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Abstract. The results of reservation of strained state in PbSe layers grown on KCl, BaF$_2$, NaCl, CaF$_2$ substrates during several years and revealing of the peculiarities of two-stage growth of layers, the creation of supercritical structures, the study of the broadening of elastic deformation at layers doping with impurities of varying valence show that it is reasonable to regulate in detail the strains (deformations) in nanolayers. For definite groups of layers with the thicknesses in the range of <100 nm and 100-200 nm, as well as at not high – 1 nm/s and high ≥10 nm/s rates of growth there appear the new means to control the deformations in PbSe nanolayers.

1.Introduction

For application of the supercritical strained PbSe layers at "negative" pressures suggested earlier in [1] for the solution of new technical problems, i.e. the development of high-temperature and high-sensitive photodetectors [2], it is interesting to consider the problems of interconnection of the thickness of layers and the rate of their growth with the deformations taking place in them [3]. PbSe layers were fabricated on BaF$_2$, NaCl, CaF$_2$ and KCl substrates with different mismatch. The special interest was caused by PbSe/KCl structures, as in this case maximal deformation of stretching was realized that will find new application in IR optoelectronic devices. The choice of the method of molecular epitaxy with a "hot-wall" [4-7] gives a possibility to control the rate of layer growth and to show the importance of this parameter for obtaining the maximum deformation also at the maximum thickness of the layer. The development of the method of controlling the growth of layers will additionally allow to define the peculiarities of their growth [8-9] and to investigate in detail the properties of layers at each step of the two stages of the growth. The investigation of these problems is the subject of the given work.

2. Experimental methods

For the planned investigations the layers of PbSe were obtained by the method of molecular epitaxy with a "hot-wall". The flux of molecules to the KCl (100) substrate is formed by heating of polycrystalline PbSe in the range of temperature 450-510^{0}C. KCl substrate was heated in the range of temperature 240-320^{0}C. The rate of growth was controlled both by the change of the temperature of the source of epitaxy and by the distance from the opened edge of quartz ampule with the source to the substrate in the range of 1-20 mm. The lattice constant of layers and their thickness, and the half-width of X-ray line were determined by registration of X-ray diffraction patterns at the reflection from (200),

(400) and (600) planes [10]. Deformation ε in PbSe layers was determined via the lattice constant of strained and unstrained layers of PbSe α_l and α_{PbSe} as $\varepsilon=(\alpha_l-\alpha_{PbSe})/\alpha_{PbSe}$. Electrical properties (concentration of current carriers and their mobility) of the layers were determined by Van der Paw method.

3. Results and discussion

PbSe layers with <200 nm thickness were mainly investigated.
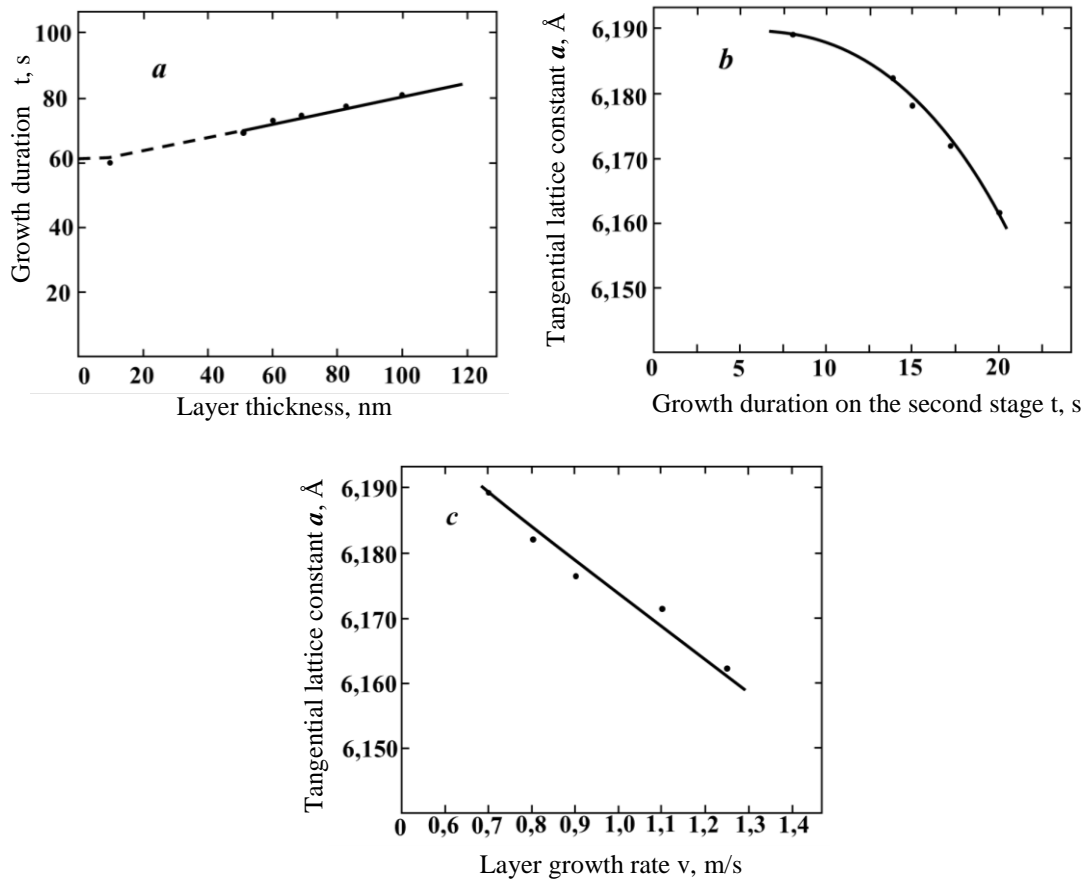
Figure 1. Dependence of tangential lattice constant and layer thickness on
growth rate and duration (*a*,b,c)

Figure 1a presents the dependence of the thickness of layers (with <100nm thickness) on the time of growth for specific regimes: at the temperatures of source 470^0C and of KCl substrate - 300^0C (320^0C) and at the distance from the open edge of quartz ampule to the substrate 12 mm. On the basis of such five layers in the row SL 742 – SL 763 the data are presented in the table. The duration of growth (t), depending on the thickness of layers, is limited to 60 sec at the decrease of the thickness of layer to 0, more exactly, to 10 nm, being the sensitivity of the X-ray method of measuring a thickness. Probably, the time 60 s for the specific conditions is the time of "delay" – corresponds to the first stage of growth. On the first stage, emerging and merging of nuclei islands, on the second stage – layerwise growth, their duration depends on the conditions of growth (temperatures of source and substrate, distance between ampule and substrate, mismatch). If we suppose that within the thicknesses of 100 nm, the second stage

of layerwise growth starts not at the thickness above 10 nm, but even at higher thickness, i.e. 40-50 nm, as the estimations show, this will cause the change of the full rate of growth – 0.1 nm/s. The similar investigations at the distance between the open edge of quartz ampule with the epitaxy source and the substrate equal to 1mm, 2.5 mm and 20 mm made it possible to determine the duration of the first stage of emerging and merging of nuclei islands – 2, 9, 100 s respectively [11]. For the layers SL 742-763 distance between ampule and substrate was 12 mm, for the layers SL 781-284 – 2.5 mm, for the layers SL 613, 616 – 1mm.

Table. Data on the conditions of growth and characteristics of strained
PbSe layers on the KCl(100) substrate

| N	Layer	Temperature of the source $T,^0C$	Temperature of the substrate $T,^0C$	Growth duration t, s	Layer thickness d, nm	Tangential lattice constant a, Å	Layer growth rate v, nm/s	X-ray dif. line half-width Δ, min	Relative mismatch-deformation $\varepsilon = \dfrac{a_l - a_{PbSe}}{a_{PbSe}} \cdot 10^2$
1	SL-742	470	300	80	101	6,162(3)	1,25	17	0,59
2	SL-758	470	300	77	83	6,172(1)	1,1	17	0,75
3	SL-756	470	300	75	68	6,178(4)	0,9	18	0,83
4	SL-751	470	320	74	59	6,185(8)	0,8	19	0,95
5	SL-763	470	300	67	48	6,188(2)	0,7	20	1,01
6	SL-781	470	240	10	35	6,210(2)	3,5	22	1,38
7	SL-783	470	240	13	98	6,145(6)	6,7	24	0,29
8	SL-215	450	240	300	189	6,129(7)	0,6	21	0,05
9	SL-578	470	240	30	181	6,149(0)	6,1	25	0,38
10	SL-284	470	240	15	175	6,136(7)	11,7	31	0,16
11	SL-613	510	240	11	204	6,138(8)	18,7	33	0,21
12	SL-616	510	240	19	435	6,131(9)	22,8	34	0,10

Such analysis allowed to determine the rate of layer growth at the second stage, with the exception of the thickness equal to 10 nm and the time of delay at the first stage equal to 60 s, as well as the rate of growth at the second stage ranged within 3.5-5.4 nm/s and the average rate was 4.5±1 nm/s. Thus, one can think that the deformation in layers connected with tangential lattice constant will be changed according to the growth duration at the second stage (the average rates of growth at the second stage are taken to be the same for all layers).

Figure 1b shows the dependence of tangential lattice constant on the growth duration at the second stage. It is seen that at the increase of growth duration from 7 to 20 s the tangential lattice constant decreases from 6.190Å to 6.160 Å. Within such an approach one can determine the dependence of tangential lattice constant on the full rate of layer growth. This rate of growth can be determined in two ways: by the relation of layer thickness to the growth time, and by the share of growth rates contributed at the first and the second stages.

For instance, the full average rate of growth can be estimated as the relation of growth rate 4.5 nm/s at the second stage (for layer SL – 742) to the value 0.9/0.25 – the resultant rate makes 1.25 nm/s and corresponds to the rate calculated from the relation 101(d)/80(t) = 1.25nm/s. It is important to note that 60s as a delay time is rough value (real is slightly more, Figure 1α). This is a result that in estimation was considered average value of the growth rate. The dependence of tangential lattice constant on the growth rate, presented in Figure 1c shows the decrease of the full growth rate with the increase of tangential lattice constant. This is connected with the fact that such result is achieved in the layer with the thickness of 48 nm (SL-763) and at the second stage a significantly less time is spent for the growth of this layer than in the case of SL-742 layer, when the full average rate of growth increases because of

more contribution of much higher rate at the second stage (with the increase of the rate 90 nm layer increases).

The following two layers on the table: SL-781 and SL783 (with the thicknesses $\leq$ 100 nm) are obtained at much higher growth rate at the expense of the decrease of the distance from the open edge of quartz ampule with the source of epitaxy to the substrate down to 2.5 mm. By way of example of these two layers it is seen that with the increase of growth rate, the layer SL-781 with the thickness of 35 nm is growing without transferring the elastic energy to the dislocations and its lattice constant reaches 6.210(2) Å and the deformation – 1.38×10^{-2}. For the layer SL-783 the thickness reaches 98 nm and, in this case, on the contrary, the nonstoichiometric defects have no time to retard the motion of dislocations and, correspondingly, the loss of layer energy increases and the lattice constant decreases to 6.145(6) Å, and the deformation decreases to 0.89×10^{-2}.
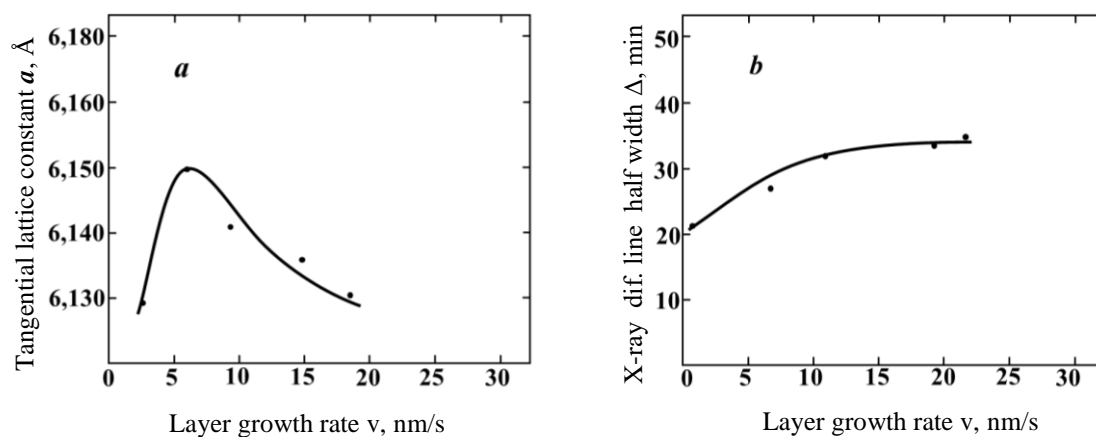

Figure 2. Dependence of tangential lattice constant (*a*) and X-ray dif.
line half-width(b) on growth rate

For the second group of layers SL-215, 578, 284, 613, 616 (mainly, with the thicknesses 100-200nm) the dependence of tangential lattice constant on the growth rate has of nonmonotonic character: at the full rate of growth 6nm/s it passes through the maximum with the slow decrease at the increase of growth (Figure 2*a*). With the increase of thickness of layers in the strained state, their elastic energy increases so that at the concentration of nonstoichio-metric defects 10^{18}- 5×10^{18} cm^{-3} is not sufficient to create barriers against the shifting of formation dislocations. This is well shown by SL-215 layer, when the lattice constant makes 6.129 (2) Å at the little rate of growth. With the increase of growth rate there appears the tendency of disordered distribution of dislocations, and the cloud of nonstoichiometric defects around the dislocations can retard their motion and the lattice constant reaches 6.149(0) Å at the 6 nm/s growth rate. With the further increase of growth rate, the breaks between the clouds appear, and on the other hand, with thickening of layers the dimensions of subgrains increase in them, and with the increase of growth rate - the mismatch on their boundaries increases as well. Conditions of the growth for all layers were found for receiving single-crystal layers.

The critical dimensions connected with such mismatch become less than the dimensions of subgrains themselves and besides the boundary substrate – layer there appears an additional channel for relaxation of strains. For the layer with 204 nm thickness (SL-613) the lattice constant decreases to 6.138(8) Å at the rate of growth 18.5 nm/s. Figure 2α shows how the mismatch between subgrains increases at the

increase of growth rate for the mentioned layer, i.e. the half-width of X-ray diffraction line reaches 33'(Figure 2b) .

In the case of layer SL-616, the mutual influence of mismatch between the subgrains and of breaks in clouds of nonstoichiometric defects on the decrease of lattice constant down to 6.131(9) Å at the growth rate 22.8 nm/s is illustrated. The deformation, probably, is kept up to the thickness 500 nm.
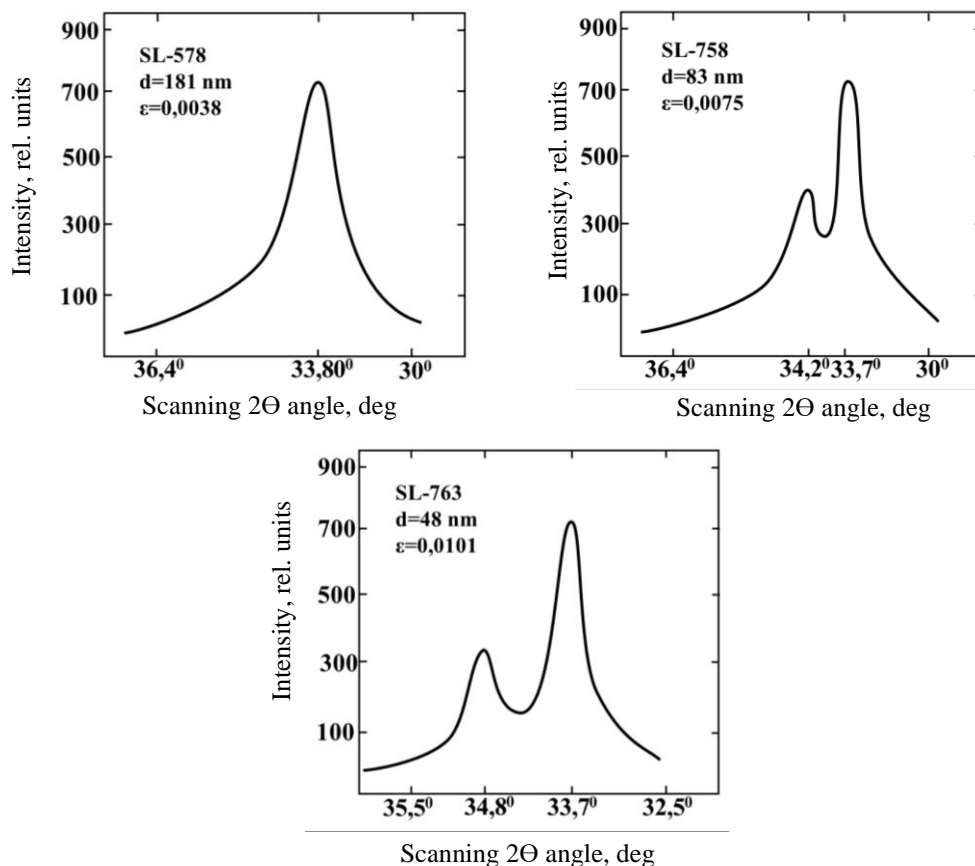
Figure 3. Diffractograms Ɵ-2Ɵ scanning of layers with different thicknesses

It is interesting to note, that comparing the data on layers SL-284 and SL-613, some increase of the lattice constant in the second case is connected with the detection of pores on the edge of SL-284 layer and its real thickness is higher than the mentioned above determined by X-ray method. The pores were revealed by optical microscopy.

Thus, for the second group of layers with high thicknesses the tangential lattice constant decreases and the increase of growth rate leads to its additional decrease because of less influence of nonstoichiometric defects (breaks in clouds) and because of relaxation of strains in subgrains. In general, at "negative" pressure, the deformation developed in the layer with 35 nm thickness, makes $1.38 \cdot 10^{-2}$, and for the layer with thickness, i.e. 70 nm – $0.8 \cdot 10^{-2}$.

Figure 3 presents the X-ray diffractograms 2θ of scanning from plane (200) for three PbSe layers of different thicknesses. For the thickness <100 nm the spectra are splitting and an additional peak appears at larger 2θ angles. The splitting between the main line and that of appeared again increases with the decrease of layer thickness – the increase of deformation. Such difference can be used for estimation of

deformation in layers. As the estimations show, at such deformations the pressure of 10-15 kbar is developed and the texture of tetragonal phase appears in the layer.

The investigations of the spectra of optical absorption of the strained PbSe layers plotted according the transmission spectra showed that the tetragonal phase in deformed PbSe layer leads to the appearance of a new level in the conduction band and to the additional absorption connected with it alongside with the main band-to-band absorption [12]. This peculiarity was also caused by strained nanolayers of lead selenide.

4. Conclusions

The influence of layer thickness and of the growth rate on the tangential lattice constant is considered for the thicknesses <100nm and 100-200 nm at the growth rate ~1 nm/s and ≥10nm/s. The peculiarity of the growth for the layers of <100nm and at the growth rates ~1 nm/s is that the tangential lattice constant can be controlled depending on the duration of growth at the second stage – the rate of shifting of nonstoichiometric defects is slightly slower than the rate of growth. With the increase of growth rate for the same thicknesses of layers, the rate of shifting of nonstoichiometric defects is already noticeably less than the rate of growth and the rate of shifting of dislocations and the lattice constants begin to decrease.

For the thicknesses of layers within 100 -200 nm, the dependence of tangential lattice constant on growth rate is of nonmonotonic character. In this case, with the increase of growth rate the disordered distribution of dislocations takes place and now they are retarded by the cloud of nonstoichiometric defects. The dimensions of subgrains and mismatch between them are increased leading to the additional relaxation of strains. In view of the fact that the rate of the transfer of elastic energy increases with the increase of layer thickness, it is reasonable to decrease the rate of delivery of evaporating molecules to the substrate, e.g., by a smooth increase of the distance from the open edge of quartz ampule with the source of epitaxy to the substrate. Wide possibilities of the regulation of the conditions of growth were allowed to choose two parameters: thickness and growth rate of the layers for the analysis of the process for reaching maximal deformations.

In nanolayers at the increasing deformations there appears a tetragonal phase leading to the appearance of a new level in the conduction band and to the additional absorption in the optical spectrum.

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