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/cm² 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, 1-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 1-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 1-Si.

This paper reports the first observation of the Labsorption 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 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 7×10^{-8} Torr and at around 220 °C to prevent in-diffusion of O₂ and H₂O. 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 paper⁹; 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 $TEM_{00} + TEM_{01}$. The irradiation energy density was varied from 0.1 to 3.6 J/cm² with an uncertainty of $\pm 30\%$. To do time-resolved measurements, the irradiation laser pulse on the foil was followed by the xray 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 Å 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 $E_{\rm th}$. Range II is from 0.17 to approximately 1.0 J/cm², where the *l*-Si phase is produced so that annealing takes place.² Range III is above 1.0 J/cm², 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/cm²; i.e., (a) without laser irradiation, (b) 0.12, (c) 0.30, (d) 0.60, and (e) 3.6 J/cm². 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_1 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 ± 0.10 Å, which shows a good agreement with literature values (2.35 Å).

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/cm² 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_1 (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- $L_{\rm ILIII}$ 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_1 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 1-Si can no longer be determined. For the EXAFS amplitude to become equal to the noise level, a temperature rise to \geq 1400 K is required, which is to be compared to the Si melting point of 1690 K.

At an energy density of 3.6 J/cm² (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 observed 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 $E_{\rm F}$, while *p*-like states occur both below and above $E_{\rm F}$.^{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 3*d*-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 $E_{\rm F}$. On the other hand, the small change in the Si- L_1 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- $L_{\rm I}$ edge to lower energy may be explained by the core-level shift due to screening effects of the conduction electrons in the metallic *I*-Si. A similar shift should occur also for the Si- $L_{\rm II,III}$ 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/cm² 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 $\tau_d = 60$ 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/cm², 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 xray 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 ± 0.04 J/cm². 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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