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VAN DER WAALS INTEGRATION OF SILICENE AND HEXAGONAL BORON NITRIDE


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Abstract
Silicene, the silicon analogue of graphene, consists of an atomically buckled honeycomb lattice of silicon atoms. Theory predicts exceptional electronic properties, including Dirac fermions and a topological spin Hall insulator phase. An important obstacle impeding exploration of such properties in electronic devices is the chemical sensitivity of silicene, hampering its incorporation in layer stacks. Here we show experimentally that epitaxial silicene and hexagonal boron nitride (h-BN) can be stacked without perturbing the electronic properties of silicene. Intercalated silicene underneath epitaxial h-BN on ZrB2(0001) substrate films is obtained by depositing Si atoms at room temperature. Using (angle resolved) photoelectron spectroscopy (ARPES, PES) and scanning tunneling microscopy (STM) we find that the intercalated silicene exhibits the same electronic properties as epitaxial silicene on ZrB2, while it resists oxidation in air up to several hours. This is an essential step towards the development of layer stacks that allow for fabrication of devices.
1. Introduction

The buckled nature of silicene,\textsuperscript{1, 2} the silicon analogue of graphene,\textsuperscript{3} is predicted to allow for electrostatic tuning of its electronic properties across a range of behaviors, including that of a topological insulator.\textsuperscript{4} However, silicene is chemically reactive and oxidizes upon exposure to air. While this property can be favorably exploited for chemical surface modification, it hinders \textit{ex situ} characterization and the integration of silicene in an electronic device. This can be solved by an insulating encapsulation layer, functioning as both a protective layer and a gate dielectric layer. Epitaxial ZrB\textsubscript{2} thin films grown on Si(111) substrates have the unique property to spontaneously form a layer of epitaxial silicene on their surfaces upon annealing.\textsuperscript{5} In addition, the ZrB\textsubscript{2} surface can also be terminated with an epitaxial hexagonal boron nitride (h-BN) monolayer by plasma nitridation and subsequent annealing at 900 °C.\textsuperscript{6} Hexagonal BN is an inert, wide-bandgap semiconductor and is as such a suitable template as well as an encapsulation layer. Further, theoretical simulations studying silicene on or between h-BN layers found that silicene is stable, interacts weakly with h-BN, and retains the electronic properties of free-standing silicene.\textsuperscript{7-14} This combination of experimental findings and theoretical predictions motivated us to explore the vertical integration of epitaxial silicene with h-BN on the ZrB\textsubscript{2}(0001) surface.

Figure 1: (a) (10 nm × 5 nm, V = 80 mV, I = 1.2 nA, room temperature) STM images of a pristine h-BN-terminated ZrB\textsubscript{2} surface showing the (1×1)-h-BN lattice, (b) (10 nm × 5 nm, V = 0.1 V, I = 1 nA, room temperature) the h-BN/ZrB\textsubscript{2} moiré pattern, depending on the sample bias voltage, and (c) (95 nm × 95 nm, V = -1.1 V, I = 0.4 nA, room temperature) a differentiated STM image after deposition of 4 ML of Si, resulting in near-complete coverage by a 2D Si layer.
2. Results and discussion

The as-annealed h-BN terminated ZrB$_2$ surface (hereafter referred to as pristine) exhibits a short periodic corrugation of 2.5 Å corresponding to the (1×1) unit cell of h-BN and a periodicity of 11.7 Å corresponding to a moiré pattern, as shown in Fig. 1. The moiré pattern is the result of the overlay of the h-BN lattice on ZrB$_2$(0001), the latter having a lattice constant of 3.186 Å. It follows that 5 unit cells of h-BN are almost commensurate with 4 unit cells of ZrB$_2$. The pristine surface also contains some residual Si, mostly residing in crystalline 2D islands as observed by STM (see Fig. S1), with lattice periodicity and crystal orientation identical to that of the (√3×√3)-reconstructed silicene layer on ZrB$_2$ without h-BN. The (1×1) lattice constant of the latter was previously reported as 3.65 Å.

Figure 2: PES spectra of the Si 2p core-level region before and after deposition of Si on the h-BN-terminated ZrB$_2$ surface. The spectra are presented in chronological order: (1) pristine h-BN-terminated ZrB$_2$ surface, (2) after deposition of 1.6 ML of Si, (3) after deposition of an additional 3.2 ML of Si. Spectrum 0 corresponds to epitaxial silicene on ZrB$_2$ without h-BN, included here for comparison. The Si 2p spectra are shown together with peak-fitting results. The sum of the fitted data is plotted behind the measured data, while the individual components and the background are offset.
The Si 2p spectrum of the pristine surface, shown in Fig. 2 (spectrum 1), shows two clearly resolved doublets and a tail. The sharp peaks are attributed to the crystalline 2D Si islands. The Si 2P$_{3/2}$ peaks of the two doublets are at a binding energy of 99.05 eV and 98.75 eV, where the latter doublet has a higher intensity.

Upon deposition of Si on the surface at room temperature, the 2D Si islands increase in number and size, while their lattice periodicity and crystal orientation remain unchanged. Although the surface coverage by the Si islands increases and nearly reaches full coverage, as shown in Fig. 1(c) for a deposition of 4 ML of Si (see also Fig. S2), no nucleation of additional layers on top of this layer, which would yield a stepped surface, was observed by STM. The deposited Si that is not incorporated into the 2D Si layer most likely forms three-dimensional (3D) disordered structures on the surface, or is incorporated into pre-existing ones (see Fig. S3). The 2D Si layer shown in Fig. 1(c) exhibits three types of defects: holes ranging in size from one to few tens of unit cells, trenches, and anti-phase boundaries (see Fig. S2). Trenches of a few (√3×√3)-cells wide and oriented along crystallographic axes remain in the 2D Si layer regardless of Si surface coverage, most probably to relieve strain. As we show below, the 2D Si layer is formed by intercalation of Si atoms underneath h-BN, such that a competition between h-BN interacting with ZrB$_2$ and h-BN accommodating the intercalated Si might play a role as well. We expect that defects in the h-BN layer facilitate the intercalation process. Here “defects” refers to any kind of imperfection in the epitaxial h-BN layer, including point defects, domain boundaries, and “open” spaces where we have silicene termination instead.

After deposition of Si, the Si 2p spectrum shows a significant change (see Supporting Information for changes to core levels of other elements), as shown in Fig. 3 (spectrum 2, 1.6 ML of Si deposited). Two sharp doublets are again resolved, but their intensity ratio is now such that the doublet at higher binding energy is most intense. The spectrum appears to be very similar to the Si 2p spectrum of epitaxial silicene on the ZrB$_2$ surface without h-BN, shown in Fig. 2 (spectrum 0), which has been previously studied. This is confirmed by least-squares peak fitting (see Methods for details), which shows that the sharp Si 2p features can be fitted with $\alpha$, $\beta$, and $\gamma$ components with similar binding energies and area ratios: 98.75 eV, 98.99 eV, and 99.11 eV with area ratios of 1.8:3.0:0.6, respectively, for epitaxial silicene layer on ZrB$_2$, and 98.76 eV, 99.03 eV, and 99.15 eV, with area ratios 1.6:3.0:0.6 for 1.6 ML of Si on the h-BN-terminated ZrB$_2$. This shows that the corresponding Si atoms in both 2D layers are in essentially the same chemical environment. This is strong evidence for the intercalation of deposited Si underneath the h-BN layer, where it forms epitaxial silicene on the ZrB$_2$ surface. The broad component $A$ is attributed to disordered Si on top of the h-BN-terminated surface. Upon deposition of a total of 4.8 ML of Si, this broad contribution becomes the dominant feature of the spectrum, as shown in Fig. 2 (spectrum 3), while the two sharp doublets can still be resolved (fitted binding energies of the $\alpha$, $\beta$, and $\gamma$ components are 98.73 eV, 99.01 eV, and 99.16 eV, and their area ratios are 1.4:3.0:0.8). The increase of component $A$ relative to the silicene-related peaks suggests that the intercalation of Si has saturated, leaving most of the deposited Si in a disordered phase on the surface. It is noted that all Si 2p spectra, shown in Fig. 2, contain broad contributions at higher binding
energies, attributed to oxidized or disordered Si. A comparison of the Si 2p spectra after Si deposition with that of the pristine h-BN-terminated ZrB$_2$ surface, which showed a different spectral line shape, is discussed in the Supporting Information.

We now demonstrate that the h-BN layer does not affect the electronic properties of silicene, based upon the valence electronic structures of pristine h-BN terminated ZrB$_2$ and intercalated silicene, characterized by ARPES. The same notation used in previous studies of the low binding-energy region of silicene on ZrB$_2$ is used to mark the individual features in the ARPES spectra.$^5,18-20$ The ARPES spectrum, measured along the Γ-M-Γ direction of ZrB$_2$, of the pristine h-BN/ZrB$_2$ surface is shown in Fig. 3(a). The spectrum was measured using a photon energy of 50 eV. It features band S$_2$ (see Fig. 3(c)), associated with ZrB$_2$ surface states. Features associated with the π-electronic bands of epitaxial silicene are not observed, suggesting that there is either little or no silicene at all on the surface.
Figure 3: ARPES spectra of (a) pristine h-BN-terminated ZrB$_2$ measured with 50 eV photon energy, and (b-c) after deposition of 1.6 ML of Si measured with 43 eV photon energy, sample temperature 10 K. (d) ARPES spectrum of silicene on ZrB$_2$ measured with 45 eV photon energy and sample temperature 22 K.

The ARPES spectrum of the h-BN/ZrB$_2$ surface with 1.6 ML of Si deposited is shown in Figs. 3(b-c), and is also measured along the Γ-M-Γ direction of ZrB$_2$. The spectrum is measured with a photon energy of 43 eV. It shows ZrB$_2$-derived bands S$_1$ and S$_2$. In addition, the silicene-related bands X$_2$ and X$_3$ are now observed. The band structure is in good agreement with that of epitaxial silicene on ZrB$_2$ without an h-BN layer, shown in Fig. 3(d). This can be explained by the intercalation of the deposited Si underneath the h-BN monolayer, where it forms epitaxial silicene on the ZrB$_2$ surface. Importantly, the close similarity of the band structures indicates that the silicene exhibits negligible hybridization with the h-BN on top.

In order to determine the effectiveness of encapsulation by the h-BN monolayer, intercalated silicene, formed by deposition of 0.7 ML of Si on an h-BN-terminated ZrB$_2$(0001) surface at room temperature, was exposed to air at atmospheric pressure in the loadlock (vented with N$_2$ gas, and subsequently opened for 10 seconds) for 5 minutes. For the purpose of comparison, spontaneously-formed silicene$^5$ and single-domain silicene$^{18}$ on ZrB$_2$(0001) thin films, grown on Si(111) substrates, were also exposed to air for 5 minutes in the same way. Si 2p spectra of these samples are shown in Fig. 4(a).
Figure 4: (a) PES spectra of the Si 2p core-level region of spontaneously-formed silicene on ZrB$_2$, single-domain silicene on ZrB$_2$, and intercalated silicene on h-BN-terminated ZrB$_2$, before and after exposure to air. It is noted that the intensities of the spectra have been individually rescaled. The binding energy scale has been calibrated using the $\beta$ component of silicene on ZrB$_2$. (b) (8 x 30 nm$^2$, V= -700 mV, I=100 pA, room temperature) STM image of intercalated silicene on h-BN-terminated ZrB$_2$, recorded after exposing the sample to air for 5 minutes.

Exposure of the intercalated silicene layer to air for 5 minutes results in the appearance of a broad component centered at 102 eV, attributed to Si sub-oxide.$^{21}$ Interestingly, the silicene spectrum has become sharper. This can be explained by the preferential oxidation of the disordered Si (which most probably has not intercalated), which moved the associated spectral intensity towards higher binding energies. Furthermore, when spontaneously-formed silicene or single-
domain silicene was exposed to air for 5 minutes, as shown in Fig. 4(a), all silicene-related intensities disappeared, and a broad component appeared at 103.3 eV, attributed to SiO$_2$. This suggests that both non-encapsulated silicene layers became fully oxidized. In comparison, the spectrum of the silicene layer encapsulated by h-BN shows relatively little Si oxide, even after prolonged air exposure for 1 hour. This provides evidence for the encapsulation of the silicene layer and its effectiveness, as is also demonstrated by the STM measurement of an air-exposed sample shown in Fig. 4(b), which still exhibits atomic resolution. Exposing the encapsulated silicene layer again to air for 15 hours in total (by storing the sample in air outside the loadlock) results in the near-complete disappearance of the silicene spectrum and the appearance of a broad component at 103.2 eV, also observed for the non-encapsulated silicene layers after just 5 minutes, suggesting that most of the silicene layer has become oxidized. This demonstrates a limit to the effectiveness of the h-BN encapsulation layer, which nevertheless allows for enough time (at least 1 hour) for ex situ sample transfer, characterization, or processing.

3. Conclusions

In conclusion, we find that the deposition of Si atoms onto a monolayer of h-BN on a ZrB$_2$ thin film at room temperature leads to the formation of an intercalated, self-terminating, epitaxial silicene layer underneath the h-BN monolayer. From an electronic structure perspective, there is no indication of interaction between the h-BN layer and the silicene layer, demonstrating vertical integration of h-BN and silicene without perturbing the electronic properties of the latter. However, the large-scale domain structure of silicene is affected, characterized by islands separated by trenches. The intercalated silicene layer also exhibits edges which corresponds to armchair edges of the silicene honeycomb lattice, in contrast to the continuous sheet of silicene on ZrB$_2$ without h-BN. Importantly, the h-BN encapsulation layer hinders the oxidation of the silicene layer underneath and enables ex situ sample transfer, characterization, or processing.

4. Methods

Sample preparation and STM measurements took place at JAIST (Japan). ZrB$_2$ thin films are grown on Si(111) substrates by ultra-high vacuum chemical vapor epitaxy (UHV-CVE), which is described elsewhere.$^{15}$ It was previously found that the surface of the ZrB$_2$ thin film is terminated with a spontaneously-formed monolayer of silicene upon annealing at 800 °C in UHV, with the Si atoms originating from the Si substrate.$^5$ Subsequently, in a separate UHV system, an h-BN monolayer is formed by nitridation of the surface using a nitrogen plasma and a subsequent annealing treatment at 900 °C in UHV, as reported in previous work.$^6$ This system consists of a molecular beam epitaxy chamber equipped with an RF plasma source, a chamber with a PES system (base pressure of 1×10$^{-10}$ mbar), and a chamber with an STM system (base pressure of 1×10$^{-10}$ mbar). Si deposition was carried out by exposing the h-BN surface, held at room temperature, to the Si flux from the deposition source made of a narrow Si strip that is resistively heated by direct-current, during which the pressure in the chamber was 3×10$^{-10}$ mbar. It is noted that during deposition the sample is slightly heated by radiative heating from the Si deposition source, such
that the substrate temperature is somewhat higher than room temperature. STM measurements were performed in constant-current mode and at room temperature using a Pt-Ir tip. The Si deposition rate was calibrated by depositing Si on a Si(111)-(7×7) surface and measuring the coverage of epitaxial growth using STM. The deposition rate of the Si source was 1 monolayer (ML), defined as 1 bilayer of Si(111), per 30 minutes.

Additional STM measurements were performed at the STM lab at ISEM (University of Wollongong, Australia). The system consists of three interconnected UHV chambers: a loadlock, preparation chamber, and analysis chamber. The preparation chamber (1×10⁻¹⁰ mbar base pressure) was used to anneal the sample by e-beam heating, and also has a Si source made of a narrow Si strip that is resistively heated. The deposition rate was 1 ML of Si per 30 minutes. The analysis chamber (6×10⁻¹¹ mbar base pressure) contains the STM system. The STM measurements were performed in constant-current mode using a Pt-Ir tip and a sample temperature of 77K.

PES and ARPES measurements were recorded at two synchrotron facilities: beamline I05 at Diamond Light Source (UK) and beamline BL6U at UVSOR (Japan). The end station at the HR-ARPES branch of beamline I05 at Diamond Light Source consists of four interconnected chambers: a loadlock, a preparation chamber, and an upper and lower chamber. Another UHV system could be accessed through the preparation chamber to reach a Si deposition source (3×10⁻¹⁰ mbar during deposition), consisting of an e-beam heated Si rod, that was calibrated using the (5×2) LEED pattern of Si on Ag(110). The deposition rate was 0.8 ML of Si per 5 minutes. The upper chamber also connects to the preparation chamber, and features a LEED system and access to the lower chamber (2×10⁻¹⁰ mbar base pressure) for (AR)PES measurements. During measurements the sample was always at a temperature of 10K. The end station of BL6U at UVSOR consists of three interconnected UHV chambers: a loadlock, a preparation chamber, and an analysis chamber. The preparation chamber (3×10⁻¹⁰ mbar base pressure) features the Si deposition source made of a narrow Si strip that is resistively heated. The deposition rate was 1 ML of Si per 5 minutes. The analysis chamber (8×10⁻¹¹ mbar base pressure) features a LEED system and a detector and photon source to perform (AR)PES measurements with the samples at a temperature of 15 K. The binding energy scales of the Si 2p spectra were calibrated with respect to the Fermi level by measuring both the Si 2p core level and the Fermi edge with a photon energy of 150 eV. The Zr 3d and B 1s, and N 1s core levels (see Supporting Information) were calibrated by measuring them together with the Si 2p core level with a photon energy of 240 eV and 500 eV, respectively.

Least-squares peak fitting of Si 2p core level spectra was performed using a Shirley background and symmetric line shapes, with each component consisting of a doublet with an area ratio of 1:2 for the Si 2p₁/₂ and Si 2p₃/₂ peaks and 0.60 eV spin-orbit splitting. The epitaxial silicene layer on ZrB₂ has a honeycomb lattice with three unique atomic sites that each contribute a Si 2p doublet to the Si 2p spectrum. The three atomic sites are referred to as A, B, and C and occur in the ratio of 2:3:1 with corresponding Si 2p₃/₂ core levels α, β, and γ. The three components α, β, and γ associated with silicene, and the two components associated with the 2D Si islands, are fitted with a line shape based on a Gaussian-Lorentzian sum function with a 40-50% Lorentzian
character. The other components, e.g. tail features that can be explained by Si sub-oxides that remained after the annealing treatments to remove native Si oxide from the sample surfaces, are Gaussian line shape.

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References