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## 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<sup>2</sup> significant differences are found from the spectrum of amorphous Si. The disappearance of the characteristic Si *L*<sub>II,III</sub> 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,<sup>1,2</sup> electrical conductivity,<sup>3</sup> and x-ray diffraction<sup>4</sup> 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,<sup>1,2</sup> 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<sup>1,2</sup> and explosive crystallization,<sup>3,5</sup> it is important to study both electronic and geometric structure of *l*-Si. TR electron diffraction,<sup>6</sup> TR low-energy electron diffraction,<sup>7</sup> and TR x-ray diffraction<sup>4</sup> 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.*<sup>8</sup>).

Amorphous Si (*a*-Si) films of 600 Å thickness were produced by electron-beam evaporation of Si and deposition on carbon films of 440 Å thickness (on a NaCl film deposited on glass) in a vacuum of  $7 \times 10^{-8}$  Torr and at around 220°C to prevent in-diffusion of O<sub>2</sub> and H<sub>2</sub>O. 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 paper<sup>2</sup>; 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 TEM<sub>00</sub>+TEM<sub>01</sub>. The irradiation energy density was varied from 0.1 to 3.6 J/cm<sup>2</sup> 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  $\tau_d$  of 12, 30, and 60 ns.

Figure 1 shows typical x-ray absorption spectra ranging from 90 to 300 eV at  $\tau_d$  of 12 ns for various annealing energy densities. Note that identical results were obtained for free-standing *a*-Si foils of 600 Å thickness. The laser energy density can be roughly divided into three ranges. Range I is below approximately 0.17 J/cm<sup>2</sup>, 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<sup>2</sup>, where the *l*-Si phase is produced so that annealing takes place.<sup>2</sup> Range III is above 1.0 J/cm<sup>2</sup>, 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

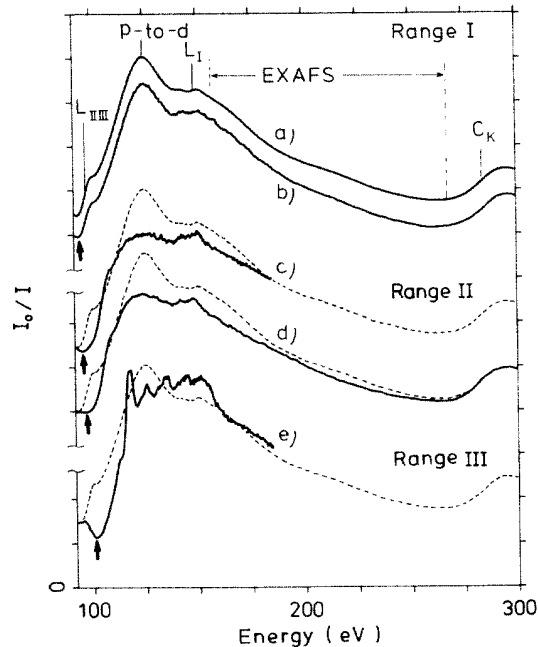


FIG. 1. Typical x-ray absorption spectra of the Si/C foil at  $\tau_d$  of 12 ns for laser energy densities from 0 to  $3.6 \text{ J/cm}^2$ ; i.e., (a) without laser irradiation, (b) 0.12, (c) 0.30, (d) 0.60, and (e)  $3.6 \text{ J/cm}^2$ . The edge at 280 eV is due to the carbon foil C-K absorption. 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.<sup>10</sup> 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.<sup>10-12</sup> The broad absorption is thought to be due to the so-called “centripetal barrier” for  $p$ -to- $d$  transitions.<sup>11</sup> 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.<sup>10,11</sup> 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  $\text{\AA}$ ).

At an energy density of  $0.12 \text{ J/cm}^2$  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  $0.60 \text{ J/cm}^2$  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

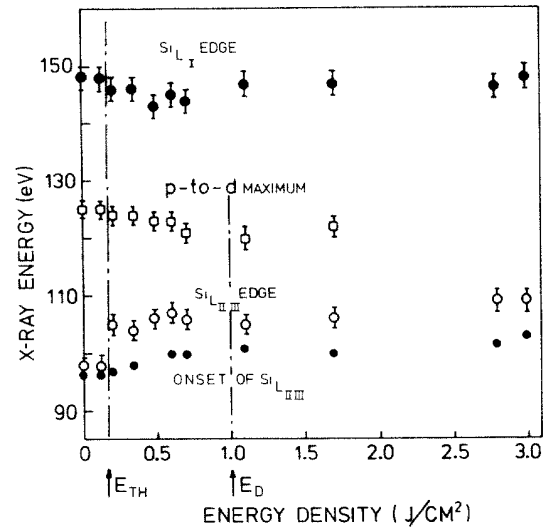


FIG. 2. Onset of the Si- $L_{II,III}$  absorption, Si- $L_{II,III}$  and Si- $L_I$  (effective) edges, and  $p$ -to- $d$  maxima as functions of the laser energy density. ( $E_{th}$  = annealing threshold;  $E_d$  = damage threshold.)

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  $3.6 \text{ J/cm}^2$  (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  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiH}_4$ , etc.<sup>10</sup>

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.<sup>12,13</sup> 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  $E_F$ .<sup>13,14</sup> 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 calculations<sup>14</sup> 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  $0.30 \text{ J/cm}^2$  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  $0.30 \text{ J/cm}^2$ , partial resolidification takes place at  $\tau_d$  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  $1.0 \text{ J/cm}^2$ , 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

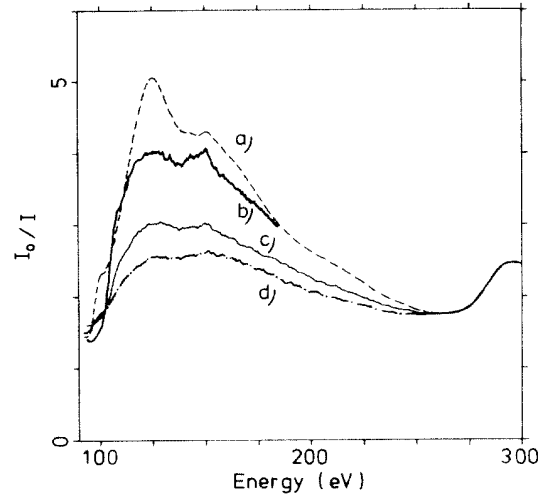


FIG. 3. Time evolution of the x-ray absorption spectra of short-lived *l*-Si produced by irradiation at  $0.30 \pm 0.04 \text{ J/cm}^2$ . Delay times are (b) 12 ns, (c) 30 ns, and (d) 60 ns. Spectrum (a) is a reference, recorded without laser irradiation.

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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