CVD Formation of Graphene on SiC Surface in Argon Atmosphere

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We investigate the microscopic processes leading to graphene growth by the chemical vapor deposition of propane in the argon atmosphere at the SiC surface. Experimentally, it is known that the presence of argon fastens the dehydrogenation processes at the surface, in high temperature of about 2000 K. We perform ab-initio calculations, at zero temperature, to check whether chemical reactions can explain this phenomenon. Density functional theory and supporting quantum chemistry methods qualitatively describe formation of the graphene wafers. We find that the 4H-SiC(0001) surface exhibits large catalytic effect in the adsorption process of hydrocarbon molecules, this is also supported by preliminary molecular dynamics results. Existence of the ArH+ molecule, and an observation from the Raman spectra that the negative charge transfers into the SiC surface, would suggest that presence of argon atoms leads to a deprotonization on the surface, which is necessary to obtain pure carbon add-layer. But the zero-temperature description shows that the cold environment is insufficient to promote the argon-assisted surface cleaning.

I. INTRODUCTION

Recent progress in nanotechnology attracts much attention to graphene.1–3 Due to its elastic and electronic properties, this material is a very good candidate for novel devices with extraordinary features4–8. Preparation of pure, good quality, and large graphene wafers is of main technological interest. For many years, the SiC surfaces have been used for the graphene sheets growth in the epitaxy process by the Si sublimation2. This method, however, introduces many defects and causes that graphene does not possess satisfactory electronic transport properties. Structure of the epitaxial graphene and its interactions with the SiC surface have been studied by Raman spectroscopy.9–11

A new method of the epitaxy, by the chemical vapor deposition (CVD), is much less sensitive to the surface defects and enables to obtain high electron mobilities in the graphene layers (up to 1800 cm²/Vs) and the grown wafers are large of even 150 mm in diameter12. Additionally, the graphene multilayers may be oriented in many stacking sequences13. A difference between the graphene growth on SiC by the sublimation and the CVD process is pronounced14. Very recent analysis of the experimental parameters in the CVD growth of the graphene and graphite sheets has been reported15. The CVD method has been also applied on the silicon dioxide substrate (SiO2)16, copper17,18, nickel19, and iron20. It enables to transfer graphene onto arbitrary substrates21.

In the technology, the gas mixture of Ar and propane (C3H8), in a role of carbon precursor, is used as an ingredient in the graphene epitaxy by the CVD process.13,24,25, Propane is used in role of carbon precursor in graphene layer creation process. It is desirable to understand how these compounds participate in the formation of the carbon layers, and especially, what is the mechanism of the removal of the hydrogen atoms from the Si-terminated SiC surface. The substrate surface must be very clean in order to obtain a good quality graphene. A possible functionalisation of graphene with the adsorbed hydrogen is a different issue.26–27.

In this work, the chemical reactions behind the CVD process are described, and mechanisms of the surface dehydrogenation are checked. These mechanisms are closely related with the noble gases tendency to form the diatomic molecules with protons or, in specific conditions, with the neutral hydrogen atom. The propane molecule, obviously, chemisorbs neither on the Si- nor the C-terminated 4H- or 6H-SiC surface (4H and 6H means the hexagonal crystal structure with the stacking period in the z-axis of 4 and 6, respectively). This is because C3H8 is a molecule with all chemical bonds saturated. It will be shown that it is absolutely sufficient to remove whichever hydrogen atom from the propane molecule in order to adsorb such created specie at the SiC surface. Further dehydrogenation of the molecule makes the adsorption stronger. The problem that arises is what is the propane dehydrogenation initialization event, since there are only the saturated propane molecules present in the gas phase. Therefore, we start from investigations of the reactions with isolated propane in the gas phase, and later we model the following chemical reactions at the surface. The possible role of argon in deprotonization reactions will be discussed. If the deprotonization scenario was true, then it would explain the Raman measurements, whose show that the charge transfers from the adsorbates to the SiC surface.28

II. CALCULATION DETAILS

All calculations in this work were performed with the density functional theory (DFT)29, using the plane-wave package QUANTUM ESPRESSO30. In order to verify the correctness of the results obtained by the DFT tool, used in the further studies, the solutions for the specific reac-
A. Molecular reactions in the gas phase

Initially, we investigated a scenario with the C₃H₈ → C₃H₇ + H and C₃H₈ → C₃H₆ + H₂ reactions in vacuum. The reaction energies presented in Table I were obtained with the schemes: restricted (open shell) Hartree-Fock, R(O)HF, without and with the second order perturbation corrections for the dynamical correlations at a level of the Möller-Plesset, MP2, method (both by GAMESS) and the DFT (by QUANTUM ESPRESSO). Additionally, the dissociation energies of H₂ were calculated to complete a description of the reactions energetics. Details of a set-up used in the calculations are given in the supporting information.

Independently on the approximation level, the removal of one hydrogen from propane needs a considerable amount of energy provided into the system (ca. 4 eV). In a case of the propene molecule (C₃H₆), a part of the energetical cost has been consumed by a formation of the H₂ diatomic bond. Because of high Ar concentration in the gas mixture, it is quite plausible that argon atoms could assist in the above reactions leading to free the hydrogen atom or a proton. This statement would be supported by the results of the quantum chemistry work on the dissociation of the HeH⁺ molecule, led by Wohliewicz, where the separation of proton is an exothermic reaction with about 2.04 eV achieved. Thus, a possibility of argon binding with a proton in our system was calculated. The results are presented in Table I.

III. RESULTS

The energy gained from ArH⁺ formation is still smaller than the energy amount needed to remove one of the hydrogen atoms from the propane molecule. However, the hydrogen ionization energy is still necessary to be taken into account. Some energy might be obtained from any of the kinetic processes, which occur at high temperatures, or from the catalytic reaction with the SiC surface. Indeed, our preliminary results obtained with the MD support that fact. At averaged simulation temperature of Nosé thermostat around 1500 K, C₃H₈ releases one hydrogen with the kinetic energy around 5 eV and the remaining C₃H₇ moiety with the kinetic energy of 1.5 eV hits the surface zone and binds at the Si-site.

Fragmentation of the propane molecules might be also caused by the electron transfer from the neutral propane into the positively charged noble gases (with unpaired electrons in the valence shell), as it has been demonstrated experimentally. On the other hand, at high temperatures in the range of 1300-1700 K, a similar decomposition of propane could be obtained without noble gases. This process was studied with IR laser absorption kinetic spectroscopy and discussed without any role of argon. However, in the aforementioned experiment, the gas mixture of C₃H₈ and Ar (as a major compound) has been used.

To complete overview of the argon role in the investigated microscopic mechanisms, it is needed to consider a possibility of the dehydrogenation assisted by the formation of the neutral ArH molecule. Such process seems to be forbidden, since the noble gases have closed valence shell and are expected not to form molecules with other atoms. We have checked, using the DFT and the ROHF methods, that indeed the neutral system ArH does not bind. However, the Van der Waals complexes of Ar with propane have been studied, and also the HeH⁺ and ArH⁺ charged molecules can be formed due to this type of interaction. Moreover, there are also known the diatomic molecules of NeH⁺, KrH⁺ and XeH⁺ with the corresponding dissociation energies 2.08, 4.35 and 4.32 eV respectively. Even more interesting are the molecules containing the noble gases and some other atoms, where one or more ingredients are in the excited state. It is known from the experiment that the molecule HArF occurs as stable, and existence of HArCl and HHeF molecules have been predicted theoretically to be stable too. Recently, the next two new molecules FArcCh and FArsIf₃ have also been proposed.

The crucial information for our investigations of argon role comes from the multiconfigurational calculations for a dissociation of the ArH⁺ molecule in the excited state, performed by Vance and Gallup. The main results of the work mentioned above are summarized in the supporting information. Focusing on those data, we suppose that it is impossible that argon could build a diatomic molecule with neutral hydrogen in our system. This is because the curve minima, in the dissociation channels of the excited argon, are shallow with 1-1.5 eV energy.

| Reaction                             | R(O)HF | MP2    | DFT | exp. |
|--------------------------------------|--------|--------|-----|------|
| C₃H₈ → C₃H₇ + H                     | 3.538  | 4.128  | 4.208 | -    |
| C₃H₇ → C₃H₆ + H                     | 1.671  | 1.341  | 1.850 | -    |
| C₃H₈ → C₃H₆ + H₂                    | 1.662  | 1.450  | 1.563 | -    |
| H₂ → H + H                          | 3.547  | 4.018  | 4.466 | 4.75 |
| rₑ (H₂)                             | 0.730  | 0.738  | 0.753 | 0.741|
| ArH⁺ → Ar + H⁺                      | 2.825  | 3.048  | 4.151 | -    |
| rₑ (ArH⁺)                           | 1.310  | 1.328  | 1.339 | -    |
FIG. 1. Adsorption geometries of propane and all transition $C_3H_{8-n}$ species, where $n=1,2,...,8$ (up to the "naked" carbons) at the Si-terminated SiC surface. The starting and final configurations, $C_3H_8$ and $C_3$, are in the first row. The second and third rows present the symmetric and the nonsymmetric cases, respectively, for the descending number of hydrogen atoms from the left- to the right-hand side.

![Adsorption geometries of propane and all transition $C_3H_{8-n}$ species](image)

FIG. 2. Adsorption energies of the first three neutral and charged species at the surface obtained from a removal of the hydrogens from propane.

![Adsorption energies of the first three neutral and charged species](image)

Energy is much less than the hydrogen binding energy to the surface or hydrocarbon, and the argon excitations are about 11.5 and 11.7 eV. Such energy excitations of the system cannot be accessible on this scale without a strong laser beam.

## B. Adsorption at the surface

Assuming that, in a high temperature process, one hydrogen is removed from propane, the $C_3H_7$ system can be adsorbed at the surface. Two possibilities of creating such specie were defined: by 1) symmetric or 2) nonsymmetric removal of the hydrogen atom from the original hydrocarbon molecule. Since an adsorption at the 4$H$-SiC(0001) surface occurs for the both cases, the symmetric $CH_3-CH-CH_3$ molecule and the nonsymmetric $CH_2-CH_2-CH_3$ molecule, further removals of the hydrogen atoms were considered and the adsorption energies were calculated. Following this procedure, the adsorption of a series of the species $C_3H_{8-n}$, with $n=1,...,7$, was calculated. Finally, the hydrogen-free system, $C_3$, was adsorbed at the 4$H$-SiC(0001) surface. This type of hydrocarbon molecular residues might serve as precursors for the graphene layer or a graphitic buffer layer.

The studied adsorbent species build one, two or three valence bonds with the Si-terminated SiC surface. For any studied molecule, the bond order formed with the surface atoms is strongly dependent on the species–surface geometry and on number of hydrogens. Some of the adsorbent created C-C bonds have a double bond character. The relaxed geometries of the adsorbed species are presented in Figure 1.

All calculated adsorption energies, except the $C_3H_8$ molecule, are negative, which means binding state. The modeled surface was considered to be metallic due to a saturation of the surface with hydrogens.

Adsorption energies were obtained from a formula valid for the neutral and charged systems:

$$E_{ads} = E_{slab/mol} - E_{slab} - E_{mol} - N\mu_e,$$

(1)

where $N$ is the number of additional electrons in the charged systems ($N \neq 0$ only in the cases presented in Figure 2). In the adsorption of charged molecules the total energies $E_{slab/mol}$ and $E_{mol}$ were calculated with additional electrons, and the energy $E_{slab}$ corresponds to the neutral surface. For the chemical potential of electrons, i.e. $\mu_e$, we assumed the Fermi level of the pure slab (without the adsorbent) obtained from the quadrature of the electronic density to the proper number of valence electrons in the system with the used pseudopotentials. Modeling interactions in crystals, using the periodic supercells, introduces spurious interactions between periodic images especially in the case of charged cells with the...
compensating charge uniform background. In order to take account of these effects, we use the Makov and Payne method\textsuperscript{18} implemented in the QUANTUM ESPRESSO code. All geometries of the systems, taking a part in the adsorption process, were optimized separately and non of the configurations was fixed.

The resulting values of the energies for the first three species: C\textsubscript{3}H\textsubscript{7}, C\textsubscript{3}H\textsubscript{5} and C\textsubscript{3}H\textsubscript{4} are depicted in Figure\textsuperscript{[2]}. Since it has been assumed, that the dehydrogenation could be assisted by the ArH\textsuperscript{+} molecule formation, the calculations for charged systems were also performed. It follows, that negatively charged species bind weaker to the surface. The binding energy depends on the number of bonds, but also on the local surface strain induced by the adsorbed molecules. For example, the symmetric configuration of C\textsubscript{3}H\textsubscript{6} group binds much stronger than the nonsymmetric one, due to a match of the Si-terminated SiC surface lattice with the molecular C-C-C chain. On the other hand, the C\textsubscript{3}H\textsubscript{7} nonsymmetric molecule binds much stronger than the symmetric one, because the CH\textsubscript{3} group in this species is more distant from the surface when the terminal hydrogen is removed from propane.

There exists a proposal of the charge transfer scenario from the deprotonized site to the SiC surface states (which have extended delocalized character) assisted by formation of the ArH\textsuperscript{+} molecule. The experimental data shows\textsuperscript{16}, that the charge distribution near the SiC surface is enhanced after the graphene layer adsorption. Also the binding energy of ArH\textsuperscript{+}, of order 4.15 eV, is slightly larger than the adsorption energy of the hydrogen atom at the Si-site of the 4H-SiC(0001) surface, which amounts to 3.92 eV (from the DFT results). On the other hand, the energy of removal of a proton from the surface is higher of the H ionization potential, about 13.6 eV, minus the work-function of the SiC surface, circa 3.87 eV. Thus, the dissociation energy of a proton amounts to around 13.65 eV. This fact indicates that the zero temperature scenario with the argon-assisted surface chemical reactions does not take place.

Further, the adsorption energies of the species with four or less hydrogens were compared with the adsorption energies of rich hydrogenated molecules. In this comparison, the hydrogens dissociated from a molecule were adsorbed at the surface Si-sites nearby the molecule (somewhere in the middle of the primitive cell used in the calculations). The adsorption sites were distant enough that the adsorbed species do not interact chemically. Although, in an indirect way the surface deformations around the adsorbed molecules affect the adsorption energies. Thus, the final reaction was not just a sum of two separate reactions with the surface. Such picture corresponds to the experimental situation much better than a very separate adsorptions scenario, with hydrogens in the infinite distance from the molecule. The results of calculations for the aforementioned processes are included in the supporting information, since the barriers were calculated via the reactant in vacum, and they do not include the catalytic role of the surface.

C. Energy barriers for the surface catalyzed dehydrogenations

Since the dehydrogenation processes which occur via the geometric configurations in vacuum show very high transition energies (see the supporting information), we calculated also the minimum-energy paths for chosen reactions which take place at the surface. In order to obtain the barriers for the reactions close to the surface, we applied the climbing-image nudged-elastic-band method (NEB), implemented in the QUANTUM ESPRESSO code\textsuperscript{19}. The results for chosen reactions are presented in Table\textsuperscript{[II]} Barrier energies are collected in columns corresponding to the symmetric and nonsymmetric geometries and to forward and backward reaction directions. The difference between the highest energy on the reaction path and the energy of the starting (or the final) geometric configuration gives the barrier for the reaction forward \( \rightarrow \) (or backward \( \leftarrow \)). The energy differences between the starting and the final configurations can be obtained from the differences \( \rightarrow \) - \( \leftarrow \). The barriers obtained on the minimum-energy path are not high. This implies, that the surface acts as a strong catalyzer in the dehydrogenation process of the hydrocarbon molecules.

The preliminary MD simulations of processes after the adsorption of C\textsubscript{3}H\textsubscript{7} show also cascade of dissociations. First, the released hydrogen from C\textsubscript{3}H\textsubscript{4}, or some other H from the atmosphere, collides with the remaining middle H of C\textsubscript{3}H\textsubscript{7}, dissociating it and effectively creating H\textsubscript{2} outgoing back to the atmosphere. In the following dynamical evolution (time scale of 90-280 fs), one H atom from the tail CH\textsubscript{3}-group of remaining at the surface C\textsubscript{3}H\textsubscript{6} specie is released, and immediately attracted to the surface Si-site neighbouring to the adsorption site of just deprotonized C\textsubscript{3}H\textsubscript{5}.
IV. CONCLUSIONS

Role of argon and the SiC surface as catalysts in the dehydrogenation processes has been investigated. We started with a removal of one hydrogen atom from the C$_3$H$_6$ molecule and found it to be sufficient to initiate the adsorption reactions, which may continue with further dehydrogenation of molecules and more strong binding, up to the C$_3$ moiety at the 4H-SiC(0001) surface. Barriers for the dehydrogenation of molecules at the surface, with one of the reactants in vacuum and other at the surface, are very high; except the first dehydrogenation of propane (see supporting information). On the other hand, the barriers obtained on the minimum-energy path for the hydrogen transfer from the adsorbed hydrocarbons onto the nearest Si-site at the SiC surface are rather low. We conclude, that the SiC surface should act as a strong catalyst in graphene epitaxy by the chemical vapor deposition process.

For the first time, we studied the chemical character of the dehydrogenation of molecules at the SiC slab, and not just the mechanical removing of the H atoms by the floating gas. We check a microscopic mechanism for the dehydrogenation of the SiC surface, assisted by the binding reaction of a proton to argon forming the ArH$^+$ molecule. After this process, the electronic charge could remain on the surface. The zero-temperature description, however, indicates that all proposed chemical reactions cannot occur without additional processes caused by the high temperature kinetics or by a strong laser beam.

Preliminary MD simulations without Ar in the atmosphere above the surface, performed at high temperature of about 1500 K, confirm the scenario with a cascade of dehydrogenations of the adsorbed hydrocarbons, and the fact that some of the dissociated hydrogens remain at the surface.

V. ACKNOWLEDGEMENT

We would like to thank Jacek Majewski for many useful discussions. This work has been supported by the European Funds for Regional Development within the SICMAT Project (Contract No. UDA-POIG.01.03.01-14/05/09) and by the European Union in the framework of European Social Fund through The Didactic Development Program of The Faculty of Power and Aeronautical Engineering of The Warsaw University of Technology. Calculations have been performed in the Interdisciplinary Centre of Mathematical and Computer Modelling (ICM) of the University of Warsaw within the grant G47-7 and in Polish Infrastructure of Informatic Support for Science in European Scientific Space (PL-Grid) within the projects nr POIG.02.03.00-028/08-00 and MRPO.01.02.12-479/02.

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