

# CVD Formation of Graphene on SiC Surface in Argon Atmosphere

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## Supporting information

The molecular calculations presented in Table 1, for methods R(O)HF and MP2, were performed with the GAMESS package. We used the gaussian basis set of 6-31G type, which includes the lobe functions as follows: for Ar (6S,10L) functions contracted to [1S,3L], for H (4S)/[2S], and for C (6S,4L)/[1S,2L]. For the closed shell calculations, for the systems with even number of electrons in the ground singlet state, we applied the RHF method, and for the open-shell systems we used the ROHF method. Further, we performed the MP2 calculations on top of the Hartree-Fock results. The molecular geometries were optimized within the frameworks of the applied methods.

The DFT calculations were performed within the generalized gradient approximation (GGA) with the Perdew-Wang (PW91) functional<sup>1</sup>. The ultrasoft pseudopotentials, generated with the Vanderbilt's code<sup>2</sup>, have been used. The energy cut-offs of 20 Ry and 200 Ry have been set-up for the plane-waves and the density respectively. Brillouin zone (BZ) integrations have been done with the uniform Monkhorst and Pack mesh<sup>3</sup> of (2,2,2) points, and a smearing technique<sup>4</sup> near the Fermi surface has been applied with the broadening parameter of 0.01 Ry.

The DFT molecular calculations were done with the spin-polarized approach for the cases with odd number of electrons, by setting the starting magnetizations appropriate to the required multiplet states (doublets in this work).

The surface calculations were performed with the slabs of 4H-SiC(0001) unit cells, repeated twice in the direction perpendicular to the surface (which gives 19 monolayers saturated with hydrogens at the bottom) and 3 times in the two directions parallel to the surface (3x3 surface unit cells, which gives 171 atoms of the slab in total). The vacuum space, above the surface in the supercells, had the thickness of about 10 Bohr. All geometries were optimized without the symmetry constraints using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method<sup>5</sup>.

In the calculations for charged negative systems, the positively charged uniform background has been applied, for the neutrality of the calculated cells, according to the Makov-Payne method<sup>6</sup>.

The graphics with molecular geometry has been prepared with the XCRYSDEN package<sup>7</sup>.

In the molecular-dynamics approach with the DFT framework, the motion of atoms is calculated directly from the underlying electronic structure of the systems. The fictitious dynamics of electronic wave function is treated in the same manner as the classical Newton-type dynamics of the atoms<sup>8,9</sup>. Wave functions must be known for each instantaneous configurations of atoms in the ground state and they reside on the Born-Oppenheimer surface. The Nosé thermostat is a method used for simulations of the canonical ensemble at predetermined temperature in quantum-mechanical molecular dynamics calculations of equilibrated systems<sup>10</sup>. In the approach of Nosé, the heatbath with the fixed temperature is introduced in the hamiltonian describing the system with an extra degree of freedom<sup>11</sup>.

The minimum-energy paths, for the dehydrogenation processes at the SiC surface, were calculated within the climbing-image nudged-elastic-band method<sup>12</sup>, assuming 7 images including the starting and the final configurations.

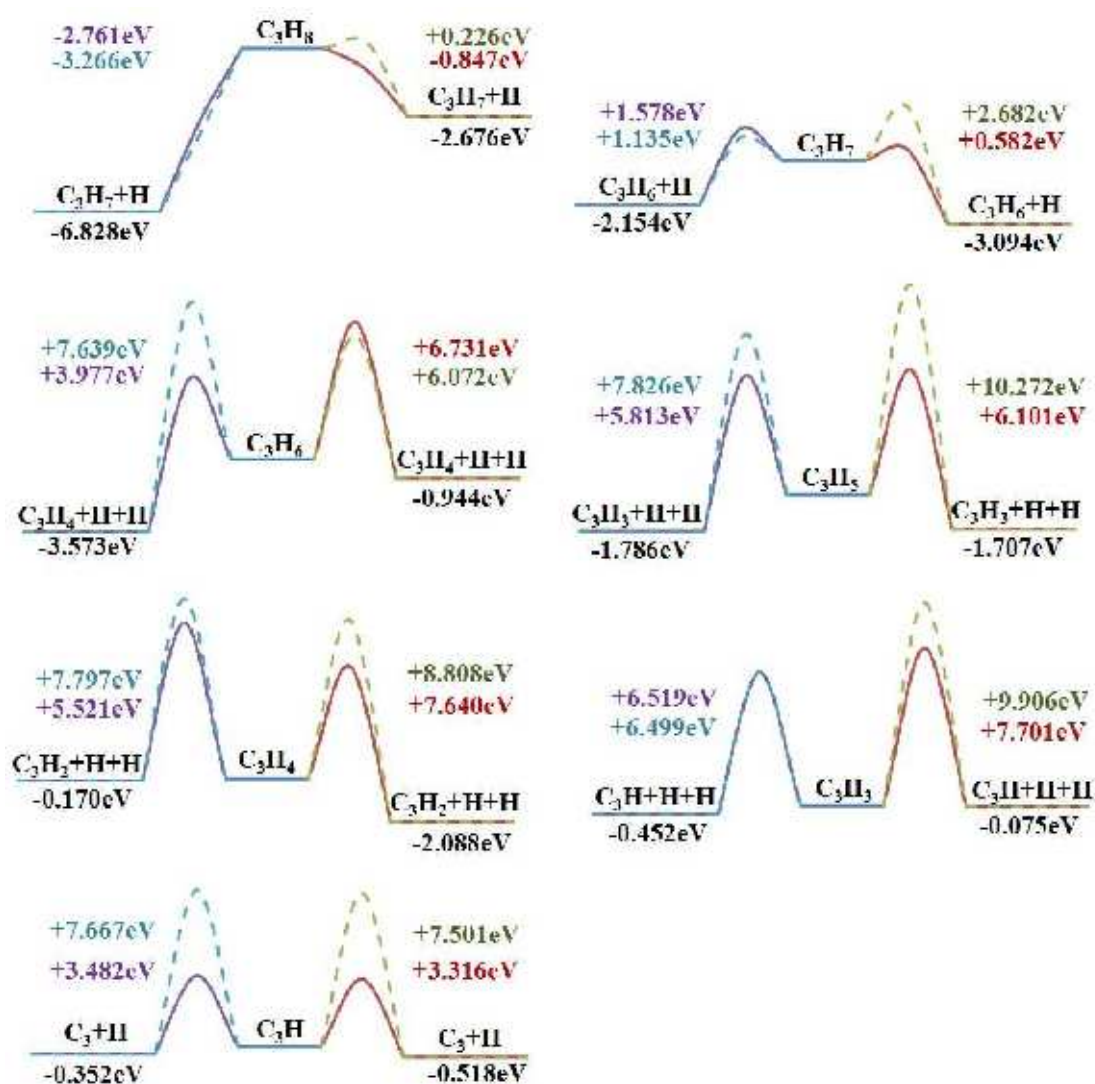
Main results of the work by Vance and Gallup<sup>13</sup> are used in our work in the context of the adsorption energy of the hydrogen atom at the SiC surface and we collect them here. The argon atom in the excited triplet states, <sup>3</sup>P<sub>2</sub> and <sup>3</sup>P<sub>0</sub>, has two unpaired electrons, characterized by the atomic configurations 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>4s<sup>1</sup> and 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>4p<sup>1</sup> respectively. These states lay about 11.55 eV and 11.72 eV above the ground <sup>1</sup>S<sub>0</sub> state. On the other hand, the hydrogen excited states (2s, 2p) lay about 10.2 eV above the ground state (1s). Therefore, the excited molecule ArH\* may dissociate into the two channels: Ar+H\* or Ar\*+H. The channel with the excited hydrogen is lower in the energy and it consists of a manifold of 3 states, with the deepest minimum of the dissociation-curve of about 2.44 eV, calculated within the multiconfiguration valence bond (MCVB) method. The same curve minimum obtained by means of the SCF-CI method amounts to 3.86 eV. The above numbers should be compared with the experimental result of 4.17 eV obtained from the elastic differential cross section data at a separation of 2.42 a.u. between the reactants. We note that such energy could conquer the H binding energy at the slab, of 3.92 eV. However, a requirement that H should be in the excited state is difficult to check theoretically

in the calculations for a surface, since the DFT method describes the ground state only. The time-dependent DFT, on the other hand, is known to perform better for molecules than for solids. Further, if one takes into consideration the higher dissociation limits of  $\text{ArH}^*$ , with an excited argon – in the two closely laying channels:  $\text{Ar}(^3P_2)+\text{H}$  and  $\text{Ar}(^3P_0)+\text{H}$  – then the manifold of four states should be examined due to molecular symmetry. Their minima, however, are shallower and do not exceed the energy of 1–1.5 eV, which is much below the H binding energy to the surface. From the above analysis of Vance and Gallup results<sup>13</sup>, it is clear that argon cannot build a molecule with neutral hydrogen in the experiment which we describe theoretically in this work.

In addition to the minimum-energy-path barriers, we calculated also the geometric configurations with one of the reactants in vacuum, with all the geometries being optimized separately. The energies of these configurations are depicted in Figure S1 included here. There was spotted an unique process, which seems to occur spontaneously, namely the removal of hydrogen from the terminal carbon of  $\text{C}_3\text{H}_8$  and the adsorption of  $\text{C}_3\text{H}_7$  radical at the surface. On the other hand, here, we did not calculate any intermediate geometric configurations with the reactants being unbound but still close to each other. Therefore, in this calculation, we do not see a small barrier found by the NEB approach which we reported in Table 2. All other energies, of the configurations with molecules calculated in vacuum, monotonically increase with the descending number of hydrogens contained in the adsorbed system. Although, the adsorption sites for the hydrogens were chosen in a different way for the NEB paths and for the configurations described here, one may compare these energies, since they have similar physical meaning. The barriers obtained on the minimum-energy path are much lower than the energies of configurations with the reactants calculated in vacuum, and this is a manifestation of the surface catalytic properties.

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**Fig. 1** Dehydrogenation reactions:  $C_3H_x@slab \rightarrow C_3H_{x-n}@slab + nH@slab$  where  $x=8,7,6,5,4,3,1$  and  $n=1$  or  $2$ . The transition energies are defined as: B1)  $C_3H_x@slab \rightarrow C_3H_{x-n}@slab + nH$  in vacuum (dashed line) and B2)  $C_3H_x@slab \rightarrow nH@slab + C_3H_{x-n}$  in vacuum (solid line). The middle levels describe the moieties bound to the slab surface for the both symmetric and nonsymmetric cases, with the adsorption energies set to zero as the reference energies (the absolute values of these adsorption energies are negative, except for the  $C_3H_8$  case for which it is around  $0.8$  eV at the distance from the surface similar to the  $C_3H_7$  bond with the surface Si atom). The energy levels of the species on the left-hand and the right-hand sides, in the figure, from the proper reference energy correspond to the symmetric and the nonsymmetric cases, respectively. The adsorbed hydrogens at the surface are at the Si-surface atoms chosen among "free" unadsorbed sites, somewhere between the adsorbed  $C_3H_x$  species within the calculated cells and their periodic analogs.