

Layer intermixing in epitaxial PbSe–PbS superlattices

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The diffusion intermixing of layers in epitaxial PbSe–PbS superlattices has been studied by X-ray diffraction technique. The interdiffusion coefficients was determined basing on changing of the intensity of near-Bragg peak satellites in X-ray diffraction pattern. Two stages of diffusion — fast (at the initial annealing stage) and slow are found out. The diffraction reflection curves have been simulated by numerical solution of the Takagi-Taupin equation for superlattices under account for its profile smoothing due to diffusion.

Методами рентгеновской дифракции исследованы процессы диффузионного перемешивания слоев в сверхрешетках PbSe–PbS. По изменению интенсивности рефлексов-сателлитов определены коэффициенты взаимодиффузии слоев. Обнаружены два этапа диффузии — быстрая (на начальных этапах отжига) и медленная. Проведено моделирование кривых дифракционного отражения путем численного решения уравнения Такаги-Таупена для сверхрешетки с учетом диффузионного сглаживания ее профиля.

The IV–VI superlattices offer wide opportunities both in the field of fundamental researches in solid state physics [1–4], and in creation of new functional elements for microelectronics, IR-engineering, thermoelectricity [5–6]. For such structures with superthin layers, of highest importance is the state of interfaces — their roughness, sharpness of transition from one layer to another, the presence and extension of intermixed zones, and also time and temperature stability of their structure and properties. The diffusion processes in such superthin layers with a high gradients of element concentrations may differ significantly from those in bulk materials [7–8]. Therefore, the investigation of layer interdiffusion in superlattices (SL) is of great importance both in theoretical and in practical aspect.

One of the most effective methods for SL investigation is the X-ray diffraction, which allows, basing on the changing of

near-Bragg peak satellite intensity, not only to trace the layer intermixing processes but also to determine their interdiffusion coefficients [9–10]:

$$\ln[I_n(\tau_2)/I_n(\tau_1)] = -8n^2\pi^2D(\tau_2 - \tau_1)/H^2, \quad (1)$$

where D is diffusion coefficient; H , period of SL; n , the satellite order; I_n , relative intensity of n -th satellite normalized to zero satellite intensity; τ , the annealing time.

The study subjects of this work are PbSe–PbS SL made in an oil less vacuum (10^{-4} – 10^{-5} Pa) by thermal evaporation of lead chalcogenides from tungsten boats and their consecutive condensation onto (001) KCl at 473 K. The layer thickness and condensation rate were monitored using a calibrated quartz resonator located near to the substrate. SL were made with equal thickness of layers and with periods $H = 19$ – 22 nm (number of periods 20). The samples

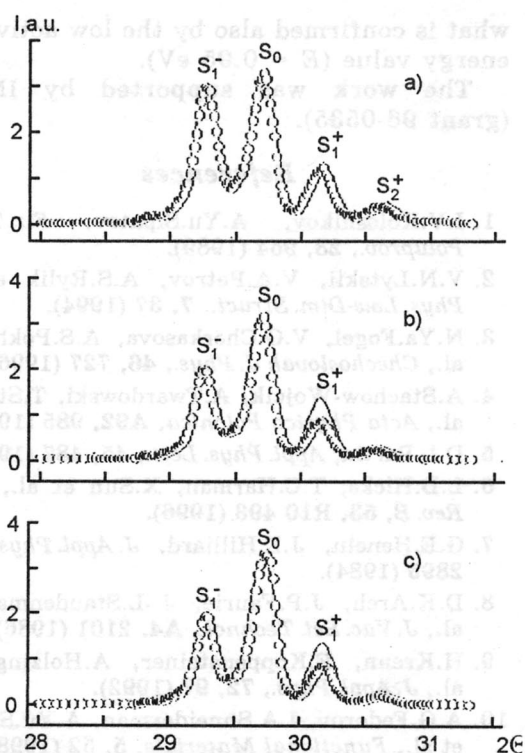


Fig.1. Experimental (dots) and calculated (lines) X-ray diffraction curves for (200) reflection of SL PbSe-PbS with a period 22 nm as-deposited (a) and after an annealing with temperature 543 K within 10 hours (b) and 78 hours (c). S_n — satellites.

were separated from substrates by dissolution of KCl in distilled water and transferred onto amorphous quartz object plates. The structure studies (electron microscopy and X-ray diffraction) have shown that PbSe-PbS SL consist of monocrystalline layers with (001) orientation and sharp interfaces; that is evidenced by the presence of satellites up to 3-rd order on X-ray diffraction patterns (Fig.1a). The samples were annealed in vacuum at constant temperatures 543 K, 593 K and 623 K. The samples were taken out from the vacuum chamber periodically for X-ray diffraction examinations. Diffraction curves were taken using a double-crystal spectrometer in $\text{Cu-K}\alpha_1$ radiation and $\theta - 2\theta$ scanning mode (the (400) reflection of the silicon monochromator crystal was used).

Theoretical curves of the diffraction patterns for superlattices were obtained by solution of the Takagi-Taupin equation [12] for symmetrical diffraction:

$$dY/dX = i\pi[Y^2 - 2(\eta - f)Y + 1]/L_e, \quad (2)$$

where Y is the amplitude ratio of diffracted beam to primary one; L_e , the extinction length; η , the normalized angular variable; f , the normalized change of interplanar distance along the X axis normal to layers. The absorption was neglected due to the small superlattice thickness.

The superlattice profile and its smoothing in the course of annealing are defined by the parameter

$$f = 2\varepsilon(X,t)\sin^2\theta/\chi_{hr}, \quad (3)$$

where: $\varepsilon(X,t)$ is distribution of relative interplanar distance across the SL which changes during the diffusion intermixing; χ_{hr} , the real part of polarisation.

The equation (2) was solved by the Runge-Kutta method for each point of the angular range at a constant η . The accurate solution of (2) for a layer with a known constant f value (in this case, for the buffer PbS layer) was used as the initial condition; then the equation was solved step-by-step numerically passing from the buffer layer-superlattice interface to the free surface. The product of the complex conjugated amplitudes on the SL surface gives the reflection coefficient at a specified θ . Fig.1 presents experimental and calculated diffraction curves for several annealing stages at 543 K.

It is seen from Fig.1 that during an annealing the intensity of lateral satellites decreases and central (zero) satellite grows, thus evidencing the mutual intermixing of layers. More illustratively, the process of layer intermixing at 543 K is displayed in Fig.2 where it is seen that there are two diffusion stages, namely, the fast (on the initial annealing stage) and the slow ones. Similar dependences of the satellite intensity changing are observed at temperatures 593 K and 623 K.

The layer interdiffusion coefficients were determined using expression (1):

for fast diffusion, $D = 3.6 \cdot 10^{-19} \text{ cm}^2/\text{s}$ (543 K); $2 \cdot 10^{-18} \text{ cm}^2/\text{s}$ (593 K); $4.9 \cdot 10^{-18} \text{ cm}^2/\text{s}$ (623 K);
for slow one, $D = 1.6 \cdot 10^{-19} \text{ cm}^2/\text{s}$ (543 K); $4 \cdot 10^{-19} \text{ cm}^2/\text{s}$ (593 K); $2.15 \cdot 10^{-18} \text{ cm}^2/\text{s}$ (623 K).

Taking into account the Arrhenius law ($D = D_0 \exp(E/kT)$), the values of activation energy E and pre-exponential coefficient D_0 were determined to be:

for fast diffusion, $D_0 = 2.4 \cdot 10^{-10} \text{ cm}^2/\text{s}$; $E = 0.95 \text{ eV}$;

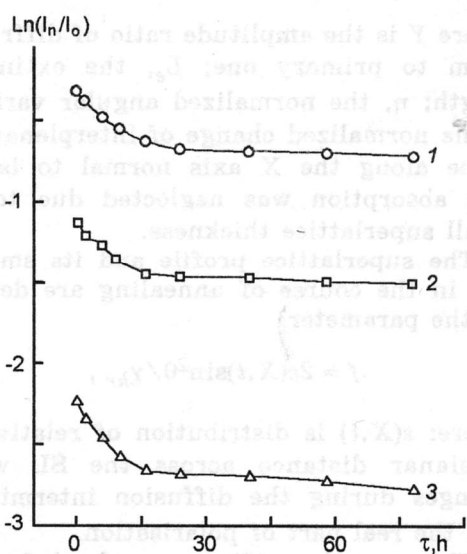


Fig.2. Variation of satellite relative intensity for first S_1^- (1), S_1^+ (2) and second S_2^- (3) order due to annealing time at 543 K for SL PbSe-PbS with period of 22 nm.

for slow one, $D_0 = 5.3 \cdot 10^{-4}$ cm²/s; $E = 1.78$ eV.

The fast diffusion on the initial annealing stage, seems to be connected with the presence of nonequilibrium nonstoichiometric point defects in lead chalcogenides [11],

what is confirmed also by the low activation energy value ($E = 0.95$ eV).

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Взаємодифузія шарів в епітаксціальних надгратках PbSe-PbS

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Методами рентгенівської дифракції досліджено процеси дифузійного перемішування шарів в надгратках PbSe-PbS. За зміною інтенсивності рефлексів-сателітів визначено коефіцієнти взаємодифузії шарів. Виявлено два етапи дифузії — швидка (на початкових етапах відпалів) та повільна. Проведено моделювання кривих рентгенівського відбиття шляхом чисельного рішення рівняння Такагі-Тапена для надгратки з урахуванням дифузійного згладжування профілю.