Electronic decoupling by h-BN layer between silicene and Cu(111): A DFT-based analysis

Mao Kanno¹, Ryuichi Arafune², Chun Liang Lin¹, Emi Minamitani³, Maki Kawai¹ and Noriaki Takagi¹

¹ Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, 5-1-5 Kashiwa, Kashiwanoha, Chiba 277-8561, Japan
² International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 304-0044, Japan
³ Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
E-mail: n-takagi@k.u-tokyo.ac.jp

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Abstract

Geometric and electronic structures of silicene on Cu(111) covered with a monolayer of hexagonal boron nitride (h-BN) were investigated by \textit{ab initio} density functional theory calculations. We found that a $\sqrt{3} \times \sqrt{3} R30^\circ$ silicene with a regularly buckled configuration is stabilized on $\sqrt{7} \times \sqrt{7} R19.1^\circ$ h-BN layer stacking commensurately to the Cu(111) substrate. The electronic band structure projected to Si 3pz orbital clearly shows a band crossing similar to a Dirac cone emerging in the band structure of freestanding buckled silicene. This is in contrast to the silicene on Cu(111), in which the Dirac fermion features disappear entirely due to the strong interactions at the interface. These examples demonstrate that the h-BN monolayer effectively prevents silicene from interacting with the underlying Cu(111) substrate and that the h-BN monolayer on Cu(111) is a promising candidate for use as a substrate on which to realize silicene hosting the Dirac fermion features.

Keywords: silicene, DFT calculation, boron nitride
Introduction

Silicene is a two-dimensional (2D) honeycomb lattice of Si atoms and a new allotrope of Si. Freestanding silicene is theoretically predicted to acquire the Dirac fermion as well as graphene [1, 2]. In addition, silicene is a candidate for use as a 2D topological insulator because spin–orbit coupling of Si is a thousand times stronger than that of C; thus, a sizable topological gap opens [3]. These theoretical predictions have triggered and fueled competition to realize the Dirac fermion in silicene.

Experimentally, the formation of silicene has been investigated on several substrates such as Ag(111) [4–10], ZrB_2-covered Si(111) [11], Ir(111) [12], etc. Of these examples, silicene grown on Ag(111) has been the most extensively studied. Recently, we have found that the interactions between the single layer of silicene and the Ag(111) substrate negatively affect the Dirac fermion character of silicene [8]. In our previous work, scanning tunneling spectra of silicene on Ag(111) were measured under a magnetic field. The characteristic Landau levels that are the reliable evidence for the Dirac fermion did not appear in the spectra. We have theoretically confirmed the absence of the Landau levels in the tunneling spectra; the calculated electronic band structure of silicene on Ag(111) is significantly modified through hybridization with the electronic states of the Ag(111) substrate. At present, our calculation have been reproduced by many theoretical groups [13–15], which justifies our findings. Thus, it is highly desired to find a way to block the interface coupling between silicene and the substrate to realize Dirac fermion in silicene and explore its exotic properties.

Recently, Guo et al [13] proposed that hydrogen terminated Si(111) and bulk hexagonal boron nitride (h-BN) are suitable substrates for preserving the Dirac fermion character in silicene. Since silicene does not exist in nature, we must evaporate and deposit Si atoms onto a substrate to synthesize it. If one succeeded in transferring silicene grown on the substrate mentioned above to another substrate, the H-terminated Si surface would provide a proper stage on which to investigate the exotic characteristics arising from the Dirac fermion. However, the H-terminated Si surface is unsuitable for the evaporation procedure because it is probable that ‘hot’ Si atoms arriving at the substrate break the Si-H bonds to directly interact with the substrate Si atoms. The bulk h-BN also has a drawback originating from the low electric conductivity associated with a large band gap. This characteristic prevents us from monitoring the geometric and electronic structures of silicene on h-BN by using various kinds of surface science techniques such as low-energy electron diffraction (LEED), scanning tunneling microscopy, photoelectron spectroscopy, etc.

It is well accepted that ultrathin insulating sheets are useful for tuning and tailoring the activity of the metal surfaces [16]. The monolayer h-BN, which can be grown on various metal surfaces [17–19], is well accepted as a suitable substance for this purpose. The chemical inertness and the wide band gap are preserved even in the monolayer on the metal surfaces. These characteristics allow us to electronically decouple adsorbed species from the electrons of the metallic substrates. Recently, h-BN has been used as a substrate for promoting the properties of graphene [20, 21]. We expect that the h-BN-covered metal is also an appropriate substrate for realizing the silicene that acquires the Dirac fermion.

In this paper, to confirm the above expectation, we have investigated the geometric and electronic structures of silicene on Cu(111) covered with the h-BN monolayer (hereafter we denote this composite substrate as h-BN/Cu(111)) by means of *ab-initio* calculations. The calculations show that silicene is stable on the h-BN/Cu(111) and that the h-BN sheet
effectively acts as a buffer layer to reduce interactions between silicene and the underlying metal substrate.

**Calculational details**

All the calculations were carried out by using the Vienna Ab Initio Simulation package (VASP) [22, 23] with the projected augmented wave (PAW) [24] potentials within the generalized gradient approximation (GGA) method. We took into account van der-Waals (vdW) interactions [25] by using optimized the B86b exchange functional [26]. Recently, this functional has been successfully applied to model the adsorption geometry and electronic structure of $\pi$-conjugated molecules on metal surfaces [27].

The total energy of freestanding silicene is rapidly converged with respect to the kinetic energy cutoff. We found that the difference between the total energy obtained from the 400 eV cutoff and that from the 450 eV was within the order of 0.1 meV. Consequently, we determined the kinetic energy cutoff for the plane wave basis set to be 400 eV. The calculated lattice constant is 3.60 Å for the bulk Cu, 2.51 Å for single layer h-BN, and 3.86 Å for the single layer silicene.

Silicene on h-BN/Cu(111) was modeled by using a supercell that consists of a silicene layer on the h-BN-covered 5-layer Cu slab with a vacuum of 15 Å thick along the surface normal. Since the lattice constant of the h-BN layer is very close to that of the Cu(111) surface, the h-BN layer is expected to take a commensurate $1 \times 1$ structure on the Cu(111) surface. Actually, the STM image of the h-BN/Cu(111) shows a moiré pattern [15], which indicates that the h-BN monolayer does not crystallize in the perfect $1 \times 1$ structure on the Cu(111) surface. In this work, the slightly stretched ($1 \times 1$) h-BN layer was assumed because the superstructure corresponding to the moiré pattern requires huge calculation resources. The lattice constant of silicene significantly differs from that of the Cu(111) surface as well as that of h-BN layer. This means that silicene cannot be formed on the h-BN/Cu(111) substrate with the $1 \times 1$ structure, within the reasonable range of the Si–Si bond length in silicene (2.1–2.3 Å) [5, 28, 29]. In our previous work [5], we provided a systematic recipe for constructing a superstructure that consists of a 2D triangular lattice commensurate to a hexagonal lattice. By using this formula, we have found that $\sqrt{3} \times \sqrt{3} R30^\circ$ silicene on $\sqrt{7} \times \sqrt{7} R19.1^\circ$ h-BN monolayer lying on Cu (111) is the smallest superstructure in which all the bond lengths are within reasonable ranges.

Here we describe the periodicities of silicene and the h-BN monolayer with respect to the $1 \times 1$ unit cell of silicene and Cu(111), respectively. This supercell is composed of 35 Cu, 7 B, 7 N and 6 Si atoms. The positions of atoms in silicene, h-BN, and the top four layers of the Cu slab were optimized without any constraint until the forces on individual atoms were less than 0.01 eV Å. In the self-consistent total energy calculations, the Brillouin zone was sampled with $(9 \times 9 \times 1)$ Monkhorst pack k-points\(^4\). An inadequate size of k-point sampling sometimes causes a significant problem. For example, according to Guo and Oshiyama [30], a structural model proposed by Chen et al [31] for the $\sqrt{3} \times \sqrt{3}$ silicene on Ag(111) that is usually assigned to multilayer silicene [5, 32, 33] becomes unstable with the increases of the k points. To check the validity of our k-point sampling, we have performed the identical calculations with $(15 \times 15 \times 1)$

\(^4\) In the preliminary calculations for investigating stable commensurate structure of silicene/h-BN and silicene/h-BN/Cu(111), we used $(5 \times 5 \times 1)$ k-points mesh. We found that the structure relaxation using $(5 \times 5 \times 1)$ and $(9 \times 9 \times 1)$ converge the identical structure essentially, but those of the electronic structure is considerably different.
k-points. The results obtained with the (9 × 9 × 1) k-points, especially the band structure, do not significantly change compared with the (15 × 15 × 1) k-points. Thus, we believe that the (9 × 9 × 1) k-point mesh is sufficient and present the results calculated with (9 × 9 × 1) k-points in this paper.

Results and discussion

Firstly, we optimized the geometric structure of the h-BN monolayer on Cu(111). We have systematically tested 70 patterns of geometry where the h-BN layer stacks differently on the Cu(111) surface. The most stable structure is that in which B and N atoms are located in the on-top and three-fold hollow sites (B-hollow, N-top), respectively. On the other hand, the (B-top, N-hollow) and the (B-hollow, N-hollow) structures are unstable. The difference in the total energy between the (B-hollow, N-top) structure and the others is about 20 meV. These results are essentially identical with the work of Joshi et al [15]. Hereafter, we use the (B-hollow, N-top) structure as the substrate for silicene.

Figure 1 shows the structure model of silicene on h-BN/Cu(111). The superstructure consists of the buckled silicene with $\sqrt{3} \times \sqrt{3} R30^\circ$ periodicity stacking on $\sqrt{7} \times \sqrt{7} R19.1^\circ$ h-BN/Cu(111). We have found that the total energy very weakly depends on the horizontal position of silicene with respect to the h-BN/Cu(111) substrate. We examined the various
geometries, in which the atomic arrangement of h-BN/Cu(111) is identical. The difference of the total energy was 3 meV at most. The calculated lattice constants of h-BN and silicene are 2.55 and 3.89 Å, respectively. This means that h-BN and silicene are slightly stretched on the Cu(111) surface compared with the freestanding ones (2.51 and 3.86 Å, respectively). The bond length and the angle between neighboring Si atoms are 2.29 Å and 102.2°, respectively, which are essentially identical with those for freestanding silicene (2.28 Å and 101.8°).

Figure 1(b) shows the side view of the silicene on h-BN/Cu(111). The layer distance between silicene and h-BN is 3.74 Å, which is slightly longer than that calculated without the Cu(111) slab (3.69 Å). This elongation can be explained by the enhanced Pauli repulsion reflecting higher density of states of Cu. The distance between h-BN and the first layer of Cu (3.08 Å) is essentially independent of the presence of silicene. Note that no surface rumpling appears on Cu(111). The distances between Cu layers with and without a silicene/h-BN layer are essentially identical; the difference is 0.003 Å at most. The silicene directly interacting with the Cu(111) surface (silicene/Cu(111)) shows a completely different structure from that on h-BN/Cu(111). As shown in figure 1(c), one of the six Si atoms in the unit cell is located at a much higher position compared with the other five Si atoms. This structure is in good agreement with the previous study [34]. The Cu atom beneath the high Si atom also shifts upward, which indicates strong interaction between Si atoms and the Cu surface. The major difference in the structure and surface rumpling of Cu(111) between silicene/h-BN/Cu(111) and silicene/Cu(111) is evidence that the h-BN layer effectively blocks the strong interaction between silicene and Cu(111). Incidentally, such surface rumpling also appears in silicene on Ag(111), which has been recently verified by tensor-LEED structure analysis [9].

Figure 2(a) shows the calculated electronic band structure of silicene on h-BN/Cu(111). Since the superstructure corresponds to $\sqrt{3} \times \sqrt{3} R30^\circ$ periodicity relative to silicene lattice, K and K’ points for freestanding silicene agree with Γ point as shown in figure 2(b). The flat bands located at −1.5 to −2.0 eV below the Fermi level are associated with the 3d states of the Cu deeper layers. Except for this feature, the many dispersion curves overlap with each other and...
the band structure looks quite complex, especially around the Fermi level. This complexity comes from the mixing of the contributions from the electronic states of silicene, h-BN, and the Cu substrate.

The projection of each dispersion curve to the atomic orbitals of Si, B, N, and Cu allows us to distinguish which atomic orbitals are dominant contributors. Figures 3(a)–(c) show the contributions from the silicene, h-BN, and Cu first layer to the band structure, respectively. For comparison, the contributions of Si 3pz to band structures of silicene/h-BN and silicene/Cu (111) are shown in figures 3(f) and (g). The h-BN layer has a wide band gap and then the contributions from the h-BN layer to the electronic band structure are negligible in this energy range as shown in figure 3(b). One sees that the Si-projected band structure essentially reproduces that of freestanding silicene.

Similarly to the freestanding silicene, the linear bands originating from the Si 3pz orbital cross at the $\Gamma$ point near the Fermi level (Dirac point) as clearly shown in figure 3(a). The band structure for silicene/Cu(111) shows that the contribution of the Si 3pz orbital spreads into the bands entirely as shown in figure 3(g). This indicates that the Dirac fermion character in silicene dissipates due to the strong hybridization with Cu when silicene interacts directly with the Cu (111) surface. Thus, the preservation of the Dirac fermion character shown in figure 3(a) is the outstanding feature realized by introducing the h-BN layer between silicene and Cu(111). The most important difference distinguishing the band structure from the freestanding silicene (figure 3(d)) is the position of the Dirac point. The Dirac point is located around 200 meV below the Fermi level, whereas the Dirac points of freestanding silicene and silicene on the h-BN layers are just at the Fermi level [13]. The Fermi velocity is $4.2 \times 10^5$ m s$^{-1}$ whereas that of freestanding silicene is $5.2 \times 10^5$ m s$^{-1}$.

In figure 3(c), the Shockley surface state appears as parabolic band dispersion with the bottom located at 131 meV below the Fermi level. On the clean Cu(111) surface, the bottom of the Shockley surface band was located at 253 meV below the Fermi level, which agrees fairly well with the experimental value (418 meV). The upward shift is caused by the so-called 'pillow effect' derived from the Pauli repulsion as observed for the Cu(111) surface covered with rare gas atoms and organic molecules [35]. The existence of the h-BN layer prevents the sp electrons at the Cu surface from extending and delocalizing to the vacuum, and then the Shockley state shifts upward. In spite of a relatively high density of states for the Shockley surface states, the parabolic band does not appear in the Si-projected band (figure 3(a)). This indicates that the h-BN layer effectively reduces the coupling of Si 3pz with the Cu electronic states to preserve the Dirac fermion features.

Finally, let us discuss the downward shift of the Dirac point as shown in figure 3(d). The Dirac point of silicene on h-BN without Cu(111) is located at 56 meV above the Fermi level (figure 3(f)), which is close to the value reported by Kaloni et al [36]. Thus, for silicene on h-BN/Cu(111), the shift of the Dirac point is induced by introducing the Cu(111) surface. To reveal the origin of the shift, we calculated the differential charge distribution of silicene on h-BN/Cu(111) as shown in figure 4. The differential charge distribution shows that the electron transfer from Cu(111) to silicene is small. This is reasonable because the Dirac fermion features are essentially preserved on Cu(111) by inserting the h-BN layer. Although the electron doping from the substrate to silicene does not appear distinctly in mapping the differential charge distribution, one would see the charge redistribution in silicene and the h-BN layers, which can induce an interface dipole layer between silicene and h-BN to cause the downward shift. Since the interface dipole changes the work function, it would be meaningful to compare the shift of
Figure 3. (a), (b), and (c) show the band structure projected to silicene, h-BN, and the first layer of Cu, respectively. (d) Magnified view of (a) showing the shift of the Dirac point. (e) Band structure calculated for the freestanding silicene. The Dirac point of silicene on h-BN/Cu(111) is approximately 200 meV below the Fermi level (d), whereas that of the freestanding silicene is located just at the Fermi level (e). (f) and (g) are the band structures of the silicene on h-BN and silicene on Cu(111), respectively. The color scale indicates the orbital contributions to each band.
the Dirac point with the work function change. The work function of the Cu(111) surface is calculated to be 4.98 eV, which is close to the experimental value (4.95 eV[37]). The calculated work function of freestanding silicene is 4.70 eV, whereas that of the silicene on h-BN/Cu(111) is 4.56 eV. One would see that the reduction of the work function of silicene by introducing h-BN/Cu(111), approximately 140 meV, is close to the magnitude of the downward shift of the Dirac point. We have concluded that the shift of the Dirac point significantly arises from the surface potential change introduced by the underlying metal substrate. One may find that the work function change does not exactly match with the shift of the Dirac point. This difference may originate from hybridization between silicene and the underlying layers. As a matter of fact, the band structure and the Fermi velocity of silicene are weakly changed by being in the vicinity of the metal surface. It would be very interesting to distinguish between the effect of the interface dipole and that of hybridization on the position of the Dirac point.

**Conclusion**

In summary, we have discussed the geometric and electronic structures of silicene on h-BN/Cu (111) through DFT calculations. Our calculations show that the h-BN/Cu(111) surface provides a suitable platform on which to preserve the Dirac fermion in silicene, which is expected theoretically in freestanding geometry. We emphasized here that the h-BN layer acts as an electronic buffer at the interface of silicene and the metal substrate. The h-BN layer can be grown on various metal surfaces, and we expect that similar effects will be observed on such surfaces. Therefore, we propose that the h-BN monolayer on any metal surface, not only Cu(111), will provide an ideal substrate for synthesizing Dirac fermion silicene.
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