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# Effect of K doping on the quasifreestanding graphene formed on Au/Ni(111): Density-functional calculations

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We investigated the atomic and electronic structure of the K-adsorbed graphene/Au/Ni(111) surface by using density-functional calculations. The role of the K adsorbates is verified as a simple donor: the adsorption of K induces a rigid shift of the graphene $\pi$ bands with preserving the quasifreestanding Dirac-cone shape. The $\pi$ character of the Dirac-cone bands, however, undergoes some weakening due to the hybridization with Ni $d$ bands, especially in the energy range of 0.5–0.8 eV (0.1–0.3 eV) below the Fermi level for the majority (minority) spin band structure. This weakening of the $\pi$ character could possibly account for the reduced photoemission intensity of the Dirac cone, which was experimentally reported as a band gap of 0.6 eV.

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## I. INTRODUCTION

Graphene reveals the so-called Dirac-cone band structure featuring linearly dispersive bands near the Fermi level, thus being an exceptional material with potential applications for electronic transport, spintronics, and optoelectronics devices [1–3]. Since the Dirac point, where the graphene $\pi$ and $\pi^*$ bands touch, is exactly on the Fermi level, we need certain band engineerings for successful device applications: for example, we need a tunable band gap for turn-on/turn-off devices [4] and an up/down shift in the Dirac point for $p$-$n$ junction devices [5].

Doping of alkali metals has widely been used for manipulating the graphene band structure. It is generally accepted that alkali-metal adsorbates donate electrons to graphene without disturbing its atomic structure, resulting in a rather rigid shift of the graphene $\pi$ bands [6,7]. As a representative dopant element, potassium (K) has recently been employed in the electronic-structure study of graphene systems. In their angle-resolved photoelectron spectroscopy (ARPES) study of graphene/SiC(0001) systems, Bostwick and coworkers showed that K deposition shifts the graphene bands rigidly to higher binding energies for single-layer graphene [8], while for bilayer graphene the band gap could be manipulated by K deposition through asymmetric carrier concentration in each layer [9]. density-functional theory (DFT) calculations also reported that K atoms adsorbed on freestanding graphene cause a rigid band shift below the Fermi level while preserving the ideal Dirac-cone shape [10,11]. The rigid band shift by K doping was successfully used to identify the Dirac-cone shape of $p$-doped graphene formed on the Au/Ru(0001) substrate, which otherwise cannot be directly measured by ARPES [12].

Notable in this regard is a recent ARPES study of the K-doped graphene/Au/Ni(111) surface [13], where the K doping was used to explore the Dirac-cone shape of the graphene/Au/Ni(111) surface. The graphene on Au/Ni(111) is known as a quasifreestanding graphene showing almost ideal graphene $\pi$ bands, as was verified by an ARPES study [14] and a DFT study [15]. Since the graphene is slightly $p$ doped by the substrate effect, however, the detailed Dirac-cone shape, i.e., the position of the Dirac point ($E_D$) relative to the Fermi level or the presence of a band gap ($E_g$) or not, could not be measured in the ARPES study [14], while the DFT study predicted $E_D = +0.02$ eV and $E_g = 0.07$ eV [15]. In their ARPES study, Varykhalov *et al.* reported that the K-doped graphene/Au/Ni(111) surface, prepared and measured at a low temperature of 30 K, displays not only a band shift of $-0.4$ eV but also, more interestingly, a large band gap of 0.6 eV, while the Gd-doped graphene/Au/Ni(111) surface well preserves the Dirac-cone shape with a negligible band gap [13]. They concluded that, unlike Gd atoms, the adsorption of K atoms newly introduces a band gap in the otherwise quasifreestanding Dirac-cone shape of graphene/Au/Ni(111). This band-gap opening in K/graphene/Au/Ni(111), however, contrasts with similar K-doped graphene/SiC(0001) and graphene/Au/Ru(0001) systems [8,12], where the Dirac-cone shape is known to be little affected by the K doping, and also with previous DFT calculations that K doping on freestanding graphene introduces no band gap [10,11]. In addition, in their combined ARPES and DFT study [16], Haberer *et al.* reported that no band gap opens for K doping on graphene/Au/Ni(111), although their work was focused on the K phases intercalated between graphene and Au/Ni(111) after annealing at 350 K, rather than adsorbed K phases expected for low-temperature depositions [13]. Thus, the experimentally reported band-gap opening in K/graphene/Au/Ni(111) is very exceptional.

In this paper, we investigate the effect of K doping on the atomic and electronic structure of graphene/Au/Ni(111) by using DFT calculations. Our calculations demonstrate that the graphene $\pi$ bands shift rigidly by K depositions, well preserving the Dirac-cone shape with a negligible band-gap opening, thus verifying the role of the K atoms as a simple donor. One noticeable change in the graphene $\pi$ bands is a weakening of the $\pi$ character near the Dirac point, which is due to the hybridization with the Ni $d$ bands widely distributed below the Fermi level. It is thus suggestive that the experimentally reported band gap could possibly be related to the $\pi$ character weakening due to the interaction with the substrate, rather than directly induced by K doping.

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## II. METHOD

We perform DFT calculations using the Vienna *ab initio* simulation package [17]. We use a spin-polarized local-density approximation (LDA) for electron-electron interactions [18] and ultrasoft pseudopotentials for electron-ion interactions [19]. The Ni(111) surface is simulated by a periodic slab geometry with a slab of five atomic layers and a vacuum spacing of about 16 Å. Carbon and Au atoms are introduced on the top of the Ni(111)-$4 \times 4$ supercell. We expand the electronic wave functions in a plane-wave basis set of 287 eV and carry out Brillouin-zone integrations by using a $3 \times 3 \times 1$ $k$-point mesh. All atoms but the bottom two Ni layers held fixed at bulk positions are relaxed until the residual force components are within 0.03 eV/Å. A similar method was successfully used for the study of the graphene/Au/Ni(111) surface [15], where the calculated structural properties of graphene and the Ni(111) surface can be found. We have examined the effect of van der Waals interactions in the graphene on Au/Ni(111) by employing the density functionals (vdW-DF) developed by Dion *et al.* [20]. The calculated graphene adsorption energy and the graphene-substrate distance are 0.02 eV per C atom and 3.69 Å, respectively, which compare well with the LDA values of 0.03 eV and 3.33 Å [15]. The differences between vdW-DF and LDA are not substantial, and, above all, the band structure is insensitive to the choice, which sufficiently justify the present use of LDA in studying the graphene band engineering by K doping.

## III. RESULTS

Figure 1 shows the employed structural model for the graphene/Au/Ni(111) surface, featuring a hexagonal layer of Au atoms intercalated between graphene and the Ni(111)-($2 \times 2$) surface. It was demonstrated in our previous DFT study [15] that this model is energetically favored and well reproduces the experimental, quasifreestanding graphene band structure [13]. In the present study, we define the coverage of 1 ML as one K atom per eight C atoms, which is known as the coverage of the most densely packed K phase on graphite [21].

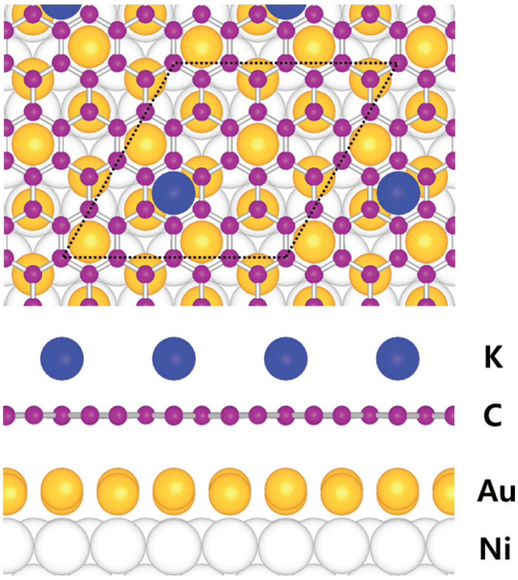

FIG. 1. (Color online) Atomic structure of the K-adsorbed graphene/Au/Ni(111) surface at 0.25 ML. Dashed lines represent the used ($4 \times 4$) supercell.

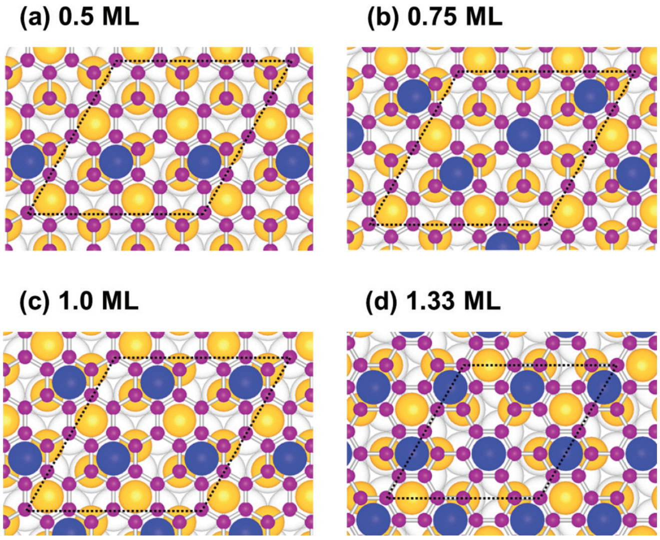

FIG. 2. (Color online) Atomic structures of the K-adsorbed graphene/Au/Ni(111) surface at high coverages.

We begin with the K adsorption of 0.25 ML, chosen as a representative low-coverage system in view that, when adsorbed on a freestanding graphene, K atoms up to 0.25 ML remain ionic by the total charge transfer to graphene [22]. Figure 1 shows the most stable adsorption geometry at 0.25 ML. The K adsorbate prefers the hollow sites over the on-top sites of graphene with an energy gain of about 0.1 eV. There are two inequivalent hollow sites depending on the presence of Au atom below, but we found that they are equally stable in energy and show no difference in the calculated graphene band structure. The equilibrium distance of K from graphene is 2.44 Å, and its adsorption energy is 1.42 eV per K atom. The adsorbed K atoms slightly increase the rumpling of the graphene layer from 0.01 Å to 0.05 Å, but little affect the Au/Ni(111) substrate (less than 0.01 Å in the graphene-Au and Au-Ni layer spacings).

Figure 2 shows the optimized K/graphene/Au/Ni(111) structures at higher K coverages. Each structure represents the most energetically stable of various K-adsorption configurations considered for the given coverage. A $4 \times 4$ supercell was used for the coverages 0.5, 0.75, and 1.0 ML and a $2\sqrt{3} \times 2\sqrt{3}$ supercell for 1.33 ML. Their adsorption properties are summarized in Table I. The adsorption energy is the largest for the lowest K coverage (here, 0.25 ML) and decreases by about 0.3 eV for higher coverages. We can understand this change in adsorption energy as that the first-stage decrease with coverage due to the repulsive interactions between ionic K atoms is soon balanced by the formation of K-K metallic bonding at higher coverages. The equilibrium distance of K from graphene is also affected by the K-K interactions: A stronger K-K metallic bonding leads to a weaker bonding between K and graphene, so the distance of K from graphene increases by about 0.2 Å. Even at these high K coverages, there is no significant change in the

TABLE I. Properties of the K/graphene/Au/Ni(111) surface at different K coverages. $E_a$ (eV) represents the adsorption energy of K. $d$ (Å) is the specified interlayer spacing, where a layer height is averaged over all atoms in the layer. $\Delta z$ (Å) is the rumpling in the layer (for Ni, the topmost layer) defined as the maximum vertical separation among atoms. $E_g$ and $E_D$ (eV) represents the band gap and the Dirac point of the graphene $\pi$ bands, respectively, obtained for the majority-band structure. Figures in parenthesis refer to the values for the minority-spin bands. $E_D$ is defined as the midpoint of the band gap.

| Systems | $E_a$ | $d_{\text{(K-C)}}$ | $d_{\text{(C-Au)}}$ | $d_{\text{(Au-Ni)}}$ | $\Delta z_{\text{C}}$ | $\Delta z_{\text{Au}}$ | $\Delta z_{\text{Ni}}$ | $E_g$ | $E_D$ |
|---|---|---|---|---|---|---|---|---|---|
| clean | | | 3.334 | 2.323 | 0.011 | 0.221 | 0.049 | 0.024 (0.002) | 0.057 (0.106) |
| 0.25 ML | 1.418 | 2.443 | 3.334 | 2.324 | 0.056 | 0.221 | 0.054 | 0.061 (0.016) | −0.827 (−0.800) |
| 0.50 ML | 1.088 | 2.525 | 3.307 | 2.323 | 0.079 | 0.234 | 0.054 | 0.019 (0.026) | −1.046 (−1.061) |
| 0.75 ML | 1.112 | 2.636 | 3.294 | 2.305 | 0.040 | 0.238 | 0.048 | 0.053 (0.005) | −1.103 (−1.111) |
| 1.00 ML | 1.164 | 2.653 | 3.337 | 2.327 | 0.032 | 0.227 | 0.051 | 0.033 (0.301) | −1.109 (−1.124) |
| 1.33 ML | 1.139 | 2.643 | 3.357 | 2.317 | 0.022 | 0.237 | 0.048 | 0.085 (0.071) | −1.122 (−1.124) |

structure of the graphene/Au/Ni(111) substrate: except a rumpling of 0.08 Å in the graphene layer at 0.5 ML and a change of 0.04 Å in graphene-Au distance at 0.75 ML, changes in layer spacings and rumplings are all negligible within 0.02 Å.

Table 1 also shows the effect of K on the electronic structure of the graphene: the band gap and the Dirac-point energy were taken from the majority-spin band structures of the K/graphene/Au/Ni(111) surfaces. The Dirac-cone shape is well preserved in all coverages (0.25–1.33 ML) as will be shown below, and the induced band gaps around the Dirac point are very small within 0.1 eV. The Dirac point, initially at +0.06 eV, shifts down to −1.12 eV with increasing the K coverage up to 1.33 ML. The Dirac-point shift is subject to the amount of charge transfer to graphene and is thus expected to be proportional with the K coverage in the ionic regime. Indeed, the Dirac-point shift is rapid early at about 0.25 ML, but it is soon saturated to about −1.1 eV at more than 0.5 ML, reflecting the onset of K-K metallic bonding. The minority-spin bands show the same behavior as the majority-spin bands with negligible differences within 0.05 eV in $E_g$ and $E_D$.

Figure 3 shows the band structures of the K/graphene /Au/Ni(111) surface at three different coverages. We will discuss the majority-spin band structures first. In Fig. 3(a), the $\pi$ bands of the clean graphene/Au/Ni(111) surface form an almost ideal Dirac-cone structure with a negligible band gap of 0.02 eV and a small shift of +0.06 eV from the Fermi level, well revealing the quasifreestanding nature of the graphene. In Fig. 3(b), the K adsorption of 0.25 ML results in a large shift of the $\pi$ bands by −0.83 eV while preserving the Dirac-cone shape with a small band gap of 0.06 eV. The K adsorbates little affect the energy levels and dispersions of the Au- and Ni-derived bands and only produce a K-derived nondispersive band at around 0.6 eV above the Fermi level, strongly indicating a rather complete charge transfer from K to the graphene layer. We also considered the adsorption of K on the top of a C atom: This structure is locally unstable, but its band structure was tried because it breaks the A-B sublattice symmetry of graphene, unlike the hollow-site adsorption, and thus could possibly open a larger band gap. Even this symmetry breaking, however, was found to produce basically the same band structure as that shown in Fig. 3(b) with $E_g = 0.06$ eV and $E_D = -0.79$ eV. In Fig. 3(c), the K adsorption of 1 ML further shifts the Dirac point to −1.11 eV. At this high coverage, the K-derived bands become metallic due to the enhanced K-K interactions, but the graphene $\pi$ bands still retain the Dirac-cone shape with a small band gap of 0.03 eV, and the Au- and Ni-derived bands also remain intact. It is, therefore, clear that the Dirac-cone structure of the quaifreestanding graphene on Au/Ni(111) is robust for K adsorptions: a simple charge transfer from K to graphene rigidly shifts the Dirac cone below the Fermi level. The minority-spin bands also show the same picture for the effect of K but a difference that the Ni $d$ bands are a little less bound by about 0.4 eV.

One interesting observation in the band structures is that the $\pi$ character of graphene bands undergoes a weakening by hybridization when crossing the substrate metal bands. Especially notable are the Ni $d$ bands bound between −0.5 and −0.8 eV near the K′ point, which results in a significant $\pi$-character weakening just below the Fermi level as seen in Figs. 3(b)–3(c). This weakening of the $\pi$ character is apparently a substrate effect, and its extent and energy level is specific to the given substrate. In our independent study, we found that the K-adsorbed freestanding graphene also preserve the Dirac-cone shape: the rigid shift of the Dirac cone at each coverage is almost the same within 0.1 eV as the value for the K/graphene/Au/Ni(111) surface. In the band structure of K/graphene, however, the $\pi$ character of graphene is intact with no weakening, which ensures that the $\pi$-character weakening in K/graphene/Au/Ni(111) is solely the effect of the Au/Ni(111) substrate.

It is interesting to check whether the $\pi$-character weakening depends on the lateral position of graphene with respect to the Au/Ni(111) substrate, in view that the reported Moiré pattern of the graphene/Au/Ni(111) surface is indicative of a graphene on the Au/Ni(111)-(9 × 9) superstructure [13]: Here, the C atoms occupy various relative positions with respect to Au or Ni atoms in the substrate, unlike in our simplified (2 × 2) model. For this purpose, we examined the band structure of the K(1.0 ML)/graphene/Au/Ni(111)-(2 × 2) surface with displacing the graphene layer along the in-plane direction. We found that the $\pi$-character weakening due to the hybridization between C bands and Ni bands little depends on the lateral position of the C atoms, while the Dirac point somewhat fluctuates in a small range of 0.2 eV.

The present result of no K-induced band gap contrasts with the experimental report of a large $\pi$-band gap of 0.6 eV in the K/graphene/Au/Ni(111) surface. In their ARPES study, Varykhalov *et al*. found that the graphene $\pi$ bands

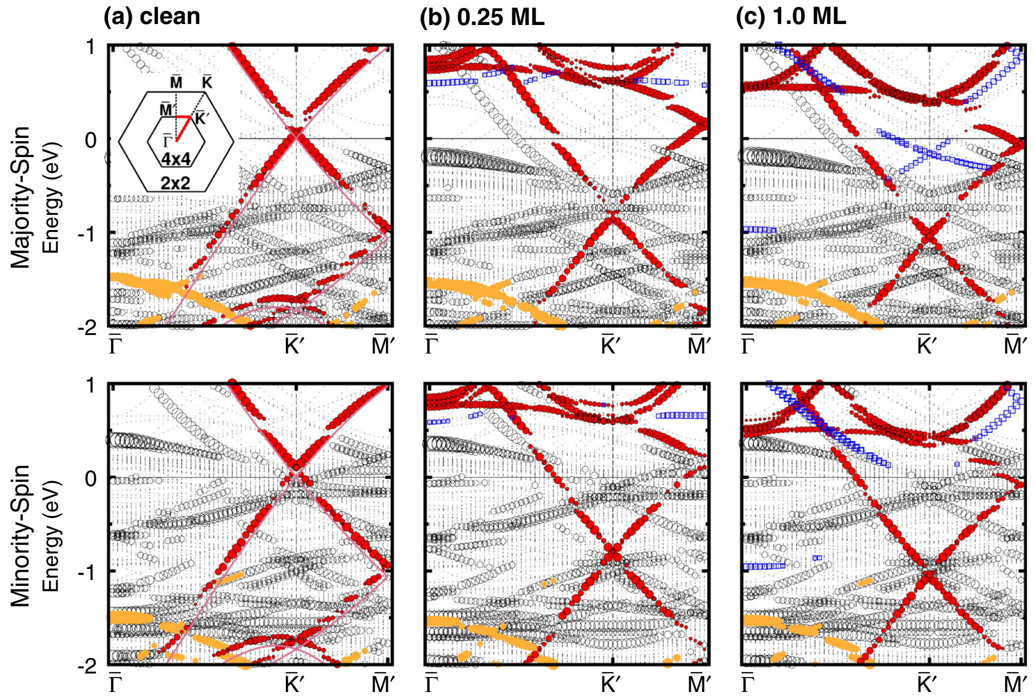

FIG. 3. (Color online) Band structures of the K-doped graphene/Au/Ni(111) surfaces: (a) clean, (b) 0.25 ML, and (c) 1 ML. In (a), the $(4 \times 4)$ surface Brillouin zone is shown, and the bands of freestanding graphene are given by solid lines as a reference. Dark (red) filled circles, gray (yellow) filled circles, open circles, and open squares represent C-, Au-, Ni-, and K-derived states, respectively, and their size is proportional to the amount of charge localized in the corresponding atoms.

shift downward by K doping, and the $\pi$-band intensity is dramatically reduced in between $-0.1$ and $-0.7$ eV [13]. This low-intensity region was interpreted as a K-induced band gap, and the center of the gap, $-0.4$ eV, was assigned to the Dirac point. In view of our calculations, however, the K adsorbates are unlikely to directly induce such a large band gap on graphene. We may suspect that the experimental finding is related to the weakening of the $\pi$ character due to the hybridization with Ni $d$ bands: The relevant Ni $d$ bands distribute in the energy range between $-0.5$ and $-0.8$ eV on the K$'$ point in the majority-spin band structure and between $-0.1$ and $-0.3$ eV in the minority-spin band structure, which largely overlaps with the experimental region of low $\pi$-band intensity. It should be mentioned, however, that we are not in a position to discuss the total disappearance of intensity in experiment, since the calculated density of states has no straightforward relation to the photoemission intensity without doing rigorous photoemission simulations. The present theory calls for a more refined analysis of the reduced ARPES intensity of the Dirac cone.

Varykhalov *et al*. also reported that, unlike the case of K, Gd plays a role of simple donor on the graphene/Au/Ni(111) surface by preserving the gapless Dirac-cone shape with $E_D = -0.4$ eV [13]. Since the Dirac point appears at the same level as the value estimated for the K doping, it is interesting why the $\pi$-character weakening is absent in the Gd case. If we examine the measured band structures carefully, however, the lower Dirac cone of the K-doped system appears to be 0.2 eV higher binding than that of the Gd-doped system. This suggests that the experimental Dirac point of K/graphene/Au/Ni(111), estimated from the incorrectly assigned band gap, should be corrected as $-0.6$ eV. While the $\pi$ bands near the Dirac point ($-0.6$ eV) of the K-doped system undergo a weakening by touching the Ni $d$ bands between $-0.5$ and $-0.8$ eV, the $\pi$ bands near the Dirac point ($-0.4$ eV) of the Gd-doped system could be intact with no overlap with the Ni $d$ bands. Shortly, both K and Gd well preserve the Dirac-cone band structure as simple donors, but their $\pi$-band intensities appear differently, depending on the relative position of the Dirac point with respect to the substrate metal bands.

## IV. SUMMARY

We have shown by DFT calculations that K doping does not disturb the Dirac-cone shape of the quasifreestanding graphene on Au/Ni(111) but results in a rather rigid band shift. This suggests that the experimentally reported band gap of 0.6 eV is not a direct band gap induced by K doping but is related to the $\pi$-character weakening of rigidly shifted graphene bands due to the interactions with the substrate Ni $d$ bands. This interpretation is also compatible with the experimental finding of no band gap in the Gd-doped graphene/Au/Ni(111) surface.

## ACKNOWLEDGMENTS

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