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Evidence for a Self-Propagating Melt in Amorphous Silicon upon Pulsed-Laser Irradiation

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A double-peak structure is observed in the Cu concentration profile after low-energy pulsed-laser irradiation of Cu-implanted Si. From the Cu surface segregation a primary melt depth is inferred. In addition, Cu segregation at the depth of the amorphous-crystal interface gives evidence for a secondary melt propagating through the amorphous layer towards the crystalline substrate. The results imply a large difference in melting temperature, heat of melting, and heat conductivity between amorphous Si and crystalline Si.

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Although amorphous silicon (a-Si) is widely used in semiconductor device processing, its thermodynamic and kinetic properties are not yet well established. The melting temperature especially is still an issue of considerable controversy. Experiments with solid phase regrowth suggest that the melting temperature of a-Si is close to that of the crystalline material.[1] On the contrary, experiments with pulsed–electron-beam annealing and pulsed-laser annealing indicate a lowering of the melting temperature of a-Si by 200–500 K.[2–4] Moreover, after pulsed-laser irradiation at laser energy densities below the threshold for epitaxial regrowth (≈ 1 J cm^{-2}) the originally amorphous film exhibits two kinds of polycrystalline structure,[3, 5–7] coarse grained near the surface and fine grained underneath, the origin of which is not yet clear. Two mechanisms have been proposed to explain this structure. It has been suggested[3] that the initial melt, produced by the absorbed laser light, solidifies to form coarse-grained polycrystalline silicon. The latent heat released drives a thin self-propagating liquid layer through the underlying a-Si, producing fine-grained polycrystalline Si. On the other hand, bulk nucleation of the highly undercooled liquid phase has been proposed to explain the fine-grained polycrystalline silicon.[5, 6]

In this paper we report on segregation effects in Cu-implanted Si after nanosecond pulsed-laser irradiation in the energy region below the threshold for epitaxial regrowth, ≈ 1 J cm^{-2}, which show that crystallization of the amorphous layer takes place via melting and resolidification at two fronts. A primary melt depth, produced by the absorbed laser light, is inferred from the surface segregation of copper. There is a plateau in the functional behavior of melt depth versus laser energy density which is consistent with the suggestion that a-Si has a melting temperature and heat conductivity much lower than that of crystalline silicon (c-Si). In addition, copper segregation near the (a-Si)–(c-Si) interface gives evidence for a secondary melt propagating through the amorphous layer towards the crystalline substrate. As will be shown, the results are consistent with the mechanism proposed in Ref. 3.

Si(100) was implanted at room temperature by 170-keV Cu^+ ions to a dose of 2×10^{15} cm^{-2}. Copper exhibits strong segregation effects and diffuses very fast in liquid silicon.[8] Therefore the as-implanted profile will be very sensitive to melting and crystallization within the amorphous layer. Changes in the Cu profile can thus be used to infer melt depths. Pulsed-laser annealing was performed using a Q-switched ruby laser, with wavelength of 694 nm, and pulse length of 20 ns. Laser energy density was varied between 0.1 and 2.0 J cm^{-2} using volume-absorbing neutral-density filters. A guide diffuser[9] was used to obtain 5% uniformity over a 5-mm laser spot. The mean energy density was calibrated to within 5% by use of calorimetry. Laser irradiation was performed at room temperature. A new location on the implanted samples was used for each value of energy density.

Copper concentration profiles were determined by Rutherford backscattering spectrometry (RBS)[10] using 2-MeV He^+ in a random direction of the sample close to its surface normal. Reflected He particles were detected and energy analyzed by a surface-barrier detector (energy resolution 12 keV) at a scattering angle of 110°, giving a depth resolution of about 10 nm. The depth of the (a-Si)–(c-Si) interface could be inferred from the high-yield portion in the RBS spectra under channeling conditions and was found to be 225 nm. Channeling was also used to determine the threshold laser energy density for which epitaxial recrystallization of the originally amorphous layer was achieved. The threshold for surface melting could be inferred (± 0.01 J cm^{-2}) from a surface color change after pulsed-laser irradiation, due to the conversion of a-Si to polycrystalline Si.

Figure 1 shows a comparison of Cu profiles after implantation at 170 keV and after irradiation at different laser energy densities. In contrast to pulsed–electron-beam experiments reported earlier,[2] in which no dopant redistribution is observed below the threshold for complete recrystallization of the amorphous film, we find a remarkable effect on the copper profile at very low laser energy densities. The threshold for surface melting was found to occur at 0.10 J cm^{-2}. Figure 1(a) shows that already at 0.12 J cm^{-2} the copper profile is changed drastically over a thickness of about 175 nm. Figure 1(b) shows the copper profile after irradiation at 0.14 J cm^{-2}; in this case changes can be observed to a depth of 210 nm. This result is remarkable because in the times involved in pulsed-laser heating the Cu implanation profile can only change as a result of liquid-phase diffusivity, yet 0.14 J cm^{-2} is not sufficient to heat the entire layer of 210-nm thickness to its melting point and melt it.[11,12]

A possible explanation for these changes far below the surface, as observed in Figs. 1(a) and 1(b), is the following. At energy densities just above the threshold for surface melting, only a very thin layer of the amorphous film is melted but the temperature in the entire film is raised above its initial value. When crystallization starts, this will lead to the release of latent heat, ΔH_c. Because ΔH_c is larger than the heat needed to melt a-Si (ΔH_a),[2,11-13] the released energy may be used both to heat previously unmelted material to its melting point and to melt it if the heat conductivity is not too high, which does not seem to be the case (see also Refs. 4 and 5). During crystallization of this secondary melted silicon, again heat is released and the process proceeds, with a self-propagating layer of melted silicon moving from the surface region towards the (a-Si)–(c-Si) interface. Depending on the temperature gradient in the amorphous material, this "explosive" crystallization may either quench at a certain depth or proceed through the entire layer. From the direction in which the secondary melt front moves it is clear that this will lead to a segregation of copper toward the (a-Si)–(c-Si) interface, which is indeed observed.

Both Figs. 1(a) and 1(b) show very little surface accumulation of copper. From this we conclude that initially only a thin surface layer has been melted by the absorbed laser light, since melting in this region of low copper concentration will not result in detectable segregation effects. Cross-section transmission-electron-microscopy pictures of an a-Si film after laser annealing at low-energy densities show a dual grain structure which may be related to this twofold crystallization,[3] while time-resolved conductivity measurements during pulsed-laser irradiation indicate the presence of a buried melted layer.[3] To explain the difference in grain structure

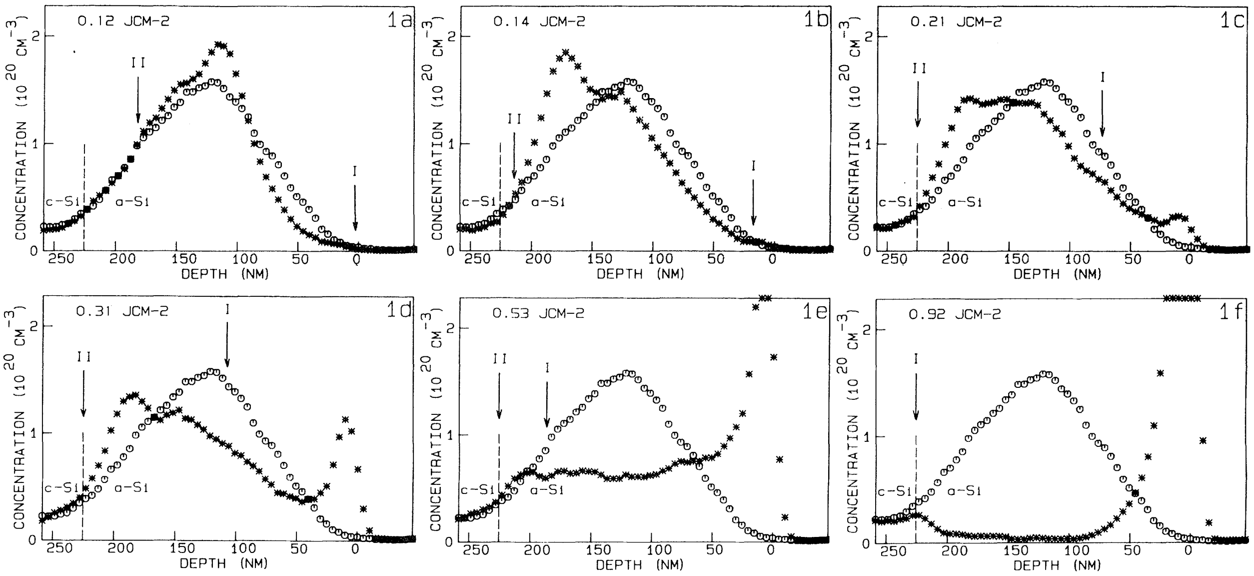

FIG. 1. Cu concentration profiles in Cu-implanted silicon, before (circles) and after (asterisks) pulsed-laser irradiation at various energy densities. Indicated are primary (I) and secondary (II) melt depths (see text). Implantation: 2×10^{15} cm^{-2}, 170 keV.

between the two polycrystalline regions, Lowndes, Wood, and Narayan[5] and Wood, Lowndes, and Narayan[6] suggest the formation of one melted layer in which two kinds of crystallization occur: bulk nucleation in that part of the liquid where the temperature is below a certain nucleation temperature and crystallization via a melt front in that part where the temperature is above this value. The nucleation temperature lies between the melting temperature of *a*-Si and that of *c*-Si. Bulk nucleation, however, should not lead to copper accumulation at the (*a*-Si)–(*c*-Si) interface and thus cannot acount for the present observations.

Figures 1(c) and 1(d) show the copper profile after irradiation at 0.21 and 0.31 J cm^{-2}, respectively. In both cases, a clear double-peak structure is observed, which for 0.31 J cm^{-2} coincides with the primary melt front reaching to half of the amorphous layer thickness. An appreciable amount of copper appears on the surface as a result of segregation in the primary melt. Copper is taken to the (*a*-Si)–(*c*-Si) interface because of segregation at the resolidification front which moves inward with the secondary melt. Figure 1(e) shows the result of a 0.53-J-cm^{-2} pulse; the primary melt depth is 185 nm. As a result of the small width of the remaining amorphous layer (40 nm) and the low copper concentrations in this region the secondary melt causes only minor changes in the profile near the interface.

The large amount of copper which is still present after crystallization of the primary melt [see Figs. 1(c)–1(e)] can be explained by solute trapping due to a very high speed of the resolidification front. When *a*-Si melts at a lower temperature than the melting temperature of *c*-Si, it forms a liquid which is undercooled with respect to *c*-Si and crystallization may occur very fast.[14] The same argument may hold for the copper which remains behind after crystallization of the secondary melt [see Figs. 1(a)–1(d)], but in this case there is a second possibility. When the liquid layer which propagates the secondary melt is thin, the copper concentration in the melt becomes very high and an appreciable amount of copper can be built in the crystal. However, at this moment, we cannot distinguish between these two effects.

For 0.70 J cm^{-2}, the copper concentration profile is found to be reduced over the full depth of the amorphous layer and segregated at the surface. From this we conclude that the primary melt has reached the depth of the (*a*-Si)–(*c*-Si) interface, which has been confirmed also by the observation of channeling in the recrystallized layer. Increasing the energy density further to 0.92 J cm^{-2} leads to improved channeling, but the spectra still reveal some dechanneling due to disorder at the position of the original interface. Between 0.70 and 0.92 J cm^{-2} the primary melt depth does not change, but the temperature in the liquid layer (the thickness of which is that of the originally amorphized layer) rises. This results in a lower rate of crystallization and a very effective segregation of copper to the surface at 0.92 J cm^{-2} [see Fig. 1(f)]. Dechanneling at the original interface is absent when pulsed-laser irradiation is performed at 1.01 J cm^{-2}, at which energy density good epitaxial regrowth is obtained, indicating that melting beyond the depth of the (*a*-Si)–(*c*-Si) interface has occurred.

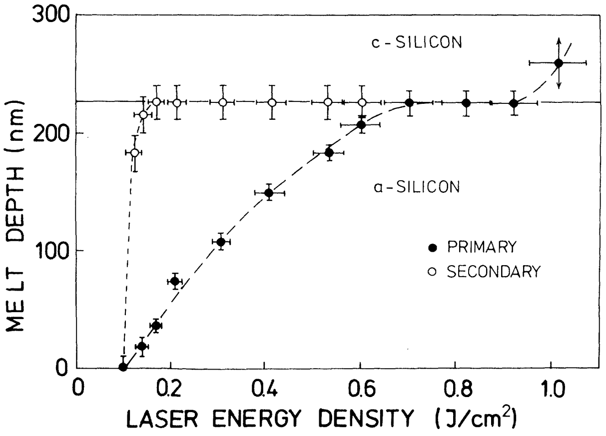

FIG. 2. Primary (solid circles) and secondary (open circles) melt depth as a function of pulsed-laser energy density.

All measurements of the primary and secondary melt depth as a function of laser energy density are summarized in Fig. 2. We have calculated the primary melt depth by subtracting the as-implanted spectrum from the spectrum which is taken after irradiation and integrating the difference spectrum from the surface region down to some depth between the surface and the (*a*-Si)–(*c*-Si) interface. By varying the second boundary, the integral of the difference spectrum is found to go to zero at a particular depth, which we have taken as the primary melt depth. All changes in the copper profile are assumed to be due to melting and segregation during resolidification. We also assume that after crystallization of the primary melt no copper is moved into or taken out of this region by the secondary melt. The secondary melt depth was calculated in a similar way.

As is shown in Fig. 2, surface melting starts at 0.10 J cm^{-2}, while crystallization of the 225-nm amorphous layer is completed at an energy density as low as 0.17 J cm^{-2}! However, it takes 0.7 J cm^{-2} for the primary melt front to reach the (*a*-Si)-(*c*-Si) interface and over 0.9 J cm^{-2} to obtain epitaxial regrowth. Although from these measurements it is not possible to calculate directly the difference in melting temperature between *a*-Si and *c*-Si, the occurrence of a plateau in the relation between laser energy density and primary melt depth is in qualitative agreement with an appreciable melting-point reduction in *a*-Si during pulsed-laser annealing.[11] Both the very low onset for surface melting and the slope in the relation between energy density and melt depth close to the plateau indicate a large difference in heat conductivity between *a*-Si and *c*-Si.[4,5]

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[1] G. L. Olson, J. A. Roth, L. D. Hess, and J. Narayan, in Proceedings of the U. S.-Japan Seminar on Solid Phase Epitaxy and Interface Kinetics, 1983 (to be published), and references therein.

[2] P. Baeri, G. Foti, J. M. Poate, and A. G. Cullis, Phys. Rev. Lett. **45**, 2036 (1980).

[3] M. O. Thompson, G. J. Galvin, J. W. Mayer, P. S. Peercy, J. M. Poate, D. C. Jacobson, A. G. Cullis, and N. G. Chew, Phys. Rev. Lett. **52**, 2360 (1984).

[4] H. C. Webber, A. G. Cullis, and N. G. Chew, Appl. Phys. Lett. **43**, 669 (1983).

[5] D. H. Lowndes, R. F. Wood, and J. Narayan, Phys. Rev. Lett. **52**, 561 (1984).

[6] R. F. Wood, D. H. Lowndes, and J. Narayan, Appl. Phys. Lett. **44**, 770 (1984).

[7] J. Narayan and C. W. White, Appl. Phys. Lett. **44**, 35 (1984).

[8] P. Baeri, S. U. Campisano, G. Foti, and E. Rimini, Phys. Rev. Lett. **41**, 1246 (1978).

[9] P. Baeri and S. U. Campisano, in *Laser Annealing of Semiconductors,* edited by J. M. Poate and J. W. Mayer (Academic, New York, 1982), p. 500.

[10] W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).

[11] See Ref. 9, p. 95.

[12] B. G. Bagley and H. S. Chen, in *Laser-Solid Interactions and Laser Processing — 1978*, edited by S. D. Ferris, H. J. Leamy, and J. M. Poate, AIP Conference Proceedings No. 50 (American Institute of Physics, New York, 1979), p. 97.

[13] F. Spaepen and D. Turnbull, in *Laser-Solid Interactions and Laser Processing—1978,* edited by S. D. Ferris, H. J. Leamy, and J. M. Poate, AIP Conference Proceedings No. 50 (American Institute of Physics, New York, 1979), p. 73.

[14] See Ref. 9, p. 32.