On the Thermal Stability of Graphene

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ABSTRACT

Molecular dynamics simulation is used to study thermally activated migration of hydrogen atoms in graphone, a magnetic semiconductor formed of a graphene monolayer with one side covered with hydrogen so that hydrogen atoms are adsorbed on each other carbon atom only. The temperature dependence of the characteristic time of disordering of graphone via hopping of hydrogen atoms to neighboring carbon atoms is established directly. The activation energy of this process is found to be $E_a = (0.05 \pm 0.01)$ eV. The small value of $E_a$ points to extremely low thermal stability of graphone, this being a serious handicap for practical use of the material in nanoelectronics.
1. INTRODUCTION

Graphene [1], a hexagonal monolayer of carbon atoms, is of great interest for both fundamental physics (Dirac fermions in solids) and practical applications (nanoelectronics [2]). At present, attention is being attracted to various derivatives of graphene. Among these are such as, e.g., graphane CH, a graphene monolayer with both sides completely saturated with hydrogen [3, 4]; diamane, double-layered graphene with hydrogen atoms adsorbed on its external surfaces [5]; etc.

Recently [6], the existence of another graphene-based hydrocarbon, graphone C$_2$H, was predicted. Graphone is a graphene monolayer on which hydrogen atoms are adsorbed at only one side (rather than at both sides, as in graphane), being attached to carbon atoms of one graphene sublattice. According to the DFT calculations performed in Ref. [6], graphone, like graphane, is an insulator, but with the much narrower band gap $E_g \approx 0.5$ eV (in graphane, $E_g \approx 5$ eV [7]). It is of interest that, as follows from the theory [6], graphone exhibits magnetic properties, in contrast to nonmagnetic graphene and graphane. The local magnetic moments of nonhydrogenated carbon atoms are ordered ferromagnetically at the Curie temperature $T_C = 300-400$ K. Due to this property, graphone may offer considerable promise for use in various nanoelectronic (e.g., spintronic) devices.

The range of possible applications of graphone depends to a large extent on the degree of its thermal stability. In fact, thermally activated hopping of hydrogen atoms between neighboring carbon atoms can induce substantial structural distortions of graphone and, as a consequence, uncontrollable changes in its magnetic characteristics (including their irregular distribution over the sample and even total loss of magnetic properties). In Ref. [6], the stability of graphone at the temperature $T = 300$ K was demonstrated by DFT molecular dynamics simulation. However, the time of the “computer experiment” during
which graphone retained its structure was only 3 ps. It is clear that this time is not long enough for final inferences on the stability of graphone to be made.

It is known that the ab initio calculations in simulations of dynamic processes demand very heavy computational resources and, therefore, allow one to study the evolution of a system of \(\sim 100\) atoms (a cluster or a supercell with periodic boundary conditions) over a rather short time \((\sim 10\) ps) inadequate to provide the sufficient statistics. The goal of this study is to implement molecular dynamics simulation of thermally activated migration of hydrogen in graphone in the tight-binding model [8] that presents a rational compromise between the stricter ab initio approaches and the oversimplified approaches involving classic potentials of interatomic interaction. The tight-binding model adequately describes both small-sized carbon clusters [9-13] and macroscopic systems [8]. In combination with the molecular dynamics method, the model allows one to bring the time of simulation up to 1 ns - 1 \(\mu\)s [9-14]. Previously, this model was successfully used to study thermal desorption of hydrogen from graphane [13] and the effect of spontaneous regeneration of the disordered graphene/graphane interface [14] as well as to calculate the dependence of the band gap of graphane nanoribbons on their width [15]. We show that the activation energy of hopping of hydrogen atoms between neighboring carbon atoms in graphone is extremely low (almost two orders of magnitude lower than the activation energy of hydrogen desorption) and, as a result, the characteristic time of disordering of the graphone structure is no longer than 1 ns even at liquid nitrogen temperature.

2. METHODS OF CALCULATIONS

The molecular dynamics simulation of thermally activated migration of hydrogen in graphone was implemented for the \(C_{54}H_{60}\) cluster. This cluster represents a graphene
fragment, the edges of which are passivated with hydrogen (the number of passivating peripheral hydrogen atoms is 48); in addition, the fragment contains 12 “inner” hydrogen atoms adsorbed at one of its sides, thus forming a graphene fragment (Fig. 1). Passivation is required to saturate dangling bonds of the sp- and sp$^2$-hybridized edge carbon atoms and, thus, first, to reduce the effects of finite dimensions and, second, to exclude (or minimize) hopping of hydrogen atoms from inner carbon atoms to edge ones.

At the initial point in time, random velocities and displacements were imparted to each atom (so that the momentum and angular momentum of the cluster as a whole are zero). Then the forces acting on the atoms were calculated and the classical equations of motion were solved numerically, with the step in time $t_0 = 2.72 \times 10^{-16}$ s. In the process of simulation, the total energy of the system remained unchanged (a microcanonical ensemble [16, 17]), so that the role of temperature was played by the so-called dynamic temperature, the measure of energy of relative motion of atoms. The dynamic temperature was calculated by the formula [17, 18] $\langle E_{\text{kin}} \rangle = \frac{1}{2} k_B T(3n - 6)$, where $\langle E_{\text{kin}} \rangle$ is the time-averaged kinetic energy of the system, $k_B$ is the Boltzmann constant, and $n = 114$ is the number of atoms in the cluster (corrections for the finite dimensions of the thermal reservoir [19, 20] were disregarded because of the large number of atoms, $n > 100$).

To calculate the forces acting on atoms at each step of molecular dynamic simulation, we used the nonorthogonal tight-binding model [8] modified from the model used in Ref. [21]. This model explicitly includes the quantum-mechanical (“band”) contribution of the electron subsystem to the total energy. We took into account all valence electrons of the system, one electron of each hydrogen atom ($1S$) and four electrons of each carbon atom ($2S$ and $2P$).

To calculate the height $U$ of the energy barrier that hampers migration of hydrogen
over graphene, we investigated the hypersurface of the potential energy of the system $E_{pot}$ as a function of coordinates of the constituent atoms. The stationary points of $E_{pot}$ (local minimums and saddle configurations) were determined by the method of structural relaxation and by searching in normal coordinates [22, 23].

3. RESULTS

By analyzing atomic configurations created in the course of simulation of graphene dynamics, we have found directly the time of hydrogen migration $\tau$ for 66 different sets of initial atomic velocities and displacements corresponding to the temperatures $T = 50$-$400$ K. The time $\tau$ was determined as the time interval from the beginning of simulation to the hop of 1 of 12 nonpassivating hydrogen atoms (Fig. 1) to a neighboring carbon atom. As a result of such a hop, one covalent C-H bond breaks and another bond is formed. The process of bond “switching” occurs within a time of $\sim 10$ fs. No reverse hop of the migrating atom has been ever observed; i.e., in graphene, migration of hydrogen is an irreversible process, as distinct from migration in the graphane/graphene structure [14]. The physical reason of such irreversibility is that migration lowers energy; i.e., graphene presents a metastable configuration (corresponding to a local energy minimum rather than to the global minimum) and the hydrogen atoms gain energy if they form bonds with neighboring carbon atoms belonging to different graphene sublattices. We will return to this issue later.

Figure 2 shows the calculated dependence of the logarithm of $\tau$ on inverse temperature. From Fig. 2, it is evident that this dependence can be rather adequately approximated with a straight line, suggesting that the standard Arrhenius formula is applicable to the
description of hydrogen migration:

\[
\tau^{-1}(T) = A \exp \left( -\frac{E_a}{k_B T} \right).
\]  

Here, \( A \) is the frequency factor independent of (or slightly dependent on) temperature and \( E_a \) is the migration activation energy determined from the slope of the straight line in Fig. 2. As the temperature is lowered from 400 to 50 K, the time of migration \( \tau \) exponentially increases by four orders of magnitude, from \( \sim 0.1 \) ps to \( \sim 1 \) ns. Statistical analysis of the results of the computer experiment yields \( E_a = (0.05 \pm 0.01) \) eV and \( A = 10^{13.5 \pm 0.1} \) s\(^{-1}\).

We draw attention to the very small value of \( E_a \) that is about 50 times lower than the activation energy of hydrogen desorption from graphane [13]. Physically, this difference arises from the fact that desorption necessitates the breakdown of the strong covalent C-H bond, whereas migration occurs if the C-H bond only “switches over” from one carbon atom to another.

Since the activation energy of migration is defined by the height \( U \) of the barrier that hampers the migration process, we have calculated the value of \( U \) in graphone. This was done for a graphone \( C_{200}H_{100} \) supercell composed of 100 C\(_2\)H unit cells with periodic boundary conditions. The dependence of the potential energy of the system on the reaction coordinate is shown in Fig. 3. From Fig. 3, it can be seen that the barrier for migration of a hydrogen atom is very low, \( U = 0.058 \) eV, in agreement with the low activation energy (as a rule, \( U \approx E_a \) [10]). In the coordinate space, this barrier is closer to the carbon atom forming the C-H bond that breaks upon migration than to the carbon atom involved in the new C-H bond. It should be emphasized that migration results in a sharp (by 1.46 eV) decrease in energy and, therefore, the barrier for reverse hopping of the hydrogen atom is very high, see Fig. 3. This is the cause of the above mentioned irreversibility of the migration process.
4. DISCUSSION

According to the calculations, the time of migration of hydrogen atoms in graphone at $T = 300 \text{ K}$ is $\tau = 0.1$-1 ps (the rather large spread of the values of $\tau$ at a particular temperature is due to the fact that the process of migration is probabilistic in nature and, therefore, the value of $\tau$ can be markedly different for different sets of initial atomic displacements and velocities, even if these sets correspond to the same temperature). At first glance, this seems in contradiction with the results of Ref. [6], wherein the authors also used molecular dynamics simulation and showed that, at $T = 300 \text{ K}$, graphone retained its structure for 3 ps. However, it should be noted that the authors of Ref. [6] reported the results of only one “computer experiment” at one temperature, these data being insufficient for an unambiguous conclusion to be drawn on the degree of thermal stability (particularly because of the above-mentioned probabilistic character of the process of migration). In contrast, in this study, we have carried out a comprehensive analysis of the dynamics of graphone in a wide temperature range and, on this basis, we have gained a rather large set of statistics and determined the temperature dependence of the migration time. One more factor that could influence the results obtained in Ref. [6] was the overly small dimensions of the system ($\text{C}_8\text{H}_4$) for which the simulation was implemented.

It is worth noting that the results obtained in this study for the activation energy of hydrogen migration and for the height of the barrier hampering the migration, $E_a = 0.05 \pm 0.01 \text{ eV}$ and $U = 0.06 \text{ eV}$, are in excellent agreement with the value of $U = 0.06 \text{ eV}$ determined for graphone in Ref. [24] by ab initio calculations. In addition, the lowering of the energy of graphone on migration of one hydrogen atom over a distance corresponding to the C-C bond length (1.46 eV) is very close to the value of 1.44 eV obtained in Ref. [24].
We believe that the extremely low degree of thermal stability of graphone makes this nanocarbon material unpromising for practical use in electronic devices. In fact, as follows from the estimates obtained by the above formula and from the above-determined parameters $A$ and $E_a$ entering in this formula, the characteristic time of structural disordering of graphone becomes macroscopic ($\sim 10^{10}$ s), only if graphone is cooled down to $T \approx 10$ K. At higher temperatures (Fig. 1), because of migration of hydrogen, the atomic configuration of graphone breaks down very quickly (the time of migration is no longer than 1 ns even at $T = 77$ K). This can lead to the irregularity in the distribution of electronic and magnetic characteristics over the sample. In addition, the possibility of phase separation of graphone into regions enriched with and depleted of hydrogen should not be ruled out. This issue calls for further investigations.

5. CONCLUSIONS

It is inferred that, in contrast to graphene and graphane, graphone is an inappropriate material for use in nanoelectronics because of its low stability even at liquid-nitrogen temperature. An alternative to graphone as a nanocarbon magnetic semiconductor may be represented by, e. g., fluorinated graphene [24], wherein fluorine is substituted for hydrogen.

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References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).

[2] A. K. Geim and K. S. Novoselov, Nature Mater. 6, 183 (2007).

[3] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, Phys. Rev. B 75, 153401 (2007).

[4] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, Science 323, 610 (2009).

[5] L. A. Chernozatonskii, P. B. Sorokin, A. G. Kvashnin, and D. G. Kvashnin, Pisma Zh. Eksp. Teor. Fiz. 90, 144 (2009) [JETP Lett. 90, 134 (2009)].

[6] J. Zhou, Q. Wang, Q. Sun, X. C. Chen, Y. Kawazoe, and P. Jena, Nano Lett. 9, 3867 (2009).

[7] S. Lebegue, M. Klintenberg, O. Eriksson, and M. I. Katsnelson, Phys. Rev. B 79, 245117 (2009).

[8] M. M. Maslov, A. I. Podlivaev, and L. A. Openov, Phys. Lett. A 373, 1653 (2009).

[9] L. A. Openov and A. I. Podlivaev, Fiz. Tverd. Tela 50, 1146 (2008) [Phys. Solid State 50, 1195 (2008)].

[10] M. M. Maslov, D. A. Lobanov, A. I. Podlivaev, and L. A. Openov, Fiz. Tverd. Tela 51, 609 (2009) [Phys. Solid State 51, 645 (2009)].

[11] M. M. Maslov, Khim. Fiz. 28, 43 (2009) [Russ. J. Phys. Chem. B 28, 211 (2009)].
[12] M. M. Maslov, Khim. Fiz. 29, 92 (2010) [Russ. J. Phys. Chem. B 29, 170 (2010)].

[13] L. A. Openov and A. I. Podlivaev, Pisma Zh. Tekh. Fiz. 36, 69 (2010) [Tech. Phys. Lett. 36, 31 (2010)].

[14] L. A. Openov and A. I. Podlivaev, Pisma Zh. Eksp. Teor. Fiz. 90, 505 (2009) [JETP Lett. 90, 459 (2009)].

[15] L. A. Openov and A. I. Podlivaev, Fiz. Tekh. Poluprovodn. 45, 644 (2011) [Semicond. 45, 633 (2011)].

[16] E. M. Pearson, T. Halicioglu, and W. A. Tiller, Phys. Rev. A 32, 3030 (1985).

[17] L. A. Openov and A. I. Podlivaev, Pisma Zh. Eksp. Teor. Fiz. 84, 73 (2006) [JETP Lett. 84, 68 (2006)].

[18] C. Xu and G. E. Scuseria, Phys. Rev. Lett. 72, 669 (1994).

[19] J. V. Andersen, E. Bonderup, and K. Hansen, J. Chem. Phys. 114, 6518 (2001).

[20] L. A. Openov, D. A. Lobanov, and A. I. Podlivaev, Fiz. Tverd. Tela 52, 187 (2010) [Phys. Solid State 52, 201 (2010)].

[21] J. Zhao and J. P. Lu, Phys. Lett. A 319, 523 (2003).

[22] V. F. Elesin, A. I. Podlivaev, and L. A. Openov, Phys. Low-Dim. Struct. 11 – 12, 91 (2000).

[23] A. I. Podlivaev and L. A. Openov, Fiz. Tverd. Tela 48, 2104 (2006) [Phys. Solid State 48, 2226 (2006)].

[24] D. W. Boukhvalov, Physica E 43, 199 (2010).
Fig. 1. The C\textsubscript{54}H\textsubscript{60} cluster as a fragment of graphone. The large and small balls are carbon and hydrogen atoms, respectively.
Fig. 2. The dependence of the logarithm of the migration time $\tau$ (sec) for one hydrogen atom in the $C_{54}H_{60}$ cluster on the inverse temperature $T$ ($K$$^{-1}$). Symbols refer to the results of calculations; the solid line is the linear approximation by the least squares method.
Fig. 3. The dependence of the potential energy $E_{pot}$ of the $C_{200}H_{100}$ supercell with periodic boundary conditions on the reaction coordinate for migration of a hydrogen atom over a distance equal to the C-C bond length. For the origin, the energy of the initial atomic configuration (before migration) is taken. The reaction coordinate is a straight line passing through two carbon atoms, between which the hydrogen atom migrates. Circles refer to (1) the initial configuration of graphone, (2) the saddle point that defines the energy barrier for the migration process, and (3) the configuration after the migration.