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A. A. CHERNOV

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Abstract

Full Text

CRYSTALLOGRAPHY

A. A. CHERNOV

ON THE THEORY OF NONEQUILIBRIUM CAPTURE OF IMPURITIES DURING CRYSTAL GROWTH*

(Presented by Academician A. V. Shubnikov, 26 January 1960)

The sectorial structure of crystals ([1]) indicates that the impurity concentrations in all growth pyramids, with the possible exception of any one of them, are not equilibrium concentrations. Therefore, thermodynamic considerations are insufficient for determining them; one must take into account kinetic effects, to one of which the present note is devoted.

In the case of a thermodynamically equilibrium distribution of an impurity, its concentration is not the same inside the crystal, but has at least three, generally speaking, different values: the concentration in the bulk of the crystal, the concentration in its surface layer, and the concentration along steps on the surface (Fig. 1). If the growth rate of the crystal is much smaller than the rate of diffusion of the impurity in it, then in all three of the mentioned "phases" (three-dimensional, two-dimensional, and one-dimensional) the impurity concentrations are equal to the equilibrium values.

Fig. 1. Diagram of different positions of an impurity atom (black square): *a* —in a step, *b* —in the surface layer

At high growth rates, equilibrium has time to be established only in the surface layer and in the steps. But as new layers of substance are deposited, the former surface layers become bulk layers, and the impurity concentration in them, i.e., in the bulk of the crystal, ceases to be an equilibrium one. An analogous argument is valid for steps moving in the course of growth. Finally, crystallization conditions are possible under which none of the three concentrations indicated above is attained.

When diffusion of the impurity in the crystal proceeds slowly, for example at

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Fig. 2. Distribution of the concentration in the crystal at the first instant after deposition of a new layer

Figure 2: Fig. 2. Distribution of the concentration in the crystal at the first instant after deposition of a new layer

Fig. 3. Dependence of the coefficient of nonequilibrium impurity capture on the crystal growth rate

Figure 3: Fig. 3. Dependence of the coefficient of nonequilibrium impurity capture on the crystal growth rate

low temperatures, the resulting nonequilibrium impurity distribution is "frozen in" and persists for a long time. If, however, the diffusion coefficient has a considerable magnitude (at high temperatures), then the impurity, tending toward an equilibrium distribution, will diffuse out of the crystal or into the crystal. Such a case was encountered by Hall ([2]) in his experiments on determining the coefficient of nonequilibrium capture of impurities in germanium and silicon.

Here the coefficient of impurity capture will be calculated under the following assumptions: the crystal grows by successive deposition on its surface of new layers of substance of identical thickness and at equal time intervals. The speed of motion of the steps by which these layers terminate is infinitely large in comparison with the rate of diffusion of the impurity in the crystal.

* Reported at the Second All-Union Conference on Crystal Growth in March 1959.

Let $c(x,t)$ be the impurity concentration in the crystal; $c_0(x)$, its equilibrium value; $u(x,t) = c(x,t) - c_0(x)$; c_1, the initial concentration of the impurity in a new layer at the moment $t = 0$; h, the thickness of each of the deposited layers; V, the normal growth rate of the face. Then, during the time interval between depositions of successive layers, i.e., for $0 < t < \tau = h/V$, the impurity distribution in the crystal is described by the solution of the following problem:

Fig. 2. Distribution of the concentration in the crystal at the first instant after deposition of a new layer

Fig. 3. Dependence of the coefficient of nonequilibrium impurity capture on the crystal growth rate

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2}; \tag{1}$$

$$\frac{\partial u}{\partial x} = pu \quad \text{for } x = 0; \tag{2}$$

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$$u(x,0) = \begin{cases} c_1 - c_0(x), & 0 < x < h, \\ c_\tau(x), & x > h. \end{cases} \tag{3}$$

The coefficient p in (2) characterizes the rate of exchange of impurity particles between the surface layer of the crystal and the medium.

By virtue of the periodicity of the problem in time with period τ,

$$c_\tau(x) = c(x-h,\tau) \equiv u(x-h,\tau) + c_0(x-h). \tag{4}$$

As an approximation to the true equilibrium distribution of the impurity in the crystal, we shall take the following function $c_0(x)$:

$$c_0(x) = \begin{cases} c_S, & 0 < x < l, \\ c_V, & x > l, \end{cases} \tag{5}$$

where l is the thickness of the near-surface layer in which the equilibrium impurity concentration c_S differs from the equilibrium concentration c_V in the bulk. Consequently (see Fig. 2):

$$u(x,0) = \begin{cases} c_1 - c_S, & 0 < x < l, \\ c_1 - c_V, & l < x < h, \\ u(x-h,\tau) + c_S - c_V, & h < x < h+l, \\ u(x-h,\tau), & x > h+l. \end{cases} \tag{6}$$

The solution of equation (1) with boundary condition (2) and initial condition (6) has the form

$$u(x,t) = \int_0^\infty G(x,\xi,t) u(\xi,0)\, d\xi, \tag{7}$$

where the Green' s function is

$$G(x,\xi,t) = \frac{1}{2\sqrt{\pi D t}} \left\{ \exp\left[-\frac{(x-\xi)^2}{4Dt}\right] + \exp\left[-\frac{(x+\xi)^2}{4Dt}\right] - 2p \int_0^\infty \exp\left[-ps - \frac{(x+\xi+s)^2}{4Dt}\right] ds \right\}.$$

Using the periodicity of the problem in time with period τ, we obtain the following integro-difference equation for determining the function $u(x,\tau)$:

$$u(x,\tau) = \int_h^\infty [u(\xi-h,\tau) + c_0(\xi-h) - c_0(\xi)] G(x,\xi,\tau)\, d\xi +$$

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$$+\int_0^h [c_1 - c_0(\xi)] G(x, \xi, \tau)\, d\xi. \tag{8}$$

Since an exact solution of this equation is apparently difficult to find, we shall confine ourselves to the zeroth approximation, taking

$$u = u_k = \text{const}.$$

To determine the unknown constant u_k, we use the following argument. When a new layer of thickness h is deposited, an amount $c_1 h$ of impurity enters the crystal. During the time τ, an amount of impurity

$$-D \int_0^\tau \left.\frac{\partial u}{\partial x}\right|_{x=0} dt$$

leaves the crystal. On the other hand, according to the definition of u, the change in the amount of impurity in the crystal during the time from $t = 0$ to $t = \tau$ is equal to

$$\int_0^\infty [u_k + c_0(x)]\, dx - \int_h^\infty [u + c_0(x-h)]\, dx = (u_k + c_V)h.$$

Consequently,

$$c_1 h - D \int_0^\tau \left.\frac{\partial u}{\partial x}\right|_{x=0} dt = (u_k + c_V)h. \tag{9}$$

After transforming this expression with the aid of (7), we obtain

$$u_k[h + g(h)] = c_1[h - g(0) + g(h)] + c_V[g(l) - g(h+l) - h] +$$

$$+ c_S[g(0) - g(l) + g(h+l)], \tag{10}$$

where

$$g(b) = \frac{1}{p} \exp\left[-\frac{b^2}{4D\tau}\right] \exp\left[\left(\frac{b}{2\sqrt{D\tau}} + p\sqrt{D\tau}\right)^2\right] \operatorname{erfc}\left(\frac{b}{2\sqrt{D\tau}} + p\sqrt{D\tau}\right) -$$

$$- \left(b + \frac{1}{p}\right) \operatorname{erfc}\left(\frac{b}{2\sqrt{D\tau}}\right) + 2\sqrt{\frac{D\tau}{\pi}} \exp\left[-\frac{b^2}{4D\tau}\right]. \tag{11}$$

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In order now to obtain the value, averaged over the volume of the crystal, of the impurity capture coefficient k, it is necessary to divide the average impurity concentration in the crystal, $u_k + c_V$, by the impurity concentration in the liquid phase c_L. Expressions (10) and (11) can be simplified in two limiting cases of small and large crystal-growth rates $V = h/\tau$. Namely, denoting $k_0 = c_V/c_L$, $k_S = c_S/c_L$, $k_1 = c_1/c_L$, we obtain the following formulas for the capture coefficient:

$$k = k_0 + (k_S - k_0)\frac{lV}{4D} + (k_1 - k_0)\left(h + \frac{2}{p}\right)\frac{V}{4D} \quad \text{for } V \ll \frac{D}{h}; \tag{12}$$

$$k = k_1 + k_0\frac{l}{h} - (k_1 - k_S)\frac{pD}{V} \quad \text{for } V \gg \frac{D}{h}. \tag{13}$$

It is necessary to emphasize that the use of (12) and (13) is meaningful only at such rates V for which the assumption made at the beginning about the instantaneous deposition of a new layer of material is not violated. Since, however, the rate of motion of the step substantially exceeds the normal growth rate V, formulas (12) and (13) may be applied over a wide range of values of V.

The coefficient k_1 entering into (12) and (13) is not constant and must depend on the growth rate according to a law analogous to (12) and (13). Indeed, a high step may be represented as an accumulation of parallel elementary monatomic steps, and the calculation of k_1 reduces to solving the problem just considered, with h replaced by the height of an elementary step and k_1 by the coefficient of capture of the impurity by this step. Therefore, at low growth rates the third term in (12) is in fact quadratic in V, and the entire curve of the dependence $k(V)$ will have the character shown in Fig. 3.

An important consequence of (12) and (13) is the possibility of determining the dependence of the capture coefficient on the crystallographic orientation of the face. This dependence enters above all through the quantities k_S and k_1. The values of the parameter p and of the diffusion coefficient D, which determine the magnitude of the impurity-capture coefficient by this surface, also depend on the indices of the growing surface. Since the principal values of the diffusion tensor may differ from one another by several times, diffusion anisotropy must have a substantial effect on the nonequilibrium part of the capture coefficient.

A very important consequence of (12) and (13), in our opinion, is the dependence of the impurity-capture coefficient on the step height h, which is one of the principal characteristics of the stepped structure of the crystal surface. Owing to this, factors affecting the stepped roughness of the face (surface energy ([3]), supersaturation ([3,4]), temperature, impurities, etc.) can change the capture coefficient. In this case the stepped structure of the crystal surface must be an intermediary between the growth conditions of the crystal and its properties. Since, however, (12) and (13) were obtained for the simplest model of equally spaced steps of identical height, refinement of the conclusion drawn requires

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solving the problem for an arbitrary function of the distribution of steps by height ([5]) and by distance from one another.

Institute of Crystallography
Academy of Sciences of the USSR

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