Electronic-structure modification of graphene on Ni(111) surface by the intercalation of a noble metal

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First-principles calculations based on the density functional theory supplemented with an empirical van der Waals interaction are used to explore the effect of Ag-atom intercalation on the electronic structure of graphene on Ni(111) surface. We first confirm that in the most stable configuration graphene is chemisorbed on Ni(111) with binding distance in good agreement with experiments. We also clarify the conflicting interplay of symmetry breaking of the graphene sublattice and hybridization of graphene π orbitals with Ni d states in the bandgap opening of graphene. Upon intercalation of Ag atoms in the interface of graphene/Ni(111), the characteristic energy bands of graphene recover with or without a bandgap depending on Ag coverage. The bandgap is largest for fractional Ag coverage of ~ 1.3 monolayer (ML) and is appreciable for fractional Ag coverage. These bandgap openings are consistent with the recent experiments [Varykhalov, Scholz, Kim, and Rader, *Phys. Rev. B* **82**, 121101(R) (2010)], which, however, have been claimed to be the results for 1 ML Ag coverage. Our calculations also demonstrate that an appreciable bandgap does not open when intercalated Ag atoms of high concentration form a flat layer, which mimics the situation of graphene/Ag(111). These results imply that the actual Ag coverage achieved in the experiments was different from 1 ML. A key role may be assigned to such a fractional Ag coverage, for which graphene–Ag distances are intermediate between those of chemisorption and physisorption, and a bandgap is induced by rather strong interactions with Ag atoms. The Ni(111) substrate plays only a role of supporting such a sparse Ag-atom distribution. Similar arguments also apply to the recent experiments on graphene/Au/Ru(0001) [Enderlein, Kim, Bostwick, Rotenberg, and Horn, *New J. Phys.* **12**, 033014 (2010)] in which a substantial bandgap also opened in graphene for the *claimed* 1 ML Au coverage.

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I. INTRODUCTION

Since its successful isolation by exfoliation from graphite,¹ graphene has attracted growing attention owing to its unique properties² and possible applications.^{3–5} The most striking feature of graphene is that quasiparticles are described by the relativistic Dirac equation and behave as massless Dirac fermions in the vicinity of the Dirac point located at the K points, i.e., the corner points in the first Brillouin zone. Freestanding graphene with this feature is a zero-gap semiconductor with vanishing density of states (DOS) at the Fermi level, which coincides with the Dirac point energy and electronically behaves like a semimetal.² Electronic properties of this pristine nanostructure are easily modified by mechanical strains, deformations, metal contacts, adsorption of foreign atoms or molecules, external fields, and other physical contacts with environment. These influences are unavoidable in most experiments as well as possible applications and easily impair intrinsic, novel properties of graphene. However, we can also make use of these effects to modulate electronic properties, thereby extending a range of technological applications. One of these examples is a bandgap opening, which is essential for graphene to be used for semiconductor devices. A substantial bandgap can be induced in several ways. Early examples are bandgap openings in epitaxial graphene on SiC (Refs. 6 and 7) and graphene on hexagonal boron nitride (h-BN).⁸ A bandgap is also induced by electron confinement (nanoribbon),^{9,10} biasing^{11,12} or doping¹³ bilayer graphene, patterning graphene with periodic holes (nanomesh or antidote lattice),^{14,15} or Moiré-patterned hydrogen adsorption,¹⁶ and so on. These

bandgap openings can be interpreted in terms of either the hybridization of electronic states at K and K' points in the Brillouin zone or the symmetry breaking of A and B sublattices by external or internal perturbations.⁶

In this paper, we are concerned with the interface structure and electronic properties of graphene on metals, which have been attractive issues since as early as the 1990s,^{17–19} before the successful isolation of a single graphite layer.¹ Numerous investigations, both experimental and theoretical, have been made, and some of these results are reviewed in Refs. 19–22. First-principles calculations based on the density functional theory (DFT) have been used to predict that graphene is physisorbed on the surfaces of noble metals (Au, Ag, and Cu), Al, Pt, and Ir, and its linear-dispersion band near the K points (Dirac crossing) is preserved, although graphene is p - or n -doped to a varying degree, primarily depending on the work-function (WF) difference.^{23–27} These results are in agreement with available experiments.^{28–30} In contrast to these features of physisorbed graphene on metals, electronic structure of graphene contacted to most transition metals shows a strong modification due to the hybridization of its π orbitals with metal d states, resulting in bonding formation and hybridized surface bands.^{31–34} We focus on a particular case, graphene/Ni(111), which is an exceptional system in that the unit cell of graphene matches that of Ni(111) surface with a very small ($\sim 1.3\%$) tensile strain of graphene and, owing to this small mismatch, epitaxial graphene on Ni(111) is quite flat without Moiré patterns,^{20,35} providing a useful platform for both

theoretical and experimental studies. Among six symmetrical configurations of graphene/Ni(111), the so-called top-fcc or bridge-top structure is the most stable with the binding distance of ~ 2.1 Å (Refs. 18 and 36–39), a typical distance in chemisorption, but the binding is weak and comparable to that of physisorption.⁴⁰ This apparent inconsistency has been analyzed using DFT calculations, in which a van der Waals (vdW) interaction is taken into account and plays a crucial role in determining energetics of the interface.^{40,41} In this chemisorption, graphene π orbitals are hybridized with Ni d states to make bonding, and characteristic energy bands of freestanding graphene are lost. The intact Dirac cone recovers if the graphene-substrate distance is increased up to ~ 3.0 Å or larger, which is the case of physisorption and has actually been accomplished in graphene/Ni(111) by intercalating noble metals in the interface.^{32,42–46} Recent experiments using angle-resolved photoemission spectroscopy (ARPES) have actually shown that the gapless Dirac cone of freestanding graphene recovers when Au atoms are intercalated in the interface of graphene/Ni(111),^{32,46} whereas a bandgap opens upon intercalating Ag or Cu atoms.⁴⁶ According to the recent DFT calculations for graphene/Au/Ni(111), a gapless graphene band is preserved only for high Au coverage, and a bandgap opens only for lower Au coverage.⁴⁷ Similar results have also been obtained for graphene/Cu/Ni(111) by the DFT calculations.⁴⁸ Decoupling of graphene and Ni(111) can also be achieved by intercalating Al atoms in the interface⁴⁹ and by alloying the Ni substrate with Sn atoms,⁵⁰ which weakly interact with graphene.

In the present work, we use the DFT supplemented with an empirical vdW interaction to explore electronic-structure modification in graphene on Ni(111) by the intercalation of Ag atoms in the interface, for which the largest bandgap and the highest doping level have been observed in ARPES measurements.⁴⁶ Our results for ~ 1.3 monolayer (ML) Ag coverage are consistent with this observation, which, however, have been claimed to be the results for 1 ML Ag coverage, implying that the Ag coverage achieved in experiments was actually larger than 1 ML and fractional. Similar decoupling and bandgap opening have also been observed in graphene/Au/Ru(0001) with the *claimed* Au coverage of 1 ML,⁵¹ which is in contrast to gapless graphene on Au/Ni(111) (Refs. 46 and 47). The present work is aimed at resolving these seemingly inconsistent observations through the analyses for a particular case of graphene/Ag/Ni(111). We argue on the basis of our calculations that an appreciable bandgap is unlikely to open in graphene on Ag/Ni(111) with a flat Ag layer similar to that of Ag(111) surface, which may be defined as the actual 1 ML Ag coverage, as we discuss later. In fact, such a configuration is similar to graphene/Ag(111) in which graphene is physisorbed on Ag(111) surface, and, as actually confirmed by the present and previous calculations,²³ the Dirac cone of graphene is preserved without a bandgap.

II. COMPUTATIONAL METHOD

We considered graphene on Ni(111) surface, which was modeled by an ABC-stacked five-layer slab. The lattice constant of graphene was matched to that of Ni(111) surface

(2.489 Å), which corresponded to only 1.3% tensile strain of graphene and enabled us to construct a supercell of arbitrary size. We used a (2×2) supercell graphene/Ni(111), and Ag atoms were intercalated in the interface of this structure. Consecutive slabs were separated by a vacuum space of ~ 15 Å or more to nullify the interactions with periodic images. It would have sufficed to use a unit cell, (1×1) graphene/Ni(111), if we were not concerned with the intercalation; however, we used a (2×2) supercell for the convenience of comparing the results with graphene/Ag/Ni(111). We also used a larger cell, (3×3) graphene/Ni(111), to observe a variety of Ag coverage.

We used the Perdew–Burke–Ernzerhof (PBE)⁵² exchange-correlation functional in the spin-polarized DFT electronic structure calculations, which was supplemented by an empirical atom–atom vdW interaction within the Grimme scheme⁵³ (DFT-D2), as implemented using the Vienna *Ab initio* Simulation Package (VASP).⁵⁴ The electron–ion interaction was modeled using the projector-augmented wave (PAW) method,^{55,56} and the plane wave expansion was limited by the cutoff energy of 400 eV. The Brillouin zone sampling was made using the Monkhorst–Pack method,⁵⁷ in which $6 \times 6 \times 1$ and $24 \times 24 \times 1$ Γ -centered $\mathbf{k}$ -point meshes were used in the structural optimization and electronic structure calculations, respectively, for the (2×2) graphene/Ni(111) cell with or without intercalated Ag atoms. Structural optimizations were made within the accuracy that the residual force acting on each atom is smaller than 0.01 eV/Å and the dipole corrections appropriate for slab geometry were added in all the calculations.

It may be useful at this stage to comment on the effect of vdW interaction on the structural and electronic properties in a particular case of layered structures such as graphene on metals. The local density approximation (LDA) generally tends to overestimate binding, but it predicts proper binding distance between layers as actually it does for graphite and graphene/Ni(111). This result has been interpreted as a result of a fortunate balance between the Pauli repulsion and vdW attraction, which are not properly taken into account in the LDA. On the other hand, the generalized gradient approximation (GGA) generally underestimates binding and fails in describing weakly bound layered structures. These limitations of the local and semilocal approximations imply that vdW interaction must be taken into account, especially in treating weakly coupled systems. This problem has been tackled, and several DFT-based methods have been proposed in recent years.⁵⁸ Several vdW density functionals (vdW-DF) have actually been used in the studies of the adsorption geometries and nature of bonding in the graphene/metal interfaces.^{59,60} The equilibrium binding distances predicted with such functionals are ~ 3.50 Å, indicative of physisorption even for graphene on Co(0001), Ni(111), and Pd(111) surfaces,⁵⁹ and are in contradiction to the experiments. Hamada and Otani⁶⁰ have shown that the predicted interfacial properties depend on the type of vdW-DF, and the best one yields an equilibrium separation in good agreement with available experiments. However, the method of using vdW-DF is computationally rather heavy and is not necessarily suitable for a wide range of applications. The DFT supplemented with an empirical vdW interaction has been proposed to avoid such an inconvenience and was actually used in the calculations for graphene/Ni(111). Several schemes have

been proposed in treating empirical vdW interaction and DFT-D2, one of such schemes, used in the present work, is probably the most widely used method to account for vdW interaction at present.⁵⁸ A more elaborate approach is to use the random phase approximation (RPA)^{40,62} in which nonlocal vdW contribution is automatically taken into account. Computationally cheaper methods within the RPA have also been developed and applied to the calculations for graphene/Ni(111).⁴⁰ These methods account for vdW interaction, and their performances are reviewed in more detail in Refs. 58 and 61. The LDA has most often been used in the calculations for interfaces and might still be useful in predicting interface structures, which are crucial in determining electronic properties of interfaces. We note, however, that binding energies predicted in the LDA are too small (in the case of physisorption) or too large (in the case of chemisorption) and, as we show later, the interface structure of graphene/Ni(111) with intercalated Ag atoms are, in some cases, strongly affected by vdW interaction, indicating a limitation of LDA calculations.

III. RESULTS AND DISCUSSIONS

A. Graphene/Ni(111)

Figure 1 shows the adsorption energy, E_{ads} , of graphene/Ni(111) obtained by the DFT-D2 method and their comparisons with the LDA results. Here, E_{ads} is defined as the energy of graphene/Ni(111) with respect to the configuration in which graphene-Ni(111) separation, d , is infinite. The so-called top-fcc structure, as illustrated in Fig. 2(a), is the most stable in the present calculations, and the equilibrium binding distance, $d = 2.09 \text{ \AA}$, of this structure is in good agreement with experiments, $d = 2.11 \pm 0.07 \text{ \AA}$ (Ref. 18). This result for d , a crucial parameter in determining electronic structure of interface, and the adsorption energy, $E_{\text{ads}} = -0.16 \text{ eV/C-atom}$, are consistent with the recent calculations by the same method⁴⁹ and are compared to the LDA results,⁶³ $d = 2.01 \text{ \AA}$ and $E_{\text{ads}} = -0.19 \text{ eV}$. These results for the binding distance in graphene/Ni(111) are in the range of the previous results, $d =$

FIG. 1. (Color online) Adsorption energies E_{ads} vs adsorption distance d of graphene/Ni(111) obtained by using the DFT-D2 method and their comparisons with the LDA results. Top-fcc and fcc-hcp configurations are assumed. The results for top-hcp are not appreciably different from those for top-fcc.

FIG. 2. (Color online) (a) Top view and (b) side view of the optimized top-fcc structure of graphene/Ni(111) and electronic band structures in the surface Brillouin zone for (c) the optimized configuration and (d) an artificial geometry with a large graphene-Ni(111) separation, $d = 3.0 \text{ \AA}$, both the results for the (2×2) cell. Only the top layer and upper three layers of Ni substrate are shown in (a) and (b), respectively. Solid and dashed lines in (a) show (2×2) and (3×3) supercells, and small (brown) and medium (gray) balls represent C and Ni atoms, respectively. Top, fcc, and hcp sites are indicated by the arrows and the side view direction is along one of the lattice vectors, **b**. Solid circles in (c) show the energy bands of hybridized states originating from graphene π states and Ni d states, and open circles in (d) show the energy bands mostly originating from graphene.

$2.02\text{--}2.10 \text{ \AA}$, obtained by similar LDA calculations,^{23–25,37,38,47} and are also compared with some other results: $d = 2.14 \text{ \AA}$ in the GGA (Ref. 36); $d = 2.10 \text{ \AA}$ (Ref. 41), $d = 2.20 \text{ \AA}$ (Ref. 61), or $d = 2.12 \text{ \AA}$ (Ref. 64) in the DFT-D2; or $d = 2.17 \text{ \AA}$ (Ref. 40), $d = 2.3 \text{ \AA}$ (Ref. 62) in the RPA. We note that the stabilities of top-fcc and bridge-top structures are comparable, as predicted by earlier LDA calculations.³⁷ More recently, Zhao *et al.*³⁹ have used combined high-resolution x-ray photoelectron spectroscopy and DFT calculations to show that coexistence of both structures is plausible. Also shown in Fig. 1 are the adsorption energies for the fcc-hcp structure [see Fig. 3(b)] as a function of binding distance. This structure is stabilized at $d = 2.98 \text{ \AA}$, a typical binding distance of physisorption, and the linear-dispersion band near the Dirac point is preserved, as illustrated in Fig. 3(c). In this structure, graphene π orbitals are hybridized with Ni d states only at a substantially small separation because no C atom is atop a Ni atom. Therefore, the fcc-hcp structure is stabilized at a relatively large separation without hybridization by the balance of weak Pauli repulsion and vdW attraction,⁴¹ which is nothing but physisorption. In the top-fcc structure,

FIG. 3. (Color online) (a) Top view and (b) side view of the metastable fcc-hcp structure of graphene/Ni(111) and the electronic band structures for (c) the lowest-energy configuration and (d) an artificial configuration with a small graphene–Ni(111) separation, $d = 2.0$ Å. Other details are the same as those in Fig. 1.

this type of stabilization also starts to occur at $d \sim 3.0$ Å, but already appreciable hybridization prevents this tendency, yielding a flat part or second minimum in the E_{ads} vs d curve (Fig. 1). These adsorption mechanisms imply, as argued by Kozlov *et al.*,⁴¹ that either chemisorption or physisorption occurs, depending on the nature of substrate or adsorption configuration; however, any intermediate adsorption between the two does not occur. Similar features are also found in the LDA results, which are interpreted as resulting from fortuitous compensation of the Pauli repulsion and vdW attraction. The LDA adsorption energy of the stabilized fcc-hcp structure is smaller in magnitude than the DFT-D2 result, in accordance with the general trend that LDA underestimates adsorption energy in the case of physisorption in which vdW interaction plays a dominant role. Interlayer binding in graphite is a typical example of such a case.⁶⁵ The fcc-hcp structure is much less stable than the top-fcc structure at small separations, but the stabilities of both structures are comparable for $d > 4$ Å, implying that the fcc-hcp structure is also possible in a situation where graphene–Ni(111) separation is expanded by, e.g., intercalation of foreign atoms. This actually happens in graphene/Ag/Ni(111), as we see later.

The electronic structures of (2×2) graphene/Ni(111) near the $\bar{K}'$ point, on which the $\bar{K}$ point in the surface Brillouin zone of unit (1×1) cell is folded, are depicted in Figs. 2 and 3. The surface band of the stabilized top-fcc structure [Fig. 2(c)] is essentially the same as the previous LDA calculations.⁴⁷ In this structure [Fig. 2(a)], A and B graphene sublattices are clearly asymmetric with respect to the Ni atoms in the top layer, implying that the bandgap in graphene opens. However, in this structure, graphene π orbitals strongly hybridize with Ni d states to make bonding, and charges of hybridized band

states are distributed on both graphene and Ni atoms, as explicitly shown in the earlier calculations.⁴⁷ We can no longer specify a graphene band in such a situation. If graphene is artificially separated to a larger distance, e.g., $d = 3.0$ Å, characteristic Dirac crossing with a small gap (~ 0.06 eV) recovers, as shown in Fig. 2(d). This result indicates that in the top-fcc structure, hybridization is ineffective at large graphene–Ni(111) separations, $d > 3.0$ Å, where the asymmetric sublattice potentials due to Ni(111) substrate are also not strong enough to induce a substantial bandgap in graphene. These indications for the roles of hybridization and symmetry breaking are somewhat different for the metastable fcc-hcp structure [Fig. 3(a)] in which Ni atoms in the top layer are positioned below the centers of graphene hexagonal rings. In this structure, A and B sublattices of graphene are clearly symmetric with respect to the top layer of Ni(111). At the optimized separation, $d = 2.98$ Å, the nearest C–Ni distance, 3.33 Å, is large enough to prevent hybridization of graphene π orbitals with substrate d states, and the Dirac crossing with vanishing energy gap is almost completely preserved [Fig. 3(c)]. Now we make graphene closer to the substrate, e.g., $d = 2.0$ Å, where the nearest C–Ni distance, ~ 2.5 Å, is much smaller than that of the top-fcc structure with $d = 3.0$ Å [Fig. 2(d)], but the bandgap is much the same (~ 0.06 eV). The bandgap of the fcc-hcp structure remains unchanged even at a much shorter distance, $d = 1.48$ Å, where the nearest C–Ni distance, 2.09 Å, is the same as that in the top-fcc structure in Fig. 2(c). These results for the fcc-hcp structure with sublattice symmetry may be explained by a weak hybridization combined with sublattice symmetry. In fact, hybridization of vertically oriented graphene π orbitals with Ni d states is suppressed in this structure, in which C atoms are not atop Ni atoms, and another mechanism of bandgap opening is excluded by sublattice symmetry. In summary, even if we can manipulate the structure of graphene/Ni(111), a substantial bandgap does not open in graphene on Ni(111) because of the conflicting interplay of hybridization and symmetry breaking. In fact, in the case where hybridization is sufficiently weak for the Dirac cone to be preserved, symmetry breaking of the graphene sublattice does not occur or the graphene–substrate interaction is not strong enough to induce a substantial bandgap in graphene. This situation can be changed by intercalating foreign atoms in the interface of graphene/Ni(111), as we see in the following subsection.

B. Graphene/Ag/Ni(111)

We used a model (2×2) graphene/Ni(111) cell, which was assumed to be a top-fcc structure [Fig. 2(a)] as the starting point, and Ag atoms were intercalated in the interface. Figure 4 shows the optimized structures of graphene/Ag/Ni(111) with 0.25–1.0 ML Ag coverage after structural relaxations and their surface-band structures near the $\bar{K}'$ point. Following the previous work,⁴⁷ we tentatively defined 1 ML by referring to the number of Ni atoms in the surface layer, which is four in the case of a (2×2) cell. For 1/4 ML Ag coverage, the top-fcc structure remains the most stable, and the Ag atom is intercalated on the fcc site [Fig. 4(a)]. Once Ag atoms are intercalated with this coverage, graphene–Ni(111) separation is expanded to $d > 4.5$ Å, and the graphene electronic structure

FIG. 4. (Color online) Top views (upper panel) and side views (central panel) of the optimized configurations and band structures (lower panel) of graphene/Ag/Ni(111) with Ag coverage of (a) 1/4 ML, (b) 1/2 ML, (c) 3/4 ML, and (d) 1 ML. Small (brown), medium (gray), and large (red) balls show C, Ni, and intercalated Ag atoms, respectively. Solid circles in the lower panel show the energy bands originating from graphene. The atomic configuration in (b) shows the most stable fcc-hcp structure with intercalated Ag atoms on the fcc and hcp sites. Ag2 in (d) shows the Ag atom, which starts to form a second layer. The intercalated Ag layer in (c) is similar to that of the Ag(111) – $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface structure.

is not directly affected by the Ni substrate, which may be obvious from the results for graphene/Ni(111), as illustrated in Fig. 2. A small bandgap of ~ 0.1 eV is interpreted as arising from the symmetry breaking of graphene sublattices with respect to the interactions with the intercalated Ag atoms. Hybridization of graphene π orbitals with Ag s or d states may be excluded as a mechanism of bandgap opening because the latter states are not in the range of Dirac crossing. However, the argument for bandgap opening due to symmetry breaking in a graphene (1×1) cell, in which each sublattice consists of one C atom, cannot directly be applicable to a (2×2) cell with four C atoms in each sublattice, which are not necessarily equivalent with respect to external or internal perturbations. Bandgap opening in such a situation has yet to be explored and may be an important issue. Hence, the argument for the bandgap opening due to the symmetry breaking in a large cell is inevitably not definite at this stage. For 1/2 ML Ag coverage, the optimized structure after structural relaxation was fcc-hcp, and two Ag atoms are intercalated on the fcc and hcp sites [Fig. 4(b)], although both positions are slightly off-center. This structure with intercalated Ag atoms of 1/2 ML coverage is slightly more stable than the corresponding top-fcc structure, in accordance with the suggestion we made earlier in relation to the stability of fcc-hcp structure with a large

graphene–Ni(111) separation (Fig. 1). In this configuration, A and B sublattices of graphene are locally asymmetric with respect to each Ag atom but are symmetric as a whole because half of both C and Ag atoms are on either the fcc or hcp site. A relatively small bandgap of ~ 0.05 eV may be explained by such a weak symmetry breaking, although this argument is not definite, as we have discussed previously. In the case of 3/4 ML Ag coverage, top-fcc configuration is again the most stable, and Ag atoms are intercalated on the top, fcc, and hcp sites [Fig. 4(c)] and form a rather flat layer, which is similar to that of the Ag(111)– $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure-matched (2×2) graphene cell. This supercell structure with small lattice mismatch has been used in the studies of interfaces of graphene on fcc metals such as Al, Au, and Ag,^{23,25–27} whose lattice constants are much the same. This structure of graphene/Ag/Ni(111) implies that 3/4 ML in the *tentative* definition is the maximum coverage for those metal atoms to form a flat layer and may be defined as the actual 1 ML achieved in experiments. For this coverage, the separation between the graphene and intercalated Ag layer is larger than 3.0 Å, and the Dirac crossing of graphene is almost completely preserved. This situation is quite similar to that of graphene/Ag(111), as we discuss later. These results imply that a flat layer, if any, of intercalated Ag atoms with 1 ML

coverage (in the tentative definition) is subject to compressive strain amounting to 15% in the lateral plane and is unlikely to be stable even if the strain is compensated by the interactions with the graphene and Ni substrate. In fact, for 1 ML coverage, three of the intercalated Ag atoms form a flat layer similar to that of 3/4 ML, though somewhat corrugated, and the excess Ag atom starts to form second layer [Fig. 4(d)]. In this configuration, a substantial bandgap opens in graphene, which may be interpreted as the result of the asymmetric interactions with the excess Ag atom in the second layer and is similar to the bandgap opening for 1/4 ML Ag coverage [Fig. 4(a)]. We note that in the LDA calculations quite a different result is obtained for the optimized structures of graphene/Ag/Ni(111) with 1 ML Ag coverage, in which all Ag atoms are intercalated on the fcc sites and form a flat layer.⁶³ A similar result has also been obtained in the LDA calculations for graphene/Au/Ni(111),⁴⁷ suggesting that the vdW interaction plays a crucial role in the calculations for this type of interface.

The results in Fig. 4 show that once Ag atoms are intercalated in the interface of graphene/Ni(111), the graphene and Ni(111) surface are decoupled and the Dirac crossing of graphene with or without a bandgap recovers depending on the Ag coverage. The separations between the graphene and Ni substrate are quite large even for the smallest Ag coverage shown in Fig. 4, indicating that Ni substrate has no direct influence on the bandgap opening, as implied by the results for graphene/Ni(111) illustrated in Figs. 2 and 3. An appreciable bandgap does not open for high Ag coverage, as it does not in Fig. 4(c) where intercalated Ag atoms form a flat layer and graphene is physisorbed on the Ag layer with a large binding distance. This situation is quite similar to that of graphene/Ag(111) in which an appreciable bandgap does not open in our DFT-D2 (Ref. 63) and previous LDA (Refs. 23, 25, and 26) calculations. This similarity between graphene/Ag/Ni(111) and graphene/Ag(111) is explored in more detail in the next subsection. In other configurations, such as those in Figs. 4(a), 4(b), and 4(d), separations between graphene and Ag atoms, ~ 2.5 Å, are somewhere between those of chemisorption and physisorption. These intermediate separations are favorable for the interactions between Ag atoms and fairly remote C atoms at the cost of the nearest-neighbor C–Ag repulsion. As discussed previously, it is realistic and convenient to define 3/4 ML in Fig. 4(c) as the actual 1 ML, and hereafter we follow this definition unless otherwise stated.

We also used a large supercell consisting of a (3×3) graphene/Ni(111) cell and considered Ag coverage of 1/9 and 8/9 ML (in the tentative definition). For this large system, we used $4 \times 4 \times 1$ and $16 \times 16 \times 1$ Γ -centered Monkhorst–Pack $\mathbf{k}$ -point meshes in the structural optimizations and electronic structure calculations, respectively. Other computational details in these calculations are the same as before. The K point in the Brillouin zone of the (1×1) cell is folded on the Γ point of the (3×3) cell. The bandgap, E_g , and Fermi-level shift, ΔE_F , of graphene were determined using band structure calculations. All of these results are summarized in Fig. 5. The bandgap is the largest, $E_g \sim 0.2$ eV, with $\Delta E_F \sim -0.65$ eV for 1.33 ML Ag coverage [Fig. 4(d)]. These results are consistent with the ARPES measurements⁴⁶ $E_g = 0.32$ eV

FIG. 5. (Color online) Energy gap (circles), E_g , and the Fermi-level shift (squares), ΔE_F , of graphene on Ni(111) surface as functions of intercalated Ag coverage. ARPES results are $E_g = 0.32$ eV and $\Delta E_F = -0.56$ eV (Ref. 46) for the claimed Ag coverage of 1 ML, which probably corresponds to 0.75 ML in this figure (see discussion in the text).

and $\Delta E_F = -0.56$ eV, which, however, have been claimed to be the results for graphene/Ag/Ni(111) with 1 ML Ag coverage. This correspondence implies that the Ag coverage achieved in the experiments could have been fractional, such as ~ 1.33 ML or 0.33 ML, rather than 1 ML with a flat Ag layer. In fact, as we have already discussed, the bandgap of graphene on Ag/Ni(111) with 1 ML Ag coverage is unlikely to open as it is on Ag(111). Similar results have been obtained by the LDA calculations for graphene/Au/Ni(111) with 1 ML Au coverage,⁴⁷ in which an appreciable bandgap actually does not open. This result for the Au intercalation may also be explained by the similarity between this system and graphene/Au(111). In contrast with the Ag-atom intercalation, this LDA result for graphene/Au/Ni(111) is consistent with the ARPES experiments,⁴⁶ suggesting that the Au coverage was actually 1 ML, as claimed in the experiments. We note that DFT-D2 and LDA calculations yield essentially the same results in the case of 1 ML coverage of Ag atoms⁶³ and, probably, of Au atoms. Gapped and gapless graphene observed experimentally for the claimed 1 ML intercalations of Ag and Au atoms can be explained, as discussed previously, if the actual coverage of Ag atoms had been fractional, where an appreciable bandgap opens as we have demonstrated. Another explanation for the inconsistency between our predictions and experiments for graphene/Ag/Ni(111) may be that Ag atoms were not uniformly intercalated for some reason. In fact, inhomogeneous or disordered distribution of intercalants could have a strong effect on the bandgap opening through symmetry breaking of the graphene sublattice. Shikin *et al.*⁴⁵ have also observed that the intercalations of Ag and Cu atoms in the interface of graphene/Ni(111) are accompanied by partial disruption of the graphene coating, while Au atom intercalation does not bring about such a disruption. These observations are consistent with the results of ARPES experiments.⁴⁶ However, there are also conflicting observations that the limiting concentration of

Ag atoms intercalated in the interface of graphene/Ni(111) is 1 ML, which is in contrast with what happens to the systems graphene/Au/Ni(111) and graphene/Cu/Ni(111), where the intercalant concentrations reached 1–2 MLs.⁴⁴ More detailed examinations of the interface structures will be required before these consistencies and inconsistencies between the predictions and experiments can be resolved.

C. Phenomenological analysis

As we discussed previously, a bandgap in graphene on Ni(111) is unlikely to open for a flat layer of intercalated Ag atoms with high coverage. In fact, graphene/Ni(111) with one layer of intercalated Ag atoms [Fig. 4(c)] is such a case and is quite similar to graphene/Ag(111) in which the bandgap of graphene is not appreciable, as actually demonstrated by the LDA and DFT-D2 calculations.^{23,25,26,63} Electronic structure in graphene on Ag/Ni(111) is virtually not affected by Ni substrate because graphene–Ni(111) separation is quite large (>5 Å). The WF of Ag/Ni(111) is different from that of Ag(111) surface, and this is the only difference. These similarities and differences can be explored in more detail using a phenomenological model. Figure 6(a) shows the DOS in graphene/Ag/Ni(111) and its projection (PDOS) on the Ag atoms and graphene, and Fig. 6(b) shows a schematic representation of the Fermi-level alignment. We first note the characteristic feature of the results in Fig. 6(a). Spin-polarization effect brings about splitting of majority and minority spin bands, amounting to ~ 0.65 eV near the Fermi level. Magnetic moment (m) largely comes from Ni atoms and is $\sim 0.55\mu_B$ per Ni atom, which is compared to the Ni bulk value, $m = 0.66\mu_B$. This reduction in magnetic moment can be explained by the reduced value in the Ni surface layer, $m = 0.61\mu_B$, and further reduction caused by overlayers of Ag atoms and graphene. These reductions of magnetic moment in graphene/Ni(111) have been studied in detail (Refs. 36 and 61), and our calculations are consistent with those results. Upon intercalation of the Ag layer in the interface, its PDOS shifts to a lower energy by ~ 0.8 eV with respect to the DOS of the isolated Ag layer, indicating that the Fermi level as well as the energy band of Ag layer shifts to lower energy by that amount, $\Delta E_{Ag} \sim -0.8$ eV. Here, we note that PDOS and DOS of the Ag layer shown in Fig. 6(a) are given as functions of energy measured with respect to the Fermi level of graphene/Ag/Ni(111) and that of the isolated Ag layer, respectively. These results imply that the WF of Ag/Ni(111) is reduced by ~ 0.8 eV compared with that of the isolated Ag(111) layer (not a bulk surface). We compare the PDOS and DOS of graphene, which are shown in Fig. 6(a), to find that the whole graphene band, including the Dirac crossing, rigidly shifts to a lower energy by 0.63 eV, which also can be seen in Fig. 4(c) and is nothing but the Fermi-level shift of graphene.

We now use the WF reduction in Ag/Ni(111) in the equation²⁶ $\Delta E_F = (1/2)(\Delta W - \Delta V_c)$, which has been obtained by a phenomenological analysis for the physisorption of graphene on metals, with the assumption that the Dirac crossing in graphene remains unchanged without a bandgap opening. Here, ΔW is the WF difference, $\Delta W = W_M - W_G$, where W_M and W_G are the WFs of metal substrate

FIG. 6. (Color online) (a) Density of states of graphene/Ag/Ni(111) with 3/4 ML Ag coverage [Fig. 3(c)]. Solid (red) and dashed (blue) curves show, respectively, the total DOS of majority and minority spin states, which are split by ~ 0.65 eV near the Fermi level (taken to be zero). Also shown are PDOS of Ag atoms (solid green curve) and graphene (solid black curve) and DOSs of the isolated Ag layer (dotted green curve) and freestanding graphene layer (dotted black curve). These PDOS and DOS of Ag atoms and graphene are those for majority-spin states, which are almost indistinguishable from those for minority-spin states. The Fermi level of each freestanding layer is also taken to be zero. The Fermi-level shift of graphene, ΔE_F , and energy-band shift (as a whole) of Ag layer, ΔE_{Ag} , are found to be -0.63 and ~ 0.80 eV, respectively. (b) Schematic representation of the Fermi-level alignment in graphene/Ag/Ni(111) as described in (a). ΔV_{Ag} and ΔV_G represent the potential drops in Ag and graphene layers with respect to Ni(111) and Ag surfaces, respectively. The work functions of the Ni substrate, Ag layer, and graphene are denoted by W_{Ni} , W_{Ag} , and W_G . E_F and E_D are the Fermi level of the whole system and the Dirac point energy of graphene, respectively.

and graphene, respectively, and ΔV_c is the Pauli repulsion between graphene and substrate. These quantities are involved in the Fermi-level alignment, which is schematically illustrated in Fig. 6(b). The potential drop in graphene with respect to the Ag layer is given by $\Delta V_G = \Delta V_c + \Delta V_{tr}$, where ΔV_{tr} is the dipole barrier induced by charge transfer. Using DFT-D2 calculations, we obtained $\Delta E_F = -0.57$ eV for graphene/Ag(111), which is reproduced using $\Delta W = 30$ eV and $\Delta V_c = 1.44$ eV in the previous equation. These results for ΔE_F and ΔV_c are somewhat different from the previous LDA calculations ($\Delta E_F = -0.30$ eV, $\Delta V_c = 0.90$ eV),^{23,26}

implying that the effect of the vdW interaction is significant in the calculations for interfaces. We have also found that W_M of Ag/Ni(111) is reduced by ~ 0.14 eV compared with that for Ag(111) surface (not a layer), which we have obtained using similar DFT-D2 calculations. The WF difference, ΔW , is reduced by the same amount, and we have $\Delta W \sim 0.16$ eV. Using this value in the previous equation with the assumption that ΔV_c remains unchanged, we have $\Delta E_F \sim -0.64$ eV, which is in good agreement with the result $\Delta E_F = -0.63$ eV, obtained by the present DFT-D2 calculations for graphene/Ag/Ni(111). These analyses demonstrate that electronic structure of graphene on Ag/Ni(111) with a high-coverage Ag layer is essentially the same as that of graphene on Ag(111) surface, and the difference, if any, can be explained by the change in WF difference. More explicitly, if the bandgap does not open in graphene on Ag(111) as actually predicted, it also would not in graphene on Ag/Ni(111) with high Ag coverage, which is the case and in agreement with the results in Fig. 4(c).

IV. CONCLUSIONS

In conclusion, we have elucidated electronic-structure modifications in graphene/Ni(111) by the intercalation of Ag atoms in the interface. We found that upon intercalation of Ag atoms, the graphene and Ni(111) surface are electronically decoupled, and the characteristic energy band of graphene recovers with or without a bandgap. An appreciable bandgap opens for fractional coverage of intercalated Ag atoms but not for a flat Ag layer with high coverage. The bandgap opening in graphene can be explained by symmetry breaking of graphene sublattices with respect to the interactions with the intercalated Ag atoms. However, the interactions between graphene and the intercalated Ag atoms are strong enough to induce an appreciable bandgap in graphene only for fractional Ag coverage. A mechanism of bandgap opening due to hybridization between graphene π orbitals and Ag states can be excluded. The Ni(111) substrate only supports a rather sparse distribution of intercalated Ag atoms and has no direct influence on the bandgap opening. A substantial bandgap and n doping predicted in graphene/Ag/Ni(111) with 1.33 ML Ag coverage are consistent with those of ARPES measurements,⁴⁶ which have been claimed to be the results

for 1 ML Ag coverage. We have demonstrated that even if symmetry breaking is prominent, an appreciable bandgap does not open in graphene/Ag/Ni(111) with a flat layer of *high* Ag coverage because the interaction between graphene and the intercalated Ag atoms is weak, which is ensured by the absence of hybridization between them. We have also argued that an invisibly small bandgap in graphene/Ag/Ni(111) with a flat Ag layer of high coverage can be explained by the similarity between this system and graphene/Ag(111). The inconsistency between our predictions and experiments for the Ag coverage suggests that the ARPES measurements might have been made for graphene/Ag/Ni(111) with fractional Ag coverage of ~ 1.3 ML, although it is not clear how the actual coverage was specified in the experiments. It is also possible that ARPES measurements have been made for a small Ag coverage, for which the bandgap predicted by the present calculations is not substantial compared with the experiments but could be much larger if we assume strong symmetry breaking of graphene sublattices due to inhomogeneous or random distributions of intercalated Ag atoms. Other possibilities such as defect formation or disruption in the graphene may also be suggested as the source of inconsistency between our predictions and ARPES measurements. Similar arguments also apply to graphene/Cu/Ni(111) (Ref. 46) and graphene/Au/Ru(0001) (Ref. 51), in which substantial bandgaps of 180 and 200 meV have also been observed for the *claimed* 1 ML coverage of intercalants. These results could also be understood if we assume small or fractional coverage of the intercalants. Finally, gapped graphene on Ni(111) surface with intercalated Ag atoms is highly n doped and is a metallic semiconductor in the sense that the Dirac point, which is assumed to be the midgap, is located far below the Fermi level. Such graphene does not form a Schottky contact, in which the Fermi level is in the energy gap, and it is useful to explore such a gapped graphene contacted to metals.

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