First-principles study of coronene adsorption on hexagonal boron nitride substrate

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A B S T R A C T

The adsorption energy of coronene on hexagonal boron nitride (h-BN) substrate has been calculated using the first-principles calculation with van der Waals interaction. As a benchmark for validating our computational calculations, the adsorption energy of coronene on graphene was also calculated. Our calculations indicate that the adsorption energy of the AB-stacked configuration of coronene on h-BN, where N-atom is located below the center of coronene, is slightly larger than the adsorption energy of that on graphene substrate, and consequently the AB-stacked coronene on h-BN can be pinned to a specific in-plane rotation angle at room temperature. A simple explanation of the stable coronene configuration is provided in terms of the repulsive interaction with substrates.

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1. Introduction

In industrial applications, graphene has attracted much attention as a promising material for nanoelectronic devices. Since its characteristic properties come from the C_6 rotational symmetry of carbon lattice, it is important to make graphene films of high quality at the atomic scale. In particularly, for an application of graphene nanoribbon (GNR) such as spin devices, it will become even more necessary to keep a hexagonal arrangement along a specific orientation.

To fully realize the functionality of graphene, many efforts have been devoted to bottom-up approaches such as epitaxial chemical vapor deposition (CVD) on metal substrate [1–5]. Recently, the seed-assisted growth of graphene on metal substrate have been proposed by several authors [6–8]. In Ref. [8], coronene is chosen for the nucleation seeds in consideration of thermal tolerance and avoidance of defects in the initial nucleation stage. Although these techniques seem to be effective for low-cost fabrication of large-scale graphene films, the grain boundaries (GBs) due to the randomly oriented grain-grain collision are unavoidable. In order to make the ideal uniform graphene with the help of seed-assisted growth, commensurate stitching [9] between aligned seeds is important. Therefore, a technique for pinning seed molecules on substrate may become a key issue. In regard to suppression of GBs, the directly oriented growth of GNRs on Ge(001) via the CVD method was performed [10,11]. In light of the above, it is suggested that pin-

ning and anisotropic growth can be controlled by introducing a strong interaction with substrates.

In this short paper, a possibility of anisotropic pinning of seed molecules on substrates has been investigated theoretically. Coronene was set as the seeds, and hexagonal boron nitride (h-BN) was chosen as the substrates. Considering that the lattice inversion symmetry of h-BN is broken compared with graphene, anisotropic adsorption of coronene is expected to occur through an interaction with the symmetry-breaking lattice of the h-BN substrates. Some configurations of coronene/h-BN were set, and their adsorption energy was calculated using first-principles calculation.

Here, we should refer to previous work. In recent decades, theoretical studies of electronic and structural properties of graphene/h-BN heterostructures and superlattices have been already performed by many authors [12–19], and various interesting physical phenomena were observed experimentally [20–22]. As a result of more recent experimental studies [23,24], it has been reported that graphene flakes on h-BN become thermally stable at a specific in-plane rotation angle. However, to the best of our knowledge, a detailed theoretical study of adsorption energy between a small PAH molecule like coronene and h-BN substrate has not yet been reported except for the case of graphene substrate [25,26].

The remainder of this paper is organized as follows: in Section 2, our numerical conditions are briefly explained. In Section 3, the adsorption energy of the coronene/graphene system is calculated as a benchmark
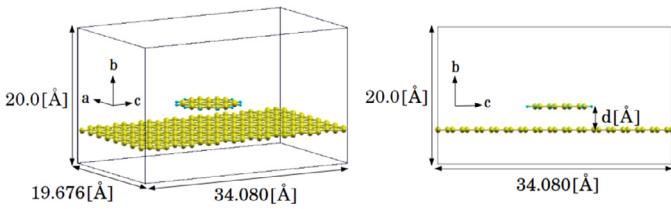

Fig. 1. A unit cell of the coronene/graphene system.

for validating our calculations, and then, the coronene/h-BN system is discussed. Finally, the results are summarized in Section 4.

2. Computational details

In this section, we explain the first-principles calculations using density functional theory [28,29] to investigate the structural properties of the coronene/h-BN system. We have used the spin-polarized density functional theory code, OpenMX [30,31]. For the exchange-correlation potential, Generalized Gradient Approximation (GGA) was used within the Perdew-Burke-Ernzerhof (PBE) [32] functional. The van der Waals interaction is treated within the DFT-D3 method [33,35] for GGA/PBE functional. The electron-ion interaction was described by norm-conserving pseudopotentials [36] with partial core correction [37]. Pseudoatomic orbitals (PAOs) centered on a atomic sites are used as the basis function set [31], and then the PAO basis functions are specified by C-s2p2d1, H-s2p2d1, B-s2p2d1, and N-s2p2d1, where s2 indicates the use of two orbitals for s component. Fig. 1 shows a unit cell of the coronene/graphene system in this study. We have used the k-points $4 \times 1 \times 4$ for the unit cell. Here, we chose one k-point, the gamma point, for b-axis because the slab of coronene/substrate is repeated in the b-axis direction and separated by a vacuum layer with a thickness of about 20Å. The convergence criteria for total energy E were set as 1.0×10^{-8} Hr. The adsorption energy is calculated by the difference of total energy between coronene/graphene (or h-BN) and each isolated system; $E_{\text{coronene/graphene(h-BN)}} - (E_{\text{coronene}} + E_{\text{graphene(h-BN)}})$. To take account of basis set superposition error caused by localized orbitals, the counterpoise method [38] was applied to estimation of the adsorption energy. The equilibrium lattice constant of the supercell for coronene/graphene (or h-BN) system was set as $a = 19.676$ (20.036)Å, $b = 20.0$ (20.0)Å, and $c = 34.08$ (34.704)Å, respectively. This cell size is large enough to neglect an interaction of coronene with its images in neighboring supercells.

3. Results and discussion

First, the equilibrium distance between coronene and substrate is discussed. The adsorption energy was calculated with a fixed distance d between coronene and substrate. The geometry of coronene and the substrate is optimized individually using molecular dynamics with the convergence criteria for total energy and forces on atoms being 1.0×10^{-8} Hr and 1.0×10^{-4} Hr/bohr, respectively. Fig. 2 shows the adsorption energy per C-atom of coronene as a function of the distance d. We start with a benchmark calculation of AB-stacked coronene on graphene substrate. Then, the equilibrium distance is estimated as 3.4 Å, and its adsorption energy is estimated as 59.1 meV per C-atom of coronene (in other words, 1.42 eV per coronene molecule). This value is consistent with the previous work, where the adsorption energy was estimated to be about 58.0 meV per C-atom of coronene [25] by the DFT-D2 method [34]. The other DFT calculations [25,26] using the vdW-DF method [39,40] show that the adsorption energy per coronene is estimated about to be 65 meV [25] per C-atom, or 1.78 eV per coronene [26]. Although a discussion of the accuracy between these DFT functionals is beyond the scope of the present work (see in Ref. [27] for a detailed study), it is noted that the adsorption energy obtained by the DFT-D3 method is a smaller value
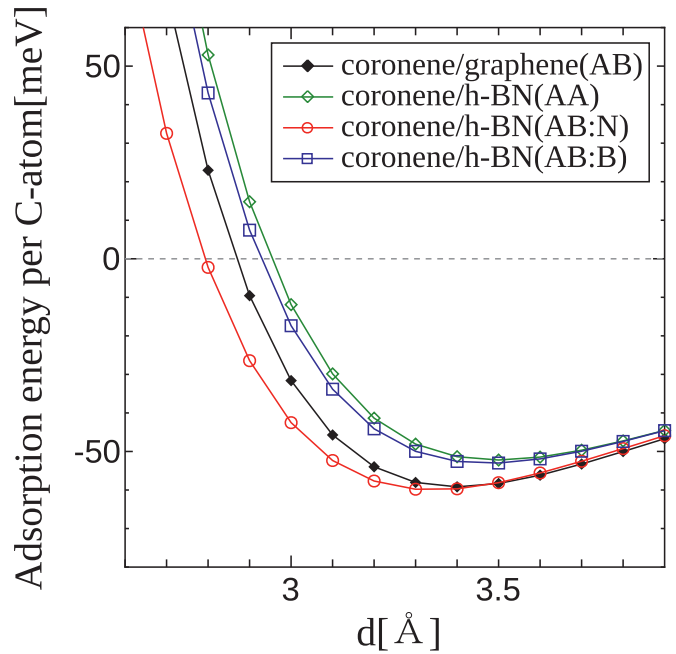

Fig. 2. Adsorption energy of the coronene/substrate system per C-atom of coronene as a function of the distance d between coronene and substrate: AB-stacked coronene on graphene (black), AA-stacked coronene on h-BN (green), AB-stacked coronene on h-BN where N-atom is located below the center of the coronene (red), AB-stacked coronene on h-BN where B-atom is located below the center of the coronene (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

than that obtained by the vdw-DF method in this system. Next, let us proceed to the h-BN substrate case. Here, two AB-stacked configurations were considered: one is a configuration where B-atom is located below the center of coronene (AB:B) and the other is a configuration where N-atom is located below the center of coronene (AB:N). In both cases of AA-stacking (AA) and AB:B, the equilibrium distance is estimated to be 3.5 Å. This value is larger than that in the case of the above-mentioned graphene substrate. In contrast, AB:N has a smaller equilibrium distance, 3.3 Å. The adsorption energy in each equilibrium configuration indicates that the AB:N configuration is the most stable. In the region of d < 3.3, AB:N gives a slightly smaller adsorption energy than in the case of AB-stacked coronene on graphene. These results are consistent with the previous theoretical studies of graphene film on the h-BN system [12,14–17].

Second, in-plane rotation angle dependence of the adsorption energy is discussed. A model of AA- and AB-stacked coronene on graphene substrate at a rotation angle θ is illustrated in Fig. 3. Here, the distance of d was fixed with the equilibrium value. Fig. 4 shows the θ-dependence of the adsorption energy by the DFT-D3 method. The most stable state is AB-stacking at $\theta = 0°$ and the meta-stable state is AA-stacking at $\theta = 30°$. The energy difference between the most stable state and the meta-stable state is estimated to be about 16.9meV per coronene molecule. This indicates that the stability of AB- and that of AA-stacked coronene on graphene substrate are equivalent at room temperature ($k_B T \sim 25$ meV). According to the previous study [41] using classical molecular dynamics, the energy gap between AA- and AB-stacking is 0.36 meV/atom. Our results are obtained by a factor of two compared to the molecular dynamics simulation. The stability between AB-staking and AA-stacking configuration becomes inverted at around $\theta = 20°$, and then the activation energy is estimated to be 61meV. These results suggest that coronene seeds on graphene substrate can have random orientation at the initial adsorption stage, and subsequently are weakly anchored at room temperature.