

THE INFLUENCE OF PRESSURE ON INDIUM DIFFUSION
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As noted previously (1), the investigation of single interphase boundaries in bicrystals permits data to be obtained about the dependence of different properties of interphase boundaries on their crystallographic parameters. In the preceding work (2) we studied the temperature dependence of indium diffusion coefficients for tin-germanium interphase boundaries in the temperature range 40-160°C at atmospheric pressure. High values of the activation energy and preexponential factor show that the mechanism of diffusion along interphase boundaries differs from that of bulk diffusion. Characteristics of an elementary diffusion act (activation volume) can be obtained in studying diffusion under pressure. The purpose of this work is to investigate the pressure dependence of indium diffusion coefficients along the same boundaries as in (2) at a constant temperature.

A set of 25 tin-germanium bicrystals with single interphase twist boundaries (001) in the range of misorientation angles 0-45° was used in the measurements. An indium layer was deposited on sample surfaces by electroplating. Diffusion annealing was conducted at a constant temperature: 161-200°C. The furnace with samples was placed in the high-pressure chamber with variable external mechanical supply and liquid medium. Silicon oil was used as a liquid medium for producing hydrostatic pressure. The distribution of indium concentration over the sample transverse section was determined by the electron microprobe analysis. The coefficients of bulk and boundary diffusion were obtained from the concentration distribution (the latter with the aid of the Fisher method (2)).

As it follows from Le Clair's analysis (4), the Fisher formulae can be used if $(D'/D) \ll 1$, $\beta = (D'\delta / (2D\sqrt{\delta t})) > 1$, $1 \geq c_s/c_0 \geq 0.5$, and $(\gamma/\sqrt{\beta}) = \gamma/\sqrt{\beta \delta t} \leq 1.5$, where D' and D are boundary and bulk diffusion coefficients, δ is boundary width, t the annealing time, c_s/c_0 the concentration interval (c_0 the solubility of In in Sn), γ the boundary diffusion depth. In these experiments the conditions are as follows: $10^4 < D'/D < 2 \cdot 10^7$; $300 < \beta < 10$ for special boundaries and $50 > \beta > 1$ for the misorientations lying far from special angles; $1 \geq c/c_0 \geq 0.2$; $0.1 \leq (\gamma/\sqrt{\beta}) \leq 2$. In our experiments another criterion of the Fisher analysis was also used: the straightness of $(\ln c_s) - (\gamma)$ plots. Thus the conclusion can be made that the Fisher approximation can be applied to our case. In (5) the conditions of indium diffusion along the Sn-Ge boundaries are considered in details.

Four diffusion annealings were performed at different pressures: atmospheric and 3.9, 7.2, 11.5 kbar. The annealing time was 144, 36, 75, and 28 hours, respectively. The pressure in the chamber was held with an accuracy of ± 0.2 kbar. The coefficient of indium diffusion along interphase boundaries was found to depend nonmonotonously on the misorientation angle (Fig. 1). The maximum values of the diffusion coefficient are observed on special boundaries with the misorientation angle 1°, 31°, and 40° (the values of the reciprocal density of coincidence sites Σ being equal for these boundaries to 1, 17, and 5, respectively).

The coefficients of the bulk and boundary diffusion decrease with the increasing pressure (Figs 2 and 3, respectively), and on special interphase boundaries the diffusion coefficients drop more rapidly than on non-special boundaries. The activation volume V^* of diffusion along interphase boundaries is obtained from the pressure dependence of the diffusion coefficients

$$V^* = -kT \left(\frac{\partial \ln D}{\partial p} \right) \quad (1)$$

Our experiment shows that the activation volume V_b^* is $4.0 \text{ cm}^3/\text{mol}$ for bulk diffusion of indium in tin parallel to C axis. (At the temperature of the experiment the diffusion flow of indium from the interface occurs only into the tin bulk, the coefficient of bulk diffusion of indium into germanium being negligible (2)). The ratio of the activation volume V^* to the molar vo-

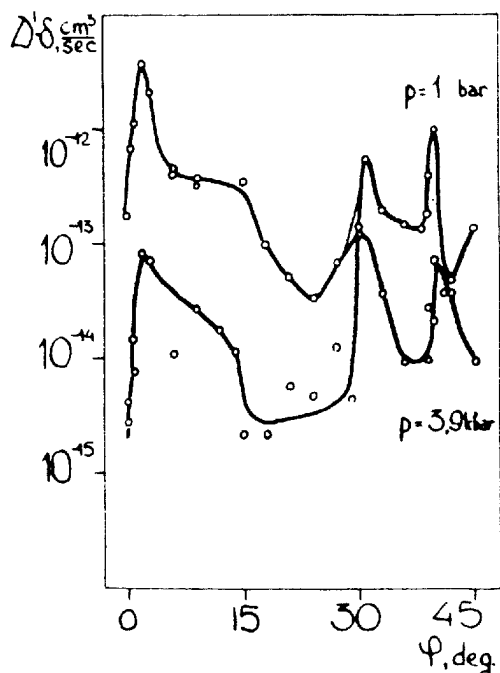


FIG.1

The dependence of the product of the indium diffusion coefficient and the boundary width $D\delta$ on the misorientation angle ϕ for pressures 1 bar and 3.9 kbar.

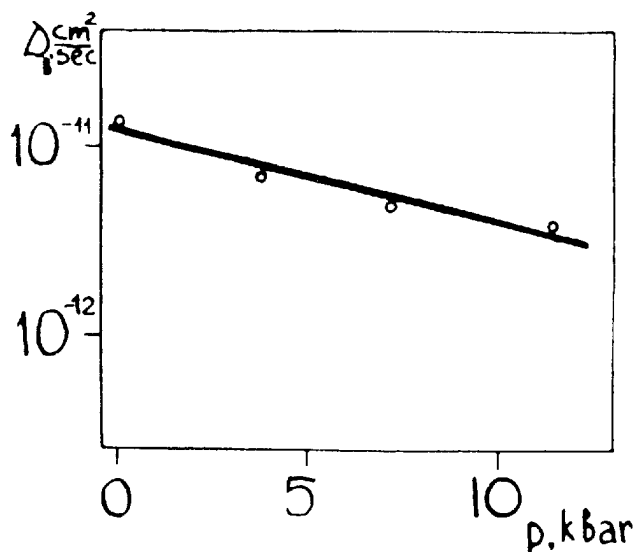


FIG.2

The pressure dependence of the bulk diffusion coefficient of indium in tin.

lume of tin Ω is 0.25. For self-diffusion in tin this ratio is $(V^*/\Omega) = 0.32$ (3).

The value of the activation volume of interface diffusion is different for various boundaries and changes nonmonotonically with the misorientation angle (Fig.4). The activation volume maxima correspond to special interphase boundaries. The ratio of the interface diffusion activation volume to the activation volume of bulk diffusion of indium in tin varies from 1.5 to 5.5. This means that diffusion along interphase boundaries seems to be a collective process.

The logarithm of the product of the diffusion coefficient along interphase boundaries at zero pressure D_{0p} and the diffusion boundary width δ as a function of the activation volume is shown in Fig.5 for the boundary set investigated. The linear relationship observed between these quantities may be called the pressure compensation effect in analogy with the temperature compensation effect (1). As it follows from the linear relationship between $D_{0p}\delta$ and V^*

$$\ln(D'_{op} \cdot \delta) = a + bV^* \tag{2}$$

(where a and b are experimental coefficients) there is a certain "pressure of compensation" p_c at which the diffusion coefficients along all the boundaries are equal, i.e.

$$\ln(D'_{op} \cdot \delta) = \ln(D'_{op} \cdot \delta) - pV^*/kT \tag{3}$$

$$\ln(D'_{op} \cdot \delta) = a + bV^* - pV^*/kT \rightarrow \text{at } p=p_c, b=p_c/kT \tag{4}$$

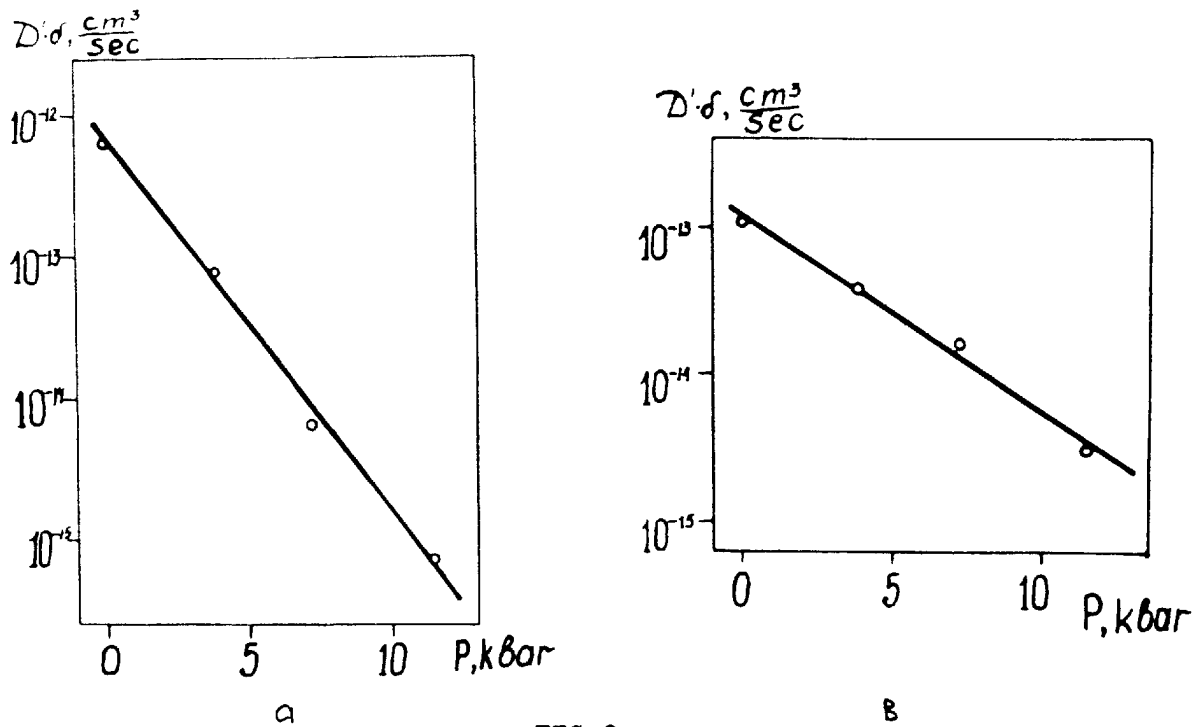


FIG. 3

The dependence of the product of the indium diffusion coefficient and the boundary width $D'_{op} \cdot \delta$ on pressure p . a) the Sn - Ge twist boundary, $\varphi = 4^\circ$; b) $\varphi = 18^\circ$.

In our case $p_c = 8.3$ kbar. This means physically that at pressures higher than p_c the coefficients of diffusion along special boundaries are higher than along non-special boundaries (Fig. 3).

In our case the driving force of boundary diffusion is a sum of entropy term and boundary segregation term. So the measured values $D'_{op} \cdot \delta$ are the products of "true" boundary diffusivities and segregation ratios β ($\beta \sim \exp(u/kT)$, where u is the heat of adsorption). These contributions cannot be separated in our experiments.

In high pressure experiments we also measure the sum of the "true" activation volume of interphase diffusion and the adsorption volume V_{ad}^* . V_{ad}^* is the volume change in the transition of indium atom from lattice to the boundary. In the same time one tin atom migrates to the lattice from the boundary. We mean that volume change of this process is negligible:

$$V_{ad}^* = V_b^{Sn} - V_b^{In} + V_L^{In} - V_L^{Sn} \tag{5}$$

where $V_b^{Sn, In}$ and $V_L^{In, Sn}$ are atomic volumes that correspond to the positions of atoms in the boundary and lattice, respectively. Let us imagine that indium atom migrates from the lattice site into the boundary interstitial.

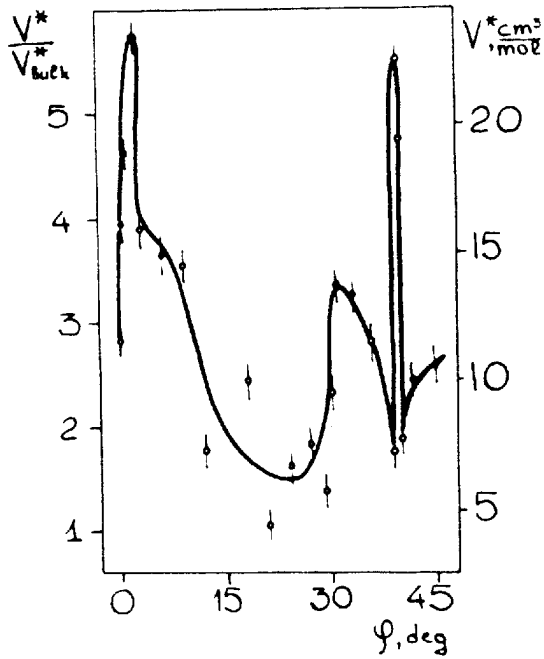


FIG. 4.

The dependence of the activation volume V^* of indium diffusion along Sn-Ge interphase boundaries on the misorientation angle φ .

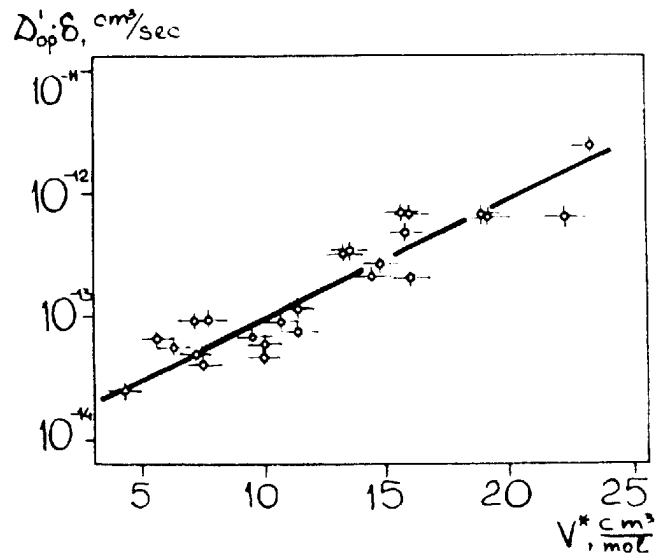
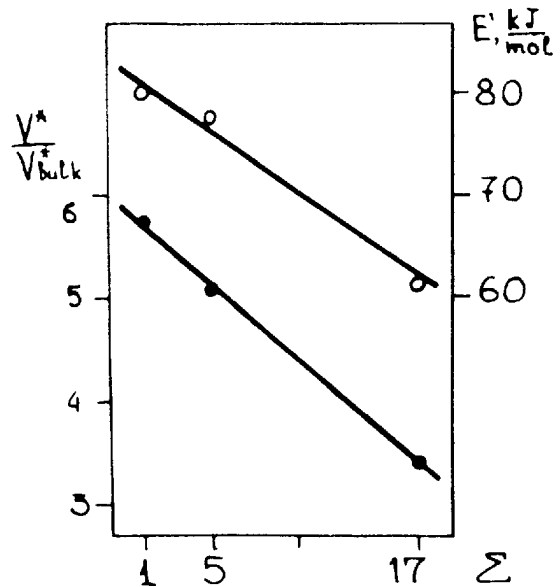


FIG. 5.

The dependence of the product of the diffusion coefficient and the boundary width at zero pressure Δ_{op} on the activation volume V^* .

FIG. 6.

The dependence of the activation volume and activation energy of diffusion along special Sn-Ge interphase boundaries on the reciprocal density of coincidence sites Σ .



Even in this case the value of V_{ad}^* is probably less than atomic volume.

The values of β are proportional to C_0^{-1} (6), C_0 is the bulk solubility of I_n in S_n . The value of C_0 is relatively great: $C_0 \approx 6\%$ at. Thus we can say that in our case the adsorption contributions do not affect significantly our basic results.

Thus, we have shown that the activation volume of diffusion along interphase boundaries is much higher than the activation volume typical of vacancy single diffusion mechanism. This effect is most pronounced for special boundaries, and with the increase in the interface perfection (with the decreasing the reciprocal density of coincidence sites Σ) the activation volume (and the activation energy) rises (Fig.6).

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