DECORATION CRITERIA FOR SURFACE STEPS*

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The criterion derived by Chakraverty and Pound for preferential nucleation of vapour condensation at macroscopic steps upon a crystalline substrate is generalized to apply to steps of any angle. For small included step angles nucleation can occur on steps even under unsaturated conditions so that they are always decorated; for intermediate step angles the degree of preference for nucleation at steps decreases as the vapour supersaturation is increased. Decoration is most easily achieved with a condensate whose contact angle on the substrate is either less than the complement of half the included angle of the step or else approximately 90°.

CRITERES DE DECORATION POUR LES MARCHES DE SURFACE

Le critère donné par Chacraverty et Pound pour la germination préférentielle de la condensation de la vapeur sur les marches macroscopiques d'un substrat cristallin, est généralisé et appliqué aux marches d'angle quelconque. Pour des angles petits la germination peut se produire sur les marches, même dans des conditions d'insaturation, de sorte qu'elles sont toujours décorées; pour les angles intermédiaires le degré de préférence pour la germination aux marches diminue quand la sursaturation de la vapeur augmente. La décoration est aisément réalisée avec un condensat dont l'angle de contact sur le substrat est ou bien inférieur au complément de la moitié de l'angle de la marche, ou bien approximativement 90°.

DEKORATIONSKRITERIEN FÜR OBERFLÄCHENSTUFEN

Das von Chakraverty und Pound abgeleitete Kriterium für die bevorzugte Keimbildung bei der Kondensation aus der Dampfphase an makroskopischen Stufen an der Oberfläche des kristallinen Substrats wird verallgemeinert, so daß es für Stufen mit beliebigem Winkel gilt. An Stufen mit kleinem Winkel kann die Keimbildung selbst bei ungesättigter Dampfphase erfolgen, so daß diese Stufen immer dekoriert werden; bei mittleren Stufenwinkeln nimmt der Grad der Bevorzugung der Keimbildung an Stufen mit zunehmender Dampfübersättigung ab. Dekoration wird am leichtesten mit einem Kondensat erreicht, dessen Kontaktwinkel auf dem Substrat entweder kleiner als der Komplementärwinkel des halben Stufenwinkels oder etwa 90° ist.

INTRODUCTION

For many studies of the topography of crystal surfaces it is common practice to observe the decoration patterns produced by the preferential condensation of a material such as gold onto steps and other surface features. It is known that not all combinations of substrate and condensate are equally effective in this process and it is therefore of interest to examine the reasons for these differences in behaviour.

Chakraverty and Pound[1] have applied classical nucleation theory to this problem for the particular case of steps which are large in height compared with the diameter of a critical condensate nucleus and which meet the substrate with an included angle of 90°. As with many applications of nucleation theory, this approach ignores the molecular nature of substrate and condensate and can therefore only approach validity when the critical nuclei contain very many atoms. Useful approximate results can, however, be generally obtained by ignoring these complications and simply extrapolating the essentially macroscopic theory to arbitrarily small nuclei.

It is the purpose of the present paper to generalize the results of Chakraverty and Pound to steps of arbitrary included angle and, from this treatment, to make certain general statements about decoration behaviour.

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THEORY

As shown by Chakraverty and Pound,[1] the ratio of nucleation frequency I_L upon the steps on a substrate surface to that on the neighbouring plane surface itself, I_F, is given by

$$\frac{I_L}{I_F} = g \exp\,[(\Delta G_F{}^* - \Delta G_L{}^*)/kT] \tag{1}$$

where g is the fraction of surface sites occupied by steps (of which there may be many), k is Boltzmann's constant and T the absolute temperature of the substrate. $\Delta G_F{}^*$ and $\Delta G_L{}^*$ are the free energies of formation of critical nuclei on the flat surface and the step respectively and are given by

$$\Delta G_F{}^* = (4\pi\sigma_{cv}{}^3/3\,\Delta G_v{}^2)\,K(\alpha) \tag{2}$$

$$\Delta G_L{}^* = (4\pi\sigma_{cv}{}^3/3\,\Delta G_v{}^2)\,F(\eta, \alpha) \tag{3}$$

where σ_{cv} is the condensate–vapour interfacial free energy per unit area of interface, ΔG_v is the free energy change on condensing vapour to form unit volume of condensate, and α is the contact angle of the condensate c on the substrate s as defined by Young's relation

$$\sigma_{sv} = \sigma_{cs} + \sigma_{cv}\cos\alpha \tag{4}$$

where σ_{ij} are interfacial free energies. $F(\eta, \alpha)$ is a geometrical factor which depends upon the contact angle α and the angle of the step η shown in Fig. 1.

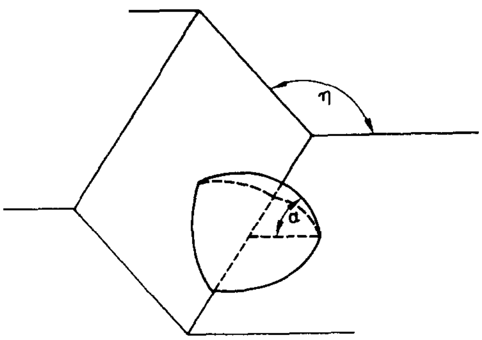

FIG. 1. Nucleus with contact angle α on a step of angle η.

$K(\alpha)$ is the corresponding function for a flat surface and is given by

$$K(\alpha) = F(\pi, \alpha) = 2 - 3\cos\alpha + \cos^3\alpha \qquad (5)$$

Chakraverty and Pound[1] have evaluated F for the case $\eta = \pi/2$ and obtain (after correction of a typographical error)

$$F\left(\frac{\pi}{2}, \alpha\right) = \sin\alpha - \cos\alpha + \frac{2}{\pi}\cos^2\alpha\sqrt{\sin^2\alpha - \cos^2\alpha}$$
$$+ \frac{2}{\pi}(\cos\alpha\sin^2\alpha\sin^{-1}\cot\alpha - \cos\alpha\sin^2\alpha)$$
$$- \frac{2}{\pi r}\int_{r\cos\alpha}^{r\sin\alpha}\sin^{-1}\left[\frac{r\cos\alpha}{(r^2 - y^2)^{1/2}}\right]dy \qquad (6)$$

It is this factor which we must first generalize and simplify.

Classical nucleation theory is based on the assumption that the surface free energies of the phases involved are isotropic so that the condensate embyro has the form shown in Fig. 1, with a spherical boundary surface. The generalized geometrical factor F is then given by

$$F(\eta, \alpha) = \frac{3V}{\pi r^3} = \frac{1}{\pi r^2}(A_c - 2A_f\cos\alpha) \qquad (7)$$

where V is the volume of the nucleus, r the radius of curvature of its surface, A_c is the area of the curved part of the nucleus surface and A_f is the area of the interface between the nucleus and one of the two planes of the step. It is required, therefore, to evaluate A_c and A_f in terms of α and η.

Referring to Fig. 2, A_f follows from the expression for the area of a sector of a circle

$$A_f = \tfrac{1}{2}r^2\sin^2\alpha(\psi - \sin\psi) \qquad (8)$$

where

$$\cos\frac{\psi}{2} = \cot\alpha\cot\frac{\eta}{2} \qquad (9)$$

A_c can be calculated by choosing the centre of the sphere as origin and evaluating the surface integral in spherical polar coordinates

$$A_c = 2r^2\int_0^{\psi}d\phi\int_{\theta_1(\phi)}^{\alpha}\sin\theta\, d\theta \qquad (10)$$

where

$$\cos\theta_1 = \cos\left(\phi - \frac{\psi}{2}\right)\Big/\left[\tan^2\alpha\cos^2\frac{\psi}{2} + \cos^2\left(\phi - \frac{\psi}{2}\right)\right]^{1/2} \qquad (11)$$

The integration is straightforward and the expression for A_c is

$$A_c = r^2\left[-2\psi\cos\alpha + 4\sin^{-1}\left(\sin\frac{\psi}{2}\sin\frac{\eta}{2}\right)\right] \qquad (12)$$

The volume V can be found by choosing the centre of the line of intersection of the two planes as origin and evaluating the volume integral in spherical polar coordinates

$$V = 2\int_0^{\eta/2}d\phi\int_0^{\pi}\sin\theta\, d\theta\int_0^{\rho(\theta,\phi)}r^2\, dr \qquad (13)$$

where

$$\rho(\theta, \phi) = -r\cos\alpha\sin\theta\cos\phi/\sin\frac{\eta}{2}$$
$$+ r\left[1 - \cos^2\alpha(1 - \sin^2\theta\cos^2\phi)/\sin^2\frac{\eta}{2}\right]^{1/2} \qquad (14)$$

Evaluating first the r-integral, then the θ-integral and

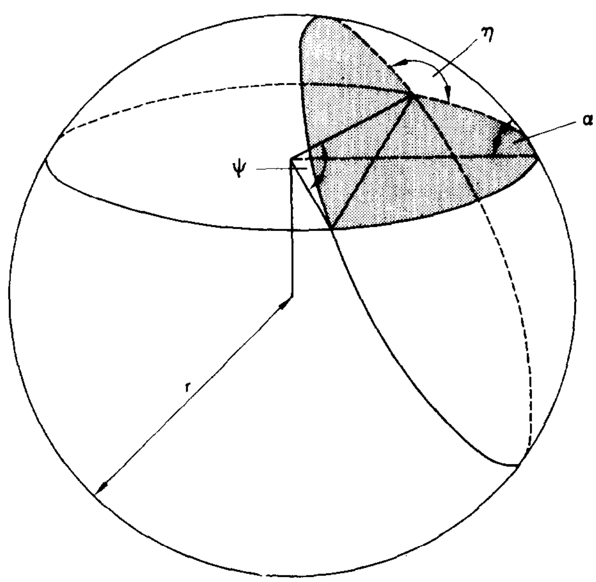

FIG. 2. Geometry used in evaluating $F(\eta, \alpha)$.

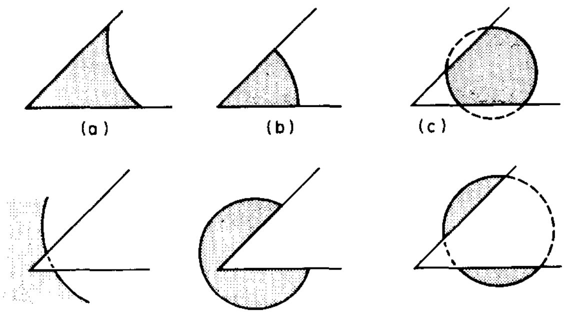

FIG. 3. Physical situations corresponding to entries in Table 1.

finally the ϕ-integral is straightforward, though tedious, and leads finally to

$$V = \frac{r^3}{3}\left[\cos\alpha\sin^2\alpha\sin\psi - \cos\alpha(3-\cos^2\alpha)\psi + 4\sin^{-1}\left(\sin\frac{\psi}{2}\sin\frac{\eta}{2}\right)\right] \quad (15)$$

These expressions (8), (12) and (15) verify the form of the equation (7) and we find

$$F(\eta, \alpha) = \frac{1}{\pi}\left[\cos\alpha\sin^2\alpha\sin\psi - \cos\alpha(3-\cos^2\alpha)\psi + 4\sin^{-1}\left(\sin\frac{\psi}{2}\sin\frac{\eta}{2}\right)\right] \quad (16)$$

where ψ is given by equation (9). This general expression is, surprisingly, more simple than the original form (6) given by Chakraverty and Pound[1] for the special case $\eta = \pi/2$. It can be verified, however, that the two expressions are equivalent for this special case and also that (16) reduces to the simple form (5) for $\eta = \pi$.

The expression (16) is valid only if

$$\frac{\pi-\eta}{2} \leq \alpha \leq \frac{\pi+\eta}{2} \quad \text{and} \quad 0 \leq \eta \leq \pi \quad (17)$$

It is, however, simple to deduce from the discussion above the appropriate form for $F(\eta, \alpha)$ when the inequalities (17) are not satisfied. These are summarized in Table 1, and sketches of the physical situation involved in each case are given in Fig. 3.

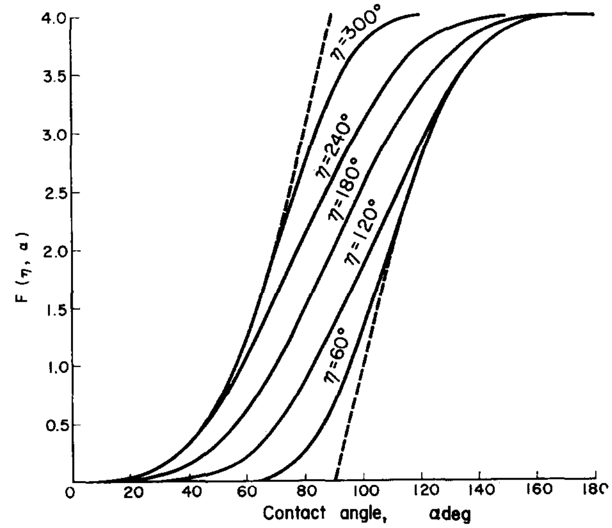

FIG. 4. $F(\eta, \alpha)$ as a function of contact angle for representative values of step angle.

There are two entries in the table for which the volume V diverges and the effective radius r is negative—we shall return to these later. In the final entry the embryo splits into two spherical caps and the situation is equivalent to nucleation on a plane surface.

The function $F(\eta, \alpha)$ is plotted in terms of α for several representative values of η in Fig. 4. Chakraverty and Pound appear to have made some numerical errors in evaluating their more complicated expression (6) since $F(\pi/2, \alpha)$ does not coincide exactly with their curve.

DISCUSSION

The experimental quantity we wish to determine is the ratio of the amount of material deposited upon the steps on a surface to that deposited upon the featureless plane surface, for it is this quantity which determines the visibility of the steps and hence the effectiveness of the decoration process. Since, once a supercritical embryo has formed, its growth rate will be essentially independent of its location, it will suffice if we determine the ratio of the nucleation rates on steps and on the plane surface, as expressed by equation (1).

TABLE 1

Conditions on η and α	Replace $F(\eta, \alpha)$ by	Physical situation
$0 \leq \eta \leq \pi$, $2\alpha \leq \pi - \eta$	Unstable	Fig. 3(a)
$0 \leq \eta \leq \pi$, $\pi - \eta \leq 2\alpha \leq \pi + \eta$	$F(\eta, \alpha)$	Fig. 3(b)
$0 \leq \eta \leq \pi$, $\pi + \eta \leq 2\alpha \leq 2\pi$	$4 - 2K(\pi - \alpha)$	Fig. 3(c)
$\pi \leq \eta \leq 2\pi$, $2\alpha \leq 3\pi - \eta$	Unstable	Fig. 3(d)
$\pi \leq \eta \leq 2\pi$, $\eta - \pi \leq 2\alpha \leq 3\pi - \eta$	$4 - F(2\pi - \eta, \pi - \alpha)$	Fig. 3(e)
$\pi \leq \eta \leq 2\pi$, $2\alpha \leq \eta - \pi$	$K(\alpha)$	Fig. 3(f)

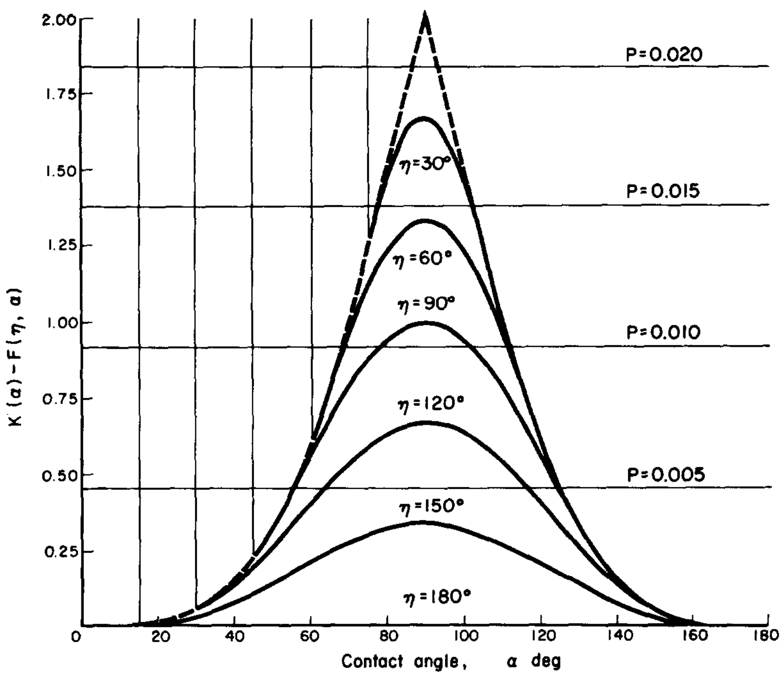

FIG. 5. Difference between the geometrical factor on a flat surface, $K(\alpha)$, and that on a step of angle η, $F(\eta, \alpha)$, as a function of contact angle for representative values of step angle.

Taking the logarithm of this equation and substituting from (2) and (3) we have

$$\ln \frac{I_L}{I_F} = \ln g + \frac{4\pi\sigma_{cv}^3}{3\Delta G_v^2 kT} [K(\alpha) - F(\alpha, \eta)] \quad (18)$$

Thus decoration is effective if $I_L > I_F$ or

$$K(\alpha) - F(\eta, \alpha) > -\frac{3\Delta G_v^2 kT}{4\pi\sigma_{cv}^3} \ln g \equiv -P \ln g \quad (19)$$

From the discussion given by Chakraverty and Pound, a typical value for g is 10^{-4}, and a typical value for the factor P multiplying $\ln g$ in (19) is 0.01. This factor P depends critically, of course, on the temperature of both vapour source and substrate since these control the vapour supersaturation near the substrate, which is measured by ΔG_v.

Figure 5 shows $K(\alpha) - F(\eta, \alpha)$ plotted as a function of α for several values of η. Also shown are horizontal lines giving the value of the right hand side of (19) for various vapour supersaturations, assuming $g = 10^{-4}$. Decoration is effective whenever the curve lies above the line specifying these experimental conditions.

From these curves several things are immediately obvious. The K–F curves rise to infinity as soon as $\alpha < (\pi - \eta)/2$ as given by (17). Under these conditions vapour condensation can occur at the step even under unsaturated conditions, since the curvature of the embryo surface is negative. This will always lead to effective decoration. When this condition is not satisfied, then decoration is most effective for a small range of contact angles around $\alpha = 90°$. For a given step geometry η and contact angle α, the decoration is most pronounced for a small value of P and hence for a small vapour supersaturation. Alternatively, for a given vapour supersaturation, steps of small re-entrant angle are more effectively decorated than are steps of larger η. The convex edges of steps, for which $\eta > 180°$, are never decorated.

REFERENCE

1. B. K. Chakraverty and G. M. Pound, *Acta Met.* **12**, 851 (1964).