coating (*b*) manufactured of it

At that moment the diffraction pattern of the coating is an unstructured curve with a halo over the entire range of Bragg angles (Fig. 1 *b*). We observe the same picture both in the case of the initial sample of the Ge-Sb₂Se₃ system and for the coating made of it.

The structure of the Ge-Sb₂Se₃ layer additionally was studied by the TEM [2] using a JEOL JEM-2200FS [3]. The high-angle annular dark field detector (HAADF) used in TEM scanning mode mainly collects Rutherford

scattered electrons and therefore exhibits elemental contrast. Fig. 2 shows the cross-section of the sample, which reveals layers of several tens of nanometers with different elemental compositions due to variations in the contrast. However, changes in concentrations could not be resolved by EDX measurements (Fig. 3). The line scanning showed strong fluctuations in Ge, Se and Sb concentrations, even though the measurement time was chosen sufficiently high for individual spectra to have a

good signal to noise ratio. High-resolution TEM confirmed the amorphous nature of the coating obtained by thermal evaporation in vacuum of the CVD-composite $\text{Ge-Sb}_2\text{Se}_3$, where no crystalline regions were found.

The elemental composition of the coating is ~ 40 at.% for Sb and for Se, and about 10 at.% for Ge, and practically does not change within its thickness (Fig. 3 b).

Only when reaching the surface of the glass substrate, there is a characteristic leap in the content of Si and a decrease to zero in the content of the above-mentioned components. As for the elemental composition, according to the data [4], the coating should be glassy. In addition, a significant decrease in the Ge content in the coating

compared to the starting material (about 17 at. %) indicates a higher volatility of the antimony selenides compared to GeSe [5, 6].

The results of studying the properties of coatings [6] indicate the following values: refractive indices $n(500 \text{ nm}) = 3.00$ and $n(940 \text{ nm}) = 3.66$, short-wavelength limits of the optical transparency region $\lambda_1 = 430 \text{ nm}$ and $\lambda_1 = 890 \text{ nm}$ for Ge-ZnS and Ge-Sb₂Se₃, respectively, and the mechanical durability – group 0. As can be seen from the Table, the value of the relative volatility $f = d/\tau^2$ for the system Ge-Sb₂Se₃ is much (8.6 times) larger than that for the Ge-ZnS system.

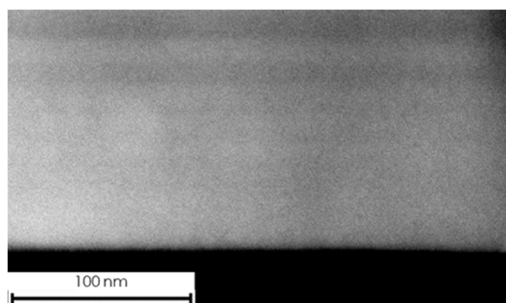


Fig. 2. TEM image of a CVD-composite $\text{Ge-Sb}_2\text{Se}_3$ coating on a glass substrate

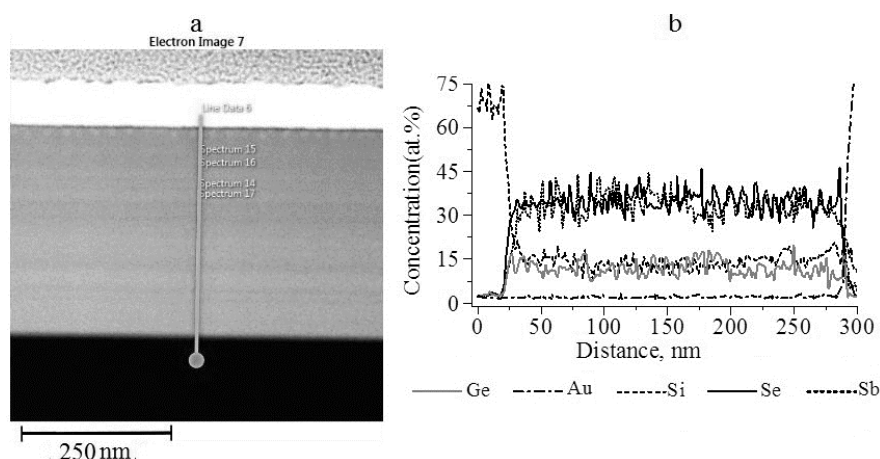


Fig. 3. TEM image (a) and corresponding EDX line scan (b) for coating deposited from $\text{Ge-Sb}_2\text{Se}_3$ CVD-composite on a glass substrate

Table. Evaporation regimes and optical and operational properties of the coatings from the CVD-composites

System	Evaporation regime			$f \cdot 10^3$	$n(\lambda)$	$\lambda_1, \text{ nm}$	Adhesion	Mechanical durability, rot/group
	$I, \text{ A}$	$\tau, \text{ min}$	$d, \text{ nm}$					
Ge-ZnS	130	20	793	2.35	3.00	~ 430	+	8000/0
Ge-Sb ₂ Se ₃	110	2	493	20.2	3.66	890	+	7000/0

Qualitative correlation between the values of the short-wavelength limits of the optical transparency region (λ_I) and the refractive indexes of the coating takes place according to the Moss rule [7]:

$$\lambda_I / \lambda'_I = (n_1/n_2)^4. \quad (3)$$

The coatings have quite good performance properties, in particular, high mechanical strength (group 0).

CONCLUSIONS

A new method for obtaining nanostructures from germanium-metal chalcogenide composites has been proposed. Coatings produced by thermal evaporation in vacuum and condensation

on a glass substrate have different degrees of amorphization – from X-ray amorphous (Ge-ZnS system) to glassy (Ge-Sb₂Se₃ system). The content of elements in the coatings qualitatively corresponds to the content of the original composite, but there is a certain deviation from the stoichiometry.

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Аморфні наноструктуровані покриття, виготовлені з CVD-композитів

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Основна ідея роботи – це розробка дешевого та простого способу виготовлення наноструктурованих систем, що базуються на випаровуванні композитів систем германій – халькогенід (оксид) металу за CVD (Chemical Vapor Deposition) – механізмом із започаткуванням нового класу матеріалів для інтерференційної оптики ІЧ (інфрачервоного) діапазону спектра. Як приклади досліджено системи Ge-ZnS та Ge-Sb₂Se₃, які випаровуються у вакуумі конгруентно, а при конденсації на підкладці утворюють наноструктуровані тонкоплівкові покриття. У першій зі систем покриття має рентгеноаморфний характер: утворення нанодисперсного композиту у плівці Ge-ZnS підтверджується відсутністю властивих для Ge та ZnS піків на рентгенівській дифрактограмі, натомість має місце утворення характерного гало. У той же час при випаровуванні та конденсації зразка системи Ge-Sb₂Se₃ утворюється склоподібна структура; це підтверджується методом просвічуючої електронної мікроскопії (ПЕМ) високої роздільної здатності, якою не виявлено області кристалічності. Вміст компонентів у покритті, визначено методом енергодисперсійної рентгенівської (ЕДР) спектроскопії (біля 10 ат. % Ge, по 40 ат. % для Sb і Se, відповідно), вказує на певне відхилення від стехіометрії, властивої для вихідного зразка системи. Це може свідчити про децю нижчу легкість селенідів германію у порівнянні з селенідами стибію. Сканування вздовж певної лінії (ЕДР) за товщиною покриття вказує на сильні флуктуації концентрації елементів, а отже – неоднорідність покриття за складом. Обидва покриття мають високу механічну міцність (група 0). У той же час їхні оптичні властивості суттєво різняться: показники заломлення становлять 3.0 та 3.66 для систем Ge-ZnS та Ge-Sb₂Se₃, відповідно. Вважається, що наноструктурування у зазначених вище системах зумовлено високою здатністю германію до аморфізації при конденсації на скляній підкладці.

Ключові слова: CVD-механізм, композит, аморфне наноструктуроване покриття, механічна міцність, оптичні властивості

REFERENCES

1. Zinchenko V.F., Sobol' V.P., Sviridova O.V. Structural and spectral features of Germanium – based interference optics for infrared range of spectrum. *Phys. Chem. Solid State*. 2012. **13**(1): 197.
2. <https://www.jeol.co.jp/en/science/em.html>.
3. <https://www.jeol.co.jp/en/products/detail/JEM-2200FS.html>.
4. Bletskan D.I. *Crystalline and glass-like Si, Ge, Sn chalcogenides and alloys based on them*. V.1. (Uzhgorod: VAT “Zakarpattia”, 2004). [in Russian].
5. Gerasimov Ia.I., Krestovnikov A.N., Gorbov S.I. *Chemical thermodynamics in color metallurgy*. V. VI. (Moscow: Metallurgii, 1974). [in Russian].
6. Zinchenko V.F., Chygrynov V.E., Magunov I.R., Stoyanov A.O. Effect of interaction in M_2Se_3 -Ge(M-In, Sb) systems on the properties on thin-film coatings. *Ukr. Khim. Zhurnal*. 2014. **80**(8): 96. [in Ukrainian].
7. Moss T.S. Relation between the refractive index and energy gap of semiconductors. *Phys. Stat. Solidi B*. 1985. **131**(2): 415.

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