THE EFFECT OF CRYSTALLOGRAPHIC PARAMETERS OF INTERPHASE BOUNDARIES ON THEIR SURFACE TENSION AND PARAMETERS OF THE BOUNDARY DIFFUSION

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Abstract—Aiming to study the effect of crystallographic parameters of interphase boundaries on their properties the method has been developed of growing bicrystalline specimens with single interphase boundaries, whose misorientation parameters are given by the single-crystal seeds. The system of the \( \langle 001 \rangle \) tin-germanium twist interphase boundaries has been chosen for the study, being similar geometrically to the \( \langle 100 \rangle \) twist grain boundaries. The orientation dependences of the surface tension of these boundaries has been obtained, as well as those of the parameters of the boundary diffusion of indium at various temperatures and pressures. The minima of surface tension and maxima of activation parameters of the boundary diffusion (energy and entropy of activation, activation volume) correspond to the positions of special boundaries within the frameworks of coincidence sites theory. It has been also shown, that special interfaces may correspond to both minimum and maximum diffusion coefficient at a maximum values of activation parameters. The real situation is determined by the position of the so called compensation temperature with respect to the temperature interval studied. The numeric values of preexponential factor and activation volume of the boundary diffusion obtained make it possible to assume, that diffusion mechanism along special interphase boundaries differs from that of noncorrelated random walks of diffusing atoms. This is, to our opinion, connected with the ordered structure of special interphase boundaries.

Résumé—Pour étudier l'influence des paramètres cristallographiques des joints de phases sur leurs propriétés il a été élabore un procedé de croissance des échantillons bicristallins aux joints de phases isolés dont les paramètres de miseorientation sont détermind à l’aide des germes monocrystallins. Pour l'étude il a été choisi le système des joints de phases de torsion \( \langle 001 \rangle \) etain-germanium analogue, en sens géométrique, aux joints de grans de torsion \( \langle 100 \rangle \). Sont obtenues les dépendances d'orientation de la tension superficielle de ces joints de phases ainsi que celles des paramètres de la diffusion intergranulaires de l'indium à des températures et pressions différentes. Les minima de la tension superficielle et les maxima des paramètres d'activation de la diffusion intergranulaire (l'énergie et l'entropie d'activation, du volume d'activation) correspondent aux positions des limites particulières dans le cadre de la théorie des réseaux de noeuds coïncidants. Il est montré qu'aux interfaces particulières peuvent correspondre tant les minima que les maxima du coefficient de la diffusion à des valeurs maximales des paramètres d'activation; la situation réelle est déterminée par la position de la température dite de compensation par rapport à l'intervalle étudiée de températures. Les valeurs numériques obtenues du facteur préexponentiel et du volume d'activation de la diffusion intergranulaire laissent à supposer que le mécanisme de diffusion par les joints de phases particuliers diffère du mécanisme des migrations accidentelles non correlationnelles de l'atome en diffusion. Cela est lié, à notre avis, à la structure ordonnée de joints de phases particuliers.

1. INTRODUCTION

In the recent 20–30 years considerable progress has been achieved in the study of interfaces in solids: grain boundaries and interphase boundaries. Most fundamental feature of interfaces is a considerable dependence of their structure and properties on crystallographic parameters of the boundary (misorientation axis, misorientation angle, etc.). Up to now a certain amount of experimental data is obtained dealing with the structure of grain boundaries and interphase boundaries in crystals. Theoretical models of these interfaces are already created [1, 2]. At the same time the properties of the interphase boundaries and of grain boundaries were studied quite differently. For the grain boundaries the effect of crystallographic parameters on their properties is studied rather thoroughly: mobility [3, 4], characteristics of boundary diffusion [5, 6], surface tension [7].

This is not the case for the interphase boundaries. The reason is that the grain boundaries’ properties were studied for a long time on bicrystals, whose methods of growth are well developed. The interphase boundaries so far were studied only in polycrystalline specimens. Only in recent years the works appeared dealing with the study of the properties of the interphase boundaries on bicrystals, obtained by diffusion from melts [8], sintering of crystals, followed by interdiffusion of components [9]. However, there was no method, enabling to grow the equilibrium two-phase bicrystal with given crystallographic characteristics of boundaries from melts, similar to the method of growing bicrystals with the grain boundaries.

The method developed of obtaining the bicrystals with the single interphase boundary, all whose crystallographic parameters may be controlled on growing (the idea of the method is given below) made it possible to obtain the orientational dependences of thermodynamic and kinetic properties of the interphase boundaries.

2. METHOD OF GROWING BICRYSTALS WITH A SINGLE INTERPHASE BOUNDARY

Our method of growing is suitable for a limited number of systems whose components form a simple eutectic diagram, where eutectic temperature $T_e$ is close to the melting point of one of the components $T_i$ (component A), while mutual solubility of the components in a solid state is negligibly small (Fig. 1). During solidification of such systems the so called anomalous eutectic is formed. The value of the ratio of the solidification entropies $\Delta S_{\text{sol}}/\Delta S_{\text{liq}}$ in such systems is not equal to unity. Since $T_e \approx T_i$, the solidification of A starts only after completion of solidification of component B. Let us put the crystal of component B into contact with the melt of component A at a temperature of $T$, slightly exceeding the eutectic temperature $T_e$. In this moment the crystal B dissolves partly in the melt of component A because the temperature of the melt exceeds the eutectic temperature. The crystal of component B will serve as a primary crystal occurring on solidification of the melt based on A and B. Directional solidification of this system leads to the formation of a bicrystal with a single interphase boundary between the crystals A and B. On sufficiently slow solidification the excess of B, solved in the melt of A again crystallizes on the surface of B. Crystallographic parameters of the interphase boundary obtained are determined by the orientation of a single crystal B and a single-crystal seed A.

We have chosen for the study the system tin-germanium where $(\Delta S_{\text{sol}}/\Delta S_{\text{liq}}) = 0.53$ [11], $T_e \approx T_{\text{melt}}$ [12], while mutual solubility in a solid state is negligibly small [12]. Long single crystals of germanium were placed on the single crystal of tin, whose end was set on the water-cooled holder.

According to the equilibrium phase diagram of Sn–Ge [12] about 1–1.5 at $\%_o$ of germanium dissolves in tin melt at 240 C. The thickness of dissolved germanium layer exceeds 20 $\mu$m, because the thickness of tin crystal is about 2 mm. Thus the contamination layer has been removed and dissolved in the melt before the formation of the tin-germanium interphase boundary. From this viewpoint the method proposed is equivalent to the classic method of growing bicrystals from the melt in single phase systems. The process of directional solidification was carried out in a graphite crucible under pure argon at the melt temperature not exceeding 240 C and solidification rate of $\approx 10^{-3}$ mm/s. Equilibrium of the phase composition and absence of germanium precipitations in the bulk of crystallized tin were analysed with the help of the electron probe microanalysis and scanning electron microscopy (with magnification up to 40,000 $\times$). The crystals of both phases were found to have equilibrium composition up to the interphase boundary, the boundary being plane and there were
no eutectic layers or germanium precipitates in tin crystal. Theoretical estimations show, that even after formation of such layers or precipitations with the size less than 1-1.5 \mu m, these nonequilibrium formations due to the action of the surface tension by means of the bulk or surface diffusion should disappear respectively in 10 or 0.1 s [13]. This time it is by several orders less than the period during which the bicrystals are subjected to the premelting temperature on growing.

The specimens were grown with the twist interphase boundaries, whose plane was perpendicular to the (100) axis of germanium and (001) axes of tin. Misorientation angle \( \varphi \) varied from 0 up to 45°. At \( \varphi = 0 \) the directions (100) of tin and germanium are parallel. The lattice parameters of tin and germanium in the boundary plane differ by 3%\( \gamma \), therefore, there exists a geometrical analogy between these interphase boundaries and twist grain boundaries with a common (100) axes.

### 3. SURFACE TENSION OF THE SINGLE INTERPHASE TWIST (001) TIN-GERMANIUM BOUNDARIES

The surface tension of the interphase boundaries in many cases determines the character and evolution of the microstructure of the multiphase systems. However the surface tension of interphase boundaries is known only for a limited number of systems. The method of measurement applied allowed to determine only values averaged over all boundaries in a crystal, while there are no data concerning the effect of crystallographic parameters on the surface tension of the interphase boundaries.

We determined the value of the surface tension of the interphase boundaries \( \sigma_s \) using the parameters of the thermal groove [12], which is formed at the site where the interphase boundary meets the specimen surface. To form the groove, preliminary polished specimens were annealed in the argon atmosphere of high purity at 220°C for 35 h. This time is quite enough for the dihedral angles at the groove top to reach the equilibrium value. Development of the groove profile at the exit of the interphase boundary to the specimen’s surface differs from the process of formation of groove in the grain boundary: the groove on the interphase boundary is asymmetrical. The dihedral angles between the boundary plane and the outer surfaces of germanium and tin (\( \theta_{\text{ge}} \) and \( \theta_{\text{sn}} \), accordingly) differ from one another, and here \( \theta_{\text{ge}} < \theta_{\text{sn}} \). If initially the specimen surface was plane, the interphase boundary was perpendicular to it, and surface tension of the interphase boundary \( \sigma_s \) was less than surface tension of germanium \( \sigma_{\text{ge}} (\sigma_s < \sigma_{\text{ge}}) \), then the development of the groove profile is limited by the process of thermal etching of germanium (since the annealing temperature is \( \sim 0.4 T_{\text{ge}} \)). Surface tension of the interphase boundary is determined from the condition of equilibrium of forces in the place of the interphase boundary show on the surface (Herring’s equation)

\[
\sigma_s = \sigma_{\text{ge}} + \sigma_{\text{sn}} + 2 \sigma_{\text{ge}} \sigma_{\text{sn}} \cos(\theta_{\text{ge}} + \theta_{\text{sn}})
\]

where \( \sigma_{\text{ge}} \) is surface tension of tin. Besides, for \( \cos \theta_{\text{sn}} \approx 1 \) we have

\[
\cos \theta_{\text{sn}} = \frac{X_{\text{ge}}}{X_{\text{sn}}} = \beta
\]

where \( X_{\text{ge}} \) and \( X_{\text{sn}} \) are the linear sizes of the groove along the \( X \) axis. In the case when the formation of the groove of thermal etching is controlled by a surface diffusion, and the mutual diffusion of components on the interphase boundary can be neglected, then, accordingly to [15] the magnitude \( \beta \) is equal to

\[
\beta = \left( \frac{D_{\text{ge}} \sigma_{\text{ge}} \Omega_{\text{ge}}}{D_{\text{sn}} \sigma_{\text{sn}} \Omega_{\text{sn}}} \right)^{1/4}
\]

where \( D_{\text{ge}}, D_{\text{sn}} \) are the surface diffusion coefficients, \( \nu_{\text{ge}}, \nu_{\text{sn}} \) are the surface atomic densities, \( \Omega_{\text{ge}}, \Omega_{\text{sn}} \) are the atomic volumes of germanium and tin accordingly.

Combining (1) and (2), for the magnitude of relative surface tension of this interphase boundary we obtain

\[
\left( \frac{\sigma_s}{\sigma_{\text{sn}}} \right)^2 = \left( \frac{\sigma_{\text{ge}}}{\sigma_{\text{sn}}} - 1 \right)^2 + \sigma_{\text{sn}} \left( 1 + \frac{1}{\beta} \right) \cos \theta_{\text{sn}}.
\]

The magnitudes \( \cos \theta_{\text{sn}} \) and \( \beta = X_{\text{ge}}/X_{\text{sn}} \) are determined experimentally. The magnitude \( \sigma_s \) was constant in our experiments and equal to surface tension for the (100) plane of tin.

We had carried out the calculation of the orientation dependence of \( \sigma_{\text{ge}} \) assuming that \( \sigma_{\text{ge}} \) is proportional to a reticular atomic density. The calculation showed that besides the narrow field of the \( \varphi \) angles (\( \varphi = 0 + 2\° \) and \( \varphi = 4 + 45\° \), where surface tension is lower) the average value can be used \( \sigma_{\text{ge}}/\sigma_{\text{sn}} = 1.61 \), calculated for \( T \approx T_{\text{ge}} \) by the data of [16]. Thus we can assume that the torque terms in Herring’s equation are negligibly small. The groove profile was measured with the help of Le markers, using a helium-neon laser as a source of light. For more precise determination of \( \sigma_s \) up to 250 profiles were measured on each specimen. When calculating the absolute values of \( \sigma_s \) for the interphase boundaries the surface tension of tin was taken 0.650 J/m² [16].

Figure 2 shows the dependence of surface tension of the (001) twist interphase tin-germanium boundaries on misorientation angle. This dependence is nonmonotonous. The surface tension varies within a given angle interval from 4.427 up to 0.45 J/m². The boundaries with the angles \( \varphi = 2 \° \) and \( 40 \° \) correspond to the minimum of the surface tension. Angles \( 30 \° \) and \( 40 \° \) are close to those corresponding to the special grain boundaries with (100) axis. Within the frameworks of the coincidence site lattices (CSL) theory, the grain boundaries with the value of
\(\Sigma = 13\) and \(\Sigma = 5\) have the misorientation angles with respect to the common axis \((100)\) equal, respectively, to \(\phi = 28^\circ\) and \(\phi = 37^\circ\) [1].

Relatively high values of the surface tension of the interphase boundaries studied with respect to the value of the surface tension \((\sigma = 0.7\sigma_c)\) and small variation interval of this value is due to that the tin-germanium boundaries belong to the so-called weak bonded boundaries, i.e., those between the substances of different type, metal and semiconductor. Formation of these boundaries does not lead to the formation of large elastic stresses over the crystal volume and dislocation relaxation of these stresses [18]. According to the authors of [18] these are the very boundaries among which the presence of the boundaries with the misorientation angles predicted by the CSL theory, should be most pronounced. In fact, our experiments show, that the surface tension of special interphase boundaries of the type of special misorientation angles of \(30^\circ\) and \(40^\circ\) is close to that of the epitaxial boundary with \(\Sigma = 1\), corresponding to the coincidence of the planes (001) and parallel directions of \((100)\) in tin and germanium.

When analysing the orientation dependence obtained one can conclude, that the special interphase boundaries with misorientation angles corresponding to high density of coinciding sites, in fact, possess the special properties—lower surface tension, as compared to the rest, random boundaries.

The orientation dependence of the surface tension obtained makes it possible to correctly analyse the data on kinetic properties of the interphase boundaries: the possibility appears to compare the data obtained not only with the prediction of geometrical models, but also with known structural positions of the boundaries with low surface tension.

### 4. DIFFUSION ALONG THE SINGLE INTERPHASE \(<001>\) TWIST TIN–GERMANIUM BOUNDARIES AT ATMOSPHERIC PRESSURE

In the next stage we study the diffusion of a third component [19] along the same interphase twist \((001)\) tin–germanium boundaries, whose surface tension was measured in a previous section.

Indium was chosen as a diffusion element. When choosing it we bear in mind, that diffusional removal from the boundary will occur only in the tin bulk, since the diffusion mobility of germanium below the tin melting point is negligibly small. Solubility of indium in tin weakly depends on temperature and is quite large to enable the measurements with the help of the electron probe microanalysis. However, the measurements of diffusion coefficients were hampered, because of the formation and growth on diffusion anneal of the layer of intermediate \(\gamma\) phase of the composition Sn–(12–15) at.\% In. In the boundary region this layer has the shape of a wedge. We have solved the diffusion problem, describing this process. Thereby, it was assumed, that the coefficient of diffusion along the interphase boundary is much more, than those of the bulk diffusion in tin and \(\gamma\)-phase. Movement of the boundary between tin and \(\gamma\)-phase was determined by the difference of diffusion flows of indium atoms. It was assumed, that diffusion into volume from the surface and diffusion flows in the volume parallel to the phase boundary may be neglected. Diffusion flow along the interface between tin and \(\gamma\)-phase was also neglected. Solution of the problem and testing experiments are described in detail in [20]. It was shown, that below the intermediate \(\gamma\)-phase layer for the determination of the coefficients of boundary diffusion (as an asymptotical form of the Wipple solution) the Fisher’s solution is applicable, modified on the basis that diffusion permeability of one of the phases is negligibly small. Correctness of the Fisher’s approximation for our case was analysed [24, 25] and confirmed, in particular, by the linearity of the dependence of indium concentration at the boundary \(C\), on the depth \(\gamma\).

The indium layer was put on the surface of bicrystals electrolytically. Diffusion annealing below 100 \(\text{C}\) were carried out in a fluid thermostat, while at \(T > 100\ \text{C}\), in the muffle furnace in the argon atmosphere. Four diffusion annealing treatments were carried out: at 40, 80, 120 and 161 \(\text{C}\) with the duration 1360, 290, 362 and 144 h respectively. In order to avoid additional annealing at room temperature, the indium layer was put on the specimen’s surface directly before diffusion annealing in a cold (5–8\(^\circ\)C) electrolyte. After annealing the specimens were kept in the vessel with liquid nitrogen to be taken from it only for preparing polishes and measurements with aid of the electron microprobe analysis. The accuracy of keeping the annealing temperature was \(\pm 0.5\ \text{C}\).

\(\Sigma\) is the CSL unit cell volume divided by the atomic volume.
Figure 3 shows the dependences of the product of the coefficient of boundary diffusion of indium and the boundary width $D\delta$ upon the misorientation angle $\phi$ for four temperatures: 40, 80, 120 and 161°C. When reducing the temperature the diffusion coefficients on all the boundaries decrease. All orientation dependence of $D\delta$ are nonmonotonous. Each of them has three maxima at the angles $\phi = 2^\circ$, 31° and 40°. The angular positions of the maxima do not change with temperature. With the decrease of temperature over the interval from 161°C down to 40°C the differences between the diffusion coefficients along the boundaries with different misorientation angles decrease, while the curves become more smooth. Let us note, that the special boundary with a low surface tension corresponds to the diffusion coefficient maxima.

The temperature dependence of diffusion coefficients for the boundaries with various misorientation angles were used to determine the activation energy and preexponential factor of the boundary diffusion $D_0\delta$. Orientation dependences of these values are given respectively in Figs 4 and 5. These curves, like the dependences of $D\delta$ on misorientation angle are nonmonotonous. The positions of special boundaries with misorientation angles $\phi = 2^\circ$, 31° and 40° correspond to the maxima of $E$ and $D_0\delta$.

There exists a linear dependence between $E$ and $D_0\delta$ (Fig. 6). The slope of this straight line gives the so called compensation temperature, i.e. the tem-
temperature at which the diffusion coefficients at all the boundaries are equal. In our case this temperature equals 27 ± 1 °C and is below the temperature interval studied. Therefore (see scheme in Fig. 7) the special boundaries with higher activation energy correspond to the maximum values of the diffusion coefficients. When the compensation temperature is below the temperature interval studied, like is the case, e.g. of diffusion of zinc along grain boundaries of aluminium, then special boundaries with maximum values of $E$ correspond to the minima of diffusion coefficients $D$ [5, 6].

In order to measure the coefficients of the boundary diffusion we also determined that of the bulk diffusion of indium in tin $D_0$ over the temperature interval 40–220 °C. The temperature dependence of this value is given in Fig. 8. Above 180 °C our data coincide with those literature [23]. Below 160 °C the activation energy of the bulk diffusion decreases down to 49 kJ/mol (preexponential factor $D_0 = 2.10^{-4}$ cm$^2$/s). In [24] this anomaly and features of the compensation effect in the system we discuss in terms of the Frenkel heterophase fluctuations.

The values of the activation energy of the boundary diffusion of indium in tin do not exceed those of the bulk diffusion of indium in germanium (232 kJ/mole) and equal (0.17–0.34) of this value.

Let us also note high values of preexponential factor $D_0$ of the boundary diffusion for special boundaries, which correspond to the interval of the values of coefficients $D_0$ from 2.10$^7$ up to 2.10$^6$ cm$^2$/s (the boundary width is taken, as usually, equal to 5.10$^{-6}$ m). Thus, this value is by several orders more, than the interval of the values of preexponential factor of the bulk diffusion, being characteristic of the bulk diffusion, occurring by means of noncorrelated random walks (10$^{-3}$–10$^{-5}$ cm$^2$/s).

Thus, when studying the diffusion of indium along individual interphase tin-germanium boundaries over the temperature interval of 40–160 °C a number of interesting features of this process has been revealed: relatively high values of $E'/E_0$ where $E_0$ is the activation energy of bulk diffusion of indium in tin, anomalously high values of the preexponential factor and unusual position of compensation temperature with respect to the temperature interval studied.

5. DIFFUSION ALONG THE INDIVIDUAL INTERPHASE TWIST ⟨001⟩ TIN-GERMANIUM BOUNDARIES AT HIGH PRESSURES

The results obtained in the first section of this study make it possible to assume, that the mechanism of diffusion along interphase boundaries, and, in particular, along special ones, differs from the mechanism of noncorrelated random walks, the idea originates from extremely high values of preexponential factor of the boundary diffusion. In order to identify the mechanism of the boundary diffusion more fundamentally it is necessary to measure some value directly connected with the number of atoms, participating in the elementary diffusion act. This is the activation volume of diffusion $V^*$—being the difference of the system volumes in the ordinary and activates states. The value of $V^*$ for the bulk and boundary diffusion was determined in [25]

$$V^* = -\frac{K T}{\left(\frac{\partial \ln D_0}{\partial (E'/E_0)}\right)}.$$  

In our experiments the coefficients of diffusion of indium was measured at 161 ± 2 °C and pressures of 1, 3.9, 7.2 and 11.5 kbar. Duration of annealings was respectively equal to 144, 36, 75 and 28 h. Annealings at high pressures were carried out in the chamber with variable external mechanical supply. The silicon oil served the medium, producing a hydrostatic pressure. The pressure in the chamber was measured with the help of a managanin resistance temperature by the chromel–alumel thermocouple. The accuracy of keeping the pressure was about ±0.2 kbar.

Figures 9 and 10 show the dependences of the product $D/\delta$ on the misorientation angle for indium diffusion along the interphase twist ⟨001⟩ tin germanium boundaries at constant temperature 161 °C and various pressures (1 bar, 3.9, 7.2 kbar) with the increase of pressure the diffusion coefficient decreases along all the boundaries. Three maxima, corresponding to special boundaries may be noticed.
on these dependences. With the increase of pressure the orientation dependences become more smooth. Let us note, that when at atmospheric pressure the compensation temperature at which the diffusion coefficients along all the boundaries are equal was out of the temperature interval studied then "the compensation pressure", at which they are also equal along all the boundaries, is inside the pressure interval studied and equals 8.3 kbar.

The value of activation volume of the bulk diffusion of indium in tin according to our data, was equal to $V^*_b = 4.0 \text{ cm}^3/\text{mol}$, this being 0.25 of the specific atomic volume of tin $\Omega = 16.3 \text{ cm}^3/\text{mol}$. For comparison let us note, that for the bulk self-diffusion in tin $V^*_b$ equals $0.33 \Omega$ [26]. It should be noted that the activation energy of the bulk self-diffusion in tin and of diffusion of indium in tin are also close and differ less, than by $10 \text{%}$. Figure 12 shows the orientation dependence of the activation volume of indium diffusion along interphase twist $\langle 001 \rangle$ tin-germanium boundaries. The same figure shows the values of the ratios of $V^*$ to the activation volume of diffusion. The value of $V^*$ is inside the interval 1.5–5.5 $V^*_b$. The orientation dependence of the activation volume is nonmonotonous, the maxima on it correspond to the positions of special interphase boundaries. The activation volume of diffusion along the ordinary boundaries practically does not differ from the respective value of the bulk diffusion of indium in tin.

In our experiments on diffusion under pressure a linear dependence is observed between the activation volume and $\ln D_{0b} \delta$ logarithm of the product of the coefficient of boundary diffusion under zero pressure $D_{0b}$ and the boundary width $\delta$. In this case the value of $D_{0b}$ plays the role of the analogue of the preexponential factor, while $V^*$ is similar to the activation energy. Using the slope of this dependence (Fig. 13) one may determine the so called compensation pressure $P_c$, which is equal to 8.3 kbar. Below the compensation pressure the boundaries with a maximum activation volume correspond to the maximum diffusion coefficients (above $P_c$ to the minimum ones).

Similar linear dependences are observed also for the pairs $V^*$ and $E'$ and $V^* - \ln D_{0b} \delta$. However, in these cases the scattering of the values around the regression lines is much more, than in Figs 6 and 13, since these pairs were determined in the independent experiments, thereby the measurements of $V^*$ were carried out at the maximum temperature of the interval for determination of $E'$ and $D_{0b} \delta$.

6. DISCUSSION

The results of measurements of the surface tension of the interphase boundary have shown, that the boundaries with misorientation angles close to the angles for special grain boundaries and those with expitaxial misorientation angle, in fact, possess lower surface tension then random boundaries. The differences of $\delta_p$ between the special and random boundaries are small. However, the tin germanium boundaries are the boundaries with a weak bond, therefore, small differences of $\delta_p$ correspond to large changes of the boundary structure and, hence, they strongly effect the kinetic properties.

It so occurred, that special boundaries correspond to the maximum of the activation diffusion parameters: activation energy $E'$, preexponential factor $D_{0b} \delta$ (or entropy of diffusion activation $S' \sim \ln D_{0b} \delta$) as well as the activation volume of diffusion $V^*$. The
maxima of $E'$ and $D_0 \delta$ were observed at special boundaries also in the experiments dealing with diffusion along grain boundaries [5, 6]. Earlier it was assumed [5], that since special boundaries are more packed, they should be related to higher activation energy barrier and lower values of diffusion coefficients, since an atom experiences the maximum "difficulties" when moving along such boundaries. Our results show, that the ratio of the diffusion coefficients for special boundaries to those for the random ones are determined by the position of compensation points with respect to the temperature and pressure intervals studied. The physical reasons, determining the value of compensation temperature and pressure are so far not quite clear. Their discussion is out of the scope of this study. We shall only note, that the compensation temperatures, obtained when studying the indium diffusion along the interphase tin-germanium boundaries are close to the tin melting point and temperature of the allotropic transformation of $\alpha$ tin into $\beta$ tin. Connection of the diffusion process with the formation of heterophase fluctuations in these systems is discussed in more detail in [24].

Let us further note, that the values $E'$, $D_0 \delta$ and $V^*$ for the random boundaries practically do not differ from the respective values for the bulk diffusion of indium in tin. At the same time the activation parameters of special boundaries are considerably higher. As it was already mentioned, the preexponential factor of diffusion along the special boundaries is by several orders higher, than those for the bulk diffusion while their activation volume is several times as much as $V^*_0$. It is known, that the bulk diffusion occurs by means of noncorrelated random walks of a single atom. Thereby, the maximum diffusion rate is determined practically by the frequency of atomic oscillations, close to Debye frequency. The fact, that the preexponential factor of the boundary diffusion is by several orders more, than that of the bulk diffusion may be explained only by the difference in the mechanism of diffusion along special boundaries from that of the random walks of a single atom. The elementary act of diffusion along special boundary is determined, apparently, by the correlated motion, with the group of several atoms participating; this is also confirmed by high value of activation volume of diffusion along special boundaries.

What are the physical reasons, which may explain the difference of the mechanism of diffusion along special boundaries from that of noncorrelated random walks?

Some answer can be obtained concerning the results of the atomistic studies of boundary vacancies structure and the process of boundary diffusion [10, 17, 33–35]. These results may be summarized as follows:

(a) The vacancy concentration in boundaries is higher than in the bulk [10, 17]. In other words we can talk about "a binding energy" between the vacancies and the boundaries.

(b) The vacancy concentration in random boundaries is higher than in the special ones [10].

(c) In special boundaries there are certain energetically favorable sites for the vacancies and impurities [17].

(d) When the binding energy between the vacancy and boundary defects or between the vacancy and impurity atom increases the correlation factor of diffusion rapidly decreases [34, 35].

This set of results clarifies the interphase boundary diffusion data obtained in our work:

(1) According to (a) and (d) the diffusion coefficient $0'$ along the boundary is much higher than in the bulk ("across" the boundary).

(2) According to (b) and (c) the summarized energies for vacancy formation and vacancy migration are higher in the special boundaries than in the random ones. This is why the values of $E'$ for special boundaries are higher.

(3) From the viewpoint of diffusion the special boundaries differ from the volume and random interphase boundaries in that they possess the sites of different sort, in which the diffusing atom has different surroundings [10, 17]. In the volume and at the boundary of ordinary types all lattice sites are equivalent. When the lattice sites, along which the diffusion takes place, become nonequivalent and position of the sites with different energy differs from that random one, then also may arise the deviations from the mechanism of random walks. Then with the increase of a degree of ordering of the boundaries, i.e. with the increase of the energetical difference between different positions of diffusing atom at the boundary the deviations should also increase of the activation

Fig. 12. Dependence of the activation volume $V^*$ of indium diffusion along the twist (001) tin-germanium interphase boundaries on misorientation angle.
parameters from the values characteristic of the ordinary boundaries. In fact, with the increase of degree of ordering of the boundaries the values \( E^* \), \( D_0^* \delta \) and \( V^* \) nonmonotonously increase. This is clearly seen from the Fig. 14, where the dependences are given of the activation parameters of indium diffusion along special tin-germanium interphase boundaries on the value of reciprocal density of coinciding sites \( \Sigma \). The higher the density of coinciding sites \( \Sigma^{-1} \), i.e. the higher the perfection of the boundary the higher are the values of \( E^* \), \( D_0^* \delta \) and \( V^* \).

A similar situation is observed also during bulk diffusion, when the positions of a diffusing atom in the volume become nonequivalent. For example, during transition of brass from disordered state into ordered the activation energy increases as much as 1.5–2 times and preexponential factor increases by 4–6 orders [27]. The activation volume of diffusion also increases during transition from the systems with lesser energetical differences in atomic positions in the lattice to those with larger ones. For example, on transition from most metallic in properties alcali-halid crystals (such as KI) to those most metalloid ones (such as LiF) the ratio of the activation diffusion volume to the atomic volume increases from the value close to a unity (0.86 for KI) to 8.41 (NaF) and even to 12 for LiF [28].

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