Quench rate enhancement in pulsed laser melting of Si by processing under water

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The thermal quench rate during pulsed laser heating of Si can be enhanced by immersing the sample in a liquid (e.g., water) during irradiation. The liquid in contact with the irradiated surface acts as an additional heat sink increasing the thermal quench rate. The heat transfer processes and phase transformations were studied in real time using transient optical reflectance and electrical conductance techniques. Measurements of the melting and solidification dynamics of the Si reveal that the quench rate may be enhanced by 30% for deep melts. The measurements also indicate that a steam or superheated water phase is formed near the Si surface during the laser pulse. The observed phenomena are analyzed in terms of standard heat flow.

Pulsed laser irradiation provides a convenient means to induce rapid and often nonequilibrium phase transformations in solids.[1-3] During irradiation with nanosecond laser pulses, very rapid heating and melting of a shallow surface layer can be achieved. As heat is conducted into the substrate, the molten layer resolidifies, often epitaxially. The velocity of this liquid-solid interface during solidification is of fundamental interest both theoretically and applied. From a theoretical viewpoint, the velocity is central to the study of nonequilibrium liquid-solid interface dynamics. From applied viewpoints, the solidification velocity, or equivalently the quench rate, is the primary parameter in determining segregation and trapping of impurities and the structural phase of the material following solidification. It is therefore of considerable interest to develop new methods for controlling the solidification velocity during pulsed laser melting.

In conventional nanosecond laser melting experiments, the solidification velocity v is typically several m/s, and is given to first approximation by $(\kappa/\Delta H)(\partial T/\partial z)$, where $(\partial T/\partial z)$ is the temperature gradient in the solid just behind the moving interface, ΔH is the enthalpy of melting, and κ is the thermal conductivity of the solid. For a given experimental configuration, the thermal gradient is limited by "intrinsic" parameters such as the laser absorption depth, pulse length, and thermal properties of the substrate and hence limits the maximum quench rate or velocity. It is desirable to have an additional, external parameter which may enhance this quench rate. Such enhancements may allow the formation of doped or compound layers with nonequilibrium compositions and structures. For example, in shallow junction processing using ion implantation and laser annealing, impurity redistribution by diffusion is minimized by rapid solidification velocities.[4] Also, if the quench rate can be enhanced above the critical value for interface breakdown[5] (15 m/s for regrowth of crystalline Si $<100>$), it becomes possible to produce thick amorphous layers directly by laser irradiation.

In this letter, we present a novel method of laser processing in which the solidification velocity can be increased by up to 30%. In this method, samples are irradiated while immersed in a liquid medium such as water. The liquid in contact with the irradiated surface acts as an additional heat sink and influences the heat transfer processes. Earlier experiments, which measured the impurity redistribution after irradiation, suggested that the quench rate could indeed be enhanced using this method.[6] In this work, we present direct measurements of the melting and solidification dynamics which quantify the influence of a liquid water layer on the quench rate in Si during irradiation. The melting and solidification dynamics in the Si were monitored in real time using transient conductance techniques[7] while transient optical reflectance techniques[8] were used to study the heat diffusion and phase transformations in the water layer.

Silicon on sapphire (SOS) samples (500 nm Si ⟨100⟩ oriented) were patterned photolithographically to yield samples for transient conductance measurements. The transient conductance technique, utilizing the 30-fold increase in conductivity of Si upon transformation to the liquid phase,[9] monitors the molten Si thickness in real time. In addition, the optical properties of the Si-water interface were probed by transient optical reflectance using a continuous wave semiconductor laser operating at $\lambda \simeq 780$ nm. Reflectance experiments were also performed on bulk single-crystal Si ⟨100⟩ samples. Both conductance and reflectance data were acquired with >500 MHz bandwidth. Samples were irradiated with a single pulse from a Q-switched frequency-doubled Nd: YAG laser operating at $\lambda = 532$ nm and a pulse width of 4 full width at half-maximum.

Samples were positioned in a transparent reservoir which was filled with de-ionized water at room temperature. Laser energy was coupled into the sample through a quartz guide diffusor.[10] Sample to light-guide distance was typically 1–2 mm with an estimated nonuniformity of $\pm$ 10% over the 6-mm-diam spot. Reference samples were irradiated in air in the same configuration just prior to the introduction of water. The Si-water interface reflectivity was probed at a glancing angle of 11° through the side walls of the reservoir.

Comparisons of the melt and solidification dynamics for SOS samples irradiated in air and in water are shown in Fig.

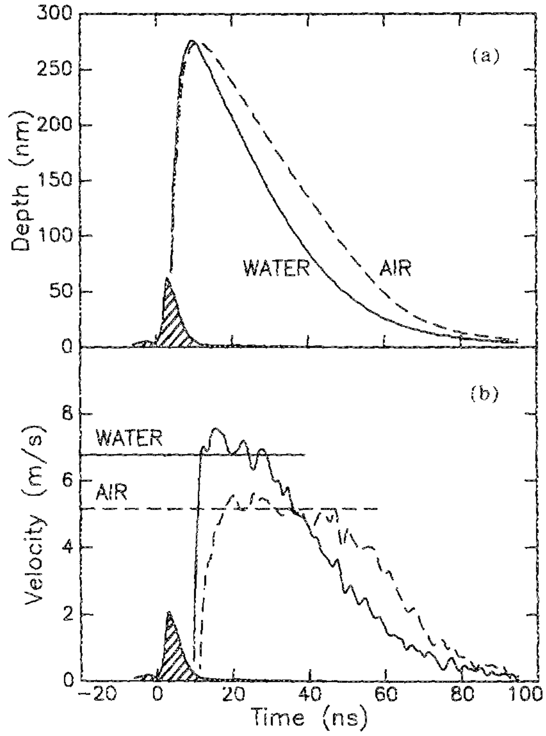

FIG. 1. (a) Melt depth transients for samples irradiated in air (dashed) and under water (solid). The hatched region indicates the relative timing of the laser pulse. (b) Liquid-solid interface velocities calculated from the curves in Fig. 1(a).

1. The two transients shown in Fig. 1(a) were selected to show comparable maximum melt depth. Figure 1(b) shows the corresponding liquid-solid interface velocities during solidification obtained by numerical differentiation of the curves in Fig. 1(a). For this peak melt depth of 270 nm the regrowth behavior differs in the two experimental situations with the maximum quench velocity enhanced from 5.2 to 6.8 m/s. As a consequence, the total duration of the melt, obtained by extrapolating the slope in the straight part of the transients to zero thickness, is reduced by 25%. Tails observed for $t > 60$ ns are attributed to slight inhomogeneities in the irradiation energy density and finite conduction in the underlying hot solid Si.

Figure 2 shows the maximum regrowth velocity as a function of maximum melt depth for a series of samples irradiated in air and water. The behavior of samples irradiated in air is similar to earlier work.[11] The use of peak melt depth as the abscissa minimizes the effect of differences in the energy coupling in the two configurations. For shallow (< 150 nm) melts, the effect of the water is insignificant compared to the scatter of the data. However, for deeper melts all the regrowth velocities under water are substantially enhanced above those for the same melt depth in air, increasing to as large as 30% for 300 nm melts.

Figure 3 shows typical transients of the Si-water interface reflectivity during irradiation of single-crystal Si samples. Both the s and p polarizations were monitored. The energy density was chosen to create a peak melt depth of ≈ 65 nm and a total melt duration of ≈ 15 ns. The reflectance observed for p-polarized light on a sample irradiated in air under comparable conditions is also shown for comparison. In air, the well-known high-reflectivity plateau corresponding to the duration of the Si surface melt is observed.[8,11] Under water, however, the reflectance shows considerably different structure. The reflectance for p-polarized light increases near the end of the laser pulse and remains constant at a high level for a time much longer than the surface melt duration. The s-polarized reflectance changes only slightly during the laser pulse and also remains near 100%. The long term reflectivity behavior under water

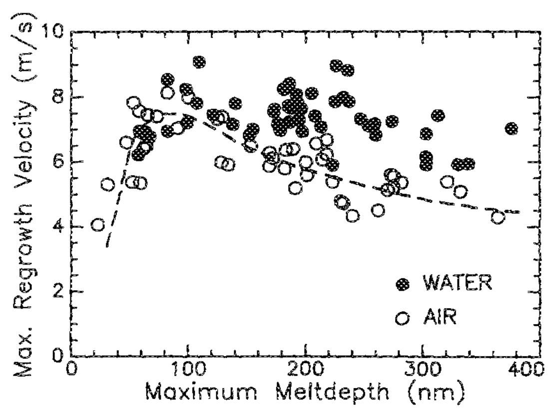

FIG. 2. Maximum regrowth velocities as a function of maximum corresponding melt depth for a series of samples processed at various energy densities either in air (open circles, dashed line) or in water (closed circles).

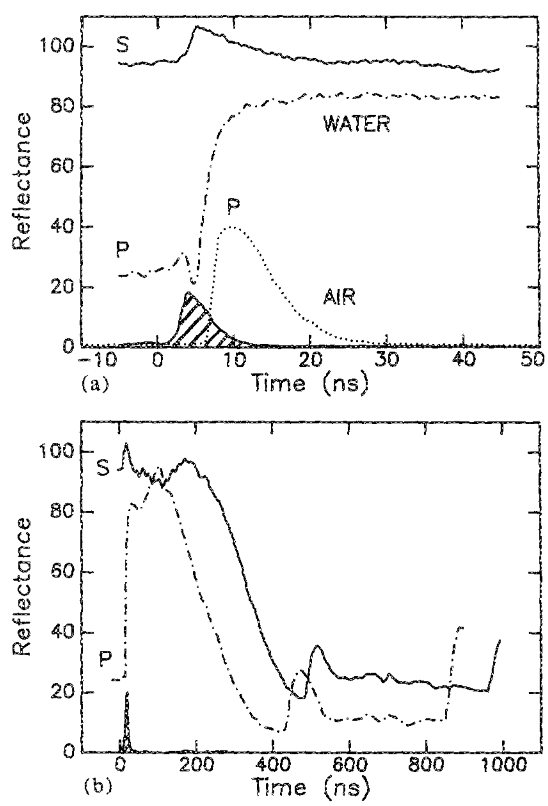

FIG. 3. Typical transient reflectivity traces for s and p polarizations of the cw laser measured on crystalline Si ⟨100⟩ upon irradiation under water (solid and dashed) and in air (dotted) are shown for short (a) and for long (b) times. Uncertainty in absolute reflectivity levels is $\pm 4\%$ and $-4/+17\%$ for s and p, respectively. Pulsed laser irradiation intensity was above the threshold for surface melting.

is shown in Fig. 3(b). After 200 ns, both s and p reflectance decrease; however, a variety of small changes in the reflectance is observed later in time. The precise structure of these oscillations was found to change with the distance between the light diffusor and sample and will be discussed further below.

The conductance and reflectance measurements provide a consistent picture for the phase changes in both Si and water. During irradiation, only the Si absorbs laser energy and is rapidly heated and melted. Heat from the melt is transported to the water, resulting in an enhancement of the quench rate. Standard heat flow considerations support the observed enhancement of 30% for deep melts; however, these cannot explain the behavior as a function of melt depth (Fig. 2). As a result of the heat flow, the water near the interface is rapidly superheated and its optical properties are changed. Variations in the reflectance (Fig. 3) present a real-time probe of the modified properties and hence the phase changes in the water. Assuming that the optical properties change only in a thin layer of uniform composition at the Si-water interface, the high p and s reflectance correspond to a refractive index near the Si surface which is lower than that of water at room temperature.[12] Indeed, the data suggest that total internal reflection occurs near the interface with corresponding high reflectivities. For the glancing angle used in these experiments, total internal reflection can be achieved for an index decrease of only $\approx 2\%$. We conclude from Fig. 3(a), therefore, that a low index phase of steam or superheated water is formed near the end of the laser pulse and remains low for at least 150 ns. Once total internal reflection occurs, the probe beam does not monitor the Si surface and hence the surface liquid–solid transformation cannot be observed. Slight nonplanarity of the reflecting interfaces and inaccuracy in the absolute reflectivity levels would explain the deviation from exactly 100%.

The p and s reflectivities both decrease discontinuously 200 ns after the Si surface solidifies, indicating an increase in the effective refractive index near the interface. The reflectivity traces return to their initial values after several microseconds. Using a large distance between sample and diffusor (several mm) it has been found that this relatively long high index phase of water "echos" back to the interface after several microseconds. The timing of the echos corresponds to a wave propagating with the sound velocity in (liquid) water which is reflected from the diffusor light guide. Several subsequent echos corresponding to the round-trip transit time can be observed. In the experiments described in Fig. 3, the sample-diffusor distance was only 0.6 mm and the round trip time is less than the total duration of the low-reflectivity phase. This results in the small oscillations being superimposed on the signal.

These phenomena suggest that the increase in the refractive index corresponds to the formation of a high-pressure liquid phase of water.[12,13] This could be initiated by expansion of the primarily formed steam or superheated water phase. The high-pressure phase travels as a shock wave through the fluid generating the observed echos. Details of these phenomena will be given in later publications.[14]

In conclusion, we have demonstrated that the thermal quench rate during nanosecond pulsed laser heating of Si can be enhanced by immersing the sample in water during irradiation. The enhancement is as large as 30% for 300 nm deep melts. A steam or superheated water phase is formed on a nanosecond time scale at the Si-water interface. This phase can last over several hundred nanoseconds and initiates a high-pressure liquid phase of water propagating as a shock wave through the fluid. This new method may allow the formation of novel doped or compound layers with nonequilibrium compositions and phases not attainable with lower quench rates.

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