X-ray diffraction investigation of diffusion in PbTe–PbSe superlattices

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Abstract

Diffusion intermixing in PbTe–PbSe epitaxial superlattice was investigated with help of the double-crystal X-ray diffractometry. Diffusion coefficients were defined for different annealing temperatures from the regular fading of satellites intensities on the X-ray diffraction patterns in the course of annealing. Theoretical grounds and computational treatment of experimental data are presented. Diffraction patterns have been simulated by numerical solution of the Takagi–Taupin equation and calculated curves were fitted to experimental ones accounting the superlattice profile smoothing due to diffusion. Diffusion coefficients determined by both procedures are in a good agreement. © 1999 Published by Elsevier Science B.V. All rights reserved.

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Epitaxial superlattices based on $A^{IV}B^{VI}$ compounds are promising for different applications because of the peculiarities of current transport. In all cases the sharpness and flatness of interfacial boundaries and the stability of the superlattice profile have a substantial importance. In this work the investigation of interdiffusion through the boundaries in PbTe–PbSe superlattices is presented.

The specimens were prepared by alternate thermal evaporation and condensation of lead telluride and lead selenide onto the single crystal KCl substrates of (1 0 0) orientation with a 100 nm PbS buffer layer. Twenty periods of PbTe–PbSe bilayers were deposited in vacuum of 10^{-5} Pa at 573 K substrate temperature. The condensation rate and the film thickness were monitored with a calibrated quartz resonator. The films so obtained were separated from the substrate in distilled water and transferred to the glass bearers.

The samples were annealed in vacuum at constant temperatures in the range 533–643 K. Throughout annealing the samples were taken out periodically from the vacuum chamber for X-ray diffraction examinations. X-ray diffraction patterns were obtained on a double-crystal spectrometer in the Cu K_{α_1} radiation and ϑ–2ϑ scanning mode.

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Along with second- and fourth-order Bragg reflections from the (1 0 0) planes, the satellites disposed equidistantly on the sides of the Bragg peaks were observed in the diffraction patterns which is characteristic for a single-crystalline superlattice. Diffraction curves in the region of (2 0 0) reflection were selected for further measurements. The superlattice period H was determined from the angular distance $\Delta(2\vartheta)$ between the satellite and the Bragg peak

$$H = \frac{57.3\lambda}{\Delta(2\vartheta)\cos\vartheta}$$

and amounted to 8.5 nm.

The interdiffusion through layer boundaries on annealing leads to smoothing of the superlattice profile and is accompanied by satellite fading. It is obvious that only the Bragg peak in the position corresponding to the PbTeSe solid solution lattice period would remain if the intermixing would complete. Smoothing of the periodical interplanar distance variation in the normal direction z, $\varepsilon(z, t) = \Delta d/d$, in the course of diffusion is described by the solution of the diffusion equation [1]

$$\varepsilon(z, t) = \varepsilon_0 \sum_n a_n \cos\left(\frac{n\pi z}{H}\right)\exp\left(\frac{-n^2\pi^2 Dt}{H^2}\right) \quad (1)$$

(where D is the diffusion coefficient, t is the annealing time) obtained for periodic boundary conditions

$$\frac{\partial\varepsilon}{\partial z}_{z=0} = \frac{\partial\varepsilon}{\partial z}_{z=H/2} = \frac{\partial\varepsilon}{\partial z}_{z=H} = \cdots = 0.$$

At the initial moment, $\varepsilon(z, 0)$ is the Fourier expansion in cosines of the initial rectangular superlattice profile

$$\varepsilon(z, 0) = \varepsilon_0 \sum_n a_n \cos(n\pi z/H), \quad \varepsilon_0 = \frac{d_{PbTe} - d_{PbSe}}{d_{PbTe}}$$

with expansion coefficients

$$a_0 = k, \quad a_n = \frac{2}{n\pi}\sin(n\pi k),$$

where k is the symmetry factor of the superlattice, introduced as $k = d_{PbTe}/H$.

Thus, the profile smoothing due to diffusion is described by the dependence of the expansion coefficients on Dt

$$a_n(t) = a_n(0)\exp(-n^2\pi^2 Dt/H^2).$$

Let us consider the satellites intensity fading in the course of annealing and superlattice profile smoothing. The scattering amplitude for a crystal, G, is the sum of those for unit cells. In the reciprocal space with coordinates h^*, k^*, l^*

$$G(h^*, k^*, l^*) = F\sum_j \exp\left(2\pi i\frac{h^*x_j + k^*y_j + l^*z_j}{d}\right),$$

where x_j, y_j, z_j is the position of jth unit cell and F is the cell structure amplitude. It is shown [2] that, if the crystal interplanar distance along a certain direction is modulated sinusoidally with a period H, that is

$$z_j = jd + \frac{H\Delta d}{2\pi d}\cos\frac{2\pi jd}{H}$$

then,

$$G(l^*) = F\sum_j \exp\left[2\pi i\left(jl^* + \frac{Hl^*\Delta d}{2\pi d^2}\cos\frac{2\pi jd}{H}\right)\right]$$

along that direction.

In our case, interplanar distance modulation is given by expression (1) and then

$$G(l^*) = F\sum_j \exp(2\pi ijl^*)\exp\left[2\pi i\frac{Hl^*\Delta d}{2\pi d^2}\right.$$
$$\left. \times \sum_n \frac{a_n}{n}\exp\left(-\frac{4n^2\pi^2 Dt}{H^2}\right)\cos\frac{2\pi jnd}{H}\right].$$

Following Ref. [2], on expanding the second exponent in a series and restricting to the first two terms because $\Delta d/d \ll 1$, one obtains after transformations

$$G(l^*) \approx F\sum_j \exp(2\pi ijl^*) + iF\frac{H\Delta dl^*}{2d^2}$$
$$\times \sum_j \sum_n \frac{a_n}{n}\exp\left(-\frac{4n^2\pi^2 Dt}{H^2}\right)\exp 2\pi ij\left(l^* + \frac{nd}{H}\right)$$
$$+ iF\frac{H\Delta dl^*}{2d^2}\sum_j\sum_n \frac{a_n}{n}\exp\left(-\frac{4n^2\pi^2 Dt}{H^2}\right)$$
$$\times \exp 2\pi ij\left(l^* - \frac{nd}{H}\right).$$

The second and third terms of the sum take maximum values at $l^* \pm nd/H = u$, where u is an integer. It is just satellites of number n on each side of the Bragg peak that is defined by the first term at an integer l^*. When the sinusoidal superlattice profile was supposed, then one satellite appeared on either side of the Bragg peak; now, their number on each side corresponds to a number of not too small Fourier coefficients in the expression for the superlattice profile. The profile smoothing due to interdiffusion results in a fast attenuation of far satellites. The intensity of an nth satellite is proportional to

$$\left[F \frac{H \Delta d(u \pm nd/H)}{2d^2} \frac{a_n}{n} \exp\left(-\frac{4n^2\pi^2 Dt}{H^2} \right) \right]^2.$$

In the course of annealing, the satellite intensity decays during the time $\Delta t = t_2 - t_1$ according to a relationship similar to that used in Ref. [3]

$$\frac{I_n(t_2)}{I_n(t_1)} = \left[\frac{\exp(-4n^2\pi^2 Dt_2/H^2)}{\exp(-4n^2\pi^2 Dt_1/H^2)} \right]^2 \quad \text{or}$$

$$\ln \frac{I_n(t_2)}{I_n(t_1)} = 8\frac{n^2\pi^2}{H^2} D(t_1 - t_2).$$

The last expression is used to calculate the diffusion coefficient. Fig. 1 shows the satellite intensity decrease relatively to that of the Bragg peak during the superlattice samples annealing at different temperatures. Experimental data were approximated by a straight line in the logarithmic scale using the least-squares method. The values of diffusion coefficients determined are presented in Table 1. The activation energy of diffusion Q calculated from these data amounted to 1.5 eV, pre-exponential factor $D_0 = 1.61 \times 10^{-6}$ cm^2/s. These results are not far from the appropriate values for bulk materials: self-diffusion of Te in PbTe is characterized by $Q = 0.75$ eV and $D_0 = 2.7 \times 10^{-6}$ cm^2/s, and for self-diffusion of Se in PbSe $Q = 1.2$ eV, $D_0 = 2.1 \times 10^{-5}$ cm^2/s. Comparing with the results of our previous work [4] confirmed the slow diffusion process, probably by substitution, in PbTe–PbSe superlattice samples under study.
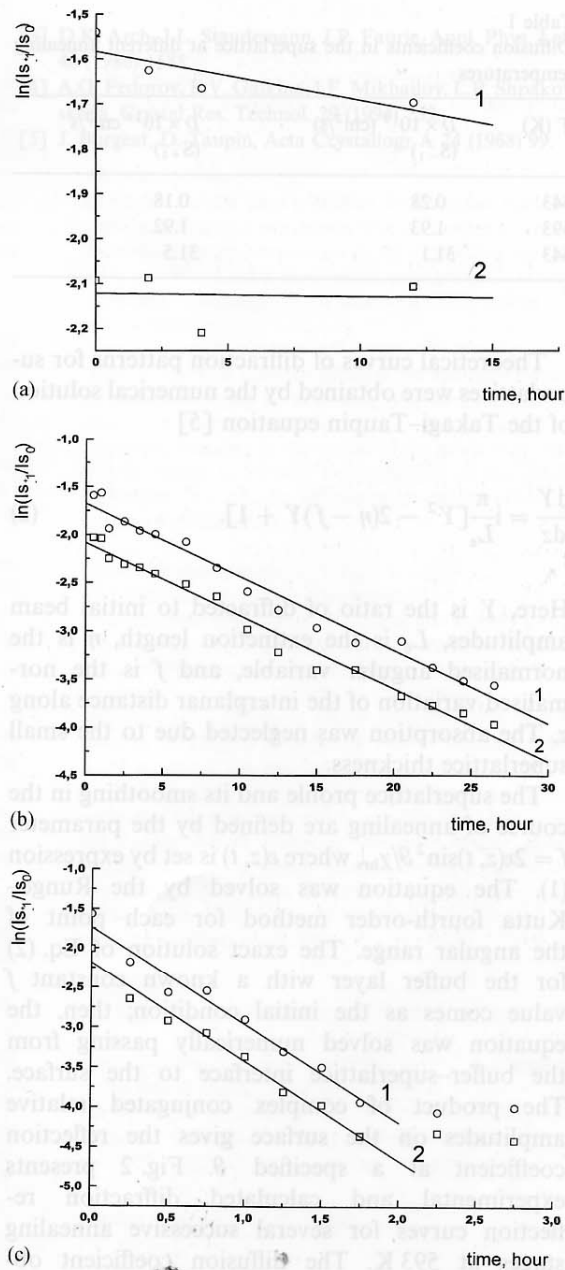

Fig. 1. Decrease of satellites intensity as a consequence of annealing at 543 K (a), 593 K (b), 643 K (c): left-hand satellite S_{-1} (1), right-hand one S_{+1} (2).

Table 1
Diffusion coefficients in the superlattice at different annealing temperatures

T (K)	$D \times 10^{19}$ (cm^2/s) (S_{-1})	$D \times 10^{19}$ cm^2/s (S_{+1})
543	0.28	0.18
593	1.93	1.92
643	31.1	31.5

Theoretical curves of diffraction patterns for superlattices were obtained by the numerical solution of the Takagi–Taupin equation [5]

$$\frac{dY}{dz} = i\frac{\pi}{L_e}[Y^2 - 2(\eta - f)Y + 1]. \qquad (2)$$

Here, Y is the ratio of diffracted to initial beam amplitudes, L_e is the extinction length, η is the normalised angular variable, and f is the normalised variation of the interplanar distance along z. 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 $f = 2\varepsilon(z, t)\sin^2 \vartheta / \chi_{hr}$, where $\varepsilon(z, t)$ is set by expression (1). The equation was solved by the Runge–Kutta fourth-order method for each point of the angular range. The exact solution of Eq. (2) for the buffer layer with a known constant f value comes as the initial condition; then, the equation was solved numerically passing from the buffer–superlattice interface to the surface. The product of complex conjugated relative amplitudes on the surface gives the reflection coefficient at a specified ϑ. Fig. 2 presents experimental and calculated diffraction reflection curves for several successive annealing stages at 593 K. The diffusion coefficient obtained by fitting of experimental and calculated diffraction curves is 8.9×10^{-19} cm^2/s at 593 K.

To conclude, epitaxial superlattices of A^{IV}B^{VI} compounds and of allied rare earth chalcogenides in different applications may meet different demands, and their tendency to diffusion intermixing
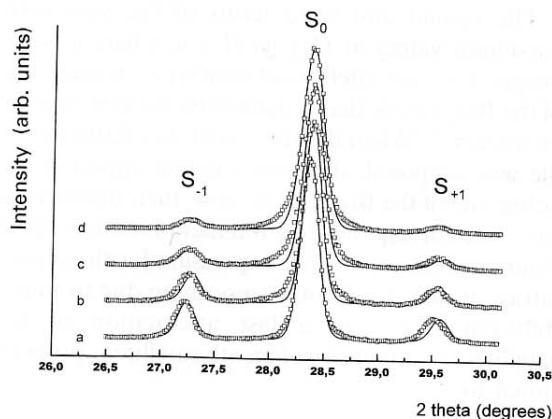

Fig. 2. Experimental (dots) and calculated (lines) diffraction curves for (2 0 0) reflection of the superlattice sample: as-deposited (a) and annealed at 593 K for 2.5 h (b), 8.5 h (c) and 14.5 h (c).

is of signficant interest. For example, the outstanding properties of novel thermoelectric devices based on carrier redistribution in the superlattice (offered by EuS–PbTe) depends on its structural stability at elevated temperatures and current flow. On the other hand, the superlattice of PbTe–SnTe composition being subjected to diffusion intermixing gives a PbSnTe solid solution layer of strictly predetermined composition for IR device applications.

Examination of diffusion in epitaxial superlattice was demonstrated in this work on the PbTe–PbSe example. It is important that two different methods of diffusion parameters determination (namely, based on temperature dependence plot of satellite intensities and on direct simulation of the diffraction curve with supposed diffusion parameters) gives close results. Superlattices of another structure may give more complex and not so regular a diffraction pattern (PbTe–SnTe [4] or mentioned EuS–PbTe). In this case the last method ought to be used. The diffusion investigation in the EuS–PbTe superlattice is underway and will be presented in future.

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