A time-resolved x-ray absorption study of amorphous Si during pulsed laser irradiation

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We report the first time-resolved x-ray absorption measurements on pulsed laser irradiated Si in the photon energy range from 90 to 300 eV, at irradiation energy densities up to 4 J/cm², and at several delay times between irradiation pulse and x-ray probe pulse. The absorption spectra recorded at a delay time of 12 ns can be classified in three categories. Below ≈ 0.17 J/cm² only thermal damping of extended x-ray absorption fine-structure (EXAFS) oscillations is observed. Between ≈ 0.17 J/cm² and ≈ 1 J/cm² annealing takes place. Several changes are observed, among which a ≈ 7 -eV $L_{II,III}$ edge shifts towards higher energy, while the L_I edge remains approximately at the same position. This edge shift behavior is explained by a largely reduced 3s density of states of the conduction band. This supports the idea that pulsed laser molten Si has a metalliclike structure. Thermal damping in this region is so strong that EXAFS oscillations are no longer visible. This is consistent with a lattice temperature above or equal to the melting temperature of Si. Above 1 J/cm², the damage region, further edge shifts and the development of several peaks are observed. Clear cooling effects are visible at long delay times (60 ns) between irradiation and x-ray probe pulse. Cooling on this time scale can only be explained by evaporation of Si.

I. INTRODUCTION

Although Si is a semiconductor in the solid state, molten Si exhibits the electronic properties of a metal. For example, the electrical resistivity and reflectivity of molten Si reach the values of metals. X-ray diffraction measurements recorded slightly above the melting point of Si show large structural changes; in the liquid phase a bond distance of 2.6 Å and a coordination number of 6.5 are reported.¹ In the solid phase these values are 2.35 Å and 4, respectively. Furthermore, liquid Si shows a 10% contraction compared to the solid state.

Pulsed laser irradiation of Si causes an extremely fast temperature rise and solid-liquid-phase transition. Time-resolved (TR) measurements showed an enhanced optical reflectivity and conductivity during pulsed laser annealing (PLA).^{2,3} Several other time-resolved techniques, like TR-x-ray diffraction,⁴ TR-low-energy electron diffraction (LEED),⁵ and TR electron diffraction,⁶ have been applied to the study of PLA Si. Nevertheless, it is still not established unequivocally that Si molten by PLA has the same structure as steady-state molten Si. This problem is an important key to the understanding of the extremely fast phase transition upon pulsed laser irradiation.

For a review of pulsed laser irradiation we refer to Ref. 7. At present the normal melting model⁸ is the most commonly accepted one. However, some observed effects have been explained with a plasma model,⁹ in which a dense electron hole plasma is created by laser irradiation. In this model the lattice temperature is hardly raised during annealing.

In this paper we report the first time-resolved x-ray absorption measurements on pulsed laser irradiated Si. Our measurements differ from the usual anneal experiment in

two aspects. First of all, thin Si foils were used instead of wafers. Second, the measurements were carried out in vacuum, while common anneal experiments take place under atmospheric pressure. Similar experiments, using reflection-mode EXAFS around the Si K edge, are in progress at the Rutherford Appleton Laboratory.¹⁰

We performed x-ray absorption measurements at irradiation energy densities up to ≈ 4 J/cm² and delay times between irradiation pulse and probe pulse of 12, 30, and 60 ns. The time resolution amounts to 18 ns, i.e., the x-ray pulse duration.

The measurements are performed on amorphous Si films in the photon energy range between 90 and 300 eV, with an energy resolution of ≈ 4 eV. This energy range includes the Si- $L_{II,III}$ edge as well as the Si- L_I edge. In general, the structure in the x-ray absorption around the edge gives information about the density of final states while, at the same time, effects like multiple scattering affect this region. The absorption region starting about 30 eV above the edge shows damped oscillations (EXAFS). From the period and amplitude of the oscillations neighbor distances and coordination numbers can be derived. We note that this technique, in contrast to the earlier mentioned techniques, is sensitive for the local atomic arrangement.

II. EXPERIMENT

An outline of the experimental arrangement is shown in Fig. 1. X-ray pulses are generated by focusing the output of a frequency doubled Nd-YAG/glass laser (7 J, 18 ns, 532 nm), on a metal target (Ta). In this way a hot plasma is created which emits an intense continuum of x rays. A total of $\approx 10^{16}$ photons/shot is emitted in our energy range, ≈ 90 –300 eV, over 2π sr, in ≈ 18 ns. A toroidal mirror creates a stigmatic image of the source, which acts as the object for a grating polychromator. The grating disperses the whole

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FIG. 1. Experimental setup for time-resolved x-ray absorption. A 20-J 18-ns YAG/glass laser pulse is frequency doubled (SHG) twice to give a 1-J "pump" beam and a 8-J "probe" beam. The latter can be delayed by up to 60 ns. (BS = beam-splitter.) The 8-J probe beam creates a plasma which emits a continuum of soft x rays. After transmission through the (Si) sample foil, the x rays are dispersed by a polychromator and detected by a multi-channel x-ray detector. Complete x-ray absorption spectra from 90 to 300 eV are recorded in one laser shot.

spectrum from 90 to 300 eV on a multichannel x-ray detector. The energy resolution of the total system amounts to 4–6 eV. The system was calibrated on a number of well-known plasma emission lines from Ti and Al targets.

The stigmatic image created by the mirror has a diameter of 0.17 mm and is used as an x-ray probe for the Si foils. At this position the x-ray beam is not yet dispersed, therefore this setup is insensitive for inhomogeneities in foil thickness.

In the time-resolved studies on laser irradiated Si foils, the x-ray beam is crossed with a laser beam (3–4 mm diam) at the position of the foil. This pump and probe setup is aligned in the following way: first of all, the foil is positioned such that the toroidal mirror images green laser light scattered from the x-ray generating plasma exactly in the center of the Si foil. To align the irradiation beam, a He–Ne laser is coaligned with the center of the irradiation beam. Now the He–Ne beam is adjusted such that it coincides with the green spot visible on the Si foil. We note that the misalignment between the x-ray beam and the visible light scattered from the plasma is less than 0.2 mm.

To obtain the irradiation beam, the fundamental output of the first frequency doubling crystal was separated from the doubled light by means of a beam splitter. This part is frequency doubled by a second frequency doubling crystal, after which this beam is directed to the Si foil. The use of two doubling crystals, which are nonlinear devices, makes the intensity of the probe beam somewhat less stable than the rest of the laser system. We estimate an error of about 15% in the total irradiation energy due to shot-to-shot fluctuations and the accuracy of the laser energy measurement. The laser itself is very stable; output energy fluctuations of typically less than 4% are measured. Furthermore, it has a top-hat beam profile (TEM_{00} and TEM_{01}) without any visible hot spots in a burn-paper pattern. Energy measurements behind a 0.4×0.5 -mm² slit revealed intensity variations of less than 25% over the 4-mm-diam laser irradiation beam. This combined with the total energy fluctuations yields an accuracy of 30% for the irradiation energy density at the

probe spot on the foil. To check the influence of intensity variations on a smaller scale, we performed a number of x-ray absorption measurements using a diffuser plate. The results of measurements using this diffuser did not reveal any changes compared to the measurements without diffuser.

In order to probe the Si foil at variable delay times between the irradiation beam and the probe beam, an optical delay line was inserted in the beam which creates the x-ray emitting plasma. Delay times between 12 and 60 ns can be realized without any problems; large delay times are not practical since the required delay line is very long (> 20 m).

This x-ray absorption apparatus is of novel design and was especially designed to perform EXAFS and surface-EXAFS measurements in the soft x-ray region. A detailed description of x-ray source, polychromator, and multi-channel detector can be found in Refs. 11–13.

Due to the small absorption length in the soft x-ray region, the Si foil has to be very thin. Consequently, the foils are very vulnerable. In order to obtain sufficient mechanical strength, a C backing is used to support the Si foils. The height of the C_k edge can be used for normalization purposes. Possible effects of the C backing will be discussed later.

The amorphous Si foils were prepared by electron gun evaporation of 660-Å Si on top of a 440-Å-thick C foil. The C foil was supported by a glass substrate with a layer of NaCl in between the glass and the C. To avoid contamination of the Si by H₂O and O₂, evaporation was done at a pressure < 10^{−8} Torr and at a substrate temperature of $\approx 220^\circ\text{C}$. The Si–C foils were floated off in distilled water, after which they were picked up on stainless-steel supports with holes of 3–4 mm diam.

To check the influence of the C layer, a number of foils were electron gun evaporated on a glass substrate with only NaCl. In this case the foils were picked up on a 70% transparent Mo mesh.

III. RESULTS

A. Unirradiated Si

Two Si absorption spectra in the energy range of 90–300 eV are shown in Fig. 2. Both spectra were recorded in the following way: first, a reference spectrum (I_0) was recorded, without a Si–C foil in the x-ray beam. Second, a raw absorption spectrum (I) was recorded with the Si foil in the beam. By dividing the reference spectrum by the raw absorption spectrum, all instrumental effects cancel. The absorption coefficient times foil thickness is obtained by taking the logarithm of I_0/I . In steady-state measurements many shots can be accumulated to improve the statistics. In this way more accurate information can be derived from the EXAFS part of the spectrum.

The lower curve of Fig. 2(a) is the result of 10 shots each for raw absorption and reference spectrum, and the upper curve (shifted upward for clarity) is the result of one shot for the raw absorption and 10 for the reference.

All the essential Si features¹⁴ are present in the 10-shot as well as in the single-shot measurement. The Si–L_{II,III} edge (2p to conduction-band transition) is visible around 100 eV. We clearly observe an onset located at ≈ 96 eV, and a shoul-

FIG. 2. (a) Lower curve: result of an x-ray absorption measurement around the Si $L_{II,III}$ edge, recorded by dividing a reference spectrum (10 accumulated shots, with the Si foil in the x-ray beam) by a raw Si absorption spectrum (10 accumulated shots, with the Si foil in the x-ray beam). All essential Si structures are visible ($L_{II,III}$ edge at ≈ 98 eV, L_I edge at ≈ 151 eV); additionally, EXAFS oscillations are visible above 151 eV. Upper curve: same as lower, but shifted upward and recorded using 1 laser shot for the raw Si absorption spectrum. In both curves the C_k edge is visible at ≈ 285 eV due to the carbon backing of the foil. (b) Lower curve: the EXAFS oscillations of the lower curve of (a), after a background subtraction and transformation to electron wave-vector space. Upper curve: same as lower curve, but displaced upward, for the single-shot measurement. (c) Fourier transform (FT) of the EXAFS oscillations in the lower curve of (b). The FT peaks at ≈ 2.11 Å. After a phase shift correction a Si bond distance of 2.32 ± 0.08 Å is found, which compares well with the x-ray diffraction value of 2.35 Å. Inset: single-shot measurement.

der at ≈ 101 eV. The point of maximum slope, which we will from now on call the effective edge, is located at ≈ 98 eV. A hump around 125 eV is due to the maximum in p -to- d transition probability and the Si- L_I edge (2s to conduction-band transition) is visible at ≈ 151 eV. Additionally, we observe EXAFS oscillations in the region above the L_I edge. The range over which the oscillations can be observed is limited by the presence of the C_k edge at 285 eV.

An absorption spectrum recorded from Si supported by a mesh showed an identical absorption behavior, the only difference being a largely reduced C_k edge. The absence of any difference in spectral shape indicates that no significant amount of SiC is formed in the Si-C foil.

Our unirradiated Si spectra, multishot as well as single shot, are in excellent agreement with the Si x-ray absorption spectra reported by Brown *et al.*,¹⁴ which were recorded with use of synchrotron radiation. In our spectra less detail of the edge structure is resolved due to a lower resolution. On the other hand, our spectra cover a much broader energy range such that EXAFS oscillations are observable.

1. EXAFS analysis

EXAFS oscillations arise from interference of an outgoing photoelectron wave with its backscattered component from neighboring atoms. Usually EXAFS is described in terms of the function $\chi(k)$ defined as¹⁵

$$\chi(k) = (\mu - \mu_0)/\mu_0$$

$$= (-1)^l \sum_j A_j(k) \sin[2kR_j + \Delta_j(k)] \quad (1)$$

Here μ is the total absorption coefficient and μ_0 the absorption of the isolated absorber atom, which does not show EXAFS oscillations. In this way the EXAFS signal is normalized to a per atom scale. The summation extends over all neighbor shells j with bond distance R_j . l is the angular momentum of the final state(s) and k the photoelectron wave vector. The wave vector can be found from $k = \sqrt{(h\nu - E_0)2m/\hbar}$ with $h\nu$ the photon energy and E_0 the binding energy of the electron. In the sin term an energy dependent phase shift $\Delta_j(k)$ is present to take into account the phase shift introduced by the potentials of the absorbing and backscattering atom. $A_j(k)$ contains all factors determining the amplitude of the oscillations. In case the neighbor shell j contains identical atoms, $A_j(k)$ is given by

$$A_j(k) = (N_j/kR_j^2)F_j(k)e^{-2\sigma^2k^2}e^{-2R_j/\lambda(k)} \quad (2)$$

For isotropic systems, like amorphous materials, N_j denotes the number of atoms at distance R_j . Two exponential damping terms are present in $A_j(k)$, the first one being a Debye-Waller term to take into account thermal vibrations. The second one includes damping due to the finite mean free path $\lambda(k)$ of the photoelectrons.

To extract structural information from the EXAFS part of the Si absorption spectrum [Fig. 2(a)], a smooth background, in our case a spline polynomial, is subtracted. The remaining oscillations are converted to oscillations in the electron wave vector (k) space. For the zero kinetic energy of the photoelectron we used a binding energy of 98 eV, corresponding to the energy separation between the 2p level and the bottom of the conduction band. The resulting function is shown in the lower curve of Fig. 2(b) for the 10-shot measurement, the result for the single-shot measurement being shown in the upper curve (shifted upward for clarity). In both curves the EXAFS oscillations are clearly visible. To obtain bond distance information the spectrum is frequency analyzed by Fourier transformation. This yields the so-called radial distribution function. This function for unirradiated Si [Fig. 2(c)] peaks around 2.11 Å for the 10-shot measurement. The single-shot measurement [see inset in Fig. 2(c)] shows approximately the same result. The Fourier transforms show a relatively high value at 0 Å. This is due to the fact that only one and a half period is transformed, such that the average value of $\chi(k)$ is not equal to zero.

In order to obtain the bond distance a phase-shift correction has to be added. For $L_{II,III}$ edges the phase shifts are complicated by the fact that transitions are possible from the initial p state to a final state of s or d symmetry. From the tables of Teo *et al.*¹⁶ we calculated a bond distance correction of 0.21 Å. So after the phase correction we find a first-neighbor bond distance of 2.32 ± 0.08 Å, which compares well

with the x-ray diffraction value of 2.35 Å.

The error quoted arises from several sources. First of all the background subtraction may introduce errors. This is especially the case when the background shows structure and/or the amplitude of the oscillations is small compared to the noise level. The choice of E_0 also introduces an error, which, in general, is not very large. In our case this error amounts to ≈ 0.02 Å/eV; with an estimated error in E_0 of 2 eV this yields an error of ≈ 0.04 Å. Another error, introduced by using calculated values for the phase correction, is of the order of 0.02 Å. In our case the limited range over which the oscillations are usable also influences the accuracy. It makes it difficult to determine the background and leads to peak broadening in the Fourier transform.

We estimate an overall accuracy of ≈ 0.08 Å for the 10-shot measurement and ≈ 0.1 Å for the single-shot measurement. The largest contribution to this error is due to the background subtraction.

From this analysis we conclude that although the region in which the EXAFS wiggles can be observed is rather small, we are still able to derive the proper bond distance, even with single-shot measurements. Furthermore, it is noteworthy that the absorption spectrum of Si supported by a mesh yields the same bond distance as the Si-C foils, indicating that no significant amount of SiC is present at the interface (SiC has a bond distance of ≈ 1.86 Å).

B. Pulsed laser irradiated Si

1. Time-resolved optical transmission

In order to assist the interpretation of the TR-x-ray absorption, we first performed some simple preliminary measurements on the behavior at optical wavelengths.

A well-known phenomenon during pulsed laser irradiation is the occurrence of a high reflectivity phase (HRP) for visible light during the molten state.⁷ Time-resolved measurements of the HRP can be used to determine the anneal threshold and the time required to melt the surface. In our case reflectivity measurements turned out to be very difficult due to geometrical constraints. We therefore used time-resolved optical transmission measurements to estimate the amount of energy and time required to melt the Si foil. The amount of transmitted light does not only depend on the reflection but also on the absorption by the foil. Since the absorption of liquid Si is larger than that of amorphous Si by a factor of 10,¹⁷ absorption as well as reflection will reduce the transmission in the molten phase. Calculations based on numbers listed in Table I predict a transmission of 35% for the amorphous Si layer (440-Å C is nearly 100% transparent), and 0.03% during the molten phase. For all our thermodynamical calculations we used the values listed in Table I, most of the values are adopted from Ref. 17.

The foils were pulsed laser irradiated in vacuum with the earlier described irradiation beam. For the probe beam a He-Ne laser was used and for the detection of transmitted light a fast photodiode in combination with a storage oscilloscope. To avoid detection of the irradiation beam an interference filter was placed in front of the photodiode. The result of such measurements showed that ≈ 0.17 J/cm² is required

TABLE I. Data used in our thermodynamical calculations, adopted from Ref. 17.

Melting point	
crystal	1685 K
amorphous	≈ 1400 K
Boiling point	3540 K
Latent heat	
crystal	1790 J/g K
amorphous	1250 J/g K
Heat capacity	≈ 1 J/g
Reflectivity	
amorphous	0.44
liquid	0.70
Absorption coefficient at 633 nm	
[assumed to be equal to absorption at 694 nm (ruby)]	
amorphous	7×10^{-4} cm ⁻¹
liquid	7×10^{-5} cm ⁻¹

to melt the foil (i.e., to observe reduced transmission). Furthermore, we found that the high reflectivity phase already exists at the time the laser pulse reaches its maximum, i.e., within less than 10 ns. In Fig. 3 the laser pulse and optical transmission measurements, at irradiation energy densities of ≈ 0.2 and ≈ 1.1 J/cm², are shown. Both measurements show a strongly reduced transmission, close to 0%, at the time the laser pulse reaches its maximum. The value of the transmission before irradiation is $\approx 35\%$. These values are in good agreement with the calculated values. However, the 1.1 J/cm² measurement shows a rapid rise of the transmission to a value significantly higher than the value before laser irradiation, while the 0.2 J/cm² measurement remains low for several hundred ns.

2. Energy density dependence

In Fig. 4 a number of absorption spectra recorded at a delay time of 12 ns and at several irradiation energy densities are shown. All the spectra of Fig. 4 have been recorded with one laser shot, except for the reference spectrum of unannealed Si, further called "reference," which was recorded using 10 laser shots.

The first changes in the absorption spectrum are found at laser energy densities larger than 0.17 J/cm². Between this

FIG. 3. Results of time-dependent optical transmission measurements of 633-nm light. (a) The irradiating laser pulse (FWHM 18 ns). (b) Optical transmission after irradiation at ≈ 0.2 J/cm². (c) Same as (b) at ≈ 1.1 J/cm².

FIG. 4. Si x-ray absorption spectra recorded at a delay time of 12 ns between irradiation pulse and x-ray probe pulse and several irradiation energy densities. The upper curve is a reference recorded by accumulating 10 shots. The other curves are single-shot measurements recorded at 0.3, 0.6, and 3.6 J/cm². Arrows indicate the first onset of $L_{II,III}$ absorption. An effective $L_{II,III}$ edge (steepest part above onset) as well as the p -to- d maximum and the L_1 edge are indicated. The reference spectrum is reproduced as a dashed curve for direct comparison with the curves recorded at different irradiation energy density.

value and 1 J/cm² the spectral shape remains more or less constant. Examples of this are visible at 0.3 and 0.6 J/cm² in Fig. 4. We note the following: first of all the total absorption, i.e., the total area below the absorption curve, is clearly reduced. The constant height of the C_K edge shows that we are not dealing with an artifact. The shoulder at ≈ 101 eV has disappeared and the effective edge is shifted by ≈ 7 eV to higher energy. However, the absorption onset is shifted less than the effective edge; at 0.3 J/cm² only a small shift of less than 3 eV is visible. Furthermore, a shoulder has developed around 105 eV, the p -to- d maximum is largely reduced, and the L_1 edge remains approximately at the same position. Finally, we observe that the EXAFS oscillations seem to have vanished completely.

Above 1 J/cm² the absorption spectrum is drastically changed. An example of such a spectrum, recorded at ≈ 3.6 J/cm², is shown in the bottom curve of Fig. 4. The onset for absorption is clearly shifted: below 1 J/cm² the first onset is situated around 97 eV, while in this case the first onset occurs around 102 eV. In general, we find a gradual shift of the onset to higher energy above 1 J/cm². A complicated structure, with at least four peaks, is present between 110 and 150 eV. Peaks are visible at 116, 124, 133, and 142 eV. This structure develops gradually above 1 J/cm², starting with the ap-

pearance of the peaks on the low-energy side of the absorption spectrum. Furthermore, the 105-eV shoulder shifts upwards to 110 eV.

In Fig. 5 the (effective) edge shifts are summarized. The data points are derived from measurements at 12-ns delay in the energy density range of 0–3 J/cm². A clear edge shift is visible for the $L_{II,III}$ edge, while the L_1 edge remains at the same position within the error bars. Possibly a small shift to lower energy takes place.

3. Time dependence

The results of measurements at delay times between irradiation and probe pulse of 12, 30, and 60 ns and at an irradiation energy density of ≈ 0.3 J/cm² are shown in Fig. 6. The spectra are displayed on the same scale, and shifted with respect to each other.

The upper curve is a reference spectrum. The 12-ns delay measurement shows the absorption as discussed in III B 2. After 60 ns the shoulder at 101 eV (indicated in Fig. 6 by the arrows) is reappearing. Although the shoulder reappears, the p -to- d maximum is not visible at 60-ns delay time.

At this irradiation energy density the total area below the absorption curves shows a gradual decrease in time. Besides this reduced height and change in edge structure, the spectra do not show any changes as a function of time.

The time behavior at 4 J/cm², Fig. 7, has a more complicated character. The upper curve is again the reference spectrum, and the 12-ns delay time measurement is the one discussed earlier (Sec. III B 2). The 30-ns delay time spectrum shows a peak height reduction of the peaks between 115 and 150 eV. In the spectrum recorded after 60 ns, the additional structure has almost vanished completely. This spectrum

FIG. 5. The $L_{II,III}$ and L_1 (effective) edge shifts and $L_{II,III}$ onset shift as a function of the irradiation energy density at a delay time of 12 ns, derived from spectra like Fig. 4. E_{TH} = threshold energy density for annealing. E_D = damage threshold.

FIG. 6. Time dependence of the x-ray absorption, after irradiation at 0.3 J/cm^2 . The upper curve is a reference, while the other curves are recorded 12, 30, and 60 ns after the irradiation pulse. The vertical scale refers to the 30-ns spectrum; other spectra are shifted for clarity. The arrows indicate the 56 shoulder at 101 eV, which is characteristic for the $L_{II,III}$ absorption edge of solid Si.

starts to resemble the spectrum recorded at irradiation energy density 0.6 J/cm^2 and a delay of 12 ns (compare with Fig. 4). Besides the disappearance of the complex structure, the $L_{II,III}$ edge is shifted back to the position which was found for the 0.6 J/cm^2 , 12-ns delay measurement. Furthermore, we note that the total absorption is approximately constant in time.

4. EXAFS

In order to isolate the EXAFS oscillations from the rest of the absorption spectrum, a smooth background was subtracted from the absorption spectra (see Sec. III A 1). The results for reference and an annealed foil, after transformation to the electron wave vector space, are shown in Fig. 8. The spectra are normalized to equal total area of absorption. Due to different normalization constants the noise levels of the spectra show differences.

In Fig. 8(a) the isolated oscillations of the reference are visible. The Fourier transform (FT) of the reference is visible in Fig. 9(a). Figure 8(b) is derived from a measurement performed at 0.3 J/cm^2 and a delay time of 60 ns, the spectrum which showed the reappearing shoulder at 101 eV. Although the noise level is high, the FT of this spectrum [Fig. 9(b)] shows a clear peak at approximately the Si-Si bond distance.

A same background subtraction and transformation to

FIG. 7. Time dependence of the x-ray absorption, after irradiation at 4 J/cm^2 . The upper curve is a reference, while the other curves are recorded 12, 30, and 60 ns after the irradiation pulse. The vertical scale refers to the 30-ns spectrum; other spectra are shifted for clarity.

FIG. 8. Absorption spectra after transformation to the electron wave-vector space, taken from spectra normalized to equal L -absorption area. (a) unirradiated reference, showing clear EXAFS oscillations. The smooth solid line is a theoretical fit. (b) spectrum recorded 60 ns after irradiation at 0.3 J/cm^2 . The smooth line shows calculated EXAFS oscillations at $T = 1685 \text{ K}$, the melting point of crystalline Si.

k -space was performed for other spectra recorded shortly after pulsed laser irradiation. Only at long delay times (60 ns) and modest irradiation energy densities the vague kind of EXAFS oscillations of Fig. 8(b) could be observed. Successive measurements on one foil, in order to improve the statistics, are not possible since the foil disintegrates shortly after the irradiation pulse.

IV. DISCUSSION

A. Energy density dependence

The time-resolved optical transmission measurements indicate that the anneal threshold (E_{TH}) is located at about 0.17 J/cm^2 ; this coincides with the first changes in the absorption spectra. Another argument that the anneal threshold is located around this energy is provided by thermodynamical calculations, which show that sufficient energy is deposited in the foil to melt it completely at about 0.2 J/cm^2 .

We can clearly distinguish three irradiation energy density ranges, each with its own specific absorption spectrum. The first region, at irradiation energy densities below $\approx 0.17 \text{ J/cm}^2$, shows no changes except for some temperature effects in the EXAFS part of the spectrum. We believe that no

FIG. 9. The Fourier transforms of the EXAFS oscillations of Fig. 8. (a) Unirradiated reference spectrum, after a phase correction the proper bond distance of $2.3 \pm 0.1 \text{ Å}$ is obtained. (b) Result for irradiation at 0.3 J/cm^2 and a delay time of 60 ns. This FT shows a peak at approximately the solid Si bond distance, indicating re-solidification.

annealing takes place in this region. The second region is that between ≈ 0.17 and 1 J/cm^2 ; in this region the first significant changes in edge shape and position are observed. It seems reasonable to assume that annealing takes place in this region. Finally, there is the region above 1 J/cm^2 (E_D), which shows a number of new absorption structures, likely connected with damage⁷ of the Si foil. From now on we will refer to this region as the "damage" region.

1. Edge behavior in anneal region

The observed edge shifts cannot be explained by a chemical shift. A chemical shift should be in the same direction and approximately of the same magnitude for the $L_{II,III}$ and L_I edge. Therefore, the explanation must be found in a changed electronic structure of the final state upon annealing.

In solid Si [see Fig. 10(a)] the valence and conduction band consist of sp^3 and $(sp^3)^*$ hybridized orbitals, respectively.¹⁸ The $L_{II,III}$ edge and the L_I edge are due to transitions from $2p$ and $2s$ states to the bottom of the antibonding conduction band $(sp^3)^*$.

A metallic electronic structure for molten Si can account qualitatively for the observed edge shift behavior. In metals, the s -like states lie, in general, below the Fermi level; the p -like states, on the other hand, are present above and below the Fermi level. By applying the dipole selection rule we find that the lowest level that can be reached from the $2p$ level is not the p -like conduction band but the higher lying $3d$ - and $4s$ -like states. The L_I edge is not affected by this change in electronic structure, since the $2s$ -to-conduction-band transition is still possible. Additionally, screening effects may introduce small shifts for both edges, which can explain a possible small shift to lower energy of the L_I edge.

The above-mentioned model for the electronic structure of pulsed laser annealed Si is supported by theoretical calculations by Gaspard *et al.*¹⁹ In these calculations a crystalline

structure with coordination number 6 is assumed. The calculated density of final states of molten Si shows a dominant p character for the conduction band, while most of the s character is found below the Fermi level. The small amount of s -like states left in the conduction band can account for the fact that the actual onset of the $L_{II,III}$ edge shifts little, even though the effective edge does undergo a considerable shift. An energy-level diagram to illustrate this electronic configuration is shown in Fig. 10(b).

We conclude that the edge behavior supports earlier indirect observations, in TR-reflectivity and TR-conductivity measurements, that pulsed laser annealed Si has a metallic-like electronic structure.^{2,3} These measurements are the first direct observations of changes in the electronic structure of PLA Si.

2. Damage region

Several mechanisms have been considered to explain the peaks in the absorption spectra recorded at high irradiation energy densities (e.g., Fig. 4; 3.6 J/cm^2). Thermodynamical calculations show that an irradiation energy density of 1.2 J/cm^2 is high enough to evaporate the foil completely. Furthermore, ions have been observed during annealing.²⁰ UV emitting laser generated plasmas are generated already at power densities of the order of 10^8 W/cm^2 ,²¹ while 3.6 J/cm^2 corresponds to $2 \times 10^8 \text{ W/cm}^2$. Therefore, models involving ions have to be considered seriously.

Of all the possible Si ions the ion species up to Si^{4+} are most likely since the ionization energies required to create these ions are all between 8 and 45 eV, while 167 eV is required to ionize Si^{4+} .

In principle, the absorption edges of ions are shifted to higher energies with respect to the neutral atom due to reduced screening effects analogous to chemical shifts. A mixture of neutrals and ions (Si , Si^+ , Si^{2+} , Si^{3+} , and Si^{4+}) will give rise to a superposition of the absorption spectra of the individual neutral and ions, i.e., a spectrum containing several structures. Although this may account for some of the observed structures, models based on edge shifts do not give rise to equidistant peaks as we observe.

Of the possible ion species only Si^{4+} shows line absorption at the positions of the peaks in our absorption spectra. The lower ion species do not have any absorption lines in our energy window. In Table II the absorption lines of Si^{4+} (Ref. 22) are listed together with the positions of the peaks in our spectra. Although a reasonable agreement is found for the absorption peaks at and above 124 eV, the peak at 116 eV is not explained. However, sharp absorption edge structures are common and are explained by effects like multiple scattering. The absence of a strong absorption peak at $\approx 105 \text{ eV}$ is more serious. Only a small shoulder is visible at this position, while two very strong line transitions of (ground-state) Si^{4+} are located around this energy.

To see whether it is energetically possible to create enough Si^{4+} ions to observe significant Si^{4+} absorption, consider the following: to melt and evaporate the whole foil 1.2 J/cm^2 is required. The ionization potentials of Si , Si^+ , Si^{2+} , and Si^{3+} are 8, 16, 33, and 45 eV, respectively. From this we calculated that 30.1 J/cm^2 is required to turn the whole foil

FIG. 10. (a) The electron configuration of solid Si. (b) The metalliclike electronic configuration of molten Si which qualitatively explains our measurements and which is supported by calculations by Gaspard *et al.* (Ref. 19).

TABLE II. Comparison between transitions in Si^{4+} and peaks in our x-ray absorption spectra (from Ref. 22).

Energy of Si^{4+} transition (eV)	Average peak position at 4-eV resolution (eV)	Observed peak position (eV)
104.2	105	105 (shoulder)
105.2		116
126.3	128	124
127.6		
128.6		
136.5	137	133
137.1		
144.9	145	142
145.6		
152.9	153	150
153.4		
157.1	157	(near L_1 edge)
157.7		

into Si^{4+} . At 3.6 J/cm² at most 12% of the foil can be turned into Si^{4+} . Such an amount of Si^{4+} could account for significant absorption.

Other models which involve (charged) clusters also have to be considered seriously. Clusters have been observed at high irradiation power densities.²³ To our knowledge, little is known about the absorption properties of clusters in the soft x-ray region.

B. Time dependence

1. Optical transmission

The time-resolved transmission measurements indicate that the anneal threshold is located at about 0.17 J/cm², and that the foil is molten within the duration of the laser pulse. At this energy density the transmission behavior is analogous to that of reflection measurements.² However, the transmission at 1.1 J/cm² shows an unexpectedly rapid rise after an initial decrease. If we assume a reasonable velocity for the Si particles ($< 10^6$ cm/s) and take into account the diameter of the probe beam (< 0.5 mm diam) and that of the irradiation spot (3–4 mm diam), we see that no optical density change takes place within ≈ 100 ns. Therefore, we will have to look for an explanation which excludes the transportation of Si out of the probe zone.

The results of a recent optical reflectivity experiment on pulsed laser irradiated Si by Downer *et al.*,²⁴ have been explained by the formation of clusters of small particles. The occurrence of clusters is also consistent with the work of Bloomfield *et al.*²³ Particles which are small compared to the He–Ne probe laser wavelength (633 nm) do not possess any longer the absorption properties of the liquid material. If we assume spherical particles uniform in size, we can calculate the absorption and scattering by applying the Mie theory to the case of conductive absorbing spheres analog to the method described in Refs. 24 and 25.

For the above-mentioned particles the light intensity

transmitted through a cloud of small particles is completely dominated by absorption. Using the numbers quoted in Ref. 24, we calculated an effective absorption coefficient of $1.3 \times 10^5 \text{ cm}^{-1}$ for small particle absorption. If the whole (600-Å) Si film is converted into small particles, this yields a transmission of 42%. This number is in reasonable agreement with the measurement of Fig. 3(c). If only a part of the foil is transformed into small particles, a highly reflective (70% reflection) and absorbing (absorption coefficient $7 \times 10^5 \text{ cm}^{-1}$) layer remains, such that the transmission of the foil remains low.

2. X-ray absorption

The time behavior of Fig. 6 clearly shows a lowering of the absorption in time. We note that this does not only occur for Si–C foils but also for Si foils supported by a mesh.

For reasons discussed earlier (see Sec. IV B 1) removal of Si out of the probe area does not play a role. This is also supported by the time behavior of the absorption at high irradiation energy density. For instance, in the case of Fig. 7 the total area below the absorption curve remains approximately constant in time. If removal of Si would play a role, the absorption reduction effect should be larger since higher velocities are expected at higher temperatures (irradiation energies).

If we assume a redistribution of matter, like the formation of droplets, we can explain the observed results. Simple calculations in which the foil is transformed in a set of rectangular bars while keeping the total volume constant, show a significant reduction of the total absorption. The exact change in absorption depends on the size of the bars. Cohesive forces will play an important role in such a redistribution of matter.

The absorption behavior at higher irradiation energy densities does not show this decrease in time. This is likely to be due to the higher temperature of the liquid Si, which will decrease the effect of cohesive forces. We note that at high irradiation energy densities ($> 1.2 \text{ J/cm}^2$) enough energy is deposited in the foil to evaporate it completely. To check whether material is ejected, the probe beam was lead parallel to a Si wafer. During pulsed laser irradiation of the wafer at $> 3 \text{ J/cm}^2$, a clear absorption signal, containing some of the damage region absorption structures, was visible. For a thin foil less energy is required to obtain the same result. We conclude that a significant amount of Si is ejected in the damage region. See Ref. 26.

Our measurements suggest that at low irradiation energy densities relatively large droplets are formed (compared to the x-ray wavelength). On the other hand, the optical transmission measurements suggest that a highly dispersed cloud of small particles (clusters) is formed at high irradiation energy densities. Our data are consistent with the data obtained by Bloomfield *et al.*²³ and Downer *et al.*²⁴ However, our measurements do not give sufficient information to arrive at an estimate of the size of the particles under different irradiation conditions.

C. Cooling

In the anneal region we clearly see that the characteristic $L_{II,III}$ edge structure reappears in the 60-ns measure-

ments (Fig. 6), and in the measurements above the damage threshold the characteristic absorption spectrum of the anneal region reappears after 60 ns (Fig. 7). Both effects can only be explained by rapid cooling. Cooling on this time scale cannot take place by radiation or conduction to the foil support, since their characteristic time scales differ by several orders of magnitude from that of the observed cooling time. Another mechanism that can play a role is evaporation of Si. Experimental results of Ref. 27 indeed show that Si is evaporated upon irradiation already at moderate power densities.

The heat capacity of liquid Si amounts to $\approx 3 \text{ J/cm}^3 \text{ K}$, while about $2.5 \times 10^4 \text{ J/cm}^3$ is needed for the liquid-gas-phase transition. From this we calculated that evaporation of a 7-Å-thick layer reduces the temperature by 100 K. We conclude that evaporation of material is a very efficient way of cooling. Probably evaporation is the dominant cooling mechanism in our case. We note that the reappearance of EXAFS oscillations in Fig. 8(b) is extra evidence for rapid cooling.

D. EXAFS

In EXAFS several damping mechanisms play a role: first of all there is thermal damping, which is described in Sec. III A 1. Furthermore, damping occurs due to structural disorder. This type of damping can be included by adding an extra term of the Debye-Waller factor. The structural disorder will definitely increase upon the solid-liquid-phase transition. Unfortunately, it is difficult to estimate the influence of this effect. Nevertheless, a large part of the observed damping can already be explained by thermal effects. In Eq. (2) we see a Debye-Waller damping term

$$e^{-2\sigma^2 k^2},$$

where k is the electron wave vector and σ^2 a factor to take into account the thermal motion of the atoms. Due to the k dependence in the damping term, the EXAFS oscillations will first vanish at high k values.

In order to estimate the damping of the EXAFS oscillations as a function of temperature, we fitted the reference spectrum of Fig. 8(a) with a theoretical spectrum. We assumed the square of the vibration amplitude to be proportional to T and added an extra damping term to account for the other damping effects and the monotonically decaying backscattering amplitude.¹⁶ The Debye-Waller factor was derived from x-ray diffraction values ($\sigma^2 = cT$, with T the temperature in K and $c = 4 \times 10^{-5}$).

The fit with the reference spectrum is shown in Fig. 8(a) as the solid line. The effect of thermal damping is demonstrated by using the same values for the fit parameters and increasing the temperature to 1685 K, the melting temperature of crystalline Si. The result is visible as the smooth solid line in Fig. 8(b). The damping of the EXAFS signal in the annealed spectrum of Fig. 8(b) is explained already by thermal effects. Although the strong damping seriously degrades the signal to noise ratio, the Fourier transform of the measured spectrum [Fig. 9(b)] shows a clear peak near the expected Si-Si bond distance.

We conclude that the EXAFS behavior is explained by a

largely increased lattice temperature during and shortly after irradiation at energy densities above the anneal threshold. This confirms the normal melting model⁸ for pulsed laser irradiation.

V. CONCLUSIONS

We have reported the first time-resolved x-ray absorption measurements on Si. Our measurements are the first direct observations of electronic changes in Si during PLA. The behavior of the Si- $L_{II,III}$ and L_I absorption edges in pulsed laser irradiated Si can be explained by a metalliclike electronic configuration during the molten phase.

The anneal and damage thresholds were measured to be ≈ 0.17 and 1 J/cm^2 , respectively. In the anneal and damage region the time dependence of the x-ray absorption can be explained by a redistribution of Si into droplets and the formation of clusters, respectively.

From the thermal damping of the EXAFS signal we conclude that the lattice temperature is above the melting temperature during pulsed laser irradiation. Clear cooling effects of the thin foils are observed in the absorption spectra recorded 60 ns after the irradiation pulse. The rapid cooling is probably due to evaporation of Si.

The statistics of our measurements are much better than is required for edge measurements. At the price of intensity loss, our laser system can be operated in a 30-ps pulse mode. Further experiments are planned to measure time-resolved (edge) absorption with a resolution of several tens of ps.

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