

## Pulsations in optical directional melting of semiconductors

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We study the pulsations observed in halogen-lamp zone melting of silicon films in terms of a simple heat-flow model, including the reflectivity difference between solid and liquid. A steady state of the model exists in which the solid just ahead of the advancing melting front is superheated. This state can have oscillatory or morphological instabilities, either of which could lead to the observed behavior of the melting front. The observed pulsations are due to the morphological instability, and so are intrinsically a nonlinear effect. The calculation also describes the linear stability of a straight *solidification* front for a material whose reflectivity differs in the solid and liquid phases.

### I. INTRODUCTION

In a recent experiment on zone melting of a thin polycrystalline silicon film, Dutartre noted<sup>1</sup> that the melting front advanced in a series of bursts, rather than moving continuously at the same speed that the halogen lamp, which was being used as a heat source, was scanned across the film. He suggested that these melting pulsations indicate the unexpected presence of superheated solid ahead of the advancing melting front, and that the reflectivity difference between liquid and solid silicon plays a role in their occurrence. In this paper, we report calculations based on a simple model of the melting process, which indicate that the pulsations are related to a morphological instability of an advancing planar melting front, which appears when the incident flux drops off sufficiently slowly ahead of the melting front. Although the calculation also predicts the possibility of an oscillatory instability of the front, this instability does not occur for the values of the experimental parameters relevant to Dutartre's experiments. The reflectivity difference between liquid and solid silicon—the liquid being more reflective than the solid—is necessary for the oscillatory instability to occur, but not for the experimentally relevant morphological instability; it does, however, have a pronounced quantitative effect on the latter instability, and may also be responsible for the fact that the instability is obvious to the observer. The calculation also applies to the problem of the stability of a planar solidification front.

Unlike directional solidification, directional melting has received rather little theoretical attention. The stability of an advancing planar melting front has been considered by Turland and Peckover<sup>2</sup> in the case in which heat is being fed into the sample from the boundaries, and by Lacey and Shillor<sup>3</sup> when a source, such as a moving heat lamp, is present. In the latter paper it was shown that a morphological instability such as that mentioned above should occur whenever the heat flow from the solid to the melting front exceeds that from the liquid. However, since the model used there did not include surface tension and so lacked a mechanism for cutting off the short-wavelength

instability, the calculation showed that the problem is ill posed under these conditions. In particular, it was not possible to calculate the wave number of the marginal mode. In addition, the model did not include a reflectivity difference between phases, nor did it include interface kinetics. All three of these effects are considered in the present paper. The relatively more complicated case of melting of a binary system has been studied by Woodruff<sup>4</sup> and by Wollkind and Raissi<sup>5</sup> using linear and nonlinear stability analysis, respectively.

Earlier experiments by Bosch and Lemons<sup>6</sup> and by Hawkins and Biegelsen<sup>7</sup> had shown that when a thin film of silicon is illuminated by a *stationary* cw laser, the film can melt partially, breaking up into coexisting liquid and solid regions with sizes on the order of 10  $\mu\text{m}$ . This patterning is also attributed<sup>7</sup> to the reflectivity difference between liquid and solid phases. Jackson and Kurtze<sup>8</sup> studied this problem theoretically, and showed that the liquid regions are supercooled and the solid superheated, and that such a state can be thermally stable. Such a situation occurs when the flux from the laser or heat lamp is not sufficient to melt the material completely. In this regime, Biegelsen *et al.*<sup>9</sup> observed that when the laser was moved, the solid regions grew by having filaments solidify from an existing solid region into previously liquid regions.

Grigoropoulos *et al.*<sup>10</sup> have studied the effect of a reflectivity difference between the two phases on the directional solidification of silicon films. They derived an expression for the linear growth rates of sinusoidal perturbations of a steadily advancing, straight-line solidification front in terms of the temperature gradients on either side of the front. For fixed solid and liquid reflectivities and an exponential heat-lamp profile, they then obtained the growth rate numerically as a function of the wave number of the perturbation for various values of the (spatial) decay constant of the heat-lamp profile. To date, however, the effect of the reflectivity difference on directional *melting* has not been studied theoretically.

### II. THEORETICAL MODEL

We wish to model the directional melting of a thin film of a pure substance, of thickness  $h$ , on an inert, insulating

substrate, accomplished by scanning a heat lamp across its surface at a constant speed  $V$  in the  $x$  direction. We work in a frame of reference moving with the lamp, which then provides an energy flux  $J(x)$  to the film. We also assume that the lamp illuminates a broad area, so that  $J$  does not depend on the coordinate  $y$  perpendicular to the scanning direction. By this we actually mean that the flux does not vary significantly over distances in the  $y$  direction which are of the order of the wavelength of the morphological instability which will appear in the next section. In addition, we discount the possibility of a significant variation in temperature through the thickness of the film, since for a silicon film of thickness  $h \sim 1 \mu\text{m}$  with an incident flux  $J \sim 1000 \text{ W/m}^2$ , this temperature difference is of order  $0.1 \text{ K}$ .<sup>8</sup> Under these assumptions, the temperature  $T(x, y, t)$  of the film satisfies the two-dimensional diffusion equation,

$$\frac{\partial T}{\partial t} = \nabla \cdot (D \nabla T) + V \frac{\partial T}{\partial x} - \frac{T - T^0}{\tau} + (1 - R) \frac{J(x)}{hC\rho} - \frac{L}{C} V^b \delta(x - x^b), \quad (2.1)$$

where  $D$  is the thermal diffusion constant of the film,  $C$  is the specific heat and  $\rho$  the density of the material,  $L$  is the latent heat of melting, and  $R$  is the reflectivity of the film. For simplicity, we assume that  $D$ ,  $C$ , and  $\rho$  are the same for the liquid and solid phases, but allow the reflectivities of the two phases to differ. We model heat loss, both by conduction into the substrate (whose temperature is  $T^0$ ) and by radiation into the ambient, by the simple linear damping term<sup>10,11</sup>  $-(T - T^0)/\tau$ , where  $\tau$  is a phenomenological damping rate; this term turns out to have only a minor effect on the stability. The importance of this heat loss term is most naturally measured by the dimensionless parameter  $\beta$ , defined by<sup>11</sup>

$$\beta^{-1} = 1 + (4D/V^2\tau), \quad (2.2)$$

which varies from 0 to 1 as the damping rate  $\tau$  grows from 0 to  $\infty$ .

In modeling the latent-heat release by the  $\delta$ -function term in (2.1), we are taking the melting front to be a single curve, given by  $x = x^b(y, t)$  and advancing at a local normal velocity  $V^b(y, t)$ . This is not generally correct for melting; since solids tend not to support superheating, the region of a sample in which melting is taking place is usually a "mushy zone,"<sup>12</sup> with a complicated structure of small coexisting areas of solid and liquid. The appearance of the mushy zone is further complicated for polycrystalline materials by the existence of a distribution of melting temperatures arising from the different surface energies and strains in the various crystallites, as well as by the fact that differently oriented crystallites can have different reflectivities, diffusion coefficients, etc. Such a zone is clearly visible in Dutarte's experimental pictures. However, the idealization of a simple, well-defined front does serve to illustrate the instability of the melting front, and, as we discuss below, it is probably not as bad an approximation for semiconductors as it would be for other substances which do not have greater reflectivities in the liquid phase than in the solid. Further work is currently

under way to incorporate the existence of a mushy zone into the model used here.

We allow for nonequilibrium interface kinetics by taking the temperature at the melting front to be a general function of the rate of advance of the front and of its curvature  $\kappa$ :

$$T(x^b) = T^b(V^b, \kappa). \quad (2.3)$$

In general, we expect that  $T^b$  will be a very slowly increasing function of  $V^b$ , and a decreasing function of  $\kappa$  if  $\kappa$  is defined to be positive when the solid bulges into the liquid. In a more detailed model of a melting polycrystalline film, we would also allow a dependence of  $T^b$  on crystal orientation. If the melting front is in equilibrium, and the equilibrium melting temperature  $T_M$  and solid-liquid surface tension  $\gamma$  are independent of crystal orientation, then  $T^b$  is given by

$$T^b = T_M \left[ 1 - \frac{\gamma}{L\rho} \kappa \right], \quad (2.4)$$

which is the classical Gibbs-Thomson condition. We will ultimately find that the curvature dependence of the melting temperature is crucial for setting the transverse length scale of morphological instabilities of the melting front, but that the dependence on growth velocity has no qualitatively important effect.

It is easy to find a steady-state solution of Eq. (2.1) with a straight melting front,  $x^b = x_{SS}^b = \text{constant}$ . The front velocity  $V^b$  in the laboratory frame of reference must be equal to the scan speed  $V$  of the lamp, and the temperature of the film is given by

$$T_{SS}(x) = T^0 + T_J(x) - \frac{L}{C} V G_{SS}(x - x_{SS}^b), \quad (2.5)$$

where  $G_{SS}$  is the steady-state Green's function for diffusion in one dimension,

$$G_{SS}(x) = (\beta^{1/2} / |V|) \exp \left[ -\frac{1}{2D} (Vx + \beta^{-1/2} |Vx|) \right], \quad (2.6)$$

and  $T_J$  is the contribution of the heat source to the temperature field,

$$T_J(x) = \int_{-\infty}^{\infty} G_{SS}(x - x') [1 - R(x')] \frac{J(x')}{hC\rho} dx'. \quad (2.7)$$

Note that the latent heat term in  $T_{SS}$  produces a discontinuity in temperature gradient of  $LV/CD$  at the melting front.

Equations (2.5)–(2.7) leave the position  $x_{SS}^b$  of the melting front undetermined. We can find it graphically, however, from the boundary condition (2.3): matching the value of  $T_{SS}(x_{SS}^b)$  obtained from Eq. (2.5) with the value  $T^b(V, 0)$  coming from this boundary condition gives us an implicit equation which determines the front position  $x_{SS}^b$ .

As pointed out by Lacey and Shillor,<sup>3</sup> it is possible for a superheated solid to exist in steady state: from the solution (2.5) for the temperature field, we see that this occurs when  $dT_J/dx$  is greater than  $-LV(1 + \beta^{1/2})/2CD$ , for then  $dT_{SS}/dx$  is positive on the solid side at the melting

front. This is rather surprising, especially when viewed in the laboratory frame of reference. A positive gradient of  $T_{SS}$  near the front means that a piece of solid material first becomes superheated before the melting front approaches it, then *cools* as heat diffuses from it toward the front to provide latent heat for melting, and then finally melts when it has cooled to the melting temperature (or the nonequilibrium melting temperature appropriate for a melting front advancing at the speed  $V$ ). This effect is, of course, a consequence of the assumption that there is a single melting front. One would normally expect that if the model predicts the existence of superheated solid, then the region of hot solid ahead of the melting front will actually break up into a mushy zone, in which small solid and liquid regions coexist at the melting temperature. However, the fact that the reflectivity of a semiconductor rises upon melting impedes the formation of such a region: under illumination by a stationary heat lamp, silicon films form relatively large ( $10\ \mu\text{m}$ ) superheated solid and supercooled liquid regions in stable coexistence, rather than mushy zones.<sup>8</sup> Thus superheating can occur more easily than usual for such materials when the film is heated optically.

In fact the contribution  $T_J$  of the lamp to the temperature field can itself have a positive gradient at the melting front. For example, if we consider the case of exponential flux,  $J \propto \exp(-x/l)$ , we find that in the limit  $l \rightarrow \infty$  ( $J$  constant) the derivative  $dT_J/dx$  at the melting front is a positive multiple of  $(R_L - R_S)$ , and so is positive for semiconductors. This is because the dominant contribution to  $T_J(x)$  comes from the region within a few diffusion lengths of  $x$ ; a point just *ahead* of the melting front sees more solid in this region than a point *at* the front does, so the heat input to the former point is larger, tending to make its temperature higher. This effect can be counteracted by a sufficiently sharp decrease in  $J(x)$  with increasing  $x$  near the front. This is made evident by the fact that as the decay length  $l$  decreases, the slope  $dT_J/dx$  at the front also decreases, passing through zero at a definite value of  $l$  which depends on  $R_S$ ,  $R_L$ , and  $\beta$ . Thus,  $dT_J/dx$  provides a measure of the general trend of  $J(x)$  with  $x$ . In the stability analysis to follow, this derivative arises naturally in the dimensionless parameter

$$G = -(2DC/L |V| \beta^{1/2}) dT_J/dx. \quad (2.8)$$

The solid will be superheated for  $G < 1 + \beta^{-1/2}$ . The reflectivity difference between the liquid and solid phases occurs in the dimensionless parameter

$$\Delta = 2D(R_L - R_S)J(x_{SS}^b)/\rho LhV^2, \quad (2.9)$$

which will be positive for semiconductors, which are more reflective when liquid than solid. For the case of uniform illumination, we have  $G = -\Delta$ ; and so we will use  $G + \Delta$  instead of  $G$  itself to present our results; positive  $G + \Delta$  generally means that the flux  $J(x)$  is decreasing at the steady-state melting front  $x - x_{SS}^b$ .

### III. STABILITY ANALYSIS

In order to investigate the stability of the steady state (2.5), we consider the fate of an infinitesimal perturbation

about that solution. To this end we write

$$x^b = x_{SS}^b + \epsilon \exp \left[ \frac{i |V|}{2D} qx + \frac{V^2}{2D} \omega t \right], \quad (3.1a)$$

$$T(x, y, t) = T_{SS}(x) + \hat{T}(x)(x^b - x_{SS}^b), \quad (3.1b)$$

where  $q$  and  $\omega$  are the dimensionless wave number and linear growth rate of the perturbation. We insert this perturbation into the diffusion equation (2.1) and boundary condition (2.3), linearize in  $\epsilon$ , and solve the resulting equations to obtain a relation between  $\omega$  and  $q$  which must be satisfied in order for the form (3.1) of the perturbation to be consistent. This relation involves the parameters  $\beta$ ,  $\Delta$ , and  $G$  introduced above and two further dimensionless parameters characterizing the sensitivity of the temperature of the front to its velocity and curvature,

$$\alpha = (C |V| / L \beta^{1/2}) \partial T^b / \partial V^b, \quad (3.2)$$

and

$$d_0 = -(C |V| / 2DL \beta^{3/2}) \partial T^b / \partial \kappa. \quad (3.3)$$

If the melting front is in equilibrium, then  $\alpha$  will be zero and  $d_0$ , in view of Eq. (2.4), will equal  $C |V| \gamma T_M / 2DL^2 \rho \beta^{3/2}$ , which is approximately equal<sup>8</sup> to  $V / (10^7\ \text{cm/s})$  for silicon. Thus we expect both  $\alpha$  and  $d_0$  to be small and positive. In terms of these parameters, the stability relation is

$$\omega + \Delta + 1 = (1 - G - \alpha\omega - d_0\beta q^2)(1 + \beta q^2 + 2\beta\omega)^{1/2}, \quad (3.4)$$

where the square root must be chosen to have a positive real part.

The regions of stability and instability of the steady state obtained from this equation are plotted in Fig. 1 for

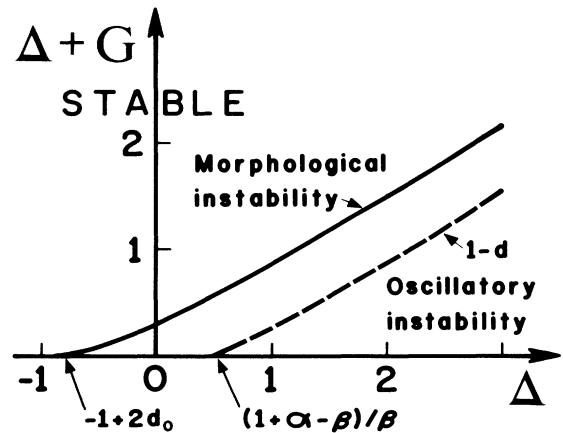


FIG. 1. Stability plot for the steady state given by Eq. (2.5). The  $\Delta$  axis to the left of  $\Delta = (1 + \alpha - \beta)/\beta$  and the dashed curve, which is given by Eqs. (3.5) and (3.6), form the stability boundary for a one-dimensional system, with the instability at the dashed curve being oscillatory. The axis to the left of  $\Delta = -1 + 2d_0$  and the solid curve, which is given by Eq. (3.8), form the stability boundary for a two-dimensional system, with a morphological instability setting in at the solid curve.

fixed values of  $\beta$ ,  $\alpha$ , and  $d_0$  as functions of  $\Delta$ , which measures the reflectivity difference between liquid and solid, and  $\Delta + G$ , which measures the rate at which the illumination falls off as one moves into the solid from the melting front. By setting  $q = 0$ , we obtain the stability relation for a one-dimensional system. The resulting equation has a solution  $\omega = 0$  for  $\Delta + G = 0$ . As stated above, this value of  $\Delta + G$  occurs for constant illumination, in which case this mode is a Goldstone mode, coming about because there is no variation in  $J(x)$  to define an origin. For  $\Delta + G < 0$ , there is a solution of (3.4) having positive  $\omega$ , so that the steady state is unstable if the illumination increases ahead of the melting front. This is to be expected, since under these conditions, if the melting front should move slightly ahead of its steady-state position, then even more energy becomes available to provide latent heat to melt the material. The front would then presumably rush ahead, pass the point of maximum light intensity, and finally reach another steady state on the forward side of the illuminated region with the illumination falling off ahead of the front, for which the relevant value of  $\Delta + G$  would be positive.

By taking the square root in Eq. (3.4) to be the basic variable, one can show that there are solutions of (3.4) with  $q = 0$  having a complex growth rate  $\omega$  for appropriate values of  $G$  and  $\Delta$ . The growth rate  $\omega$  has positive real part, indicating an oscillatory instability, for points below and to the right of the curve given parametrically by

$$\Delta = (2\alpha P^3 + P^2 - \alpha P - \beta) / \beta, \quad (3.5)$$

$$\Delta + G = P(P - 1)(2\alpha P + 1 + \alpha) / \beta, \quad (3.6)$$

with  $P \geq 1$ . On this curve, the real part of  $\omega$  vanishes and the imaginary part is given by

$$\text{Im}(\omega) = P(P^2 - 1)^{1/2} / \beta. \quad (3.7)$$

Note that this oscillatory instability occurs only for positive  $\Delta$ , i.e., only when the liquid is more reflective than the solid.

For nonzero wave number  $q$ , the picture changes somewhat. Oscillatory instabilities with nonzero  $q$  occur only within the region in which the  $q = 0$  oscillatory mode is already unstable. However, morphological instabilities with real growth rates do occur at values of  $\Delta$  and  $G$  for which the one-dimensional modes are stable. It is easy to show from (3.4) that these instabilities occur below and to the right of the curve

$$\Delta + G = 1 + \Delta + d_0 - \frac{3}{2}[2d_0(1 + \Delta)^2]^{1/3}, \quad (3.8)$$

for  $\Delta > -1 + 2d_0$ . Along this curve, a mode whose wave number is given by

$$\beta q^2 = [(1 + \Delta) / 2d_0]^{2/3} - 1 \quad (3.9)$$

is marginally unstable. In analyzing the case  $\Delta = 0$  without surface tension or heat loss, Lacey and Shillor<sup>3</sup> found that the steady state would be unstable for  $G < 1$ , meaning that heat transport to the melting front from the solid is faster than from the liquid. Here their result is modified by surface tension: for  $\Delta = 0$ , the instability sets

in when  $G$  is equal to  $1 - 3(d_0/4)^{1/3} + d_0$ , which can be significantly lower than 1 even if  $d_0$  is quite small. The curves marking the onset of morphological instability and of  $q = 0$  oscillatory instability do cross provided  $\alpha$  is less than  $27\beta d_0$ , but only at a value of  $\Delta$ , which is of the order of  $d_0^{-2}$ . Thus, for reasonable values of the parameters, morphological instabilities with real growth rates always exist whenever an oscillatory instability does.

#### IV. DISCUSSION

Clearly, an oscillatory instability of the steady state could produce the pulsating advance of the melting front observed by Dutartre. On the other hand, it is also possible for a morphological instability to lead to melting pulsations. To see this, suppose the melting front is prepared as a straight line. If the steady state is morphologically unstable, then protruberances of liquid form and start to grow rapidly into the solid region. Their growth is sustained mainly by heat transport from the superheated solid, and as they grow ahead of the straight-line melting front they encounter solid at higher and higher temperatures. This is as far as the linear stability analysis can probe. However, as the protruberances grow, they absorb heat from the solid and also eventually reach regions in which the solid is becoming cooler. As a result, they must eventually slow down, leaving a solid region next to them which is cooler than it would be in steady state. This surviving solid then waits for the advancing heat source to raise its temperature again so that it can melt.

Although it is tempting to associate the oscillatory instability with the melting pulsations observed by Dutartre, it is in fact the morphological instability which is manifesting itself there. The experimental pictures<sup>1</sup> appear to show a wavy melting front with a transverse wavelength of 300–400  $\mu\text{m}$ . Using the data of Ref. 10 for the properties of silicon, Dutartre's values<sup>1</sup>  $h = 0.5 \mu\text{m}$  and  $V = 0.01 \text{ cm/s}$ , and the fact<sup>13</sup> that the 150 W halogen lamp is focussed onto an ellipse of dimensions  $1 \times 1.5 \text{ cm}^2$  leads to a value of  $\Delta$  in the range  $10^2 - 10^3$ . From (3.8) we then find that the morphological instability occurs for  $G \sim 0.80 - 0.95$ , corresponding to  $dT_J/dx > -20 \text{ K/cm}$  (a range which includes 0!). Finally, from (3.9) we find that the morphological instability first occurs with a wavelength of about 400–800  $\mu\text{m}$ . On the other hand, the oscillatory instability does not occur until  $G$  is reduced to about  $-15$ , and then has a period of about 150 s, much longer than the observed times of order 1 s. Thus it appears that, although oscillations do occur within the linear stability analysis of this process, the observed periodic melting bursts are actually an intrinsically nonlinear result of an instability which initially is not oscillatory.

The model used in this paper to study the directional melting of materials which undergo a reflectivity change on melting could equally well be used to describe the directional solidification of such materials. In fact, it is probably a better model for solidification than for melting, since it is easier to produce supercooled liquids than superheated solids, so that the idealization of a single, connected transition front is more realistic. To analyze solidification, we would simply make the scanning veloci-

ty  $V$  negative in the diffusion equation (2.1). The calculation would continue as in Secs. II and III, with the same dimensionless parameters  $\Delta$ ,  $G$ ,  $\beta$ ,  $\alpha$ , and  $d_0$  arising from the stability analysis. The definitions of these quantities appearing in the earlier sections were given in forms valid for  $V$  positive or negative, in order for the results to be applicable both to melting and solidification. We then find that the stability relation (3.4) holds for both problems, and so Fig. 1 doubles as a stability plot for solidification of these materials. Our results then generalize those of Grigoropoulos *et al.*,<sup>10</sup> which were obtained only for a specific (exponential) form of the lamp flux  $J(x)$ . The major difference between the stability proper-

ties of the two processes is that we would expect the parameter  $G$ , given by (2.8), to be considerably smaller for solidification than for melting; this is because the lamp's contribution to the temperature field does not fall off as rapidly on the trailing side of the lamp, where solidification is taking place, as it does on the leading side, where melting occurs.

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