

Dynamics of ultrashort pulsed laser radiation induced non-thermal ablation of graphite

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Abstract We report on the dependence of a laser radiation induced ablation process of graphite on the applied pulse duration of ultrashort pulsed laser radiation smaller than 4 ps. The emerging so-called non-thermal ablation process of graphite has been confirmed to be capable to physically separate ultrathin graphitic layers from the surface of pristine graphite bulk crystal. This allows the deposition of ablated graphitic flakes on a substrate in the vicinity of the target. The observed ablation threshold determined at different pulse durations shows a modulation, which we ascribe to lattice motions along the *c* axis that are theoretically predicted to induce the non-thermal ablation process. In a simple approach, the ablation threshold can be described as a function of the energy penetration depth and the absorption of the applied ultrashort pulsed laser radiation. Based on the analysis of the pulse duration dependence of those two determining factors and the assumption of an invariant ablation process, we are able to reproduce the pulse duration dependence of the ablation threshold. Furthermore, the observed pulse duration dependences confirm the assumption of a fast material specific response of graphite target subsequent to optical excitation within the first 2 ps.

1 Introduction

As a direct consequence of the sustained interest on graphene for electronic and optoelectronic applications, the development of a simple, cost-effective and reproducible production process of pristine graphene remains an ongoing objective of research [1]. Deriving advantage from the spatial asymmetry in bond strength, optical excitation has developed to a promising approach to physically isolate graphene layers from the surface of a bulk graphite crystal [2] and enables the direct deposition on a transparent substrate with a spatial resolution limited by the accuracy of the positioning system only [3]. This technique stands out due to its principle to selectively break the van der Waals bonds between adjacent layers at the surface of a graphite target, while the layer internal sp^2 -hybridization and therefore the intrinsic, desirable properties of the ablated graphene layer are maintained.

However, the underlying physics responsible for this unique ablation process is controversially discussed [4, 5].

On the one hand, density functional theory in combination with molecular dynamics simulations attributes the ejection of graphitic flakes to be induced by Coulomb explosion within about 100 fs after the laser pulse [5]. On the other hand, pure molecular dynamics simulations predict an effective ablation process characterized by a lattice dynamics induced spallation of intact graphene layers on a picosecond timescale [4]. In both cases, the so-called non-thermal ablation process of graphite is induced by a single femtosecond laser pulse. The energy density, necessary to induce the ablation process, is below the classical thermal ablation threshold, which corresponds to the fragmentation of graphite planes [6]. Recently, the experimental validation of this theoretically predicted non-thermal ablation of

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graphite as well as the deposition of sp^2 -hybridized graphitic layers has been demonstrated [3].

The observed modulation of the ablation threshold on a picosecond timescale gives evidence for the substantiated assumption of optically induced lattice dynamics. Therefore, we emphasize the analysis and the corresponding discussion of our experimental results on the comparison with the latter theoretical approach based on lattice dynamics. The mechanism of this process is described to be initialized by the optical excitation of the π -electron system due to absorption of the laser radiation. In consequence of the collective excitation of electrons into antibonding π^* -states, the attractive interlayer potential is weakened [7, 8]. The collective excitation of the electron system and the energy relaxation from the excited electron system to phonons and anharmonic motions are suggested to induce lattice dynamics of the graphite layers along the c axis [4, 6, 8]. Subsequent to these lattice distortions, collisions of adjacent, oscillating graphene layers are proposed to permit a sufficiently high momentum transfer to ablate the top-most graphene layers from the irradiated graphite target [4, 6].

Applying ultrashort pulsed laser radiation, the sub-picosecond electron–phonon thermalization time of 500 fs of the irradiated graphite target and the relaxation time of the excited phonon branches are in the same order of magnitude [8–18]. Hence, a change in the pulse duration exceeding an intrinsic interaction time of the graphite target has a crucial impact on the grade of distortion of the thermodynamic equilibrium and the subsequent energetic relaxation dynamics [6].

In this work, we present the investigation of the impact of pulse duration on the non-thermal ablation of graphite. Recently, theoretical simulation and experimental results assigned lattice dynamics to originate changes in material specific properties, for instance, the absorption. As the ablation threshold mainly depends on the energy penetration depth δ_E and the absorption A , we measure both values in dependence on the applied pulse duration. Grounding on the results of these two graphite specific properties, we calculate the ablation threshold and show the coincidence of our calculations with the observed modulation of the ablation threshold. This coincidence leads to the conclusion of an invariant ablation mechanism in dependence of the pulse duration and a constant energy amount that has to be applied to initiate the ablation process.

2 Experimental

In this study, a Ti:Sapphire CPA (Chirped Pulse Amplification) laser system (Coherent, Libra) is applied to carry out ablation experiments of graphite. The

graphite targets are highly oriented pyrolytic graphite (HOPG) of grade ZYH. They are irradiated with pulsed laser radiation at a wavelength of $\lambda = 800$ nm, fluences up to $2,300$ mJ/cm² and pulse durations between $\tau = 100$ fs and $\tau = 4$ ps.

2.1 Non-thermal ablation threshold

Optical microscopy images of the graphite surfaces irradiated by single ultrashort laser pulses are analyzed to determine the diameter D of the ablation crater serving as fundamental basis to calculate the non-thermal ablation threshold $F_{\text{threshold}}$ [19]. The focal diameter used for this experiment is $2w_0 = 34$ μm .

The non-thermal ablation threshold is determined for 40 different pulse durations. For each investigated pulse duration, we generate ablation craters for 16 pulse energies in the range of 8 μJ up to 21 μJ and measure the corresponding diameter D of the modified, non-thermal regime [3] (Fig. 1a). In the next step, the squares of the mean values of the diameter D^2 are plotted versus the applied pulse energies E_p (Fig. 1b). The squared diameter of the ablation crater D^2 obeys the logarithmic function $D^2 = a \ln(b \cdot E_p)$, where a and b represent fitting parameters [19]. In consequence, the ablation threshold is calculated by $F_{\text{threshold}} = 4/(\pi ab)$.

2.2 Energy penetration depth

To investigate the energy penetration depth δ_E , we perform multi-pulse ablation experiments on graphite targets with $N = 100$ pulses using a repetition rate of 1 kHz and a focal diameter of $2w_0 = 40$ μm . A laser scanning microscope (LSM, Keyence VK-9700) is utilized to measure the depth z of the ablation crater (Fig. 2a, b).

For a number of pulses $N = 100$, the crater depth increases linearly with N so the ablation rate per pulse L can be calculated by dividing the measured crater depth by N . For one selected pulse duration, 12 ablation craters for pulse energies between 2 and 16 μJ are generated. As a result of the two-temperature model, the correlation of the ablation depth per pulse L and the energy penetration depth δ_E obeys $L = \delta_E \ln(c E_p)$ [20]. Accordingly, the energy penetration depth δ_E is directly extracted from the slope of linear regression of the half logarithmic plot of the ablation depth per pulse L versus the applied pulse energy E_p (Fig. 2c).

2.3 Absorption

To determine the absorption of ultrashort pulsed laser radiation by the graphite target $A(\tau) = 1 - R(\tau)$, reflection measurements are utilized (Fig. 3). The measurements are

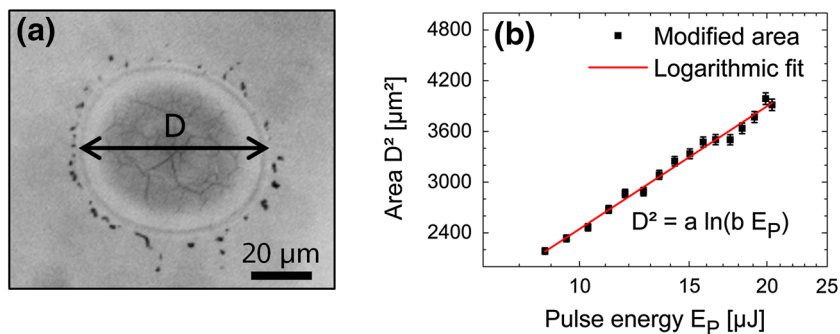


Fig. 1 **a** Ablation crater induced by a single laser pulse ($\lambda = 800$ nm, $\tau = 660$ fs, $E_p = 18$ μ J, $2w_0 = 34$ μ m) with marked diameter D of the crater. **b** Squared diameter of the ablation crater D^2

for different pulse energies (*black squares*) and logarithmic fit (*red line*) to calculate the non-thermal ablation threshold ($\tau = 660$ fs)

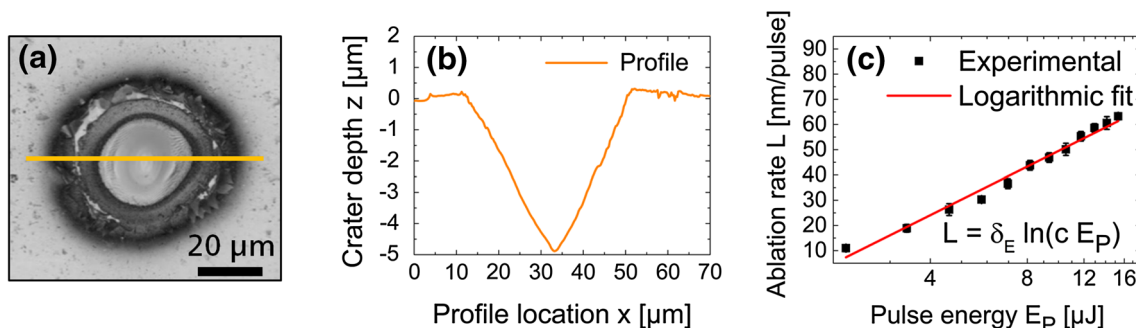


Fig. 2 **a** Ablation crater on HOPG generated by $N = 100$ pulses ($2w_0 = 40$ μ m). **b** Measured height profile of the ablation crater shown in **a**. **c** Ablation rate L for different pulse energies (*black squares*) and logarithmic fit (*red line*) to calculate the optical penetration depth

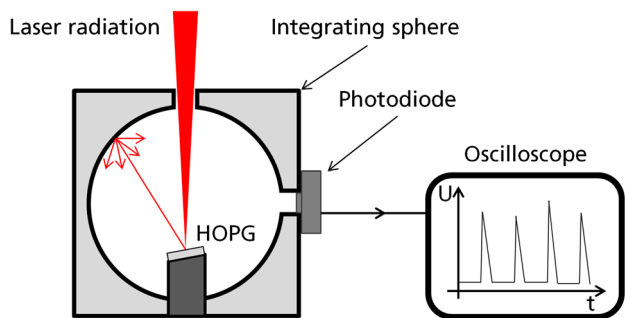


Fig. 3 Schematic setup of the reflection measurements

performed in an integrating sphere. To avoid the disappearance of directly reflected radiation through the entrance of integrating sphere, the graphite target is mounted onto the bottom of the sphere under an angle of 11° . A fast photodiode connected to an oscilloscope detects and logs the reflected intensity signal. In the following, the presented relative reflection values correspond to the reflected energy of a single laser pulse. Therefore, the reflected pulse energy is calculated on the basis of the recorded photodiode signal and divided by the total amount of applied incident pulse energy. The pulse energy or the

corresponding fluence of the applied single pulses is kept at a constant value, while the pulse duration is varied systematically. To avoid any effects on the absorption cause by the ablation of the target, the selected peak fluence of 150 mJ/cm² corresponds to the highest possible fluence applicable for all investigated pulse durations without exceeding the ablation threshold.

3 Results and discussion

3.1 Non-thermal ablation threshold

In Fig. 4, the experimentally determined non-thermal ablation threshold is presented for pulse durations up to 4 ps. For these pulse durations, the non-thermal ablation threshold oscillates around the mean value of 210 mJ/cm² with local minima around 100, 600 and 1,700 fs. Up to 600 fs, we assign the observed features to the optical excitation of the π -electron system and the ensuing electron-phonon thermalization, respectively [13]. For pulse durations longer than 600 fs, the period of the observed oscillation of approximately 1 ps matches the period of lattice dynamics along the c axis [17] and is in line with the

picture of energy relaxation in graphite subsequent to a strong optical excitation [8, 15, 17]. In contrast, for pulse durations exceeding 2.5 ps up to 4 ps, the ablation threshold is a constant value of 220 mJ/cm². Taking the aforementioned lattice dynamics as the originating effect of the observed modulation, the vanishing modulation of the ablation threshold can be attributed to the pulse duration exceeding the period of the lattice dynamics. In this case, the long pulse durations lead to a deposition of the pulse energy over multiple periods of lattice dynamics. In consequence, the resulting effects of an expanded or compressed interlayer distance on the ablation threshold equal out. The lowest ablation threshold of 180 mJ/cm² observed for a pulse duration of 100 fs is in accordance with previous experimental observations [21] as well as theoretical predicted values [4].

To shed light on the origin of the observed modulation, we approach to identify measurable physical values and determine their dependence on the pulse duration. The threshold itself is suggested in Ref [6] as follows:

$$F_{\text{threshold}}(\tau) = E_S n_A k_e \frac{\delta_E(\tau)}{A(\tau)} \quad (1)$$

Here, k_e represents the Coulomb constant, E_S is the energy needed to induce the non-thermal ablation process and $n_A = 1.14 \times 10^{23}$ atoms/cm³ is the density of atoms in graphite [6]. Assuming the energy required to induce the non-thermal ablation process as a constant value, Eq. (1) implies a pulse duration dependency determined by two factors only: the energy penetration depth $\delta_E(\tau)$ and the absorption $A(\tau)$. In the following, we experimentally estimate both values and discuss the assumption of an energy invariant ablation process.

3.2 Energy penetration depth

The energy penetration depth $\delta_E(\tau)$ is illustrated in Fig. 5 for eight selected pulse durations up to 4 ps. The selected pulse durations coincide with local extrema or distinctive positions identified in the non-thermal ablation threshold (Fig. 4). Basically, two major results can be extracted from this measurement. The first evident result is that the energy penetration depth reveals the same trends in dependence on the pulse duration compared to the non-thermal ablation threshold. Especially, the strong decrease in the energy penetration depth of the shortest applied pulse duration of 100 fs is conspicuous. Previous experimental observations describe a strong reduction in the interlayer distance subsequent to a strong optical excitation [8, 15]. In agreement with these observations, the initially reduced energy penetration depth can be interpreted as a consequence of an increased density caused by the compression of the lattice along the c axis. Secondly,

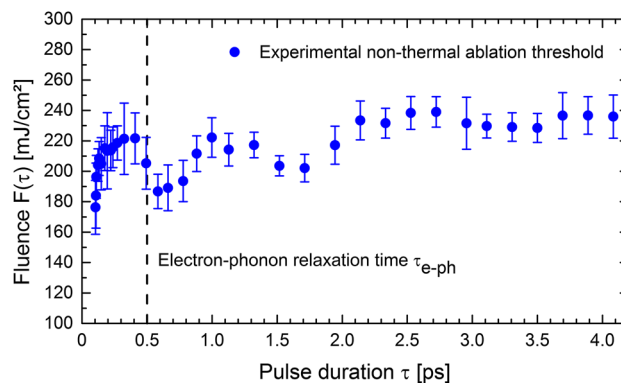


Fig. 4 Experimentally determined ablation threshold for the non-thermal ablation process of HOPG as a function of the pulse duration

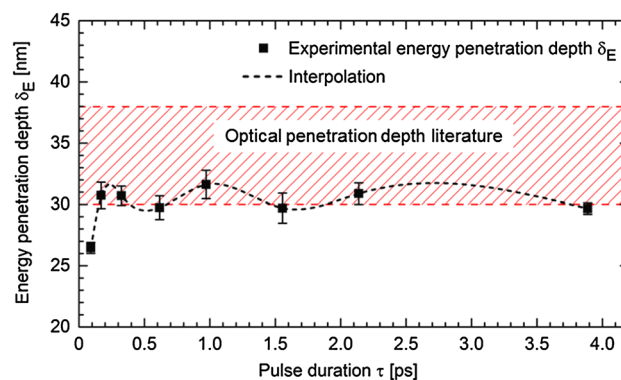


Fig. 5 Experimentally determined optical penetration depth for different pulse durations (black squares) and literature values (red hatched area)

the range of the observed penetration depth of 26 nm up to 32 nm implies a relative change of approximately 20 % and therefore matches the relative change in the non-thermal ablation threshold. Hence, these results provide evidence for the substantiated assumption that the observed changes in the non-thermal ablation threshold are strongly affected by the pulse duration dependency of the energy penetration depth. An increasing energy penetration depth equals an enlarged volume in which the absorbed energy is distributed, resulting in an increased non-thermal ablation threshold and vice versa. Beside the proposed explanation for the pulse duration dependency of the non-thermal threshold, it has to be noted that the mean value of the observed energy penetration depth of 30 nm is in agreement with the usually calculated literature values of the optical penetration depth for graphite (red hatched area in Fig. 5) [6, 15, 22]. Only the smallest penetration depth of 26 nm estimated for 100 fs deviates significantly from literature values.

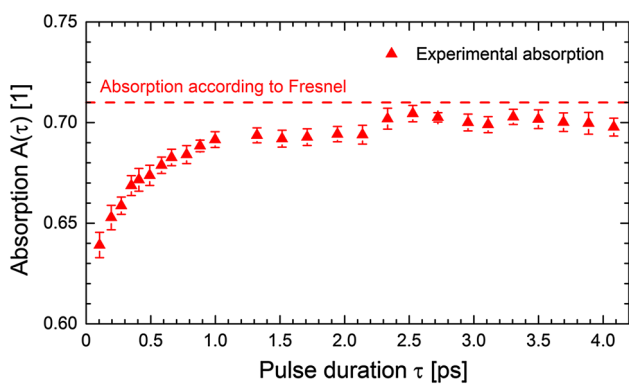


Fig. 6 Calculated absorption of HOPG for different pulse durations of ultrashort pulsed laser radiation based on reflection measurements

3.3 Absorption

The aforementioned second determining factor for the ablation threshold is the absorption $A(\tau) = 1 - R(\tau)$ of the incident laser radiation. The estimated dependence on the applied pulse duration up to 4 ps is presented in Fig. 6. For increasing pulse durations from 100 fs to 1 ps, the measured absorption increases by approximately 10 % and asymptotically approaches the theoretical value of 0.71 (red dashed line) calculated by the use of the Fresnel equations for a tilting angle 11° . The occurrence of a change in the absorption in the observed pulse duration regime coincides with our expectations grounding on the fast carrier dynamics [12, 13] and time resolved reflectivity measurements of graphite [22].

We assign the origin of this effect to the collective optical excitation of the π -electron system of graphite. Subsequent to the excitation, the energy relaxation of the electronic subsystem is described by the electron–phonon interaction time of 500 fs [13], which is of the same order of magnitude as the pulse duration. In this case, the changing occupation of electronic orbitals [23] accompanied with lattice distortions gives evidence to the assumption of strong changes in the intrinsic optical properties of the graphite target within the investigated time domain. For longer pulse durations exceeding 1 ps, the absorption is constant and confirms the calculated value except a slight difference of approximately 1–2 % only.

3.4 Calculation of the non-thermal ablation threshold

Finally, we combine the experimentally determined energy penetration depth and the absorption to calculate the ablation threshold based on Eq. (1). A comparison of the calculated and the experimentally determined ablation threshold is shown in Fig. 7. To match the data of the non-thermal ablation threshold, the energy E_S needed to induce

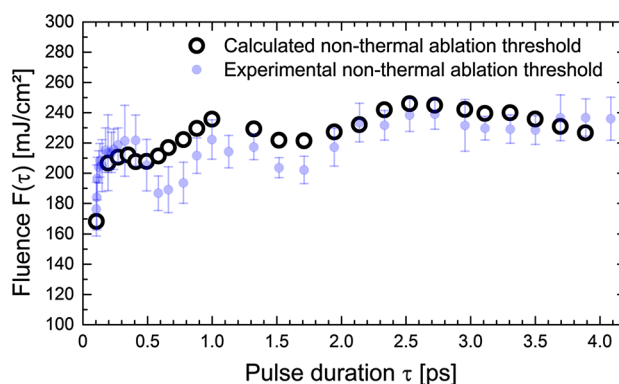


Fig. 7 Comparison of the experimentally determined (blue cycles, Fig. 4) and the calculated ablation threshold (black hollow cycles). The theoretical threshold is calculated by applying Eq. (1) with the experimentally estimated energy penetration depth (Fig. 5) and absorption (Fig. 6)

the non-thermal ablation process equals a constant value of 1.4 eV/atom, in our case. In this context, it has to be mentioned that this value differs by more than a factor of two compared to the values calculated by a molecular dynamics simulations. Here, the expected energy values for E_S are stated to range from 3.0 up to 4.1 eV/atom for the corresponding pulse durations of 100 fs up to 500 fs [6]. Based on the assumption of a constant energy sufficiently high enough to induce the ablation process, our approach is capable to reproduce the observed features of the non-thermal ablation threshold at 100, 600 and 1,700 fs. Beside the general accordance of the data sets, the occurring features are mainly attributed to the strong change in the energy penetration depth. Especially, the initial increase in the energy penetration depth of 20 % within the pulse duration regime up to 200 fs overcompensates the reduced absorption at 100 fs resulting in the lowest ablation threshold of 180 mJ/cm².

4 Conclusion

In conclusion, we determine the non-thermal ablation threshold of graphite in dependence on the pulse duration of the applied ultrashort pulsed laser radiation. It reveals a modulation for pulse duration below 2 ps owed to the fast material specific response subsequent to optical excitation. To elucidate the origin of this modulation, we measure the pulse duration dependence of the two major determining factors of the non-thermal ablation threshold. Both factors, the energy penetration depth as well as the absorption, show strong features for pulse durations below 500 fs. In accordance with previous studies, this effect is attributed to the fast relaxation of the excited electron system of graphite. Additionally, the collective excitation of the π -

electron system is assumed to weaken the c axis bond and to induce c axis lattice dynamics. The ablation threshold and the energy penetration depth show an oscillation which matches a period consistent with lattice motions along the c axis between 500 fs and 2 ps. An alternating interlayer distance is assigned to explain the varying energy penetration depth and the correlated effects on the non-thermal ablation threshold.

In contrast to theoretical predictions, we demonstrate the reproduction of the observed pulse duration dependency of the ablation threshold by the use of the experimentally determined energy penetration depth and the absorption only. This especially implies the assumption of an invariant amount of energy of 1.4 eV/atom necessary to induce the non-thermal ablation process. To the best of our knowledge, this is the first time the ablation threshold is experimentally determined on the basis of this simple approach.

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References

1. F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, A.C. Ferrari, *Mater. Today* **15**, 564 (2012)
2. P. Kumar, *RSC Adv.* **3**, 11987 (2013)
3. M. Reininghaus, D. Wortmann, J. Finger, O. Faley, R. Poprawe, C. Stampfer, *Appl. Phys. Lett.* **100**, 151606 (2012)
4. H. Jeschke, M. Garcia, K. Bennemann, *Phys. Rev. Lett.* **87**, 015003 (2001)
5. Y. Miyamoto, H. Zhang, D. Tománek, *Phys. Rev. Lett.* **104**, 208302 (2010)
6. H.O. Jeschke, M.E. Garcia, *Appl. Surf. Sci.* **197–198**, 107 (2002)
7. A. Marinopoulos, L. Reining, A. Rubio, V. Olevano, *Phys. Rev. B* **69**, 245419 (2004)
8. F. Carbone, P. Baum, P. Rudolf, A. Zewail, *Phys. Rev. Lett.* **100**, 035501 (2008)
9. N. Bonini, M. Lazzeri, N. Marzari, F. Mauri, *Phys. Rev. Lett.* **99**, 176802 (2007)
10. F. Carbone, G. Aubeck, A. Cannizzo, F. van Mourik, R.R. Nair, A.K. Geim, K.S. Novoselov, M. Chergui, *Chem. Phys. Lett.* **504**, 37 (2011)
11. F. Carbone, *Chem. Phys. Lett.* **496**, 291 (2010)
12. K. Ishioka, M. Hase, M. Kitajima, L. Wirtz, A. Rubio, H. Petek, *Phys. Rev. B* **77**, 121402 (2008)
13. T. Kampfrath, L. Perfetti, F. Schapper, C. Frischkorn, M. Wolf, *Phys. Rev. Lett.* **95**, 187403 (2005)
14. I. Chatzakis, H. Yan, D. Song, S. Berciaud, T.F. Heinz, *Phys. Rev. B* **83**, 205411 (2011)
15. M. Lenner, A. Kaplan, C. Huchon, R. Palmer, *Phys. Rev. B* **79**, 184105 (2009)
16. T. Mishina, K. Nitta, Y. Masumoto, *Phys. Rev. B* **62**, 2908 (2000)
17. R. Nicklow, N. Wakabayashi, H.G. Smith, *Phys. Rev. B* **5**, 4951 (1972)
18. H. Yan, D. Song, K.F. Mak, I. Chatzakis, J. Maultzsch, T.F. Heinz, *Phys. Rev. B* **80**, 121403 (2009)
19. J.M. Liu, *Opt. Lett.* **7**, 196 (1982)
20. B.N. Chichkov, C.S. Momma, S. Nolte, F. von Alvensleben, A. Tünnermann, *Appl. Phys. A* **63**, 109 (1996)
21. K. Sokolowski-Tinten, S. Kudryashov, V. Temnov, J. Bialkowski, M. Boing, D.V. Linde, A. Cavalleri, in *Femtosecond laser-induced ablation of graphite*, Optical Society of America, Ultrafast Phenomena, vol. 43 (2000)
22. D.H. Reitze, H. Ahn, M.C. Downer, *Phys. Rev. B* **45**, 2677 (1992)
23. R. Raman, Y. Murooka, C.-Y. Ruan, T. Yang, S. Berber, D. Tománek, *Phys. Rev. Lett.* **101**, 077401 (2008)