Nucleation of Boron-Nitrogen on Transition Metal Surface: A First-Principles Investigation

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Boron nitrogen (BN) monolayer has attracted considerable attention because of their successful incorporation with graphene based nanodevices. However, many important aspects of the growth mechanisms are still not well explored. Using density functional theory (DFT) calculations, we found that Cu(111) surface is more suitable to be used as a substrate to grow BN monolayer compared with Ni(111) surface. Moreover, we explored that one-dimensional (1D) BN chain configuration is dominant to the two-dimensional (2D) BN ring formation from one pair to five BN pairs deposited on Cu(111) surface. Energetically stable structure transformation of BN monolayer from 1D BN chain to 2D BN ring occurs when the number of pairs is \( n > 5 \). It is suggested that, as the number of BN pairs increases the energetically stable structures achieve.

Key words: Growth mechanism, Density functional theory, BN monolayer

I. INTRODUCTION

During the past decade, such as graphene and hexagonal boron nitride (h-BN), two-dimensional (2D) materials have attracted attentions of physicists and material scientists because of their unique electronic properties, high thermal conductivity, high electrical resistivity, and other promising future industrial and potential applications [1–5]. Boron and nitrogen based 2D materials can be used in different future applications such as atomically thin capacitors, light emitting diodes and laser diodes [6, 7], neutron detectors [8, 9], coating [10] and other related technologies [11]. Besides, in the case of 2D BN monolayer, the bulk compound has excellent properties, such as high-temperature stability, low dielectric constant, large thermal conductivity, and high mechanical strength [12]. Boron and nitrogen have very similar radii as carbon and the lattice mismatch between hexagonal boron nitride (h-BN) and graphene is very small (<1.7%) [13, 14]. Thus, 2D BN monolayer is a promising substrate for graphene electronics [15]. Consequently, high-quality and large scale BN monolayer is necessary for all of these practical applications.

Among the established methods of synthesizing these 2D materials, chemical vapor deposition (CVD) is the most promising method for the synthesis of high-quality 2D materials [16]. Recently, intensive theoretical and experimental efforts have been made to synthesize 2D h-BN monolayer on various transition metals such as Ni [17–19], Ru [19, 20], Cu [21], Pt [22], and Pt [23]. Mostly for all transition metal substrates, recent density-functional theory (DFT) studies state that the N atom in the BN layer is repelled from the metal while the B is attracted toward the metal [24]. Strong covalent sp\(^2\) bonds in BN monolayer make it mechanically stronger [21]. Experimental studies of deposition of hexagonal BN on the metals mentioned above show that Cu is a crucial substrate for the synthesis of BN films [25] which in turn are crucial ingredients in graphene-based devices [26]. Also, Cu is attractive due to its high purity and relative cheapness. However, the atomic growth mechanisms of the 2D h-BN monolayer on various transition metals surfaces are still not well explored.

To improve the quality of 2D materials by using CVD, it is necessary to have a theoretically deep understanding of nucleation mechanism of BN pairs with the stepwise increment on transition metals surfaces. Since Cu(111) and Ni(111) are broadly adopted as substrates to grow 2D materials, here, we will study the mechanism of BN pairs on such surfaces. Our findings will be very helpful for synthesizing BN monolayer on transition metal surface experimentally.

II. MODELS AND THEORETICAL METHODS

First-principles calculations were performed with the Vienna \textit{ab initio} simulation package (VASP) [27], using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [28]. All structures were opti-
mized by a conjugate gradient method until the force component on every atom was less than 0.01 eV/Å. The plane-wave basis kinetic energy cutoffs of 400 eV and convergence criterion of $10^{-5}$ eV were used in all calculations [29]. In order to accurately describe the van der Waals interactions (vdWs) between BN pairs and the metal surface, the vdWs correction (DFT-D2) has also been used [30]. In this study, more than 3 layers of Cu atoms were used to build as substrates with 20 Å vacuum slabs perpendicular to the surface. To investigate the nucleation of paired BN monolayer on Cu(111), we have considered various possible chain and ring structures which consist of 1-8 BN pairs. The Cu(111) slab was gradually expanded to make sure the distance between two neighboring BN clusters was more than 9 Å with the size increasing of clusters. A climbing-image nudged elastic band method [31] was employed to predict the energy barrier of one BN pair diffusing on surfaces.

III. RESULTS AND DISCUSSION

First of all, a wise choice of the precursor is very important for the CVD process. Considering that on the surface of a transition metal substrate, B and N atoms are very easy to form BN monolayer. Here we choose the BN pairs as the precursor to study the CVD process of h-BN. To study the diffusion of BN pairs, which is important for the nucleation, we firstly consider the possible adsorptive sites of single BN pair on the surface of Cu(111) and Ni(111). By placing BN pair on various adsorption sites such as on hcp and fcc positions, we optimized the structures to find the optimal adsorptive positions. Through total energy calculations, we find that binding energy of BN pair is larger on Ni(111) surface, compared with Cu(111) surface. To gain more details of such interactions, we plotted the partial density of states (PDOS) of BN pair and the top surface. From FIG. 1 (a) and (b), one sees that, for one BN pair on Cu(111) surface, the main peaks of PDOS for BN pair are close to the Fermi level (around $-1.5$ eV) and those for Cu atoms are far away from the Fermi level (around $-3$ eV). While for the case of Ni(111) surface, the main peaks of PDOS for BN pair shift left in energy (around $-4$ eV) and those for Ni atoms shift right closer to the Fermi level (around $-1$ eV). These imply that the Ni(111) surface transfers more electrons to the BN pairs than the Cu(111) surface does. This can be understood that Ni has lower electronegativity than Cu. Due to this, a BN pair bindings stronger with the Ni(111) surface than the Cu(111) surface. Generally, the larger binding energy of precursors means that energy barrier of diffusion becomes higher. Consequently, it is unfavorable to the fast growth of large scale mono-layer.

To confirm the above conclusions, it is necessary to analyze one BN pair diffusing on Cu(111) and Ni(111) surface to see the behavior of nucleation process. Here, we explored the diffusion of a BN pair from one optimal adsorptive site to the nearest one on Cu(111) and Ni(111) surfaces by using climbing image-nudged elastic band calculations. The computed energy barrier is 0.50 and 0.66 eV for Cu(111) and Ni(111) surfaces, respectively. FIG. 2 (a) and (b) represent the transition barrier and relaxed geometries of initial state, transition state and final state on the Cu(111) and Ni(111) surfaces respectively.

The computed energy barrier for Cu(111) substrate is lower as compared to Ni(111) substrate, which means that the process of diffusion on the surface of Cu(111) substrate is faster and easier than Ni(111) substrate, consistent with our former analysis. Note that, the BN pairs can also diffuse in the sublayers of the substrates, but this process is usually more difficult than that on the surface and the diffusion barrier is much larger. Thus in the present work, we mainly discuss the diffusion process on the surfaces. Our study shows that the BN monolayer atoms on the surface of Cu(111) are stable and have low energy barrier of 0.50 eV as compared to Ni(111). Here we can predict for experimental research that, during the deposition process, the metal substrate not only works as a catalyst to lower the energy barrier of the reaction but also determines the BN atoms deposition mechanism, which ultimately affects the quality of BN on a substrate.

Next, we study the nucleation process of BN pairs. For each size of BN clusters on Cu(111) surface, various different configurations were explored, and the optimized structures with the lowest energy were taken as the ground state. By reviewing all these optimized structures, we find that they can be classified into two categories: (i) BN chains and (ii) BN rings. Our results demonstrate that 1D BN chains formation on a transition metal surface is favored when the size of BN clusters is small. As the size of BN cluster increases, the ground state structure transforms from 1D BN chain to the 2D BN ring. The critical point occurs at $x=6$, where $x$ is the number of BN pairs forming a cluster. For quantitative analysis, we calculate the adsorption energy of each BN cluster with a step-wise increment of BN pair. The adsorption energy $E_a$ is presented as:

$$ E_a = \frac{E_{\text{total}} - E_{\text{Cu}} - xE_{\text{BN}}}{x} $$

where $E_{\text{total}}$ is the total energy of $x$(BN) adsorbed on Cu(111) surface, $E_{\text{Cu}}$ and $E_{\text{BN}}$ are the energies of the isolated Cu substrate and BN pair respectively, and $x$ denotes the number of BN pairs. The process of BN nucleation is considered to start by using a stepwise increment of BN pair on the surface of Cu(111) as shown in FIG. 3.

FIG. 3 shows the representative chain and ring structures and their adsorption energies for BN clusters with different sizes, which shows that for $x<6$, the energetically optimized stable structure with the lowest adsorp-
FIG. 1 Projected density of states for one BN pair on (a) Cu(111) surface and (b) Ni(111) surface, respectively.

FIG. 2 (a) Minimum energy path for one BN pair on Cu(111) surface with an energy barrier of 0.50 eV, (b) minimum energy path for one BN pair on Ni(111) surface with an energy barrier of 0.66 eV.

tion energy is 1D BN chain structure, but when \( x \geq 6 \), the energetically optimized stable structure with the lowest adsorption energy is 2D BN ring structure. The most optimized stable structures of paired BN cluster with \( x \geq 6 \) always have a few (i.e. one to three) rings in their formation, which originates from the requirement to reduce the number of edge BN atoms. Atoms of one BN pair on the surface of Cu(111) have adsorption energy of 7.62 eV and distance between B and N is 1.346 Å, while adsorption energy of two BN pairs on Cu(111) is 7.97 eV, the distance between two BN pairs is 1.341 Å. The adsorption energy for two BN pairs is higher than one BN pair on Cu(111) surface but less than the summation of two isolated BN pair on Cu(111) surfaces. This means that as the number of BN pair increases, the surface of the substrate becomes more stable for the nucleation of BN. The two end atoms of boron and nitrogen chain bind to the hollow sites of Cu(111) surface strongly and stabilize the BN chain formation on the surface of a substrate. Interestingly, for 4 BN pairs, the adsorptive energy of ring structure is much smaller than the other cases. After carefully studying the structure, we found that the fourth BN pair added lowers the adsorptive energy which is due to the weak interaction with the other pairs. For BN atoms up to 5 pairs, the possible ring formation is unstable on Cu(111) surface as compared to the formation of a chain, which is stable and has lowest adsorption energy as compared to a ring structure. When the number of pairs exceeds 5, the ring structure becomes more favored than the chain structure. Further analysis showed that the stable ground state structure transformation from 1D BN chain to the 2D BN ring plays an important role in the nucleation of BN monolayer on Cu(111). Hence, during the nucleation step of BN growth on Cu(111) surface, a short BN chain is initially formed and then transformed into two-dimensional BN ring with the further increment of BN pair. With the deposition of paired BN atoms, BN rings act as a nucleation center and the number of rings will increase by the continuous increment of BN pair. In FIG. 3 a few snapshots represent the growth of BN rings with the increment of those added pairs.

For chain structures up to 6 pairs, we can see that BN atoms make a bridge on the surface of Cu(111) where boron and nitrogen atoms prefer the hcp and fcc sites respectively. In all configurations, up to 5 BN pairs, the chain configuration is favored over a ring configuration. On the other hand, if we analyze on the basis of single and double arch structure which are formed in the optimized structures from 3 to 8 BN pairs as shown in...
FIG. 3 Optimized geometries and their respective adsorption energies (under each configuration) for chain and ring configuration for BN pairs on Cu(111) surface where $x$ ranges from one to eight.

FIG. 4. FIG. 4 (a) shows the graphical comparison of deposition of BN chain and ring structures on Cu(111) on the basis of formation energy and number of BN pairs. This means that up to 5(BN) all the chain configurations are dominant over the ring configurations. The transition of energetically stable configuration from chain to ring structure occurs when the number of BN pairs is greater than or equal to six. So, for BN pairs number greater than five, the BN ring configurations are dominant over chain configurations because of long unstable BN chain and dislocation centers.

Aside from the energetic comparison, FIG. 4 also shows that from 3 BN pairs to 5 BN pairs chain configurations single arch shapes are formed and height of arch is also increased, while double arched shapes are formed for 7 and 8 BN pairs configurations. The transition of a single arch to double arch occurs because of lattice mismatch and dislocation between the substrate and deposition atoms as reported by Fan et al. [32]. It states that the chain stability fluctuates as more atoms are added to the chain because additional dislocations are formed. Chain breakage and initiation of two-dimensional (2D) always start again at dislocation centers which can be clearly observed in FIG. 4 (b) for 7 and 8 BN pairs on Cu(111). During the formation of BN chain configurations, chain always grow along the direction on the surface of the substrate where the mismatch is minimal. In this work, the formation of BN chain structure in the shape of arch depends upon the bonding between BN atoms and substrate. The formation of an arch in chain configurations is just because of strong bonding between B and N as compared to the interaction between BN and Cu(111) substrate. BN atoms in the middle have weak interaction with the Cu substrate while strong boron and nitrogen bonds with the neighbor. In this scenario, arch formation in BN chains is expected to be a common feature in the growth of BN pairs on Cu(111) substrate or any other metal substrate.

As we know that, similar to carbon, the $sp^2$ hybridizations in a BN compound are usually more stable than the $sp$ hybridizations. As a consequence, an isolated 1D BN chain cannot exist theoretically while an isolated 2D BN monolayer can. But why the 1D BN chain is more favored than the 2D BN rings in a small size cluster on the Cu(111) surface? According to the above analysis, this can be understood that, although the $sp^2$ bond of BN is energetically more favored, when

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the size of BN cluster is small, the number of edged B and N atoms, that is to say, the number of dangling sp$^2$ bonds is too large compared to that of the saturated sp$^2$ bonds, which greatly reduces the stability of the sp$^2$ systems. While for the chain configurations, there are only two dangling bonds (start and end of the chain), which makes this sp system preferred to the sp$^2$ system. When the size of BN cluster increases, the ratio of dangling to saturated sp$^2$ bonds becomes small enough, then the sp$^2$ system will be more stable.

IV. CONCLUSION

In this present work we carry out a systematic first principles study of an initial stage of paired BN monolayer nucleation on Cu(111) and Ni(111) substrates. Energetically stable structure transformation of the 1D chain of BN pair to 2D ring of BN-pair occurs at a critical number of pairs $x \geq 6$. Where boron (B) atoms prefer to bind at fcc surface sites and nickel (N) atoms prefer to bind at hcp surface sites. The most optimized stable structures of BN pair $x \geq 6$ always have a few (more than one) rings in their formation with the increment of BN pair. The edge atoms of BN monolayer strongly interact with the surface of Cu(111) substrate to form chain and ring structures respectively. Our calculations also revealed that, in the chain formation on Cu(111) surface transition of a single arch to double arch occurs because of lattice mismatch and dislocation between substrate and deposition atoms.

Apart from Cu(111) substrate, we also compute, analyze and compare nucleation of only one BN pair on Ni(111) surface which shows the same behavior as Cu(111) but computed energy barrier for BN monolayer atoms diffusion on Ni(111) surface is higher as compared to Cu(111) surface. This means that Cu(111) substrate is good for BN deposition as compared to Ni(111) substrate. Thus, according to our results, we predict that high temperature is necessary to produce high-quality BN monolayer on Cu(111) substrate. We expect that our present theoretical findings will stimulate future experimental investigations.

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