The PbSe metastable phase. I. The growth mechanism

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Abstract. PbSe and PbSe:Cd films, grown by two different non-equilibrium growth techniques, laser-assisted deposition and electron-beam evaporation, on two different types of substrate, KCl and BaF$_2$, are investigated. The crystal structure of the films is studied by x-ray and reflecting high-energy electron diffraction. On the basis of the structural investigations it is found that the films grown by both non-equilibrium techniques represent heterophase junctions between the metastable CsCl-type phase and the stable FCC phase. The growth mechanism is semiquantitatively discussed in the framework of Sirota's examinations of the formation of the metastable phases. The substrate type is found to influence only the metastable-phase lattice constant, which in turn determines the thickness of the metastable-phase sublayer.

1. Introduction

PbSe, like the other lead salts, crystallizes into the FCC NaCl-type structure (O_h^5) at ambient conditions. It is reported to undergo a high-pressure-induced structural phase transition to the orthorhombic TlI-type phase (D_{2h}^{16}) at pressures of about 4.5 GPa and another one to the CsCl-type (O_h^1) phase at about 16 GPa [1, 2]. Thus PbSe is a material that possesses two high-pressure (HP) metastable crystal modifications. We have demonstrated the possibility of growing films with metastable phases from a material possessing such a phase or phases using non-equilibrium techniques of growth in the case of PbTe. The PbTe films deposited by laser-assisted deposition (LAD), which is a highly non-equilibrium growth technique, contain GeS- and CsCl-type PbTe metastable phases. These films turned out to represent heterophase junctions between the metastable phases and the stable one. The metastable-phase sublayers were thick enough for their properties to be studied [3–7]. The growth of a metastable phase of a certain material in the form of a film, in other words obtaining it without applying pressure (when the metastable phase is a HP one) is of both fundamental and practical importance, as: (i) the properties of the metastable phase, representing a new material, in fact, can be studied and (ii) the films consisting of two well defined sublayers with different crystal phases represent heterophase junctions—a new type of semiconductor structure. As far as PbSe possesses two metastable phases it can be expected that, using non-equilibrium growth techniques, PbSe metastable phases can be obtained in the form of films. With this work we aim: (1) To show that the reason for the growth of metastable phases really is the non-equilibrium growth process and that films with metastable phases can be grown from each material possessing such a phase or phases. Here along with LAD we have used another non-equilibrium growth technique, namely electron beam evaporation (EBE), and another material possessing metastable phases—PbSe. (2) To study the role of the substrate and the target doping on the metastable phase formation.

X-ray diffraction and reflecting high-energy electron diffraction (RHEED) investigations are used to detect the presence of the HP PbSe CsCl-type phase.

2. Samples and experimental results

2.1. Growth processes

The films investigated are deposited by two different non-equilibrium growth techniques—LAD and EBE. The non-equilibrium processes of growth of thin films are widely spread because of their simplicity. LAD is based on the interaction of pulsed laser radiation with a solid target and the subsequent ejection of a new phase, condensing on a substrate in the form of a thin film. Our set-up for the technical realization of the LAD is described elsewhere [8]. The technological parameters varied in this technique are substrate temperature T_s, substrate-to-target distance L, laser energy E_J per pulse and the number N of laser pulses. It is found that the film stoichiometry reproduces that of the target when the distance from the substrate to the target is between 3 cm and 6 cm and the energy of the laser pulse E_J between 2 J/pulse and 5 J/pulse [8,9]. Films with mirror surfaces and satisfactory adhesion to the substrates are grown at substrate temperatures maintained in the range 100 °C–300 °C.

In the case of EBE the ejection of a new phase, condensing on the substrate and forming the film, is provided by the interaction of an accelerated electron beam with a solid target [10]. The technological conditions varied in this technique are substrate temperature T_s, substrate-to-target distance L and electron beam power E_J. The deposited films have the same stoichiometry as the source material and mirror-like surfaces when L is about 20 cm, E_g is in the range between 100 W and 300 W and T_s is maintained at different temperatures between 150 °C and 350 °C.

2.2. Samples

PbSe films are grown by LAD and EBE on (100)-oriented KCl and (111)-oriented BaF_2 substrates. PbSe films doped with 2 mol% Cd are deposited on the two types of substrate by LAD, as well, in order to investigate the influence of the dopant (Cd in our case). The film thicknesses are determined from the pictures of the cross-sections taken with an electron scanning microscope. The carrier concentrations and the mobilities of the films are calculated from the Hall coefficient and the electrical conductivity measured by the standard Van der Paw technique. A great number of films were investigated. In table 1 the data on the films, typical representatives of each of the groups investigated are given. In the labelling of the samples, given in table 1, K stands for the KCl substrate, B for the BaF_2 one, S for PbSe, the notation 2C means that the samples are doped with 2 mol% Cd and the * means that the film is deposited by EBE.

2.3. X-ray diffraction

X-ray diffraction measurements are undertaken in order to investigate the volume crystal structure of the films. The x-ray diffractograms are obtained by a standard x-ray diffractometer URD-6 with Co Kα radiation with a graphite mononchromator and a step size of 0.05°. The angular range is varied from 25° to 75°. The lattice constants and the peak intensities are obtained using the PULVERIX program as implemented by H Moller, Institut fur Experimental Physik, Technische Universitat, 1040 Wien, Austria. Figure 1(a) shows the diffraction patterns of PbSe (K12S) and PbSe:Cd (K2C74S) films deposited on KCl substrates. Figure 1(b) gives the diffractograms of PbSe (B82S) and PbSe:Cd (B2C60S) films deposited on BaF_2 substrates. The most intensive peaks in all diffractograms indicate mainly FCC NaCl-type structure with (100) direction of crystallization in spite of the fact that the two substrates have different orientations: (100)KCl and (111)BaF_2. The lattice parameter a of the FCC PbSe determined from the diffractograms is $a = 6.124$ Å, in good

Table 1. Technological parametres—substrate temperatures T_s, number of N laser pulses, laser energy E_J per pulse, electron beam power E_B, substrate-to-target distance L, thickness d and transport coefficients—carrier concentrations N and Hall mobilities μ of the samples.

Samples	T_s (°C)	N	E_J (J)	E_B (W)	L (cm)	d (μm)	N (10^{-18} cm^{-3})		μ (cm^2 V^{-1} s^{-1})	
							77 K	320 K	77 K	320 K
K12S	210	50	2.2	—	5	0.50	—	—	—	—
K170S	220	50	3.0	—	3	0.85	—	—	—	—
K172S	220	400	3.0	—	3	4.70	7.8	7.5	3936	803
K189S	220	800	0.75	—	3	2.05	1.7	1.6	12900	1100
B82S	300	100	3.0	—	3	1.00	0.096	2.6	16	54
B86S	270	100	5.0	—	3	3.30	—	0.52	—	110
B89S	250	1	3.0	—	3	0.035	—	—	—	—
B91S	250	50	3.0	—	3	1.50	—	—	—	—
B186S	220	400	3.0	—	3	4.70	9.8	9.8	2660	640
K2C10S	220	85	3.0	—	5	8.30	—	—	—	—
K2C21S	250	150	5.0	—	3	2.80	—	8.9	—	63
K2C22S	300	200	5.0	—	3	3.20	6.4	2.9	350	230
K2C39S	150	150	3.0	—	2	0.75	—	—	—	—
K2C73S	250	100	3.0	—	3	1.20	—	9.0	—	120
K2C74S	250	100	3.0	—	3	0.60	3.9	4.0	1800	430
B2C60S	220	100	0.5	—	3	0.40	—	—	—	—
B2C61S	250	100	3.0	—	3	2.00	0.2	0.44	17	31
B2C212S	250	600	3.0	—	3	5.80	0.2	0.44	17	30
K12S*	300	—	—	150	20	2.53	1.22	1.28	4500	700
K20S*	350	—	—	250	20	4.20	0.8	0.84	13000	1070
B13S*	300	—	—	150	20	3.00	0.92	1.00	6400	950

agreement with the value for bulk material [1]. The value of the FCC lattice constant is found to be identical in undoped samples and doped with 2 mol% Cd PbSe with accuracy ± 0.005 Å. In the diffractograms in figure 1 some additional reflections are seen. These reflections cannot be indexed either in the stable PbSe FCC structure or in the corresponding substrate reflections. We succeeded in indexing them into the CsCl-type HP PbSe phase crystallizing in the (100) direction. In figure 1 the experimental x-ray spectra are compared to the calculated ones. The full vertical lines represent the intensities of the reflections of the (100)FCC and the (100)CsCl-type phases. The broken vertical lines represent the intensities of the reflections of the (100) oriented KCl substrate and the (111)-oriented BaF$_2$ substrate. The lattice parameter of the CsCl-type phase in PbSe and PbSe:Cd films and the variation of the unit cell volume given by the ratio V/V_0 of the CsCl-type phase volume V to the FCC phase volume V_0 are given in table 2. From the V/V_0 pressure dependence of PbSe reported by Chattopadhyay *et al* [2] we have found that the CsCl-type phase volume in the films deposited on KCl substrates corresponds to atmospheric pressure, while that of the CsCl-type phase grown on BaF$_2$ corresponds to pressures of about 5.5 GPa. Obviously, as in the case of PbTe films [5], the metastable CsCl-type phase in the films can exist at pressures much lower than the pressure of the phase transition from TlI- to CsCl-type phase in a bulk material.

The experimentally obtained intensities of the FCC-phase (200) and (400) reflections are about three orders of magnitude higher than those of the (100)CsCl-type phase reflections. This fact indicates that the upper sublayer is the one that crystallizes into the stable FCC phase, while the metastable CsCl-type phase is obviously formed in the initial stage of growth. The very low intensive reflection seen in the diffractogram of sample B2C60S can be indexed as (220)FCC-phase reflection. A growth with (110)FCC phase most probably
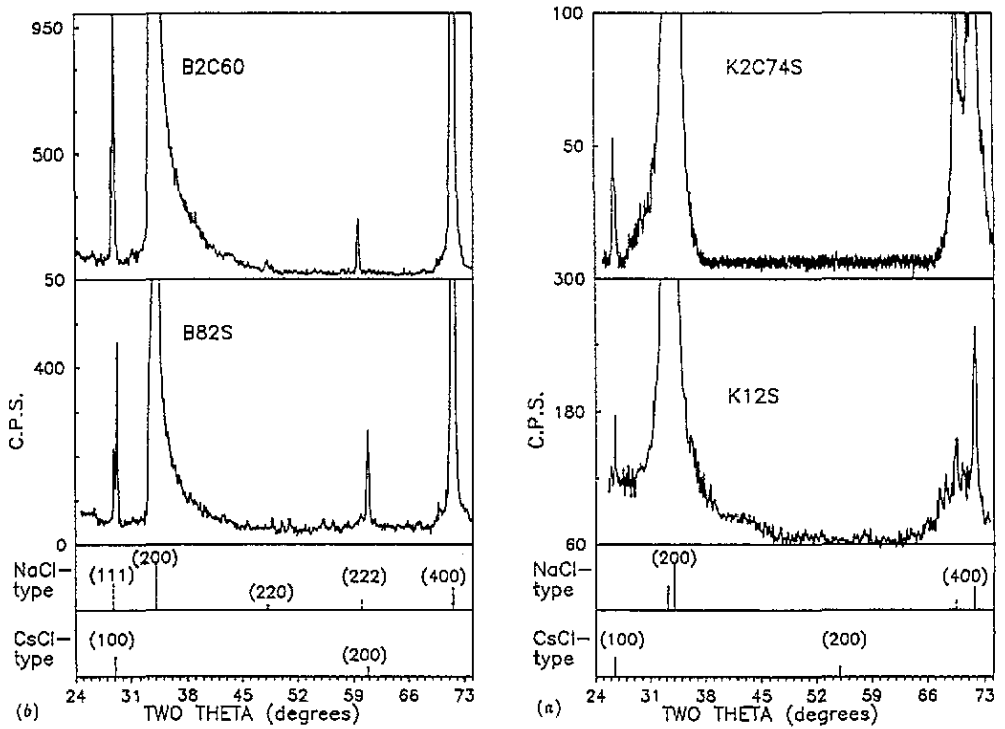
Figure 1. X-ray diffraction spectra of PbSe and PbSe:Cd films deposited on (*a*). KCl substrates and (*b*). BaF$_2$ substrates. The FCC phase reflection intensities are calculated with $a = 6.124$ Å and the CsCl-type phase (100) direction reflections intensities are calculated with $a = 3.536$ Å. The reflection intensities for the FCC and the CsCl-type phases are represented by full vertical lines. The broken vertical lines represent the intensities of the reflections of the (100)-oriented KCl ($a = 6.293$ Å) and the (111)-oriented BaF$_2$ ($a = 6.200$ Å) substrates.

takes place in the junction region with thickness d_j (see figure 2), between the sublayer of the (100)CsCl-type phase with thickness d_m and the sublayer of the (100)FCC phase with thickness d_r.
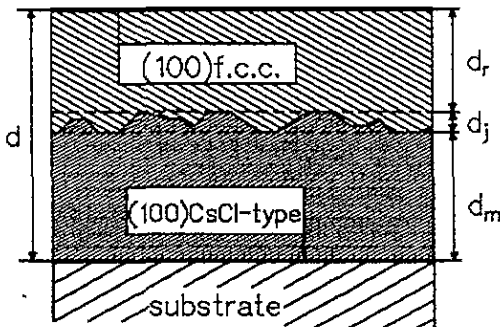

Figure 2. Schematic represention of the crystal structure over the thickness of the films.

In the case of PbTe, along with the CsCl-type phase the intermediate metastable GeS-type phase is detected in all films deposited at substrate temperatures T_s higher than

Table 2. Surface and volume crystal structure characteristics of the films.

Samples	Surface structure (RHEED)	volume structure (x-ray)	Ratio of metastable and stable phase volumes V/V_0	Lattice constants of the CsCl-type phase (Å)
B91S	(111)CsCl type	—	—	—
B89S	polycrystal	—	—	—
	(111)CsCl type	—	—	—
	(100)FCC	—	—	—
B2C212S	(111)CsCl type	—	—	—
B86S	polycrystal	—	—	—
	(110)FCC	—	—	—
B82S	—	(100)FCC (100)CsCl type	0.77	3.536
B2C60S	—	(100)FCC (100)CsCl type	0.83	3.622
K2C74S	—	(100)FCC (100)CsCl type	1.04	3.909
K2C39S	(100)FCC	(100)FCC (100)CsCl type	1.04	3.908
K2C73S	(100)FCC	(100)FCC	—	—
K170S	(100)FCC	(100)FCC (100)CsCl type	—	—
K12S	—	(100)FCC (100)CsCl type	1.02	3.888
K12S*	(100)FCC	(100)FCC (100)CsCl type	0.95	3.788
B13S*	—	(100)FCC (100)CsCl type	0.76	3.527

50–100 °C and with increase of T_s its quantity increases [5,7], while the metastable orthorhombic PbSe TlI-type phase is not seen even in the samples deposited at T_s as high as 300 °C. Thus the x-ray investigations indicate that in the initial stage of growth undoped and doped PbSe films, both on KCl and BaF$_2$ substrates, crystallize into monocrystal (100)CsCl-type structure at all substrate temperatures and laser pulse energies investigated. The TlI-type phase is not detected in the films grown by EBE either which means that even if it is present its quantity is very small.

2.4. Reflecting high-energy electron diffraction (RHEED)

The crystal structure of the films surfaces is studied by RHEED using an electron microscope type EF, Carl-Zeiss, Jena, at an accelerating voltage of 65 kV and an incident angle of the electron beam of about 89°. The results of RHEED investigations may be interpreted as follows.

(i) The electron diffraction patterns of PbSe and PbSe:Cd films deposited on KCl substrates indicate in general perfect monocrystal (100)FCC NaCl-type structure as shown in figure 3, for sample K170S. In the figure the experimental electron diffraction pattern is compared to the calculated reflections of the PbSe FCC phase crystallizing in (100) direction, with lattice parameter $a = 6.124$ Å determined from the x-ray measurements. The fact that the upper sublayers of these films always have FCC structure means that their thicknesses are greater than or at least of the order of the electron penetration depth (40 Å). The presence of the stable FCC phase on the surface of comparatively thin films, $d \simeq 0.6$ μm, does not mean that thicker sublayers with metastable phase cannot be grown. It merely signifies that
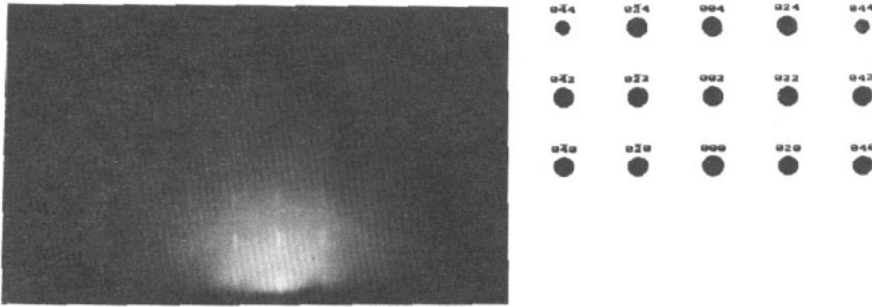
Figure 3. A typical electron diffraction pattern (sample K170S) of PbSe films deposited on KCl substrates indicating perfect monocrystal (100)FCC structure. The calculated reflections of the FCC PbSe structure in the (100) crystal direction ($a = 6.124$ Å) are given in the inset.

the metastable phase grown on KCl substrates, with lattice constant corresponding to V/V_0 $\geqslant 1$, easily relaxes to the stable FCC phase and the thickness of the relaxed sublayer is higher than 40 Å.

(ii) The electron diffraction patterns of PbSe and PbSe:Cd films grown on BaF$_2$ substrates are quite different from those of the films deposited on KCl substrates. As is seen from the electron diffraction pattern (figure 4(a)) of sample B89S with thickness about 35 nm, the metastable phase does not relax entirely to the stable FCC phase. On the polycrystal background the reflections of (100)FCC phase, as well as reflections of different crystal directions of the metastable CsCl-type phase, are seen—(111), in particular. The reflections of the (100)FCC and (111)CsCl-type phases, given in the left and the right insets, respectively, are calculated with the corresponding lattice constants; $a_{FCC}^{PbSe} = 6.124$ Å, a_{CsCl}^{PbSe} $= 3.536$ Å.

The electron diffraction pattern of a PbSe film with thickness about 3 μm (sample B86S, figure 4(b)) confirms the fact that the metastable PbSe phase deposited on a BaF$_2$ substrate does not relax easily to the stable phase. The reflections on this electron diffraction pattern indicate (110)FCC phase structure, as is shown in the inset. The CsCl-type phase, which has a smaller lattice constant ($V/V_0 = 0.77$ in this case) obviously cannot relax to the thermodynamically more favourable (100) direction of crystallization of the FCC phase over a thickness of about 40 Å. The junction region (d_j), where the growth with (100)CsCl-type phase changes to further growth with the (100) FCC phase, is obviously polycrystal. Nevertheless the (111) direction of the CsCl-type phase and/or the (110)FCC phase prevail in this region. So the (110)FCC phase, detected in some samples by x-ray diffraction as well, is related to the junction region. The presence of this phase on the film surface means that the change of the film growth from the (100)CsCl-type phase to the (100) stable FCC phase really does pass through a growth with (110)FCC phase.

The RHEED investigations show that the thickness of the sublayer with the metastable phase in the films grown on Ba$_2$F substrates is about three times higher than that in the films grown on KCl substrates at one and the same laser pulse energy. The surface structure of a film as thick as about 3 μm (B86S) does not indicate the thermodynamically favourable (100) crystallization direction of the stable FCC phase as is usually the case in films grown on KCl substrates.
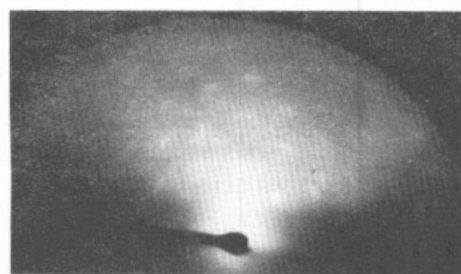
As concerns the films doped with Cd, it can be concluded that the doping makes the relaxation process even more difficult. The electron diffraction pattern of a doped film (B2C212S), figure 4(c), indicates the (111) direction of crystallization of the CsCl-type
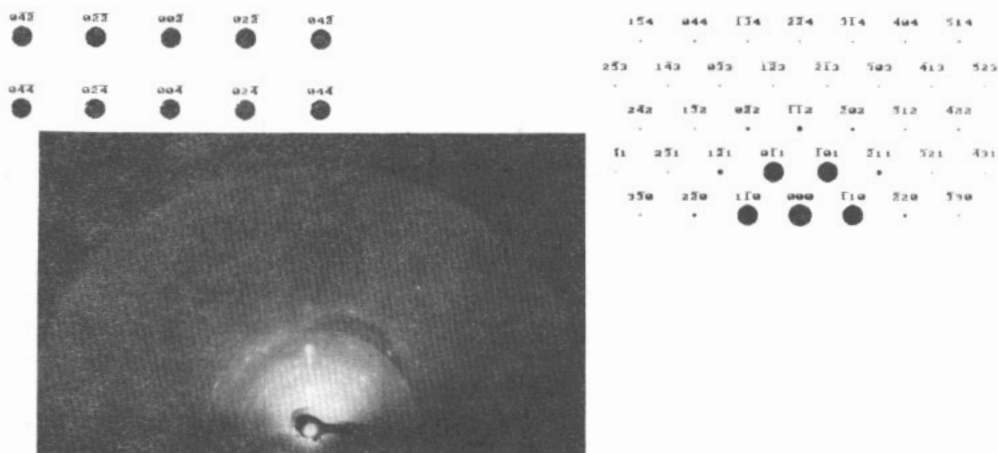
(a)

(b)

(c)

Figure 4. (a) Electron diffraction pattern of a PbSe film (sample B89S) with thickness 35 nm, deposited on a BaF$_2$ substrate. The reflections of the (100)FCC and (111)CsCl-type phases, given in the left and right insets, respectively, are calculated with the corresponding lattice constants, $a_{FCC} = 6.124$ Å and $a_{CsCl} = 3.536$ Å. (b) Electron diffraction pattern of a PbSe film deposited on a BaF$_2$ substrate (sample B86S) with thickness about 3 μm. The calculated reflections of the FCC PbSe structure in the (110) crystal direction ($a = 6.124$ Å) are given in the inset. (c) Electron diffraction pattern of a PbSe:Cd film deposited on a BaF$_2$ substrate (sample B2C212S) with thickness 5.8 μm. The calculated reflections of the CsCl-type PbSe structure in the (111) crystal direction ($a = 3.622$ Å) are given in the inset.

phase. The reflections shown in the inset in figure 4(c) are calculated with the CsCl-type phase lattice parameters determined from the x-ray measurements given in table 2. Over a thickness about 40 Å the metastable phase cannot relax to the stable phase. The relaxation consists only if a change of the crystallization direction of the CsCl-type phase from (100) to (111), the (111) direction having a packing density corresponding to that of the (100) direction of crystallization of the FCC phase. The role of the doping consists of an increase of the metastable-phase bulk modulus.

The (111)CsCl-type phase, seen on the sample surface (see also figure 4(a)) means that along with the (110)FCC phase, the junction sublayers (with thickness d_j in figure 2) also contain the (111)CsCl-type phase. Thus on the basis of the structural investigations it can be concluded that the initial stage of growth of the films occurs with the metastable (100)CsCl-type phase, which forms a sublayer with thickness d_m. Over a comparatively narrow range, the range of the junction with a thickness d_j, the growth changes from the (100) CsCl-type phase to the (100)FCC phase, passing consecutively through (111)CsCl-type and (110)FCC phase directions. Further growth is with the stable (100)FCC phase and the thickness of this sublayer depends on the laser pulse number in LAD and on the evaporation time in EBE.

2.5. Optical investigations

The interference transmittance T and reflectance R spectra are measured at different temperatures between 80 K and 320 K in the range from 400 to 4000 cm^{-1} using a UR-20 double-beam spectrometer.

It was noticed that the interference spectra of the films thicker than 2.5 μm, grown by both techniques, were usually periodically modulated. The modulated transmittance spectra of two undoped PbSe films, deposited on KCl and BaF$_2$ substrates (K20S* and B186S), and a PbSe:Cd (K2C10S) film are given in figure 5(a), (b) and (c), respectively. The periodical modulation of the spectra indicates that the films consist of two well defined sublayers with different thicknesses and optical constants. The thicknesses of the two sublayers can be evaluated easily from the modulation of the spectra on the rough assumption of equal refractive indexes in both sublayers. They are found to depend on the substrate type and the target doping. The typical thicknesses d_m of the sublayers with the metastable phases adjacent to the substrate, in the PbSe/KCl films are about 1 μm (figure 5(a)), while in the PbSe/BaF$_2$ films $d_m \simeq 3$ μm (figure 5(b)). The target doping also influences d_m: in the PbSe/KCl films $d_m \simeq 1$ μm, while in PbSe:Cd/KCl films $d_m \simeq 1.5$ μm (figure 5(c)).

The modulation of the interference spectra indicates that the films have a two-layer structure with a relatively sharp boundary, with a thickness d_j, between the metastable CsCl-type phase sublayer and the upper FCC phase one. The films with comparable thicknesses, d_m and d_r, of the sublayers with the metastable and the stable phases, represent heterophase junctions, as shown in figure 2.

3. Discussion

The structural and optical investigations of the PbSe and PbSe:Cd films produced on KCl and BaF$_2$ substrates show that they represent two-layer structures. The sublayers grown in the initial stage of growth (adjacent to the substrate) consist of the CsCl-type metastable phase with considerable thickness d_m: up to 1 μm for PbSe films grown on KCl substrates and up to 3 μm for the films grown on BaF$_2$ substrates. When the thickness of the film becomes higher its crystal structure changes to the stable FCC phase. The thickness d of
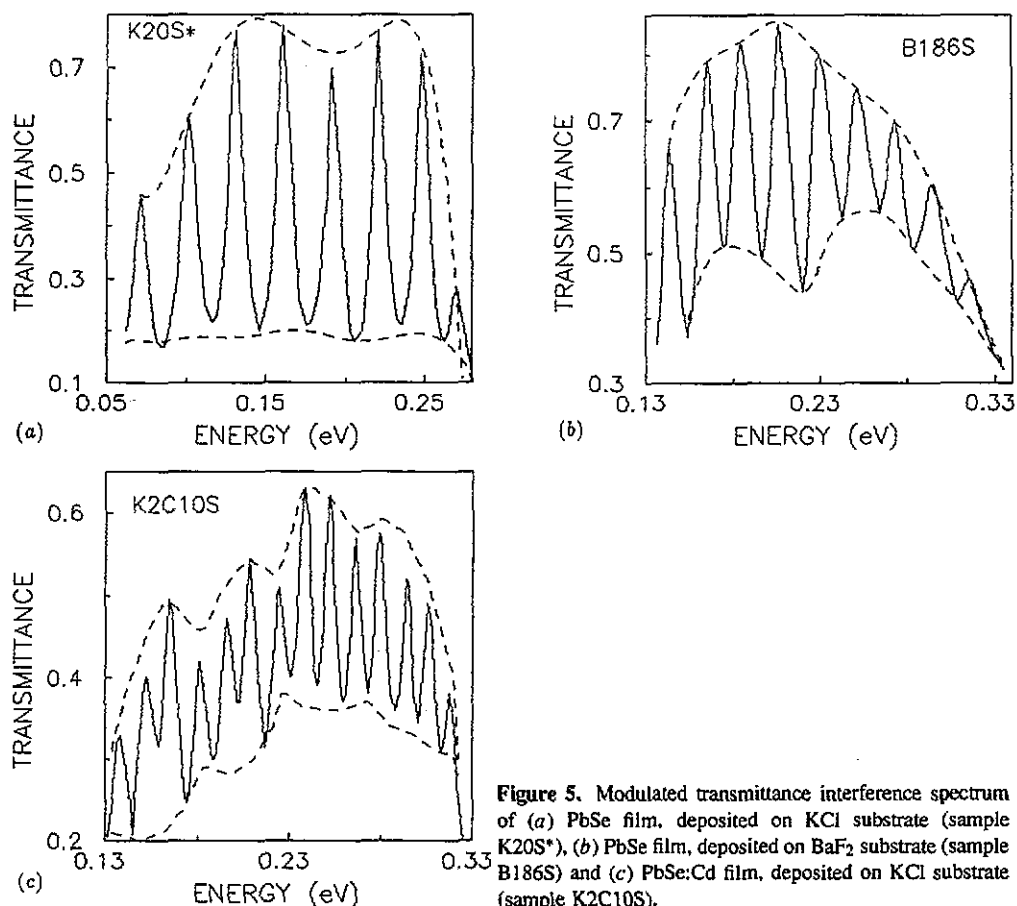
Figure 5. Modulated transmittance interference spectrum of (a) PbSe film, deposited on KCl substrate (sample K20S*), (b) PbSe film, deposited on BaF$_2$ substrate (sample B186S) and (c) PbSe:Cd film, deposited on KCl substrate (sample K2C10S).

the sublayer with the stable phase depends on the number of laser pulses and can be varied from 0 μm to about 8 μm in our set-up for LAD.

The sublayers with metastable phases with thickness of several micrometres and well defined lattice parameter and crystallization direction cannot be regarded as pseudomorphic layers, as usually observed in the films grown by the standard epitaxial growth techniques. The critical thickness of the pseudomorphic layers, even in the case of large mismatch (>4%) between the substrate and the deposited material, is not higher than several nanometres [11]. The reason for the growth of films with metastable phases has to be looked for in the growth conditions as the lattice mismatch between the KCl and BaF$_2$ substrates and the deposited material cannot account for the presence of sublayers with metastable phases with a thickness of several micrometres. We have successfully used Sirota's examinations [12] of the formation and the existance of metastable phases on the grounds of the crystallization theory for a semiquantitative explanation of the growth of PbTe films with metastable phases. In the case of PbTe films the initial sublayer contains CsCl-type phase or a mixture of CsCl- and GeS-type metastable phases, depending on substrate temperature. In the case of PbSe films, deposited in the same range of substrate temperatures, $150° \leqslant T_s \leqslant 300°C$, where the GeS-type phase quantity is predominant in PbTe films, the only metastable phase detected is that of CsCl-type. In order to decide which one of the three possible crystal phases (as in the case of PbSe) will be formed at a certain supercooling, the velocity V_2 of the

two-dimensional nucleus formation as a function of the temperature has to be considered. According to Sirota [12]:

$$V_2 = B_2 \exp{-\left(C_2 A_2/kT + n_2 G/kT + U/kT\right)} \tag{1}$$

B_2 and C_2 depend on the nature of the atoms and can be assumed to be temperature-independent constants. A_2 is the work-function of the two-dimensional nucleus formation, G is the work-function of the volume changes per atom, U is the change of the free energy as a result of the atom diffusion from a regular to an irregular site, n_2 is the number of the atoms in a nucleus and k is the Boltzman constant. The contribution of the term U/kT can be ignored in our case, where the high speed of the evaporated material and the comparatively cold substrate makes the motion or rotation of the condensed particles practically impossible.

According to Sirota [12] the work-function A_2 of the two-dimensional nucleus formation can be written in the form

$$\left(A_2\right)_n = C Q_{1n}\left(T_{kn}/\Delta T_n\right) \tag{2}$$

C depends on the crystal structure of the adjacent phases, Q_{1n} is the heat of the phase transition from a solid phase n to the liquid phase 1. Q_{1n} is proportional to the critical temperature T_{kn} of the transition ($n = 2$ corresponds to the phase transition from the liquid to the stable FCC phase, $n = 3$ to that to the intermediate metastable TlI-type and $n = 4$ to that to the CsCl-type phase), $\Delta T_n = T_{kn} - T$ is the value of the supercooling. The term A_2/kT for the nth phase can be written in the form

$$\left(A_2/kT\right)_n \simeq T_{kn}^2/T\left(T_{kn} - T\right). \tag{3}$$

The critical temperature T_{k2} of the phase transition from the PbSe FCC stable phase to the liquid one is known: $T_{k2} = 1361$ K. The critical temperature T_{k3} of the metastable TlI-type phase and that (T_{k4}) of the CsCl-type phase are unknown and cannot be easily determined. It is obvious only that we can take $T_{k4} < T_{k3} < T_{k2}$ as the higher is the pressure inducing a given phase n, the lower is its critical temperature T_{kn}: (i) The change $\Delta F_n = F_n - F_1$ of the free energy F_n during the formation of a given crystal phase n from the liquid phase 1, can be written in a rough approximation in the form

$$\Delta F_n = Q_{1n}\Delta T_n/T_{kn}.$$

(ii) On the other hand the change ΔF_n of the free energy is proportional to the pressure P inducing the phase and to the volume change $V_{1n} = V_1 - V_n$:

$$\Delta F_n = -P\Delta V_{1n}.$$

We choose $T_{k4} = 900$ K and $T_{k3} = 1100$ K. The arbitrary values of these temperatures make our considerations semiquantitative.

In figure 6 the temperature dependences of the terms A_2/kT for the three different crystal phases (the stable FCC, curve 2; the metastable orthorhombic TlI type and the metastable CsCl type, curves 3 and 4, respectively) calculated according to equation (3) are given. This figure shows which phase will be formed at supercooling to a certain temperature—the substrate temperature T_s in our case. At $T_s > T_3$ (see figure 6, T $\simeq$ 680 K) the probability of forming the stable phase (FCC PbSe) is highest as the work-function of nucleus formation
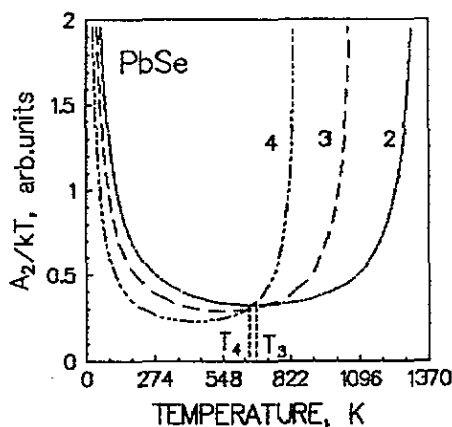
Figure 6. The temperature dependences of the terms A_2/kT, which determines the velocity of the two-dimensional nucleus formation (see (1) and (3)), for the three different PbSe crystal phases. Curve 2 corresponds to the stable FCC phase, curve 3 to the metastable TlI-type phase and curve 4 to the metastable CsCl-type phase.

with this phase is lowest. At $T_s \leqslant T_4$ ($T_4 \simeq 650$ K) the probability of growing the metastable phase 4 (CsCl-type phase) is highest. As all our samples are grown at substrate temperatures in the range between 370 K and 600 K it is easily understood why only the CsCl-type metastable phase is detected in our films. It is worth noting that the range of supercooling where the CsCl-type phase grows is shifted towards higher temperatures in comparison to that for the PbTe CsCl-type phase [7]. This is in fact a result of the higher PbSe critical temperature T_{k2}. The FCC PbSe phase melting temperature is 1361 K, while the FCC PbTe one is 1192 K. On the other hand the range of temperatures with the highest probability of growing the intermediate TlI-type phase is a very narrow one. Taking also into account the fact that a slight fluctuation of the crystallization front temperature can lead to formation of the stable FCC phase (curve 2 is very close to curve 3), one can understand why the intermediate TlI-type phase is not detected in the films.

Our investigations show that the substrate nature does not influence the type and the direction of crystallization of the metastable phase. The metastable phase sublayers on KCl and BaF$_2$ substrates differ in thickness and lattice constant. The contribution of the substrate to the velocity V_2 of the two-dimensional nucleus formation can be accounted for by the term $n_2 G/kT$ in equation (1). According to Sirota [12] the number of atoms in a two-dimensional nucleus is proportional to the critical temperature T_{kn} and inversely proportional to the volume changes ΔV, $n_2 \simeq T_{kn}/\Delta V$. The volume of the metastable phase unit cell grown on a KCl substrate is equal to or even higher than that of the stable FCC phase ($V/V_0 \leqslant 1.04$). The unit cell volume of the metastable phase grown on BaF$_2$ substrate is significantly smaller ($V/V_0 = 0.77$). Then the contribution of the term $n_2 G/kT$ to the velocity of the two-dimensional nucleus formation (see equation (1)) is much smaller in the case of KCl substrates. The term $n_2 G/kT$ contributes to the increase in the velocity V_2 of the formation of the nuclei of the metastable phase on BaF$_2$ substrates. As a result the velocity V_2 on BaF$_2$ substrates is higher than that on KCl substrates and the sublayers with the metastable phase in the films grown on BaF$_2$ substrates are thicker.

To understand the presence of the FCC phase as an upper sublayer (figure 2) in our films one also has to take into account the fact that with the increase of the number of laser pulses (i.e. with the increase of the film thickness) the temperature of the crystallization front increases. As a result at a certain critical thickness (about 1 μm in the films grown on KCl substrates and about 3 μm in those grown on BaF$_2$ substrates) when the temperature of the crystallization front becomes comparable with T_s, growth with the stable FCC phase takes place.

The influence of the dopant Cd on the film growth is twofold: (i) the doping increases the deposition rate [9] and (ii) it increases the CsCl-type-phase bulk modulus as follows from RHEED investigations. As a result, in the films doped with 2 mol% Cd, the thickness of the metastable phase sublayer can reach $d_m \simeq 5.8$ μm, as in the case of sample B2C212S.

4. Conclusion

The crystal-structure investigations of PbSe and PbSe:Cd films grown by non-equilibrium processes on different crystal substrates lead to the following conclusions. (i) Using non-equilibrium processes of growth, LAD and EBE, films with metastable phases of a material, possessing such a phase or phases, can be grown. (ii) In the non-equilibrium processes of growth the substrate does not influence the direction of crystallization as it does in the equilibrium processes. The growth process is a heterophase epitaxy—the metastable CsCl-type phase grows in the (100) direction on both (100)FCC-orienting KCl substrate and (111) FCC-orienting BaF$_2$ substrate. The substrate nature influences the metastable phase lattice constant, which in turn determines the thickness of the metastable-phase sublayer. The fact that the crystal substrate governs the metastable-phase lattice constant only means that the process of growth can be regarded rather as graphoepitaxy. (iii) The doping leads to a significant increase of the metastable phase sublayer thicknesses. (iv) It is worth noting that the PbSe CsCl-type metastable phase, which in bulk material can be obtained at pressures higher than 16 GPa, in the films grows with unit cell volume equal to that of the stable FCC phase at atmospheric pressure.

Acknowledgments

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