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TIME-RESOLVED STUDIES OF ULTRARAPID SOLIDIFICATION OF HIGHLY
UNDERCOOLED MOLTEN SILICON FORMED BY PULSED LASER IRRADIATION

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TIME-RESOLVED STUDIES OF ULTRARAPID SOLIDIFICATION OF HIGHLY UNDERCOOLED MOLTEN SILICON FORMED BY PULSED LASER IRRADIATION*

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INTRODUCTION

In this paper we report new results of nanosecond-resolution time-resolved optical reflectivity measurements, during pulsed excimer (KrF, 248 nm) laser irradiation of Si-implanted amorphous (a) silicon layers, which, together with model calculations and post-irradiation TEM measurements, have allowed us to study both the transformation of a-Si to a highly undercooled liquid (ℓ) phase and the subsequent ultrarapid solidification process.¹⁻³ The melting temperature (T_a) of a-Si is apparently some 150–300 K below the melting temperature ($T_c = 1683$ K) of c-Si;⁴⁻⁹ thus, molten ℓ -Si that is undercooled by hundreds of Kelvins can be prepared by pulsed laser melting of a-Si layers, using laser pulses of low E_ℓ . By melting only partially through an a-Si layer, the undercooled ℓ -Si remains isolated from the c-Si beneath because of the low thermal conductivity ($K_a \approx 0.02$ W/cm-K)^{1,3} of the remaining a-Si. This makes it possible to study the subsequent process of resolidification from a highly undercooled melt under relatively well-controlled experimental conditions. Preliminary studies of this kind were carried out using pulsed Nd (532 nm) laser irradiation.¹⁻³ Typical TEM micrographs^{1,10} following low E_ℓ laser irradiation of a 500-nm-thick a-Si layer on a c-Si substrate showed a region of fine-grained (FG) polycrystalline Si (p-Si) at the surface, followed at increasing depth by the remaining a-Si, the a-c interface, and the c-Si substrate. At higher E_ℓ a layer of large-grained (LG) p-Si was found at the surface, followed in order by the FG p-Si, a-Si, and c-Si. Further increases in E_ℓ resulted in further growth of the LG region, reduction in the thickness of the FG region, and displacement of the FG region to greater depth, until melting entirely through the a-Si layer was accomplished at high E_ℓ . Individual grains in the FG region are quite small (~ 10 nm) and are randomly oriented and equiaxed, indicating that there is no preferred direction of crystal growth during the formation of this region; this behavior strongly suggests that bulk nucleation occurs in the undercooled

λ -Si under these conditions. Calculations of laser melting of a-Si layers can be "calibrated" by comparison with time-resolved reflectivity measurements and used to determine temperature profiles in the undercooled λ -Si.² Comparing these profiles with the solidification structures observed by TEM, we were able to simulate that bulk nucleation in the liquid occurs at a temperature approximately 50°C higher than T_a .

RESULTS AND DISCUSSION

A number of improvements have been made in both experimental and calculational techniques for our current studies. a-Si layers of approximately 100, 190, and 440 nm were used. An excimer laser (KrF, 248 nm, ~35-nsec FWHM pulse duration) provides a much more homogeneous and reproducible laser beam while minimizing differences in the optical properties of the a-, λ -, and c-phases of Si (a significant simplification for model calculations). In-situ E_λ monitoring of every laser pulse reduced the uncertainty in individual E_λ measurements to $\pm 2\%$. A Tektronix 7912AD transient digitizer (time constant ~1 nsec) interfaced to a laboratory computer system was used to record and store both the time-resolved reflectivity (R) signals and sample laser pulses with 512-point resolution on the time axis.

As a result of these improvements, we can now accurately monitor the heating of a-Si while still in the solid phase, during absorption of the initial part of a laser pulse (Fig. 1). Together with measurements at higher E_λ of the time of onset of melting, t_m , during the laser pulse (Fig. 1), measurements in the solid phase provide data which can be used to help determine the thermal properties of a-Si, especially its thermal conductivity, K_a .^{1,2} For example, model calculations of t_m (E_λ) showed that earlier data similar to that in Fig. 1 implied a temperature-averaged $K_a \approx 0.02$ W/cm-K, compared to K_c (300 K) ≈ 1 W/cm-K for c-Si.

Earlier model calculations have been greatly improved by the development of a new computer program based on an enthalpy formulation of the heat flow and phase change problems. The formulation can be applied to situations for which it is necessary to treat the time evolution of several competing phases, with phase changes occurring at temperatures not equal to the normal (equilibrium) phase change temperatures (e.g., as a result of undercooling or overheating). Both our original^{2,3} and more recent model calculations demonstrate that the release of latent heat by bulk nucleation occurring during the melt-in process is essential to obtaining agreement with experimentally observed depths of melting and that this release of latent heat can result in the existence of buried

Fig. 1. Use of time-resolved reflectivity to monitor solid phase heating and the time of onset of melting (arrows) of a 440-nm thick a-Si layer at $E_L = 0.117$ (bottom), 0.124, 0.14, and 0.176 (top) J/cm^2 . (The reflectivity traces have been displaced vertically for clarity.)

Fig. 2. Surface melt duration vs KrF excimer laser energy density for a-Si layers.

molten layers of λ -Si in the interior of the sample even after the surface has solidified.

The importance of the thermal isolation provided by the unmelted a-Si remaining beneath any molten layer of λ -Si is illustrated in Fig. 2 where the surface melt duration, τ_s (duration of the high reflectivity phase, HRP), is plotted vs E_L for three different a-Si layer thicknesses. τ_s varies by a factor of 3 or more, between the thinnest and thickest layers, at the higher E_L values. Furthermore, τ_s does not increase monotonically with increasing E_L : Model calculations show that the plateau in τ_s for the 100-nm a-Si layer, and the actual decrease (between 0.5 and 0.65 J/cm^2) in τ_s for the 190-nm a-Si layer, are both primarily due to the increased rate of heat loss from the λ -Si that occurs when the melt front approaches the a-c interface.

The new optical measurements also appear to provide direct in-situ time-resolved evidence for the beginning of bulk nucleation and crystal-lite growth very near the highly undercooled molten surface, while penetration of the melt front into the a-Si layer is still in progress. Fig. 3 shows a series of R signals observed from a $\sim$ 440-nm-thick a-Si layer, as a function of E_L . R was monitored using a low power, cw HeNe probe laser, for which the optical skin depth in ordinary liquid Si would be about 9.6 nm at the probe's 633-nm wavelength. At the lowest E_L values, the R signal (Fig. 3) never achieves the flat-topped shape that is characteristic of the HRP associated with pulsed laser melting of c-Si (see inset), but instead decays to lower values almost immediately.

This decay we attribute to the occurrence of bulk nucleation, within a few nanoseconds after melting has occurred, in the highly undercooled melt that exists near the surface at low E_L . During this time, the optical properties of the region being observed are those of a "slush," a mixture of undercooled liquid and growing crystallites. With increasing E_L , the fall in R occurs later in the HRP (Fig. 3) and is of smaller magnitude; the model calculations associate this with a prolonged duration for the slushy region near the surface, brought about by a competition between bulk nucleation and remelting due to the release of latent heat. Finally, at about 0.44 J/cm^2 , a flat-topped HRP is observed throughout the duration of surface melting, indicating that the temperature of the melt remains above T_n throughout the shallow region sampled by the 633-nm probe beam, until a recrystallizing front returns to the surface by epitaxial regrowth from the polycrystalline silicon formed below.

Fig. 3. Decaying time-resolved reflectivity signals associated with bulk nucleation (see text).

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