Time-resolved reflectivity measurements during explosive crystallization of amorphous silicon

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Explosive crystallization of Cu implanted amorphous silicon during irradiation by a 32-ns FWHM ruby laser pulse has been studied using time-resolved reflectivity measurements and Rutherford backscattering spectrometry. From interferences in the reflectivity, the position and the velocity of the self-propagating melt have been deduced as a function of time. A maximum average velocity of 13 ± 2 m/s has been obtained. The reflectivity behavior indicates the presence of crystalline nuclei in the melt.

Explosive crystallization of amorphous silicon (*a*-Si) upon pulsed-laser irradiation has recently received considerable attention.[1-8]. Thompson and co-workers[2] proposed a model in which the absorbed laser energy melts a primary liquid layer at the surface. The latent heat released by the solidification of this liquid into large-grain polycrystalline silicon (LG *p*-Si) will melt a thin layer of the underlying *a*-Si. During crystallization of this secondary melt, latent heat is again released and the liquid will self-propagate towards the interior of the sample. The secondary melt is thought to be more undercooled than the primary one, resulting in the formation of fine-grain (FG) *p*-Si. A different model has been proposed by Wood *et al.*[7] They suggested that bulk nucleation during melting is responsible for the formation of the FG material. The release of latent heat by this process would explain the measured large melt front penetration depth. The LG *p*-Si then presumably grows from the underlying FG *p*-Si layer. Wood's model does not contain a self-propagating buried liquid layer. It is now generally believed that the FG *p*-Si is formed by a self-propagating liquid as proposed by Thompson *et al.*[2] However, it remains unclear how and when the secondary melt is formed from the primary one.

In order to study the explosive crystallization process we measured the time-resolved reflectivity (TRR)[9] during pulsed-laser irradiation of Cu implantation amorphized silicon under conditions where this process is known to occur.[3] Primary and secondary melt depths have been determined by Rutherford backscattering spectrometry (RBS) from the redistribution of copper.[3] The reflectivity shows temporal interferences due to the self-propagating liquid as well as effects attributable to nucleation and growth of nuclei in the melt.

Si(100) was implanted at room temperature with 170 keV Cu^+ ions to a dose of 2×10^{15} cm^{-2}, resulting in a 220-nm-thick *a*-Si layer. Copper was taken as an implant because it exhibits strong segregation effects at the liquid-solid interface in silicon and can therefore be used as a marker for melting and solidification.[3-5] Spots with a diameter of ~ 1.5 mm were irradiated by a *Q*-switched ruby laser ($\lambda = 694$ nm) with a pulse length of 32 ns FWHM. The mean energy was determined with an accuracy of 5% and the uniformity over the laser spot was measured to be better than 5%. The reflectivity was probed by a single-frequency HeNe laser ($\lambda = 633$ nm) focused to a ~ 0.1-mm-diam spot and incident at 13° to the sample's normal. The intensity of the reflected beam was monitored with a measured response time of less than 1 ns. Additional reflectivity measurements were made with an Ar^+ laser ($\lambda = 488$ nm), but only the HeNe data will be discussed in this letter. Cu concentration profiles were determined with a ~ 15 nm depth resolution by RBS using 2 MeV He^+.

The TRR signals for irradiation at various energy densities are shown in Fig. 1. For 0.16 J/cm^2, Fig. 1(a), the maximum reflectivity reached is about 60%, well below the value for a thick (>20 nm) liquid silicon (*l*-Si) layer at this wavelength and angle (73%).[10,11] Following the high reflectivity phase (HRP), oscillations in the reflectivity are observed which we believe to be caused by the self-propagating liquid layer while it moves into the *a*-Si towards the interface with the crystalline substrate. In this interpretation the oscillations arise from interference of the light reflected at the air-solid interface (the sample's surface) and that reflected at the solid-liquid interface of the propagating secondary melt front. The interference extrema can be used to estimate the penetration depth of the self-propagating melt as a function of time at various laser energy densities. For 0.16 J/cm^2, two minima and one maximum are observed. As the energy density is increased to 0.18 J/cm^2, Fig. 1(b), an additional maximum appears. For 0.19 J/cm^2, Fig. 1(c), the first interferences disappear in the tail of the HRP, while the maximum reflectivity has now increased to 65%. At higher energy densities, Fig. 1(d), the HRP dominates, its maximum reflectivity and duration increase. At these energy densities the thickness and duration of the strongly absorbing primary melt are such that the interference effects can no longer be observed. The simultaneously recorded reflectivity at 488 nm did not show oscillations, which is in agreement with experiments by Thompson *et al.*[2]

After pulsed-laser irradiation RBS has been used to determine the changes in the Cu profile. In the range of energy densities used in this work, the originally Gaussian implantation profile has changed into a double-peak structure. Cu is accumulated at the surface due to segregation during so-

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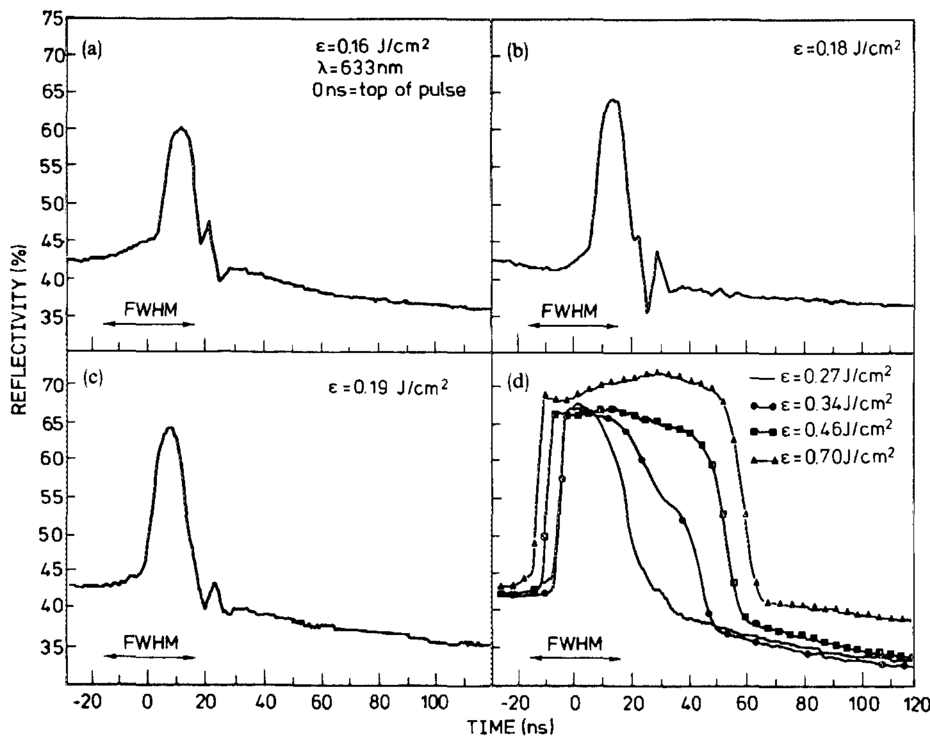

FIG. 1. Time-resolved reflectivity (TRR) measurements of Cu implanted a-Si upon pulsed-laser irradiation for various energy densities. Times before the top of the laser pulse are taken as negative.

lidification of the primary melt and at greater depth due to transportation by the self-propagating secondary melt. As was shown before[3] this double-peak structure can be used to infer the primary and secondary melt depths. The results for the present study are shown in Fig. 2.[12] Apparently, surface melting starts at 0.14 J/cm^2 and for 0.16–0.19 J/cm^2 the primary melt depth is approximately 35 nm. As the energy density is increased to 0.27 J/cm^2, the primary melt depth increases to 65 nm. The secondary melt front penetration is much greater. From 0.14 to 0.16 J/cm^2 it exhibits a steep increase from 0 to 135 nm. Above 0.20 J/cm^2 it almost reaches the a-Si/c-Si interface.

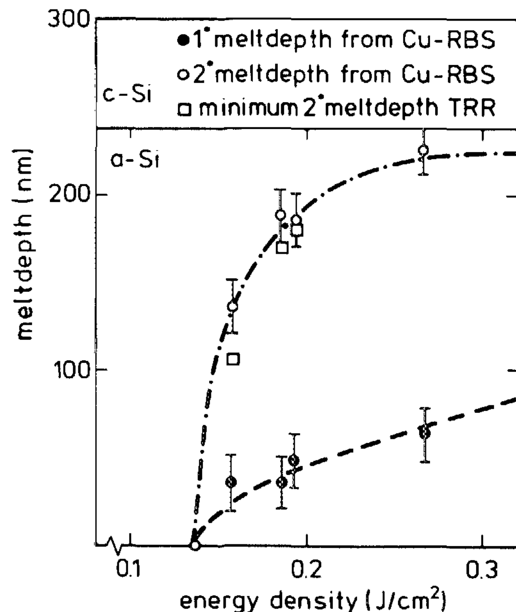

FIG. 2. Primary (solid circles) and secondary (open circles) melt depth as a function of energy density as measured by RBS together with estimates for the secondary melt depth from TRR (open squares).

Comparison of the reflectivity and RBS results leads to a number of interesting observations. Figure 2 implies that the primary melt depth for 0.16, 0.18, and 0.19 J/cm^2 is in excess of 20 nm, yet in Fig. 1 the maximum in the HRP does not reach 73%, expected at 633 nm for a l-Si layer thickness of more than 20 nm.[10,11] In fact, all HRP values in Fig. 1 stay significantly below this value. We believe that this is caused by the presence of p-Si nuclei in the melt. The melting temperature of a-Si is approximately 200 K below that of c-Si.[2] When a melt is produced from a-Si, it is undercooled with respect to the melting temperature of c-Si; therefore, p-Si nuclei may form and grow. An estimate of the transient time needed to obtain steady-state nucleation[13] gives a value of less than 1 ns, indicating that p-Si nuclei can be formed on the time scale of our experiments. The changes in the effective optical properties of the medium by the increasing p-Si fraction result in a lower high reflectivity value, which decreases in time.[8] Moreover, these nuclei may introduce a certain amount of scattering, which also effectively lowers the specular reflectivity. Thus the primary melt can reach thicknesses beyond 20 nm, while its reflectivity stays below 73%. Near the end of the laser pulse, the primary melt reaches its maximum thickness and the remaining liquid solidifies by further growth of the p-Si nuclei. At the same time these nuclei can act as nucleation sites for explosive crystallization of the remaining a-Si via the self-propagating melt.

The presence of p-Si nuclei in the primary melt is further substantiated by the following arguments. Firstly, not one of the HRP measurements in Fig. 1 contains a flat plateau. This observation signifies that the optical properties of the primary liquid are never constant in time. Secondly, the decrease in the reflectivity at the end of the HRP is not as

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abrupt as would be expected for a uniform solid-liquid front moving towards the surface. This is especially clear for the two lowest energy densities presented in Fig. 1(d), where a distinct shoulder is visible in the falling edge of the reflectivity. For 0.70 J/cm^2, the shoulder has changed into an even increasing reflectivity which reaches the value of 73%, indicating that for this high-energy density the *p*-Si nuclei in the top layer of the primary melt can be molten again, giving the reflectivity of pure *l*-Si. For the energy-density range of Fig. 1(d), the measured reflectivity behavior at 488 nm resembled that at 633 nm, showing the same effects of the presence of *p*-Si nuclei in the primary melt.

One might argue that the decreased high reflectivity value and its behavior as a function of time and energy density can also be explained by assuming a temperature-dependent reflectivity of pure *l*-Si without any nuclei. This cannot be excluded, but an extrapolation of the *l*-Si reflectivity data from Lampert *et al.*[14] seems to suggest that the reflectivity increases with decreasing temperature, which would give an effect of opposite sign.

The depth of the self-propagating molten layer can be estimated from the observed reflectivity oscillations.[15] Calculations showed that the first minimum in the reflectivity occurs at a depth of about 20 nm, while every additional extremum adds another 40 nm to this value (1/4 wavelength $\sim$40 nm). The penetration depths of the secondary melt obtained from the interferences in the reflectivity and from the Cu profiles are compared in Fig. 2 and show reasonable agreement. Since the interferences have been measured as a function of time, we can estimate the velocity with which the explosive crystallization proceeds. The maximum value obtained is 13 ± 2 m/s which is large but still below 15 m/s, the solidification velocity that is known to yield *a*-Si.[16]

The following conclusions can be drawn from the above described TRR and RBS measurements. At all energy densities used, the HRP value starts significantly below 73%, expected at 633 nm for a primary melt depth of more than 20 nm as measured by RBS. This indicates the presence of *p*-Si nuclei in the melt. The growth of these nuclei is responsible for the solidification of the primary melt. This process will start at the interior, where undercooling is greatest, thus initiating the self-propagating secondary melt. This secondary melt is measured to proceed with a maximum average velocity of 13 ± 2 m/s, which is as expected below the critical value of 15 m/s at which amorphous growth has been found to occur.

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