Asymmetric Melting and Freezing Kinetics in Silicon.

Citation	Tsao, Jeff Y., Michael J. Aziz, Michael O. Thompson, and Paul S. Peercy. 1986. Asymmetric Melting and Freezing Kinetics in Silicon. Physical Review Letters 56(25): 2712-2715.
Published Version	doi:10.1103/PhysRevLett.56.2712
Accessed	February 17, 2015 5:49:08 PM EST
Citable Link	http://nrs.harvard.edu/urn-3:HUL.InstRepos:2839211
Terms of Use	This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA

(Article begins on next page)

Asymmetric Melting and Freezing Kinetics in Silicon

Jeff Y. Tsao,[1] Michael J. Aziz,[2] Michael O. Thompson,[3] and Paul S. Peercy[1]

[1] Sandia National Laboratories, Albuquerque, New Mexico 87185
[2] Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[3] Department of Materials Science, Cornell University, Ithaca, New York 14853
(Received 10 February 1986)

We report measurements of the melting velocity of amorphous Si relative to that of (100) crystalline Si. These measurements permit the first severe experimental test of theories describing highly nonequilibrium freezing and melting. The results indicate that freezing in Si is inherently slower than melting; this asymmetry can be interpreted in terms of an entropy-related reduction in the freezing rate.

PACS numbers: 64.70.Dv

Virtually all commonly encountered melting and solidification phenomena are heterogeneous, i.e., mediated by the motion of a liquid-solid interface. The velocity $v(T)$ at which this interface moves in response to overheating or undercooling is a fundamental unanswered question in materials science.[1,2] Recently, real-time measurements[3-6] of melting and freezing in Si under pulsed laser irradiation have begun to provide insights into $v(T)$; however, to date these measurements have not provided meaningful tests of theories for these functions. In this Letter, we describe new measurements of the relative melting velocities of amorphous Si (a-Si) and crystalline Si (c-Si). These measurements lead to the first quantitative discrimination between kinetic models for highly nonequilibrium melting and freezing.

Two transition-state theory models are formulated and tested. The difference between the two models can best be understood in the limit of vanishing activation enthalpy. In the "collision limited" growth model, both melting and freezing are assumed to be fundamentally limited only by collision frequencies at the interface. This leads to a "symmetric" formulation in which maximum melting and freezing rates are identical. In the "entropy limited" growth model, proposed here, only melting is assumed to be so limited. This leads to an "asymmetric" formulation in which the maximum freezing rate is lower than the collision-limited maximum melting rate by an entropic factor. We find the measurements to be consistent only with the asymmetric model. Furthermore, we are able to limit the important physical parameters of this model, viz., the fundamental attempt velocity and the activation enthalpy, to narrow, but plausible, ranges of values.

Experiments were performed on (100) silicon-on-sapphire samples photolithographically patterned for transient-conductance measurements,[3,4] and ion implanted with Si to amorphize the near-surface material to depths from 0.16 to 0.46 μm. Samples were irradiated through a fused-quartz homogenizer[7] with 20- to

30-ns pulses from a Q-switched ruby laser at 694 nm. An example of the measured melt depth versus time is shown in Fig. 1(a). A plateau is observed at the depth of the a-Si/c-Si interface, due to the difference between the melting temperatures of a- and c-Si. Indeed, the melting-temperature difference $T_{lc} - T_{la}$ can be extracted from the duration of the plateau.[8]

The present analysis focuses on the velocity transients, shown in Fig. 1(b), associated with the plateau. The melting velocity in the a-Si is determined by steady-state heat flow; the interface temperature T_i adjusts according to the $v_a(T)$ relationship for a-Si. Im-
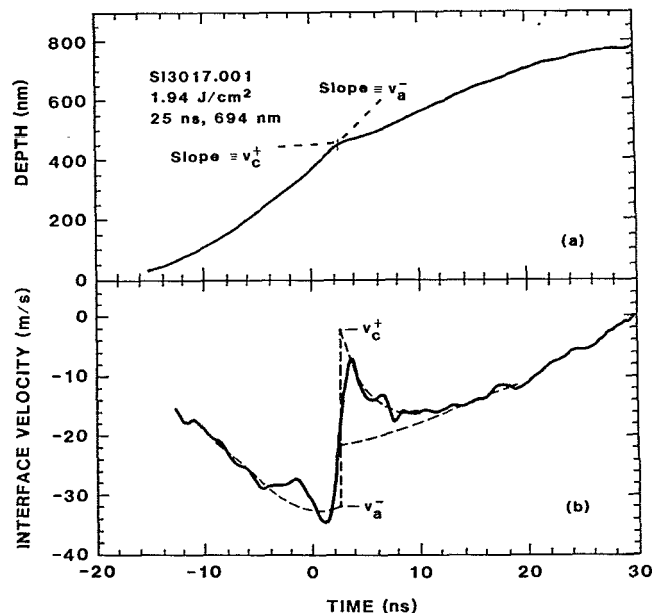

FIG. 1. Real-time transient-conductance measurement, during pulsed laser melting, of (a) melt depth and (b) solidification velocity, obtained by numerical differentiation. The dashed lines are velocities extrapolated to the original a-Si/c-Si boundary. The sample was 1 μm silicon on sapphire, implanted with Si to produce an amorphous layer 460 nm thick.

mediately after the interface passes into the c-Si, T_i has not changed, but the melting velocity in the crystal is now controlled by the $v_c(T)$ relationship appropriate for c-Si, and so the velocity changes almost discontinuously. After a transient period, v_c and T_i decay to new steady-state values.

Velocities immediately before (v_a^-) and after (v_c^+) the a-Si/c-Si boundary were varied by changes of the laser fluence and the thickness of the a-Si layer. These velocities are plotted versus each other in Fig. 2. For low v_a^- (where $T_i < T_{lc}$), the sign of the velocity reverses as c-Si grows into l-Si. For large v_a^- (where $T_i > T_{lc}$), the liquid/solid interface slows, but does not reverse direction, upon crossing the a-Si/c-Si boundary. The velocity v_a^- at which v_c^+ is zero is the a-Si melting velocity at T_{lc}. Any theory which describes melting and freezing of Si must satisfy the constraints defined by the value and slope of this line at $v_c^+ = 0$:

$$v_a(T_{lc}) = 29 \pm 3 \text{ m/s}, \tag{1}$$

$$dv_c/dv_a|_{T_{lc}} = 0.55 \pm 0.2. \tag{2}$$

Additional constraints provided by previous measurements can be enumerated. For example, it has been shown that l-Si can freeze to form c-Si at interface velocities at least as high as 15 m/s, but that the velocity is less than or equal to 15 m/s at the a-Si melting temperature.[10] Therefore,

$$\max\{v_c\} \geqslant 15 \text{ m/s}, \tag{3}$$

$$v_c(T_{la}) \leqslant 15 \text{ m/s}. \tag{4}$$

In addition, for 2.3-ns 694-nm laser irradiation just sufficient to melt 0.46 μm of silicon (on sapphire), the peak c-Si melting velocity has been measured to exceed 190 m/s.[11] At that peak velocity, heat-flow analyses indicate that an upper bound on the interface
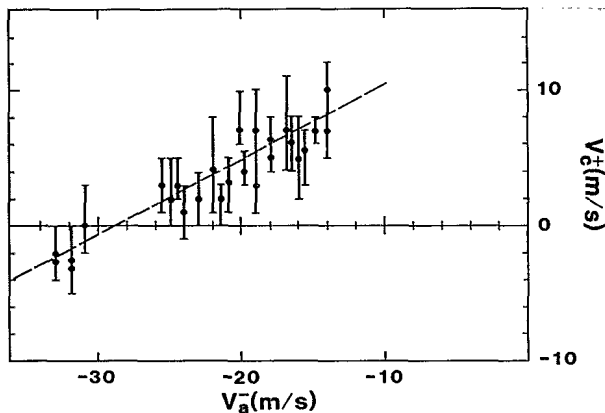

FIG. 2. The velocities just before (v_a^-), vs the velocities just after (v_c^+), kinks such as that shown in Fig. 1(b) (Ref. 9).

temperature is 3300 K.[11] Therefore,

$$v_c(3300 \text{ K}) \leqslant -190 \text{ m/s}. \tag{5}$$

Finally, interface velocities must be limited by sound velocities[12]:

$$\max\{|v_c|\} \leqslant v_{\text{sound},c} = 8300 \text{ m/s}, \tag{6}$$

$$\max\{|v_a|\} \leqslant v_{\text{sound},a} = 6370 \text{ m/s}. \tag{7}$$

These constraints allow us to compare quantitatively different models for interface response functions. In the classical transition-state theory for continuous crystal growth,[1,13,14] the response function is the difference between simultaneous freezing and melting rates:

$$v = v_0 f[\exp(-\Delta G_{l*}/kT) - \exp(-\Delta G_{s*}/kT)]. \tag{8}$$

Here, v_0 is an attempt, or collision, velocity, f is an active site fraction, $\Delta G_{ab} = G_b - G_a$, $\Delta H_{ab} = H_b - H_a$, and $\Delta S_{ab} = S_b - S_a$ are Gibbs free energy, enthalpy, and entropy differences, respectively, and an asterisk refers to the transition state. In standard notation,[1,13,14] the maximum freezing velocity, $v_f = v_0 f \times \exp(\Delta S_{l*}/k)$, is factored out of Eq. (8) to give

$$v = v_f \exp(-\Delta H_{l*}/kT)[1 - \exp(-\Delta G_{sl}/kT)]. \tag{9}$$

In systems for which f approaches unity and ΔH_{l*} approaches zero, it has been suggested[1] that v_f, rather than v_0, be identified as the collision velocity. However, the implication of this identification is that the maximum melting velocity may *exceed* the collision velocity by a factor $\exp(\Delta S_{sl}/k)$. Examination of the bracketed thermodynamic factor in Eq. (9) suggests an explanation for this unphysical behavior. For $T < T_{ls}$, the Gibbs free energy decreases for freezing and increases for melting. In this case, consistent with expectation, the freezing part of the thermodynamic factor is saturated at unity, whereas the melting part is decreased by the factor $\exp(-\Delta G_{sl}/kT)$. For $T > T_{ls}$, the Gibbs free energy increases for freezing and decreases for melting. In this case, however, the freezing part of the thermodynamic factor is still saturated at unity, whereas the melting part is *increased* by the factor $\exp(\Delta G_{sl}/kT)$. To avoid this unphysical behavior, reflected in excessive melting velocities, we force the melting part of the thermodynamic factor to saturate at unity, while decreasing the freezing part by $\exp(-\Delta G_{ls}/kT)$. This symmetrizes Eq. (9) according to

$$|v| = v_f e^{-Q/kT}[1 - e^{-|\Delta G_{sl}|/kT}]. \tag{10}$$

We call this the symmetric, or "collision limited" growth, model because in the absence of an activation enthalpy Q, both freezing and melting may approach collision velocities.

We also propose a second possibility: that only the maximum melting velocity, $v_m = v_0 f \exp(\Delta S_{s*}/k)$, but not the freezing velocity, approaches the collision velocity. Factoring this maximum melting velocity out of Eq. (8) gives

$$v = v_m e^{-Q/kT}[e^{-\Delta S_{sl}/k} - e^{-\Delta H_{sl}/kT}]. \tag{11}$$

We call this the asymmetric, or "entropy limited" growth, model, because in the absence of an activated enthalpy Q, the maximum freezing velocity is lower than the maximum melting velocity by the factor $\exp(-\Delta S_{sl}/k)$.

Written in this manner, the model can be seen to be one in which the enthalpic and entropic contributions to the Gibbs free energy appear to enter *inequivalently* into the kinetics of freezing and melting, and therefore do not counteract each other, as is implicit in Eq. (10). The origin of this inequivalence can be interpreted as follows: On the one hand, there is a large energetic driving force for liquid atoms to solidify; however, there is only a small domain in configurational and vibrational phase space for which this is possible. The collision-limited freezing rate is therefore decreased by an entropic factor $\exp(-\Delta S_{sl},)$. On the other hand, virtually the entire domain of phase space available to solid atoms is also available to atoms in the more disordered liquid state; however, transformation to the liquid is energetically unfavored. The melting rate is therefore decreased by the Boltzmann factor $\exp(-\Delta H_{sl}/kT)$.

To test the two models, represented by Eqs. (10) and (11), respectively, we consider the behavior predicted by each for both the a-Si $\leftrightarrow$ l-Si and the c-Si $\leftrightarrow$ l-Si transformations. The relevant thermodynamic quantities have been determined previously.[15] The three free parameters are v_{fc} and v_{fa} (or v_{mc} and v_{ma}), which are taken to be temperature independent, and Q, which is expected to be similar for the two transformations.[16] By use of constraint (1), v_{fa} (or v_{ma}) can be eliminated, which leaves only two free parameters. All remaining constraints, except the line constraint (2), then represent allowed half-planes in the two-dimensional parameter spaces defined by v_{fc} (or v_{mc}) and Q.

The boundaries of these half-planes are drawn for the two models in Figs. 3(a) and 3(b). The shaded regions correspond to parameter values consistent with these boundaries. For the symmetric model [Fig. 3(a)] the allowed region is extremely small; since the boundaries represent extreme possibilities rather than best estimates, this model can immediately be considered unlikely. Physically, the allowed region is restricted for the following reasons: For a given v_{fc}, $\max\{v_c\} \geq 15$ m/s places an upper bound on Q; however, $v_c \leq 15$ m/s at T_{la} places a lower bound on Q. The allowed window increases as v_{fc} decreases, but the
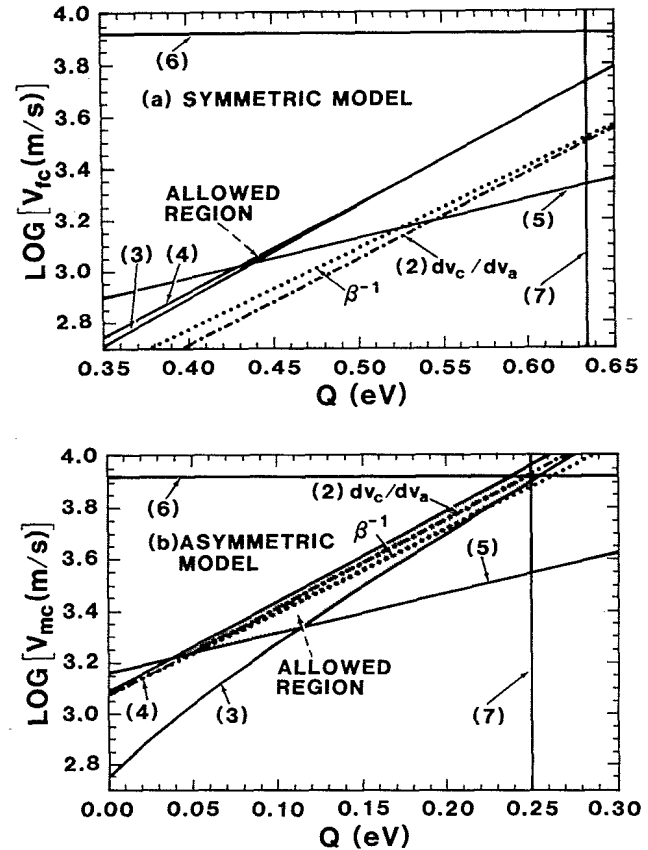

FIG. 3. Plots of the restrictions placed on the two-dimensional parameter spaces (a) v_{fc} and Q for the symmetric model, and (b) v_{mc} and Q for the asymmetric model. The shaded (allowed) regions define the parameter values consistent with the half-plane constraints (3)–(7). The dash-dotted lines define the line constraint (2), labeled dv_c/dv_a. The dotted lines define the parameter values consistent with the slope $\beta = [dv_c/dT]_{T_{lc}} = \frac{1}{15}$ m/s·K, from transient-conductance measurements (Ref. 17).

requirement that $v_c = -190$ m/s at $T_l \leq 3300$ K places a lower bound on v_{fc}.

The line constraint (2) is drawn dash-dotted in Figs. 3(a) and 3(b). Even when broadened by experimental uncertainty, the line constraint does not pass through the allowed region of the symmetric model, indicating *a fortiori* that this model is inconsistent with experiment. Mathematically, the constraints imply a greater asymmetry between melting and freezing rates than can be introduced into the symmetric model by a simple activation enthalpy. Indeed, we speculate that symmetric models in general, for which nonactivated maximum melting and freezing rates are the same, may be inconsistent with experiment.

In contrast, constraint (2) does pass through the allowed region of the asymmetric model [Fig. 3(b)]; therefore, this model *is* consistent with experiment. Three interesting conclusions can be drawn from the

parameter values allowed by the boundaries in this model. First, $1600 \leq v_{mc} \leq 8300$ m/s, which bounds $f \exp(\Delta S_{s*}/k)$ between 0.19 and 1.0. Therefore, if the fraction of double-bond growth sites on the (100) c-Si surface is ~ 0.5, then the entropy of the transition state is near that of the solid. Second, $0.3 \leq Q \leq 0.25$ eV; despite the low measured freezing velocities relative to the sound velocity, the transformations are not strongly thermally activated. Thus, the observation that freezing of Si is slower than that of metals[1] is attributed mainly to a greater liquid/solid entropy difference rather than to a higher activation energy for interfacial atomic rearrangement. Third, for this model to satisfy the half-plane constraint (4), the slope $[dv_c/dT]_{T_{lc}}$ must be less than $\frac{1}{12}$ m/s·K. Of four independent measurements of this slope, this is consistent with the two transient-conductance measurements (dotted lines in Fig. 3),[18,19] but not with optical[5] and x-ray diffraction[6] measurements.

In conclusion, we have measured directly the relation between the melting velocities of a-Si and c-Si. This has led to the first severe experimental test of theories describing velocity/temperature interface response functions far from equilibrium. The measurements are inconsistent with a symmetric, collision-limited growth model, but are thus far consistent with an asymmetric, entropy-limited growth model which we have proposed here.

Although not elaborated here, both models can be shown to differ formally only in the thermodynamic properties of the transition state.[17] In the symmetric model, the transition state has a Gibbs free energy $G_* \geq \max\{G_s, G_l\}$; thus G_* follows G_l below the melting temperature and G_s above. In the asymmetric model, $G_* \geq H_l - TS_s$; the enthalpy of the transition state is greater than or equal to that of the liquid, while its entropy is less than or equal to that of the solid. It should also be noted, however, that although transition-state theory is commonly used to describe phase transformations, its validity may be limited for weakly activated condensed-phase processes. A detailed comparison with the results of molecular-dynamics simulations[20] would be particularly illuminating.

[1]F. Spaepen and D. Turnbull, in *Laser Annealing of Semiconductors,* edited by J. M. Poate and J. W. Mayer (Academic, New York, 1982), pp. 15–42.

[2]K. A. Jackson, in *Surface Modification and Alloying by Laser, Ion, and Electron Beams,* edited by J. M. Poate, G. Foti, and D. C. Jacobson (Plenum, New York, 1983), pp. 51–79.

[3]Michael O. Thompson, G. J. Galvin, J. W. Mayer, and R. B. Hammond, Appl. Phys. Lett. **42**, 445 (1983).

[4]G. J. Galvin, M. O. Thompson, J. W. Mayer, P. S. Peercy, R. B. Hammond, and N. Paulter, Phys. Rev. B **27**, 1079 (1983).

[5]P. H. Bucksbaum and J. Bokor, Phys. Rev. Lett. **53**, 182 (1984).

[6]B. C. Larson, J. Z. Tischler, and D. M. Mills, in *Energy Beam-Solid Interactions and Transient Thermal Processing/1984,* edited by D. K. Biegelsen, G. A. Rozgonyi, and C. V. Shank (Materials Research Society, Pittsburgh, 1985), p. 187.

[7]A. G. Cullis, H. C. Webber, and P. Bailey, J. Phys. E **12**, 688 (1979).

[8]Michael O. Thompson, G. J. Galvin, J. W. Mayer, P. S. Peercy, J. M. Poate, D. C. Jacobson, A. G. Cullis, and N. Chew, Phys. Rev. Lett. **52**, 2360 (1984).

[9]The velocities do not change discontinuously at the kinks because of slight nonuniformities in the laser beam and because of a finite measurement bandwidth. Therefore, v_a^- and v_c^+ are extrapolations of the velocities to the position of the original a-Si/c-Si boundary. The error bars and scatter in the data reflect uncertainties in these extrapolations.

[10]Michael O. Thompson, J. W. Mayer, A. G. Cullis, H. C. Webber, N. G. Chew, J. M. Poate, and D. C. Jacobson, Phys. Rev. Lett. **50**, 896 (1983).

[11]J. Y. Tsao, M. O. Thompson, and P. S. Peercy, unpublished.

[12]We use the values measured in I. R. Cox-Smith, H. C. Liang, and R. O. Dillon, J. Vac. Sci. Techol. A **3**, 674 (1985).

[13]D. Turnbull, J. Phys. Chem. **66**, 609 (1962).

[14]K. A. Jackson, in *Treatise on Solid State Chemistry,* edited by N. B. Hannay (Plenum, New York, 1975), Vol. 5, pp. 233–282.

[15]We use the values $\Delta H_{cl} = 0.525$ eV (at 1685 K), $\Delta S_{cl} = \Delta H_{cl}/1685$ K, and $\Delta H_{al} = 0.385$ eV (at 1442 K). The melting temperature of a-Si, T_a, is taken to be 1442 K—between the estimates of Donovan, *et al.,* 1420 K [E. P. Donovan, F. Spaepen, D. Turnbull, J. M. Poate, and D. C. Jacobson, J. Appl. Phys. **57**, 1795 (1985)] and of Thompson, *et al.,* 1485 K [Ref. 8]. ΔS_{al} at T_{la} is then deduced to be $\Delta S_{al} = \Delta H_{al}/T_{la}$. Small errors in this value, and minor effects due to the temperature dependences of ΔH_{sl} and ΔS_{sl}, will not affect our conclusions.

[16]D. Turnbull, J. Phys. (Paris), Colloq. **43**, C1-259 (1982).

[17]J. Y. Tsao, M. J. Aziz, Michael O. Thompson, and P. S. Peercy, to be published.

[18]Michael O. Thompson, P. H. Bucksbaum, and J. Bokor, in Ref. 6, p. 181.

[19]G. J. Galvin, J. W. Mayer, and P. S. Peercy, Appl. Phys. Lett. **46**, 644 (1985).

[20]J. Q. Broughton, G. H. Gilmer, and K. A. Jackson, Phys. Rev. Lett. **49**, 1496 (1982).