Orientational dependence of the surface tension at tin–germanium phase boundaries

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Bicrystals with single phase boundaries of given crystallographic orientation were used to determine the surface tension at phase boundaries by producing a thermal etching groove. A nonmonotonic orientational dependence of the surface tension was observed. The results were analyzed using the theory of coincident-site lattices.

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Phase boundaries represent an important and extremely interesting class of objects. However, although considerable progress has been made in the theoretical and experimental investigations of the structure and properties of grain boundaries, very little information is available on the thermodynamic and kinetic properties of these boundaries and, moreover, there are practically no data on the relationship between these properties and the crystallography of phase boundaries. We think that this is because of the absence of a method for investigating single phase boundaries of a given crystallographic orientation, whereas studies of grain boundaries in bicrystals have a long history.[1]

We developed a method for preparing bicrystals with a single phase boundary and for ensuring directional crystallization of one phase on the surface of a single crystal of another phase.

The investigated system was the tin–germanium pair with a low mutual solubility of the components in the solid state.[2] This was a necessary condition for a pair of metals when bicrystals were grown by our method. Single boundaries formed in this way were in equilibrium in the thermodynamic sense, since liquid tin, solid tin, and solid germanium were all in equilibrium during crystallization. The absence of second-phase inclusions was indicated by the results of a local x-ray microemission analysis. The process of growth was sufficiently slow for the phase boundary to have its natural roughness (with corners, steps, etc.) as a result of diffusion in the liquid and for this boundary to be in a structural equilibrium.

An important thermodynamic property of an equi-

librium phase boundary is its surface tension. It is interesting to know how the surface tension of a phase boundary depends on its crystallographic parameters. For example, it is known how the crystallography of grain boundaries affects the surface tension.[3] Therefore we began a study of the properties of single phase boundaries by investigating the orientational dependence of their surface tension.

We grew a batch of Sn–Ge bicrystals in which the phase boundary was oriented at right-angles to the four-fold rotation axes in Sn ($\langle 001 \rangle$ axis) and in Ge ($\langle 100 \rangle$ axis), and the angle of rotation φ about the axis perpendicular to the boundary was varied from 0 to 45° (Fig. 1). In the $\varphi = 0°$ case the $\langle 010 \rangle$ direction in Ge was parallel to the $\langle 100 \rangle$ direction in Sn. These boundaries were selected because in the geometric sense they were similar to the grain boundaries (twist boundaries with the $\langle 100 \rangle$ rotation axis): the ratio of the lattice periods in the (100) plane of Ge and the (001) plane of Sn was 0.970. However, this was not a full analogy because the chemical properties of the phases were quite different and, moreover, the lattice periods in the direction of the $\langle 001 \rangle$ axis in Sn and
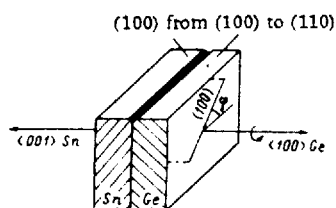
(100) from (100) to (110)

FIG. 1. Schematic representation of an Sn–Ge bicrystal with a single phase boundary and a thermal-etching groove.

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$\langle 100 \rangle$ axis in Ge, i.e., at right-angles to the boundary, differed by a factor of 1.78.

The surface tension of a phase boundary was determined by measuring the parameters of a groove formed by thermal etching at the points where the boundary emerged on the surface of a sample. This method was preferable to, for example, the method of determining the surface tension at triple contacts because the mobility of the boundaries was low: considerable annealing times were required before angles at the point of triple contact between the phase boundaries could be measured. A groove was formed by annealing polished samples in an atmosphere of spectroscopically pure argon for 35 h. The depth of the groove was $\sim 0.5\,\mu$, which was sufficient for measurement purposes. In fact, this method allowed us to determine the equilibrium values of the angles because an increase in the duration of annealing to 200 h did not alter the dihedral angles.

The profile of the thermal etching groove at the points of emergence of the phase boundary on the surface had a number of special features distinguishing it from a corresponding grain-boundary groove. The phase-boundary groove was asymmetric, in contrast to the grain-boundary case,[4] and the dihedral angles between the plane of the boundary and external surfaces of germanium and tin (θ_{Ge} and θ_{Sn}, respectively, in Fig. 2b) differed from one another and it was found that $\theta_{Ge} < \theta_{Sn}$. If the initial surface of a sample was plane, the boundary was perpendicular to this surface and the surface tension of the phase boundary σ_{ph} was less than the surface tension of germanium σ_{Ge} ($\sigma_{ph} < \sigma_{Ge}$), it was found that the kinetics of the groove profile was controlled by thermal etching of germanium (since the annealing temperature was $0.41 T_{mp}^{Ge}$). The surface tension at the phase boundary was deduced from the conditions of equilibrium of the forces at the points of emergence of the phase boundary on the surface:

$$\sigma_{ph}^2 = \sigma_{Ge}^2 + \sigma_{Sn}^2 + 2\sigma_{Ge}\sigma_{Sn}\cos(\theta_{Ge}+\theta_{Sn}), \quad (1)$$

where σ_{Sn} is the surface tension of tin. For $\cos\theta_{Sn,Ge} \ll 1$, we found that

$$\frac{\cos\theta_{Sn}}{\cos\theta_{Ge}} = \frac{X_{Ge}}{X_{Sn}} = \beta, \quad (2)$$

where X_{Ge} and X_{Sn} are the linear dimensions of the groove in the direction of the x axis (Fig. 2b). If the formation of the thermal-etching groove was controlled by

surface diffusion and one could ignore the mutual diffusion of the components across the phase boundary, one could define a quantity β

$$\beta = \frac{B_{Ge}}{B_{Sn}}, \quad (3)$$

where B_{Ge} and B_{Sn} are, by analogy to a grain-boundary groove,[4]

$$B = D_s \Omega \rho^s, \quad (4)$$

where D is the surface diffusion coefficient; ρ^s is the surface density of atoms; Ω is the atomic volume. Combining Eqs. (1) and (2) we found the relative surface tension at the phase boundary from

$$\left(\frac{\sigma_{ph}}{\sigma_{Sn}}\right)^2 = \left(\frac{\sigma_{Ge}}{\sigma_{Sn}} - 1\right)^2 + \frac{\sigma_{Ge}}{\sigma_{Sn}}\left(1 + \frac{1}{\beta}\right)^2 \cos^2\theta_{Sn}. \quad (5)$$

We determined experimentally[1] the quantities $\cos\theta_{Sn}$ and $\beta = X_{Ge}/X_{Sn}$ (Fig. 2b). The value of σ_{Sn} was constant in our experiments and it was equal to the surface tension of the (100) plane of tin.

The value of σ_{Ge} was not constant: when the angle φ was varied, the germanium plane emerging on the surface of the sample also varied (Fig. 1). For $\varphi = 0°$ it was the (100) plane of Ge, whereas for $\varphi = 45°$ it was the (110) plane of Ge. We calculated the orientational dependence of σ_{Ge} employing a simple model according to which the surface tension was proportional to the surface density of atoms. This calculation demonstrated that, apart from a narrow range of angles φ ($\varphi = 0-2°$ and $\varphi = 43-45°$), where the surface tension was lower, one could use the average value $\sigma_{Ge}/\sigma_{Sn} = 1.61$ calculated for $T \approx T_{mp}^{Sn}$ on the basis of the results of Ref. 5.

The profile of the thermal-etching groove (Fig. 2a) was photographed for each sample using a double-beam Linnik microinterferometer and a coherent light source (a helium-neon laser emitting at $\lambda = 6328$ Å). Constant-intensity fringes represented a thermal-etching profile of a groove magnified by the ratio $2a/\lambda$, where a is the distance between the fringes (Fig. 2b). The value of $\cos\theta_{Sn}$ was deduced from the angle θ_{Sn}' in a photomicrograph using the condition

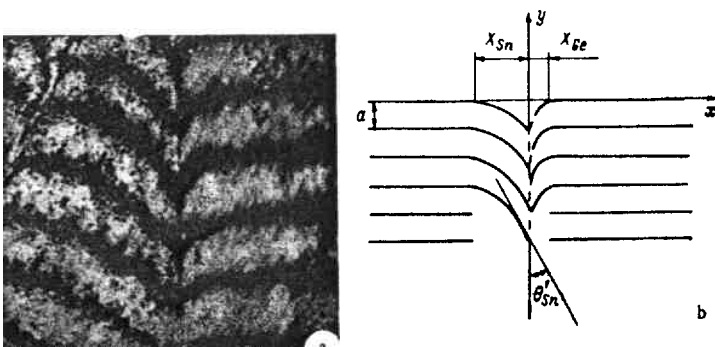$$\tan\theta_{Sn}' = \frac{2a}{\lambda}\tan\theta_{Sn}. \quad (6)$$

FIG. 2. Thermal-etching groove at the points of emergence of a phase boundary on the surface: a) interference pattern; b) schematic representation of the method of analysis of this pattern.
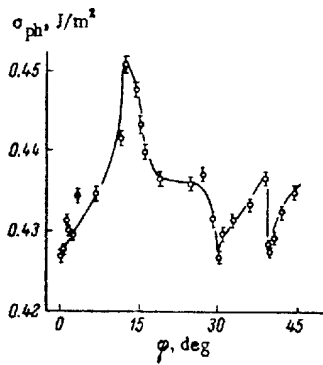
FIG. 3. Dependence of the surface tension σ_{ph} at a twist phase boundary in an Sn−Ge bicrystal on the angle of rotation φ around a common fourfold axis.

FIG. 4. Triple contact between a phase boundary ($\varphi = 0°$), a grain boundary ($\varphi' = 15°$), and a phase boundary ($\varphi = 15°$).

The experimental accuracy was improved by measuring this angle at a large number (30-250) of points and then analyzing the results statistically. This reduced the relative error in the determination of $\cos\theta_{Sn}$ to an average value of 15%. The ratio $\beta = X_{Ge}/X_{Sn}$ varied from sample to sample and it amounted to 0.39 ± 0.03. These measurements were carried out on 26 samples in the range of angles 0-45°.

Figure 3 shows the orientational dependence of the relative surface tension of a twist phase boundary with a common fourfold rotation axis in the Sn—Ge system obtained for $\sigma_{Ge}/\sigma_{Sn} = 1.61$ and $\beta = 0.39$ (the absolute values are given for $\sigma_{Sn} = 0.650$ J/m^2 − Ref. 5).

We found that the orientational dependence of the surface tension of the Sn—Ge phase boundary was nonmonotonic. In the investigated range of angles it varied from 0.427 to 0.451 J/m^2. Minima were found at angles 0, 30, and 40°. These were close to or identical with the angles corresponding to special grain boundaries with the $\langle 100\rangle$ rotation axis predicted by the theory of coincident sites ($\Sigma = 1$, $\varphi = 0°$; $\Sigma = 13$, $\varphi = 28°$; $\Sigma = 5$, $\varphi = 36°$), indicating that the theory as a whole could be applied to phase boundaries. In the experiments on crystallization of molybdenum drops on the surface of fluorite[6] it was also found that boundaries with a high density of coincident sites were formed.

One should point out that some of the results obtained did not fit the theory of coincident-site lattices. In particular, the depth of the minima, i.e., the surface tension of the "special" phase boundaries, was not correlated with the density of coincident sites Σ^{-1}. Moreover, the curve $\sigma(\varphi)$ exhibited a maximum. This was in no way predicted by the theory.

Our nonmonotonic dependence of the surface tension of the grain boundaries on the misorientation angle allowed us to predict the direction of motion of grain boundaries in tin along a phase boundary and to find the surface tension at grain boundaries when the surface tension of
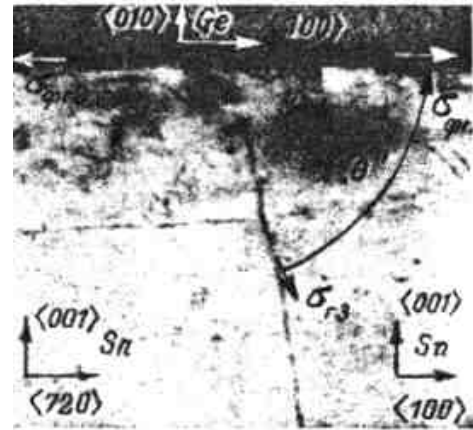
the phase boundary and the angle approach of the grain boundaries θ^n were known: $\sigma_{gr} \approx 0.3\sigma_{Sn}$. In Fig. 4 to the left and right of the grain boundaries (a tilt boundary with the $\langle 001\rangle$ axis, $\varphi = 15°$) we can see phase boundaries with different crystallographic properties and, consequently, different surface tensions ($\varphi = 0°$, $\sigma_{ph} = 0.427$ J·m^{-2} and $\varphi = 15°$, $\sigma_{ph} = 0.451$ J/m^2). The high mobility of the grain boundaries ensured that the phase boundaries remained plane and one could then use the relationship $\Delta\sigma_{ph} = \sigma_{gr}\cos\theta$).

We thus established by direct experiments that the surface tension at grain boundaries could vary considerably depending on the mutual orientation of the neighboring phases.

The experiments indicated directly that the boundaries with a specific phase misorientation were characterized by a low surface tension, which probably indicated a low concentration of defects.

[1]The ratio X_{Ge}/X_{Sn} could be measured more accurately than the angle θ_{Ge}.

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