Bridge structure for the graphene/Ni(111) system: A first principles study

Miguel Fuentes-Cabrera,[1,*] M. I. Baskes,[4] Anatoli V. Melechko,[1,2] and Michael L. Simpson[1,2,3]

[1]*Center for Nanophase Materials Sciences and Computer Science and Mathematics Division, Oak Ridge National Laboratory,*
P.O. Box 2008, Oak Ridge, Tennesse 37831, USA
[2]*Materials Science and Technology Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennesse 37831, USA*
[3]*Materials Science and Engineering Department, University of Tennessee, Knoxville, Tennessee 37996, USA*
[4]*Los Alamos National Laboratory, MST-8 MS G755, New Mexico 87545, USA*

The structure of graphene on Ni(111) is studied with density functional theory (DFT). Six different structures, i.e., top-fcc, top-hcp, hcp-fcc, bridge-top, bridge-fcc, and bridge-hcp, were investigated. Bridge-top, bridge-fcc, and bridge-hcp are studied here. Top-fcc and hcp-fcc have been considered before, experimentally and theoretically, and regarded as energetically stable structures. The calculations employed the local density approximation (LDA) and the Perdew, Burke, and Ernzerhof (PBE) generalized-gradient approximation to DFT. The results showed that with PBE, none of the structures is stable at the experimentally relevant temperatures; with LDA, only bridge-top and top-fcc are stable. These findings suggest that it will be worthwhile to carry on new experimental studies to revisit the structural determination of the graphene/Ni(111) system, with special emphasis on testing whether bridge-top could exist by itself or coexist with other structures.

I. INTRODUCTION

Understanding the structure of the interface between graphene and a metal has recently gained a considerable attention. One of the reasons is that the studies of graphene itself have generated a range of new phenomena caused by the uniqueness of such a low dimensional material.[1] However, the interest on the graphene-metal interface stems mostly from the problem of catalytic synthesis of carbon nanostructures, such as carbon nanotubes[2] and carbon nanofibers (CNFs).[3]

Recently, Helveg *et al.*[4] gained an insight into the mechanism of catalytic synthesis of a CNF on Ni using *in situ* electron microscopy. From these experimental observations, they concluded that the nanofiber growth is driven by the formation and restructuring of mono-atomic step edges at the Ni surface. Helveg *et al.* and later, in more detail, Abild-Pedersen *et al.*[5] performed *ab initio* calculations on the diffusion barriers for the transport of C and Ni adatoms along the graphene-Ni interface. These calculations led to the conclusion that Ni-step edges act as graphene growth centers.

Investigating the dynamics of CNF growth would allow probing further which role the Ni step edges play. One could use *ab initio* molecular dynamics simulations (MDs) for this purpose, but such calculations are computationally expensive. The computational limitations can be overcome by employing techniques other than *ab initio*. For example, one can use modified embedded atom method (MEAM)[6] potentials to mimic the interactions between C and Ni, and then use these potentials to perform MDSs. The reliability of the MEAM, or any other potential, is usually ensured by fitting to experimental and *ab initio data*, the latter being relatively inexpensive to obtain. So far, the available data for the graphene/Ni(111) system do not allow one to reach consensus over what is the most stable structure.

Three possible structures have been considered so far for graphene on Ni(111). These are known as top-hcp, top-fcc, and hcp-fcc, and they are shown in Figs. 1(a)–1(c), respectively. In top-hcp, the C atoms are placed directly above the Ni atoms of the first (top site) and the second (hcp site) layers. In top-fcc, the C atoms are situated above the Ni atoms of the first and third (fcc) layers. In hcp-fcc, the C atoms are placed on hcp and fcc sites. There is not consensus yet on which of these structures is more energetically stable. The experimental studies of Rosei *et al.*[7] and Klink *et al.*[8] found that the most stable structure is hcp-fcc, whereas those of Gamo *et al.*[9] found that it is top-fcc. The situation is not better for the theoretical studies. Bertoni *et al.*[10] used density functional theory (DFT) with the Perdew, Burke, and Ernzerhof generalized gradient approximation (GGA-PBE)[11] and found that top-fcc is the most stable structure. Kalibaeva *et al.*[12] also performed DFT-PBE studies and found that top-fcc has the lowest energy surface, whereas hcp-fcc is unstable
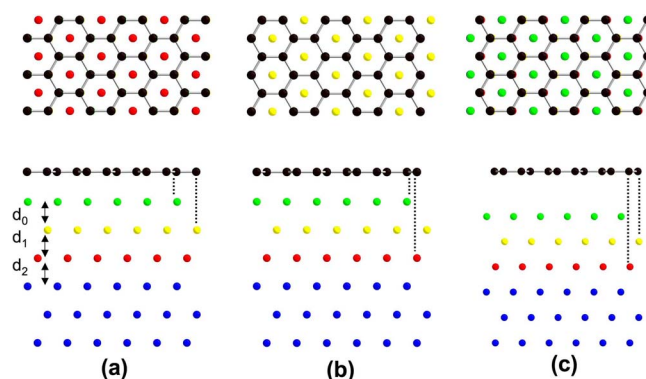

FIG. 1. (Color online) Structures considered so far for graphene over the Ni(111) surface seen from above (top) and from the side (bottom). (a) top-hcp, (b) top-fcc, and (c) hcp-fcc. Color code: Ni, green, yellow, red, and blue; C, black. Ni in the first (top), second (hcp), and third (fcc) layers are shown in green, yellow, and red, respectively. The arrows define the parameters d_0, d_1, and d_2, see Table I. The dashed lines are used as a visual aid to show how a C atom is placed with respect to a Ni atom.

TABLE I. Structural parameters for the graphene/Ni(111) system collected from the literature. d_0 gives the distance between graphene and the first Ni layer. The two values for d_0 indicate the distance between C1, C2, and the first Ni layer; C1 and C2 are nonequivalent C atoms. d_1 gives the distance between the first and second Ni layers. d_2 gives the distance between the second and third Ni layers. d_0, d_1, and d_2 are given in Å.

	Ref.	top-hcp	top-fcc	hcp-fcc
d_0	Expt.[a]		2.16/2.11	
	Expt.[b]			2.80
	Theor.[c]	2.113/2.120	2.122/2.130	3.050/3.050
	Theor.[d]	2.132/2.137	2.127/2.132	
	Theor.[e]			3.2
d_1	Expt.[a]		1.96	
	Theor.[c]	2.034	2.011	1.975
d_2	Expt.[a]		2.09	
	Theor.[c]	2.015	2.014	1.999

[a]Reference 9.
[b]Reference 7.
[c]Reference 10.
[d]Reference 12.
[e]References 4 and 5.

(during the optimization of this structure, graphene is drawn away from the Ni surface). Abild-Pedersen *et al.*[5] and Helveg *et al.*[4] only investigated hcp-fcc and found it to be stable with local density approximation (LDA)[13] and unstable with revised PBE.[14] Table I summarizes all these findings.

Clearly, employing the data in Table I to fit a MEAM potential requires making compromises. Which experimental result one should choose and why? And the same questions can be asked about the theoretical results, with the added complication that different authors use different techniques and neither uses two different techniques at once. This controversy affects the fitting of potentials, preventing further attempts at understanding the graphene/catalyst interface and its role in the CNF growth.

The objective of this paper is twofold. First, we aim to provide a better understanding of the interface of the graphene/Ni(111) system. Second, we reveal the shortcomings that will be encountered when trying to generate a MEAM potential that one could use to investigate the dynamics of the CNF growth process. With these goals in mind, we have performed a comprehensive *ab initio* study of six different structures, three of them have not been considered before, to the best of our knowledge.

II. METHODS

The *ab initio* calculations are based on DFT with the use of pseudopotentials and a plane-wave expansion. All plane waves up to 400 eV and projected augmented-wave pseudopotentials[15] for Ni and C were used. The exchange-correlation potential was approximated with LDA[13] and PBE.[11] An $8 \times 8 \times 1$ grid within the Monkhorst-Pack[16] scheme was used to sample the Brillouin zone; this sampling

used 16 k points. The calculations are spin polarized. We used the Vienna *ab initio* simulation package (VASP) (Version 4.6.28).[17]

When defining the initial structure of the Ni (111) slab, one needs to be aware of the fact that LDA fails to reproduce the experimental Ni lattice constant a_0. LDA gives an a_0 of 3.43 Å versus 3.52 Å experimentally. PBE gives an a_0 that coincides with the experimental value. We chose the PBE's a_0 to define the Ni (111) slab. The slab is made of six layers, each with two atoms, with an interlayer separation of 2.034 Å. Consecutive slabs are separated by a vacuum space of 15 Å. The graphene layer, which contains four atoms, was added on one side of the Ni(111) slab and it is commensurate with the Ni surface. The distance between the upper Ni layer and graphene is initially 2.034 Å. When graphene is added, the vacuum space is reduced to approximately 13 Å. During the optimizations, we allowed the graphene and three upper Ni layers to relax in all three directions.

The binding energy ΔB between graphene and Ni(111) is given by the following expression:

$$\Delta B = (E_{graphene} + E_{\mathrm{Ni(111)}}) - E_{graphene/\mathrm{Ni(111)}}, \qquad (1)$$

where $E_{graphene/\mathrm{Ni(111)}}$ is the energy of the graphene/Ni(111) system and $E_{graphene}$ and $E_{\mathrm{Ni(111)}}$ are the energies of graphene and Ni(111) surface, respectively. The graphene/Ni(111) system, graphene, and the Ni(111) surface all have the same volume. A positive ΔB means that graphene is bound to the Ni surface, unbound if ΔB is negative.

III. RESULTS

In addition to top-hcp, top-fcc, and hcp-fcc, we have also studied three additional structures which we call bridge-top, bridge-fcc, and bridge-hcp. In these structures, the C atoms are not placed in top, hcp, and fcc sites but in between. Denoting the nonequivalent C atoms as C1 and C2 and their bond as C1-C2, we can describe the bridge structures as follows. In bridge-top, C1-C2 is above a Ni atom of the top layer, C1 is placed between top and fcc sites, and C2 is placed between top and hcp. In bridge-hcp, C1-C2 is above a Ni atom of the second layer and C1 (C2) is placed between hcp and top (hcp and fcc). In bridge-fcc, C1-C2 is above a Ni atom of the third layer and C1 (C2) is between fcc and hcp (fcc and top). Bridge-top, bridge-hcp, and bridge-fcc are shown in Figs. 2(a)–2(c), respectively. To the best of our knowledge, none of the bridge structures have been studied before. Kalibaeva *et al.*[12] studied C compounds on Ni(111) with C atoms placed in bridge positions, but they did not consider graphene.

Table II contains the structural parameters d_0, d_1, and d_2 that we have obtained for top-hcp, top-fcc, and hcp-fcc. d_0 gives the distance between graphene and the first Ni layer. There are two values for d_0, one for each nonequivalent C atom. d_1 gives the distance between the first and second Ni layer and d_2 gives the distance between the second and third Ni layers. In Table II, there are no LDA data for top-hcp because during relaxation, graphene undergoes a lateral displacement that yields a new structure. This new structure will
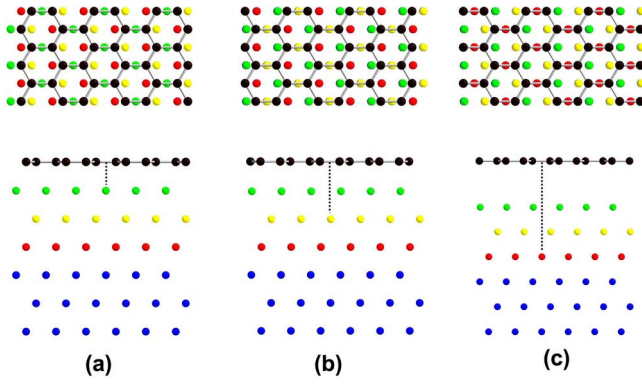
FIG. 2. (Color online) Bridge structures of graphene over the Ni(111) surface seen from above (top) and from the side (bottom). (a) bridge-top, (b) bridge-hcp, and (c) bridge-fcc. Color code: Ni, green, yellow, red, and blue; C, black. Ni in the first (top), second (hcp), and third (fcc) layers are shown in green, yellow, and red, respectively. The dashed lines are used as a visual aid to show how a C1-C2 bond is placed with respect to a Ni atom.

be discussed later. For now, we will compare the data in Tables I and II.

The d_0 values in Table II for top-fcc are in a reasonably good agreement with the experimental values in Table I. On the other hand, for hcp-fcc, LDA and PBE overestimate d_0 by about 0.3 and 0.8 Å, respectively. When our PBE data are compared to previous PBE data, good agreement exists, except for hcp-fcc. Specifically, we have obtained a d_0 of 3.6 Å for this structure: Bertoni et al.[10] obtained 2.8 Å, a value that coincides with the experimental d_0 obtained by Rosei et al.;[7] Kalibaeva et al.[12] did not report the value of d_0 but found that graphene moves away from the Ni surface during the relaxation, indicating that this structure is unstable; similarly, Helveg et al.[4] found that with PBE, graphene is not bound to the Ni(111) surface. As for the LDA data, comparisons can only be made with the work of Helveg et al.[4] and Abild-Pedersen et al.[5] They found a d_0 of 3.2 Å versus the 3.083 found here.

A surprising result was obtained when we investigated the new structure that resulted from relaxing top-hcp with LDA. This new structure is the one we have termed as bridge-top and its energy indicated to us that it was likely to be very

TABLE II. Structural parameters for top-hcp, top-fcc, hcp-fcc, and bridge-top as obtained with LDA and PBE. d_0, d_1, and d_2 are given in Å.

	top-hcp	top-fcc	hcp-fcc	bridge-top
		PBE		
d_0	2.169/2.172	2.131/2.130	3.611/3.612	2.074/2.075
d_1	2.028	2.021	2.000	2.035
d_2	2.029	2.014	2.020	2.030
		LDA		
d_0		2.009/1.992	3.083/3.083	1.945/1.948
d_1		1.941	1.909	1.953
d_2		1.932	1.931	1.936

TABLE III. Binding energies ΔB per C atom (in eV) for each structure as calculated with PBE and LDA (see the text for a description of how ΔB was computed). A positive (negative) ΔB means that the graphene is bound (unbound) to the Ni surface. The symbol † (‡) means that the structure becomes top-fcc (top-hcp) after being relaxed; ¶ (*) means that the structure becomes almost-top-almost-fcc (almost-top-almost-hcp) after being relaxed.

Structure	PBE	LDA
top-hcp	−0.019	
top-fcc	−0.007	0.19
hcp-fcc	0.005	0.030
bridge-top	−0.004	0.205
bridge-fcc	−0.009†	0.188¶
bridge-hcp	−0.019‡	0.174*

stable. Further inspection of the symmetry of the system revealed the existence of two other bridge structures, i.e., bridge-fcc and bridge-hcp. The last column of Table II contains the structural parameters for the bridge-top structure. These are very similar to those of top-hcp and top-fcc. The parameters for bridge-fcc and bridge-hcp are not reported because during their relaxation, graphene undergoes a lateral displacement that yields a different graphene/Ni(111) structure, although one that is equal or close to others that have already been considered. Specifically, with PBE (LDA), bridge-fcc and bridge-hcp become top-fcc (almost-top-almost-fcc) and top-hcp (almost-top-almost-hcp), respectively. By almost-top, almost-fcc, and almost-hcp, we mean that the C atom is placed in a site that is very close to being a top, fcc, or hcp site. Next, we discuss the binding energy ΔB of top-fcc, top-hcp, hcp-fcc, and bridge-top.

The binding energies per C atom are shown in Table III. For simplicity, we will discuss first the binding energies of top-hcp, top-fcc, and hcp-fcc. Then, we will include in the discussion the bridge-top structure. Clearly, PBE and LDA disagree significantly. For PBE, hcp-fcc is the only stable structure, whereas for LDA, top-fcc is the most stable structure followed by hcp-fcc. Comparisons with previous theoretical results are complicated since in some cases, surface energies instead of binding energies were calculated[12] or only hcp-fcc was studied[4,5] or relative energies instead of binding energies are reported.[10] Still, one can try drawing some comparisons with the data in Refs. 4, 5, and 10. In Refs. 4 and 5, when hcp-fcc is studied with LDA, its binding energy per C atom is 0.05 eV, but if studied with PBE, it is unbound. Here, hcp-fcc is bound by 0.030 eV if studied with LDA and weakly bound (0.005 eV) if studied with PBE. In Ref. 10, the relative energies are given and top-fcc is the most stable structure, followed by hcp-fcc, with a relative energy of +0.062, and top-hcp at +0.066 eV. The relative energies calculated here depend on whether one uses LDA or PBE. With LDA, we obtain top-fcc (0.00) and hcp-fcc (+0.64); with PBE, we obtain hcp-fcc (0.00), top-fcc (+0.05), and top-hcp (+0.10). We now include in the discussion the bridge-top structure. Now, one finds that for PBE, hcp-fcc remains the only stable structure, with bridge-top's energy being +0.036 eV higher. On the other hand, for LDA,

the most stable structure is bridge-top, and the relative energy ordering has also changed, being now bridge-top (0.0), top-fcc (+0.062), and hcp-fcc (+0.70). Therefore, LDA and PBE give very different binding energy trends. Not only that, LDA finds that there is a structure, bridge-top, not considered up to this point, which is the most stable one. Before discussing this issue further, we will compare the binding energies to kT, where T is the temperature at which the experiments are done.

The temperature varies from one experiment to another. For example, T is higher or equal to 873 K in Ref. [9], whereas in Ref. [7], it is above 573 K. At these temperatures, kT are approximately 0.075 and 0.05 eV, respectively. With PBE, hcp-fcc is bound by about 0.005 eV, which means that with PBE hcp-fcc is actually unstable at the experimental conditions. The small binding energy found might be an artifact of the calculation. Similarly, it is unlikely that hcp-fcc as given by LDA would exist at the experimental conditions, for its binding energy is 0.030 eV. As for bridge-top and top-fcc as given with LDA, their binding energy values suggest that they will be stable at the experimental conditions.

IV. DISCUSSION

The use of PBE and LDA for investigating the graphene/Ni(111) system is probably not sufficient since PBE tends to underestimate the binding, and LDA to overestimate it. Instead, it is likely that van der Waals interactions are needed for obtaining an accurate description. Indeed, it is known that LDA and PBE fail in describing layered structures such as graphite, where van der Waals interactions are relevant.[18,19] Despite this, the results we present here are meaningful in the sense that they provide a comparison between PBE and LDA studies of the graphene/Ni(111) system. Such comparison has never been done before and the theoretical data are quite scattered, as it can be seen in Table I. It is then convenient to put these two techniques on the same footing. This, in turn, should help deciding in the future which type of data one wishes to use, if any, for fitting potentials that could be used to perform MD simulations.

When one compares the PBE and LDA results, the following is observed. In general, the structural parameters obtained with PBE agree with the experimental ones, however, that none of the structures is bound with PBE questions its suitability. With LDA, the situation is slightly better: not only does it give structural parameters that are in better agreement with the experimental ones (see, for example, hcp-fcc) but also out of the two experimental structures so far reported, i.e., top-fcc and hcp-fcc, top-fcc is bound at the experimental conditions. Now, using LDA, bridge-top, a new structure, is most stable. It remains to be seen how plausible this is, but it also seems worth pondering whether bridge-top can exist by itself or coexist with top-fcc. For example, for the hexagonal BN/Ni(111) system, there are theoretical[20] indications and experimental evidence[21] on the coexistence of

two structures (which resemble top-fcc and top-hcp); each occupies a different domain. Similarly, it would be interesting to experimentally investigate whether there are different domains on the graphene/Ni(111) system and whether they contain top-fcc, bridge-top, and perhaps an almost-top-almost-hcp structure. As mentioned above, the almost-top-almost-hcp structure appears after relaxing bridge-hcp, and its binding energy, which is also reported in Table III, is close to that of top-fcc.

Finally, we would like to comment on the meaning that these results have in the context of CNF growth. Helveg *et al.*[4] and Abild-Pedersen *et al.*[5] performed *ab initio* calculations of transport of C and Ni adatoms on the interface of the graphene/Ni(111) system. These calculations showed that Ni-step edges act as a growth center for graphene. This result, in turn, supported the experimental conclusion that CNF growth is driven by the restructuring of monatomic step edges at the Ni surface. However, Helveg *et al.* and Abild-Pedersen *et al.* chose the hcp-fcc structure for performing their *ab initio* calculations. Our results indicate that hcp-fcc is the least stable structure with LDA and unstable with PBE. Furthermore, according to LDA, hcp-fcc is unlikely to exist above 873 K, which is the temperature at which Helveg *et al.* performed the experiment. It seems then that choosing hcp-fcc for performing transport calculations of C and Ni adatoms might not be the best choice and that other structures, for example, top-fcc, should be considered instead.

V. CONCLUSIONS

An *ab initio* study of six different structures of the graphene/Ni(111) showed that LDA and PBE disagree significantly on the binding energy trend, although, in general, the structural parameters are in good agreement with previous experimental studies. This discrepancy signals the need to include van der Waals interactions and also reveals the shortcomings that one needs to bear in mind when employing LDA or PBE data to fit potentials that could be used to perform MDSs, e.g., simulations of CNF growth. On the other hand, we have also found that with LDA, there is a structure, not considered until now, that we have termed bridge-top and is more stable than top-fcc and hcp-fcc. It appears that it is worth revisiting experimentally the problem of the graphene/Ni(111) structure, specifically evaluating the existence of the bridge-top structure, or its coexistence with top-fcc and perhaps an almost-top-almost-hcp structure. We hope that our results will encourage such experiments.

*fuentescabma@ornl.gov

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