Supercooling and Nucleation of Silicon after Laser Melting

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Bulk nucleation of crystalline Si at a supercooling of 505 K was observed following pulsed-laser–induced melting of thin films. If the nucleation was homogeneous, the estimated nucleation rate of 10^{29} events/m^3·s implies a liquid-Si–crystalline-Si interfacial energy of 0.34 ± 0.02 J/m^2. In addition, observation of crystalline nucleation bounds the interface energy between amorphous Si and liquid Si to be > 0.20 J/m^2. This laser melting technique is applicable to nucleation studies in a wide variety of materials.

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Recent studies of pulsed-laser irradiation of Si have dramatically changed our understanding of rapid phase transformations under large deviations from equilibrium.[1] For example, amorphous Si (*a*-Si) can be directly quenched from the liquid phase at interface velocities exceeding $\simeq 15$ m/s,[2-4] indicating an interesting competition between the kinetic growth rate and nucleation at a moving interface. More recently, investigations of explosive crystallization of *a*-Si have led to the development of quantitative models for the transformations among amorphous, liquid, and crystalline phases.[5-9] Tsao and Peercy[7] suggested that explosive crystallization proceeds by nucleation of crystalline Si (*c*-Si) at a moving amorphous-liquid interface, a model which can only be valid if the interface energies, and hence the competing nucleation rates, fall within a limited range. Other models[8,9] suggest that homogeneous nucleation of *c*-Si occurs during explosive crystallization at temperatures near the melting temperature of *a*-Si ($\simeq 250$ K below the crystalline melting temperature[5]). Evaluation of these various models requires determination of the supercooling[10] required for homogeneous nucleation and the corresponding interfacial energies.

Homogeneous nucleation has been traditionally studied in droplet experiments, with typical volumes of ≤ 1 mm^3 and nucleation occurring on time scales of seconds.[11,12] These conditions correspond to nucleation rates of 10^6–10^{12} events/m^3·s. With use of known bulk values for the enthalpy (ΔH_m) and temperature (T_m) of melting, the energy associated with the liquid-solid interface can be determined from measurements of the nucleation rate and temperature. The nucleation rate is normally assumed to increase so rapidly with supercooling that a unique nucleation temperature can be specified.

This Letter reports the first measurements of the supercooling required for bulk nucleation in Si at extremely high nucleation rates ($\simeq 10^{29}$ events/m^3·s). These conditions are established by the rapid thermal quench following pulsed-laser–induced melting. The supercooling of 505 K required for nucleation under these conditions greatly exceeds the 275-K supercooling achieved in droplet experiments[13] because of the different rates. If the observed nucleation was homogeneous, these results indicate a liquid-Si [*l*-Si/*c*-Si interface energy of 0.34 J/m^2 (0.16 eV/atom)]. These observations have implications for both the mechanism of direct quenching of *a*-Si from the melt and the detailed mechanism which governs explosive crystallization.

Thin films (< 1 μm) of Si on suitable nonreactive substrates were completely melted with a 30-ns *Q*-switched pulsed ruby laser ($\lambda = 694$ nm). Conduction of heat into the substrate results in a thermal quench of $\simeq 5 \times 10^9$ K/s and eventually leads to nucleation in the liquid. During melting and nucleation, the thickness of the liquid layer and the phases in the surface region were monitored with transient conductance[14] and surface optical reflectance[15] at 488 nm near Brewster's angle. Various Si-layer thicknesses and substrate materials were studied, including films of 500- and 600-nm Si on sapphire, 300-nm polycrystalline Si (*p*-Si) on 250-nm thermal SiO_2 on a Si substrate, and 300-nm zone-melt-recrystallized (ZMR) Si[16] on 250-nm thermal SiO_2 on a Si substrate. Microstructures of the resultant films were examined by planar and cross-sectional transmission electron microscopy (TEM). All of these Si-layer thicknesses and substrate materials yielded essentially identical results.

Typical transient-conductance and optical-reflectance data are shown in Fig. 1 for irradiation of a ZMR sample at 1.01 J/cm^2. During irradiation, the Si-surface layer is completely melted as indicated by the plateau at 5.8 mmho in the conductance (equivalent to 304 nm of *l*-Si). The film remains molten for $\simeq 100$ ns as the liquid cools

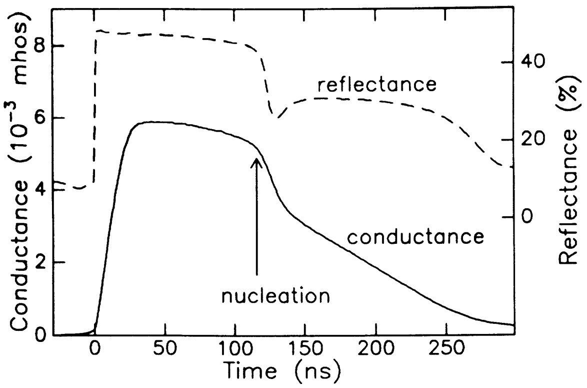

FIG. 1. Transient-conductance and optical-reflectance traces for irradiation of a 300-nm ZMR film at 1.01 J/cm^2. The entire Si film is melted, with subsequent nucleation indicated by the arrow. The reflectance scale is approximate.

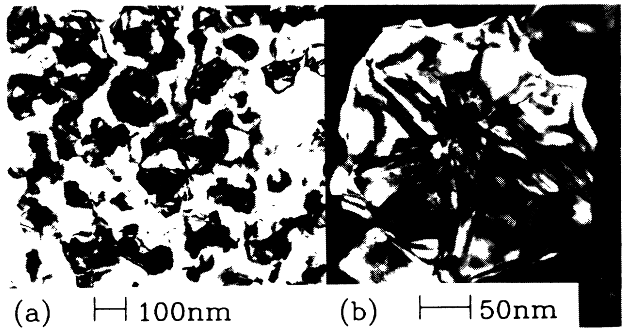

FIG. 2. (a) Planar TEM view of a ZMR sample after nucleation and solidification. The microstructure shows uniform 150–250-nm grains. (b) Planar view of a nucleation site.

by thermal conduction into the substrate. Because of the relatively high thermal conductivity of l-Si, the liquid layer is essentially isothermal during the cooling period (< 10-K difference across it). Following this delay, there is a simultaneous and rapid decrease in both the conductance and reflectance signals. These decreases are interpreted as marking the onset of nucleation and recalescence (reheating to near T_m); the timing and magnitude of this event can be related to the supercooling at nucleation as discussed below. Following recalescence, growth of the solid continues under steady-state conditions as heat is conducted into the substrate. The surface reflectance, a complex spatial average of the liquid and solid phases present in the top 20 nm, remains approximately constant during the subsequent growth, indicating that crystallization proceeds from the cooler substrate region toward the surface.

The conductance signal observed in Fig. 1 is also a complex average of the conductivities and volume fractions of the phases present. Although nonlinear, the conductance decreases monotonically with the volume fraction of solid present. The volume of material which solidifies during recalescence is hence directly related to the magnitude of the discontinuity in the conductance. The ratio of the conductance level following recalescence to the fully liquid value is approximately constant at 0.64 ± 0.03 over an incident energy-density range of 1.0–2.5 J/cm^2, where the uncertainty reflects the standard deviation of the twenty samples studied. This result indicates that a constant volume fraction of Si is consumed during recalescence. Since the heat released in recalescence raises the temperature of the film from the nucleation temperature (T_n) to the steady-state growth temperature (near T_m), nucleation occurred at approximately the same temperature in all cases.

The volume fraction of solid remaining after recalescence, χ, may be obtained by our assuming two-phase conduction of spherical solid particles dispersed in a continuous liquid matrix.[17] The observed conductance ratio of 0.64 indicates solidification of $\simeq 29\%$. The nucleation temperature is estimated by our equating the enthalpy released during recalescence to the heat required to raise the liquid from T_n to the steady-state temperature, T_{ss}:

$$\int_{T_n}^{T_{ss}} C_p^{\mathrm{liq}}(T)\,dT = \chi \Delta H_m.$$

With bulk parameters of Si,[18] the supercooling prior to nucleation is 505 ± 45 K. Similar estimates may also be obtained if we numerically model the heat transfer prior to nucleation. Numerical simulations for solid-on-solid films indicate that nucleation occurred at 550-K supercooling, approximately 45 K greater than estimated above. Heat transfer through SiO_2 at high temperatures could not be accurately modeled because of scatter in experimentally measured thermal parameters,[19] and the possibility of a phase transition near the melting temperature of Si. The heat-balance result of 505 K is considered to be more accurate and, at worst, provides a lower estimate for the supercooling required for nucleation.

A planar TEM view, Fig. 2(a), reveals that the microstructure after solidification consists of uniform polycrystallites 150–250 nm in diameter. An example of a site where nucleation appears to have occurred is shown in Fig. 2(b). Electron diffraction confirms that the grain in this region is a single crystal, apparently originating from a single nucleation site with no observable second-phase particles. Cross-sectional views of similar samples show the microstructure to be uniform in depth also with no evidence of preferential nucleation at either the free surface or the Si-substrate interface.

These TEM and time-resolved measurements provide strong evidence for bulk nucleation. First, the surface reflectance qualitatively indicates that a partial phase transformation occurred at the surface during recalescence. Preferential nucleation at either the free surface or the buried interface would result in either a complete drop in the reflectance to the crystalline value or no change at all, respectively. Secondly, TEM shows uniformly distributed grains throughout the Si film with no evidence of particles associated with the nucleation events. Furthermore, since nucleation occurred at the same temperature for all film thicknesses and substrate materials, we conclude that the nucleation occurred uniformly and possibly homogeneously throughout the film.

An estimate of the nucleation rate observed in this experiment may be obtained by determination of the grain density and the approximate time scale for nucleation. First, a nucleation density of $\simeq 2\times 10^{20}$ events/m^3 is estimated if each grain in the final microstructure results from a separate nucleation event. Since the enthalpy released by crystallization heats the surrounding liquid, thus suppressing further nucleation, the estimated nucleation density requires all nucleation to occur within a time scale on the order of a nanosecond. Thus, the estimated nucleation rate is $\simeq 10^{29}$ events/m$^3\cdot$s. This is an upper limit on the homogeneous nucleation rate since either dynamic nucleation effects[20] or crystallite fracture during growth may result in numerous grains associated with a single homogeneous nucleation event. If we assume spherical nuclei, classical nucleation theory[21] estimates the homogeneous nucleation rate, Γ, as

$$\Gamma \approx 10^{39} e^{-\Delta G^*/kT}\ \text{events/m}^3\cdot\text{s},$$

where

$$\Delta G^* = 16\pi T_m^2 \sigma^3 / 3\Delta H_m^2 \Delta T^2,$$

and σ is the interface energy, ΔT is the supercooling, T is absolute temperature, and k is Boltzmann's constant. Since ΔH_m and T_m are well known, a nucleation rate of 10^{29} events/m$^3\cdot$s at 505 ± 45 K supercooling implies an interface energy ($\sigma_{c\text{-}l}$) of 0.34 ± 0.2 J/m^2 (0.16 eV/atom).[22]

The nucleation rate versus temperature for $\sigma_{c\text{-}l}=0.34$ J/m^2 is shown in Fig. 3. Experimental results from this work and from a droplet examined by Devaud and Turnbull[13] are also shown. While the nucleation rate is a very steep function of temperature, a difference of $\simeq 10^{20}$ in nucleation rate required markedly different supercoolings. The agreement between these experiments appears excellent; however, more careful consideration of the nucleation conditions in the laser experiment are necessary before detailed comparisons can be made.

The 505-K interfacial undercooling immediately following nucleation observed in these experiments is substantially greater than any undercooling previously observed at a l-Si interface. Indeed, the undercooling exceeds the $\simeq 250$ K obtained during a-Si quenching directly from l-Si.[4] Under these extreme undercoolings, a-Si is expected to form during solidification. However, TEM investigations reveal no evidence either of a-Si or of very fine-grained (10 nm) p-Si, a usual signature of explosive crystallization of a-Si. These observations imply that the rate of crystalline nucleation exceeds that of the amorphous phase under these experimental conditions. With bulk parameters for a-Si in the nucleation rate equation, a minimum a-Si/l-Si interfacial energy ($\sigma_{a\text{-}l}$) of $\simeq 0.20$ J/m^2 is required for the amorphous nucleation rate to be less than 10^{29} events/m$^3\cdot$s at T_n. The dashed curve in Fig. 3 shows this maximum permissible rate.

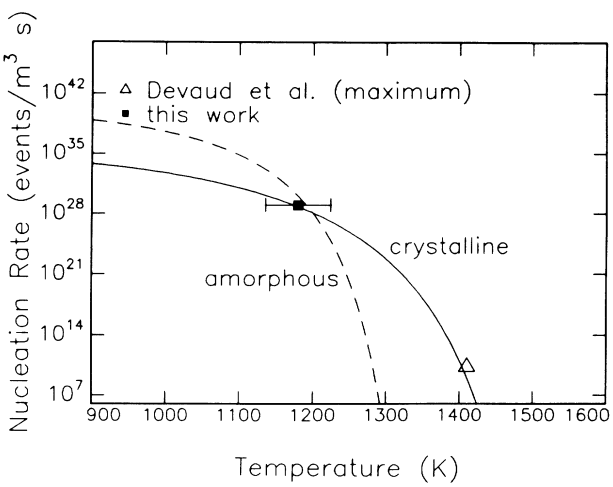

FIG. 3. Nucleation rate vs temperature for $\sigma_{c\text{-}l}=0.34$ J/m^2. Nucleation rates and temperatures for this work and Ref. 13 are shown. Dashed curve indicates maximum nucleation rate for a-Si consistent with c-Si nucleation in this experiment.

Since the l-Si temperature during explosive crystallization is never below the melting temperature of a-Si, our observation of a 505-K supercooling firmly rules out homogeneous or surface nucleation during explosive crystallization.[8,9] The measured surface energies are, however, consistent with the mechanism suggested by Tsao and Peercy.[7]

These experiments, however, do pose several subtle questions for the conventional interpretation of laser amorphization of Si. As noted above, a l-Si to a-Si transformation is expected because of the severe undercooling present. If we assume that the interface response function is single valued for c-Si, the c-Si/l-Si interface must pass through conditions comparable to those present when a-Si is formed from l-Si. However, no microstructural evidence for a-Si formation was observed, leading to two possible explanations. Either a-Si did not form, or any a-Si which formed transformed to c-Si epitaxially during recalescence. Close examination of the time-resolved reflectance during recalescence reveals a dip followed by a rise to the steady-state value which may be related to this question.

It has been suggested that there is an incubation time for a-Si formation from l-Si,[4] perhaps representing a period of interface growth during which defects coalesce. Under this hypothesis, the interface may pass through the conditions for a-Si formation in a time short compared with this incubation period, preventing a-Si formation. Additionally, the presence of grain edges in the neighborhood of the growing particle may prevent the agglomeration of defects, further preventing a-Si formation.

Secondly, it is possible that following c-Si formation, a-Si is indeed formed, but transforms epitaxially by a liquid-phase process to c-Si within the recalescence time. Solid-phase regrowth kinetics are too slow to explain such a transformation ($\simeq 0.03$ nm/ns at 1600 K), but energy released in slight solid-phase regrowth may nucleate a secondary liquid phase. In this scenario, the initial deep drop in surface reflectance could correspond to surface a-Si formation with the subsequent increase corresponding to the conversion of some a-Si to l-Si. Further experiments are necessary to resolve this question.

In conclusion, it has been shown that bulk nucleation of elemental materials can be readily studied in laser melting experiments. An interface energy of 0.34 ± 0.02 J/m^2 has been estimated for the c-Si/l-Si interface, and a lower bound of 0.20 J/m^2 has been determined for the a-Si/l-Si interface. Although interface temperature conditions suggest that a-Si should have been formed from the liquid during recalescence, no microstructural evidence of such a transformation was observed. This suggests that solidification proceeds by more complex scenarios than had previously been appreciated.

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[1] See, for example, *Beam-Solid Interactions and Transient Processes,* edited by M. O. Thompson, S. T. Picraux, and J. S. Williams, MRS Symposium Proceedings Vol. 74 (Materials Research Society, Pittsburgh, PA, 1987).

[2] P. L. Liu *et al.*, Appl. Phys. Lett. **34**, 864 (1979).

[3] A. G. Cullis *et al.*, Phys. Rev. Lett. **49**, 219 (1982).

[4] Michael O. Thompson *et al.*, Phys. Rev. Lett. **50**, 896 (1983).

[5] Michael O. Thompson *et al.*, Phys. Rev. Lett. **52**, 2360 (1984).

[6] D. H. Lowndes *et al.*, J. Mater. Res. **2**, 648 (1987).

[7] J. Y. Tsao and P. S. Peercy, Phys. Rev. Lett. **58**, 2782 (1987).

[8] J. J. P. Bruines *et al.*, Appl. Phys. Lett. **49**, 1160 (1986).

[9] K. Murakami *et al.*, Phys. Rev. Lett. **59**, 2203 (1987).

[10] In this paper, we use undercooling to refer to the deviation of an *interface* from the melting temperature and supercooling to refer to the deviation of a *bulk liquid* from the melting temperature.

[11] D. Turnbull and R. E. Cech, J. Appl. Phys. **21**, 804 (1950); D. Turnbull, J. Appl. Phys. **21**, 1022 (1950).

[12] J. H. Perepezko and I. E. Anderson, in *Synthesis and Properties of Metastable Phases,* edited by E. S. Machlin and T. J. Rowland (American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA, 1980), p. 31.

[13] G. Devaud and D. Turnbull, Appl. Phys. Lett. **46**, 844 (1985).

[14] G. J. Galvin *et al.*, Phys. Rev. Lett. **48**, 33 (1982); M. O. Thompson *et al.*, Appl. Phys. Lett. **42**, 445 (1983).

[15] D. H. Auston *et al.*, Appl. Phys. Lett. **33**, 437 (1978).

[16] C. K. Chen *et al.*, Appl. Phys. Lett. **48**, 1300 (1986).

[17] J. C. Maxwell, *Electricity and Magnetism* (Clarendon, Oxford, 1892), 3rd ed., Vol. 1, p. 440; D. A. G. Bruggeman, Ann. Phys. (Leipzig) **24**, 636 (1935).

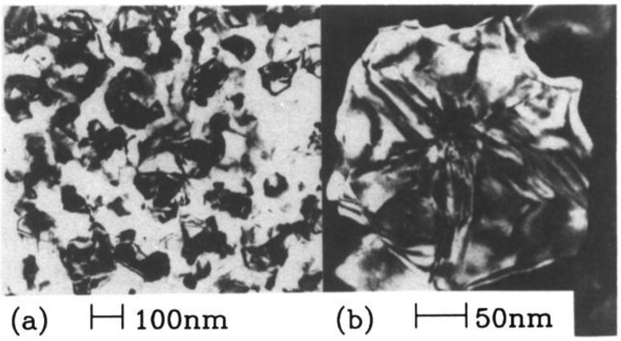
[18] C. Y. Ho, R. W. Powell, and P. E. Liley, Chem. Ref. Data **3**, Suppl. 1 (1974); *Chemical Rubber Company Handbook of Chemistry and Physics,* edited by R. C. Weast and M. J. Astle (CRC Press, Boca Raton, FL, 1981), 62nd ed.

[19] Y. S. Touloukian and E. H. Buyco, *Specific Heat, Metallic Elements and Alloys,* Thermophysical Properties of Matter Vol. 4 (IFI/Plenum, New York, 1970).

[20] J. L. Walker, in *Physical Chemistry of Process Metallurgy,* edited by G. R. Pierre (American Institute of Mining, Metallurgical and Petroleum Engineers, New York, 1961), p. 845.

[21] J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon, Oxford, 1965), p. 377.

[22] Nonspherical nuclei and size-dependent ΔH_m may result in corrections to the calculated $\sigma_{c\text{-}l}$.



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