Melting Temperature and Explosive Crystallization of Amorphous Silicon during Pulsed Laser Irradiation

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Measurements during pulsed laser irradiation indicate that amorphous Si melts at a temperature 200 ± 50 K below the crystalline value. Below energy densities required to melt the amorphous layer fully, the data are interpreted in terms of an explosive crystallization. The initial liquid layer solidifies to form coarse-grained polycrystalline Si. A thin, self-propagating liquid layer travels through the remaining amorphous Si at a velocity of 10–20 m/s, producing fine-grained polycrystalline Si.

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The pulsed-laser melting of amorphous semiconductors has raised several fundamental questions regarding the mechanism and thermodynamics involved in the process.[1,2] For example, measurements of the free energy,[3,4] indicating that the amorphous phase of Si (α-Si) should melt at a temperature several hundred degrees below the crystalline value, have prompted much work.[5,6] While the nature of single-crystal melting under laser irradiation is well understood and modeled in the nanosecond time regime,[7,8] many quantitative difficulties remain for α-Si annealing.[9,10] At a sufficiently high laser energy density (epitaxial threshold), the α-Si layer is known to melt fully and crystallize epitaxially from the underlying single-crystal Si. Below this epitaxial threshold, a portion of the α-Si is transformed into polycrystalline Si (poly-Si). Contrary to expectations, the poly-Si thickness does not increase linearly with incident energy density. Instead, this thickness approaches the amorphous-crystal interface at low energy densities, and remains relatively unchanged across a large energy-density range until the epitaxial threshold is reached.[10,11] Current interpretation has been, as in the case of single-crystal melts, that the melt front propagates to the full extent of the poly-Si layer formed.

In this Letter, we present time-resolved observations, inferred from surface-reflectance[12] and transient-conductance[13] measurements, of the amorphous-liquid interface motion during pulsed laser irradiation. The data indicate a first-order phase transition from α-Si to liquid at a temperature 200 ± 50 K below the crystalline melting point. Below the epitaxial threshold, explosive crystallization[14] of the underlying α-Si is observed.

Samples were prepared from 0.5-μm silicon on sapphire, with patterns for transient-conductance measurements (active area 1 mm^2) formed photolithographically. Amorphous Si thicknesses of 215, 330, and 400 nm were produced by ion implantation of ^{28}Si to a dose of 5×10^{15}. The samples were irradiated through a quartz homogenizer with a 28-ns full-width at half maximum *Q*-switched ruby laser (694 nm). Surface reflectance was monitored with an argon laser (488 nm) incident at glancing angle. By monitoring electrical conduction through a metallic liquid layer, the transient conductance provides a direct measurement of the molten thickness.[13] After irradiation, several samples were corss sectioned for analysis by transmission electron microscopy (TEM).

In Fig. 1, the melt depths as a function of time, determined from transient-conductance measure-

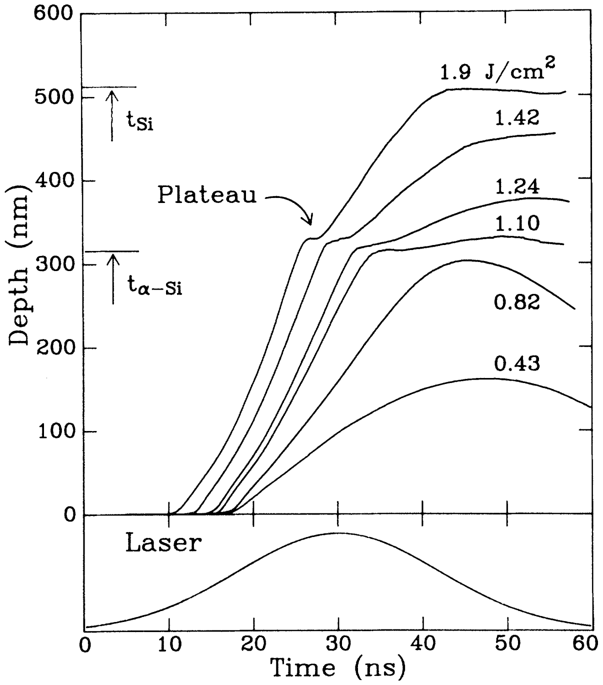

FIG. 1. Melt-depth transients for 330-nm amorphous-Si samples at various incident energies. The lower trace indicates the timing of the incident laser pulse. The 1.90-J/cm^2 pulse was adequate to melt the Si layer fully to the sapphire interface (510 nm).

ments, are shown for a series of laser energy densities incident on samples with 330-nm α-Si layers. In each case, melting occurred prior to the peak of the laser pulse and, as indicated by surface-reflectance measurements, was initiated at the surface. As the melt reached the amorphous-crystal interface, a plateau was observed with a duration between 2 and 6 ns. For the 215- and 400-nm implants, this plateau also occurred at a thickness corresponding to the original α-Si layer. Rutherford backscattering and channeling analysis confirmed that full epitaxial regrowth occurred when the observed melt depth extended beyond the crystal-amorphous interface (~ 1.10 J/cm^2 for the 330-nm α-Si).

The sharp plateaus seen in these traces are consistent with a first-order phase transition of α-Si to the metallic liquid at a reduced temperature ($T^{\alpha 1}$) relative to the crystalline melting point (T^{c1}). Melting occurs when the surface temperature exceeds $T^{\alpha 1}$ and propagates near this temperature until reaching the crystal-amorphous interface. At the interface, further melting is delayed until the laser delivers sufficient energy to raise the liquid temperature from $T^{\alpha 1}$ to T^{c1}. The absolute temperature difference (ΔT) can consequently be determined from the plateau width (Δt) and the incident laser intensity [$I(t)$]:

$$C_p d(\Delta T) + K(\partial T/\partial z)(\Delta t) = \int_{\Delta t}(1-R_1)I(t)dt,$$

where C_p is the specific heat of the liquid, d is the thickness of the molten layer, K is the thermal conductivity and $\partial T/\partial z$ the temperature gradient at the interface, and R_1 is the appropriate liquid reflectivity. The first term on the left is the specific heat associated with raising the liquid temperature from $T^{\alpha 1}$ to T^{c1}, while the second term represents the energy removed from the interface by thermal conduction into the underlying substrate. Since the thermal properties, especially the thermal conductivity, of α-Si are poorly known, the gradient in the second term is difficult to determine. However, an upper bound can be placed on the melting-temperature reduction by neglecting this thermal conduction, and a lower bound can be estimated by assuming a thermal gradient corresponding to 6-m/s regrowth velocity (an upper limit for this time regime[13]). By use of liquid reflectivity value of 72% and an average plateau for six 330-nm α-Si samples at 1.85 J/cm^2 of 2.2 ns, the temperature difference is estimated to be 200 ± 50 K. This temperature difference, with small corrections due to superheating, is equal to the equilibrium melting-point depression, $T^{c1} - T^{\alpha 1}$.

This value agrees well with the solid-phase calculations of Donovan *et al.*[4] Recently, there has been considerable interest in the possibility that several relaxed states of amorphous Si exist.[15] Amorphous samples annealed in a vacuum furnace at 570 °C for 15 min showed similar duration plateaus at a reduced depth, corresponding to the partially regrown amorphous-crystal interface. These measurements imply that little change occurs in the thermodynamics of the amorphous state after thermal annealing, despite considerable changes in the optical properties.[15]

For very low-energy-density irradiation of amorphous layers, the melting and solidification behavior are markedly different. The behavior at 0.20 J/cm^2, near the threshold for surface melting (~ 0.15 J/cm^2), is shown in Fig. 2. This double peak in the liquid thickness occurs for all energies 0.30 J/cm^2. As the energy is increased, the second peak becomes a shoulder on the first peak, and is eventually fully obscured. Both the reflectance and transient conductance indicate that surface melting occurs at 36 ns. However, the surface reflectance returns to the solid value at 54 ns, while the tran-

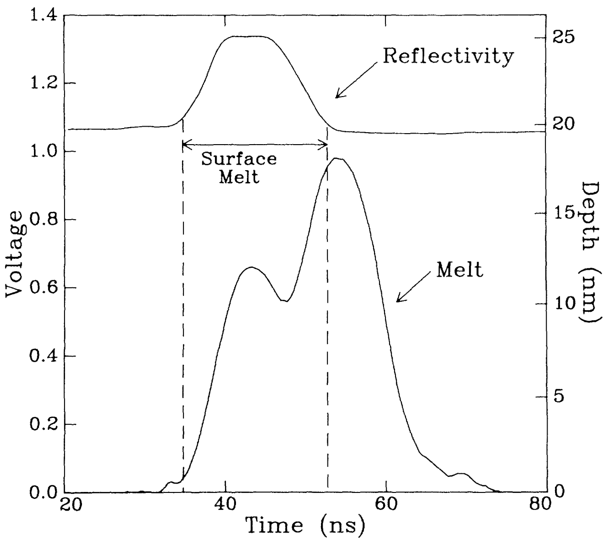

FIG. 2. The transient conductance and the surface reflectance for a 0.20-J/cm^2 pulse incident on the 320-nm amorphous film. The scale on the left axis is the observed voltage for conductance transient, with the corresponding molten thickness indicated on the right. This transient indicates a surface melt followed by an interior molten layer.

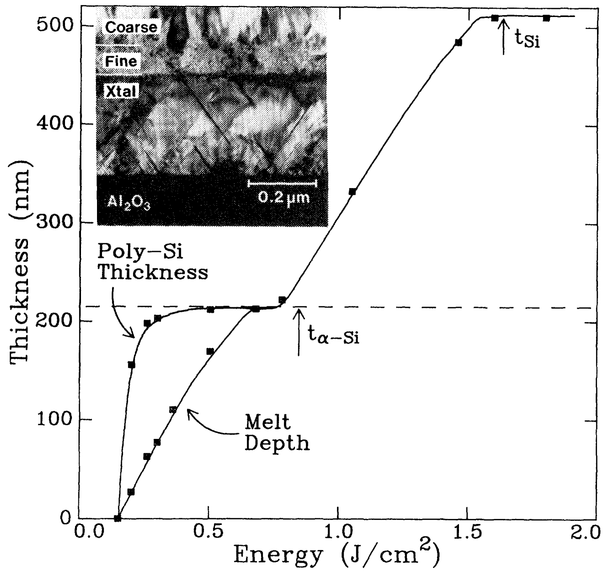

FIG. 3. The thickness of the primary melt and the total poly-Si formation as functions of the energy density incident on a 215-nm amorphous film. Inset: TEM cross section illustrating the formation of coarse- and fine-grained poly-Si at 0.5 J/cm^2. Note that the fine-grained poly-Si extends to the original amorphous-crystalline interface.

sient conductance indicates the presence of significant conductance (liquid) for an additional 10 ns. Since the reflectivity is only sensitive to the first 20 nm near the surface, the liquid indicated by the second peak in the conductance must exist within the interior of the sample. The magnitude of the conductance indicates a primary (during which the surface is molten) melt depth of 12 nm, followed by a molten layer of maximum 18-nm thickness contained within the sample. Cross-section TEM of similar samples indicates the formation of approximately 160 nm of fine-grained (5–10 nm) poly-Si at this energy density.

Previous TEM investigations have shown the formation of fine- and coarse-grained poly-Si layers during the annealing of α-Si samples.[11,16] At low energy densities (< 0.30 J/cm^2) only fine-grained poly-Si is observed. Higher energy densities result in a coarse-grained poly-Si surface layer and an underlying fine-grained layer. Figure 3 shows the primary melt depth and the total poly-Si thickness (observed by TEM) as a function of the energy density incident on 215-nm amorphous layers. Poly-Si formation is significantly greater than the maximum penetration of the laser-induced melt at low energy densities. As the energy density approaches the epitaxial threshold (0.8 J/cm^2), the poly-Si thickness and the primary melt-depth values converge. TEM measurements indicate that coarse-grained poly-Si is formed for a depth slightly less (~ 10 nm) than the primary melt depth, with the remaining thickness consisting of fine-grained poly-Si, as shown in the inset of Fig. 3.

The indication of an interior melt, and the structure of the poly-Si layers, suggests an explosive crystallization processes occurring within the sample. The recrystallization of α-Si is hypothesized to occur as described below. At low energy densities, the laser energy melts only a thin primary liquid layer near the surface. As this liquid begins to resolidify as poly-Si, the latent heat released from the liquid raises the temperature of the resolidified poly-Si above $T^{\alpha l}$, and the underlying α-Si material begins to melt. This new liquid, however, is severely undercooled with respect to the poly-Si layer and resolidifies as fine-grained poly-si. Thus, a thin liquid layer is presumed to propagate, as a result of the released latent energy, through the α-Si material. This thin liquid layer mediating the explosive crystallization, suggested previously by experiments in Ge,[14] is observed in these experiments as the secondary liquid peak in Fig. 2. Eventually, the self-sustaining explosive crystallization is quenched by the energy required to raise the temperature of the α-Si solid in front of the liquid to $T^{\alpha l}$. Because of the thermal conductivity difference between α-Si and crystalline Si, explosive crystallization can proceed to the amorphous-crystal interface at very low energy densities (Fig. 3) before being affected by thermal conduction into the underlying substrate. The velocity of the explosive melt front can be estimated from the time duration of the second peak and the thickness of the fine-grained poly-Si. For thin melts, this velocity is between 10 and 20 m/s. The delay of the peak melt depth with energy at the amorphous-crystal interface (Fig. 3) is also consistent with a reduced melting temperature for α-Si.

Transient conductance and surface reflectance have allowed the first confirmation of the reduction of the α-Si melting temperature relative to the crystalline value. These measurements imply an α-Si melting temperature of 1480 ± 50 K. Irradiation below the epitaxial annealing threshold produces polycrystalline material both from a primary melt and from explosive crystallization of the underlying α-Si initiated by this primary melt. Poly-Si formation at low energy densities is dominated by the explosive crystallization. The explosive crystallization is observed to be mediated by a thin liquid layer propagating at a velocity of 10–20 m/s, which corresponds to crystal growth at an undercooling of the depressed melting point.

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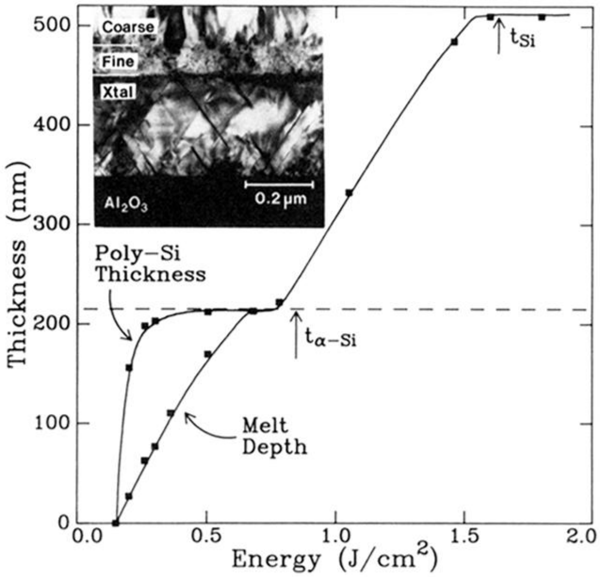

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