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Self-assembly of carbon nanoclusters on dielectric boron nitride

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ABSTRACT

Nucleation and growth of C nanoclusters on a dielectric boron nitride (BN) substrate is investigated by first-principles calculations. Monatomic C quantum wires, chemically bonded by one terminal atom to the BN substrate, are found to be stable during the initial growth stage when the number of atoms is less than 10. Monatomic C rings, physically adsorbed on the substrate dominate the second growth stage. The critical number of atoms for quantum rings is 22. Hexagonal honeycomb structures dominate the third growth stage. No critical size is found for hexagonal honeycomb nanoclusters, in contrast to the growth of C clusters on metal surfaces. The stability of hexagonal honeycomb nanoclusters increases with cluster size, and a graphene layer has the highest stability. The presence of C_5 ring units has a negative impact on a cluster's stability and also acts as the source of a magnetic moment due to the unpaired 2*p* electron. 3D-like C cluster structures are not stable on a BN substrate.

1. Introduction

Graphene is a two-dimensional hexagonal honeycomb material, composed of carbon atoms. The conjugated π electron in graphene mimics a relativistic particle with zero rest mass and has an effective speed of 10^6 ms^{-1} [1]. Graphene can be fabricated by chemical vapor deposition (CVD) on a metal or dielectric substrate [2–10]. For compatibility with current MOSFET technologies, direct growth of graphene on a dielectric substrate is preferable, as it removes the necessity of transferring graphene to a dielectric substrate or atomically depositing dielectric materials on graphene. Few-layer nano-graphene has been synthesized on MgO, Al_2O_3 and SiO_2 dielectric insulator substrates [7–11]. However, the large lattice mismatch between graphene and these three dielectric materials hinders the large-area growth of graphene layers. In addition, these oxygen-rich substrates will chemically decorate graphene and introduce strong *P* type doping effects due to the charge transfer between graphene and substrate.

Boron nitride (BN) is regarded as a natural substrate for graphene due to favorable lattice matching between the two. BN is also chemically inert and thus would not be expected to cause any significant doping effects due to its weak interactions with graphene. Experimental studies have been undertaken to fabricate crystalline graphene on BN substrates [9–11], but the corresponding microscopic nucleation and growth mechanism is not clear. Here we investigate the growth process of C nanoclusters on a hexagonal BN dielectric substrate, from a single C adatom to a full monolayer, using first-principles calculations based on density functional theory. We find that there are three dominant growth stages for C clusters on BN: monatomic quantum wires, monatomic quantum rings and hexagonal honeycomb structures.

2. Computational methods

Theoretical calculations were performed with the Quantum Espresso package [12], employing both the local density approximation (LDA) exchange-correlation functional and the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional with non-local van der Waals dispersion (vdW) corrections according to the vdW-DF2 procedure [13,14]. The cutoff energy of the plane-wave basis set was 35 Ry. A hexagonal BN layer with a 7×7 supercell was used as substrate to simulate the CVD growth of carbon nanoclusters. As the vertical C monatomic wires with up limit of 13 atoms will be considered, a 2.6 nm vacuum layer was used to eliminate the longitudinal interactions between supercells. The sampling for the Brillouin zone includes a $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh. The cohesive energy was calculated by the following equation:

$$E_{coh}(n) = \frac{-[E^{ads}_{C_n} - E_{slab} - nE_C]}{n}, \quad (1)$$

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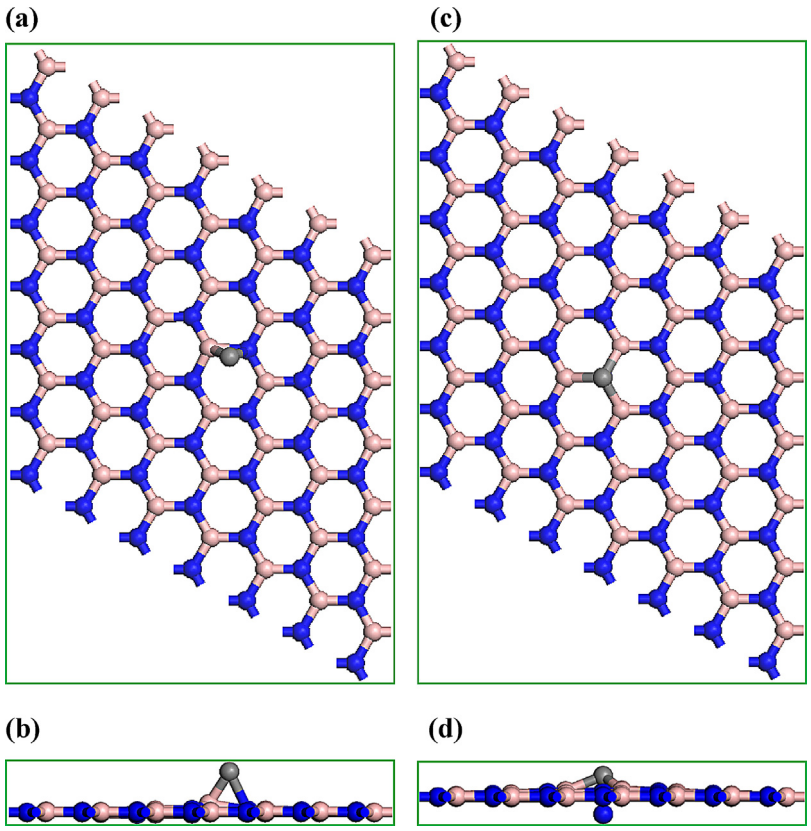

Fig. 1. Adsorption configurations of monomer on BN substrate. (a and b) Bridge configuration. (c and d) C-substitutional configuration. N atoms are blue; C atoms are gray, and B atoms are pink. This notation is used throughout this paper. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

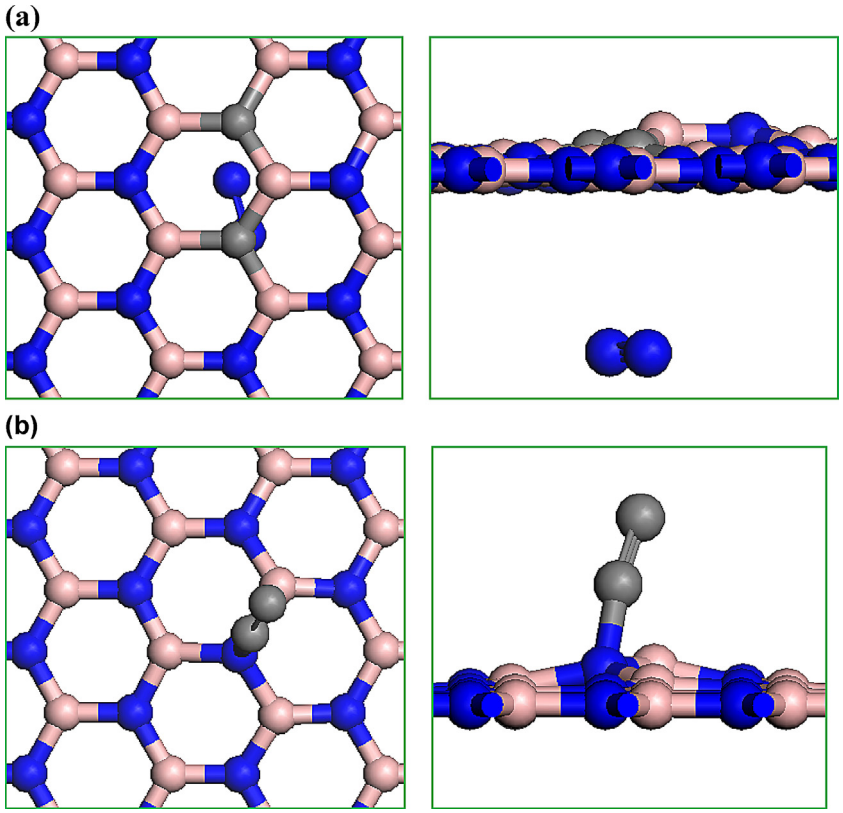

Fig. 2. Adsorption configurations of dimer on BN substrate: (a) C-substitutional configuration and (b) monatomic wire configuration.