

Pulsed-Laser-Irradiated Silicon Studied by Time-Resolved X-Ray Absorption (90–300 eV)

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We report the first x-ray absorption spectra of pulsed-laser-irradiated amorphous Si around the Si L edge, recorded with a time resolution of 18 ns. At irradiances above 0.17 J/cm^2 significant differences are found from the spectrum of amorphous Si. The disappearance of the characteristic Si $L_{II,III}$ edge structure at 100 eV and the decrease in overall absorption are interpreted in terms of the metallic character of liquid Si and the formation of droplets, respectively.

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Several time-resolved (TR) techniques such as optical reflectivity,^{1,2} electrical conductivity,³ and x-ray diffraction⁴ measurements have indicated that intense picosecond or nanosecond pulsed-laser irradiation of Si (coordination number 4) induces an abrupt temperature rise in the solid state and an extremely fast phase transition to a liquid state. It remains to be solved whether or not the short-lived liquid state, l -Si, produced on picosecond or nanosecond time scales,^{1,2} is entirely equal to normal liquid Si (coordination number 6.5). In order to clarify the nature of fast phase transitions, such as pulsed-laser annealing^{1,2} and explosive crystallization,^{3,5} it is important to study both electronic and geometric structure of l -Si. TR electron diffraction,⁶ TR low-energy electron diffraction,⁷ and TR x-ray diffraction⁴ techniques have been used to obtain information about the long-range structure of l -Si. They reveal that long-range order disappears in the liquid states produced. There have been no TR experiments on the electronic structure and local atomic arrangement of l -Si.

This paper reports the first observation of the L -absorption spectrum of l -Si under various conditions of irradiation. The spectra give direct information on the evolution of the electronic structure; in addition, an attempt is made to analyze the extended x-ray absorption fine structure (EXAFS) in order to establish the local atomic arrangement. Thus, we demonstrate that time-resolved x-ray absorption spectroscopy is a useful method for the study of the various phases of pulsed-laser-irradiated materials (see also Epstein *et al.*⁸).

Amorphous Si (a -Si) films of 600 \AA thickness were produced by electron-beam evaporation of Si and deposition on carbon films of 440 \AA thickness (on a NaCl film deposited on glass) in a vacuum of 7×10^{-8} Torr and at around 220°C to prevent in-diffusion of O_2 and H_2O . The a -Si on C (a -Si/C) films were floated off in distilled water and picked up on stainless steel sample holders with holes of 3 or 4 mm diameter.

X-ray absorption and EXAFS measurements were carried out by transmission of a broad continuum of

x-ray beam through the a -Si/C foil and dispersion of the radiation afterwards. As an x-ray source we used a plasma that was created by focusing of the output of a frequency-doubled Nd-doped yttrium aluminum garnet/glass laser (7 J, 15 ns, 523 nm) on a Ta target. The pulse width of the x rays was 15 ns. Our measuring system allows us to record an absorption spectrum in one single laser shot with good statistics. The energy resolution was approximately 4 eV. Part of the experimental technique was described in an earlier paper²; more details will be given in a later publication.

A fraction of the laser output was used to irradiate the a -Si/C foils. The laser beam was focused to 4–5 mm, while the diameter of the x-ray probe beam on the sample was approximately 0.2 mm. The laser beam has a top-hat spatial profile, i.e., close to $\text{TEM}_{00} + \text{TEM}_{01}$. The irradiation energy density was varied from 0.1 to 3.6 J/cm^2 with an uncertainty of $\pm 30\%$. To do time-resolved measurements, the irradiation laser pulse on the foil was followed by the x-ray probe pulse with a variable delay time τ_d of 12, 30, and 60 ns.

Figure 1 shows typical x-ray absorption spectra ranging from 90 to 300 eV at τ_d of 12 ns for various annealing energy densities. Note that identical results were obtained for free-standing a -Si foils of 600 \AA thickness. The laser energy density can be roughly divided into three ranges. Range I is below approximately 0.17 J/cm^2 , at which energy density we observe the first significant changes in the absorption spectra. This value is therefore thought to correspond to the annealing threshold E_{th} . Range II is from 0.17 to approximately 1.0 J/cm^2 , where the l -Si phase is produced so that annealing takes place.² Range III is above 1.0 J/cm^2 , at which density further changes in the spectra are observed. This corresponds to the damage threshold E_d , as we confirmed by TR optical transmission measurements.

For the spectrum 1(a) without pulsed-laser irradiation, a clear edge and a broad peak are seen at 98 and 125 eV, respectively. This absorption spectrum is in good agreement with x-ray absorption measurements

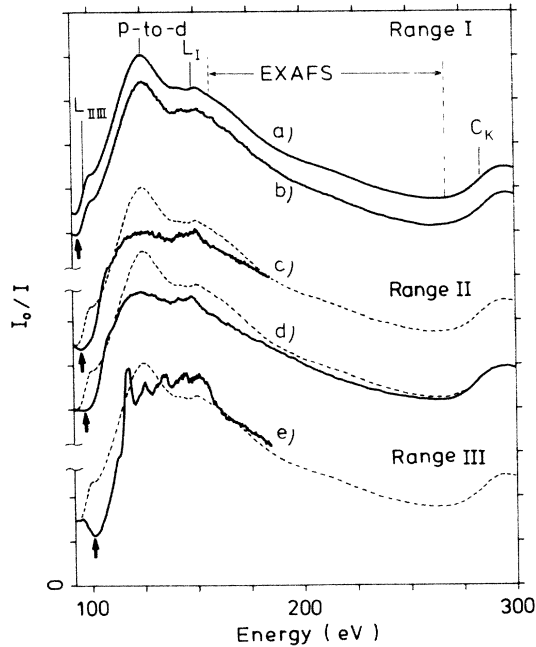


FIG. 1. Typical x-ray absorption spectra of the Si/C foil at τ_d of 12 ns for laser energy densities from 0 to 3.6 J/cm^2 ; i.e., (a) without laser irradiation, (b) 0.12, (c) 0.30, (d) 0.60, and (e) 3.6 J/cm^2 . The edge at 280 eV is due to the carbon foil C-K absorption. The dotted lines show the spectrum (a) for comparison. The arrows indicate the onset for the Si- $L_{II,III}$ absorption. The vertical axis indicates the ratio of the incident x-ray intensity I_0 to that of the transmitted x rays, I . The spectra (a)–(d) are displaced upward for clarity.

by Brown, Bachrach, and Shibowski.¹⁰ The edge comes from Si- $L_{II,III}$ absorption corresponding to excitation of an electron from the $2p$ core level to the bottom of the conduction band.¹⁰⁻¹² The broad absorption is thought to be due to the so-called “centripetal barrier” for p -to- d transitions.¹¹ Hereafter we call this the “ p -to- d maximum.” The Si- L_I edge is also observed at about 150 eV; this edge corresponds to excitation from the $2s$ core level to the bottom of the conduction band.^{10,11} It should also be stressed that in the energy range from 155 to 270 eV EXAFS oscillations can be observed. Fourier transformation of this oscillation indicates a Si-Si atomic distance of $2.30 \pm 0.10 \text{ \AA}$, which shows a good agreement with literature values (2.35 \AA).

At an energy density of 0.12 J/cm^2 in range I, there is no significant change in the spectrum, except reduction of the EXAFS signal. [See Fig. 1(b).] This is due to the temperature rise. At energy densities of 0.30 and 0.60 J/cm^2 in range II [Figs. 1(c) and 1(d)], the first observation is a decrease in total area. This will be discussed below. The structure characteristic of the Si- $L_{II,III}$ absorption at 100 eV nearly disappears. The observed spectra are much different from the original

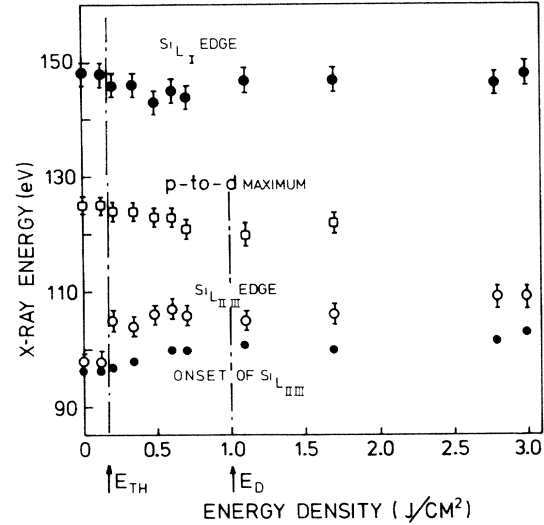


FIG. 2. Onset of the Si- $L_{II,III}$ absorption, Si- $L_{II,III}$ and Si- L_I (effective) edges, and p -to- d maxima as functions of the laser energy density. (E_{th} = annealing threshold; E_d = damage threshold.)

one for a -Si. Although the actual onset of the Si- $L_{II,III}$ absorption, shown by the arrows in Fig. 1, is not changed considerably, there is a distinctly slower rise to the p -to- d maximum. If we define simply the point of maximum slope as an “effective edge” of the Si- $L_{II,III}$ in ranges II and III, there is a clear edge shift of about 7 eV to higher energy. It should also be noticed that there is a decrease of the p -to- d maximum height and a small shift of the peak position to lower energy. The Si- L_I edge seems to be unchanged or to move slightly to lower energy, in contrast to the behavior of the Si- $L_{II,III}$ edge. The EXAFS amplitude becomes so weak that the Si interatomic distances in l -Si can no longer be determined. For the EXAFS amplitude to become equal to the noise level, a temperature rise to $\geq 1400 \text{ K}$ is required, which is to be compared to the Si melting point of 1690 K.

At an energy density of 3.6 J/cm^2 (range III), a complicated structure near the absorption peak and a large shift in the Si- $L_{II,III}$ edge can be seen in spectrum (e) of Fig. 1. The complicated peaks may be connected with the formation of a Si plasma. A detailed analysis will be published elsewhere.

The onset of the Si- $L_{II,III}$ absorption, the Si- $L_{II,III}$ and Si- L_I (effective) edges, and the p -to- d maximum have been plotted as functions of the energy density in Fig. 2. The onset shows a slight change around E_{th} and gradual change far above E_{th} . On the other hand, the Si- $L_{II,III}$ effective edge shift of about 7 eV to higher energy can be clearly seen at E_{th} . The p -to- d maxima show, however, a slight shift to lower energy and the Si- L_I edge also seems to move to lower energy by 2–3 eV. This fact indicates strongly that the ob-

served edge shifts cannot be attributed to a chemical shift of the core levels, since opposite shifts have not been observed in Si compounds such as SiO_2 , Si_3N_4 , SiH_4 , etc.¹⁰

In general, solid Si is thought to have nearly equal amounts of *s*-like and *p*-like states in both the valence (sp^3 bonding states) and conduction [$(sp^3)^*$ antibonding states] bands.^{12,13} On the other hand, in metallic solids *s*-like states tend to lie in the part of the band below E_F , while *p*-like states occur both below and above E_F .^{13,14} On the assumption that *l*-Si is metallic, as is known for normal liquid Si, the edge shifts can be interpreted as follows. According to the dipole selection rule, the final states in the conduction band above the Fermi level E_F which can be reached depend on the symmetry of the initial core state ($2s$ or $2p$) from which the transition takes place. Consequently, the observed large change in the spectra or large shift of the Si- $L_{II,III}$ edge can be attributed to a reduction of the density of $3s$ -like states just above E_F in *l*-Si; i.e., the main transition strength occurs from $2p$ to $4s$ -like and $3d$ -like states. However, the first onset of Si- $L_{II,III}$ absorption is changed little. This indicates that a small amount of $3s$ -like states remains just above E_F . On the other hand, the small change in the Si- L_I edge indicates no or little changes in the density of $3p$ -like states just above E_F for *l*-Si. Both indications are consistent with recent band calculations¹⁴ for normal liquid Si.

Finally, the small shift of the Si- L_I edge to lower energy may be explained by the core-level shift due to screening effects of the conduction electrons in the metallic *l*-Si. A similar shift should occur also for the Si- $L_{II,III}$ edge, but is obscured by the larger shift in the opposite direction, discussed above.

Figure 3 shows the time evolution of the x-ray absorption spectrum at an energy density of 0.30 J/cm^2 over the range up to 60 ns. The most striking feature is that the integrated absorption decreases with time. This is consistent with the known phenomenon of the formation of *l*-Si droplets: The droplet formation introduces a nonlinear compression of the spectra. At $\tau_d = 60 \text{ ns}$ [Fig. 3(d)], the spectrum shows a very small edge structure at 100 eV, similar to that of the solid. This is one piece of evidence that, under the irradiation condition of 0.30 J/cm^2 , partial resolidification takes place at τ_d of 60 ns. For our Si foil, the rapid cooling can only be due to evaporation.

In summary, we have reported for the first time x-ray absorption spectra of Si under intense pulsed-laser irradiation. In the energy range from 0.17 to 1.0 J/cm^2 , corresponding to the annealing range, significant changes in the edge behavior of the Si- L absorption spectra for the *l*-Si have been observed. This direct information on the change in electronic structure is consistent with a metallic character for *l*-Si. It

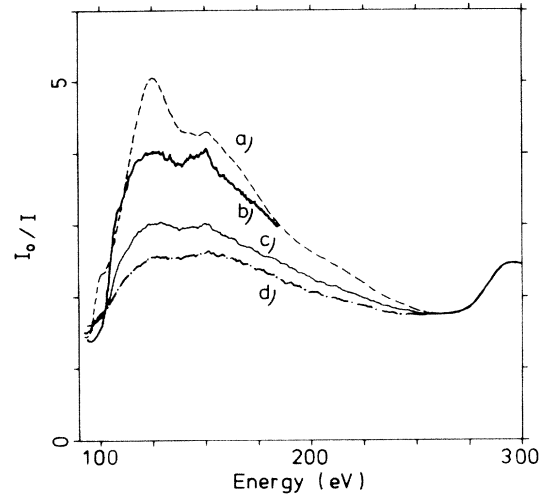


FIG. 3. Time evolution of the x-ray absorption spectra of short-lived *l*-Si produced by irradiation at $0.30 \pm 0.04 \text{ J/cm}^2$. Delay times are (b) 12 ns, (c) 30 ns, and (d) 60 ns. Spectrum (a) is a reference, recorded without laser irradiation.

was found that *L*-shell EXAFS of the *l*-Si has insufficient modulation to extract interatomic distances. Comparison with normal liquid Si is not possible with the present transmission technique. An x-ray absorption experiment in the reflection mode is in progress.

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