# Electronic structures and vibrational properties of coronene on Ru(0001): first-principles study*

Zhang Yu-Yang(张余洋), Du Shi-Xuan(杜世萱)†, and Gao Hong-Jun(高鸿钧)

*Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

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We calculate the configurations, electronic structures, vibrational properties at the coronene/Ru(0001) interface, and adsorption of a single Pt atom on coronene/Ru(0001) based on density functional theory calculations. The geometric structures and electronic structures of the coronene on Ru(0001) are compared with those of the graphene/Ru(0001). The results show that the coronene/Ru(0001) can be a simplified model system used to describe the interaction between graphene and ruthenium. Further calculations of the vibrational properties of coronene molecule adsorbed on Ru(0001) suggest that the phonon properties of differently corrugated regions of graphene on Ru(0001) are different. This model system is also used to investigate the selective adsorption of Pt atoms on graphene/Ru(0001). The configurations of Pt on coronene/Ru(0001) with the lowest binding energy give clues to explain the experimental observation that a Pt cluster selectively adsorbs on the second highest regions of graphene/Ru(0001). This work provides a simple model for understanding the adsorption properties and vibrational properties of graphene on Ru(0001) substrate.

**Keywords:** coronene/Ru(0001) interface, surface adsorption, phonon calculation, first-principles calculation

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## 1. Introduction

Since the discovery of exfoliated graphene in 2004,[1] the research on this two-dimensional material with many excellent physical properties[2−5] and great potential for future applications[6,7] has become a hot topic. Among all the fabrication methods of graphene layers,[8−13] epitaxy on transition metal surfaces has been widely used because of its high efficiency and high sample quality.[11−14] To understand the structural and physical properties of graphene on transition metals, various experimental techniques, such as low energy electron diffraction (LEED), scanning tunneling microscopy (STM), and angle-resolved photoemission spectroscopy (ARPES), have been employed.[15−17] At the same time, many calculations and simulations at different levels (from the empirical tight binding approach to the *ab initio* method) have been carried out.[18−22]

Because of the lattice mismatch between an epitaxial graphene layer and a transition metal substrate (except Ni(001)), a supercell with a moiré pattern of the combined system can be very large. Take graphene/Ru(0001) for an example, two types of supercell have been reported based on different LEED patterns and STM experiments.[9,11,14,23] One contains 25×25 graphene cells and 23×23 Ru(0001) cells, which is beyond the state-of-the-art first principles calculation.[14] The other contains 12×12 graphene cells and 11×11 Ru(0001) cells,[11] much smaller than the first one, but still very large. Based on the second supercell, Jiang *et al.* and Wang *et al.* calculated the geometric structure and charge transfer, and obtained reasonable results as compared with experimental findings.[20,21] However, because of the large size of this supercell and many local minima in the energy space, it is difficult to investigate the adsorption behaviour of molecules and metal clusters on graphene/Ru(0001) by first-principles calculations using this supercell. In addition, calculation of the vibrational properties using this supercell is almost impossible. Therefore, various methods and models have been used to reduce the size of the large supercell, and density functional theory (DFT) calculations have been applied to it. The simplest way is to use a unit cell without considering the lattice mismatch. Khomyakov *et al.* and Vanin *et al.* used this model to discuss interaction between graphene and several

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†Corresponding author. E-mail: sxdu@iphy.ac.cn

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noble metals.[18,19] Another way is to use an artificial supercell with a different lattice mismatch from the real system but with a moderate size. Sun *et al.* used an $(m \times m)$ graphene-$((m-1)\times(m-1))$ metal model to discuss the strain effect in graphene–ruthenium system.[22] For all these approaches, the graphene layer used to simulate the properties of that in graphene/Ru(0001) system is quite distorted.

In this letter, we propose to use the coronene/Ru(0001) as a model system to investigate the physical and chemical properties of the graphene/Ru(0001) system. This model gives a geometric structure and binding energy similar to those of the graphene/Ru(0001) system with the C(12×12)/Ru(11×11) supercell.[20,21] The calculated vibrational properties of this model system imply different phonon frequencies of different regions in the graphene/Ru(0001) system, which should be observable by related experiments. We further investigate the adsorption of Pt atoms on coronene/Ru(0001). It was found that a Pt atom adsorbed on coronene/Ru(0001) with moderate coronene–Ru(0001) separation is the most stable configurarion, which means at initial stage, Pt atom prefers to adsorb on the second highest region of graphene/Ru(0001) surface. This result may give clues to explain the experimently observed selective adsorption of Pt cluster on graphene/Ru(0001) system, and also provide a simple way to investigate and understand the selective adsorption of other metal atoms on a graphene/ruthenium system.

## 2. Calculation method

Quantum mechanical calculations based on DFT were performed using the Vienna *ab initio* simulation package (VASP).[24,25] A Perdew–Wang (PW91)[26] type exchange-correlation functional and the projector augmented wave (PAW) method were employed.[27,28] The Ru(0001) surface was modeled with a slab model. One coronene molecule was put on one side of a 6×6 supercell of six-layer Ru(0001) with a 15 Å vacuum gap perpendicular to the surface. The energy cutoff was set to be 400 eV and the Brillouin zone was sampled with the $\Gamma$ point only. All the atoms except those at the bottom three layers were fully relaxed until the forces on each atom were less than 0.01 eV/Å. Different initial adsorption sites were tested to calculate the Pt adsorption. The vibrational properties of the coronene/Ru(0001) system were derived by calculating the force constant with the finite displacement method and the displacement for each step is 0.02 Å. In the calculation of vibrational properties, only the molecule and the ruthenium atoms in the first layer were allowed to move, which could represent a reasonable interaction between the molecule and the substrate, and reduce the total vibration modes for analysis.

Considering the position of the central benzene ring of the coronene molecule on Ru(0001) and the corrugation of graphene/Ru(0001), we use three typical configurations with the central benzene ring of coronene molecule on the top of a ruthenium atom (TOP, Fig. 1(a)), on an fcc hollow site (FCC, Fig. 1(b)), and on an hcp hollow site (HCP, Fig. 1(c)) of the first layer to simulate the atop (the highest), hcp (the lowest), and fcc (the middle) regions of the graphene/Ru(0001) system, respectively.

## 3. Results and discussion

The adsorption configurations of coronene on Ru(0001) surface are optimized first. Figure 1 shows the top view of the three typical adsorption configurations named TOP, FCC, and HCP. The coronene molecules remain flat on the substrate for all these configurations. The distances between central benzene rings and the substrate for TOP, HCP and FCC configurations are similar to those in atop, hcp and fcc corrugated regions of the graphene/Ru(0001) with C(12×12)/Ru(11×11) supercell, respectively (see Table 1). Compared the middle part of the coronene molecule in TOP configuration with the highest part (atop region) in graphene/Ru(0001) system,[20,21] both of the central benzene rings are on the top of a ruthenium atom in the first layer of Ru(0001) and surrounded by six benzene rings whose centers are also nearly on the top of ruthenium atoms. The distance between the central benzene ring and the ruthenium substrate ($z$) is 3.90 Å (a typical distance between aromatic molecules and transition metal substrate[29]). In graphene/Ru(0001) system, it is 3.87 Å in Ref. [20] and 3.70 Å in Ref. [21]. In the same way, we compare the HCP and FCC configurations with the hcp and fcc regions of graphene/Ru(0001) system. The distance between the central benzene ring and the substrate ($z$) in HCP configuration is the lowest among these three configurations, which is in agreement with that of the graphene/Ru(0001) system.[20]

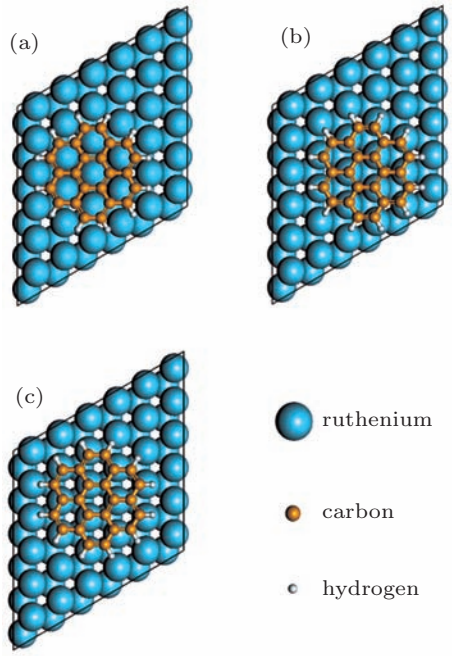



**Fig. 1.** (colour online) Adsorption configurations of coronene/Ru(0001) system (top view) for (a) TOP configuration, (b) FCC configuration, and (c) HCP configuration.

Based on the optimized geometric structures, we further calculate the adsorption energies for each configuration (see Table 1). In Table 1, $z$ is the vertical distance between the central carbon atoms in coronene molecule and the substrate, $E_{\rm b}$ is the binding energy of coronene on Ru(0001), $d$ is the length of the Pt–C bond, $E_{\rm Pt}$ is the binding energy of a Pt atom of the coronene/Ru(0001) system, and $f$ is the frequency of the vibration mode corresponding to the G mode in graphene. The adsorption energies of a coronene molecule on Ru(0001) for TOP, FCC, and HCP configurations are $-0.28$, $-0.33$, and $-0.36$ eV respectively. Therefore, we can estimate the adsorption energy caused by the central benzene ring is about 13 meV per C-atom, which is similar to that of the graphene/Ru(0001) system, which is about 11 meV per C-atom.[20] Adsorption-induced electron redistribution between adsorbates and substrate can give insightful information at the interface.[30] Our calculation results show that the electron transfers from Ru substrate and coronene molecules to the region inbetween is about 0.16, 0.40, and 0.47 electron per molecule for TOP, FCC, and HCP configurations, respectively. This electron redistribution has the same trend as that in graphene/Ru(0001) system, and will induce a surface dipole moment pointing from Ru substrate to coronene molecules.[20]

**Table 1.** Calculation results for TOP, FCC, and HCP configurations.

| | $z$/Å | $E_{\rm b}$/eV | $d$/Å | $E_{\rm Pt}$/eV | $f$/meV |
|---|---|---|---|---|---|
| TOP | 3.90 | –0.28 | 2.11 | –1.87 | 198.4 |
| FCC | 3.33 | –0.33 | 1.99 | –0.35 | 197.2 |
| HCP | 3.19 | –0.36 | 1.99 | –2.28 | 196.1 |

We then calculate the electronic structures for these three configurations. The density of states (DOS) projected on $p_z$ orbital (corresponding to $\pi$ bonds) and $s + p_x + p_y$ orbitals (corresponding to $\sigma$ bonds) attributed to the central benzene ring of a free coronene molecule, in the TOP, FCC, and HCP configurations are shown in Fig. 2. For the TOP configuration, the distance between the coronene molecule and the substrate is the largest of the adsorbed configurations, which implies a weaker adsorption. Comparing the projected DOS (PDOS) of the central benzene ring in TOP configuration with that in the free molecule, we find that the electronic structure of the TOP configuration is very similar to that of a free coronene molecule. This is a direct evidence that the coronene molecule in the TOP configuration adsorbs weakly on Ru(0001), which corresponds to the weak interaction between graphene and the substrate at atop site in graphene/Ru(0001).[21] Comparing the PDOS of the central benzene ring in the FCC and HCP configurations (see Figs. 2(c) and 2(d)) with that of the free molecule, we find that all peaks shift to the lower energy region and are slightly broaden. This phenomenon is qualitatively similar to that of the graphene/Ru(0001) system with C(12×12)/Ru(11×11) supercell.[21] Unlike the TOP configuration, the large shift of PDOS in FCC and HCP configurations indicates a strong binding between the adsorbate and the substrate, and such a system will have different physical and chemical properties, for example, different adsorption behaviour for metal clusters or molecules. The HCP configuration has a lower binding energy and shorter molecule-substrate distance than those of the FCC configuration, which indicates a stronger binding between adsorbed molecules and the Ru(0001) in HCP configuration than that in FCC. However, as shown in Figs. 2(c) and 2(d), the energy shift of the PDOS in the FCC configuration is larger than that in the HCP configuration. This behaviour is also found in the graphene/Ru(0001) system between hcp and fcc sites.[21]

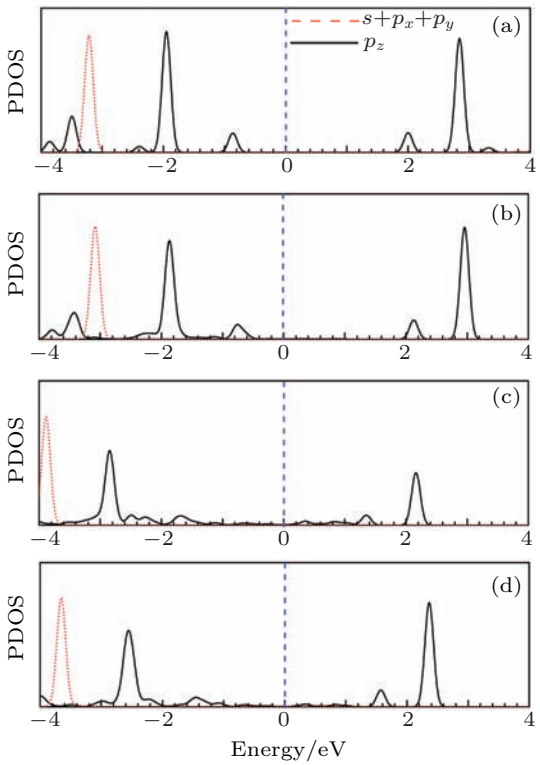



**Fig. 2.** (colour online) Projected density of states (PDOS) contributed by the center benzene ring of coronene in (a) free molecule, (b) TOP configuration, (c) FCC configuration, and (d) HCP configuration. Dashed lines are the summation of PDOS from $s$, $p_x$ and $p_y$ orbitals; solid lines are the PDOS of $p_z$ orbitals; dashed blue lines indicate the Fermi levels.

By comparing the geometric structure and electronic structure of coronene/Ru(0001) with those of the graphene/Ru(0001) system, we find that the properties of the coronene/Ru(0001) system is very similar to these of the graphene/Ru(0001) system, which makes the coronene/Ru(0001) system be an excellent model system to study the properties of the graphene/Ru(0001) system, but with a much smaller computational cost. Based on this conclusion, we use this model to investigate the vibrational properties and adsorption properties of the graphene/Ru(0001) system.

The phonon property of graphene layer could vary for different regions of graphene/Ru(0001) because the interaction between the graphene layer and Ru(0001) changes from region to region. However, to the best of our knowledge, the phonon property of the graphene/Ru(0001) system has never been reported, based on either experiment or calculation. Because of the huge size of the supercell, calculating the phonon property of a real system is far beyond the present state of the art. In order to investigate the phonon properties of graphene/Ru(0001) in different regions, we use the coronene/Ru(0001) with TOP, FCC, and HCP configurations instead.

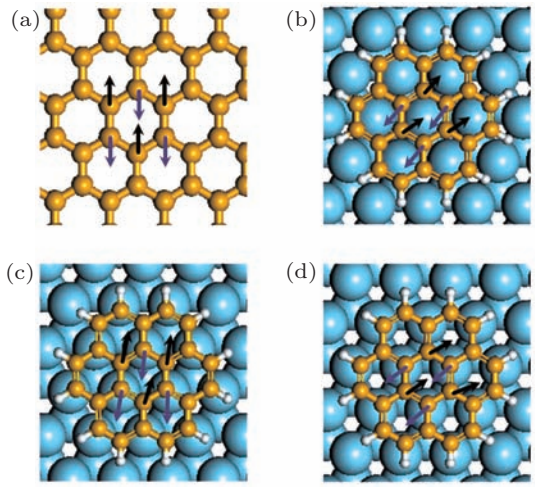



**Fig. 3.** (colour online) Schematic illustrations of the G modes in graphene and corresponding vibration in the coronene/Ru(0001) system. G mode in (a) graphene, (b) TOP configuration, (c) FCC configuration, and (d) HCP configuration. Black arrows and purple arrows indicate the vibration directions of different subsets of carbon atom A and B.

First, the vibrational modes of a free coronene molecule are calculated. The vibrational modes of its central benzene ring are used to compare with those in a graphene layer. The most important vibrational mode in a graphene system is the G mode with $E_{2g}$ symmetry at 198 meV. An example of such a vibrational mode detected at this frequency is presented in Fig. 3(a). The two carbon atoms (A and B) in one unit cell, which are in the same chemical environment, vibrate in opposite directions (black and purple arrows shown in Fig. 3(a)). For free coronene molecule, our calculation results show that the vibrational mode at 199.8 meV is similar to the G mode in graphene. Thus, we use this mode (G mode) as a reference, and investigate its change when the molecule is put on Ru(0001) surfaces with different configurations. The G modes of the central benzene ring in the coronene/Ru(0001) system are shown in Figs. 3(b)–3(d). These vibrational modes differ from that in a free coronene molecule. The environments for the two carbon atoms (A and B) are different because of the existence of the ruthenium substrate, and they no longer vibrate in exactly opposite directions. That is to say, their vibrational frequencies are also influenced by the ruthenium substrate. For a free coronene molecule, the vibrational frequency of this mode is 199.8 meV, which is higher than that of the TOP, FCC, and HCP configurations, i.e., 199.1, 197.2

and 196.1 meV, respectively. Since the HCP configuration has the strongest molecule–substrate interaction, its vibrational frequency is the lowest. The FCC configuration has a moderate interaction between the molecule and substrate, and its vibrational frequency is likewise in between. These results suggest that the vibrational properties of the graphene/Ru(0001) system should vary in differently corrugated regions. The space resolution of inelastic electron tunneling spectroscopy (IETS)[31−33] is high enough to resolve the three regions in a graphene/Ru(0001) sample. Based on our calculations, it should be possible to observe vibrational differences in the three regions of the graphene/Ru(0001) system with IETS.

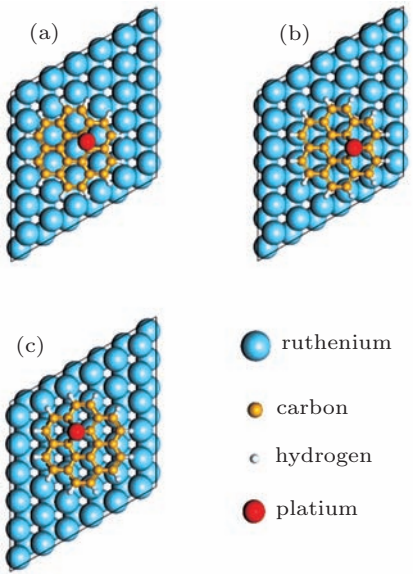



**Fig. 4.** (colour online) Most stable adsorption sites for Pt atom on coronene/Ru(0001) system for (a) TOP configuration, (b) FCC configuration, and (c) HCP configuration. Small black balls represent Pt atoms.

We also investigate the selective adsorption of Pt atom on graphene/Ru(0001) using this coronene/Ru(0001) system, which is helpful to understand the selective adsorption of Pt clusters on graphene/Ru(0001) system.[34] The most stable adsorption sites for Pt atoms in the TOP, FCC, and HCP configurations are shown in Fig. 4. For the TOP configuration, the most stable adsorption site is between two carbon atoms, as shown in Fig. 3(a). The adsorption energy for a Pt atom ($E_{\mathrm{Pt}}$) is −1.87 eV, and the Pt–C bond length is 2.11 Å (see Table 1). For FCC and HCP configurations, the Pt atom prefers to adsorb on the top of a carbon atom, as shown in Figs. 4(b) and 4(c). The Pt–C bond length is 1.99 Å in both the FCC and HCP configurations, and the adsorption energy decreases significantly to −3.50 eV in the FCC configuration and −2.82 eV in HCP configuration. The FCC configuration has a lower binding energy than the HCP region. It implies that the Pt atom prefers to adsorb on the fcc region rather than on the hcp region in graphene/Ru(0001), which is in agreement with the experimental observations.[34] In addition, because the interaction between a coronene molecule and Ru(0001) is mainly through the lowest unoccupied orbital in the molecule and the *s* orbital in Ru(0001), the closer the lowest unoccupied orbital to the Fermi level is, the more active the reactivity of the molecule is. The energy shift of the DOS of the FCC configuration is the largest among the three configurations. Thus, the lowest unoccupied state in the FCC configuration is closer to Fermi energy than that of the HCP configuration, which means a more active adsorption site in the FCC configuration for a Pt atom. Our calculation results based on the simplified model not only explain the selective adsorption observed in experiments according to the difference in binding energies between the FCC configuration (fcc region) and the HCP configuration (hcp region), but also reveal the physical origin of this selective adsorption underlying the difference of electronic structures between these two configurations. Thus, this simple model can be used to explain the selective adsorption of Pt clusters on graphene/Ru(0001) with small computational cost.

## 4. Conclusions

We have calculated the geometric and electronic structures of coronene/Ru(0001) interface. The results show that the interaction between the central benzene ring of coronene molecule and the Ru(0001) substrate is a good basis for describing the interaction between a graphene layer and the Ru(0001) substrate at regions with different corrugations. Using this model, we have predicted the vibrational difference among different regions in graphene/Ru(0001) system. It is also found that the binding energy of a Pt atom on coronene/Ru(0001) with the FCC configuration is the lowest, which means that Pt prefers to adsorb on the graphene/Ru(0001) surface in fcc region at initial stage and thus could be used to explain the selective adsorption of Pt cluster on an fcc region of a graphene/Ru(0001) system. In recent years, several van der Waals involved calculations have been carried out for graphene/metal systems to obtain a better understanding of their configurations and electronic

structures, though there is still discrepancy among different methods.[19,35] We will also extend our work to incorporate dispersion interactions into the DFT framework in the future.

# References


[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666

[2] Zhang Y, Tan Y W, Stormer H L and Kim P 2005 *Nature* **438** 201

[3] Tombros N, Jozsa C, Popinciuc M, Jonkman H T and van Wees B J 2007 *Nature* **448** 571

[4] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Maan J C, Boebinger G S, Kim P and Geim A K 2007 *Science* **315** 1379

[5] Geim A K and Novoselov K S 2007 *Nat. Mater.* **6** 183

[6] Bunch J S, van der Zande A M, Verbridge S S, Frank I W, Tanenbaum D M, Parpia J M, Craighead H G and Mceuen P L 2007 *Science* **315** 490

[7] Ang P K, Chen W, Wee A, Thye S and Loh K P 2008 *J. Am. Chem. Soc.* **130** 14392

[8] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282

[9] Pan Y, Shi D X and Gao H J 2007 *Chin. Phys.* **16** 3151

[10] Berger C, Song Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J, Marchenkov A N, Conrad E H, First P N and de Heer W A 2006 *Science* **312** 1191

[11] Pan Y, Zhang H G, Shi D X, Sun J T, Du S X, Liu F and Gao H J 2009 *Adv. Mater.* **21** 2777

[12] N'Diaye A T, Coraux J, Plasa T N, Busse C and Michely T 2008 *New J. Phys.* **10** 043033

[13] Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee S K, Colombo L and Ruoff R S 2009 *Science* **324** 1312

[14] Martoccia D, Willmott P R, Brugger T, Björck M, Günther S, Schlepütz C M, Cervellino A, Pauli S A, Patterson B D, Marchini S, Wintterlin J, Moritz W and Greber T 2008 *Phys. Rev. Lett.* **101** 126102

[15] Loginova E, Bartelt N C, Feibelman P J and Mccarty K F 2009 *New J. Phys.* **11** 063046

[16] Coraux J, N'Diaye A T, Engler M, Busse C, Wall D, Buckanie N, Heringdorf F J M zu, van Gastel R, Poelsema B and Michely T 2009 *New J. Phys.* **11** 023006

[17] Starodub E, Bostwick A, Moreschini L, Nie S, Gabaly F E, McCarty K F and Rotenberg E 2011 *Phys. Rev.* B **83** 125428

[18] Khomyakov P A, Giovannetti G, Rusu P C, Brocks G, van den Brink J and Kelly P J 2009 *Phys. Rev.* B **79** 195425

[19] Vanin M, Mortensen J J, Kelkkanen A K, Garcia-Lastra J M, Thygesen K S and Jacobsen K W 2010 *Phys. Rev.* B **81** 081408

[20] Jiang D E, Du M H and Dai S 2009 *J. Chem. Phys.* **130** 074705

[21] Wang B, Bocquet M L, Marchini S, Günther S and Wintterlin J 2008 *Phys. Chem. Chem. Phys.* **10** 3530

[22] Sun J T, Du S X, Xiao W D, Hu H, Zhang Y Y, Li G and Gao H J 2009 *Chin. Phys.* B **18** 3008

[23] Vázquez de Parga A L, Calleja F, Borca B, Passeggi M C G, Hinarejos J J, Guinea F and Miranda R 2008 *Phys. Rev. Lett.* **100** 056807

[24] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558

[25] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169

[26] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671

[27] Blöchl P E 1994 *Phys. Rev.* B **50** 17953

[28] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758

[29] Gao H J and Gao L 2010 *Prog. Surf. Sci.* **85** 28

[30] Zhang Y Y, Du S X and Gao H J 2011 *Phys. Rev.* B **84** 125446

[31] Ogawa N, Mikaelian G and Ho W 2007 *Phys. Rev. Lett.* **98** 166103

[32] Vitali L, Burghard M, Schneider M A, Liu L, Wu S Y, Jayanthi C S and Kern K 2004 *Phys. Rev. Lett.* **93** 136103

[33] Huan Q, Jiang Y, Zhang Y Y, Ham U and Ho W 2011 *J. Chem. Phys.* **135** 014705

[34] Pan Y, Gao M, Huang L, Liu F and Gao H J 2009 *Appl. Phys. Lett.* **95** 093106

[35] Stradi D, Barja S, Díaz C, Garnica M, Borca B, Hinarejos J J, Sánchez-Portal D, Alcamí M, Arnau A, Vázquez de Parga A L, Miranda R and Martín F 2011 *Phys. Rev. Lett.* **106** 186102