

**INVESTIGATION OF STRAINED LEAD SELENIDE NANOLAYERS****A. M. Pashaev<sup>1</sup>, O. I. Davarashvili<sup>2</sup>, M. I. Erukashvili<sup>2</sup>, Z. G. Akhvlediani<sup>2,3</sup>, L. P. Bychkova<sup>2</sup>, M. A. Dzaganina<sup>2,4</sup> and V. P. Zlomanov<sup>5</sup>**

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**DOI:** 10.5281/zenodo.55962**KEYWORDS:** defect annihilation model, low growth rates, refractive index, deformation, additional absorption limit, layer color, classification of layers.**ABSTRACT**

For a number of practical applications, it is necessary to fabricate strained nanolayers of IV-VI semiconductors with a high anisotropic deformation. There are presented the technological conditions for achieving the high deformations with thicker layers. Low layer growth rates were realized in accordance with the model of nonstoichiometric defect annihilation in dislocation nuclei causing their inhibition. When studying the optical properties, new approaches to the analysis of the refractive index variation with deformation and the determination of the absorption by free carriers. Additional absorption is sensitive to the concentration of free carriers in layers, and it is relatively low at the concentration of  $5 \cdot 10^{18} \text{ cm}^{-3}$ . In this case the forbidden gap width is determined more precisely with straightening of squared absorption coefficients.

**INTRODUCTION**

Nanolayers of different materials grown on substrates from foreign materials are often strained (in spite of some relaxation of strains with layer thickness growth) and possess new properties. This is true first of all for semiconductor materials designed for electronics. In particular, in previous works [1, 2] it was shown that strained lead selenide nanolayers are distinguished by a modified energy spectrum and associated changes in electrical and optical, and, with alloying, in thermal and mechanical properties. On the other hand, when PbSe nanolayers are grown on the substrates with the greater lattice constant BaF<sub>2</sub>, KCl and other, effective “negative” pressure causing the formation of completely new phases, including two-dimensional ones, could develop. Optical methods have a significant place in the investigation of the energy spectrum of current carriers. There were developed the methods of processing the optical transmission spectra with the aim of reconstruction of absorption spectra through the preliminary determination of refractive indices by interference maxima, and of reflection and absorption coefficients [3,4]. The forbidden gap width of the layers with different concentrations of current carriers was determined by straightening of the squared absorption coefficients with consideration of the degeneration of current carriers and the threshold of band-band absorption [5].

It is shown that, with decreasing layers thickness the spectrum shifts to the short wavelength side. Additional absorption was detected in the spectrum region between the basic absorption edge and the absorption by free carriers increasing with the wavelength [6]. The latter absorption is associated with indirect transitions between different branches of the allowed band and the absorption by defects at the substrate-layer heteroboundary which occur due to partial relaxation of strains. As follows from work [7], there had been no mention of additional absorption in IV-VI semiconductors before.

Besides the above-mentioned issues, in this work we also study and analyze the following: variation of the refractive index depending on the anisotropic deformation of layers, absorption by free carriers involving the data on their concentration and mobility, the range of additional absorption shift, etc.



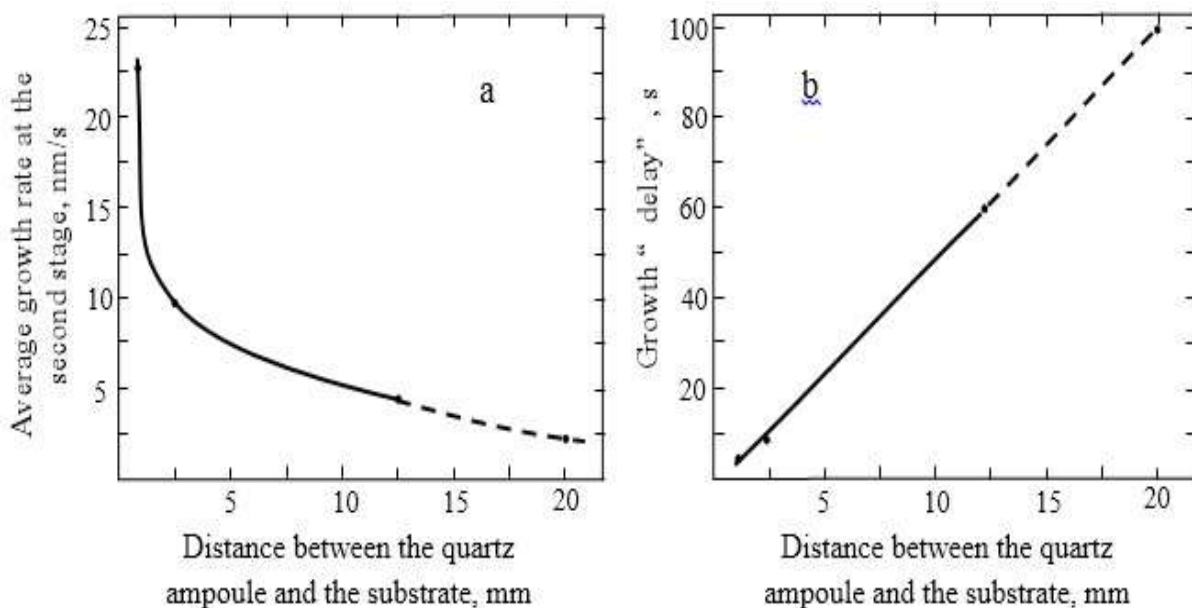
## EXPERIMENTAL

The strained lead selenide PbSe layers were grown by molecular epitaxy with “a hot wall” [8]. Polycrystalline PbSe was used as an epitaxy source, and KCl (100) was used as a substrate. The epitaxy source temperature varied over a range of 450-510°C, and the substrate temperature – over the range of 240-320°C. The growth rate of layers was varied by varying the temperature of the epitaxy source and the distance between the open end of the quartz ampoule with that source and the substrate from 1 to 12 mm. Thus the variation in the growth rate in the limits of 1-25 nm/s was achieved.

The thickness and the tangential lattice constant of layers were determined by the method of X-ray diffraction by using the  $CoK\alpha$  radiation and reflections from planes (200) and (400). The layer thickness was determined by the intensity ratio of reflections from planes (200) and (400) with the layer deposited on the substrate and without it. The tangential lattice constant was determined by the diffraction patterns recorded with reflection from plane (400). The concentration of current carriers and their mobility at 300K were determined by a four-probe method, they made up  $5 \cdot 10^{18}$ - $3 \cdot 10^{19} \text{ cm}^{-3}$  and  $5$ - $20 \text{ cm}^2/\text{V} \cdot \text{s}$ , respectively. We recorded the optical transmission spectra by using the two-beam prism-diffraction spectrophotometer SPECORD-75IR. Masks were used for calibration of the transmission scale.

## RESULTS AND DISCUSSION

The results of the investigation of lead selenide layers are presented by the example of the layer 70 nm thick. The tangential lattice constant of this layer is equal to  $a=6.175(5) \text{ \AA}$ , while the deformation referred to the PbSe monocrystal with the lattice constant  $a=6.126(4) \text{ \AA}$  is equal to  $\varepsilon=(a_1 - a_m)/a_m=0.008$ .



**Fig. 1** Dependence of the growth rate of PbSe layers (a) and the growth “delay” (b) on the distance between the open end of the quartz ampoule with the epitaxy source and the substrate

As mentioned above, the lead selenide PbSe layers were grown by molecular epitaxy with “a hot wall”. Earlier it was shown [3] that, due to the annihilation of nonstoichiometric defects in dislocation nuclei, the unrelaxed state with supercritical thickness of layers was obtained [9]. Considering the total displacement rate of nonstoichiometric defects and dislocations in the layer thickness, it turned out that deformations form effectively at low growth rates. Such conditions can be achieved at low temperature of the polycrystalline PbSe source and by increasing the distance between the open end of the quartz ampoule with the source and the substrate  $l$ , i.e. when the speed of bringing the evaporating PbSe molecules to the substrate decreases. The growth of layers proceeds in two stages. At the first stage, it takes nuclei-islands a lot of time to initiate and merge, this time is considered as the growth “delay”; at the second stage, when the deformation eventually forms, layer-by-layer



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growth of layers takes place. For the layer under consideration 70 nm thick, the temperature of the source equal to 470°C provided the saturated pressure of PbSe molecules at the level of vacuum of  $\sim 5 \cdot 10^{-6}$  mm Hg, and some excess of vacuum was obtained with the distance  $l$  of 12 mm. This led to the average growth rate of layers at the second stage equal to  $\sim 4.5$  nm/s.

*Table 1. Data on the refractive indices of the PbSe nanolayer ( $d=70$  nm) with consideration of its deformation and of the KCl substrate*

hv,eV	$N'(\text{PbSe})=N(\text{PbSe})+1$	$N(\text{KCl})$
0,285	5,50	1,470
0,304	5,66	1,470
0,310	5,71	1,471
0,316	5,76	1,471
0,322	5,81	1,471
0,329	5,87	1,471
0,335	5,93	1,471
0,341	5,99	1,471
0,360	6,10	1,472
0,378	6,19	1,472
0,397	6,25	1,473
0,415	6,28	1,473
0,434	6,33	1,474
0,453	6,33	1,474
0,456	6,33	1,474
0,459	6,33	1,475
0,462	6,33	1,475
0,465	6,33	1,475
0,471	6,33	1,475
0,477	6,33	1,475
0,484	6,33	1,475

According to the analysis, at least to achieve the same deformation  $\varepsilon=0.008$  in the layer 100 nm thick or the deformation  $\varepsilon=0.01$  in the layer 70 nm thick, the distance  $l$  must be increased to 20 mm, and the corresponding growth rate of layers at the second stage must be  $\sim 2$  nm/s. When the growth rate decreases, the growth time factor is less pronounced: the annihilation of defects in dislocation nuclei keeps up with their displacement. In Fig. 1a, b is shown the dependence of the average growth rate of layers at the second stage on the distance  $l$  (a), and the dependence of growth “delay” versus the distance  $l$  (b). When  $l$  increases up to 20 mm, the growth “delay” could make up  $\sim 100$  s (at the first stage, a layer  $\sim 10$  nm thick grows), and a layer, for instance, 70 nm thick will grow in 130 s (additional 30 s at the growth rate of 2 nm/s).



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*Table 2. Data on the absorption coefficients and their squared values for the PbSe layer (d=70 nm)*

hν, eV	λ, μm	T <sub>exp.</sub>	α, cm <sup>-1</sup>	α <sub>fr.car.</sub> , cm <sup>-1</sup>	α* = α - α <sub>fr.car.</sub> , cm <sup>-1</sup>	α* <sup>2</sup> = (α - α <sub>fr.car.</sub> ) <sup>2</sup> , cm <sup>-2</sup>	1/γ	(α̇) <sup>2</sup> = (α*1/γ) <sup>2</sup> , cm <sup>-2</sup>	(α̇·hν) <sup>2</sup> , cm <sup>-2</sup> eV <sup>2</sup>
0,285	4,348	0,190	101799	101461	338	1,14E+05	15,87	2,88,E+07	2,35E+06
0,304	4,082	0,195	87604	86890	714	5,10E+05	12,16	7,54,E+07	6,96E+06
0,310	4,000	0,195	83584	82718	866	7,50E+05	11,14	9,31,E+07	8,95E+06
0,316	3,922	0,194	80030	78816	1214	1,83E+06	10,22	1,91,E+08	1,91E+07
0,322	3,846	0,194	76211	75161	1050	1,10E+06	9,37	9,69,E+07	1,01E+07
0,329	3,774	0,193	72662	71612	1050	1,10E+06	8,61	8,17,E+07	8,82E+06
0,335	3,704	0,190	69286	68286	1000	1,00E+06	7,91	6,26,E+07	7,02E+06
0,341	3,636	0,188	66088	65166	922	8,50E+05	7,28	4,51,E+07	5,24E+06
0,360	3,448	0,181	58328	57543	785	6,16E+05	5,71	2,01,E+07	2,60E+06
0,378	3,279	0,174	51867	51307	560	3,14E+05	4,54	6,46,E+06	9,23E+05
0,397	3,125	0,168	46428	46125	303	9,18E+04	3,65	1,23,E+06	1,93E+05
0,415	2,985	0,162	42073	41886	187	3,50E+04	2,99	3,13,E+05	5,40E+04
0,434	2,857	0,156	38233	38069	164	2,69E+04	2,49	1,67,E+05	3,15E+04
0,453	2,740	0,152	35159	35005	154	2,37E+04	2,12	1,07,E+05	2,19E+04
0,456	2,721	0,152	34673	34530	143	2,04E+04	2,07	8,75,E+04	1,82E+04
0,459	2,703	0,151	34198	34065	133	1,77E+04	2,02	7,21,E+04	1,52E+04
0,462	2,685	0,151	33731	33609	122	1,49E+04	1,97	5,78,E+04	1,23E+04
0,465	2,667	0,150	33275	33163	112	1,25E+04	1,93	4,65,E+04	1,01E+04
0,471	2,632	0,147	35736	32296	3440	1,18E+07	1,84	4,01,E+07	8,91E+06
0,477	2,597	0,145	36582	31462	5119	2,62E+07	1,76	8,16,E+07	1,86E+07
0,484	2,564	0,143	37317	30661	6657	4,43E+07	1,69	1,27,E+08	2,98E+07

The optical characteristics of the PbSe layer were determined by the transmission spectra recorded at 300K. For the layer 70 nm thick, the spectrum is slightly increasing with the wavelength, with transmission T, and, at energy of 0.29-0.49 eV, the difference ΔT made up 0.04-0.05.



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Like our previous works, the transmission spectra were processed for attaining the ultimate goal of determining the forbidden gap width of the strained layer, but with consideration of the deformation dependence of the refractive index and new values of absorption coefficients by free carriers.

According to the model of Fabry- Perot interferometer, the equation for determination of absorption coefficients  $\alpha$  by the spectrum  $y=\exp(-\alpha d)$  was derived

$$T(r_1 r_2)^2 y^2 - [(1 - r_1^2)(1 - r_2^2) + Tr_1 r_2 - 4 Tr_1 r_2 \sin^2 (2\pi Nd/\lambda)]y + T=0 \quad (1)$$

To determine  $\alpha$  reflection coefficients by amplitude were preliminarily calculated

$r_1=(N_l - N_{air})/(N_l + N_{air})$ ,  $r_2=(N_l - N_{sub.})/(N_l + N_{sub.})$ , where  $N_l$ ,  $N_{air}$  and  $N_{sub.}$  are the refractive indices of the layer, air and substrate, respectively, at the corresponding wavelengths. The variation of the refractive reflection coefficients index with deformation can be determined by the relation  $dN/d\varepsilon=dN/dE \cdot dE/d\varepsilon$ , using the dispersion dependence of the refractive index in an unstrained PbSe layer [3, 10].

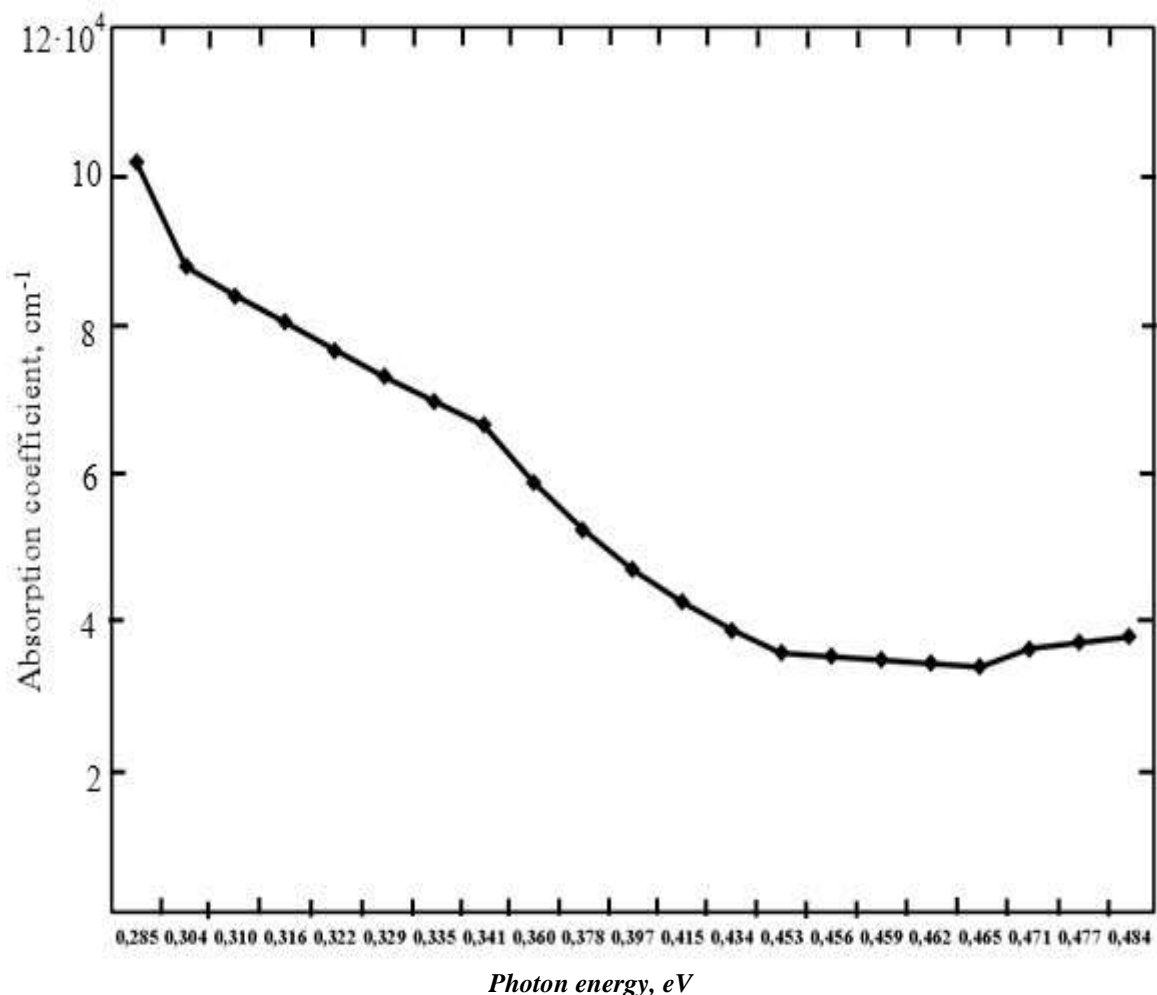


Fig. 2 Photon energy dependence of the absorption coefficient  $\alpha$

In a linear section of the dispersion dependence,  $dN/dE=5.7eV^{-1}$ . From optical investigations, the forbidden gap width of the strained layer 70 nm thick increases by 0.174 eV with deformation  $\varepsilon=0.008$ . Hence  $dE/d\varepsilon=22$  eV and  $dN/d\varepsilon=125$ . Then, with the same deformation  $\varepsilon=0.008$ ,  $\Delta N=+1$  at the energy higher than the forbidden gap width of the unstrained PbSe layer ( $E_g=0.286$  eV).



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Thus, for the strained PbSe, one adds to the values of the refractive index previously determined by interference maxima over the entire given spectrum. These data, along with the refractive indices, are given in Table 1.

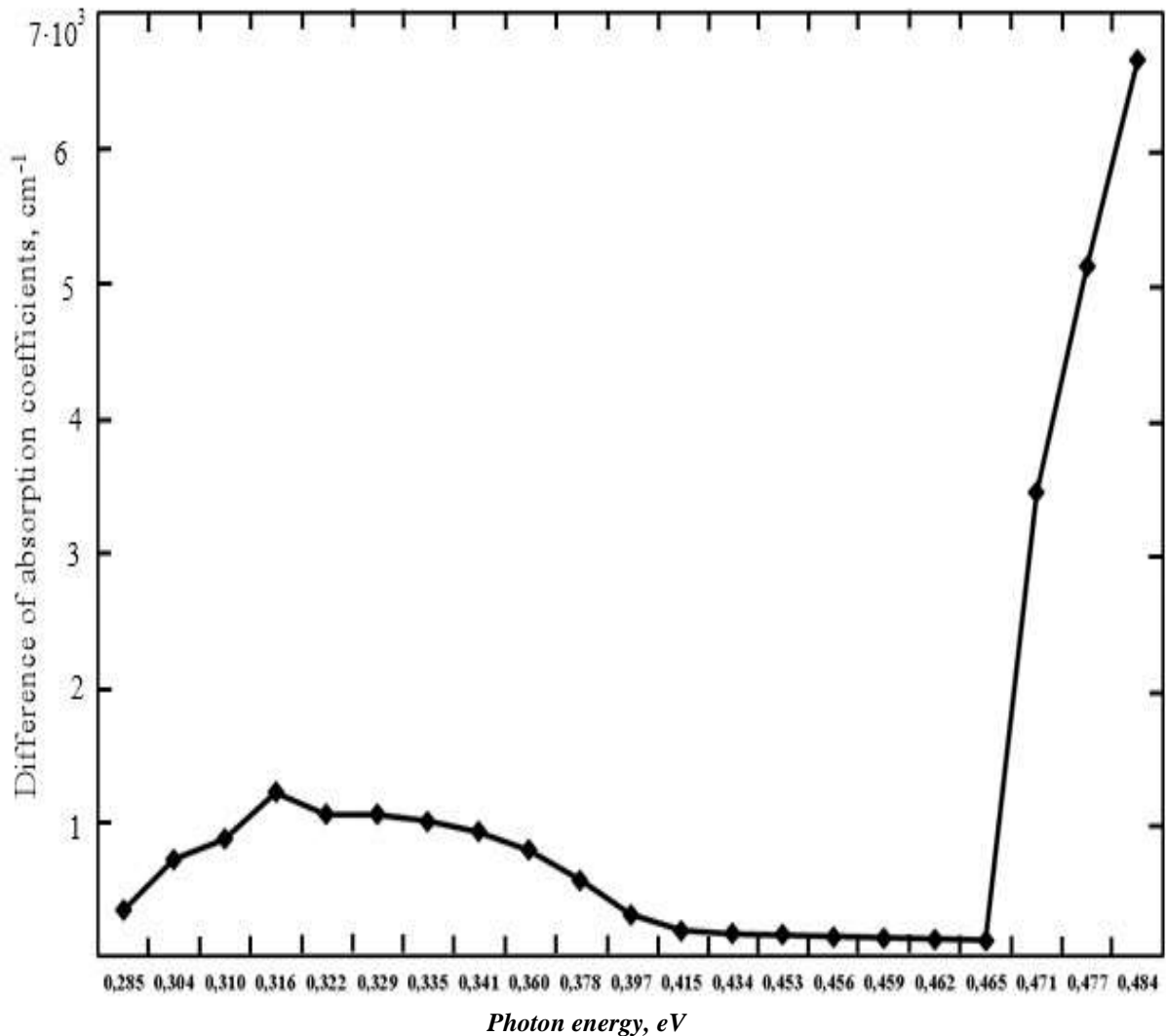


Fig. 3 Photon energy dependence of the difference of absorption coefficients  $\alpha - \alpha_{fr.car}$ .

The calculated reflection coefficients with new data on refractive indices were used for determining the absorption coefficient by Eq (1). In Table 2, along with these data, are given the absorption coefficients by free carriers calculated by formula

$$\alpha = e^3 n \lambda^2 / \pi c^3 \mu N m^{*2} \quad (2)$$

If in previous works the coefficient of relation  $\lambda^2/N$  was determined over the entire spectrum by equating of the absorption coefficient determined by Eq (1) to the absorption coefficient by free carriers, in this work the refractive index was determined by substituting the values of the concentration of current carriers  $n=5 \cdot 10^{18} \text{ cm}^{-3}$ , their mobility  $\mu=10 \text{ cm}^2/\text{V}\cdot\text{s}$ , and the effective mass  $m^*=0.06 m_0$  into Eq (2). Such a procedure is associated with the detection of additional absorption between the basic absorption edge and the absorption by free carriers. Due to the fact that the transmission in the experimental spectrum in the region of 0.285-0.484 eV varied within  $0.05 \pm 0.01$  and, as the analysis showed, it is impossible to obtain the difference of absorption coefficients  $\alpha - \alpha_{fr.car}$  of two hundred  $\text{cm}^{-1}$  or less in this case. It would be possible only if the transmission varied in this region within 0.20-0.25.



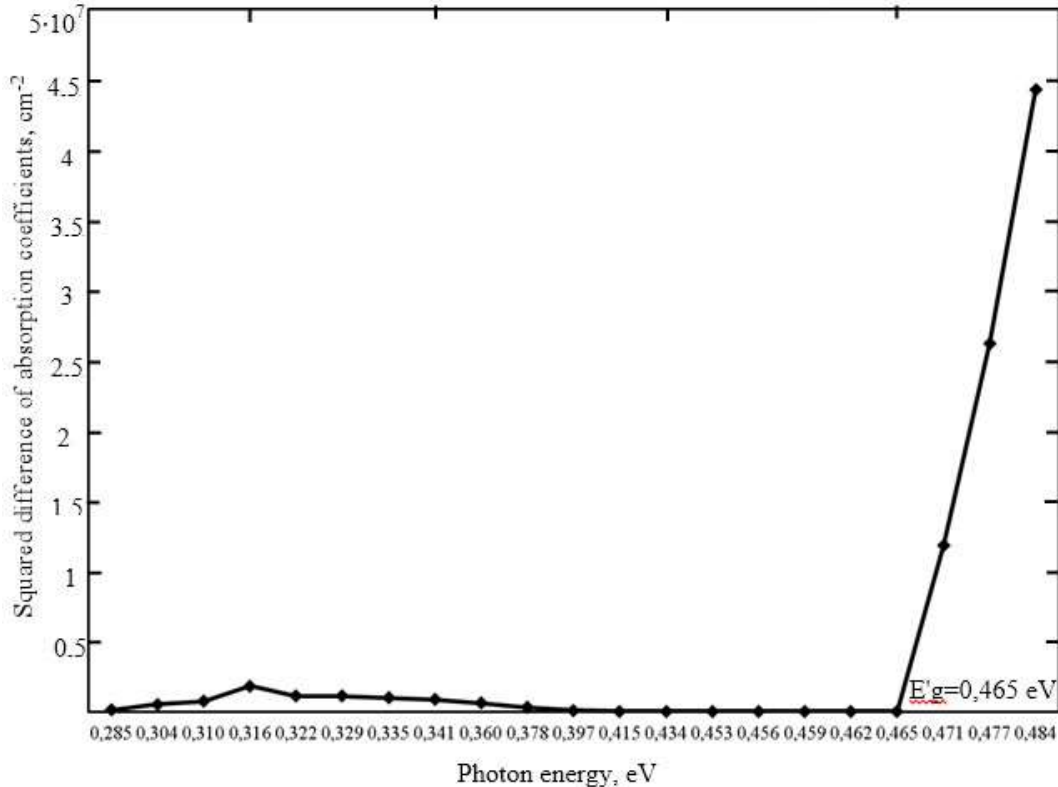


Fig. 4 Photon energy dependence of the squared difference of absorption coefficients  $(\alpha - \alpha_{fr.car.})^2$

This means that the additional absorption must be revealed in this case as well. To set the upper bound on the difference of absorption coefficients  $\alpha - \alpha_{fr.car.}$ , we adduce the following arguments: the absorption coefficient associated with additional transitions in the conduction band will firstly be less than the band-band one due to high density of states in the valence band exceeding the concentration of current carriers in the conduction band  $\sim 10^{19} \text{cm}^{-3}$ . Secondly, the spectrum shifts to the short wavelength side in nanolayers. Hence, even with addition of the absorption by the defects at the substrate-layer heteroboundary and with consideration of a strong dependence of the difference of absorption coefficients  $\alpha - \alpha_{fr.car.}$  on the transmission, the maximum value of this difference will be at the level of  $1,000-1,500 \text{cm}^{-1}$ .

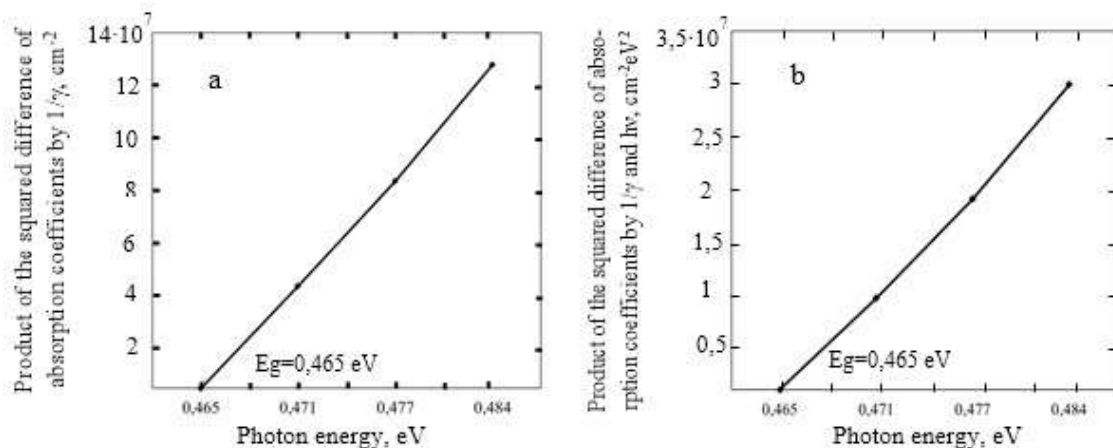


Fig. 5 Photon energy dependence of the product of the squared difference of absorption coefficients  $(\alpha - \alpha_{fr.car.})^2$  by  $1/\gamma$  (a), and by  $1/\gamma$  and  $h\nu$  (b) in the narrow spectrum region



It is obvious that the additional absorption increases with the concentration of free carriers, remaining on the whole lower than the basic band-band absorption. The data given in Table 2 were used to construct the relations  $\alpha=f(h\nu)$  and  $(\alpha-\alpha_{fr.car.})=f(h\nu)$  (Figs. 2 and 3). Low maxima of the additional absorption between the band-band absorption and the absorption by free carriers over the range 0.310-0.320 eV could point to the existence or emergence of a new level in the conduction band with deformation where the indirect transition from the basic minimum takes place.

Figure 4 shows the relation  $(\alpha-\alpha_{fr.car.})^2=f(h\nu)$ . The straightening of the squared difference  $\alpha-\alpha_{fr.car.}$  usually leads to the determination of the absorption edge, and, with degeneration, it looks like  $E_g + E_F$  (where  $E_F$  is the Fermi level). However, as is seen from Table 2 and straightening performed, from relations  $[(\alpha-\alpha_{fr.car.})1/\gamma]^2=f(h\nu)$  and  $[(\alpha-\alpha_{fr.car.})1/\gamma \cdot h\nu]^2=f(h\nu)$  (Fig. 5a,b), the value of  $E_g$  was equal to 0.465 eV in all cases. It should be noted, that the consideration of degeneration through the coefficient  $1/\gamma$  is made only in the region of the band-band absorption. Hence the straightening of the squared absorption coefficients is performed only in the narrow region of the spectrum. On the other hand, coincidence of the values of forbidden gap width by all types of straightening is associated with, besides the absence of degeneration, slight changes in the energy of radiation quanta in the given spectrum region. This also follows from the fact that the function  $1/\gamma$  takes on the value close to two in the vicinity of 0.465 eV (Table 2), i.e.  $E_F=0$ , at the concentration of free carriers  $\sim 5 \cdot 10^{18} \text{ cm}^{-3}$ , which corresponds to the results of work [11].

Finally, it should be noted that the strained PbSe layer 70 nm thick is of yellow color. In work [12] it is shown that the color of nanolayers is determined by imposing the interference peaks in accordance with the relation  $2\pi Nd/\lambda=n\pi$ , where  $n=1, 2, 3, 4, \dots$ . For the given layer, the first peak corresponded to the wavelength  $\lambda=0.58 \mu\text{m}$ , and the second – to  $\lambda=0.31 \mu\text{m}$ (ultraviolet).

In the formation of such a dependence, the refractive index at the wavelength of the first peak (corresponds to the yellow color)  $N_1=4.15$  plays an important role. Depending on the layer thickness in the range of 1120-68 nm, the color of the layers changed from metallic silver to transparent, and the deformation varied in the range of 0.0005 to 0.0084. Therefore, the color of the layers could be the primary characteristic of layers and a useful means of their classification by deformation.

## CONCLUSIONS

For achieving the high deformations in nanolayers, the growth rate of layers is decreased basically at the expense of increasing the distance between the open end of the quartz ampoule with the epitaxy source and the substrate, as the state temperature corresponds to the pressure of saturated PbSe vapor equal to the pressure in vacuum. When studying the optical spectra, the refractive index variation with deformation was assessed by analyzing the definite derivatives of the refractive index by energy, and the energy – by deformation. With the deformation  $\epsilon=0.008$ , in the nanolayer 70 nm thick, the refractive index over the spectrum higher than the forbidden gap width of the unstrained PbSe layer  $E_g=0.286 \text{ eV}$  increased by one.

The determination of absorption by free carriers via the experimental values of the concentration of free carriers led to relatively low additional absorption. Hence the forbidden gap width of the PbSe nanolayer is determined more precisely with straightening of the squared absorption coefficients and is equal to 0.465 eV.

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