SUPERCOOLING OF SILICON AND GERMANIUM AFTER LASER MELTING

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ABSTRACT

Following pulsed laser melting, supercoolings of 505 K in Si and 430 K in Ge were observed prior to bulk nucleation. These large supercoolings are obtained because of the extremely high thermal quench which follows laser irradiation. Nucleation rates were estimated to be $\sim 10^{29}$ events/m^3/s. Assuming that homogeneous nucleation was achieved, surface energies are estimated to be 0.34 J/m^2 for Si and 0.24 J/m^2 for Ge. These results are in reasonable agreement with traditional homogeneous nucleation experiments sensitive to rates of only $\sim 10^{10}$ events/m^3/s. This laser melting technique is applicable to nucleation studies in a wide variety of materials.

INTRODUCTION:

Phase transformations provide an interesting opportunity to observe the interaction between energies associated with interfaces and those associated with bulk materials. For instance, it is often observed that liquids may be cooled (supercooled [1]) considerably below their melting temperature prior to solidification. In such cases, solidification is limited by the initial formation of a crystalline nuclei, referred to as the nucleation process. Nucleation cannot occur until the energy associated with the bulk formation of solid is sufficient to overcome the energy required to create a surface between the crystallite and the remaining liquid. This initial nucleation is most often heterogeneous, occurring at either the walls of a container or from dispersed second phase particles in the liquid. If care is taken to avoid such heterogeneous nucleation sites, bulk metals such as Ni can be supercooled to roughly half the melting temperature before homogeneous nucleation and solidification occurs. Organic materials and alloys, indeed, may be cooled as liquids to room temperature forming glassy phases. The fundamental limit to such cooling experiments is the temperature at which the liquid is spontaneously unstable to formation of nuclei, referred to as the homogeneous nucleation temperature. Study of this temperature allows determination of the energy associated with the liquid-solid interface.

Study of such nucleation processes has typically been done in droplet experiments, where volumes are $\sim 10^{-3}$ mm^3 and homogeneous nucleation occurs on time scales of seconds [2-4]. These conditions correspond to nucleation rates of 10^6 - 10^{12} events/m^3/s. Using 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; for example, increasing the supercooling by 5 K increases the nucleation rate by approximately an order of magnitude.

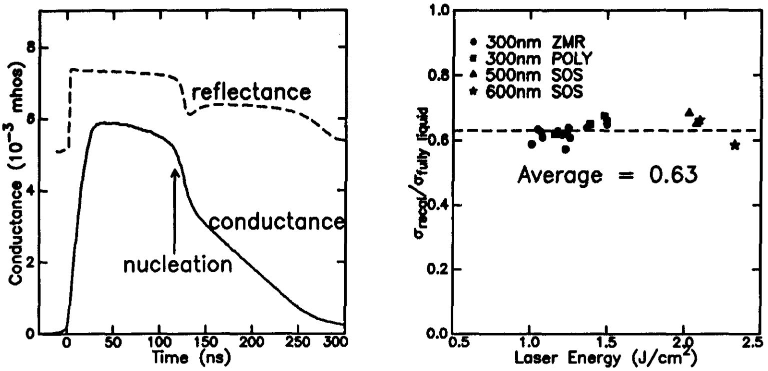
In this paper, we report measurements of the supercooling required for bulk nucleation in Si and Ge at extremely high nucleation rates. These conditions are established by the rapid quench following pulsed laser induced melting. The supercooling required for nucleation under these conditions greatly exceeds that achieved in droplet experiments on the same materials [3,5] due to the radically different rates. Implications of these experiments to several current models describing transitions among amorphous Si (a-Si), l-Si and c-Si [6-8] are also discussed.

EXPERIMENTAL PROCEDURES

Thin films (< 1um) of Si and Ge on suitable non-reactive substrates were completely melted using a 30 ns Q-switched pulsed ruby laser (λ = 694 nm). Once the film was fully molten, conduction of heat into substrate results in a thermal quench of ~5x10^9 K/s and eventually to nucleation in the liquid. During melt and nucleation, the thickness of the liquid layer and the phases in the surface region were monitored using transient conductance [9,10] and surface optical reflectance [11] (λ = 514 nm) techniques. Various Si layer thicknesses and substrate materials were studied, including films of 500nm and 600nm Si on sapphire (SOS), 300nm polycrystalline Si (p-Si) on 250nm thermal SiO_2 on a Si substrate, and 300nm zone-melt-recrystallized (ZMR) Si [12] on 250nm thermal SiO_2 on a Si substrate. All Si layer thicknesses and substrate materials examined in these experiments yielded essentially identical results. Ge experiments were performed using 350nm polycrystalline films on 350nm thermal SiO_2 on a silicon substrate. Microstructures of the resultant Si films were examined by planar and cross sectional transmission electron microscopy (TEM).

SILICON RESULTS:

Typical transient conductance and optical reflectance data are shown in Fig. 1a for irradiation of a Si 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 mmhos in the conductance (equivalent to 304 nm of molten Si). The film remains molten for ~100 ns as the liquid cools by thermal conduction into the substrate. Following this delay, there is a simultaneous and rapid decrease in the both the conductance and reflectance signals. These decreases are interpreted as marking the onset of nucleation; the timing and magnitude of this event can be related to the supercooling at nucleation as discussed below. Following nucleation and rapid growth (recalescence),



(a) (b)

Fig. 1: (a) 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 and recalescence occurring at the time indicated. (b) The ratio of the conductance after recalescence to the fully liquid value as a function of laser energy and sample type for Si.

growth of the solid continues under steady state conditions as heat is conducted into the substrate. The surface reflectance, a spatial average of the 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. 1a is a complex average of the conductivities and volume fractions of the phases present in the surface layer. Although non-linear, the conductance decreases monotonically with the volume fraction of solid present. The volume of material consumed 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 over an incident energy density range from 1.0 to 2.5 J/cm², with a value of 0.64 ± 0.03. These data are shown in Fig. 1b. This indicates that a constant volume fraction of Si is consumed during recalescence. Since the heat released during recalescence raises the temperature of the liquid layer from the nucleation temperature (T_n) to the steady state growth temperature (near T_m), nucleation occurs at approximately the same temperature in all cases.

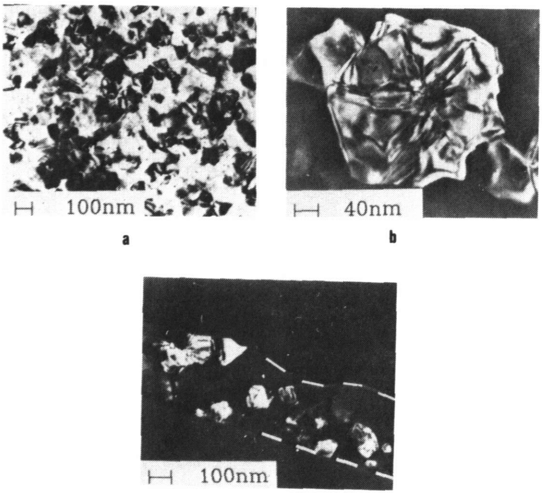
The solid volume fraction present after recalescence, χ, may be obtained by assuming that the conductance is due to two phase conduction of spherical solid particles dispersed in a continuous liquid matrix [13,14]. A conductance ratio of 0.64 in Si indicates solidification of a volume fraction of ~29%. The nucleation temperature may be estimated by equating the enthalpy released during recalescence to the heat required to raise the liquid from T_n to the steady state temperature, T_{ss}, as below:

$$\int_{T_n}^{T_{ss}} C_p(T)\, dT = \chi\, \Delta H_m \tag{1}$$

where C_p is the specific heat of the liquid. Using bulk parameters of Si [15,16], the supercooling prior to nucleation is evaluated as 505 ± 45 K. Similar estimates may also be obtained by numerically modelling the heat transfer prior to nucleation. Numerical simulations for SOS films indicate that nucleation occurred at 550 K supercooling, approximately 45 K greater than estimated above. Simulations of Si films on SiO_2 layers were considerably more difficult and considered unreliable because of scatter in experimentally measured thermal parameters for SiO_2, and the possibility of a phase transition very near the melting temperature of Si. For these reasons, heat transfer through the oxide at high temperatures could not be accurately modeled. Consequently, the heat balance results discussed above are considered to be more accurate and, at worst, provide a lower estimate for the supercooling required for nucleation.

A planar TEM view, Fig. 2a, shows the microstructure of a Si film after bulk nucleation and solidification. The microstructure is uniform and poly-crystalline with an average grain size of ~200 nm. A example of a site where nucleation appears to have occurred is shown in Fig. 2b. Electron diffraction confirms that the grain 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 (Fig. 2c) 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 indicates that a partial phase transformation occurred at the surface during recalescence, with



a b

c

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. (c) Cross-sectional TEM view of a similar sample.

~40-50% of surface solidifying. Concurrently, conductance indicates that ~30% of the bulk is transformed to solid. 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. It is concluded that a bulk nucleation phenomena was observed.

TEM analysis also provides evidence that the nucleation was homogeneous. First, there are no observable second phase particles associated with the suspected nucleation events (Fig. 2b). Also, it seems unlikely that nucleation on a second phase particle would result in the symmetric single crystal structure typical of these events. Furthermore, nucleation occurred at approximately the same temperature for all film thicknesses and substrate materials. It is therefore concluded that the nucleation occurred homogeneously.

The nucleation rate observed in this experiment may be estimated by determining the grain density and the approximate time scale for nucleation. First, each grain in the final microstructure is assumed to result from separate nucleation events, yielding a density of approximately 2×10^{20} events/m^3. Since the recalescence is completed in 10-15 ns, it is further assumed that all nucleation events occurred within a few nanoseconds. Thus, the nucleation rate is estimated to be 10^{29} events/m^3/s. In classical nucleation theory [17], assuming spherical nuclei, the rate Γ is given by:

$$\Gamma \simeq 10^{39}\ (/m^3 s) * \{\exp(-\Delta G^*/kT)\} \qquad (2)$$

where

$$\Delta G^* = 16\,\pi\,\sigma^3 \,/\, (3\,\Delta G_v^2) \qquad (3)$$

and σ is the interface energy, ΔG_v is the free energy difference between the solid and liquid on a per volume basis, T is absolute temperature, and k is Boltzman's constant. Uncertainty in the pre-exponential term may be as large as ± 4 orders of magnitude [17]. ΔG_v is given by the following:

$$\Delta G_v \simeq \Delta H_m * \Delta T / T_m \tag{4}$$

where ΔT is the supercooling. Since ΔH_m and T_m are well known, a nucleation rate of 10^{29} events/m^3/s at a supercooling of 505 ± 45 K implies a interface energy of 0.34 ± 0.02 J/m^2 (0.16 eV/atom).

GERMANIUM RESULTS

Ge films behaved similarly to Si films, however, the the drop in conductance at recalescence preceded the drop in reflectivity by ~20 ns, indicating that the nucleation may have been preferential to the sub-surface. Conductance and reflectance traces for a 330nm Ge film on 350nm SiO_2 on Si sample, irradiated with 0.76 J/cm^2 are shown in Fig. 3a. Fig. 3b shows the ratio of the conductance after recalescence to the fully liquid value as a function of laser energy. Again, this ratio is constant (0.61 ± 0.02) indicating that nucleation occurred at approximately the same temperature. Using the same analysis as for Si, a supercooling of 430 ± 30 K was achieved prior to bulk nucleation. This implies a liquid to solid interfacial energy of 0.24 ± 0.01 J/m^2 (0.12 eV/atom) in Ge.

UNCERTAINTIES:

Nucleation Temperature:

The previous analysis assumes that the subcritical nuclei are in some quasi-steady state equilibrium. Since the equilibrium distribution of these embryos is temperature dependent, there is a transient period following a change in temperature during which the nucleation rate is time dependent. In these experiments the temperature of the liquid changes rapidly with time suggesting that such transients may be important.

Christian [17] shows that the duration of this transient period, τ, is given to within an order of magnitude by:

$$\tau = n_c^2 / (q\, o_c) \tag{5}$$

where n_c is the number of atoms in a critical nuclei, o_c is the number of atoms on the surface of a critical nuclei and q is the rate of transfer of atoms into the embryo per atom on the surface (assumed to be independent of size).

Assuming spherical nuclei, one can calculate n_c and estimate o_c. The rate of transfer of atoms into the embryo is given by:

$$q = (kT/h) * \exp(-g_a/kT) \tag{6}$$

where g_a is the activation energy associated with transferring an atom from the liquid, through the interface and into the solid. This term was estimated by Turnbull to be approximately equal to the activation energy for viscous flow, yielding $\exp(-g_a/kT) \simeq 0.01$ for liquid-solid transformations in metals. The transient duration time is thus estimated to be on the order of 0.1 ns.

As this calculation is only accurate to an order of magnitude, the maximum delay in nucleation caused by non-equilibrium embryo distributions is estimated to be several nanoseconds. The cooling rate at nucleation is ~3-4 K/ns, hence transient effects could cause an overestimate of the supercooling required for nucleation by, at most, ten degrees.

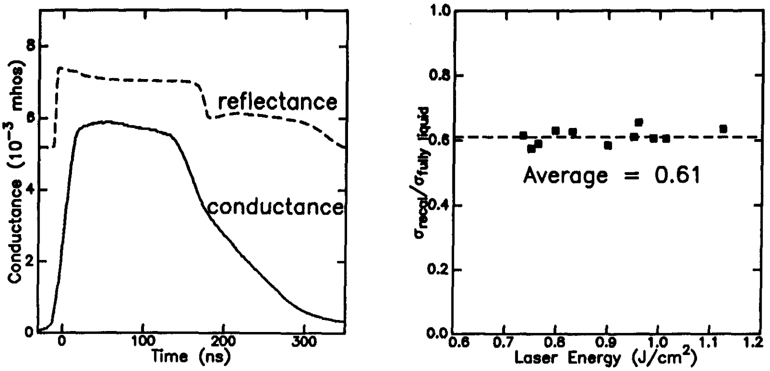
Nucleation Rate:

As previously stated, the nucleation rate was estimated assuming that each grain in the final microstructure was the result of a separate, homogeneous nucleation event. It has been suggested [18] that a single nucleation event may give rise to many seemingly disoriented grains from fracture, and subsequent displacement, of delicate dendritic arms. These dendrites are expected to form from crystal growth at a highly undercooled interface. It is also possible that the nucleation rate is overestimated due to dynamic effects. True homogeneous nucleation events may induce other nonequilibrium events via a shock-wave associated with the density change at nucleation. Experiments are planned to examine these effects.

COMPARISON WITH OTHER EXPERIMENTS:

Turnbull [3] studied homogeneous nucleation in a wide variety of materials using a small drop technique. It was observed that, on a per atom basis, the ratio of the surface energy to the enthalpy of melting was nearly constant for a particular class of materials. This ratio was found to be approximately 0.45 for metals and 0.33 for the semi-metallic elements Bi, Sb, and Ge.

Devaud et al. [5], using small Ge drops in an anhydrous B_2O_3 flux, were able to obtain maximum supercoolings of approximately 300 K. A maximum of 275 K supercooling was obtained with un-fluxed Si droplets. These correspond to $\sigma/\Delta H_m$ of 0.37 and 0.27 respectively. The same authors were later able to



(a) (b)

Fig. 3: (a) Transient conductance and optical reflectance traces for irradiation of a 330 nm Ge film at 0.76 J/cm². (b) The ratio of the conductance after recalescence to the fully liquid value as a function of laser energy for Ge.

obtain supercoolings of 420 K in Ge ($\sigma/\Delta H_m = 0.44$) [18]. To our knowledge, no other measurements of the interface energy for Si or Ge under conditions of homogeneous nucleation have been performed.

Our data indicates a ratio, $\sigma/\Delta H_m$, of 0.30 for Si and 0.32 for Ge. If the maximum (instead of the average) supercooling achieved in these experiments is used to calculate the surface energies, the ratios increase to 0.33 and 0.34, respectively. The relatively small differences between these results and those from droplet experiments is extremely encouraging; however, more accurate determination of the nucleation rate in the laser experiments is required before detailed comparisons can be made.

IMPLICATIONS:

The 505 K supercooling in Si (which becomes ~505 K undercooling following nucleation) observed in these experiments is substantially greater than any undercooling previously observed at l-Si interfaces. Indeed, the interfacial undercooling exceeds the ~250 K estimated to exist during a-Si quench directly from l-Si [19-21]. It was consequently expected that at these extreme undercoolings, a-Si should form during solidification. However, TEM investigations reveal no evidence of either a-Si or of very fine grained (10nm) p-Si, a usual signature of explosive crystallization of a-Si.

These observations imply that nucleation of c-Si, and not a-Si, was observed. The minimum value of the a-Si/l-Si interfacial energy (σ_{a-l}) consistent with the observation of crystalline nucleation in this experiment is 0.20 J/m^2. If σ_{c-l} is scaled by the enthalpies of melting for a-Si and c-Si, a more realistic estimate of 0.11 eV/atom or 0.24 J/m^2 is obtained for σ_{a-l}.

These experiments also pose several subtle questions for the conventional interpretation of laser amorphization of Si. As noted, a l-Si to a-Si transformation is expected because of the severe undercooling present; 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, indicating that the surface region initially contained a larger volume fraction of solid than is observed in steady state. Consequently, it appears that some of the solid formed during recalescence actually remelts. These questions will be discussed in a future publication.

Finally, since the l-Si temperature during explosive crystallization is never below the melting temperature of a-Si, the observation of 505 K supercooling prior to nucleation firmly rules out homogeneous or free surface nucleation during explosive crystallization [7,8]. The measured surface energies are, however, consistent with the mechanism suggested by Tsao et al. [6].

CONCLUSIONS

In conclusion, it has been shown that bulk nucleation of elemental materials can be readily studied in laser melting experiments. Interfacial energies of 0.34 J/m^2 and 0.24 J/m^2 have been estimated for the crystalline-liquid interfaces in Si and Ge, respectively. These interfacial energies (on a per atom basis) scale with the enthalpy of melting, consistent with measurements in metallic systems. These results show reasonable agreement with values obtained from droplet experiments.

Observation of c-Si nucleation at ~500 K supercooling allows the energy of the l-Si/a-Si interface to be bounded as >0.20 J/m^2. The very large supercooling prior to nucleation firmly rules out free surface or homogeneous nucleation as the mechanism which initiates explosive crystallization.

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.

ACKNOWLEDGEMENTS

We gratefully acknowledge C. K. Chen at MIT Lincoln Laboratories for providing the ZMR materials used in these experiments and the laboratory assistance of R. Blake at Sandia. Work at Cornell is supported by the NSF-PYIA (J. Hurt) and samples were fabricated at the National Nanofabrication Facility (NSF) at Cornell. Work at Sandia supported by DE-AC04-76DP00789.

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