Transitions to Defective Crystal and the Amorphous State Induced in Elemental Si by Laser Quenching

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(Received 1 February 1982)

Large-area, uniform amorphous layers have been formed on Si crystals by means of 2.5-nsec, 347-nm laser pulses. Computations indicate that amorphization at the resolidification interface occurs for isotherm threshold velocities of 18 m/sec on Si(001) and 15 m/sec on Si(111). The amorphous Si is impurity free and structurally similar to conventionally formed material. Below the amorphization velocity thresholds Si(001) reforms good single crystal while Si(111) gives twin defects down to ~ 6 m/sec—a new defect transition.

PACS numbers: 64.70.Dv, 61.40.-a, 42.60.-v

Q-switched-laser irradiation of Si can induce transient melting which leads to rapid resolidification with very high liquid/solid interface velocities, typically several meters per second. This is a new regime of crystal growth in which distinctive impurity trapping and segregation phenomena occur, as reviewed by Poate.[1] Most significantly, at sufficiently high resolidification velocities the crystal lattice itself is unable to restructure and an amorphous surface layer can be produced. Rapid resolidification can be achieved by use of short laser pulses,[2] especially with short-wavelength radiation. Indeed, the amorphization of Si directly from the melt was first demonstrated in the important work of Liu *et al.*[3] and Tsu *et al.*[4] who used, respectively, 30-psec and ≈ 10-nsec pulses of ultraviolet (uv) radiation. However, this work generated only very small and irregular patches of amorphous material; the radiation used in each case was spatially nonuniform. This situation has prohibited study of important characteristics of the material, such as the accurate assignment of formation thresholds and the determination of impurity content (laser-induced surface oxidation may occur under some conditions[5]). Therefore, the present experiments were designed to subject relatively large areas of Si to uniform, rapid-quenching conditions by use of large-diameter, uniform radiation pulses. The conditions required to achieve surface amorphization are characterized and related to specific melt resolidification (or isotherm) velocities. The amorphous phase is analyzed in detail and shown not to be impurity stabilized. Furthermore, it is demonstrated that recrystallization interface breakdown can also occur in a lower velocity regime which yields a new fundamental transition from single crystal to defective crystal.

Polished single crystals of (001) and (111) float-zoned Si were irradiated with (2.5 ± 0.2)-nsec pulses of frequency-doubled radiation at 347 nm from a pulse-chopped ruby laser system. Residual ruby radiation at 694 nm was removed from the output beam and the uv radiation, after energy measurement, was passed through a silica light guide diffuser.[6] This gave a 3-mm-diam, speckle-free spot with an exceptionally flat, uniform energy density profile (± 2% over the central 1-mm region). Sample irradiations were performed in pure Ar or N_2 atmospheres and the crystal background temperature was usually 293 K (one sample was cooled to 77 K to give an increased quench rate[7]). The crystal structure of irradiated layers was determined by transmission electron microscope (TEM) examination of plan-view and cross-sectional thinned specimens. Selected samples were also studied by Rutherford backscattering and channeling of 1.8-MeV He^+ ions.

When Si(001) was irradiated with 2.5-nsec 347-

nm radiation pulses of $\lesssim 0.16$ J/cm^2, no detectable change was produced. However, near 0.2 J/cm^2 the optical reflectivity of the annealed surface increased slightly indicating the formation of some amorphous material. This was confirmed by TEM examination which showed [Fig. 1(a)] that the amorphous layer was discontinuous, isolated islands being only ~100 Å thick. With increasing radiation energy density in the range 0.2–0.3 J/cm^2 the amorphous layer became continuous and increased in thickness up to a mean value of ~150 Å [see Fig. 1(b)]. The optical reflectivity of the surfaces also increased. However, with further slight increase in energy density above 0.30 J/cm^2 the amorphous layer thickness decreased rapidly to zero. This was a consequence of an accompanying decrease in thermal quench rate (see below) which fell below the amorphization threshold. Figure 1(c) shows a typical (001) layer annealed with an energy density above this threshold and it is clear that high-quality crystal free of extended defects re-formed upon recrystallization.

The annealing behavior of Si(111) was significantly different. Once again the onset of amorphization occurred somewhat below 0.2 J/cm^2 though at an energy density value apparently ~10% lower than for Si(001). However, for both Si orientations, it was difficult to estimate this threshold accurately since the initial reflectivity change was small. A typical Si(111) sample near this threshold is shown in Fig. 1(d) where the thin (~100 Å) nonuniform amorphous layer is evident. Increasing the radiation energy density increased the amorphous Si thickness but, in this case, it was not until ~0.55 J/cm^2 that an amorphous-to-crystal transition was observed. Thus, for Si(111), amorphous layers up to ~800 Å in thickness [Fig. 1(e)] could be produced. In addition, Figs. 1(e) and 1(f) show that amorphization ceased to occur as defects in an initially narrow band at the amorphous/crystal interface began to extend towards the surface. This high-energy-density (low-quench-rate) threshold corresponded to the point at which the melted region recrystallized to give a high density of microscopic crystal defects. These defects have been found[8] to be mainly microtwin lamellae and they persisted for annealing over a wide range of higher energy densities: Fig. 1(g) shows a typical result. Indeed, only at the low quench rate achieved, for example, by use of a 16-nsec uv pulse at 1.2 J/cm^2 was it possible to almost suppress defect formation in Si(111).

The nature of the amorphous solid produced at high quench rates was studied in a number of ways. A TEM diffraction pattern obtained from a typical amorphous layer is shown in Fig. 2(a) (chemical thinning was used to avoid ion damage). Strong diffuse scattering bands are evident—up to five were visible in the original negative. The intensity maxima of the first two are at ~0.31 and 0.57 Å^{-1}; these values and the widths of the bands themselves are characteristic of normal

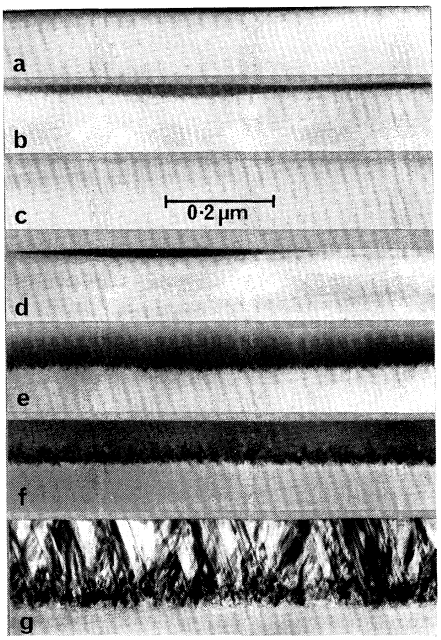

FIG. 1. Cross-sectional TEM images of Si layers irradiated with 2.5-nsec uv pulses. Si(001): (a) 0.20, (b) 0.27, and (c) 0.40 J/cm^2; Si(111): (d) 0.20, (e) 0.5, (f) 0.55, and (g) 0.9 J/cm^2.

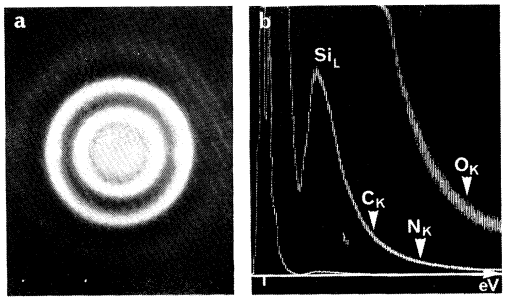

FIG. 2. (a) Transmission-electron diffraction pattern given by amorphous Si. (b) Transmission-electron energy-loss spectrum given by amorphous Si: Different curves represent different gain settings; K x-ray edge energies of C, N, and O indicated.

amorphous Si formed, for example, by ion implantation. The absence of structural units in the laser-quenched amorphous Si down to at least ~10 Å was confirmed by high-resolution TEM imaging. Direct elemental analysis was carried out by transmission-electron energy-loss spectrometry. A spectrum obtained from an amorphous layer of ~400 Å thickness is shown in Fig. 2(b). The expected Si_L loss peak is present at ~140 eV. However, no features were present in the spectrum at the loss energies of the C_K, N_K, and O_K x-ray edges. Thus, these impurities were absent down to the detection limit[9] (about 5%) of the technique.

To obtain a sensitive check on the quality of the amorphous material, the regrowth by thermal annealing at 823 K of a 250-Å mean thickness layer on Si(001) (produced by irradiation at 77 K) was studied by means of He^+-ion channeling with the detector in low-angle takeoff geometry. This demonstrated that the annealed layer regrew plane by plane to give essentially perfect crystalline Si. Such regrowth is the signature of impurity-free amorphous Si, the only impurity present being oxygen in $\lesssim 20$ Å of native surface oxide. The actual regrowth rate was somewhat slower than that of amorphous Si formed by ion implantation, as discussed elsewhere.[1] The different analytical studies taken together thus demonstrate that laser-quenched amorphous Si is substantially free of impurities and is structurally similar to amorphous material produced by conventional means. This conclusion is supported by the insensitivity[10] of the amorphization process to ambient conditions.

We have also calculated the thermal quench rates corresponding to the laser energy densities which produced the structure transition thresholds described above. The heat-flow computations employed the same model and single-crystal Si thermodynamic parameters as those used by Baeri *et al.*[11] except that, for 347-nm radiation, the assumed crystal reflectivity was 0.54 and the absorption coefficient was 2×10^5 cm^{-1}. It is important to note that the basic computer model contained the assumption that melt resolidification occurs at the crystal melting temperature (T_{c-l}, 1685 K). However, during cooling the melt will become substantially undercooled. Although, at first, the resolidification interface velocity will increase proportionately, Jackson[12] has proposed that the melt/crystal interface velocity is a peaked function of melt undercooling (because of melt viscosity effects) and has predicted that the velocity maximum for Si(001) (about 10 m/sec) is much greater than that for Si(111) (about 5 m/sec). Therefore, our calculations yield quench rates as 1685-K isotherm velocities: The actual resolidification interface velocities will be somewhat lower, except in the range below ~5 m/sec. Figure 3 summarizes the results and it is seen that the similar amorphization onsets for Si(001) and Si(111) correspond to laser energy densities just above the surface melting threshold, with calculated peak 1685-K isotherm velocities of $\gtrsim 20$ m/sec. Under these conditions the melt temperature falls sufficiently to allow the direct formation of amorphous Si (see below). For Si(001), amorphization ceases when the peak isotherm velocity is less than ~18 m/sec (at 0.3 J/cm^2) and good crystal is then formed. For Si(111), the isotherm velocity must fall below ~15 m/sec (at 0.55 J/cm^2) to inhibit the formation of amorphous Si, although twinned (and faulted) crystal is then formed and velocities of ~6 m/sec (at 1.2 J/cm^2, 16 nsec) are needed to suppress defect production. The formation of defects in Si(111) crystal over a range of moderate quench rates represents the observation of a new transition from single crystal to defective crystal. Its prevalence for

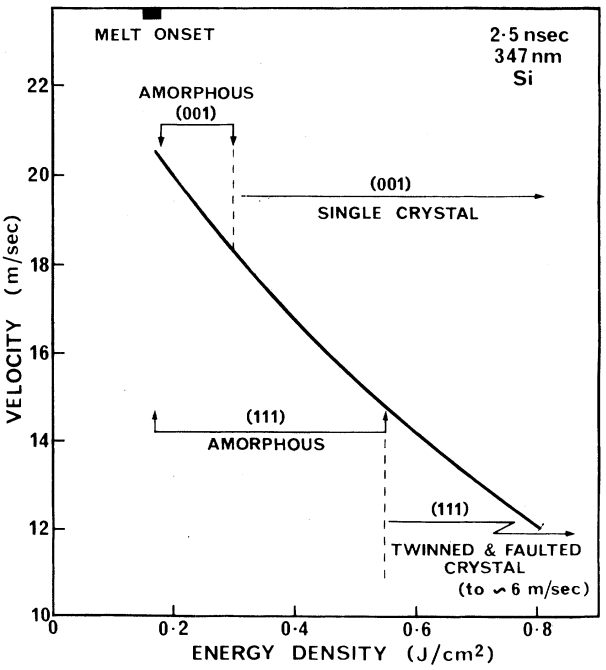

FIG. 3. Computed peak velocity of 1685-K isotherm as a function of pulse energy density showing surface melting threshold and orientation-dependent amorphization and defect formation regimes.

Si(111) is probably due to the ease with which twofold twin rotations can occur around atomic bonds normal to such a surface.

A crucial consideration in these measurements is the amount of melt undercooling as a function of interface velocity. There are predictions based on the free energy difference between amorphous and crystalline Si[13] that the melting (and hence solidification) temperature ($T_{a\text{-}l}$) of amorphous Si is substantially (~ 300 K) lower than $T_{c\text{-}l}$. Spaepen and Turnbull[14] have pointed out that it is thermodynamically possible to form amorphous Si at the recrystallization interface if the amount of undercooling exceeds $T_{c\text{-}l} - T_{a\text{-}l}$. The estimates of Jackson[12] indicate that the undercooling at the above experimentally observed amorphization velocity thresholds can approach 300 K, thus setting a limit on $T_{c\text{-}l} - T_{a\text{-}l}$. The fact that amorphous Si persists to lower quench velocities on the (111) interface will be due to the higher undercooling achieved when compared with an (001) interface moving at the same velocity. While independent rapid-pulse heating measurements[11] indicate that $T_{c\text{-}l} - T_{a\text{-}l}$ can be several hundreds of kelvins, recent work with cw-laser heating[15] does not show such a large depression, possibly because of amorphous Si superheating effects.[16] It will, therefore, be important to quantify the estimates of undercooling so that $T_{a\text{-}l}$ can be accurately determined.

The authors would like to thank Dr. D. T. J. Hurle (Royal Signals and Radar Establishment) and Dr. K. A. Jackson (Bell Laboratories) for helpful discussions, and Mr. D. C. Jacobson (Bell Laboratories) for technical assistance.

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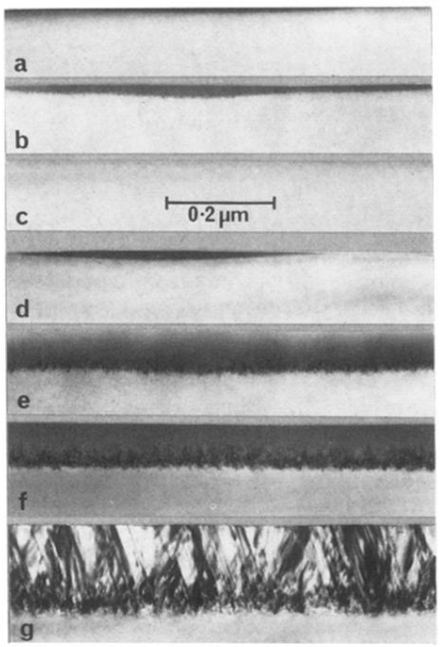

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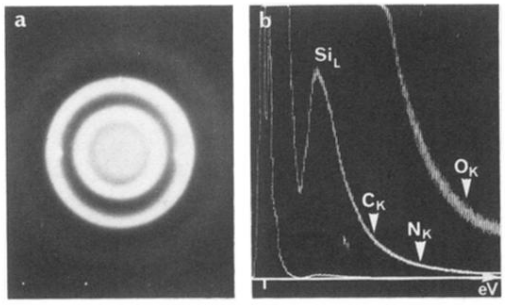

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