Available online at www.sciencedirect.com

SCIENCE DIRECT®

Computational Materials Science 35 (2006) 179–182

COMPUTATIONAL MATERIALS SCIENCE

www.elsevier.com/locate/commatsci

Laser manipulation of nanodiamonds

Aldo H. Romero [a], Harald O. Jeschke [b], Martin E. Garcia [c,*]

[a] CINVESTAV-Queretaro, Libramiento Norponiente No 2000 Real de Juriquilla, 76230 Queretaro, Mexico
[b] Institut für theoretische Physik, Johann Wolfgang Goethe-Universität, Max-von-Laue-Str. 1, 60438 Frankfurt/Main, Germany
[c] Theoretische Physik, Fachbereich Naturwissenschaften, Universität Kassel and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Received 24 April 2004; accepted 16 September 2004

Abstract

We present atomistic simulations of laser induced structural modifications in nanodiamonds. The method used is based on a microscopic approach for the interaction between femtosecond laser pulses and nanostructured materials. It allows us to describe the ultrafast change of bonding type produced in diamond-like nanostructures as a consequence of the laser excitation. In contrast to a thermal processing of nanodiamonds, an ultrashort laser pulse can eliminate all sp^3 bonds in the system on a sub-picosecond time scale, opening the possibility for the production of graphitic nanostructures and the creation of nanocontacts between carbon nanoclusters and other nanostructures.

PACS: 78.70.−g; 61.46.+w; 64.70.Nd

Keywords: Nonequilibrium structural changes; Clusters and nanostructures; Molecular dynamics simulations

In recent years many theoretical and experimental works have shown that it is possible to produce reversible and irreversible ultrafast material modifications in solids and nanostructures using femtosecond laser pulses. Such laser induced structural changes can occur in form of solid–liquid [1–3] or solid–solid transitions [4–8]. In the case of nanostructures there exists a third possibility, which consists in the "cold" removal of parts of the system, like, for instance, the ejection of clusters out of thin films [9] or ejection of the caps of a carbon nanotube [10]. These findings can become of fundamental importance since they open the possibility of manipulating lattice arrangements, bond types and general shapes of nanostructures.

One of the typical laser induced changes of bonding type is the ultrafast graphitization of diamond [11]. The excitation of a large fraction of the valence electrons across the diamond gap fills antibonding states and makes the compact sp^3 structure unstable. In contrast, the effect of the laser excitation on the stability of the sp^2 bonding type is not important. As a consequence, the system undergoes a rapid formation of graphite layers.

Based on these results one would expect that, whenever a diamond-like material is excited by a femtosecond laser pulse, formation of graphite layers is obtained. However, the formation of other, more interesting, graphitic-like structures is a priori not excluded.

In this paper we show that laser excitation of diamond-like clusters (nanodiamonds) leads to the formation of curved sp^2-bonded structures.

Recently, a study focusing on the thermal mechanism of the transition from nanodiamond to a fullerene has been reported [12]. In these investigations, tight binding molecular dynamics were employed to follow the time

---

[*] Corresponding author.
E-mail address: garcia@physik.fu-berlin.de (M.E. Garcia).

0927-0256/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.commatsci.2004.09.051

evolution of a heated nanodiamond for more than 100 ps. The authors identified a number of mechanisms working together to bring inner carbon atoms to the surface of the cluster and to form a uniform fullerene cage.

We show here that the use of femtosecond laser pulses leads to a more efficient transformation nanodiamonds to graphitic structures.

In order to simulate the dynamical process of laser-induced structural transformations, we employ a nonadiabatic MD method combined with a density matrix formulation to describe the coupled dynamics of valence electrons and ionic cores, previously employed in studies of ultrafast ablation and melting [2,7,13,14].

Briefly, our treatment is based on a microscopic electronic Hamiltonian $H_{\mathrm{TB}} + H_{\mathrm{laser}}(t)$, where H_{TB} is a tight-binding Hamiltonian with hopping matrix elements which depend on the interatomic distances $\{r_{ij}\}$, and $H_{\mathrm{laser}}(t)$ accounts for the coupling of the valence electrons of the nanostructure with a time-dependent laser field of shape $E(t)$ and frequency ω. We assume that the nondiagonal elements of the density matrix vanish rapidly in time due to dephasing effects. From the Hamiltonian H_{TB} we calculate forces $f_k(\{r_{ij}(t)\}, t)$ acting on the atoms [11]. They depend on the (time-dependent) occupations $n(\epsilon_m, t)$ of the electronic energy levels (eigenvalues of H_{TB}). Note that, while in thermal equilibrium the occupation numbers are calculated from a Fermi–Dirac distribution function $n^0(\epsilon_m) = 2/(1 + \exp\{(\epsilon_m - \mu)/k_{\mathrm{B}}T_{\mathrm{e}}\})$ at a given electronic temperature T_{e}, electronic nonequilibrium is accounted for by solving equations of motion for the occupation of electronic states:

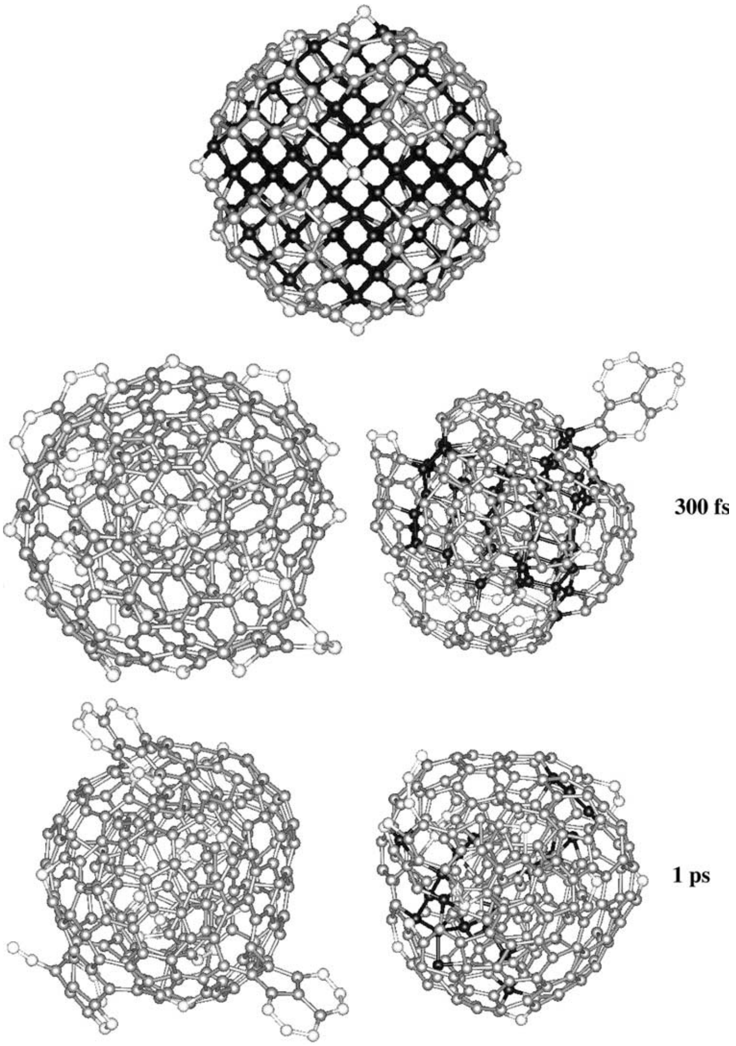

Fig. 1. Snapshots of the nonthermal and thermal transition of nanodiamond to a fullerene in comparison. The top structure shows the initial nanodiamond cluster as obtained from ab initio structure optimization and subsequent annealing with tight binding MD. The left two structures show the structure at $t = 300$ fs and at $t = 1$ ps. Note that the pulse maximum occurs at 40 fs, the pulse duration is $\tau = 50$ fs, and the intensity is $E_0 = 1.0$ eV/atom. The right two structures show the result of 300 fs and 1 ps of thermal annealing at $T = 2000$ K, respectively. Black atoms and bonds correspond to sp^3 hybridization, grey atoms and bonds to sp^2 character.

$$\frac{\mathrm{d}n(\epsilon_m,t)}{\mathrm{d}t} = \int_{-\infty}^{\infty} \mathrm{d}\omega g(\omega,t-\Delta t)\{[n(\epsilon_m-\hbar\omega,t-\Delta t) + n(\epsilon_m+\hbar\omega,t-\Delta t) - 2n(\epsilon_m,t-\Delta t)]\} - \frac{n(\epsilon_m,t)-n^0(\epsilon_m)}{\tau_1}. \tag{1}$$

This equation is derived from the equation of motion for the density matrix under the assumption described before. Thus, the electronic distribution is at each time step folded with the pulse intensity function $g(\omega,t)$. This means that at each time step, the occupation of an energy level ϵ_m changes in proportion to the occupation difference with respect to levels at $\epsilon_m-\hbar\omega$ and at $\epsilon_m+\hbar\omega$. In Eq. (1), constant optical matrix elements are assumed. The second term of Eq. (1) describes the electron–electron collisions that lead to an equilibration of the electronic system with a rate equation of the Boltzmann type for the distribution $n(\epsilon_m,t)$. Hence, with a time constant τ_1, the distribution $n(\epsilon_m,t)$ approaches a Fermi–Dirac distribution $n^0(\epsilon_m)$.

With this theoretical model, and using the previously determined tight-binding parameters for carbon [15], we have performed simulations of the response of nanodiamonds. The time step of $\Delta t = 0.1$ fs was used in treating both the electron and ion dynamics. The relaxation time $\tau_{\mathrm{e-e}}$ was taken to be $\tau_1 = 50$ fs, consistent with the value used for other carbon nanostructures [16].

We have considered a single diamond-like carbon cluster with a total of 293 carbon atoms. The initial structure has been obtained after optimizing the atomic coordinates from an ab initio calculation. This calculation was performed in the Car–Parrinello approach [17]. Norm-conserving pseudopotentials were used with s and p nonlocality for C [18]. Wave functions were expanded in plane waves with an energy cutoff of 40 Ry. Then, we have subjected the optimized structure to a thermal relaxation within a tight-binding molecular dynamics for 300 fs. It is important to mention that after the thermal equilibration was achieved, the carbon cluster kept most of the bonding features of the initial structure and only small bond length relaxations were observed. The internal carbon atoms are sp^3 hybridized, while atoms on the surface relax to sp^2 and sp hybridization. This surface reconstruction has been reported previously on carbon nanodiamond by Raty et al. [19]. There is a fullerene-like formation on the surface and the cluster core corresponds to a perfect diamond-like structure. After the thermal relaxation at 300 K was achieved, the carbon cluster was excited by a laser pulse of $\tau = 50$ fs duration and a central laser frequency of 1.96 eV (which corresponds to a typical experimental value). The peak maximum of the laser pulse was placed at $t = 40$ fs. Total energy of the laser pulse was varied to study its effect on bond breaking. The value of $E_0 = 1.0$ eV/atom that was used for the results we are reporting here is well below the threshold energy required to let atoms leave the cluster.

The application of the laser pulse leads initially to cluster expansion. This means that, similarly to the case of other nanostructures, during the first stages of laser excitation only a coherent breathing mode is active. After the pulse is over, the structure of the cluster starts exhibiting remarkable changes. Between 50 fs and 100 fs after the laser application, already more than 90% of the sp^3 carbon atoms have changed their hybridization to sp^2 in an exponential decay in time as is clearly shown in Figs. 1 and 2. Here we have defined the hybridization by the number of neighboring carbon atoms with distances of less than 1.8 Å. The bond breaking starts from the cluster inner core and after 100 fs most of carbon atoms are sp^2 or sp hybridized, as shown in Fig. 1. The top figure shows the initial configuration after the thermal equilibration and then we can see from the structures on the left of Fig. 1 that after 300 fs (the first 50 fs correspond to the laser pulse) almost no carbon atoms present sp^3 hybridization.

To confirm the advantages of the femtosecond laser pulse in performing structural transformations on carbon nanoclusters we have considered the same system but under thermal exposure only. We have started with the same initial configuration and subjected the system to a temperature of $T = 2000$ K for 1 ps. Fig. 1 shows the temperature effects on the same time scale as in the laser case. The first observation is basically that the thermal transformation also tends to decrease the sp^3 hybridization but the number of carbon atoms that have undergone this process is not as high as in the laser case. To give a more precise description, we have calculated the number of atoms with a given hybridization as function of time. Figs. 2 and 3 show very clearly that after 300 fs, the laser has been able to break 99% of the sp^3

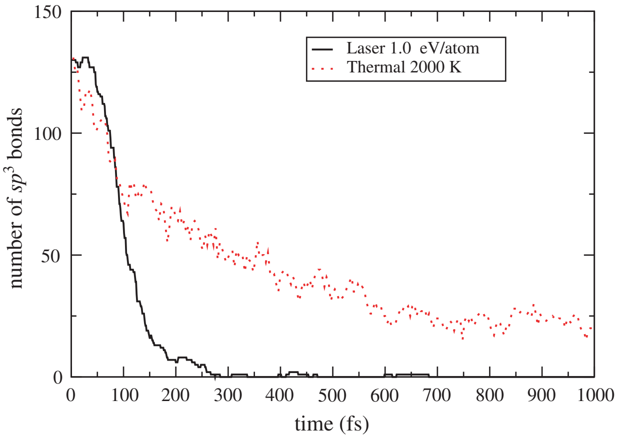

Fig. 2. Time evolution of the number of sp^3 bonds in a nanodiamond consisting of $N = 293$ atoms. The solid and dotted lines show the number of sp^3 bonds for the laser and thermally induced transitions, respectively.

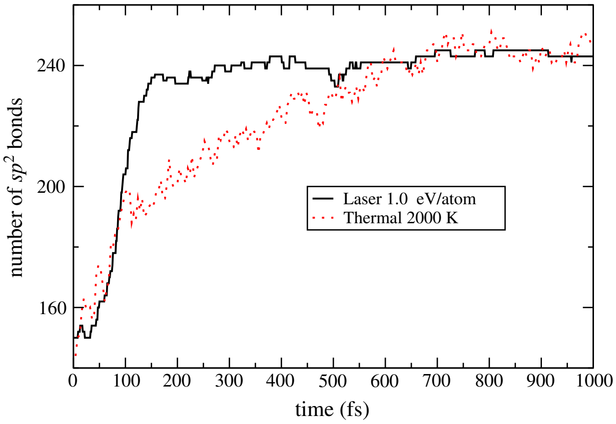

Fig. 3. Time evolution of the number of sp^2 bonds in a nanodiamond with 293 atoms. The solid and dotted lines show the number of sp^2 bonds for the laser and thermally induced transitions, respectively.

carbon bonds while in the thermal case the percentage is much lower. Another important difference is in the dynamics of the transition. While in the case of the laser pulse, the breaking of sp^3 bonds happens from the core to the surface, in the thermal case it starts from the surface with only limited bond modification in the cluster core.

In conclusion, in a series of MD simulations, we provided a microscopic picture of the response of nanodiamond to ultrafast laser pulses. We have shown that a much more efficient transformation of sp^3 to sp^2 bonding is achieved with the help of a femtosecond laser pulse than by means of thermal heating.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through the priority program SPP 1134 and by the European Community Research Training Network FLASH (MRTN-CT-2003503641). H.O.J. gratefully acknowledges support by the Emmy Noether Programme of the DFG. We acknowledge the computer time allocation on the Cray T3E at the Centro Nacional de Supercomputo—IPI-CyT. A.H.R. acknowledges support by Conacyt-Mexico under Grant 42647.

References

[1] P.L. Silvestrelli, M. Parrinello, J. Appl. Phys. 83 (1998) 2478.
[2] H.O. Jeschke, M.E. Garcia, K.H. Bennemann, Phys. Rev. Lett. 87 (2001) 015003.
[3] T. Dumitrică, R.E. Allen, Phys. Rev. B 66 (2002) 081202.
[4] A. Rousse, C. Rischel, S. Fournaux, I. Uschmann, S. Sebban, G. Grillon, P. Balcou, E. Förster, J.P. Gelndre, P. Audebert, J.C. Gauthier, D. Hulin, Nature (London) 410 (2001) 65.
[5] K. Sokolowski-Tinten, C. Blome, J. Blums, A. Cavalleri, C. Dietrich, A. Tarasevitch, I. Uschmann, E. Fvrster, M. Kammler, M. Horn-von-Hoegen, D. von der Linde, Nature (London) 422 (2003) 287.
[6] M. Hase, M. Kitajima, S. Nakashima, K. Mizoguchi, unpublished.
[7] H.O. Jeschke, M.E. Garcia, J.A. Alonso, Chem. Phys. Lett. 352 (2002) 154.
[8] A. Cavalleri, Cs. Tóth, C.W. Siders, J.A. Squier, F. Ráksi, P. Forget, J.C. Kieffer, Phys. Rev. Lett. 87 (2001) 237401.
[9] T.E. Glover, G.D. Ackerman, A. Belkacem, P.A. Heimann, Z. Hussain, R.W. Lee, H.A. Padmore, C. Ray, R.W. Schoenlein, W.F. Steele, D.A. Young, Phys. Rev. Lett. 90 (2003) 236102.
[10] T. Dumitrica, M.E. Garcia, H.O. Jeschke, B. Yakobson, Phys. Rev. Lett. 92 (2004) 117401.
[11] H.O. Jeschke, M.E. Garcia, K.H. Bennemann, Phys. Rev. B 60 (2000) R3701.
[12] G.-D. Lee, C.Z. Wang, J. Yu, E. Yoon, K.M. Ho, Phys. Rev. Lett. 91 (2003) 265701.
[13] H.O. Jeschke, M.E. Garcia, Appl. Surf. Sci. 197–198 (2002) 107–113.
[14] M.E. Garcia, H.O. Jeschke, Appl. Surf. Sci. 208–209 (2003) 61.
[15] C.H. Xu, C.Z. Wang, C.T. Chan, K.M. Ho, J. Phys.: Condens. Matter 4 (1992) 6047.
[16] A. Romero, H.O. Jeschke, A. Rubio, M.E. Garcia, to be published.
[17] R. Car, M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471, we have used the code CPMD developed by J. Hutter et al. 1990–2003.
[18] N. Troullier, J. Martins, Phys. Rev. B 43 (1991) 1993.
[19] J.-Y. Raty, G. Galli, C. Bostedt, T.W. vanBuuren, L.J. Terminello, Phys. Rev. Lett. 90 (2003) 037401.