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Structural and Spectral Features of Germanium – Based Interference Optics for Infrared Range of Spectrum

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In fabrication of the optical elements with clarifying coatings germanium is used in a double role – both as a substrate in optical structure and in the form of a layer in interference coating. It is established, that even in case of condensation on heated substrate Ge layer becomes completely amorphous. The gypsochromic shift of the edge of absorbency from 1.8 to 0.9 micrometers is observed, and the average diameter of the nanoparticles (5.7 nm) is estimated. It was established that in the range of spectrum from 7.5 to 11.5 micrometers Fresnel reflection is practically nullified due to clarifying coating and this has allowed increasing transmission to more than 95 %, (till 98 % in the range of Ge maximum transparency), i.e. it exceeded value for Ge substrate more than twice. Tests of coating operational properties confirm its high mechanical durability (group 0), thermal and climatic firmness.

Keywords: germanium substrate, Fresnel reflection, refractive index, clarifying coatings, nanostructure

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Introduction

Infrared (IR) spectrum range is an interesting and important field for working out of photo-electronic sensor controls, and also optically active devices, in particular IR - lasers and their combinations. It is caused by the existence in IR range of so-called atmosphere „transparency window" (8 – 14 micrometers), in which there are drama events of "hotbed effect" ($l_{\tilde{N}\hat{I}_2}$ = 10.6 micrometers) and other global phenomena. The passive infrared optics is based principally on optical structures from elemental germanium of high (semiconductor) purity and of deep (mirror) surface processing. Germanium has transparency domain (transmission is not below 30 % for a plate of 2 micrometers thickness) in a range of 1.8 – 23 micrometers [1]. However, because of a high refractive index (n = 4.14 at λ = 1.8 micrometers), transmittance of Ge plate does not exceed 50 % (at λ = 5.0 micrometers) because of considerable losses on Fresnel reflection:

$$R = \frac{(n-1)^2 + n^2k^2}{(n+1)^2 + n^2k^2} \qquad (1)$$

where κ is index of absorption. Thus, entirely dielectric reflectance equals to:

$$R = \frac{(n-1)^2}{(n+1)^2} = (3/5)^2 \approx 0.36, \qquad (2)$$

i. e. 36 %

The rest of the optical losses are due to optical absorbance in the plate.

It causes necessity of drawing on a Ge substrate (a plane-parallel plate or a lens) special anti-reflecting (clarifying) coatings. They consist of alternating layers of materials with high (n_h) and low (n_l) refractive indices (including a substrate), and the optimum ratio between them should satisfy the following relation:

$$n_h = n_l^2. \qquad (3)$$

I. Experimental and discussion

Optical elements with clarifying coatings on germanium were created by the method of thermal (either resistive or electron beam) evaporation in vacuum of ZnS, Ge, complex fluoride (Yb, Ce) F_3, as well as oxides of Y_2O_3 and HfO_2 (the latter are used as isolating layers of very low thickness, which did not effect on optical properties of the coating). The coating scheme was as follows: Ge (substrate) | Y_2O_3 | ZnS | Ge | ZnS | HfO_2 | (Yb, Ce) F_3 | Y_2O_3. Coatings were evaporated both on the cold substrate and substrate heated to 135 °C. In the latter case Ge layers turned out in X-ray

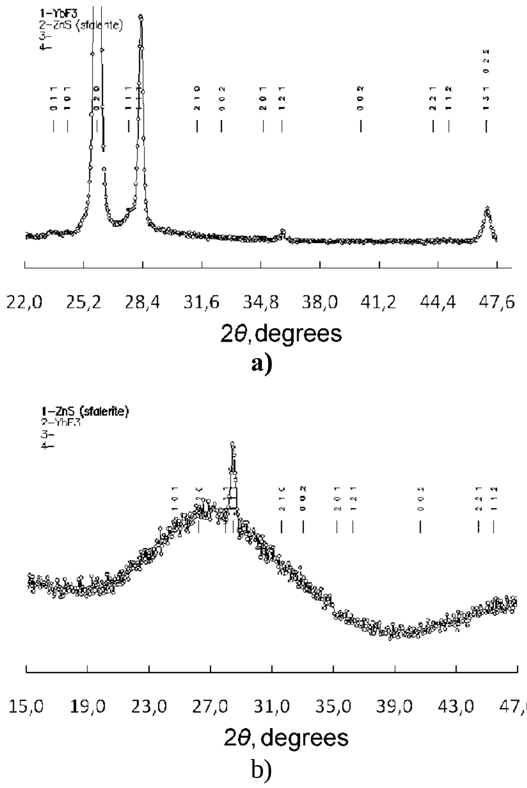


Fig. 1. Patterns of the X-ray diffraction spectra for the model of multilayered clarifying coating Y_2O_3 / ZnS / Ge / ZnS / HfO_2 / (Yb,Ce)F_3 / Y_2O_3, obtained by thermal evaporation in vacuum on the heated (135 ºC, a) and cold (b) substrates.

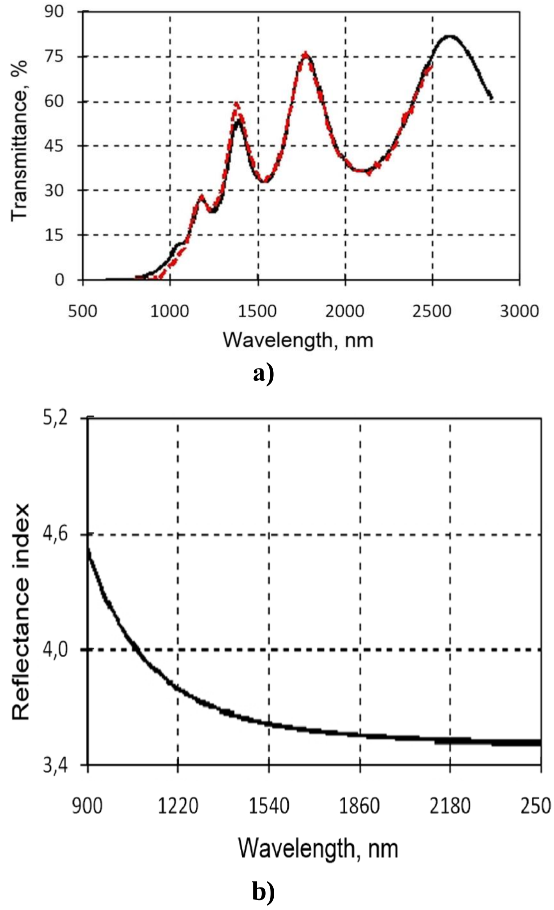


Fig. 2. Spectral reflectance (a) and refractive index (b) of Ge monolayer at various wavelengths: dashed (red) line – experiment, solid (black) line – calculation.

amorphous state, and the others – in crystalline (Fig. 1,*a*). When coating deposition was made on a cold substrate the most part of layers in coating turned out to be in X-ray amorphous (nanostructure) state (Fig. 1,*b*).

Thus, germanium is used in a double role – as a substrate in optical structure, and in the form of a layer in interference coating. It is established, that even in case of condensation on a heated substrate Ge layer becomes completely amorphous. Is of interest to establish, whether occur, and if occur, – in what direction, changes of optical properties of specified material at transition in nano – structural state. Fig. 2 represents spectral characteristics of reflection of Ge monolayer on optical glass, received by condensation on a cold substrate. As follows from the represented characteristic, the coating is transparent since 0.9 - 1.0 micrometers, i.e. the edge of transparency domain of nano – structural Ge reveals appreciable gypsochromic shift in comparison with macro crystalline material; change of band–gap width is ΔE_g = 1.30 - 0.68 = 0.62 eV. These values correspond to data of authors [2] for amorphous and crystallized coatings (1.05 and 0.65 eV, respectively). As follows from represented on Fig. 2 dispersion curve of refractive index of coating from Ge, value of n, peculiar to single - crystalline substance at λ = 1.8 micrometers, is reached at λ = 1.01 micrometers; at λ = 1.8 micrometers it is approximately 3.55. According to well-known Moss's [3] rule, the ratio between specified values should correspond to the following expression:

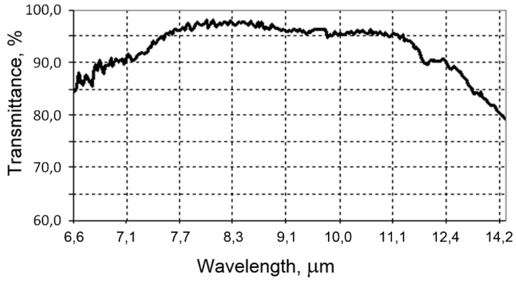
$$\frac{E_{g,1}}{E_{g,2}} = \frac{n_2^4}{n_1^4} \qquad (4)$$

Calculation shows, that the specified ratios are nearby 1.91 and 1.85, respectively, i.e. values are close to each other. Thus, the appreciable dimensional effect is observed for Ge in a coating that confirms its nano - structural nature. We attempted to estimate the average diameter ($\overline{D}$) of the nano - particles of the Ge coating, using the following relation:

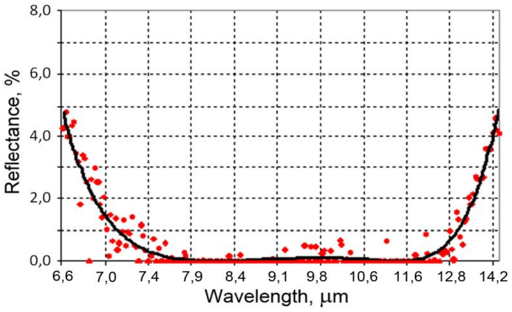
$$\overline{D} = \frac{h}{\sqrt{2\mu m_e \Delta E_g}} \qquad (5)$$

where h is Planck's constant, m_e is electron's mass, μ is effective electron – hole mass, which is defined by relation: $\mu^{-1} = m^{*-1}_e + m^{*-1}_h$, where m^*_e, m^*_h – effective masses of electron and hole, respectively [4]. Value of $\overline{D}$ is determined to be equal to 5.7 nm.

Fig. 3 represents spectral transmission curves of a plane–parallel Ge plate and reflection curves from one of germanium wedge surfaces with clarifying coatings. As follows from represented characteristics, in the range of spectrum from 7.5 to 11.5 micrometers Fresnel reflection is practically nullified, and this has allowed increasing



a)



b)

Fig. 3. Spectral characteristics of transparency for germanium parallel-sided plate (2 mm thick) with clarifying coatings on both sides (a) and reflection from one of the surfaces of germanium wedge with clarifying coating (b).

transmission to more than 95 %, i.e. to exceed more than twice value for Ge plate without clarifying coating. In the region of Ge maximum transparency, transmission of plate with coating exceeds 98 %. Tests of operational properties of the coating confirm its high mechanical durability (group 0) and adequate thermal and climatic firmness.

We have also investigated the possibility of usage zinc selenide, ZnSe in the coating instead of ZnS as the latter possesses insufficiently high transparency in IR range of a spectrum because of presence of oxide impurities [5]. Higher purity and transparency of ZnSe allows using it as a material for obtaining transparent (optical) ceramics. At the same time, the optical ceramics from ZnS, which producing was begun in the late eighties of last century, is translucent in a visible range because of various impurities. Coatings of ZnSe on germanium substrate were obtained by a thermal evaporation in vacuum. The coatings received from additionally purified ZnSe [6] possess absorption factor $k = (0.5 - 1.1)\cdot 10^{-4}$, i.e. 10 – 20 times lower in comparison with initial, crude samples.

Conclusions

1. The main material for IR optics, Germanium due to high optical losses on Fresnel reflection (more than 36%) needs in anti-reflecting (clarifying) coating.

2. Thermal evaporation of Ge in vacuum and its condensation either on cold or heated substrate produces an amorphous (nano-crystalline) coating, that results in gypsochromic shift of a band-gap energy about 0.6 eV and to respective decrease of the refractive index (from 4.14 to 3.55 at $\lambda = 1.8$ micrometers)

3. Use of clarifying coating allows increasing transmittance of the Ge plate from 45-50 % to 95-98 % in the range 7.5 ÷ 11.5 micrometers.

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Структурні та спектральні особливості германію на основі інтерференційної оптики для інфрачервоної області спектра

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При виготовленні оптичних елементів германій використано у подвійні ролі – як підкладку в оптичній структурі та у формі шару в інтерференційному покритті. Встановлено, що навіть при конденсації на підігріту підкладку шар з Ge стає цілком аморфним. Спостерігається гіпсохромний зсув порогу поглинання з 1,8 до 0,9 мкм, на основі чого оцінено середній діаметр наночасток (5,7 нм). Встановлено, що у діапазоні спектру від 7,5 до 11,5 мкм френелевське відбиття практично зведено до нуля завдяки просвітлюючому покриттю, що дозволило підвищити пропускання до більш ніж 95 %, (до 98% в області максимуму прозорості Ge), тобто його перевищено щодо підкладки з Ge більш ніж удвічі. Випробування експлуатаційних властивостей покриття підтвердили його високу механічну міцність (група 0), термічну та кліматичну стійкість.

Ключові слова: германієва підкладка, френелівське відбиття; показник заломлення; просвітлююче покриття; наноструктура