Graphene nucleation on (100)Si using toluene as carbon precursor: A DFT study on early-decomposition steps and anthracene formation

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Direct chemical vapor deposition (CVD) of graphene on industrially preferred semiconductor (such as c-Si) or dielectric substrates is a desirable approach to incorporate graphene into electronic devices, thus preventing the commonly used transfer process of graphene films from Cu foils, which inevitably leads to residual contamination and mechanical defects [1].

The CVD synthesis of graphene on Si substrates is realized using methane at high temperature (>900°C), although the low diffusivity of carbon species and the strong carbon solubility in Si lead to the unavoidable formation of SiC buffer layers, which severely hamper an efficient growth [2]. Though several strategies have been adopted to overcome such limitations, few studies have focused on the use of aromatic hydrocarbons as possible carbon precursors [3].

We recently reported on a DFT study of adsorption and most-likely decomposition paths of liquid aromatic hydrocarbons onto Cu(111) and showed that methyl dehydrogenation of toluene is the most favored one, leading to the abundant formation of adsorbed benzyl radicals onto Cu, as active species for graphene nucleation [3].

Here, we report on early decomposition steps of toluene and possible recombination pathways of as-formed active species onto the c(4x2)-reconstructed Si(100) surface through density functional theory (DFT) calculations with van der Waals corrections (DFT-D3). Toluene molecules can chemisorb with several configurations onto the Si surface by addition reactions [4]. We found the most stable configuration is the aromatic ring forming four sigma bonds with two adjacent Si dimers, having an adsorption energy of 1.39 eV, i.e. much higher than for Cu(111). Then, the minimum energy pathway (MEP) and transition state (TS) of chemical reactions (decomposition and recombination steps) were investigated through the climbing-image nudged elastic band (CI-NEB) method. As for the Cu surface [3], dehydrogenation of the toluene methyl group was found the most likely early-decomposition path with an energy barrier of 1.4 eV, while toluene demethylation is hampered by a much higher energy barrier.

Finally, the formation of anthracene (three connected phenyl rings) as possible stable graphene nuclei was investigated, for which we found a strong adsorption energy of 2.43 eV. Such carbon structure was obtained by recombination of two adsorbed benzyl radicals, although an energy barrier of ≥2.6 eV was estimated for this pathway.

References

[1] Wang H and Yu G., Direct CVD graphene growth on semiconductors and dielectrics for transfer-free device fabrication. Adv. Mater. 2016;28(25): 4956-4975.
[2] Khan A et al, New Insight into the metal-catalyst-free direct chemical vapor deposition growth of graphene on silicon substrates. J. Phys. Chem. C 2021; 125(3): 1774–1783.
[3] Tau O et al, Adsorption and decomposition steps on Cu(111) of liquid aromatic hydrocarbon precursors for low-temperature CVD of graphene: A DFT study. Carbon 2023; 206:142-149.
[4] Costanzo F et al, Theoretical study of toluene chemisorption on Si(100). J. Phys. Chem. B 2003: 107(37): 10209-10215.