Electronic structure of silicene on Ag(111): Strong hybridization effects

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(Received 25 January 2013; published 18 July 2013)

The electronic structure of the recently synthesized (3×3) reconstructed silicene on (4×4) Ag(111) is investigated by first-principles calculations. New states emerge due to the strong hybridization between silicene and Ag. Analyzing the nature and composition of these hybridized states, we show that (i) it is possible to clearly distinguish them from states coming from the Dirac cone of free-standing silicene or from the sp bands of bulk Ag and (ii) assign their contribution to the description of the linearly dispersing band observed in photoemission. Furthermore, we show that silicene atoms contribute to the Fermi level, which leads to similar scanning tunneling microscopy patterns as observed below or above the Fermi level. Our findings are crucial for the proper interpretation of experimental observations.

I. INTRODUCTION

Silicon chemistry has been compared with that of carbon, but both experimental and theoretical studies have illustrated great differences between structure and reactivity of compounds of the two group-IV elements and silicene, the silicon equivalent of graphene,[1,2] is not an exception. Unlike carbon atoms in graphene, Si tends to adopt sp^3 hybridization over sp^2 which results in a slightly buckled structure of silicene.[3–6] Despite this buckling, the free standing silicene structure has enough symmetry to preserve the linearly crossing bands around the Fermi level.[5,6] This makes electrons of silicene behave as massless Dirac fermions as in graphene.[2]

Free standing silicene has not been synthesized yet. However, experiments show growth of nanoribbons[7–13] and two-dimensional (2D) monolayers[14–21] of silicene on substrates, usually composed of silver. Interestingly, there is a debate on the structural configuration of silicene on Ag(111). Superstructures with $(2\sqrt{3} \times 2\sqrt{3})$,[14] (3×3),[15,16] $(\sqrt{3} \times \sqrt{3})$,[19,20] and other[17,21] silicene reconstructions on Ag surfaces have been experimentally reported.

Photoemission measurements show linearly dispersing bands for silicene nanoribbons[10,13] and 2D silicene sheets[16] supported on Ag substrates. Nonetheless, this intriguing aspect was not theoretically addressed in detail, but just a simple explanation was provided that linked the observed linear bands to the theoretically predicted Dirac cone of free standing silicene. More precisely, Vogt *et al.*[16] used these linear bands together with scanning tunneling microscopy (STM) images as compelling evidence for monolayer silicene. By combination of calculated and measured STM images, they have nicely shown that silicene sheets are arranged so that (3×3) silicene supercells coincide with (4×4) Ag(111) supercells, where a Si-Si bond length of 2.3 Å is in good agreement with the theoretical calculations.[6] The angle-resolved photoemission spectroscopy (ARPES) measurements show a linear band at the K point of the (1×1) silicene unit cell, which starts

0.3 eV below the Fermi level and has a Fermi velocity of $v_F = 1.3 \times 10^6$ m/s. Here the (3×3) reconstructed silicene unit cell is composed of two atomic planes with twelve Si atoms close to the Ag substrate and six Si atoms further apart. This structure is further confirmed by full structural optimization calculations and by comparing the calculated STM images with the experiment. The similarity between STM images at applied bias of −1.4 eV, −0.5 eV, and 0.6 eV was used to confirm that the origin of the observed patterns was of structural nature. However, the STM data around the Fermi level or the ARPES data over the whole Brillouin zone was not discussed. We note that a linear dispersion around the Fermi level was also observed in the band structure of $(\sqrt{3} \times \sqrt{3})$ reconstructed silicene.[20] However, the exact positioning of silicene atoms on silver is not well characterized experimentally or theoretically in these structures. Also the linear dispersion is inferred indirectly from scattering patterns measured by STM.

In this paper, we provide a simple and coherent interpretation of the main experimental observations for single-layer silicene supported on Ag. We extend the analysis of first-principles calculations performed on the structures reported by Vogt *et al.*[16] We first show that the calculated STM around the Fermi level (0.0 eV) has a similar pattern to those for −1.4 eV, −0.5 eV, and 0.6 eV, which is contributed by silicene, thus implying that silicene on Ag is metallic. We also show that the linear band at the K point of the (1×1) silicene reported by the ARPES measurement[16] can be attributed to a new state that emerges due to the strong hybridization between silicene and Ag. The character of these new states can be clearly analyzed in detail by projecting those states on specific atomic orbitals. Our results will trigger further experimental and theoretical works to consolidate our conclusions.

II. RESULTS

The first step of our calculations based on density functional theory (DFT) has been to determine the lattice parameter of
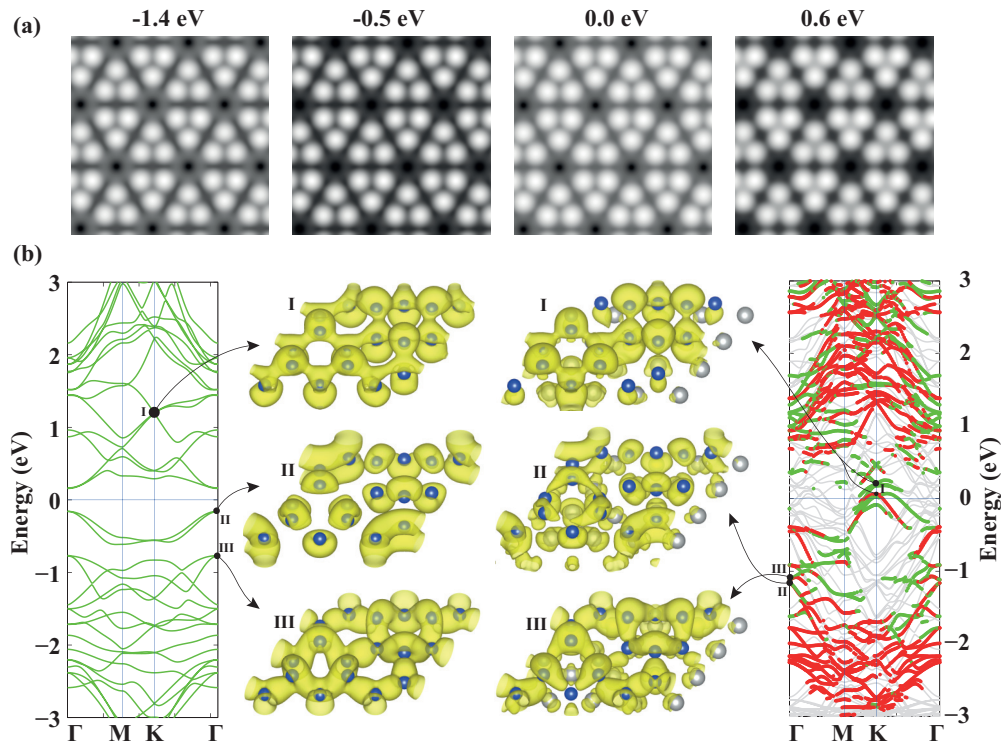
FIG. 1. (Color online) (a) Constant current STM images of reconstructed (3×3) silicene on Ag substrate calculated at -1.4 eV, -0.5 eV, 0.0 eV, and 0.6 eV. (b) The band structure (side panels) and band decomposed charge density isosurfaces (inner panels) of reconstructed silicene in the absence (left side) and presence (right side) of the Ag substrate is shown. The red color indicates the states contributed by p_z orbitals of six Si atoms pointing outwards, whereas the green and light gray lines correspond to the states contributed by Si and Ag atoms, respectively. This correspondence is found by calculating projections of each state to specific atomic orbitals. Si and first layer of Ag atoms are represented by blue and gray balls in the charge density plots. States of interest are labeled by Roman numerals. States corresponding to charge density isosurfaces are shown by arrows where the black circles with little, medium, and large sizes indicate the single, double, and triple degenerate states, respectively.

bulk Ag.[22–29] Then we put one layer of (3×3) silicene on top of 11 layers of (4×4) Ag(111) and optimized the structure by keeping the bottom eight layers fixed at the bulk Ag parameters. The resulting structure has the same configuration as reported in Ref. 16. The calculated constant current STM images are depicted in Fig. 1(a). These images are mainly contributed by Si atoms that are further apart from the Ag layer. They form a hexagonal superstructure with three Si atoms at the corners. The image at 0.0 eV is similar to those at -1.4 eV, -0.5 eV, and 0.6 eV, meaning that Si atoms do indeed contribute to the states at the Fermi level.

To understand the electronic structure of silicene on Ag we first look at the reconstructed silicene in the absence of the substrate which is referred to as unsupported silicene. The band profile of this structure is presented in the left panel of Fig. 1(b). Note that the linearly crossing bands at the K point of unreconstructed (1×1) silicene is folded to the Γ point of its (3×3) supercell. Here the reconstruction breaks the symmetry and opens a 0.3 eV gap at the Γ point. However, the linear dispersion is still present away from the Γ point. A linear dispersion is also present in the states denoted by I whose bands cross each other at the K point. These states could be linked to six Si atoms that point outwards and form a hexagonal superstructure with three Si atoms at each corner, as seen in STM images in Fig. 1(a). The band structure

presented here is in agreement with the one reported in another article.[30]

The band structure of reconstructed (3×3) silicene on (4×4) Ag substrate is shown in the right panel of Fig. 1(b). To have a better insight about the role of silicene in this band structure, we computed the relative contribution of Si atoms by calculating the projection of each state on the atomic orbitals of silicene. We marked with green dots the states with a significant projection on silicene orbitals in order for the plot to preserve its clarity and information. Furthermore, the color of each green dot is changed to red if the corresponding state has significant projection on the p_z orbitals of the six Si atoms positioned relatively further apart from the Ag substrate. On the base of this distinction, it is easy to see that there is a gap in the states contributed by Si atoms at the Γ point of (3×3) silicene. This is in accordance with the measured ARPES data. However, there are still states contributed by Si atoms around the Fermi level but at the K point of the (3×3) silicene, thus explaining the calculated STM image at 0.0 eV [see Fig. 1(a)]. Furthermore, we compare the band decomposed charge densities at K point of the (3×3) reconstructed silicene with and without the Ag substrate, denoted as I in Fig. 1(b). The similarities between these charge densities suggest that the states that contribute to the Fermi level of silicene on Ag system are coming from hybridization between Ag states and
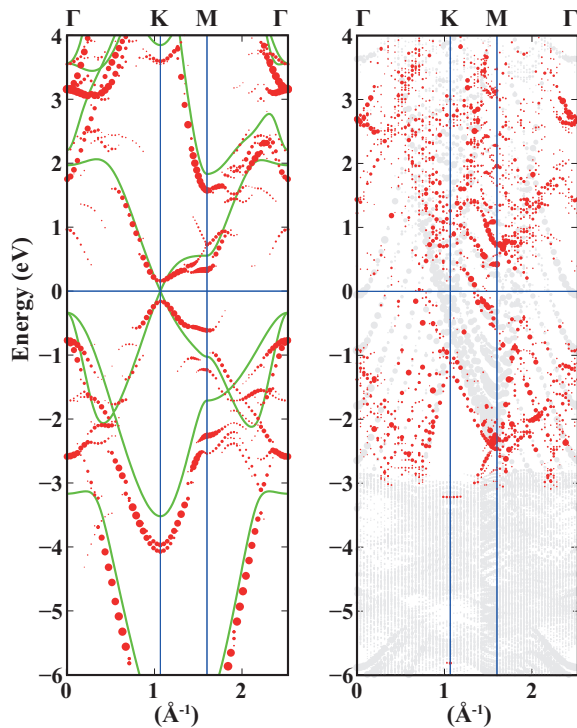
FIG. 2. (Color online) Left panel: bands of reconstructed (3 × 3) silicene in the absence of Ag substrate (unsupported silicene) unfolded to BZ of (1 × 1) silicene are shown by red dots. The radii of dots correspond to the weight of unfolding. The band structure of ideally buckled silicene is shown by green lines. Right panel: unfolded band structure of silicene on Ag. Red dots correspond to states with significant contribution from silicene.

states 1.2 eV above the Fermi level of unsupported silicene. The charge transfer from Ag to silicene which is found to be only 0.5 electron per (3 × 3) supercell cannot account for this energy shift. This issue was also discussed in Ref. 30 for states at the Γ point. Detailed charge density analysis shows that hybridization with Ag breaks the triple degenerate symmetry that this state possesses in the absence of Ag.

To provide a microscopical description of the states contributing to the observed linear dispersion in the photoemission data of Ref. 16, we unfold the band structures presented in Fig. 1(b) to the (1 × 1) unit cell of silicene. The unfolded band structure of unsupported silicene is presented by red dots in the left panel of Fig. 2. Here the states in the (3 × 3) silicene supercell are expanded in terms of the states in the (1 × 1) silicene unit cell and the weight of contribution is represented by the radii of red dots.[31] The band structure of ideally buckled silicene in which one sublattice of Si atoms are at the bottom and the other at the top is presented by green lines. For better comparison, the lattice constant and the buckling height of this structure is set to that of unsupported silicene. The symmetry of ideally buckled silicene preserves the linearly crossing bands at the K point. In the unsupported silicene, however, this symmetry is broken and the linear bands become parabolic with a 0.3 eV band-gap opening due to the structural modification induced by the Ag substrate (hybridization).

The unfolded band structure of fully relaxed (3 × 3) silicene on (4 × 4) Ag substrate is shown in the right panel of Fig. 2.

The *d* bands of Ag are located in the energy window from −6 eV to −3 eV. Here we calculate the projection of each state on the atomic orbitals of silicene and mark with red dots the states in which the magnitude of projection is above some threshold. Comparing red dots in the left and right panel of Fig. 2, one can see significant change in the character of the silicene bands. In fact, it is hard to make a direct one to one correspondence between the states in these two panels.

One can see states at the Fermi level which has contribution from silicene. These are the states that give rise to the STM patterns calculated at zero bias. They are folded to the K point of (3 × 3) silicene and are denoted as state I in Fig. 1(b).

The σ states around the Γ point are shifted down by ∼0.5 eV, while the π states around the K point are shifted down by ∼0.9 eV upon hybridization with Ag. This difference could be attributed to the larger overlap of the latter states with Ag substrate compared to the former ones. Note that, in the Brillouin zone (BZ) of the (3 × 3) silicene supercell, these two states fold to the same point. The charge densities projected on σ and π states are presented in Fig. 1(b) and they are denoted by state II and III, respectively. Here one can see that the difference in the energy shift due to hybridization inverts the band order between states II and III. This also confirms that the shifts are mainly caused by the hybridization with Ag and not by the charge transfer from Ag to silicene.[30]

Recently (after submission of the present work), it was argued that the slope and the energy range in which the experimentally observed bands[16] extend matches better to the *sp* bands of Ag states than the Dirac cone of silicene.[32] This argument, however, does not clarify why the linear bands disappear when the measurement is performed in the absence of silicene. This fundamental piece of understanding is provided below.

The coherent interpretation of experiments requires analyzing the band structure of (3 × 3) silicene on 11 layers of (4 × 4) Ag in a narrow window of the BZ and the energy range where the ARPES measurements with linear bands were reported.[16] In Fig. 3(a) we present the unfolded band structure of silicene on Ag system in this narrow window. Since the system includes 11 layers of Ag we assume that the three Ag layers in the middle can be considered as representative of the bulk Ag bands. We calculate the projection of each state on these three Ag layers in the middle and denote by blue dots the states that have magnitude of projection larger than some threshold. Then we calculate projections on three Ag layers underneath silicene and silicene itself and plot with orange dots the states having magnitude of projection above some threshold. These thresholds are defined such that the magnitude of projection divided by the number of chosen atomic orbitals is equal to 0.006. The same value is also used in Fig. 2(b) and in the rest of Fig. 3.

One can see in Fig. 3(a) that the hybridization between silicene and Ag results in a state (shown in orange) which can be distinguished from the bulk Ag state (shown in blue). We confirmed that this hybridized state completely disappears when calculation is performed with 11 Ag layers without silicene. Note that hybridization with Ag transforms the parabolic band structure with a gap into a gapless band structure with a quasilinear dispersion that resembles a Dirac cone. Comparing with ARPES measurements[16] one can see that the
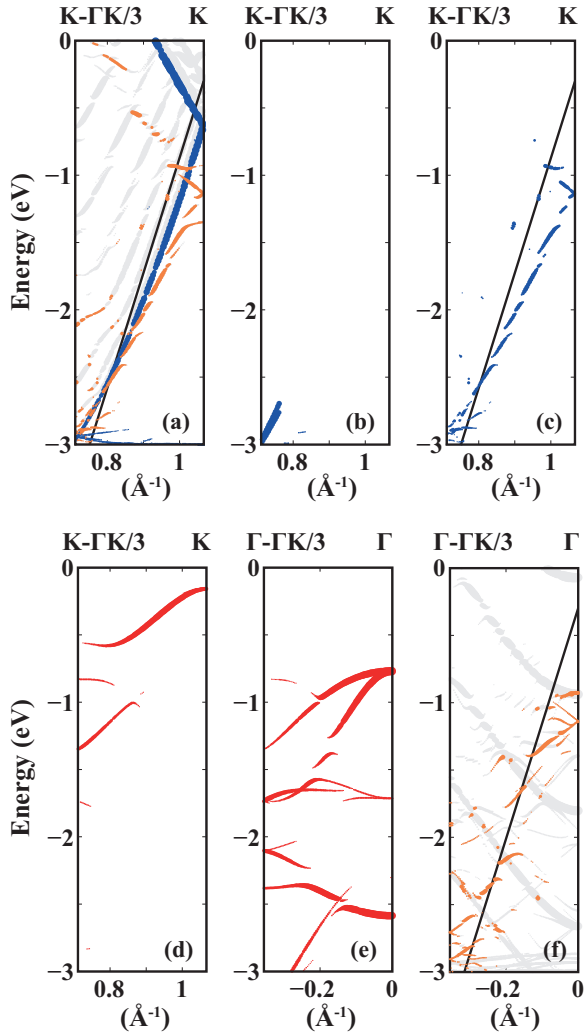
FIG. 3. (Color online) (a) Band structure of silicene with 11 Ag layers around K point. Blue and orange dots correspond to bulk Ag states and hybridized silicene/Ag states. Gray dots come from foldings of finite slab and can be ignored. Contribution of three Ag layers at the surface in the (b) absence and (c) presence of silicene. (d) π bands of unsupported silicene. (e) σ bands of unsupported silicene around Γ point. (f) Same as (a) around Γ point. The solid black lines in (a), (c), and (f) are representational sketches of the experimental data.[16] It is starting from -0.3 eV and has a slope corresponding to $v_F = 1.3 \times 10^6$ m/s. It is recommended, however, to compare our data directly with the ARPES data.[16]

bulk Ag states indeed have an impressive overlap. However, the hybridized state has also considerable reminiscence.

To simulate the ARPES measurement which is sensitive to surface states[16] we plot in Figs. 3(b) and 3(c) the states contributed by three Ag layers underneath the silicene in the absence and presence of silicene, respectively. The threshold for projections is the same as in Fig. 3(a). In this respect, it is very interesting that the bulk Ag states are absent in both plots. Moreover, the surface states of Ag have almost no contribution when the silicene is absent and the linear band appears when the silicene is present. This similarity with experiment and absence of Ag bulk contributions suggests that it is more reasonable to attribute the observed linear

bands to the hybridized states of silicene and Ag rather than bulk Ag state, despite the likeness of the latter. Note that, upon hybridization, the character of silicene states changes significantly. In this respect, unsupported silicene states presented in Fig. 3(d) can be compared with hybridized states presented in Fig. 3(a). Despite this change, the charge densities of hybridized and unsupported silicene around the K point still show considerable resemblance (for more details, see Ref. 33).

We explore also the states near Γ point because they can have contribution to experimental measurements due to the folding of (3×3) silicene BZ.[34] Here we show σ states of unsupported silicene and hybridized states around the Γ point in Figs. 3(e) and 3(f), respectively. The energy shift of states due to hybridization is less pronounced compared to π states because σ states have less overlap with Ag (see also Ref. 33). Comparing Fig. 3(f) with Figs. 3(a) and 3(c) one can deduce that hybridized σ states of silicene might also contribute to the experimental measurements.

III. DISCUSSIONS AND CONCLUSION

Finally, we point out the improvements that our work brings and shortcomings that still remain on the interpretation of experimental results related with silicene on Ag. The hybridized state presented in Fig. 3(a) extends down to -3 eV where the Ag d bands start, in accordance with experiments. The slope of the linear band presented in Fig. 3(c) corresponds to a velocity of 0.8×10^6 m/s that is considerably closer to the experimental value of 1.3×10^6 m/s than the Fermi velocity of free standing silicene ($v_F = 0.53 \times 10^6$ m/s). We found that this Fermi velocity is increased to $v_F = 0.71 \times 10^6$ m/s when $G_0 W_0$ corrections are considered.[29,35] Similar behavior was found for graphene.[36–39] The DFT slope of the hybridized state may be improved further by including those $G_0 W_0$ many-body effects in calculations of silicene on Ag, as the states that we observe here come mainly from the hybridization of the sp bands of Si with the sp bands of Ag, while d bands of Ag contribute to the screening of electron-electron interactions at the Fermi level.

In summary, by means of first-principles calculations, we showed that the (3×3) reconstructed silicene on the Ag substrate has a metallic state at the Fermi level that shares a similar calculated STM pattern as those for -1.4 eV, -0.5 eV, and 0.6 eV. As the STM at zero bias is not possible experimentally our calculation could be confirmed by scanning tunneling spectroscopy (STS) measurements, which should show no gap when bias crosses zero. Detailed band structure and charge density analysis reveal that the hybridization between silicene and Ag has substantial effect, leading to a change in the band order of some states. By calculating projections to specific atomic orbitals, we have clearly distinguished hybridized silicene/Ag states from bulk Ag states. We show that hybridized states are localized at the surface and give rise to a linear band in the presence of silicene and disappear in the absence of silicene. This is in accordance with a recent ARPES measurement which is sensitive to the surface states.[16] Moreover, the hybridization between σ states of silicene and Ag can also contribute to an experimentally observed linear band due to the folding of (3×3) silicene BZ.

In the light of our findings we conclude that it is not possible to attribute the experimentally observed linear bands solely to sp bands of bulk Ag or to Dirac cones of silicene. We attribute the experimental bands to a hybridized state localized at the surface emerging due to the interaction between silicene and Ag. This state has a resemblance to experimental bands and appears only when silicene is present. The pronounced effects of hybridization with Ag substrate presented in this paper may play a crucial role in the interpretation of the linear bands observed also in single and multilayer silicene nanoribbons[10,13] and monolayer silicene structures with other types of reconstructions.[20,40] Their origin should be analyzed in depth, instead of simply linking them to sp bands of bulk Ag or to Dirac cones of silicene.[41]

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

[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005).

[3] K. Takeda and K. Shiraishi, Phys. Rev. B **50**, 14916 (1994).

[4] E. Durgun, S. Tongay, and S. Ciraci, Phys. Rev. B **72**, 075420 (2005).

[5] G. G. Guzmán-Verri and L. C. Lew Yan Voon, Phys. Rev. B **76**, 075131 (2007).

[6] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci, Phys. Rev. Lett. **102**, 236804 (2009).

[7] A. Kara, C. Léandri, M. E. Dávila, P. De Padova, B. Ealet, H. Oughaddou, B. Aufray, and G. Le Lay, J. Supercond. Nov. Magn. **22**, 259 (2009).

[8] G. Le Lay, B. Aufray, C. Léandri, H. Oughaddou, J.-P. Biberian, P. De Padova, M. E. Dávila, B. Ealet, and A. Kara, Appl. Surf. Sci. **256**, 524 (2009).

[9] B. Aufray, A. Kara, S. Vizzini, H. Oughaddou, C. Léandri, B. Ealet, and G. Le Lay, Appl. Phys. Lett. **96**, 183102 (2010).

[10] P. De Padova, C. Quaresima, C. Ottaviani, P. M. Sheverdyaeva, P. Moras, C. Carbone, D. Topwal, B. Olivieri, A. Kara, H. Oughaddou, B. Aufray, and G. Le Lay, Appl. Phys. Lett. **96**, 261905 (2010).

[11] P. De Padova, C. Quaresima, B. Olivieri, P. Perfetti, and G. Le Lay, Appl. Phys. Lett. **98**, 081909 (2011).

[12] P. De Padova, P. Perfetti, B. Olivieri, C. Quaresima, C. Ottaviani, and G. Le Lay, J. Phys.: Condens. Matter **24**, 223001 (2012).

[13] P. De Padova, O. Kubo, B. Olivieri, C. Quaresima, T. Nakayama, M. Aono, and Guy Le Lay, Nano Lett. **12**, 5500 (2012).

[14] B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and B. Aufray, Appl. Phys. Lett. **97**, 223109 (2010).

[15] C.-L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi, and M. Kawai, Appl. Phys. Express **5**, 045802 (2012).

[16] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. Le Lay, Phys. Rev. Lett. **108**, 155501 (2012).

[17] H. Jamgotchian, Y. Colignon, N. Hamzaoui, B. Ealet, J. Y. Hoarau, B. Aufray, and J. P. Bibérian, J. Phys.: Condens. Matter **24**, 172001 (2012).

[18] A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang, and Y. Yamada-Takamura, Phys. Rev. Lett. **108**, 245501 (2012).

[19] B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Cheng, L. Chen, and K. Wu, Nano Lett. **12**, 3507 (2012).

[20] L. Chen, C.-C. Liu, B. Feng, X. He, P. Cheng, Z. Ding, S. Meng, Y. Yao, and K. Wu, Phys. Rev. Lett. **109**, 056804 (2012).

[21] H. Enriquez, S. Vizzini, A. Kara, B. Lalmi, and H. Oughaddou, J. Phys.: Condens. Matter **24**, 314211 (2012).

[22] Calculations were carried out using the projector-augmented wave (PAW) pseudopotential method[23] as implemented in the VASP software.[24] The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof form[25] was used to include the exchange-correlation interactions. A plane wave energy cutoff of 300 eV was used. The vacuum spacing between image surfaces due to the periodic boundary condition is larger than 12.5 Å. The forces on the relaxed atoms were converged to less than 10^{-3} eV/Å. In the ionic relaxation calculations, the Brillouin zone was sampled by $(3 \times 3 \times 1)$ k points,[26] while the accurate charge density was calculated by a $(9 \times 9 \times 1)$ Γ centered k-point grid. Bulk lattice constant of Ag was found to be 4.16 Å. Buckling height of silicene on Ag was found to be 0.78 Å, while the height difference between bottom Si and top Ag atoms is 2.30 Å. The Tersoff-Hamann model was used for the simulation of STM images.[27] Corrections have been made to avoid a fictitious dipole field due to the periodic slab images.[28] A single-shot perturbative G_0W_0 calculation with default parameters provided by VASP[29] and a $(36 \times 36 \times 1)$ Γ centered k-point grid was performed on top of DFT calculation of buckled (1×1) silicene with a vacuum spacing of 15 Å.

[23] P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).

[24] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); G. Kresse and J. Furthmuller, *ibid.* **54**, 11169 (1996).

[25] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[26] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[27] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).

[28] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[29] M. Shishkin and G. Kresse, Phys. Rev. B **74**, 035101 (2006).

[30] Z.-X. Guo, S. Furuya, J.-I. Iwata, and A. Oshiyama, J. Phys. Soc. Jpn. **82**, 063714 (2013).

[31] P. B. Allen, T. Berlijn, D. A. Casavant, and J. M. Soler, Phys. Rev. B **87**, 085322 (2013).

[32] C.-L. Lin, R. Arafune, K. Kawahara, M. Kanno, N. Tsukahara, E. Minamitani, Y. Kim, M. Kawai, and N. Takagi, Phys. Rev. Lett. **110**, 076801 (2013).

[33] States that do not belong to bulk Ag or hybridization with silicene (shown in gray) can be viewed as an artifact of using a finite number of Ag slabs. In fact, as the number of Ag slabs are increased these bands get more dense and converge to a gray background which can be ignored.

[34] This idea roots to discussions with Maria-Carmen Asensio and Jose Avila.

[35] S. Huang, W. Kang, and L. Yang, Appl. Phys. Lett. **102**, 133106 (2013).

[36] A. Grüneis, C. Attaccalite, T. Pichler, V. Zabolotnyy, H. Shiozawa, S. L. Molodtsov, D. Inosov, A. Koitzsch, M. Knupfer, J. Schiessling, R. Follath, R. Weber, P. Rudolf, L. Wirtz, and A. Rubio, Phys. Rev. Lett. **100**, 037601 (2008).

[37] A. Grüneis, C. Attaccalite, L. Wirtz, H. Shiozawa, R. Saito, T. Pichler, and A. Rubio, Phys. Rev. B **78**, 205425 (2008).

[38] P. E. Trevisanutto, C. Giorgetti, L. Reining, M. Ladisa, and V. Olevano, Phys. Rev. Lett. **101**, 226405 (2008).

[39] L. Yang, J. Deslippe, C.-H. Park, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **103**, 186802 (2009).

[40] L. Chen, H. Li, B. Feng, Z. Ding, J. Qiu, P. Cheng, K. Wu, and S. Meng, Phys. Rev. Lett. **110**, 085504 (2013).

[41] Y.-P. Wang and H.-P. Cheng, arXiv:1302.5759.