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Probing phase transitions under extreme conditions by ultrafast techniques: Advances at the Fermi@Elettra free-electron-laser facility

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ABSTRACT

Novel possibilities for studying matter under extreme conditions are opened by the forthcoming availability of free electron laser (FEL) facilities generating subpicosecond photon pulses of high intensity in the VUV and X-ray range, which are able to heat thin samples up to the warm dense matter (WDM) regime. Pump-and-probe ultrafast techniques can be used to study the dynamics of phase transitions and characterize the states under extreme and metastable conditions. Ultrafast (10–100 fs) bulk heating is seen as a novel route for accessing extremely high temperature regimes as well as the transition region between low-density and high density fluids, that is presently considered a no man's land in simple liquids and glasses. Here we briefly describe the present status of the TIMEX end-station devoted to those experimental activities at the Fermi@Elettra FEL facility, and some preliminary results obtained in a pilot ultrafast experiment using a laser source as a pump and a supercontinuum probe aimed to characterize the melting process of Silicon.

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1. Introduction

The forthcoming availability of free electron laser (FEL) facilities offers a unique opportunity to study states of matter under extreme conditions, obtained by exposing condensed matter to their subpicosecond photon pulses. The expected energy and intensity tunability of these potentially extremely intense pulses are able to pump selected specimens in a wide range of temperatures (up to 10^3-10^5 K) while maintaining densities typical of condensed matter under ambient conditions on a typical timescale of a few picoseconds. In the warm dense matter (WDM) regime, easily reached for intense FEL pulses, the thermal energy is comparable to that of the interatomic potential thus leading to an exotic state consisting of a dense electron plasma strongly coupled to the lattice ions [1]. Although being exotic on earth, such disordered states are those found in the interior of large planets and in stars and can be produced in devices for plasma production and inertial confinement fusion. The intensity of the FEL pulses was recently used for creating and investigating matter in the WDM regime at the fourth-generation light source FLASH (Hamburg) [2,3]. The use of FEL radiation for investigating matter under extreme conditions is particularly promising because it extends the ultrafast techniques already available using optical lasers to homogeneously bulk-heated specimens, opening the way to the study of the dynamics of transitions in ordered and disordered condensed matter. Several techniques can be used to probe matter under these extreme conditions including absorption spectroscopy, reflectivity and pump-and-probe experiments. In particular, pump-and-probe ultrafast experiments are expected to unravel details of the dynamics of phase transitions and characterize the states under extreme and metastable conditions, presently inaccessible. For example, those experiments could shed light on the occurrence of polymorphism and the hypothesis about the existence of a coexistence line and a critical point separating low-density and high-density fluids in a class of substances which include water, C, Ge, Si and their oxides [4–6].

Up to now, several ultrafast optical studies have been carried out on simple crystalline and amorphous system giving important information about melting and recrystallization of various substances (see Ref. [7] for a review on semiconductors). For example, melting of crystalline silicon has been studied since the early times of ultrafast optical spectroscopy (see [8–10] and Ref. therein), while melting, crystallization and re-amorphization were studied for various amorphous semiconductors [11,12].

In this contribution we briefly describe the main characteristics of the TIMEX end-station devoted to time-resolved experiments under extreme conditions at the Fermi@Elettra FEL facility in Trieste (see [13] and Section 2). The potential of the new instrument is illustrated in details, and the preliminary results obtained in pilot ultrafast experiments using a laser source as a pump and a supercontinuum

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probe are here presented, with the aim of characterizing the melting process of the silicon Si(100) surface.

2. TIMEX end-station design

As outlined above, new possibilities for ultrafast experiments are opened by the development of free-electron-laser facilities. Fermi@Elettra is a 4th generation light source user facility with a high brilliance and short pulse length currently under construction at Sincrotrone Trieste. It is based on a High Gain Harmonic Generation (HGHG) scheme employing multiple undulators up-shifting an initial seed signal (pulsed laser) in a single-pass that will provide an almost ideal transform limited and fully spatial coherent radiation. The duration, bandwidth and wavelength of the output radiation will be tunable. Two undulator's chains will be employed: FEL1 covering the wavelength range from 20 nm to 100 nm (down to 6.7 nm by using third harmonic) and FEL2 from 4 nm to 20 nm (down to 1.3 nm in third harmonics), with typical pulse width in the 40–100 fs range and ~10^{13}–10^{14} photons per pulse (see [14] and Ref. therein).

The FEL pulse is designed to be delivered to the beamlines through a sophisticated system (PADRes, see Ref. [15]) dedicated to the diagnostic and intensity tuning of the photon beam. A special optics with an active mirror has been designed for the TIMEX end-station providing the necessary beam-shaping capabilities for obtaining a well-defined 3–50 micron spot with the desired energy (and fluence) deposited on the sample [14]. Proper diagnostics for the temperature takes advantage of our knowledge on the shape of the pump pulse as described in Refs. [14,16].

The TIMEX end-station [13] is conceived to exploit the unique intensity, energy domain and time structure of the FEL presently under construction, to probe metastable and/or excited matter under extreme conditions. In particular, the energy and intensity of the Fermi@Elettra FEL beam is suitable for an efficient ultrafast heating of most bulk-like dense samples.

As shown in Fig. 1 the end-station design has been maintained very flexible and can accommodate various possible configurations for single-shot experiments including simple far-UV and soft X-ray absorption, and pump and probe experiments using as a probe optical lasers or the FEL pulse (and its harmonics). The optical laser can be also used as a pump. The focussed FEL pulse interacts with the sample installed on a motorized sample manipulator stage working in a Ultra-High-Vacuum (UHV) chamber designed with a variety of windows and feedthroughs (see Fig. 1, upper panel). The 5-axis motorized manipulator is conceived for single-shot measurements at 10–100 Hz rate, allowing precise alignment of the sample in the interaction region with pump and probe ultrashort pulses. Useful diagnostic for initial experiments include a long-distance (LD) microscope for fine micrometric alignments and an infra-red pyrometer [16], but further space is left for additional instrumentation. The main chamber will be equipped with a set of avalanche diode detectors for measurements of direct photon transmission. Fast CCD cameras and diode array detectors will be used for detection of optical ultrashort pulses. The use of an ultrafast streak camera is presently under consideration and tests about the dynamic range and time-resolution of the measurements are also part of the installation program. The sample chamber is fully interfaced through a translation stage with a sample preparation chamber where a fast replacement and surface-science characterization of fresh specimens can be performed.

Both transmission and pump-and-probe experiments using ultra-short photon pulses probing reflectivity and transmission will be possible using proper optical elements (see Fig. 1, lower panel). Suitable windows and space for detectors are left for experiments using harmonics as a probe as well as the possibility of measuring optical absorption of the probe pulses. A table-top supercontinuum probe system [17,18] will be installed for collecting ultrafast optical

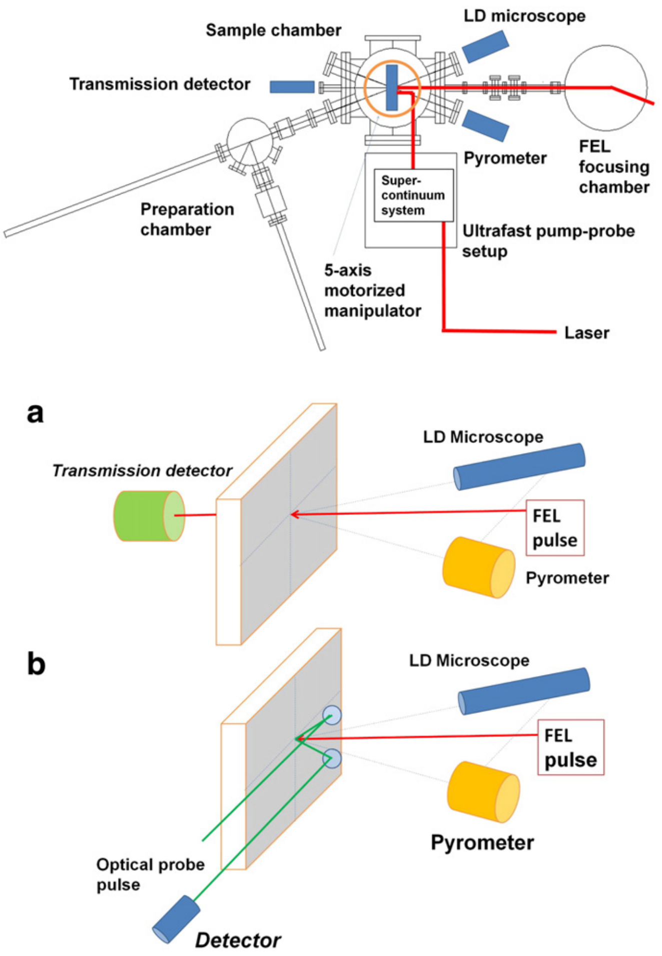

Fig. 1. Upper panel: sketch of the TIMEX end-station under construction at the Fermi@Elettra FEL facility. The FEL pulse is focussed on the sample position through a dedicated mirror set-up [14]. An UHV chamber, connected with a UHV preparation chamber, hosts a 5-axis motorized manipulator allowing for single-shot measurements at 10–100 Hz rate. Diagnostics include a long-distance (LD) microscope for fine micrometric alignments and an infra-red pyrometer [16]. Lower panel: set-up for soft X-ray absorption experiments (a); set-up for ultrafast pump-and-probe optical reflectivity and absorption experiments (b).

absorption and reflectivity data in a wide range of wavelengths in a single shot.

3. TIMEX experimental capabilities: pilot pump-and-probe experiments

The end-station design sketched in Fig. 1 can be used for a variety of experiments including simple absorption spectra at different energies (using the FEL energy tunability) and pump-and-probe experiments of optical properties of matter. An important line of research regards pump-and-probe time-resolved studies of the optical and soft X-ray properties of matter providing direct information on surfaces and bulk of samples under extreme conditions. In fact, ultrafast pump and probe experiments in the 0.1–10 ps range, performed under extreme and metastable or non-equilibrium conditions are relevant to a variety of physical and chemical phenomena for which full control and understanding are presently beyond our experimental capabilities. This includes forefront research in high-pressure and high-temperature physics, non-equilibrium and meta-stable states of matter, applied material studies, understanding of chemical reaction and catalysis paths, planetary interiors, inertial fusion, and various forms of plasma production in which energy is rapidly deposited into a solid.

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The primary difficulties in studying these physical phenomena and states of matter are that the timescales for changes are rapid (0.1–1 ps) while density of the excited sample region can be considered constant within times of the order of a few ps.

Moreover, optical pump-and-probe studies are usually limited to surface properties due to the limited penetration depth of the pump pulse in most substances. Therefore the use of higher-energy FEL radiation (far-UV, soft and hard X-ray) is particularly important for efficient ultrafast bulk heating of thin samples. We estimate that an isochore heating up to temperatures of 10 eV can be obtained for bulk-like (50–500 nm thick) samples using the Fermi@Elettra expected radiation, and the temperature range can be easily tuned by modifying the energy and the intensity of the pulses.

A primary interest in studying properties of warm dense matter is related to the fact that those are the actual conditions occurring in most planets and star interiors and approaching these states in a laboratory experiment is a crucial challenge to pursue. The little progresses made so far in laboratory experiments (see for example [1] and Ref. therein) are mirrored in the astrophysical literature where the WDM regime is found, for example, in the structural formation of large planets and brown dwarfs (see for example [19,20] and Ref. therein).

Present experimental data are scattered and largely based on single-shot shock-wave techniques while ultrafast quasi-isochore heating obtained using the FEL beam is able to sample wide regions in still unexplored extreme conditions.

Ultrafast experiments, however, represent a tool of paramount importance also in study the dynamics of phase transitions in condensed matter, and in particular those concerning disordered states of matter. The excitation induced by the pump involves the electrons with binding energies lower than the photon beam energy and the absorbed energy may be limited by the number of available electrons. In timescales of the order of 1 ps, typical of the electron-phonon coupling [21,22], part of the energy is transferred to the ionic degrees of freedom, contributing to the approach to thermal equilibrium in a high-temperature state (including the WDM regime). After a few picoseconds or even in shorter times (non-thermal melting) the atomic displacements become comparable to the inter-atomic distances and the system reaches a disordered state. After 10–100 ps the sample is either molten or vaporizes in the surrounding vacuum. The TIMEX end-station exploiting the FEL source, allows studies of phase transitions involving metastable states occurring in regions which are presently inaccessible. An important example is the occurrence of polyamorphism and the hypothesis about the existence of a coexistence line and a critical point separating low-density and high-density fluids in a wide class of substances (see for example [4–6] and Ref. therein).

In spite of the fundamental importance of these phenomena, the transition region often is located in a no man's land (see Fig. 2) where crystallization of the undercooled liquid or of the glassy phase prevents observation of the fluid structure transformation. Due to the ultrafast bulk heating nature of the pump, a simple experiment using the Fermi@Elettra beam will give access to what is presently a no man's land in simple liquid and glasses like water, C, Ge, and Si shedding light on the nature of the fluid and on the dynamics of recrystallization. In Fig. 2 a hypothetical phase diagram of polymorphic substance is depicted, assuming that the application of pressure induces a transformation from a low-density to a high-density liquid (LDL to HDL), reflected also in a corresponding change in the amorphous solid (LDA to HDA). This is exactly what it has been found to happen under certain conditions in water, Ge, Si, but the direct observation of these transitions is hindered by crystallization into the stable crystalline phase. The ultrafast bulk heating expected by using free-electron-laser pulses will be used as an effective tool for observing such transitions between disordered metastable states (see upward vertical arrow), overcoming the limitation due to the very fast nucleation rates during a rapid (even at a ms scale) quenching of the melt (see arrows in Fig. 2). An example of ultrafast heating of a surface of a simple substance is given in the next section.

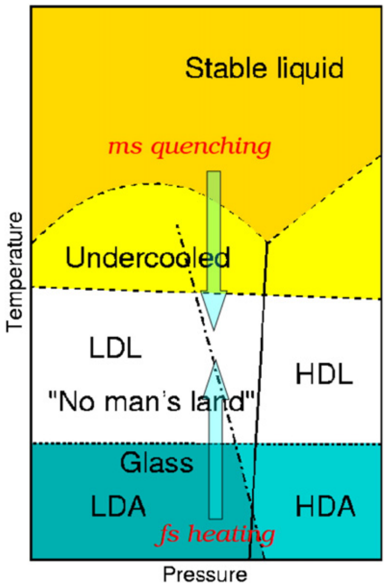

Fig. 2. Hypothetical phase diagram of a polymorphic substance showing the possible occurrence of metastable phases in the region of stability of the crystal. A high density phase is obtained at high pressure, as it happens in a variety of systems (water, Si, Ge and others, see text). A low density liquid (LDL) and a high-density liquids can exist and their coexistence line often lies in the metastability region (undercooled liquid). This polyamorphism can be extended to the corresponding amorphous systems. Very fast nucleation rates of the undercooled liquid in the stable phase prevents observation of the transition that is often located in a no man's land (quenching rates in the range of ms, see downward vertical arrow). Ultrafast bulk heating obtained by free-electron-laser pulses is here regarded as an effective tool for observing such transitions between disordered metastable states (see upward vertical arrow).

4. Experimental results: ultrafast melting of Si(100)

Pump-and-probe experiments aimed to investigate phase transitions in simple substances are a substantial part of the scientific program for the TIMEX end-station. In particular, the development of a suitable supercontinuum optical probe for ultrafast reflectivity (see Fig. 1 and Section 2) and absorption measurements is seen as an important tool for a detailed characterization of the onsets of the transitions. Such a set-up [17,18] has been recently developed at Fermi@Elettra and has been used for pilot experiments of the reflectivity changes near the melting threshold of the Si(100) surface, using an optical laser as a pump.

The source is a regenerative amplified Ti:sapphire laser working at 800 nm, frequency-doubled at 400 nm for this experiment (pulse width FWHM 80 fs, typical rate 500 Hz). The probe is obtained by focusing the laser light pulses on a CaF_2 platelet to produce supercontinuum white light (SWL) ultrashort pulses at 500 Hz repetition rate. The SWL shows a reasonable intensity in the 350–1000 nm range. The SWL is focused on the sample in spatial and temporal coincidence with the pump pulse and dispersed on a 512 pixel NMOS array, after the interaction. A complete scan of the variation in the reflectivity (or transmission) for a selected delay time is triggered by the pump pulse and completed before the next laser pulse.

Samples were commercially available Si(100) slabs (moderately B-doped, p-type, concentration below 10^{16} cm^{-3}). Typical spot sizes used during the experiment were 100 μm (pump pulse) and 50 μm (probe pulse).

The pulse structure and shape were carefully monitored during the experiment, and the time delay scale, being slightly wavelength

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dependent (geometry and optical elements both contribute to a spread of about 200 fs) was accurately calibrated with the ultrafast signal of $CuGeO_3$ [18]. The superposition of the pump and probe pulses was checked with a long-distance microscope Questar CM1 with an accuracy better than 5 μm.

The experiment was performed measuring the broadband change of reflectivity of the Si(100) surface for a given pump fluence as a function of time in the 0–20 ps and 0–500 ps ranges with different time resolutions. The experiment was performed at 500 and 250 Hz repetition rate, collecting always the signal after the pump (R) and without pump (R_0) and calculating $\Delta R = \frac{R-R_0}{R_0}$ (normalized reflectivity change) up to the damage threshold. Beyond the damage threshold, the measurements are obviously single-shot experiments and the region of the surface hit by the pump must be replaced with a fresh one. A motorized 3-axes sample stage was used for these single-shot experiments. However, due to the dimensions of the beam and to the physical limits of the sample, the statistics of the time delays was obviously limited. Moreover, precise motion of the motors required lower repetition rates in the 10 Hz range (compatible with the expected FEL performances) so limiting the useful pulses to an actual repetition rates around 8 Hz.

The effect of the high-fluence pump pulses on the Si(100) surface has been also investigated using optical microscopy. In Fig. 3 (left) we show the images of the Si(100) surface for pulse fluences above the ablation threshold, for which a permanent damage of the surface is obtained. The dimension of the damaged region is clearly correlated (see [23] and ref. therein) with the pump (and deposited) energy as shown in the upper-right plot of Fig. 3. Our estimation of the damage threshold for the given wavelength and pulse duration of the pump turns out to be in line with previous measurements using different pump pulses, as shown in the lower plot where the present estimate (fluence threshold F_{th} ~0.03 J/cm^2) for the irreversible damage is compared with various calculated (open symbols) and experimental (filled symbols) results (see [10] and Ref. therein). The fluence threshold, as previously found by calculations, depends on the energy and duration of the pump pulse.

In Fig. 4 we report the normalized reflectivity change as a function of time in the range 0–20 ps after the pump (intensity below F_{th}), at selected wavelengths (450, 600, and 750 nm). The observed changes in the Si(100) reflectivity are found to depend strongly on the (probe) wavelength. The sudden decrease of reflectivity, much larger for longer wavelengths, is realized within times shorter than 1 ps,

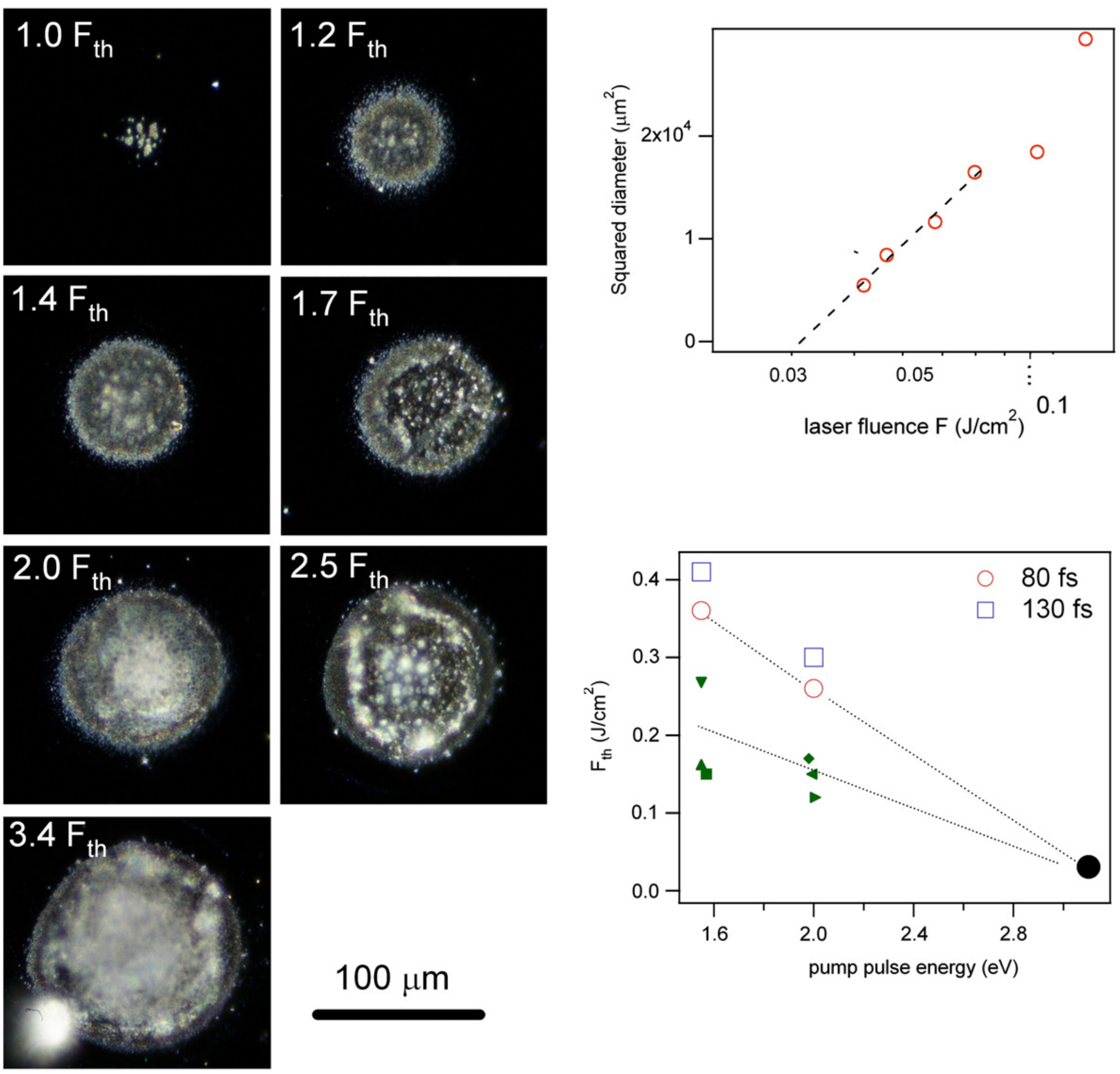

Fig. 3. Left panel: images of permanent damages induced on the Si(100) surface as by the 400 nm laser pump pulse (fluence of the pulse marked on the figures is expressed in terms of the fluence threshold for permanent damage). Images have been collected with an optical microscope in reflection mode. Right panel: square diameters of the damaged regions on the Si(100) surface as a function of the laser fluence (upper figure). The fluence threshold (F_{th} ~0.03 J/cm^2) for producing an irreversible damage is extrapolated. The present result (filled circle at 400 nm, corresponding to ~3.23 eV) is compared with various literature data at different pump wavelengths (see [10] and Refs. therein) in the lower-right figure.

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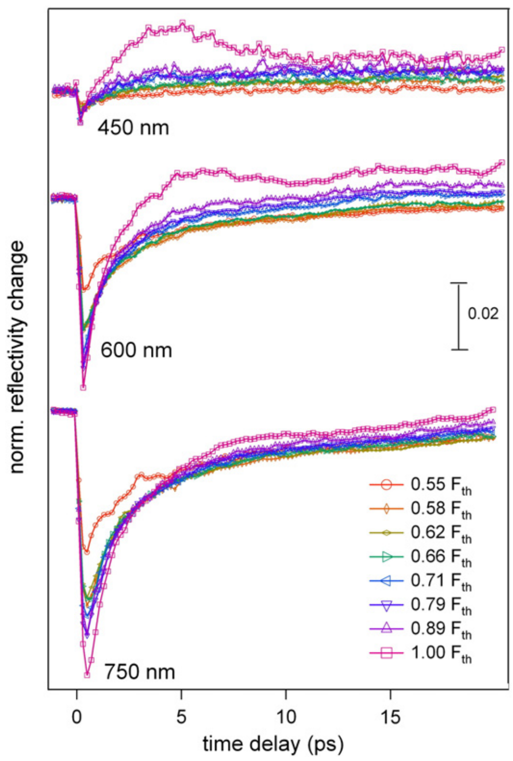

Fig. 4. Normalized reflectivity changes of the Si(100) surface as a function of the probe time delay (up to 20 ps) at different wavelengths (450, 600, and 750 nm) and pump fluences (0.55–1.0 F_{th}). Reflectance spectra at different wavelengths are shifted vertically for clarity of presentation. The maximum negative change observed at 750 nm is around 8% (0.08) at maximum pump fluence within 1 ps.

reaching up to −8% of the original reflectivity at 750 nm. The reflectivity change tends instead to be positive at longer times (after 1 ps at 400 nm, above 20 ps for longer wavelengths) approaching the equilibrium condition only for very long time delays (500 ps) for fluences below F_{th}. As discussed in Ref. [24] this behavior can be explained as a consequence of two phenomena decreasing the reflectivity: 1) a free-carrier (FC) contribution (Drude-like), 2) a state-filling (SF) associated with the absence of electrons in the valence band. Here, the positive contribution obtained for longer time delays is interpreted as mainly due to lattice heating effects as a consequence of electron thermalization (having typical lifetimes compatible with the observed increase in reflectivity). More details on a quantitative interpretation of these data will be given elsewhere [25].

In Fig. 5 we show the results of our single-shot measurements of the reflectivity change for two different pump fluences above threshold F_{th} at 450 and 650 nm, respectively. We have observed that the reflectivity drastically increases within times lower than 1 ps, reaching variations in the 20–50% of the unperturbed reflectivity after 2–5 ps with a slight decrease observed for longer delay times (200 ps), depending on the particular wavelength of the probe. Our results are consistent with those obtained in earlier works using different pump-and-probe pulse configuration [8,26]. In Fig. 5 we notice that both the maximum and the onset and shape of the positive change induced by the pump pulse depends on the wavelength of the probe. The slightly larger effect observed at 600 nm with respect to 450 nm is roughly compatible with the known difference between the reflectivity of (semiconducting) solid and (metallic) liquid Si, which increases at larger wavelengths (see Refs. [27–29]). However, as briefly discussed below, the nature of the transient disordered state (within the first few ps) induced by the pump on the silicon surface is still a matter of debate.

In Fig. 6 we show that the reflectivity increase for fluences above the threshold takes place within times less than 1 ps in the whole

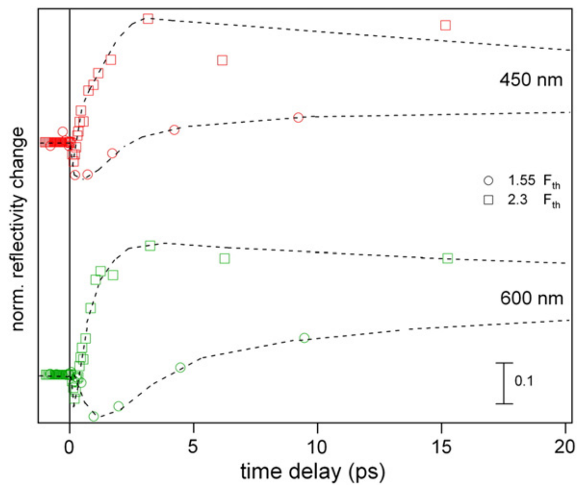

Fig. 5. Normalized single-shot reflectivity changes of the Si(100) surface as a function of the probe time delay (up to 20 ps) at different wavelengths (450 and 600) for two pump fluences above the F_{th} threshold (1.55 F_{th}—circles - and 2.3 F_{th}—squares-respectively). Reflectance spectra at different wavelengths are shifted vertically for clarity of presentation. The maximum positive change observed at 600 nm is around 30% (0.3) at 2.3 F_{th} pump fluence after about 3 ps.

wavelength range under investigation. For high fluences (2.3 F_{th}) the reflectivity change turns out to be positive after only 0.2 ps and then gradually increase within 1 ps. The high concentration of excited electrons within the typical duration of the pump pulse (100 fs) is known to drive the system in a disordered state on timescales much shorter than those of thermal melting (1–10 ps). This "plasma annealing" effect, leading to a non-thermal melting after 100–200 fs, has been studied by tight-binding and ab-initio calculations (see [30,31] and Ref. therein). Moreover, a recent detailed and realistic molecular-dynamics and Monte Carlo study [32] shows the time-evolution of a Si(100) surface after laser irradiation, describing the initial non-equilibrium super-heated states and the thermodynamical evolution of the portion of surface involved in the excitation.

The large reflectivity increase occurring within 200 fs observed in this work (data shown in Figs. 5 and 6) shows that a disordered metallic state, similar to that of liquid Si, is reached through an initial non-thermal process. A detailed analysis of the time evolution and wavelength dependence of the reflectivity spectra can be used to obtain experimental information about the nature of this metallic disordered state and further thermalization processes, as discussed elsewhere [25].

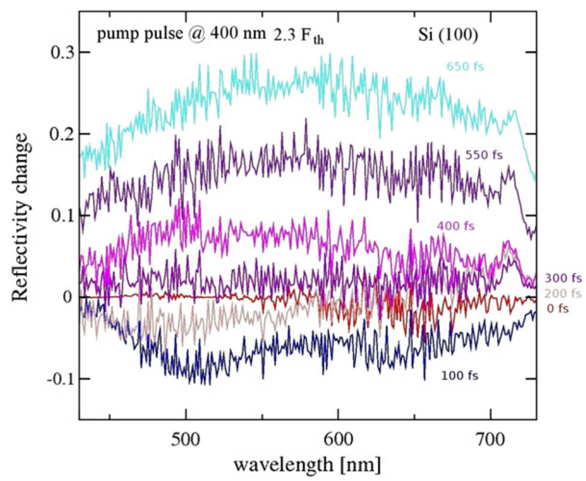

Fig. 6. Normalized reflectivity change ($\Delta R/R$) as a function of the photon wavelength in the optical range. Data collected in the range 0–650 fs are shown.

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5. Conclusions

In conclusion, we have presented in this paper the present developments for the installation of an end-station (TIMEX [13]) dedicated to ultrafast measurements of matter under extreme conditions using the Fermi@Elettra free-electron-laser facility under construction as a source for 50–100 fs pulses in the UV/soft X-ray range. The major technical and scientific issues for the realization of these challenging experiments have been briefly discussed showing that the end-station will benefit of dedicated optics and diagnostic systems, with the final aim of conducting ultrafast pump-and-probe measurements on (transient) phase transitions. The present design of the end-station is conceived to be flexible enough to allow various single-shot experiments using also an optical laser providing probe or pump ultrashort pulses. The end-station will take advantage of an optical supercontinuum probe for combined broadband reflectivity and absorption ultrafast measurements. The preliminary results of a pump-and-probe experiment on the Si(100) surface show the usefulness of these techniques for studying the dynamics of phase transitions occurring after excitations with ultrashort pulses. The excitation of the Si(100) surface using sub-picosecond optical pulses is followed by a sudden modification of the optical properties taking place within the first picosecond. Depending on the intensity of the pump pulse, an irreversible modification of the surface takes place, for which we determined the actual fluence threshold (in line with previous estimates for the present pulse pump). The time evolution of the reflectivity below this threshold shows a complex time evolution depending both on the fluence and on the probe wavelength. Results are in line with previous measurements obtained using different pump-and-probe arrangements. The new measurements, extended to several fluence values and covering the whole optical wavelength range, show that new information can be obtained on the nature of the transitions occurring at the surface. In particular, a transition to a disordered highly excited metallic state is shown to occur above the fluence ablation threshold after about 200 fs, followed by a slow thermalization at longer timescales typical of thermal melting. Present results stimulates further studies to be carried out using the FEL pulses providing bulk heating (or probe in the far UV/soft X-ray regimes) possibly reaching non-equilibrium or metastable states presently inaccessible, as briefly outlined in this work.

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