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Ultrafast structural transformations in graphite

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Femtosecond laser-induced structural transitions in graphite were studied with time-resolved optical anisotropy measurements. The decay of the anisotropic reflectivity seems to indicate a loss of long-range order on a sub-picosecond time-scale, which is much faster than the electron-phonon relaxation time. This observation confirms a non-thermal nature of the structural transition.

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Ultrafast light-induced phase transitions have been studied in a number of covalently bonded materials and with many different experimental techniques, including time-resolved measurements of the reflectivity [1 – 4] and of the reflected second harmonic [2, 5, 6] as well as by molecular dynamics simulations [7]. More recently, a direct observation of the disordering of a solid during melting has become possible through the use of ultrafast time-resolved X-ray diffraction [8 – 10]. While reflectivity measurements provide information only about the changes of the electronic properties, which can not be uniquely related to transient structural changes, time resolved X-ray diffraction has not yet been applied to the particular case of femtosecond excited graphite.

In this letter we present the results of femtosecond time-resolved optical anisotropy measurements of ultrafast order-disorder transitions in single crystalline graphite after excitation by femtosecond laser pulses. The novel time-resolved optical anisotropy technique developed in [11] was successfully applied to study the melting dynamics of superficial layers of zinc and graphite heated by picosecond laser pulses [12]. The idea of the method can be described as follows. When the p- or s-polarized electromagnetic wave is incident on a surface of an optically isotropic medium, the reflected wave has the same polarization, as the incident wave. However, when the medium is optically anisotropic, the reflected wave contains, in general, a component perpendicular to the polarization of the incident wave as well. The latter component disappears, if the crystal is converted to an isotropic state as a result of a phase transition [11, 12].

Optical anisotropy in uniaxial crystals most strongly manifests itself in the reflection from planes containing the anisotropy axis ($\mathbf{C}$), the situation realized in our experiments. A p-polarized wave with intensity I_{in} normally incident on the surface containing the anisotropy axis possesses both s- and p-polarized components after reflection. Their intensities I_s and I_p can be easily obtained using the Fresnel formula:

$$\begin{aligned} I_s &\equiv R_{ps} I_{in} = I_{in} \left| \frac{2\delta}{(n+1)^2 - \delta^2} \right|^2 \sin^2 2\varphi, \\ I_p &\equiv R_{pp} I_{in} = I_{in} \left| \frac{n^2 - \delta^2 - 1 + 2\delta\cos 2\varphi}{(n+1)^2 - \delta^2} \right|^2 . \end{aligned} \tag{1}$$

Here $n = (n_o + n_e)/2$ and $\delta = (n_e - n_o)/2$ represent an isotropic and anisotropic part of the complex refractive index with n_e and n_o being the complex refractive indices for extraordinary and ordinary waves, respectively; φ is the angle between the polarization plane and the anisotropy axis. Only a small fraction of the incident intensity is converted into the s-component: $R_{ps} \propto 10^{-2} \div 10^{-3}$ [11, 12], which is maximal at $\varphi = 45°$. The reflectivity of the parallel p-component being the ordinary reflectivity for $\varphi = 90°$ and extraordinary reflectivity for $\varphi = 0°$ remains quite high: $R_{pp} \propto 1$. The lange difference in the intensities of p- and s-components immediately gives $|\delta| \ll |n^2 - 1|$ and allows to neglect in (1) the small terms proportional to δ^2. The expressions (1) for the particular case $\varphi = 45°$ have a simple form:

$$R_{ps} \approx \frac{|2\delta|^2}{|n+1|^4}, \quad R_{pp} \approx \left| \frac{n-1}{n+1} \right|^2, \quad \text{for } R_{ps} \ll R_{pp} \propto 1, \ \varphi = 45°. \tag{2}$$

Note that the expressions (2) are different from those derived in Ref. [11] for metallic surfaces in the frame of an impedance approximation: $|\delta| \ll |n|$, $|n| \gg 1$. It

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follows from Eq. (2) that the intensity of the s-wave vanishes when the material looses order or a crystal becomes isotropic, corresponding to $\delta \to 0$.

The experimental results were obtained by time-resolved polarization microscopy, the schematic of the setup is presented in Fig.1. A p-polarized pump pulse

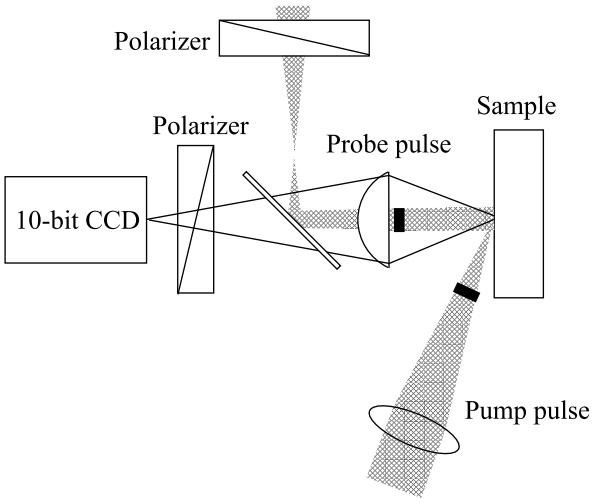

Fig.1. Schematic of the experimental setup

($\tau = 100\,\text{fs}$, $\lambda = 800\,\text{nm}$) at an angle of incidence of approximately 45 deg is used to excite the surface of a single crystalline graphite sample. The excited surface area is illuminated by a weak time-delayed p-polarized probe pulse (second harmonic, $\tau = 100\,\text{fs}$, $\lambda = 400\,\text{nm}$) normally incident on the surface through a high-resolution microscope objective (20X, NA = 0.3). A CCD-camera located in the image plane of the microscope objective was used to acquire the transient surface reflectivity images formed by the reflected probe pulse. By adjusting a polarizer placed in front of a CCD-camera the "isotropic" (p-polarized) or "anisotropic" (s-polarized) reflectivity component can be detected.

Perfect crystalline surfaces parallel to the basal plane of graphite (perpendicular to the optical axis) can be easily obtained by removal of the upper layers [4]. In contrast, the preparation of a surface which contains the anisotropy axis and has a perfect crystalline structure in a thin surface layer with a thickness of the order of the skin-depth represents a serious problem. An effective way to prepare a perfect crystalline surface is based on "laser annealing" [6]: removal of the non-perfect upper layers of the material by laser ablation. In Fig.2 we compare the angular dependence of the anisotropy signal $R_{ps}(\varphi)$ from the initially polished graphite surface with that from the annealed surface area (annealing pulse: $\tau = 100\,\text{fs}$, $\lambda = 800\,\text{nm}$, $F = 0.6\,\text{J/cm}^2$).

Fig.2. (a) Anisotropic (s-polarized) reflectivity images of laser-annealed area at different angles $\varphi = 110°$, $130°$, $160°$, $180°$; the elliptical ablation crater can be easily recognized. (b) The angular dependence of anysotropic reflectivity of the polished and laser-annealed surface

The anisotropic reflectivity images are taken at different angles φ between the optical axis and the polarization vector by rotating the sample; the annealed area can be clearly seen in the center of each image, Fig.2a. The visible scratches with a typical depth of 1 μm originate from the polishing procedure and can not be eliminated by laser annealing since only a few tens of nanometers are removed by laser ablation. Nevertheless, laser-annealing does significantly improve the crystalline structure of the surface, which is shown in Fig.2b. The anisotropy signal from the initial surface is relatively weak and contains only two maxima. In contrast, the angular dependence measured in the center of the annealed area shows four distinct maxima of equal amplitudes, which is in good agreement with the expected $\sin^2(2\varphi)$ angular dependence (see Eq. (2)). The maximal value of the anisotropy signal $R_{ps}^{\max} \approx 4 \cdot 10^{-3}$ is consistent with the value $5.5 \cdot 10^{-3}$ obtained from Eq. (2) by assuming $n_o = 2.62 - 1.28i$ and $n_e = 2.04 - 0.62i$ [13]. The nonzero minimal value of an anisotropy signal $R_{ps}^{\min} \approx 0.4 \cdot 10^{-3}$ is determined by the extinction ratio of the polarizers

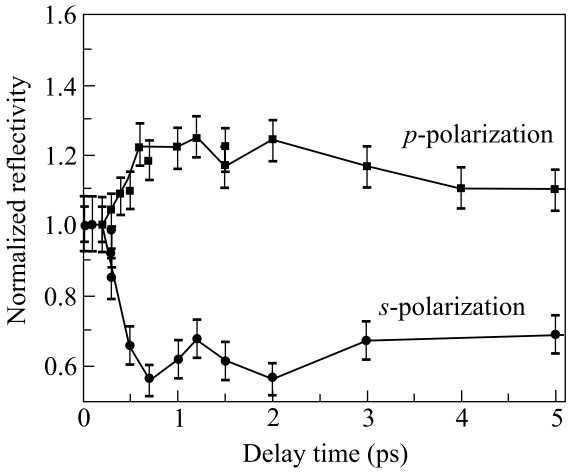

Fig.4. Temporal evolution of the isotropic (p-polarized) and anisortopic (s-polarized) reflectivity, laser fluence 0.35 J/cm^2

Fig.3. Time-resolved reflectivity images for s- and p-polarizations, laser fluence 0.35 J/cm^2, $\Delta t = 700$ fs, frame size $150 \times 120\ \mu$

in the current geometry of the experiment. A detailed surface inspection by Nomarski (differential interference contrast) optical microscopy does also indicate an improved surface morphology of the laser-annealed area as compared to the as-polished surface.

For time-resolved experiments the pump pulse with maximal fluence 0.35 J/cm^2 was focused inside the laser-annealed surface area. The orientation of the sample was set to maintain the maximal initial anisotropy signal at $\varphi = 45°$. An example of transient anisotropy measurements is shown in Fig.3, where the normalized isotropic and anisotropic reflectivity images for the delay time $\Delta t = 0.7$ ps are presented. The normalization procedure implies the division of the transient reflectivity image upon the initial reflectivity image of unexcited surface to eliminate the influence of inhomogeneous probe illumination and initial surface defects. The small increase of an isotropic (p-polarized) and significant decrease of the anisotropic (s-polarized) reflectivity can be inferred from the reflectivity images of Fig.3. The temporal evolution of normalized isotropic and anisotropic reflectivity components is summarized in Fig.4. Within a few hundred of femtoseconds after laser excitation an increase of the isotropic p-component is observed, similar to the results reported by Downer et al. [4] for the experiments performed on the basal plane of graphite. In contrast, the anisotropic s-component drops very sharply within 300–500 fs. This behavior indicates a very rapid loss of crystalline order, much faster than the electron-phonon relaxation time which is of the order of 1–2 ps [4]. Thus the destruction of crystalline order is caused by a non-thermal mechanism due to the strong electronic excitation of the material.

To summarize, we have extended time-resolved optical anisotropy measurements [11, 12] to the femtosecond time domain and applied this technique to detect an ultrafast structural transformation in fs-laser excited graphite. Laser-annealing using fs-laser ablation is proven to be a robust technique for the preparation of well ordered surfaces containing the anisotropy axis. The first time-resolved measurements indicate the disappearance of crystalline order on a sub-picosecond time scale and thus emphasize the non-thermal nature of the structural transition. A slight modification of the experimental geometry will allow to follow the temporal evolution of both, ordinary and extraordinary refractive indices. This experiment is expected to provide more insight into the physical mechanisms of the structural transformation in graphite and is currently in progress.

1. C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983).
2. K. Sokolowski-Tinten, J. Bialkowski, and D. von der Linde, Phys. Rev. **B51**, 14186 (1995).
3. L. Huang, J. P. Callan, E. N. Glezer, and E. Mazur, Phys. Rev. Lett. **80**, 185 (1998).

4. D. H. Reitze, H. Ahn, and M. C. Downer, Phys. Rev. **B45**, 2677 (1992).
5. C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **51**, 900 (1983).
6. H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz, Phys. Rev. Lett. **60**, 1438 (1988).
7. P. L. Silvestrelli and V. Parrinello, J. Appl. Phys. **83**, 2478 (1998).
8. C. W. Siders, A. Cavalleri, K. Sokolowski-Tinten et al., Science **286**, 1340 (1999).
9. A. Rousse, C. Rischel, S. Fourmaux et al., Nature **410**, 65 (2001).
10. K. Sokolowski-Tinten, C. Blome, C. Dietrich et al., Phys. Rev. Lett. **87**, 225701 (2001).
11. M. B. Agranat, S. I. Anisimov, V. E. Fortov et al., JETP **88**, 1184 (1998).
12. M. B. Agranat, S. I. Ashitkov, V. E. Fortov et al., Appl. Phys. **A69**, 637 (1999).
13. E. D. Palik, *Handbook of Optical Constants of Solids II*, Academic Press, San Diego, 1991.