

Carbon atom reactions in CVD graphene growth on nickel: A theoretical study

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1. Introduction

Chemical vapor deposition (CVD) using transition metal surface with hydrocarbon source is one of the practical methods to produce graphene. Nickel has been used most popularly among various transition metals as it is a typical catalyst for hydrocarbon reactions. The graphene growth behavior on nickel surface in the CVD production has been studied extensively because it is complicated as the carbon atoms produced by the hydrocarbon decomposition can dissolve in the bulk nickel. The nickel dissolved carbon atoms are reportedly responsible for the graphene growth via segregation [1]. This mechanism however is not straightforwardly acceptable since it is also reported that the graphene grows in different modes depending on the reaction temperature [2]. Batzil suggests that reaction via carbon segregation is valid for elevated temperature, while graphene is produced via ordinary surface nucleation at lower temperature [2]. Despite extensive experimental studies, atomistic picture of the carbon atom behaviors in the CVD reaction are not sufficiently understood. In the present study, we have performed theoretical calculations to obtain fundamental insights into the carbon atom reactions in the CVD process.

2. Carbon atom ...nickel surface bonding structures

The nickel bound atomic carbon species were studied first. We focused on the Ni(111) surface since most of the experiments are conducted using this surface. The calculated structures are a carbon atom on (111) surface, a carbon atom at corresponding subsurface and step sites, and a carbon atom in bulk nickel, and a graphene monolayer (GM) on a nickel surface which was picked up as a reaction product (Fig.1). In these calculations, nickel surface was modeled by three layer nickel slab with small unit cells (4, 6, or 9 nickel atoms in each layer). These structures were optimized by the density functional theory (PBE functional) using plane wave basis with a kinetic cutoff energy of 25 Ry.

The calculated structures and their formation energies (relative to the isolated carbon atoms and a nickel cluster) are given in Fig.1. Surface carbon atom occupies the three-fold hollow site, while carbon atoms at subsurface, step, and bulk sites occupy octahedral sites of the fcc-nickel lattice. Carbon atoms in these structures bond to neighboring nickel atoms relatively strongly with bond lengths of 1.7-1.9 Å. The GM carbon atoms are over the on-top site and three-fold hollow site. The carbon atoms in this structure are separated from the nickel atoms significantly compared with the other structures.

The formation energy per carbon atom is smaller in

the order of GM on surface (-7.56 eV), a carbon atom at step (-6.91), subsurface (-6.07), and surface (-5.95), and in bulk (-5.81). The smallest formation energy for GM on surface indicates that carbon atoms dispersed to various surface and internal sites of nickel should be finally incorporated in surface graphene. The formation energies of the other structures suggest that an atomic carbon preferably occupies step sites of the carbon-free initial state of nickel, and then subsurface, surface, and bulk sites. The least energetical preference of the bulk site, the most populated site in actual metal, means that carbon atoms substantially dissolve in nickel only at elevated temperature, which may be related to the experimentally observed temperature dependent behavior of CVD reactions [2].

Nickel bound carbon dimer species were also examined (Fig.2). The carbon-carbon bonding at surface, step, and subsurface has been found to be possible (C-C bonding structures in bulk have not been calculated because high energy was expected). The lengths of the C-C bonds at the surface and step correspond to a double bond, while that for subsurface corresponds to a conjugated double bond. Stabilities of the C-C bond dimers are in marked contrast to those of carbon monomers: the dimer is most stable on surface (-6.59 eV), and comparably stable to this at a step (-6.53); the dimer at subsurface is significantly unstable than the former two species (-6.14).

Combining the data in Figs. 1 and 2, we can discuss the energetical preference of the first C-C bonding processes. A carbon atom bonds to a surface bound carbon atom with reaction energy of -7.24 eV (to form a surface dimer), to a subsurface bound carbon atom with -6.21 eV, and to a step bound carbon atom with -6.08 eV. These data imply that the first carbon nucleation would take place over nickel surface. It may be noteworthy that the first C-C nucleation takes place on surface while carbon atoms tend to dissolve in nickel as observed experimentally.

3. MD simulations of carbon atom nucleation

Molecular dynamics (MD) simulations were performed to investigate the atomic processes of cluster growth in the later stage. In these calculations, classical force field ReaxFF [3] have been used instead of density functional theory to allow long time simulations. The accuracy of the force field was tested by calculating the structures and energies of the nickel bound atomic carbon species in Fig.1. It has been confirmed that this force field can moderately reproduce the relative energies of structures of the first principles calculation (Table 1).

NVT-constant MD simulations were started from the initial structure shown in Fig.3a. The five layer nickel of

420 atoms has two steps on both up and down sides, which were prepared since step site is supposed to be a carbon cluster growing site [4]. Carbon atoms are placed at the energetically preferred bonding sites, *i.e.*, 12 atoms at all the available step sites and 36 atoms at the 1/3 of the subsurface sites of the slab. Simulation temperature was set to 1500 °C, significantly higher than the experimental temperature (~1000°C) to accelerate the carbon nucleation. The nickel atom movement was constrained by a harmonic potential to prevent the surface structure from collapsing under the high temperature.

In the simulation, carbon atoms spend most of the time in moving around in the subsurface region, but they jump beyond surface nickel layer to the terrace at a rate of one atom in several ten picoseconds. The surface carbon atoms are long living, and they bond to a carbon atom at a step or another surface carbon atom after wandering the surface. The produced C-C bonds break seldomly, and the C-C bond species never sink into the subsurface. Thus, the number and size of the carbon clusters increase, which probably corresponds to the carbon segregation.

Snapshot at 1 ns in the MD simulation is displayed in Fig. 3b. Many of the carbon clusters are bonding to the steps, whereas some clusters reside on the terrace area without connection to steps. As of 1 ns, the largest carbon cluster is C5, which is on the terrace area. This result suggests that the carbon clusters do not necessarily grow at steps, as surface carbon atoms do not emerge through steps but through surface nickel layer.

4. Summary

We have performed theoretical calculations to understand the carbon atom behavior in the CVD graphene growth. First principles calculations for nickel bound carbon atom monomer and dimer suggest that initial carbon cluster emerges on nickel surface. The classical MD calculations suggest that carbon clusters do not necessarily grow at steps but can grow at terrace area.

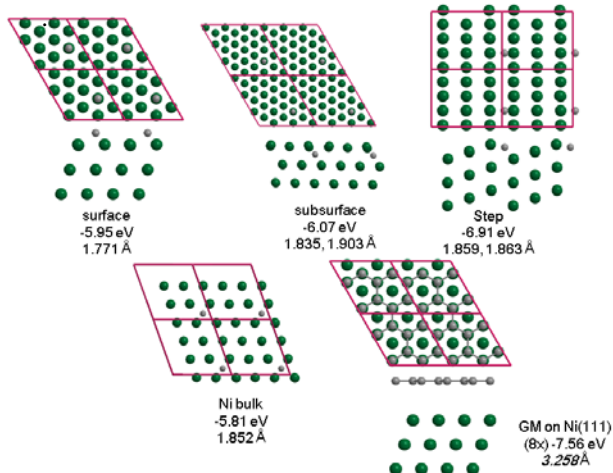


Fig.1. Calculated nickel bound carbon structures (top view and side view) and their formation energies (relative to isolated carbon atoms and nickel cluster, per carbon atom). The distances indicate the shortest Ni-C bond lengths. Lattice constants for the

periodic directions have been fixed to the calculated values for Ni crystal. The graphene...surface distance has been fixed to the experimental value in the calculations of the GM...Ni(111) model.

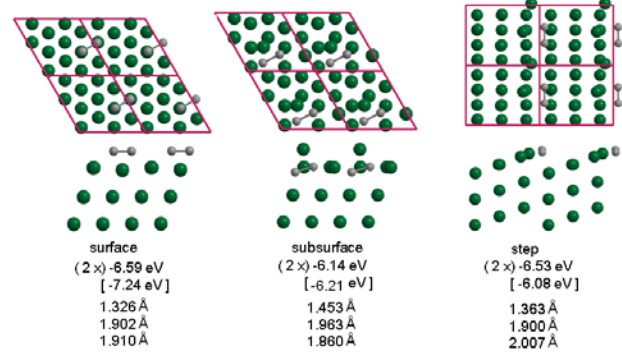


Fig.2. Calculated nickel bound carbon dimer structures and their formation energies. The values in square brackets are energies of formation from the corresponding monomer structures and a carbon atom. The distances indicate C-C bond lengths (first row) and the shortest Ni-C bond lengths (second and third row).

Table 1. Calculated formation energies (E) for the nickel bound carbon structures and their relative energies (E').

	ReaxFF*		PBE	
	E/eV	E'/eV	E/eV	E'/eV
Surface	-6.49	Ref.	-5.95	Ref.
Subsurface	-6.80	-0.31	-6.07	-0.12
step	-7.40	-0.91	-6.91	-0.96
GM on Ni(111)	-7.79	-1.30	-7.56	-1.61
Ni-bulk	-6.22	0.27	-5.81	0.14

*The lattice constants obtained from first principle calculations for Ni-bulk have been applied for the calculations using ReaxFF.

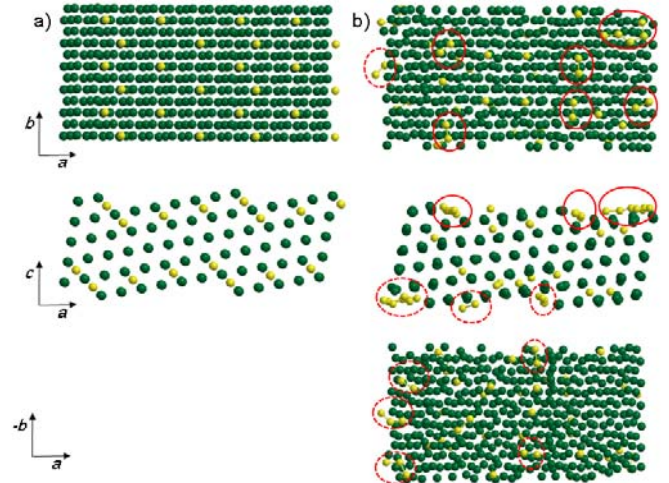


Fig. 3. Initial structure (a) and snapshots at 1 ns (b) in the MD simulations. Carbon atom clusters are marked with circles.

References

- [1] X. Li *et al.*, *Nano Lett.*, **9**, 4268 (2009).
- [2] M. Batzill., *Surf. Sci. Rep.*, **67**, 83 (2012).
- [3] J. E. Mueller, *et al.*, *J. Phys. Chem. C*, **114**, 4939 (2010).
- [4] F. Abild-Pedersen *et al.*, *Phys. Rev. B*, **73**, 115419 (2006).

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