A first principles study on CVD graphene growth on copper surface: C-C bonding reactions at graphene edges

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1. Introduction

Graphene has attracted considerable research interest owing to its potential application to future electronic devices. Large area and high quality graphene is needed for device applications. Chemical vapor deposition (CVD) using a copper surface with a hydrocarbon source is one of the practical methods to produce graphene. This method is appropriate for creating large area graphene with low cost, and the graphene growth control to obtain a high quality product is a remaining challenge. The carbon atom nucleation and cluster growth processes in the CVD reactions have been studied extensively as key steps that affect the graphene growth behavior. We have been studying the carbon atom reactions in these processes by theoretical approaches [1]. In the present study, we have focused on the later stage of CVD reaction, that is, carbon atom reactions at graphene edges by which carbon clusters grow in the Cu-CVD.

2. Computational Details

The energetics of carbon atom reactions and the carbon-metal interactions involved were analyzed by first principles (FP) molecular dynamics (MD) simulations. Molecular dynamical approach was adopeted since copper surface is active dynamically in typical graphene growth experiments at ~1000 °C [1] (cf. melting point of copper is merely 1084 °C). Since carbon atom bonding takes place rarely in plain MD simulations, constrained MD calculations with some appropriate reaction coordinates were performed to force C-C bonding. The energetics of reactions was analyzed in terms of potential of mean force using the blue moon (BM) method.

Three layer slab models of Cu(111) surface Cu₂₄₀C_{80+n} (n = 1-3) were employed in the simulations (Figure 1), where the 80 carbon atoms correspond to a graphene ribbon to form zigzag (ZZ) or armchair (AC) edge on the slab, and they react with as many as three external carbon atoms as described later. The first principles calculations employ PBE functional with ultra soft pseudo potentials. Energy cutoff was set to 18 Ry. Only gamma point was sampled. MD simulations were performed at 1000 °C, the temperature of typical Cu-CVD experiments. Simulations of 1000 time steps (dt = 2 fs) were carried out for each reaction coordinate, of which the 600 step data after the first 400 steps

of equilibration were used for the BM analyses. First principles simulator PHASE was used for these calculations [2].

3. Calculated Results

Figure 2 displays the calculated carbon atom reactions at the ZZ and AC graphene edges. They are series of reactions that construct a reaction pathway to form a new six-member ring at each graphene edge. These reaction pathways were studied in a paper [3] by static calculations (geometry optimizations) as one of the possible routes that allows recursive increase of 6-member rings at graphene edge. Although the importance of these reaction pathways are not verified, we have examined the reactions involved to understand the characteristics of the possible carbon atom reactions at graphene edges.

To illustrate our BM analysis, the mean forces and the free energy curve (potential of mean force) calculated for the reaction $1 \rightarrow 2$ at ZZ-edge are shown in Figure 3 as an example. The data points of mean force form an almost continuous curve, suggesting that our data sampling has been successful. The free energy curve shows that this process is a one-step reaction. There is an energy minimum ($r \sim 1.4$ Å) corresponding to C-C bonded structure, an energy maximum ($r \sim 2.2$ Å) corresponding to the energy barrier to C-C bondig, and an energy-flat region ($r \sim 3.8$) Å corresponding to carbon atoms' dissociated state. By fitting the data around the minimum and maximum to third order polynomials, the reaction energy is calculated as -0.69 eV, and the activation energy is calculated as 0.94 eV.

The energetics of the other reactions are analyzed in the same way as this reaction. The results obtained are summarized in the form of energy diagram in Figure 4. The data show that each elementary step has an energy barrier of ~ 1.0 eV, suggesting that the series of these reactions are possible energetically at typical experimental CVD temperature of ~ 1000 °C. These energy barriers commonly arise from the bond reorganization from Cu-C to C-C (an example for the process $1 \rightarrow 2$ at ZZ edge is shown in Figure 5), and therefore their activation energies are not so different. The calculated results imply that the barrier of the rate limiting step of graphene growth would be of around ~ 1 eV even if the graphene edges grow via other reaction pathways than those in Fig. 2. We have already studied carbon atom nucleation processes in Cu-CVD by FPMD based BM analysis elsewhere [1], where we have found that carbon atom dimerization proceeds with activation energies of 0.5-0.8 eV. The calculated results in Fig. 4 suggest that the carbon atom incorporation to graphene edges is a slightly higher-energy process than carbon atom dimerization. It is therefore suggested that the carbon atoms in the reaction system form new nuclei more preferably than react with graphene edges, until sufficiently large nuclei, with many reaction sites, appear in the later stage of CVD.

It would be worth remarking that the reactions at ZZand AC-edges in Fig. 4 are almost equally energetically favorable. This is in contrast to the reported results of static calculations [3] which suggest that an AC graphene edge is much more active to carbon atom incorporation than a ZZ edge.

4. Conclusions

We have studied carbon atom reactions at graphene edges by which carbon clusters grow in the Cu-CVD. These reactions have energy barriers of around $\sim 1 \text{ eV}$ arising from the bond reorganization from C-Cu to C-C. These activation energies are slightly higher than those of carbon atom dimerization.

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Fig.1. Copper-carbon model systems employed in the FPMD calculations (top view and side view, copper and carbon atoms in yellow and red, respectively). a) ZZ-edge and b) AC-edge graphene ribbons, and a carbon atom to react with them as an

example case, are placed on the three-layer-slab surface models of Cu(111) surface ($8x5\sqrt{3}$ supercell layer).



Fig.2. The carbon atom reactions at graphene edges that are studied in this paper by FPMD. These reactions were studied originally by static calculations in ref. 3. The inter-atomic distance between a bonding atom pair is employed as the reaction coordinate in the constrained MD simulation.



Fig.3. a) Calculated mean force for the carbon atom incorporation to ZZ-edge (reaction $1 \rightarrow 2$ in Fig. 2.) and b) its integral (potential of mean force). Energy in b) is relative to the energy minimum data at r = 3.8 Å.



Fig.4. Summaries of the reaction energies (subscript r) and activation energies (subscript a) for the reactions in Fig.2. Values without parentheses are relative energies of reaction steps to the initial state (1) for each reaction pathway.



Fig.5. An MD snapshot taken from simulations of the energy barrier regions for reaction $1 \rightarrow 2$ at ZZ edge (left), and the magnified view of the atoms around the reaction site of this snapshot (right).