Rapid Melting and Regrowth Velocities in Silicon Heated by Ultraviolet Picosecond Laser Pulses

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Direct measurements of the silicon liquid/solid interface velocity have been made during both melt-in and regrowth for crystalline silicon irradiated with a pulsed (15 psec) ultraviolet laser. The liquid films produced were up to 40 nm thick and were fully amorphized upon resolidification. Above threshold, the regrowth velocity was 25 m/sec, independent of laser fluence. The results imply a nonlinear relationship between supercooling and interface velocity.

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It is by now well established that pulsed laser irradiation of a crystal surface can result in annealing of damage to the crystal structure near the surface. This behavior is due to the epitaxial regrowth of the laser-melted liquid film. Recent studies[1,2] have demonstrated, however, that when the regrowth velocity exceeds a critical value in crystalline silicon, the crystal is supplanted by a thermodynamically unstable solid amorphous phase. Rapid solidification velocities occur under conditions of high thermal gradients and large heat flows, which require a heating source with a shallow penetration depth and short duration to allow minimum time for thermal diffusion. In this region, it is assumed[1] that the temperature of the liquid-solid interface can become supercooled below the melting temperature for amorphous silicon, semiempirically estimated at 200–260 K below the crystal melting point.[3] At some point below this temperature, interface thermodynamics begins to favor amorphous-silicon formation. In Ref. 1, a 347-nm frequency-doubled ruby laser with a pulse width of 2.5 nsec was used in the amorphization experiments. Regrowth velocities as high as 20 m/sec were observed. However, the amorphous films which were formed were significantly thinner than the measured maximum melt depths. It was speculated that this difference could be explained by considering the time required to undercool the liquid below the amorphous transition temperature but no direct information concerning the role of undercooling was obtained.

We report the results of experiments to probe laser-melted liquid-silicon films as they melt and resolidify with 20-psec time resolution. A 248-cm excimer laser with 15-psec pulse width[4] was used as the melting source to induce a large resolidification velocity to study the thermodynamics of the liquid-solid interface far from equilibrium. A much weaker 1.64-μm infrared 15-psec laser pulse, generated by use of a portion of the ultraviolet laser output, probed the liquid film in transmission and reflection. This information could be directly related to the depth of the liquid-silicon film. Comparison of the data with a new heat-flow calculation provides clear evidence for undercooling of the interface during amorphous regrowth and overheating during melt-in.

Great care was taken to produce a spatially homogeneous melt spot; typically, a spot size of 0.8 mm was used. The 1.64-μm infrared probe pulse was derived from the ultraviolet laser pulse by transient stimulated Raman scattering[5] in thallium vapor. The infrared beam was heavily attenuated, apertured, and imaged to a 100-μm spot in the center of the melt spot on the sample. The silicon wafers were mounted to a motorized raster scanner, which moved to expose a fresh crystalline surface on every pulse. Room-temperature germanium photodiodes detected infrared light transmitted and reflected from the silicon, as well as a glass surface reflection used for normalization.

The attenuation constant in metallic liquid silicon is simply related to $k(\omega)$, the imaginary part of the complex refractive index $n(\omega)$, which may be calculated with a simple Drude model. The value of $k(\omega)$ thus derived is in excellent agreement with ellipsometry measurements in the wavelength range 0.4–1.0 μm.[6] At the probe wavelength in this experiment, calculation yields $k(1.6\ \mu\text{m}) = 8.4$. Once the air, metallic liquid, and solid complex indices are known, the transmission and reflection coefficients T and R can be calculated easily.[7]

Reflection data are used to corroborate the depths obtained from transmission. The two data sets are independent, and their comparison provides a check of the experimental technique as well as the optical constants used to calculate the depth. For liquid-silicon film thicknesses between 8 and 30 nm, the reflection and transmission data agree to within 15%.

Data were taken on both (111) and (100) silicon surfaces. The maximum melt depth was a linear function of incident laser fluence, statistically independent of orientation, with a slope of $(5.6 \pm 0.3) \times 10^{-2}$ cm^3/kJ. The melting threshold, determined by extrapolating the linear fit to zero depth, was 24 mJ/cm^2. The threshold was roughly consistent with the observed threshold for amorphous silicon formation.

The melt depth as a function of time and laser fluence is displayed in Fig. 1. Zero on the time axis coincides with the peak of the melting laser pulse. This plot represents approximately 5000 individual laser shots, which are binned and averaged in fluence and time. Each line connects points with the same fluence. The time required to melt the silicon to its maximum depth is nearly independent of laser energy, and therefore the average melt-in velocity, defined as the maximum melt depth divided by the time required to reach that depth, increases linearly with the laser power, up to a maximum velocity of 750 m/sec for a 40-nm-deep melt. Resolidification of the molten silicon films was observed over a range of laser energies, up to approximately six times threshold energy for melting. At all energies, the rate of resolidification was greater than 10–15 m/sec, the threshold for amorphous silicon formation. This was corroborated by the characteristic higher reflectivity at visible wavelengths for amorphous silicon, which was always observed when the laser pulse energy was above the melting threshold.

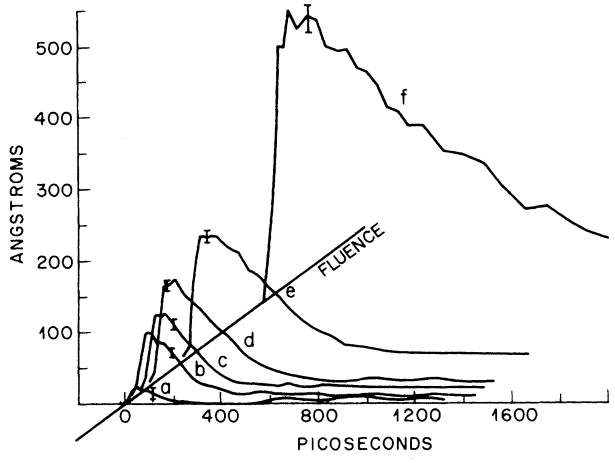

FIG. 1. Liquid-silicon thickness vs time and laser fluence. Curve *a*, 32 mJ/cm^2; *b*, 37 mJ/cm^2; *c*, 42 mJ/cm^2; *d*, 47 mJ/cm^2; *e*, 66 mJ/cm^2; and *f*, 106 mJ/cm^2.

The velocity of the liquid–amorphous-solid phase boundary was approximately constant throughout the resolidification process. This steady-state velocity was reached within 50–100 psec of the melt-in termination time and maintained throughout 80% of the melt-out duration. Near the end of the melt, all samples displayed an apparent slowing of the regrowth. Except for the two shallow melt curves that were close to threshold for melting, the regrowth velocities for all incident laser energies were approximately 25 m/sec.

Several groups have constructed models of laser annealing.[8] The simplest approach assumes that melting and resolidification of laser-irradiated material is a one-dimensional heat-flow problem in which energy is deposited near the surface of a semi-infinite medium and thermalizes immediately, forming a temperature gradient normal to the surface. A computer simulation written by M. O. Thompson which numerically integrates the heat-flow equations for an arbitrary laser heating pulse was used to simulate the present results. A version that could easily be modified for picosecond uv pulses was supplied by its author. This program has successfully predicted results of nanosecond laser melting experiments,[9] and we consider it a useful tool for comparing the physical mechanisms which determine interface velocities in these two very different time domains. The input parameters to the program are the bulk optical and thermal parameters of liquid, crystal, and amorphous silicon. We used standard literature values for heat capacity, latent heat, melting temperature, and thermal conductivity wherever possible, usually choosing the same values used in the nanosecond simulations.[10] Optical constants for the crystalline and amorphous solid phases were taken from ellipsometry measurements.[11]

When this simple model is applied to the present experiment, the predicted resolidification velocities are more than double those observed. Since this simulation requires that freezing occur at temperature $T = T_m$, this suggests undercooling of the melt front during solid phase regrowth. Actually, some undercooling of the phase boundary is necessary to drive the resolidification process itself. This effect must always be present during freezing, but the temperature difference is usually negligible for freezing on time scales much longer than a nanosecond. A simple linear relationship between interface velocity and temperature, $V(T)=a(T-T_m)$, also produces a very poor fit to the data. It does not appear possible to match the freezing interface velocity for all values of laser fluence with a single proportionality constant a.

In the simplest dynamical model of melting, the rate of mass transfer across the solid-liquid interface is proportional to the chemical potential difference between the two phases, leading to a simple exponential expression that describes the phase transition velocity[12]:

$$V(T)=V_0(T)[\exp(\Delta g/RT)-1], \qquad (1)$$

where g is the Gibbs free energy per mole. The limiting velocity $V_0(T)$, which depends on the microscopic details of melting and freezing, can be written[13]

$$V_0(T)=k\lambda f, \qquad (2)$$

where k is the collision rate between an atom in the melt and the interface (hopping frequency), λ is the interatomic spacing, and f is the fraction of growth sites on the interfacial surface. Each may be temperature dependent. In addition, if the phase transition is an activated process, a factor $\exp(-\mu/RT)$ must be included, where μ is the activation energy.[14] In Eq. (2), k is roughly equal to the vibrational frequency of an atom in the liquid. The exponential factor may be calculated with the aid of the free-energy phase diagram for silicon.[3] To first order, Δg is proportional to the latent heat of melting L and, Eq. (1) may be approximated by

$$V(T)=V_0\{\exp[(L/RT_m^2)(T-T_m)]-1\}, \qquad (3)$$

where V_0 is approximately constant.

The liquid-amorphous interface velocity $V_a(T)$ has a different temperature dependence because of its different entropy, specific heat, free energy g', and equilibrium melting temperature T_{ma}. It may have a different limiting velocity V_{0a} as well. When $V_a(T)>V(T)$, direct liquid → amorphous-solid transitions can occur. The computer simulation was modified to follow $V(T)$ in Eq. (3) for the crystal-liquid transition up to $V=15$ m/sec.[1] For higher velocities, the interface follows $V_a(T)$. Literature values were used for the amorphous melting temperature and latent heat of melting.[3] Also, the two curves were constrained to cross at 15 m/sec. This procedure resulted in a two-parameter fit, shown in Fig. 2, where the fitting parameters are V_0 and the effective surface reflectivity.[15] We find that V_0 is in the range 25–27 m/sec and V_{0a} is between 50 and 68 m/sec. The temperature at the crossing point is between 1270 and 1320 K. The effective reflectivity is 0.58 ± 0.04.

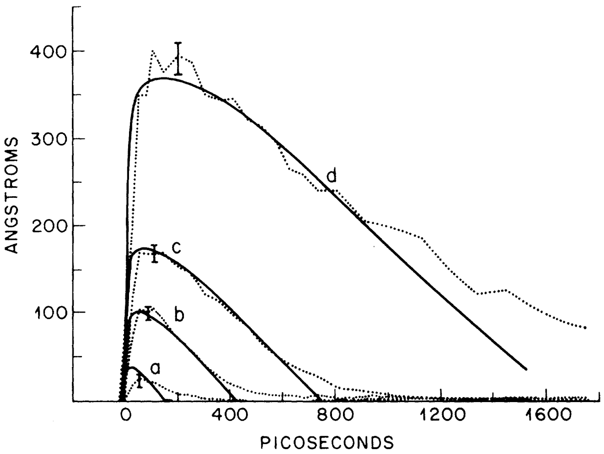

FIG. 2. Fits to the data for four values of laser fluence: curve a, 34 mJ/cm^2; b, 42 mJ/cm^2; c, 66 mJ/cm^2; and d, 106 mJ/cm^2. Fitting functions were two curves of the form shown in Eq. (3), representing amorphous and crystalline solidification, which cross at 15 m/sec.

These values may be used to place limits on the physical growth mechanisms. If the phase transformation is collision limited, then $V_0 \approx V_{\text{sound}} f$, which implies that the growth-site fraction f is a few percent for both crystal and amorphous silicon. If, however, there is an activation energy μ, then the experimental values imply an upper limit of $\mu < RT\ln(V_{\text{sound}}/V_0)$. This is 0.6 eV for the liquid-to-crystal transition, and 0.5 eV for the liquid-to-amorphous transition.

Several problems remain unresolved in these fits. Most important from the standpoint of quantitative interpretation of the data is the rapid melt-in velocities in the simulations, which are considerably slower in the data. Also, the total melt-in time is roughly independent of laser fluence in the experiment; this effect does not appear in the simulation, where deeper melts take longer to reach maximum depth. The rate of melting affects the thermal gradients during the initial phase of regrowth. Therefore, the pinning of the observed regrowth velocity may be nontrivially related to the constant melt-in time. The fits employed the simplified version of the melting curve shown in Eq. (3); however, melting rates are in better agreement if the exponential dependence of Eq. (1) is assumed, although the best overall fits employ Eq. (3). Finally, none of the simulations reproduce the long flat tail seen in the data at the end of each melt. This may be an experimental artifact, from small-scale nonuniformities in the melt depth across the probed area.

In conclusion, we have directly observed the position of the liquid–amorphous-solid interface in silicon with 20-ps time resolution, under conditions of high thermal gradients and rapid heat flow brought on by melting with a 15-ps uv laser. The interface velocity was observed to saturate at about 25 m/sec, independent of incident laser fluence. Comparison with standard heat-flow calculations that are successful when applied on nanosecond time scales shows for the first time large undercooling of the interface (up to 700 K) and indicates a nonlinear exponential dependence of interface velocity on temperature. However, systematic deviations in the fits suggest the need for a more sophisticated model of melting under these nonequilibrium conditions.

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