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STRUCTURAL TRANSFORMATIONS IN POLYCRYSTALLINE CADMIUM SELENIDE FILMS

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Study of crystalline structural types and their transformations is of considerable interest due to the effect of structural changes on the electrophysical properties of semiconductors.

Polycrystalline cadmium selenide films crystallize in a hexagonal modification with a wurtzite lattice (α -CdSe) and a cubic modification with a sphalerite lattice (β -CdSe) [1-5] or may contain both the cubic and hexagonal modifications [6]. Depending on the preparation conditions and subsequent treatment, the phase composition of the films in most cases is altered in favor of the hexagonal phase. This is a consequence of metastability of the cubic phase which is transformed to the hexagonal phase even at 403°K [5]. The possibility of the reverse transition has not been definitely established. Semiletov [7] and Shank [8] have reported on the conditions for the conversion of α -CdSe to the β -modification.

In the present work, we studied the polymorphic transformations in polycrystalline CdSe films during isothermal annealing and storage in the dark at room temperature for a prolonged period in order to establish features indicating structural changes in the films and the reasons for these changes.

The concentration of impurities in vacuum-deposited CdSe films did not exceed their concentration in the starting material (cadmium selenide powder corresponding in impurity content to ETO 021.006.TU [special purity, V4 purity class]). The impurity whose percentage composition is greatest is isovalent and the changes in the interplanar distance in CdSe caused by its presence, according to the Vegard law [9], are two orders of magnitude below the resolution of the measurement apparatus.

The cadmium selenide films were obtained by sublimation of the powder in a quasi-sealed volume of a graphite reactor with $1.33 \cdot 10^{-3}$ Pa residual pressure. As in our previous study [6], the samples were of both types. At 623°K base temperature, the films were formed with comparable amounts of the hexagonal and cubic phases. The vaporizer temperature was held at 973-1023°K. Glass with normal surface roughness was used as the base. In order to eliminate the effect of the predominant growth of crystallites perpendicular to the base, the roughness was artificially increased. The structural studies were carried out on an EG-100A electron diffraction camera and URS-50IM diffractometer using x-ray phase analysis [10, 11]. A scintillation counter with symmetrical setting of the amplitude analyzer channel was used for recording. The error in measuring the centers of gravity of the lines was 1' of arc.

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TABLE 1. Changes in the Relative Intensities of the Maxima in the Diffraction Patterns upon Structural Transformations in Cadmium Selenide Films after Isothermal Annealing at 423° and 573°K (artificial aging)

$d_{\text{tabl}}, \text{\AA}$	Comparable rel. amts. of cubic and hex. phases					Predominance of rel. amt. of hex. phase				
	$\frac{I_1}{I_0'}$, %	$\frac{I_2}{I_0''}$, %	$\frac{I_3}{I_0'''}$, %	$\frac{I_4}{I_0''}$, %	$\frac{I_5}{I_0'}$, %	$\frac{I_1}{I_0'}$, %	$\frac{I_2}{I_0''}$, %	$\frac{I_3}{I_0'''}$, %	$\frac{I_4}{I_0''}$, %	$\frac{I_5}{I_0'}$, %
3,72 (h)	18,15	9,8	82,5	17,2	125	18,2	13,3	103	22,1	149,6
3,51 (c)	28	7,4	40,2	13,6	64	5,8	5,3	157	7,4	190
3,29 (h)	100	100	154	100	132	100	100	141	100	123
2,554 (h)	32	21	100,1	38	157	32	32,2	143	48	186
2,149 (c)	13,1	12	134	17,3	168	18,2	16,1	125	30	200
2,151 (h)										
1,980 (h)	99,5	42	64	48	64	50	48,3	136	55,5	136
1,833 (c)	45,4	36	120	59	170	50	51,5	145	63	155
1,834 (h)										
1,450 (h)	36,3	30	125	35,3	128	45,5	35,5	110	40	107
1,2055 (h)	27,2	33	183	29	139	31	39	178	37	147

Note. $I_1, I_2,$ and I_3 are the intensities of the maxima in the diffraction pattern in the starting state and after isothermal annealing at 423° and 573°K, respectively; $I_0', I_0'',$ and I_0''' are the intensities of the major maxima in the diffraction pattern in the starting state and after annealing.

TABLE 2. Changes in the Relative Intensities of the Maxima in the Diffraction Patterns upon Structural Transformations in Cadmium Selenide Films after Maintenance in the Dark for 1 Month at Room Temperature (Natural Aging)

$d_{\text{tabl}}, \text{\AA}$	Comparable amts. of cubic and hex. phases			Predominance of rel. amt. of hex. phase		
	$\frac{I_1}{I_0'}$, %	$\frac{I_2}{I_0''}$, %	$\frac{I_3}{I_0'''}$, %	$\frac{I_1}{I_0'}$, %	$\frac{I_2}{I_0''}$, %	$\frac{I_3}{I_0'''}$, %
3,72 (h)	25,7	12,9	38,9	100	100	81,8
3,51 (c)	74,4	48,1	50	48,8	53,8	91,8
3,51 (h)						
3,29 (h)	41,5	22,2	41,4	38,4	46,1	100
2,554 (h)	28,6	27,7	75	8	11,5	120
2,149 (c)	28,6	25,9	70	72	71	82,2
2,151 (h)						
1,980 (h)	100	100	77,1	21,6	25,9	100
1,833 (c)	8,6	14,8	133,3	0,4	11,5	101,7
1,834 (h)						
1,2055 (h)	5,1	5,8	93,7			

Note. I_1 and I_2 are the intensities of the maxima in the diffraction pattern in the starting state and after natural aging, respectively; I_0' and I_0'' are the intensities of the major maxima in the diffraction pattern in the starting state and after natural ageing, respectively.

At 423°K annealing temperature and $1.33 \cdot 10^{-3}$ Pa vacuum, the maxima of almost all the diffraction peaks increase independently of the type of the base and condensation temperature due to recrystallization. The major maximum increases significantly and the other peaks increase relatively slightly (Table 1). Annealing at 423°K virtually entirely completes the recrystallization, and the reflection maximum from the atoms of the major plane does not undergo further change upon subsequent annealing at 573°K. In this case, the recrystallization occurs over the entire bulk of the film, as reflected in the significant increase in the secondary maxima. A decrease in the fraction of the cubic phase is observed concurrently with ordering of the crystallite structure (Table 1).

TABLE 3. Changes in the Interplanar Distances in Cadmium Selenide Film Crystallites after Maintenance in the Dark for 1 Month at Room Temperature (natural aging)

$d_{\text{tabl}}, \text{\AA}$	Comparable amts. of cubic and hex. phases		Predominance of rel. amt. of hex. phase	
	$d_1, \text{\AA}$	$d_2, \text{\AA}$	$d_1, \text{\AA}$	$d_2, \text{\AA}$
3,72 (b)	3,680	3,723	3,720	3,723
3,51 (c)	3,479	3,511	3,491	3,498
3,29 (b)	3,270	3,296	3,285	3,291
2,554 (h)	2,538	2,552	2,544	2,550
2,149 (c)	2,175	2,179	2,141	2,144
2,151 (h)				
1,980 (b)	1,969	1,975	1,970	1,972
1,833 (c)	1,823	1,833	1,826	1,828
1,834 (h)				
1,2055 (h)	-	-	1,201	1,208

Note. d_1 and d_2 are the interplanar distances in cadmium selenide film crystallites in the starting state and after natural ageing, respectively.

TABLE 4. Changes in the Interplanar Distances in Cadmium Selenide Film Crystallites after Isothermal Annealing at 423° and 573°K (artificial aging)

$d_{\text{tabl}}, \text{\AA}$	Comparable amts. of cubic and hex. phases			Predominance of rel. amt. of hex. phase		
	$d_1, \text{\AA}$	$d_2, \text{\AA}$	$d_3, \text{\AA}$	$d_1, \text{\AA}$	$d_2, \text{\AA}$	$d_3, \text{\AA}$
3,72 (b)	3,694	3,692	3,692	3,696	3,696	3,696
3,51 (c)	3,479	3,470	3,470	3,475	3,475	3,467
3,29 (b)	3,274	3,267	3,269	3,270	3,270	3,272
2,554 (h)	2,537	2,537	2,537	2,541	2,535	2,541
2,149 (c)	2,137	2,134	2,134	2,139	2,139	2,139
2,151 (h)						
1,980 (b)	1,966	1,970	1,968	1,972	1,969	1,971
1,833 (c)	1,817	1,817	1,817	1,850	1,850	1,847
1,834 (h)						
1,2055 (h)	1,202	-	1,201	1,202	1,202	1,201

Note. d_1 , d_2 , and d_3 are the interplanar distances in cadmium selenide film crystallites in the starting state and after isothermal annealing at 423° and 573°K, respectively.

The data obtained after natural aging indicate that the initial stages of recrystallization take place or there are no changes due to the low rate of recrystallization at room temperature. However, independently of the type of base and preparation conditions, the intensity of all the peaks decreases as a result of natural aging (Table 2). The intensity of the diffraction pattern "tails" also decreases and the background remains unchanged within experimental error.

The nature of the changes in the reflection intensities depends on the relative content of the cubic and hexagonal phases in the film in the starting state. Thus, in addition to the overall decrease in reflection intensities, the relative intensity of the reflections from most of the planes of samples with predominance of the hexagonal phase increases, while it decreases for samples with a large fraction of the cubic CdSe modification (Table 2). The decrease in the reflection intensities is accompanied by an increase of interplanar distance of the crystallites in the two sample types of a different extent (Table 3). The increase in interplanar distances causes a decrease in the number of sources of coherent scattering in a unit of volume, which leads to a decrease in the intensity of the diffraction peaks.

The interplanar distances immediately after preparation in all starting samples were less than the corresponding tabulated values (Tables 3 and 4), i.e., compression deformation occurs upon deposition and cooling to room temperature in the samples which gives rise to elastic stresses which may permit the crystallite structure to relax to the equilibrium state. Indeed, Table 3 shows that the interplanar distances during natural aging increase both for the major maxima and for some of the other maxima and reach the tabulated values.

The generation of compression deformation recorded upon isothermal annealing may be the result of the condensation of favorably oriented crystallites relative to the vapor streams which suppresses the growth of other crystallites [12]. The anisotropy of the CdSe wurtzite structure may also lead to elastic deformation in CdSe films upon cooling [13]. The discrepancy between the values for d and the equilibrium values and, thus, the change in diffraction pattern peak intensities during natural aging are more pronounced in films with a large content of the cubic phase (Tables 2 and 3). These tables indicate that non-uniformity of the phase composition of a film may also be a cause for deformation of the crystal lattice. We should also note that destruction and deformation occur in the film structure as a result of its interaction with the base [13].

If change in the interplanar distances is caused by nonuniformity of the phase composition, we should expect an increase in d upon annealing in vacuum when the film uniformity is enhanced (Table 1) as a result of the formation of the hexagonal phase. In the case of the predominance of the anisotropic factor of the wurtzite modification, a decrease in d relative to the starting value would be observed as result of annealing. In fact, a decrease in the interplanar distances in cadmium selenide films is observed after vacuum annealing at 573°K (Table 4), which is natural for phase rearrangement to the α -modification [14]. In this case, the number of coherent scattering sources in a unit of sample volume increases, which, in addition to recrystallization, is responsible for an increase in the intensity of the diffraction peaks.

CONCLUSIONS

Recrystallization with the formation of the hexagonal CdSe modification occurs upon thermal aging, which increases the anisotropy of a cadmium selenide semiconductor film characterized by compression of the crystallite unit cell. Relaxation of the original structural defects occurs during natural aging with restoration of the cell parameters to literature values in the course of an increase in the interplanar distances.

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PHASE DIAGRAM OF THE PbSe-CdTe SYSTEM

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Lead selenide is employed in thermogenerators and in the manufacture of photoresistors. Cadmium telluride is a promising material for x-ray spectroscopy. Therefore, the study of alloys based on these substances is of great importance.

The results of an investigation of the chemical reactions in Pb, Cd||Se, Te systems were presented in [1-9]. The boundary of the solubility region near PbSe in the PbSe-CdSe system was determined in [1]. The unit cell parameter of $(PbSe)_{1-x}(CdSe)_x$ specimens varies as $a = 6.127 - 0.42x$ Å. In [2] it was found that this system is quasi-binary. A eutectic forms at 995°C and $x = 0.46$. At this temperature regions of solid solutions lie in the ranges $0 \leq x \leq 0.3$ and $0.99 < x \leq 1$. The phase diagram of the CdTe-CdSe system is a eutectic system with a eutectic point at 1091°C and the composition $CdTe_{0.8}Se_{0.2}$ [3, 4]. The solid solutions with a sphalerite structure extend up to 26 mole % at 1000°C and up to 46.5 mole % CdSe at 800°C. The two-phase region amounts to only 3 mole %, and the remaining region belongs to solid solutions based on CdSe with a wurtzite structure. The PbTe-CdTe system is quasi-binary and of the eutectic type [5]. The maximum width of the region of solid solutions on the PbTe side is ~20 mole % at 866°C (for $Pb_{1-x}Cd_xTe$ specimens $a = 6.459 - 0.3x$ Å). The mechanism of the exchange reaction between lead selenide and cadmium telluride was investigated in [8]. Samples of the original compounds were pressed together and annealed at 500-700°C. Subsequently the distribution of the elements was studied in the direction perpendicular to the plane of contact of the samples.

A thermodynamic analysis of the nature of the exchange interaction on the basis of a calculation of the change in the Gibbs free energy in $AlIBIV-PbBVI$ systems was carried out in [9]. However, it is difficult to predict the course of the reaction $PbSe + CdTe \rightleftharpoons PbTe + CdSe$ on the basis of this analysis, and this is attributable, in the opinion of Tomashik et al., to the overestimated value of the widely accepted standard heat of formation of lead selenide.

In the present work we studied the phase equilibrium in the PbSe-CdTe system on the basis of differential thermal, x-ray diffraction, and metallographic analyses. The starting compounds were synthesized from the elements of semiconductor purity with a content of the main substance equal to 99.999 wt. %. Tellurium and lead were subjected to capillary purification. The synthesis was carried out in evacuated graphitized quartz ampuls by high-frequency heating (2-3 min), holding at 1150°C for 1 h, and subsequent cooling of the material in air. For the x-ray diffraction analysis the samples were ground, annealed at 590, 810, and 830°C to the establishment of equilibrium, and chilled in ice water.

The DTA was carried out on a system based on an ÉPP-09 six-point dc potentiometer, an R-310 potentiometer, and an F116/2 photomultiplier. This system permits the simultaneous recording of the DTA curves of three samples, which is important in resolving closely arranged

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