

# Diffusion of indium along single <001> twist phase boundaries in Sn-Ge

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The diffusion along single phase boundaries in bicrystals was investigated experimentally for the first time. The investigation was carried out on <001> twist boundaries in Sn-Ge bicrystals for misorientation angles 0-45° with steps of 1.5-2°. The diffusing impurity (indium) was detected by x-ray microspectroscopic analysis. Maxima of the orientation dependences of the diffusion permeability, activation energy, and preexponential factor of boundary diffusion corresponded to the positions of special phase boundaries. It was found for the first time that the diffusion permeability of special boundaries was higher than that of boundaries of the general type. This was explained by the fact that the diffusion annealing temperatures were above the compensation temperature. The parameters of bulk diffusion of indium in tin were also determined.

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The recent progress made in the study of grain boundaries has been achieved mainly by concentrating on single carefully investigated boundaries in bicrystals. The scarcity of data on the properties of internal phase boundaries in crystals is due to the fact that investigations have been carried out exclusively on polycrystalline samples, whereas - in our opinion - progress can only be made by investigating single phase boundaries in bicrystals with known crystallographic characteristics.

In an earlier study<sup>1</sup> we reported the orientation dependence of the surface tension on (001) twist phase boundaries in the Sn-Ge system, determined for bicrystals.

We now used the same samples to study the diffusion of indium. The indium impurity, whose solubility in tin is ~6% and varies little with temperature, was deposited electrolytically on the surfaces of the samples. The diffusion profile of indium was determined by x-ray microspectroscopic analysis in which an electron-beam probe traveled at right-angles to the phase boundary. The indium profile was asymmetric, because the diffusion coefficient of indium in germanium (at the temperatures used in our experiments) was much less than in tin. The diffusion permeability (defined as the product of the diffusion coefficient of  $D'$  of indium on a phase boundary and the thickness of the boundary  $\delta$ ) was determined by the Fisher method.<sup>2</sup> The diffusion flux of indium atoms from the boundary into the germanium part of the bicrystal could be ignored.<sup>3</sup> Therefore, the product  $D'\delta$  was found from

$$c = c_0 \exp \left[ -y \left( \frac{D}{\pi t} \right)^{1/4} (D'\delta)^{-1/2} \right] \operatorname{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right], \quad (1)$$

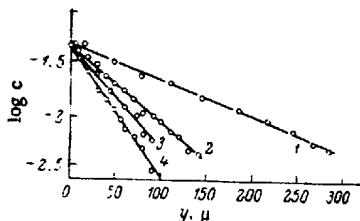


FIG. 1. Dependences of the concentration of indium near the  $c|x=0$  phase boundary on the depth  $y$ .  $T = 160^\circ\text{C}$ ,  $t = 145$  h. Misorientation angle ( $^\circ$ ): 1) 1; 2) 9; 3) 30; 4) 38.

where  $D$  is the bulk diffusion coefficient of In in Sn;  $t$  is the annealing duration;  $c_0$  is the solubility limit;  $c$  is the concentration of indium. The origin of the coordinate system was located at the point of intersection of the phase boundary with the surface of the bicrystal; the  $x$  axis was parallel to the surface and the  $y$  axis was parallel to the boundary. The diffusion took place from a constant-concentration source. The concentration curves obtained in our experiments were readily rectified by plotting the dependences of  $\ln(c/c_0)$  on  $y$  in the range  $0.3 \leq c/c_0 \leq 1$  (Fig. 1). An analysis by Le Clair<sup>4</sup> indicated that one could use in this case the Fisher solution. The determination of the boundary diffusion coefficient was complicated by diffusion growth (in the boundary region) of a wedge of an inter-

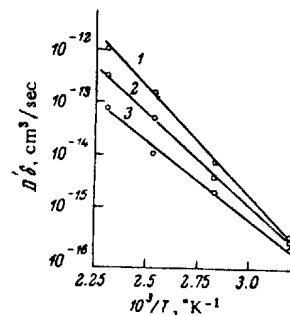


FIG. 2. Temperature dependences of the diffusion permeability of  $D'\delta$ . Misorientation angle ( $^\circ$ ): 1) 2; 2) 6; 3) 0.

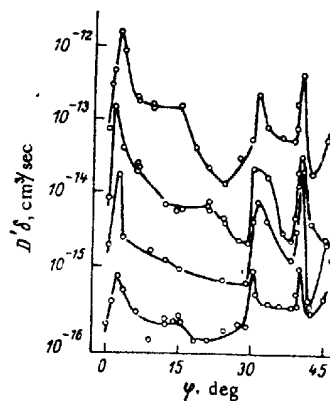


FIG. 3. Orientational dependences of the diffusion permeability  $D'\delta$ .  $T$  ( $^\circ\text{C}$ ): 1) 160; 2) 120; 3) 80; 4) 40. Diffusion period  $t$  (h): 1) 144; 2) 362; 3) 290; 4) 1366.

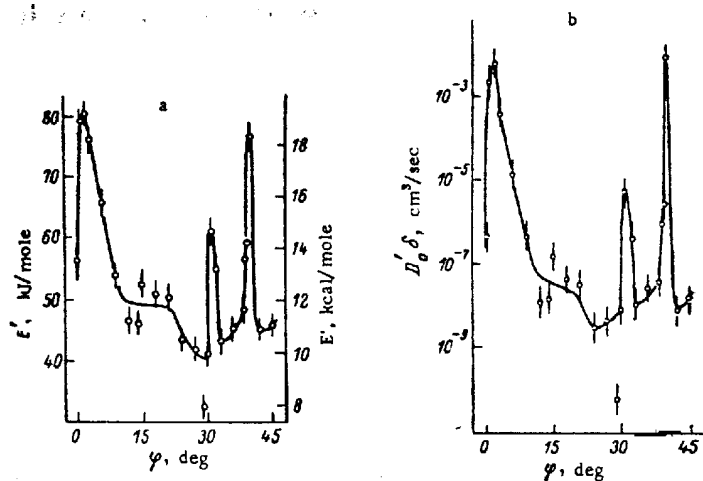


FIG. 4. Orientation dependences of the activation energy  $E'$  (a) and preexponential factor  $D_0'\delta$  (b) for the diffusion of indium along the  $\langle 001 \rangle$  phase boundaries.

mediate  $\gamma$  phase of the composition Sn + 9-15 at. % In. It was shown in Ref. 5 that in the range  $y > y_0$ , i.e., outside the  $\gamma$ -phase wedge (where  $y_0$  is the depth of the  $\gamma$ -phase wedge), one could use the solution of Eq. (1).

The bulk diffusion coefficient of In in Sn was determined for the same samples as the distribution of  $D'\delta$  and at the same annealing temperatures (160, 120, 110, 80, and 40°C). The activation energy and the preexponential factor for the bulk diffusion of In in Sn ( $12.2 \pm 0.1$  kcal/mole and  $2.2 \pm 1 \cdot 10^{-6}$  cm<sup>2</sup>/sec) differed greatly from the values determined in Ref. 6 at temperatures of 180-221°C ( $E = 25.6 \pm 0.5$  kcal/mole,  $D_0 = 12.2 \pm 2.5$  cm<sup>2</sup>/sec). Agreement was obtained only at 160°C.

The temperature dependence of the product  $D'\delta$  (Fig. 2) was used to find the activation energy  $E'$  of the diffusion along phase boundaries. The orientation dependences of the product  $D'\delta$  (Fig. 3) were nonmonotonic and the maxima occurred at angles of 2, 31, and 40°. The positions of the  $D'\delta$  maxima were independent of temperature and agreed with the positions of the minima in the orientation dependence of the surface tension found for the same boundaries.<sup>1</sup>

Since these minima correspond to special phase boundaries,<sup>2</sup> it follows that the spectral (001) twist boundaries in Sn-Ge have a higher diffusion permeability than the boundaries corresponding to the angles of rotation far from special. However, it has been assumed up to now that

special boundaries should have a lower diffusion permeability (because of fewer structural defects). This conclusion is based on the experiments on grain-boundary diffusion.<sup>7-9</sup>

The special phase boundaries correspond also to the highest values of the activation energy  $E'$  and of the preexponential factor  $D_0'\delta$  (Figs. 4a and 4b). Similar orientation dependences of  $E'$  and  $D_0'\delta$  have also been observed in the case of grain-boundary diffusion.<sup>7-9</sup> It follows that a distinguishing feature of special internal interfaces (both grain boundaries and phase boundaries) is a high value of the activation energy and of the preexponential factor of boundary diffusion. However, the diffusion permeability of special boundaries may be both higher and lower than the permeability of general boundaries.

A linear relationship between the activation energy and the logarithm of the preexponential permeability factor ("compensation effect," Fig. 5) indicates that the activation lines which are the dependences  $\ln(D'\delta) = 1/T$  shown in Fig. 2 intersect for all boundaries at the same point which is the compensation temperature  $T_C$ . In our case,  $T_C \approx 27^\circ\text{C}$ . It should be noted that the compensation effect is observed also in the case of grain-boundary diffusion, but in the case of diffusion of zinc along grain boundaries in aluminum<sup>7</sup> the compensation temperature is  $T_C \approx 450^\circ\text{C}$ . This difference in the nature of the orientation dependences of the diffusion along grain boundaries and phase boundaries (maxima of the product for these  $D'\delta$  for special phase boundaries and minima for special grain boundaries) is due to the position of the compensation tempera-

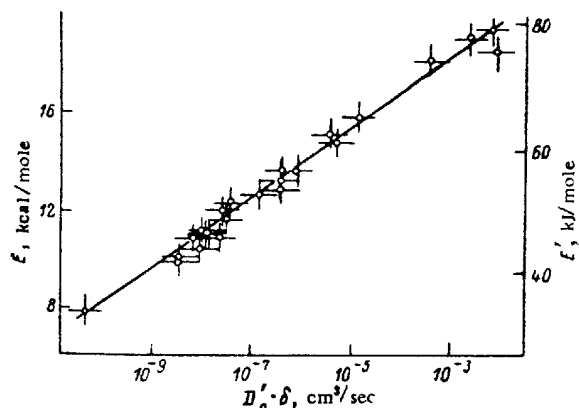


FIG. 5. Dependence of the activation energy  $E'$  on the logarithm of the preexponential factor  $D_0'\delta$  ("compensation effect").

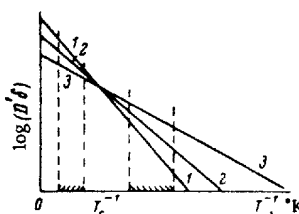


FIG. 6. Positions of temperature ranges in which the diffusion along phase boundaries ( $T > T_C$ ) and along grain boundaries ( $T < T_C$ ) was investigated, relative to the compensation point (schematic representation). 1-3)  $E_1' > E_2' > E_3'$ ,  $D_{01}' > D_{02}' > D_{03}'$ . At  $T^{-1} < T_C^{-1}$ ,  $D_1' > D_2' > D_3'$ ; at  $T^{-1} > T_C^{-1}$ ,  $D_1' < D_2' < D_3'$ .

ture relative to the investigated temperature interval. It follows from the schematic diagram in Fig. 6 that special boundaries have also a higher diffusion permeability above the compensation point, as found in our experiments.

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## Temperature dependences of the band gap and of electron spectra of ferroelectric IV-VI semiconductors

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A calculation is made of the renormalization of the electron spectra of ferroelectric IV-VI semiconductors due to the electron-phonon interactions. Allowance is made for the linear and quadratic vibronic interactions with the ferroelectrically active optical vibrations and for the interaction of the electron subsystem with acoustic vibrations. Two competing mechanisms of the temperature dependence of the band gap in ferroelectric phases have been established: the electron-phonon interaction with acoustic vibrations tends to reduce the band gap as temperature is lowered, and the vibronic interaction with the ferroelectrically active optical vibrations has the opposite effect. The dependence of the temperature coefficient of the band gap  $E_g$  on the carrier density is found for the range  $T > T_c$ . The temperature dependences of  $E_g$  are calculated for GeTe and SnTe.

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1. The electron-phonon (the vibronic) mechanism of structural phase transitions has already been invoked (see, for example, Refs. 1-4) to explain some experimental data for IV-VI systems.<sup>5-8</sup> The interband electron-phonon interaction inducing a ferroelectric phase transition<sup>1-3</sup> renormalizes the electron and phonon spectra of the system in which the transition takes place.<sup>3,9,10</sup> We shall calculate renormalization of the band gap and of the electron spectra of the valence and conduction bands of GeTe-type systems allowing for all the likely (in this case) electron-phonon interactions, including the interaction with acoustic vibrations in the deformation potential model.<sup>11</sup>

It has been demonstrated experimentally that the band gap  $E_g$  of ferroelectric IV-VI semiconductors has an anomalous temperature dependence<sup>12-14</sup> and that in the range  $T > T_c$  many of these materials exhibit a positive temperature coefficient of the band gap  $(dE_g/dT)P > 0$ , where  $P$  is the pressure,<sup>5-8</sup> contrary to the usual relationship  $(dE_g/dT)P < 0$  for semiconductors. It is natural to attribute this anomalous temperature dependence of the band gap of GeTe-type ferroelectrics to the electron-phonon interaction which induces a structural phase transition.<sup>1-4</sup>

2. We shall write down the Hamiltonian of the initial electron-phonon system in the form

$$H = \sum_{\mathbf{k}} \epsilon_{\sigma}(\mathbf{k}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + \sum_{\sigma, \sigma'} \sum_{\mathbf{k}} [P_{\sigma\sigma'}(\mathbf{k}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma'} + \text{H. c.}] +$$

$$+ N_0^{-1/2} \sum_{\sigma, \sigma'} \sum_{\mathbf{q}} [V_{\sigma\sigma'}^j(\mathbf{q}) y_{\mathbf{q}j} + N_0^{-1/2} \beta_{\sigma\sigma'}^j(\mathbf{q}) y_{\mathbf{q}j}^2] a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}-\mathbf{q}} \quad (1)$$

Here  $\epsilon_{\sigma}(\mathbf{k})$  are the initial spectra of the valence band ( $\sigma = 1$  or 2) and of the conduction band ( $\sigma = 3$  or 4), respectively, with the wave functions  $|L^{\delta'}\bar{\alpha}\rangle$ ,  $|L^{\delta'}\bar{\beta}\rangle$  and  $|L^{\delta}\bar{\alpha}\rangle$ ,  $|L^{\delta}\bar{\beta}\rangle$  ( $\bar{\alpha}$  and  $\bar{\beta}$  are the spin indices);  $a^{\dagger}$  and  $a$  are the creation and annihilation operators of electrons;  $y_{\mathbf{q}j}$  are the normal coordinates of the vibrations ( $y_{\mathbf{q}j} = \bar{y}_{\mathbf{q}j} + \hat{y}_{\mathbf{q}j}$ , where  $\bar{y}_{\mathbf{q}j}$  describes the equilibrium lattice configuration and  $\hat{y}_{\mathbf{q}j}$  the corresponding operator parts);  $j$  is the index of the vibration branch;  $j = 1$  refers to the optical vibrations active in the phase transition and  $j = 2$  refers to the acoustic vibrations;  $V_{\sigma\sigma'}$  and  $\beta_{\sigma\sigma'}$  are the constants of the linear and quadratic electron-phonon interactions;  $P_{\sigma\sigma'}$  are the matrix elements of the  $\mathbf{k} \cdot \mathbf{p}$  interaction<sup>15</sup>;  $N_0$  is the number of cells in a crystal.

We shall use  $\alpha_L^i$  and  $\epsilon_{\alpha^i\alpha^i}^{(L)}$  ( $\alpha = x, y, z$ ) for the coordinates of a ferroelectrically active optical vibration and components of the strain tensor in a system of symmetry axes referring to extrema at a given point  $\mathbf{k}_L$  in a Brillouin zone [in the Hamiltonian (1) the quantities  $\alpha_L^i$  and  $\epsilon_{\alpha^i\alpha^i}^{(L)}$  correspond to  $\bar{y}_{\mathbf{q}1}$  and  $\bar{y}_{\mathbf{q}2}$  in the limit  $\mathbf{q} \rightarrow 0$ ]. We shall select a system of coordinate axes for the  $L$  extrema oriented along the [111],  $[\bar{1}11]$ ,  $[1\bar{1}1]$ , and  $[\bar{1}\bar{1}1]$  directions