Original

Nueske, R.; Jurgilaitis, A.; Enquist, H.; Farahani, S.D.; Gaudin, J.; Guerin, L.; Harb, M.; Korff Schmising, C.v.; Stoermer, M.; Wulff, M.; Larsson, J.:

Picosecond time-resolved x-ray refectivity of a laser-heated amorphous carbon film

In: Applied Physics Letters (2011) AIP

DOI: 10.1063/1.3562967

Picosecond time-resolved x-ray refectivity of a laser-heated amorphous carbon film

R. Nüske,[1] A. Jurgilaitis,[1] H. Enquist,[2] S. Dastjani Farahani,[3] J. Gaudin,[3] L. Guerin,[4] M. Harb,[1] C. v. Korff Schmising,[1] M. Störmer,[5] M. Wulff,[4] and J. Larsson[1,a)]
[1]*Department of Physics, Lund University, P.O. Box 118, 221 00 Lund, Sweden*
[2]*MAX-lab, Lund University, P.O. Box 118, 221 00 Lund, Sweden*
[3]*European XFEL GmbH, Albert-Einstein-Ring 19, D-22761 Hamburg, Germany*
[4]*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, F-38043 Grenoble CEDEX, France*
[5]*Helmholtz-Zentrum Geesthacht, Zentrum für Material und Küstenforschung GmbH, Max-Planck-Straße 1, 21502 Geesthacht, Germany*

(Received 9 February 2011; accepted 17 February 2011; published online 10 March 2011)

We demonstrate thin film x-ray reflectivity measurements with picosecond time resolution. Amorphous carbon films with a thickness of 46 nm were excited with laser pulses characterized by 100 fs duration, a wavelength of 800 nm, and a fluence of 70 mJ/cm^2. The laser-induced stress caused a rapid expansion of the thin film followed by a relaxation of the film thickness as heat diffused into the silicon substrate. We were able to measure changes in film thickness as small as 0.2 nm. The relaxation dynamics are consistent with a model which accounts for carrier-enhanced substrate heat diffusivity. © *2011 American Institute of Physics*. [doi:10.1063/1.3562967]

X-ray reflectivity is an established technique for the characterization of the structure of thin films and multilayers.[1] Important morphological parameters that are crucial to the performance of thin film based devices, such as layer thicknesses, densities, and surface roughness, can be extracted from x-ray reflectivity curves. Until now, time-resolved x-ray reflectivity studies have focused on slowly varying states with time-resolution in the minutes to milliseconds range.[2–4] In this study, we extend the technique to the ultrafast domain by recording the x-ray reflectivity of an amorphous carbon (a-C) thin film coated on a silicon (Si) wafer with picosecond time-resolution using a pump-probe scheme in repetitive mode. The samples are models for the x-ray mirrors at the European x-ray free electron laser (XFEL). Structural changes and thermal expansion of thin films on the picosecond timescales are of importance for the beam quality of the XFEL radiation, and more generally for other thin-film based coatings used in the optical range.

The experiment was performed at beamline ID09B located at the European Synchrotron Radiation Facility. This beamline is dedicated to time-resolved x-ray diffraction and scattering techniques.[5] A high speed chopper system isolates single x-ray pulses at a rate of 986.3 Hz. A titanium:sapphire-based laser system provides excitation pulses with 100 fs duration at 800 nm center wavelength with up to 2 mJ pulse energy. For the present experiment, the laser was synchronized to the x-ray source with a jitter of approximately 100 ps. The x-ray pulse duration in 16-bunch mode was about 100 ps, which together with the timing jitter set the limit for the time-resolution in this experiment. The sample was a 46 nm thin film of sp^3 rich a-C (0.2 sp^3 ratio) on a single-crystal Si substrate.[6] The laser was focused under normal incidence on the sample to a spot size of 0.2×8.2 mm^2, where the elongated direction was parallel to the x-ray propagation direction. The induced temporal mismatch due to the crossed-beam geometry was about 30 ps, well below the x-ray pulse duration. The laser fluence was set to 70 mJ/cm^2. The damage threshold of the a-C film was found to be 100 mJ/cm^2, which is similar to what has been reported previously for a-C.[7,8] At this fluence we found no significant graphitization, which would have manifested itself as a permanent change in density and film thickness up to 20%.[9,10] In our measurement, the permanent density change was less than 0.1%. Thus, the measurements could be performed below the damage threshold, in repetitive mode. The critical angle for total external reflection for the used x-ray energy of 18 keV is 0.092°. In order to match the laser and x-ray footprints on the sample when x-rays are incident at near critical angle, the x-ray focus size was reduced to 0.18×0.02 mm^2 by closing the vertical x-ray slits. The incident x-ray flux was 2.4×10^9 photons/s. X-ray reflectivity measurements were performed by scanning the x-ray incidence angle and the delay between x-ray and laser pulses, while keeping the x-ray energy constant. The specular reflected x-ray signal was recorded using a calibrated x-ray photodiode.

Knowledge about the film can be extracted from x-ray reflectivity measurements. The period of the fringes is determined by the film thickness. The fringe contrast depends on the density of film and substrate. The roughness influences the drop of intensity for high-q values. In our experiment, the changes in film parameters were subtle and not directly evident from visual inspection of plots like the ones in Fig. 1. However, the morphological parameters could be extracted with high accuracy by fitting the raw data to the model of the specular x-ray reflectivity for a thin film on substrate described by Gibaud and Hazra.[1] Using nonlinear regression, the films average thickness, density, and root-mean-square (rms) surface roughness were extracted for each time delay. The time-dependence of these parameters is displayed in Fig. 2. The film thickness and density were chosen as independent parameters in the fitting process. We find the product of the thickness and density of the film to be approximately

a)Electronic mail: jorgen.larsson@fysik.lth.se.

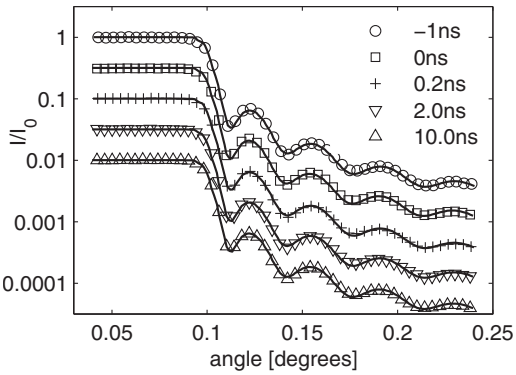

FIG. 1. X-ray reflectivity of an a-C thin film as a function of incidence angle and delays between laser excitation and x-ray probe (curves are offset for clarity). The solid lines are fits using the thin film reflectivity model.

constant for all delays. This confirms that the film was excited below threshold of permanent damage. Following excitation, the film expands rapidly by 0.3% accompanied by a corresponding decrease in density. From the measurement, we can set an upper limit of 200 ps on the timescale of this expansion process. This is equivalent to the temporal resolution of the beamline during the experiment. Subsequently, the film thickness and density relax within 2 ns. We also observe an increase in surface roughness of the film from 0.1 to 0.4 nm (rms) after laser excitation. The surface roughness of the thin film does not recover within the observed time frame of 10 ns. The lateral correlation lengths of the laser-induced roughness is expected to be significantly larger than the laser wavelength and therefore in the micrometer range. We have thus modeled the drop in reflectivity using a Debye–Waller formalism which is described by, e.g., de Boer *et al.*[11]

We interpret the results as follows. After absorption of the pulsed laser radiation, the carrier and lattice temperature

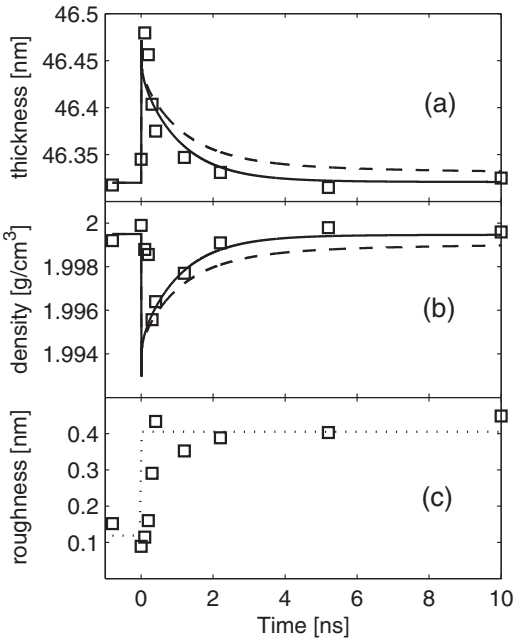

FIG. 2. Time-evolution of the a-C thin film thickness (a), density (b), and surface roughness (c) following laser excitation. Theoretically calculated dynamics using a thermoelastic model: for equilibrium heat conductivity (dashed line) and a laser-modified heat conductivity in the silicon-substrate (solid line). The dotted line is a guide for the eye.

equalize within a few picoseconds in the thin film and substrate. The interface between film and substrate acts as a barrier for carriers generated in the thin film, similar to what has been reported by Cavalleri *et al.*[12] According to Thomsen *et al.*,[13] the initial temperature increase $\Delta T(z)$ following laser excitation in the film is given by:

$$\Delta T(z) = (1-R)\frac{F}{C\xi}e^{-z/\xi}. \tag{1}$$

In Eq. (1), F is the laser incident fluence (energy per unit area), C is the heat capacity, ξ is the attenuation length, z is the distance from the surface, and R is the reflectivity of the surface at the boundary between air and a-C. The reflectivity at the boundary between a-C and Si is below 4% and has been neglected in our simulations. Since the thickness of the film is smaller than the 200 nm laser absorption depth (800 nm),[9] the excitation of the underlying substrate is substantial. We calculate the initial temperature distribution using Eq. (1). The initial temperature rise at the a-C top surface is estimated to be 1400 K, leaving the film well below the melting point of 3000 K. The initial increase in the temperature of the Si substrate at the interface is 150 K. The generated temperature profile in the thin film and substrate produces thermal stress, which is released as a strain wave starting at the surface of the film and at the interface between silicon and a-C. Since the speed of sound in a-C is about 10 km/s,[14] the timescale of this expansion process is estimated to be about 5 ps. This timescale is significantly faster than the 200 ps temporal resolution, implying that the waves have propagated out of the probed depth and the observed expansion is governed by change in temperature. Finally, the film thickness decreases due to heat diffusion into the substrate. The timescale of this process is determined by the heat conductivity and heat capacity of both film and substrate.

Below is a model describing the temporal evolution of the film thickness and density following laser excitation. Since the excitation depth ξ is negligible compared to its lateral size, the problem can be considered quasi-one-dimensional. The initial stress and following expansion is only z dependent. The problem is described by the following heat diffusion and elasticity equations:

$$\rho C\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}k\frac{\partial T}{\partial z}, \tag{2}$$

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial z}, \tag{3}$$

$$\sigma = 3\frac{1-\nu}{1+\nu}B\varepsilon - 3B\beta\Delta T. \tag{4}$$

In Eqs. (2)–(4), T denotes the temperature, σ the stress, u the displacement, and $\varepsilon = \partial u/\partial z$ the strain. The parameter k is the heat conductivity, ρ the density, B the bulk modulus, ν is Poisson's ratio, and β is the linear expansion coefficient of the medium. The calculated initial temperature profile $T(z,t=0)$ sets the initial condition for the simulation. The displacement $u(z,t)$ and temperature $T(z,t)$ values are calculated numerically from Eqs. (2)–(4) using the finite-element method. The model system is a 46.3 nm thin a-C film on a bulk Si substrate. The thermal boundary resistivity[15] at the a-C/Si boundary has been estimated to be as low as ~1

$\times 10^{-8}$ $km^2\ W^{-1}$ and is neglected in the model. The calculated time-dependent film thickness and density are plotted together with experimental values in Fig. 2. The dashed line displays the simulation results assuming the material parameters of Si and a-C under equilibrium conditions as reported in literature.[9,16–20] From this simulation, a time constant of about 3 ns is predicted for the film thickness and density relaxation. Experimentally, the thin film relaxation process is found to be about a factor 2 faster. We attribute this discrepancy to the increase in ambipolar thermal diffusivity for high carrier densities in the silicon substrate above a carrier density of 10^{19} cm^{-3} as reported by Young *et al.*[21] The photoinduced carrier density in the silicon substrate is estimated to be 7×10^{20} cm^{-3}. We find, that a fivefold or higher increase in the substrate thermal diffusivity can reproduce the thin-film relaxation dynamics more accurately. This is in good agreement with Ref. 21. The dynamics of the thin film thickness when the increase in thermal diffusivity has been accounted for is displayed in Fig. 2 (solid line).

The relaxation process of the surface roughness shows a substantially different behavior. We observe a rapid increase in roughness following laser excitation, which does not relax within 10 ns. The surface roughness is sensitive to lateral excitation inhomogeneity of both film and substrate. The total expansion of the substrate is estimated to be about 4 nm at a delay of 600 ps. This is much more than the increase in film thickness. A 10% variation in the lateral laser beam intensity is sufficient to induce the observed 0.4 nm roughness. The variation could be due to a nonuniform laser beam profile, or fringes arising from interference between the incident and reflected laser light fields.[22] The heat conduction process within the substrate is slow compared to the film due to much smaller temperature gradients. This explains the observed slow roughness relaxation. From the experimental data, we can set a lower limit of 10 ns required for the thin film roughness to recover under the used excitation conditions.

In conclusion, we have shown that x-ray reflectivity measurements of thin films can be performed with picosecond resolution. Thermal stress generated by laser excitation causes the film to rapidly expand and increases the surface roughness substantially. The subsequent relaxation of the films thickness is governed by heat diffusion into the substrate. This process is accelerated by photoinduced carriers in the substrate.

The authors would like to thank the Swedish Research Council (VR), the Knut and Alice Wallenberg Foundation, the Crafoord Foundation, and the Carl Trygger Foundation for financial support. M.H. acknowledges financial support from the Natural Sciences and Engineering Research Council of Canada.

[1] A. Gibaud and S. Hazra, Curr. Sci. **78**, 1467 (2000).
[2] M. Gonzalez-Silveira, J. Rodriguez-Viejo, M. T. Clavaguera-Mora, T. Bigault, and J. L. Labar, Phys. Rev. B **75**, 075419 (2007).
[3] A. G. Richter, M. K. Durbin, C. J. Yu, and L. Dutta, Langmuir **14**, 5980 (1998).
[4] T. Matsushita, E. Arakawa, Y. Niwa, Y. Inada, T. Hatano, T. Harada, Y. Higashi, K. Hirano, K. Sakurai, M. Ishii, and M. Nomura, Eur. Phys. J. Spec. Top. **167**, 113 (2009).
[5] M. Wulff, F. Schotte, G. Naylor, D. Bourgeois, K. Moffat, and G. Mourou, Nucl. Instrum. Methods Phys. Res. A **398**, 69 (1997).
[6] M. Störmer, C. Horstmann, F. Siewert, F. Scholze M. Krumrey, F. Hertlein, M. Matiaske, J. Wiesmann, and J. Gaudin, AIP Conf. Proc. **1234**, 756 (2010).
[7] R. Koter, M. Weise, A. Hertwig, U. Beck, and J. Kruger, J. Optoelectron. Adv. Mater. **12**, 663 (2010).
[8] T. V. Kononenko, S. M. Pimenov, V. V. Kononenko, E. V. Zavedeev, V. I. Konov, G. Dumitru, and V. Romano, Appl. Phys. A: Mater. Sci. Process. **79**, 543 (2004).
[9] J. Robertson, Mater. Sci. Eng. R. **37**, 129 (2002).
[10] A. C. Ferrari, B. Kleinsorge, N. A. Morrison, A. Hart, V. Stolojan, and J. Robertson, J. Appl. Phys. **85**, 7191 (1999).
[11] D. K. G. de Boer, A. J. G. Leenaers, and W. W. van den Hoogenhof, J. Phys. III **4**, 1559 (1994).
[12] A. Cavalleri, C. W. Siders, F. L. H. Brown, D. M. Leitner, C. Toth, J. A. Squier, C. P. J. Barty, K. R. Wilson, K. Sokolowski-Tinten, M. H. von Hoegen, D. von der Luinde, and M. Kammler, Phys. Rev. Lett. **85**, 586 (2000).
[13] C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, Phys. Rev. B **34**, 4129 (1986).
[14] A. J. Bullen, K. E. O'Hara, D. G. Cahill, O. Monteiro, and A. von Keudell, J. Appl. Phys. **88**, 6317 (2000).
[15] A. A. Balandin, M. Shamsa, W. L. Liu, C. Casiraghi, and A. C. Ferrari, Appl. Phys. Lett. **93**, 043115 (2008).
[16] R. F. Wood and G. E. Giles, Phys. Rev. B **23**, 2923 (1981).
[17] A. Champi, R. G. Lacerda, G. A. Viana, and F. C. Marques, J. Non-Cryst. Solids **338–340**, 499 (2004).
[18] M. Hakovirta, J. E. Vuorinen, X. M. He, M. Nastasi, and R. B. Schwarz, Appl. Phys. Lett. **77**, 2340 (2000).
[19] S. Cho, I. Chasiotis, T. A. Friedmann, and J. P. Sullivan, J. Micromech. Microeng. **15**, 728 (2005).
[20] M. Shamsa, W. L. Liu, A. A. Balandin, C. Casiraghi, W. I. Milne, and A. C. Ferrari, Appl. Phys. Lett. **89**, 161921 (2006).
[21] J. F. Young and H. M. van Driel, Phys. Rev. B **26**, 2147 (1982).
[22] P. M. Fauchet and A. E. Siegman, Appl. Phys. Lett. **40**, 824 (1982).