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journal or publication title	Physical review letters
volume	59
number	19
page range	2203-2206
year	1987-11
権利	(C) 1987 The American Physical Society
URL	http://hdl.handle.net/2241/104172

doi: 10.1103/PhysRevLett.59.2203

Explosive Crystallization Starting from an Amorphous-Silicon Surface Region during Long-Pulse Laser Irradiation

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(Received 3 April 1987)

A newly developed method of backside time-resolved reflectivity measurement is useful for probing the interface between solid and transient liquid Si. Measurements indicate that explosive crystallization starts very near the Si surface from a highly undercooled liquid Si layer thinner than 3 nm, for laser irradiation with long pulses ranging from 65 to 200 ns. During the laser irradiation, surface melt-in continues into fine-grained polycrystalline Si produced by explosive crystallization, followed by solidification of the surface-liquid layer.

PACS numbers: 61.50.Cj, 05.70.Ln, 64.70.Dv, 79.20.Ds

Fast phase transitions induced by pulsed-laser irradiation have been a topic of interest for the study of systems far from thermodynamic equilibrium and the formation of materials in nonequilibrium states.[1,2] At laser energy densities above the threshold E_{LPE} for liquid-phase epitaxial regrowth (~ 1 J/cm^2), a transient molten, liquid Si (l^*-Si) layer is formed at the surface for periods longer than approximately 50 ns. At energy densities just above the threshold E_{SM} for surface melting ($\simeq 0.1$ J/cm^2), melting of amorphous silicon (a-Si) results in transient, highly undercooled liquid Si (l^{**}-Si),[2] which induces interesting phenomena. For laser irradiation with pulse durations τ_p longer than about 10 ns and at energy densities between E_{SM} and E_{LPE}, explosive crystallization (EC) takes place in the a-Si layer.[3-7] As a result, the a-Si layer is changed into a region of large-grained polycrystalline Si (LG pc-Si) near the surface and one of fine-grained (FG) pc-Si at larger depth.[2,3] Thompson *et al.*[2] proposed a model in which a thin, self-propagating buried liquid layer (l^{**}-Si) is formed when a primary surface-liquid layer reaches a maximum depth and then begins to slowly solidify, leading to release of latent heat. On the other hand, solidification of the primary surface-liquid layer from the surface, resulting in amorphous states, was observed without EC for laser irradiation with τ_p shorter than 10 ns.[8,9] Furthermore, EC from the surface region was recently predicted by Wood and Geist,[4] who performed a computer simulation. The model proposed by Thompson *et al.*,[2] therefore, should be modified. Important questions to be solved are as follows: (1) How and when is the self-propagating l^{**}-Si layer initially formed from the primary surface-liquid layer? (2) What are the conditions and triggers for starting the EC? We believe that the key to these questions can be found in both the interface of liquid-solid Si and the changes in short-range ordering of l^{**}-Si.

In order to investigate the EC and l^{**}-Si, we have developed a new time-resolved optical reflectivity (TROR) measurement from the backside of a-Si. This enables us to probe the interface of l^{**}-Si and solid Si at larger depth. We also used laser outputs with longer pulse duration τ_p, ranging from 35 to 200 ns, to produce the l^{**}-Si layer effectively. In this paper, we present the first, direct, backside TROR measurements of the dynamics of the l^{**}-Si and a-Si interface, as well as the l^*-Si and c-Si interface. Simultaneous measurements of backside TROR and conventional frontside TROR are demonstrated to be useful for clarifying fast phase transitions.

To apply the backside TROR measurement, we utilized Si on sapphire (SOS) samples with Si thicknesses, d, of 600 ± 60 nm which were implanted with Zn ions. The implantations were done at room temperature with 120-keV Zn^+ to a dose of 2×10^{15}/cm^2. The thickness of the produced a-Si layer was approximately 160 nm. Zn impurities in Si have a small thermal-equilibrium segregation coefficient of $\simeq 1 \times 10^{-5}$ and, therefore, are expected to be a good marker for the EC, like Cu.[3,7] We measured the redistribution of Zn impurities after pulsed-laser irradiation by means of secondary-ion mass spectroscopy. A ruby laser ($\lambda = 694$ nm) was used to irradiate the a-Si layers. TROR measurements were carried out simultaneously from the frontside and the backside at 633 and 1152 nm, respectively, with He-Ne lasers. The spot sizes for both probe beams were about 100 μm. Each output of the pulsed laser was measured simultaneously with the frontside and backside TROR signals. The time resolution was better than 5 ns and the relative error on the time scale was less than 1 ns between both TROR signals.

Figure 1 shows typical (a) frontside and (b) backside TROR signals for unimplanted, crystalline Si (c-Si) on sapphire which was irradiated with a laser pulse with τ_p of 55 ns and an energy density of 1.3 J/cm^2. At around 20 ns the front reflectivity begins to increase slowly, while the rear reflectivity decreases from the initial level a to a point b at 33 ns. These come from a temperature rise of the Si layer which varies the refractive index n.[10] A temperature gradient, $dT(x)/dx$, is induced within the Si layer. It will, however, be small for times later than

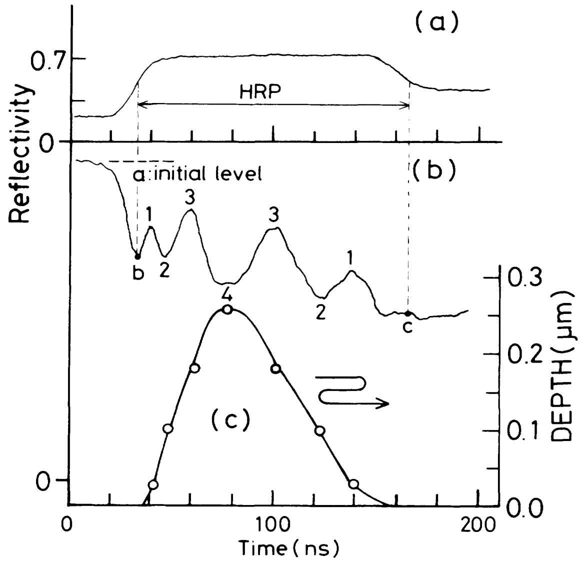

FIG. 1. (a) Frontside TROR signal, (b) backside TROR signal, and (c) obtained depth of the interface between the surface l^*-Si and the deeper c-Si.

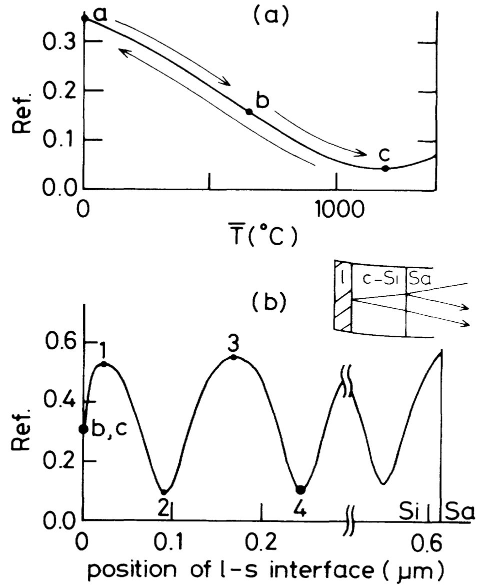

FIG. 2. Calculated curves of (a) backside reflectivity change for an air/c-Si/sapphire structure as a function of the average temperature $\bar{T}$ of the c-Si layer and (b) backside reflectivity as a function of the l-s interface position for an air/l^*-Si/c-Si/sapphire structure, where the extinction coefficients k of l^*-Si and c-Si are 7.71 and 0.02, and the n values of l^*-Si and sapphire are 5.33 and 1.75, respectively, for 1152 nm at 1200 °C.

50 ns because the thermal conductivity of the underlying sapphire is much smaller than that of Si and the Si thickness is thinner than the thermal diffusion length, L, in 50 ns; i.e., $L=(2Dt)^{1/2}=1.0$ μm, where we use a Si thermal diffusivity D of 0.1 cm^2/s at around 1000 °C. Furthermore, even if a temperature gradient exists, there is no significant reflection within the Si layer because of small changes in n, and only the probe-laser wavelength, λ/n, varies with the depth x. In this case an average temperature can be defined by the quantity $\bar{T}=(1/d)\int_0^d T(x)dx$, leading to an average refractive index $\bar{n}(\bar{T})$. By using the linear relation $\bar{n}(\bar{T})=3.51+2.2\times10^{-4}\bar{T}(°C)$ for $\lambda=1152$ nm,[11] we can calculate the change in the backside reflectivity of the Si layer as a function of $\bar{T}$, a shown in Fig. 2(a).

It can be seen from Fig. 1(a) that the high-reflectivity ($\simeq 72\%$) phase due to transient l^*-Si is retained for a period of 133 ns, from 33 to 166 ns. For that period, clear peaks of maxima and minima are seen in the backside TROR signal, due to interfering optical reflections from the Si-sapphire interface and from the moving interface between the surface l^*-Si layer and the solid Si (l-s interface), as shown in the inset of Fig. 2(b), which will be discussed later. A change from point c to the initial level was observed at times later than 166 ns, which is not shown in Fig. 1(b). This is due to a temperature fall.[10] $\bar{T}$ corresponding to point c is about 1200 °C. The Si layer is probably heated enough to reach at least this temperature at times later than 50 ns. $\bar{T}$ corresponding to point b is lower than 1200 °C, as shown in Fig. 2(a), since the Si layer is not heated enough by the laser pulse at times earlier than 50 ns.

The backside reflectivity for the c-Si with surface l^*-Si layer is also calculated [see Fig. 2(b)], on the assumption that $\bar{T}$ of the c-Si layer is 1200 °C. This shows the reflectivity change at 1152 nm as a function of position, x, of the l-s interface from the Si surface. By comparison of the backside TROR signal and the calculated reflectivity curve,[12] the interference maxima and minima observed are assigned the positions 1,2,3,4,3,2,1 in Fig. 2(b) in that order. Point 4 indicates the maximum depth of the l-s interface. The depth corresponding to each maximum and minimum is plotted in Fig. 1(c). A temperature gradient has only a small influence on the result, and the error in the obtained depth is estimated to be approximately ± 9 nm if there were an uncertainty of ± 200 °C in $\bar{T}$. From the results in Fig. 1(c) maximum melt-in and solidification velocities can be evaluated to be 9.6 and 3.7 m/s, respectively. These values are consistent with velocities which were obtained by a time-resolved conductivity measurement.[13] Thus the backside TROR measurement is found to be a very powerful method for direct observation of the l-s interface and can be applied to probe EC phenomena.

Figure 3 shows results for EC in Zn-ion–implanted a-Si during pulsed-laser irradiation [Fig. 3(a)] with τ_p of 90 ns and an energy density of $\simeq 0.08$ J/cm^2. From the frontside TROR signal, Fig. 3(b), it can be seen that a surface l^{**}-Si layer is produced during the time period

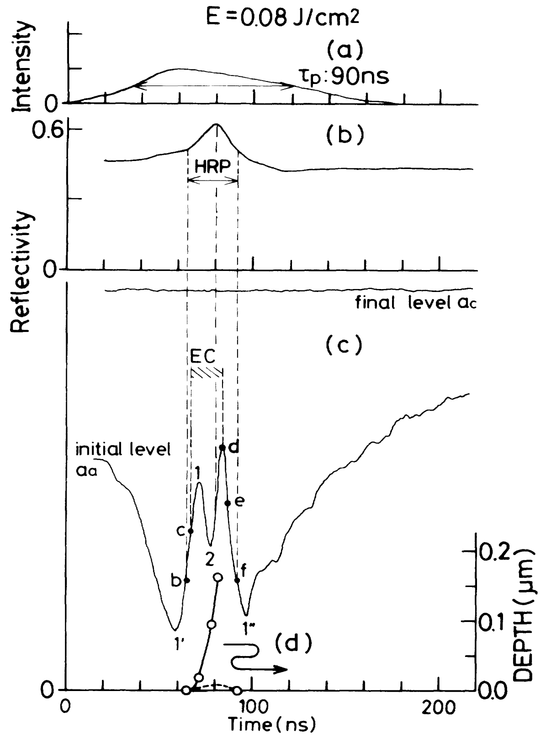

FIG. 3. (a) Laser pulse shape, (b) frontside TROR signal, (c) backside TROR signal, and (d) obtained depth of the interface between the self-propagating buried l^{**}-Si layer and inner a-Si. The duration of EC is shown in (c).

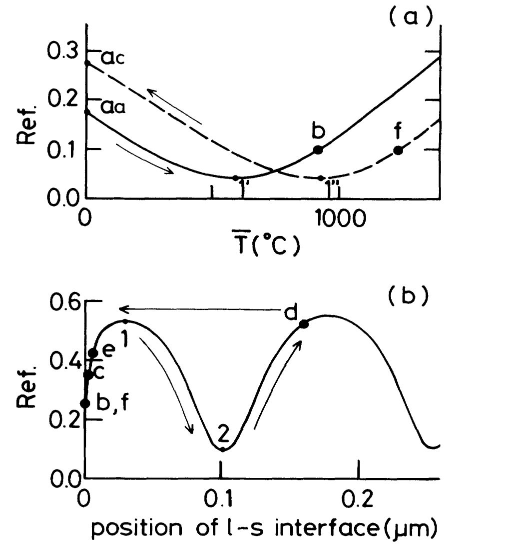

FIG. 4. Calculated backside reflectivity curves for (a) the initial structure of air/a-Si/c-Si/sapphire (solid curve) and the air/FG pc-Si/c-Si/sapphire structure obtained after EC (broken curve) as a function of average temperature $\bar{T}$, and (b) for a Si layer with inner propagating l^{**}-Si layer as a function of position of the deeper l-s interface.

from 64 to 92 ns, corresponding to points b and f in Fig. 3(c), respectively. The backside TROR signal, Fig. 3(c), clearly shows interference phenomena. Si temperature variation gives an interference background from 0 to 64 ns and for times later than 92 ns. This is compared with the change from the initial reflectivity a_a to b and with that from f to the final reflectivity a_c of polycrystallized Si in Fig. 4(a), which displays the backside reflectivity calculated as a function of $\bar{T}$. Here, we used $n = 3.56$ for a-Si [11] and $n = 3.51$ for FG pc-Si at 0 °C and 1152 nm, and assumed the same $\bar{T}$ dependence of n for a-Si as for c-Si, since no data are available. The calculated backside reflectivity curve is shown in Fig. 4(b) for the Si layer with a l-s interface, where $\bar{T}$ is assumed to be 1200 °C. For the 1152-nm probe laser, the reflection at the interface of a-Si and c-Si is so small ($< 1\%$) that this can be neglected in the calculation. It should be noticed that, from 64 to 92 ns, two interference maxima and one minimum can be seen in the backside TROR signal, Fig. 3(c), while the frontside TROR signal, Fig. 3(b) shows a maximum reflectivity of only 62% at 80 ns, corresponding to a surface l^{**}-Si layer thickness of 7 nm. If the interferences were attributed to the interface between the surface l^{**}-Si and the a-Si, the maximum interface depth would be about 80–100 nm [see Fig. 4(b)] at a time of 78 ns when the interference minimum is observed. This depth, however, is much larger than the 7 nm obtained from the frontside TROR signal. Therefore, the interference maxima and minimum in Fig. 3(c) do not come from a surface l^{**}-Si, but from a self-propagating buried l^{**}-Si layer, i.e., the moving interface between the self-propagating l^{**}-Si layer and inner a-Si.

The depth corresponding to the maximum point 1 is evaluated to be 30 nm from Fig. 4(b), while at that time the frontside TROR signal shows a reflectivity of 56%, corresponding to a surface l^{**}-Si thickness of about 3 nm. Consequently, the onset of EC is estimated to be around point c in Fig. 3(c). This suggests the idea that the self-propagating l^{**}-Si layer is first formed at a time around 64 ns, from a primary surface l^{**}-Si layer thinner than 3 nm, which is estimated by our taking into account the inaccuracy in the onset time of EC. Furthermore, the maximum point d should indicate the end of EC and the maximum depth of the propagating l^{**}-Si layer. This is likely to be equal to the a-Si thickness ($\simeq 160$ nm) because segregated Zn impurities were detected around 160 nm by secondary-ion mass spectroscopy measurements. At a time of 84 ns corresponding to point d, the front reflectivity still shows a high-reflectivity phase, indicating that the primary surface l^{**}-Si layer still exists. After the end of EC, the reflectivity moves from point d to a point around e and, furthermore, changes from the point e to a point f as the thin l^{**}-Si layer solidifies. Gradual changes observed from point d to e, as well as from point b to c, are probably due to both the time resolution of 5 ns and the spatial inhomogeneity. In the calculated reflectivity curves in Fig. 4, arrows indicate the order of the process. The average propagation velocity of the buried l^{**}-Si layer can be estimated to be about 14 m/s from the interface depth in Fig. 3(d), which was obtained by comparison of the results of Figs. 3(c) and 4(b). The main error in the obtained depth comes from an uncertainty in $\bar{T}$ of c-Si and a-Si and is again estimated to be ± 9 nm for $\pm 200\,°C$.

Similar results were obtained for laser irradiation with pulse durations from 65 to 200 ns at 0.08–0.20 J/cm^2 which produce primary surface l^{**}-Si layers up to depths from 7 to 20 nm. The results obtained indicate that the self-propagating l^{**}-Si layer is initiated from a surface l^{**}-Si layer with a thickness less than 3 nm. Surface melt-in proceeds into the FG pc-Si produced by EC, in contrast to the process proposed by Thompson *et al.*[2]

For pulsed-laser irradiation with τ_p less than 65 ns at 0.19 and 0.26 J/cm^2, we observed interferences in the frontside TROR signals similar to those reported by Lowndes *et al.*[6] and Bruines *et al.*[5] EC as indicated by both the frontside and backside TROR signals, is initiated about 20 ns after the surface begins to melt. This indicates that the EC is initiated at a deeper l^{**}-Si/a-Si interface for laser pulses shorter than 65 ns.

It is suggested from the obtained results that some kind of fast nucleation occurs in the primary surface l^{**}-Si,[5] which becomes a trigger for the formation of the self-propagating l^{**}-Si layer under some conditions. An interesting idea was recently presented by Tsao and Peercy[14] that the nucleation of pc-Si occurs at the moving l^{**}-Si/a-Si interface when velocities are below a critical one. To clarify further the fast phase transitions induced by pulsed-laser irradiation, time-resolved structure measurements such as extended x-ray-absorption fine structure,[15] as well as combined experiments of time-resolved conductivity and backside reflectivity measurements, are needed for the l^{**}-Si and l-s interfaces.

In conclusion, we have demonstrated that the backside TROR technique is useful for the investigation of the dynamics of liquid-solid interfaces. For pulsed-laser irradiation of a-Si with long pulses ranging from 65 to 200 ns, we obtained several new findings concerning explosive crystallization (EC); EC starts at the a-Si surface region from a primary l^{**}-Si layer thinner than 3 nm. During the laser irradiation, melt-in proceeds into the FG pc-Si layer produced by EC and is followed by solidification of the surface l^{*}-Si. This suggests that EC is triggered by rapid pc-Si nucleation in highly undercooled l^{**}-Si at or near the l^{**}-Si/a-Si interface.

This work was partly supported by a Grant-in-Aid for the Special Project Research (1985–1987) on Ion Beam Interactions with Solids from the Ministry of Education, Science and Culture, Japan.

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