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INTERFACE VELOCITY TRANSIENTS DURING MELTING OF a-Si/c-Si THIN FILMS

J.Y. TSAO*, M.J. AZIZ**, P.S. PEERCY* AND M.O. THOMPSON***
* Sandia National Laboratories, Albuquerque, NM 87185
** Harvard University, Cambridge, MA 02138
***Cornell University, Ithaca, NY 14853

ABSTRACT

We report transient conductance measurements of liquid/solid interface velocities during pulsed laser melting of amorphous Si (a-Si) films on crystalline Si (c-Si), and a more accurate, systematic procedure for analyzing these measurements than described in previous work [1]. From these analyses are extracted relations between the melting velocities of a-Si and c-Si at a given interface temperature, and between the temperatures during steady-state melting of a-Si and c-Si at a given interface velocity.

INTRODUCTION

How fast planar liquid/solid interfaces move in response to deviations from the equilibrium melting temperature T_m is a basic question in materials science, whose answer is contained in velocity vs temperature interface response functions $v(T)$. For highly viscous liquids, it has been found [2] that the response function scales with diffusive velocities D/a_o (D is the atomic diffusivity, a_o is the lattice constant) and is locally "symmetric" (melting and freezing rates are the same for small but equal deviations above and below T_m).

The scaling and general shape of the response function have been more difficult to establish for non-viscous (most elemental) liquids. In Si, a system which has been studied intensively recently, transient conductance measurements [3] indicate that there is global asymmetry in that the melting and freezing behavior far from equilibrium are different. Previously, we [4] and others [5] have argued that this asymmetry can at least partially be understood as a natural outcome of transition-state theory, which predicts that far from equilibrium the melting rate should be "collision-limited" (limited only by the rate at which atoms collide with the interface), while the freezing rate should be "entropy-limited" (limited further by the entropy difference between liquid and solid) [6]. Differences between the densities of liquid and solid may also play a role [7].

Even if there is global asymmetry, though, we expect local symmetry. Recently, however, elegant x-ray diffraction measurements by Larson and co-workers [8] indicate that there may be a local asymmetry to the interface response function for Si. If so, the origin of this asymmetry is an extremely interesting theoretical problem.

In this work, we present measurements of liquid/solid interface velocities during pulsed laser melting of amorphous Si (a-Si) films on crystalline Si (c-Si), and a systematic procedure for analyzing these measurements. The result of our measurements and analyses is that melting and freezing of c-Si is locally symmetric, in disagreement with the x-ray diffraction measurements.

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TRANSIENT CONDUCTANCE MEASUREMENTS

Liquid layer thicknesses were measured in real time by the transient conductance technique [9]. The samples were 0.5-μm-thick (001) silicon-on-sapphire, photolithographically patterned into a 5:1 meander pattern. The samples were implanted with 125 keV, 3×10^{15}/cm^2 ^{30}Si ions at liquid nitrogen temperature to create a surface amorphous layer approximately 270 nm thick. The samples were irradiated by spatially homogenized 694-nm-wavelength laser pulses from a Q-switched ruby laser; pulsewidths were varied from 20 ns FWHM to 40 ns FWHM. Simultaneous transient reflectance measurements were made to ensure the absence of artifacts due to explosive crystallization.

An example of these measurements is shown in Fig. 1. The measured melt depth is the solid line in Fig. 1(a); the interface velocity, determined from the measured melt depth, is the solid line in Fig. 1(b). The interface velocity displays a quasi-steady-state behavior during most of its traversal across the a-Si and c-Si films, punctuated by a short-lived transient as the interface passes through the original a-Si/c-Si boundary.

Fig. 1. (a) Measured depth-phase-time diagram and (b) numerically deduced velocities during melting with a single 30.4 ns FWHM laser pulse at 2.13 J/cm^2.
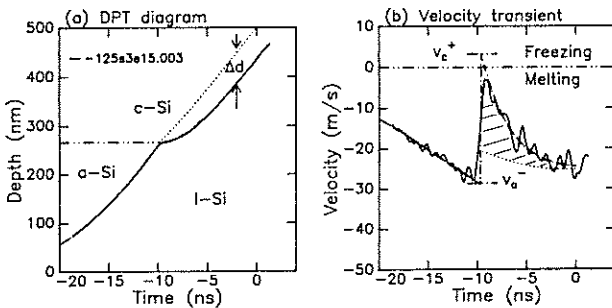
HEAT-FLOW CONSIDERATIONS

These qualitative features can be understood by simple heat-flow arguments. After melting initiates, the temperature of the liquid layer changes only if there is an imbalance between the laser power absorbed in the liquid layer of thickness d, the heat flow out into the underlying solid, and the latent heat consumed through interface motion at velocity v:

$$c_p T d = [J_{laser} - J_{solid}] + v \cdot \Delta H. \tag{1}$$

Since the laser intensity is slowly varying, quasi-steady-state holds during melting of the a-Si layer before the transient and during melting of the underlying c-Si after the transient has decayed. Then, the rate of change of the liquid layer temperature can be neglected, and the quasi-steady-state velocity is $v = -[J_{laser} - J_{solid}]/\Delta H$ [10].

Just after the liquid layer comes into contact with the underlying c-Si, however, the interface, which was moving according to the velocity-vs-temperature response function of a-Si, now moves according to the response function of c-Si. Because the equilibrium melting temperature of c-Si is higher than that of a-Si, the melt velocity will decrease; indeed, the interface may even reverse direction ("bounce back") momentarily. During this transient, the temperature of the liquid layer is changing rapidly in time according to the heat flow imbalance determined by Eq. (1). Writing the slope of the velocity vs temperature interface response function for c-Si near its melting temperature as $dv_c/dT = -\beta_c$, Eq. (1) becomes

$$(c_p d/\beta_c)\dot{v} - v\Delta H_{cl} = J_{laser} - J_{solid}. \tag{2}$$

Provided the incident laser energy and the heat flow into the underlying solid remain slowly varying, solution of this first order differential equation reveals that interface velocity transients should decay exponentially with a time constant

$$\tau = (dc_p)/(\beta_c \Delta H_{cl}). \tag{3}$$

DATA ANALYSIS

Based on these heat-flow arguments, we have fit the experimentally measured interface velocities with two quasi-steady-state Gaussian velocities, on which is superimposed an exponentially decaying velocity transient. For the Gaussian velocities we used the same shape as that of the measured laser intensity, with center heights in the ratio (0.71) of the latent heats for melting of a-Si and c-Si. Their center positions in time were taken to be identical and were determined by fitting the quasi-steady-state velocities before and well after impact. In all cases these center positions were within 1.5 ns of the measured center of the laser pulses -- approximately the triggering jitter of our system for these irradiation conditions.

The exponential transients were fit by matching τ to the measured decay times, then varying the magnitude of the transient to match the measured melt depth after the transient had largely decayed away. Over the range of pulsewidths studied here, we have found the best-fit decay times to scatter (± 0.4 ns) around a mean value of 2.65 ns. This value is consistent with Eq. (3) for $\beta_c = 1/16.1$ m/(K-s). Since, from Eq. (3), we expect the decay times to be constant, for all the data presented here we have fixed the decay time to be equal to this mean value. We find that this procedure markedly reduces the scatter in other fitting parameters.

The quasi-steady-state Gaussian velocities used to fit the data are shown as the dotted lines in Fig. 1(b). The velocity after the best-fit exponential transient has been added is shown as the dot-dashed lines. Finally, the dashed lines show the velocities after numerically convolving the velocities with an instrumental time response. The fits to the data are excellent; on the scale for which Fig. 1 is plotted the simulated and measured melt depths and velocities are virtually indistinguishable.

Two important quantities can be obtained from this data-fitting procedure. The first is the magnitude of the isothermal velocity jump at the instant the a-Si/l-Si interface impacts the underlying c-Si. For the case of Fig. 1, the velocity of the a-Si/l-Si interface just before impact is $v_a^- = -28.7$ m/s (i.e., melting); the velocity of the c-Si/l-Si interface just after impact is $v_c^+ = +3.2$ m/s (i.e., freezing).

Fig. 2.
Velocity
jumps (a)
and temp-
erature
offsets (b)
deduced
from
analysis of
measure-
ments made
over a
range of
pulse-
widths.

(a) Velocity jumps

○ 125s3e15 series

(b) Temperature offsets

○ 125s3e15 series
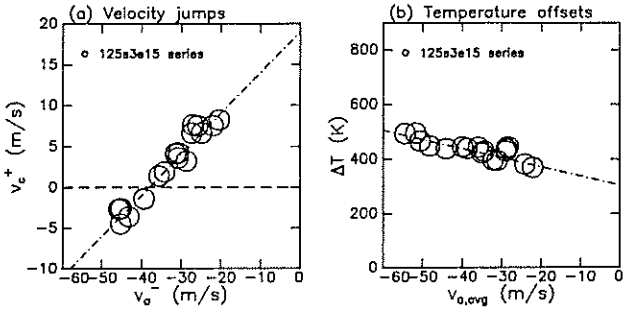
The second quantity is the difference between the interface (and molten layer) temperatures during quasi-steady-state melting of a-Si before the transient, and during quasi-steady-state melting of c-Si after the transient has decayed. If (as is implicit in our data analysis) we separate the velocity in Eq. (1) into a quasi-steady-state part $v_{QSS} = [J_{laser} - J_{solid}] / \Delta H$ and a transient part Δv, then this temperature difference ΔT can be seen to be due to latent heat "liberated" by the transient part of the velocity. Denoting the integral of the velocity transient, shown by the cross-hatched area in Fig. 1(b), as a "depth deficit" Δd [11], the temperature difference may be deduced from

$$c_p \Delta T d = \Delta H_{cl} \Delta d. \qquad (4)$$

For the case of Fig. 1, the depth deficit is 65.9 nm, which corresponds to a temperature difference of 407 K.

The results of similar measurements and analyses for a range of pulsewidths are summarized in Fig. 2. As the a-Si melting velocity just before impact decreases, the c-Si melting velocity just after impact also decreases until, at approximately 38 m/s, the velocity changes sign (freezing rather than melting). In the limit of zero a-Si melting velocity, the freezing velocity of l-Si into c-Si extrapolates to 19 m/s, in approximate agreement with the measured critical c-Si freezing velocity (15 m/s) for spontaneous formation of a-Si. The slope dv_a/dv_c is approximately 0.5, indicating that less overheating is required to achieve a given melting velocity in a-Si than in c-Si.

Fig. 3. (a)
Sequence of
events and
(b) implica-
tions of our
measurements
and analyses
on the
velocity-vs-
temperature
interface
response
function for
c-Si.

(a) Sequence of events

(b) TST Models
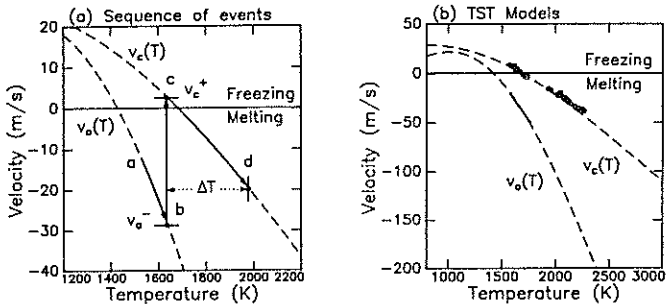
As shown in Fig. 2(b), as the a-Si melting velocity (averaged over its extrapolated value during the transient) decreases, the temperature difference ΔT decreases. In the limit of zero a-Si melting velocity, the temperature difference extrapolates to 304 K, in approximate agreement with measurements of the equilibrium melting temperature of a-Si [12].

IMPLICATIONS FOR $v_c(t)$

The implications of these measurements can be understood more clearly with the help of the schematic interface velocity response functions for a-Si and c-Si shown in Fig. 3(a). As the laser pulse heats the a-Si overlayer, the temperature increases, eventually exceeding the equilibrium melting temperature. Then, the a-Si begins to melt, and the a-Si/l-Si interface velocity and temperature increase from a to b as the laser intensity increases, according to quasi-steady-state heat-flow. As the interface passes through the original a-Si/c-Si boundary, the l-Si suddenly comes into contact with c-Si, which has a different interface response function. The melting velocity decreases isothermally from v^- at b to v_c^+ at c. At c, however, the interface velocity is too slow. Heat flow is imbalanced, and, according to Eq. (1), the interface velocity and temperature will increase from c to d until heat flow is again balanced. The temperature change ΔT during this transient period is given by Eq. (4).

The data in Fig. 2 define two relations between the relative melting velocities and temperatures of a-Si and c-Si. Therefore, given a prescribed shape for $v_a(T)$, we can deduce a shape for $v_c(T)$. Note, however, that the data in Fig. 2(a) determine the melting velocity of a-Si at the melting temperature of c-Si. Since the melting temperature of a-Si is approximately known, we can deduce the approximate shape for $v_a(T)$ shown by the solid line in Fig. 3(b). Using this shape for $v_a(T)$ and the data in Figs. 2(a) and 2(b), we deduce the data points clustered near the melting temperature of c-Si, and the data points lying to the right, respectively. The dashed line through the data is derived from our entropy-limited transition-state model, using a prefactor velocity of 1100 m/s and an activation energy of 0.2 eV.

CONCLUSIONS

The implication of these measurements is that melting and freezing of c-Si is locally symmetric, in disagreement with x-ray diffraction measurements. We do not at present understand the source of this disagreement. However, two important caveats must be made. First, our analysis of these measurements assumes that the liquid/solid interfaces are planar. If melting of a-Si is not planar, perhaps due to nucleation of liquid ahead of the "interface", then our analysis would not be valid.

Second, our analysis assumes that the contributions to the heat flow balance from absorbed laser intensity and heat flow into the underlying substrate are exactly canceled by quasi-steady-state velocities. If the thermal conductivities of a-Si and c-Si are similar near their melting temperatures, similar analyses of heat-flow simulations [13] show this assumption to be reasonable: our fitting procedure reproduces closely the velocity jumps and temperature deficits expected from the interface response functions put into the simulations, with the correct decay times.

However, if the thermal conductivity of a-Si near its melting temperature is much less than that of c-Si, then the best fit decay times were increased above the correct values. The reason is that the quasi-steady-state temperature gradient in the solid just behind the liquid would be much steeper during a-Si melting then during c-Si melting. Then, during the transient, extra heat must flow into the solid to set up the appropriate quasi-steady-state temperature profile in the c-Si, leading to longer decay times and an overestimate of the temperature offset ΔT.

It should be noted, however, that our experimental best-fit decay times agree rather closely with Eq. (3), using a $\beta_c = (1/16)$ m/(s-K). This is consistent, as discussed by Thompson [14], with the absence of a significant difference in the a-Si and c-Si thermal conductivities at high temperature.

ACKNOWLEDGEMENTS

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