Topical Review

Electronic properties of epitaxial silicene on diboride thin films

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Abstract
The Si counterpart of graphene—silicene—has partially similar but also unique electronic properties that relate to the presence of an extended $\pi$ electronic system, the flexible crystal structure and the large spin–orbit coupling. Driven by predictions for exceptional electronic properties like the presence of massless charge carriers, the occurrence of the quantum Hall effect and perfect spin-filtering in free-standing, unreconstructed silicene, the recent experimental realization of largely sp$^2$-hybridized, Si honeycomb lattices grown on a number of metallic substrates provided the opportunity for the systematic study of the electronic properties of epitaxial silicene phases.

Following a discussion of theoretical predictions for free-standing silicene, we review properties of ($\sqrt{3} \times \sqrt{3}$)-reconstructed, epitaxial silicene phases but with the emphasis on the extensively studied case of silicene on ZrB$_2$(0001) thin films. As the experimental results show, the structural and electronic properties are highly interlinked and leave their fingerprint on the chemical states of individual Si atoms as revealed in core-level photoelectron spectra as well as in the valence electronic structure and low-energy interband transitions.

With the critical role of substrates and of the chemical stability of epitaxial silicene highlighted, finally, benefits and challenges for any future silicene-based nanoelectronics are being put into perspective.

Keywords: silicene, electronic structure, photoelectron spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

As the larger cousin of carbon (C), the element silicon (Si) is right below C in the table of elements. While the chemical properties of the two elements might therefore be expected to resemble each other, there are actually very important differences that lead to distinct roles in nature and technological applications. Carbon is the essential ingredient of organic compounds and thus essential for life, and it is very well known to form a number of crystalline allotropes ranging from graphene and graphite to the fullerenes, carbon nanotubes and diamond.

On the other hand, while Si atoms are part of a number of molecular compounds, these are far less versatile than carbon-based organic materials. The only well-established crystalline Si allotrope at ambient conditions so far is diamond-structured silicon, shown in figure 1(a), and it is for this reason that in English and in many other languages the names to describe the element and the crystalline material are synonyms. In order to properly distinguish the two, in the present article, we are going to use the chemical symbol
Figure 1. Side views of structures and in-plane lattice constants of (a) the Si(1 1 1) bilayer (highlighted) in diamond-structured silicon, hypothetical and free-standing, (b) planar silicene, (c) regularly buckled silicene [16], and (d) a MoS$_2$-structured Si layer [3]. Top view is common for all the structures.

'Si' to denote the chemical element while the established allotrope shall be called 'diamond-structured silicon' or just 'silicon'. As part of ongoing, still yet very fundamental and theoretical research, novel hypothetical Si allotropes may then find new names like 'Si nanotubes' [1], 'silicene' [2] and 'MoS$_2$-structured Si' [3].

Silicon is the most commonly used material in the semiconductor industry. The scaling-down of electronic device structures by top-down approaches has, however, intrinsic limits that derive not only from the technological challenges in the fabrication process but ultimately also from the increasing relevance of quantum effects: in lower dimensions or in case of localization at atomic length scales, charge carriers and spins behave quite differently [4–6]. This generates high interest in novel types of electronic and spintronic applications.

At present, the ball is in the hands of the frontrunner graphene for which already field-effect tunneling transistor performance has been demonstrated using heterostack configurations [7]. Combined with the existing know-how and market power of the semiconductor industry, however, the possible existence of one or more well-defined, low-dimensional Si allotropes is not just of scholarly interest but may well be a stepping stone into the information technology of tomorrow.

In this review, beginning with new ideas about the chemistry of Si atoms, we will discuss the evolution of the concept of 'silicene' and its relation with experimentally realized two-dimensional, epitaxial Si adlayers. While for details about the fabrication of epitaxial silicene phases, we refer the reader to our recent review of aspects of the materials science behind the formation and chemistry of Si adlayers [8], here, the focus is on the electronic properties in relation to structural details and the interactions with substrates. While keeping an eye onto the wider field of silicene research, we will focus onto the structural, electronic and to some extent also the chemical properties of the rather well-characterized epitaxial silicene phase on ZrB$_2$(0 0 0 1) thin films. In establishing the essential role of the metallic diboride substrate by a comprehensive surface science characterization, it has been possible to verify some of the basic features predicted for silicene.

2. The concept of silicene

2.1. Bonding configurations of carbon and silicon atoms

The three-dimensional (3D) diamond structure of silicon is made of sp$^3$-hybridized Si atoms in a 4-fold configuration (figure 1(a)). In this modification, the localization of valence electrons in $\sigma$ bonds provides a high structural stability in three dimensions and is responsible for the formation of an electronic gap in between occupied and unoccupied $\sigma$ electronic states.

Similarly, for carbon, the corresponding allotrope, diamond, is well known for its hardness, transparency and reflecting surfaces.

Another important allotrope of carbon is based on the sp$^2$ hybridization and the resulting 3-fold coordination. As the ultimately thin form of graphite, graphene is an atom-thick single layer and thus two-dimensional (2D). It exhibits an extremely high structural stability within the plane spun by the planar honeycomb lattice. The $\pi$ orbitals are oriented out of plane, contain the fourth valence electron per atom and are responsible for the many exciting electronic properties of this material [9, 10]. In particular, $\pi$ electronic bands form Dirac cones just at the Fermi level, $E_F$, and at high-symmetry points classified as the $K$ points [11], making graphene a semimetal with ultra-mobile charge carriers [9, 10].

On the contrary, while the sp$^2$ hybridization of Si atoms occurs in disilene molecules [12] and at the reconstructed Si(1 1 1) surface [13], it is energetically unfavorable as compared to the sp$^3$ hybridization such that graphite-like 3D
crystals made by stacking of the planar honeycomb Si structure displayed in figure 1(b) cannot exist [14]. The main reason for this instability is found in the core–core Coulomb repulsion of the nuclei that can be reduced by about 10 eV per Si atom [15] if 2D Si honeycomb layers are ‘corrugated’ on the atomic length scale [16], or in other words ‘buckled’ [17], in a way in which the two sublattices are displaced from each other in the out-of-plane direction. Such honeycomb structures are called ‘silicene’ [17] and exist in isolated, or ‘free-standing’, forms only as hypothetical concepts. A structural model for this buckled silicene sheet is displayed in figure 1(c).

Note that originally, the term ‘silicene’ has only been used to describe the ‘planar’ analog to graphene [2], which is schematically drawn in figure 1(b), while nowadays it may be used even if the buckling could exhibit larger scale periodicities [15].

While the buckling in silicene sheets inadvertently mixes sp² and sp³ types of hybridization [16], for C atoms, a mixture of sp² and sp³ hybridizations is realized in the curved structures of the fullerens and carbon nanotubes [18] rather than by atomistic buckling.

In more recent theoretical work, it has been shown that silicene itself is not the most stable configuration of 2D Si allotropes [3]. The addition of individual Si adatoms results in the formation of a dumbbell structure that is characterized by a lower energy per Si atom [19, 20]. Towards complete coverage, the periodic dumbbells form the structure of the well-known single layer of MoS₂ shown in figure 1(d) [3]. In this structure, the Si atoms in the central part of the layer are 6-fold coordinated. Besides an extended π electronic system, cigar-shaped, so-called ‘nematic’ σ orbitals [3] are directed in the out-of-plane direction. Note that the bonding is different from that for the 6-fold coordinated Si atoms in the β-tin Si phase, which can only be stabilized under a high pressure [21].

Although hypervalent Si atoms in heteroatomic molecules have been known since the 19th century [22, 23], our prediction of the 6-fold coordination in a crystalline and extended 2D Si allotrope [3] indicates further significant differences in chemical properties between Si and C atoms.

While C atoms are able to coordinate with two, three or four nearest neighbors corresponding to the sp (realized in some linear organic compounds), sp² (or mixed sp²/sp³) and sp³ hybridizations, it remains to be seen if beside the 4-fold coordination, the predicted 3- or 6-fold coordination may be realized in free-standing, 2D crystalline Si allotropes.

There is already evidence that both previously unimagined bonding configurations, though stabilized by interactions with metallic substrates [24], must be considered to be present as epitaxial 2D Si adlayers [25, 26]. While the MoS₂-type structure (with a partially 6-fold coordination to nearest neighbor Si atoms) has just been discussed to correspond to the (√3 × √3) silicon phase formed on the Ag(1 1 1) surface [26], coordination to three nearest Si neighbors has been shown by us [25] to be realized in epitaxial silicene on ZrB₂(0 0 0 1) thin films [15]. While it may be difficult to experimentally verify some of the exotic physical effects predicted for free-standing, buckled silicene, the finding of diverse forms of π and σ bonding in 2D Si allotropes reflects by itself exciting chemistry.

2.2. The predicted electronic structure of free-standing silicene

In 1994, Takeda and Shiraishi published a study describing the hypothetical crystal and electronic structures of isolated, both planar (figure 1(b)) and ‘corrugated’ or ‘buckled’ (figure 1(c)), 2D honeycomb lattices of Si atoms together with those of C and Ge atoms [16]. In this study, all features characteristic of silicene have been pointed out. Later on, following the enormous success of graphene [9, 10], the term ‘silicene’ has been coined to highlight the conceptual similarity between the two materials [2].

In more recent years, it has been found that this buckled silicene (figure 1(c)) which is now also called ‘low-buckled’ [17] or ‘regularly buckled’ [15] silicene is calculated to be structurally stable for optimal in-plane lattice parameters [17] but only if the atomic areal density is fixed [3]. The relative stability (per Si atom) with respect to MoS₂-structured layers (figure 1(d)) [3] and diamond-structured silicon layers (figure 1(a)) is a consequence of the missing out-of-plane bonding partners that prevent the 4-fold coordination of Si atoms. The associated additional electrons are accommodated in π bonds associated with the mixed sp²/sp³ hybridization.

Electronic properties different from those of diamond-structured silicon (in the bulk made up of 4-fold coordinated Si atoms) shall also be reflected in structural differences. As such, while the calculated lattice constant of approximately 3.86 Å [16] is similar to that of 3.84 Å of the Si(1 1 1) bilayer of diamond-structured silicon (figure 1(a)), bond lengths are predicted to be shorter (2.24 Å [16]) than those of 2.35 Å in sp³-hybridized silicon. As a consequence, regularly buckled silicene (figure 1(c)) is flatter than the Si(1 1 1) bilayer (figure 1(a)). Note in this context that double bonds between Si atoms in disilenes (2.14–2.16 Å [12]) are even shorter than those predicted for silicene.

Similar to graphene, silicene has two sublattices such that the (1 × 1) unit cell of silicene contains two atoms. Due to this similarity, considering the symmetry of the atomic orbitals involved, the band structure of silicene can, in an initial approach, be derived from that of graphene [2, 15, 16]. Starting from the tight-binding description of graphene, a finite set of three hopping integrals may be used. As illustrated in figure 2, several hopping parameters describe σ-bond hopping (t₁) between two of the σ orbitals (also called sp² orbitals; each form is a combination of atomic s, px and py orbitals), π-bond hopping between px orbitals of neighboring atoms (t₂), and the pᵧ–sp³ hopping (t₃) [15].

For planar systems like graphene and hypothetical planar silicene (figure 1(b)), t₁ is zero. As a consequence, π and σ electronic states do not couple to each other. As shown in figure 3α, the low-energy band structure is formed by (bonding) π and (antibonding) π∗ bands that both cross E_F at the K point. Since both types of bands have linear dispersions in the vicinity of K, a Dirac point is formed. Due to the presence of two sublattices, the π and π∗ bands are doubly degenerate.

Following the introduction of a buckling, t₁ becomes non-zero. However, the buckling cannot lift the degeneracy of
Figure 2. Nearest-neighbor-hopping integrals within a simple tight-binding model for a Si honeycomb lattice considering only the $\sigma$-bond hopping ($t_1$), $p_z$–$p_z$ hopping ($t_2$), and the dominant $p_z$–$sp^2$ hopping ($t_3$). $t_3$ is zero for the planar structure but can reflect the strength of buckling between the two atoms in the unit cell. $t_4$, $t_5$ and $t_6$ denote other hopping integrals not discussed here. Reproduced from [15]. Article published under a Creative Commons Attribution 3.0 Unported (CC BY 3.0) License.

Figure 3. The electronic band structures of free-standing (a) planar, (b) regularly buckled, and (c) planar-like silicene phases as unfolded from the ($\sqrt{3} \times \sqrt{3}$) unit cell ($a = 6.35$ Å, using the in-plane lattice constants of the (2×2) unit cell of ZrB$_2$(001) into the first BZ of (1×1) silicene. The $s$ and $p_z$ characters of bands are colored in magenta and black, respectively, and that of $p_x$ and $p_y$ orbitals in green. Reproduced from [15]. Article published under a Creative Commons Attribution 3.0 Unported (CC BY 3.0) License.

Since despite the induced buckling, the electronic structure of silicene resembles that of graphene [16], silicene is expected to possess massless charge carriers known as Dirac fermions. On the other hand, a major difference to graphene is the amount of spin–orbit coupling (SOC). This large SOC originates from the buckled nature of silicene [28], but it is large because it scales with the fourth power of the atomic number [29]. The large SOC is predicted to lead to an experimentally observable quantum spin Hall effect. The SOC-induced transition to the quantum spin Hall insulator (QSHI) state is therefore expected to take place at a much higher temperature as compared to graphene [28, 30]. The QSHI state could lead to spin accumulation at the edges of a stripe when a charge current is passed through, and to Majorana fermions in edge states when the QSHI is in contact with a superconductor [31]. Since these edges relate to 2D topological insulator properties in silicene [28, 30, 32], opportunities in spintronics applications and in topological quantum computing arise [33].

2.3. The crystal and electronic structures of ($\sqrt{3} \times \sqrt{3}$)-reconstructed, free-standing silicene

Inspired by the discovery of large-scale reconstructions of 2D Si adlayers on metallic substrates that have been called ‘epitaxial silicene’ [34–38], and the subsequent
consideration of \((\sqrt{3} \times \sqrt{3})\)-reconstructed phases of free-standing silicene [15], nowadays, the term ‘silicene’ is used to describe any 2D honeycomb structure made of Si atoms. In this context, the term ‘reconstruction’ refers to variations of the local buckling that are variations on the atomic length scale that go beyond the out-of-plane displacements of the two sublattices. The unit cell then contains more than two atoms.

Since the local symmetry around each Si atom is broken once the lattice is reconstructed, the degeneracy of \(\pi\) bands at the \(K_{Si}(1 \times 1)\) point is lifted. Bands are folded into the reduced Brillouin zone (BZ) such that the \(K_{Si}(1 \times 1)\) and \(M_{Si}(1 \times 1)\) points coincide with the \(\Gamma_{Si}(\sqrt{3} \times \sqrt{3})\) and \(M_{Si}(\sqrt{3} \times \sqrt{3})\) points of the repeated BZ of the reconstructed layer, respectively. This is illustrated in figure 4.

Any discussion of the electronic properties of reconstructed phases in terms of the ‘unreconstructed’, \((1 \times 1)\), regularly buckled silicene unit cell does not respect the symmetry of reconstructed phases. However, the band structures of \((\sqrt{3} \times \sqrt{3})\)-reconstructed phases can be unfolded into the larger BZ of \((1 \times 1)\) silicene [39]. This turns out to be useful for the comparison of the characteristic electronic states in terms of the predictions made for free-standing, unreconstructed silicene [25].

For a certain range of lattice constants, slightly compressed with regard to the equilibrium conditions of the unreconstructed, ‘regularly buckled’ phase, a particular \((\sqrt{3} \times \sqrt{3})\)-reconstructed phase, called the ‘planar-like’ phase [15], has been calculated to be quite stable. The crystal structures of the two phases are shown in figures 5(a) and (b), respectively. As discussed in our earlier work by Lee et al [15], the relative stability of this phase especially with respect to the planar one in terms of the total energy derives from a reduction of the core–core Coulomb repulsion of the nuclei. This repulsion is lowered by the substantial amount of about 50 eV and 60 eV per Si atom, as compared to the regularly buckled and planar phases, respectively [15]. This highlights the essential role of the atomic positions and the bond lengths for the stability of silicene phases. As already discussed in section 2.2, bond lengths are expected to represent the type of hybridization occurring in the particular Si structure.

Note that while not being the ground state in its free-standing form, the planar-like phase is stabilized under epitaxial and slightly strained conditions on substrates: in its form with stripes [40], it forms the ground state on the ZrB_2(0001) surface [15, 25]. It has also been discussed to form on the Ag(1 1 1) surface [41] and on ZrC(1 1 1) [42].

The planar-like phase has a peculiar structure displayed in figure 5(b): one of the Si atoms per hexagon is kicked out of the single plane spun by all the others. As compared to planar silicene (figure 1(b)), in this way, the bond lengths can be longer and closer to those of the regularly buckled one (figure 1(c)) [15]. As can be seen in figure 3(c), unfolded into the \((1 \times 1)\) BZ, it still resembles to some extent the band structure of unreconstructed silicene. As such, cone-like band dispersions in the vicinity of the \(K_{Si}(1 \times 1)\) point can still be recognized. A small band gap is opened, however, accompanied by a small up-shift of the corresponding features.

3. Epitaxial silicene phases

3.1. The experimental realization of Si honeycomb structures on surfaces

As we have discussed so far, the theoretical understanding of possible low-dimensional Si structures and of the physical effects emerging in isolated, free-standing silicene is progressing fast. In aspiring to the expectations raised, in recent years, various efforts undertaken to synthesize and characterize such Si honeycomb lattices have paid off. These efforts, which we reviewed in a recent article [8], provided a wealth of novel materials science but so far could not find convincing and verifiable agreement with essential properties predicted for free-standing silicene. The main reason for this fact is that epitaxial silicene phases are always stabilized by
interactions with metallic substrates in a way in which their electronic states are hybridized with those of the respective substrate surfaces. They are thus not well defined in terms of ‘ideal’ silicene.

The research is further complicated because of the lack of a single reliable identification method for epitaxial silicene. A comprehensive experimental characterization in combination with first-principles calculations covering both structural and electronic properties is then always required [8, 38]. These characterization techniques include scanning tunneling microscopy (STM) performed under ultra-high vacuum (UHV) conditions which in combination with an electron diffraction technique [24, 43, 44] provides information on the surface reconstruction and possibly on the in-plane structure of the Si adlayer if atomic resolution could be achieved or once a model with reasonable assumptions for the bond lengths is applied. It has therefore been used in most of the initial studies of Si adlayers as the primary [34–38, 45–47] and often the only characterization method. High-resolution, core-level (XPS) [38, 48, 49]) and angle-resolved valence band (ARPES) [24, 25, 36, 38, 48, 50] photoelectron spectroscopies, on the other hand, are essential for the determination of the elemental composition and chemical environment of Si atoms and the bond structure, respectively.

Already for a while, Si honeycomb structures have been known to sandwich layers of metal atoms in disilicides [51–53], to exist in Si sheets exfoliated from Ca disilicides [54] and even as a single sheet on an Er-covered Si(1 1 1) single-crystal surface after thermal annealing [55]. The electronic structure of this ‘2D Er silicide’ is characteristic of a semimetal with a small density of states at $E_F$ that derive from a small hole pocket at the $\Gamma$ point and a small electron pocket at the $M$ point [55]. Moreover, the surface electronic structure of a buckled honeycomb Si sheet on (\sqrt{3} \times \sqrt{3})-reconstructed epitaxial ErSi$_{1.7}$ layers on Si(1 1 1) has been characterized using ARPES. It was found that prominent bands at low binding energies can be explained by (1 x 1) bands of 2D Er silicide back-folded into the reduced (\sqrt{3} \times \sqrt{3}) BZ, thus resulting in the appearance of cone-like dispersions and of half-an-eV gap centered at 0.7 eV below $E_F$. Due to the reconstruction, they are located at the $M(1 \times 1)$ and reconstructed $M$ points [53].

These Si sheets in disilicides are characterized by charge transfer and a large degree of hybridization between the low-binding-energy valence electronic states of the Si and metal subsystems [51–53, 55]. It is therefore important to keep in mind that the classification of epitaxial Si honeycomb lattices in terms of epitaxial silicene requires an understanding of the strength and type of interactions between the Si sheets and the substrate surface.

More recently, Si nanoribbons with an internal honeycomb structure have been prepared on the Ag(1 1 0) surface [56–60]. Along the long direction of the ribbons, cone-like dispersive electronic states, split with a gap of 0.5 eV and centered at 0.6 eV below the Fermi level, $E_F$, at the high-symmetry point corresponding to $K_S(1 \times 1)$, have been observed by ARPES [59]. They are reminiscent of $\pi$ electronic states in graphene. In the short direction, their minor dispersion indicates a localized character of the states expected for 1D nanostructures.

Following a highly contested earlier report [46], in 2012, several groups described details of 2D Si honeycomb structures on substrate surfaces with hexagonal symmetry: on the Ag(1 1 1) surface of single crystals [34–37] and on ZrB$_2$(0 0 0 1) surfaces of thin films prepared on Si(1 1 1) wafers [38]. While the latter are formed by surface segregation at high temperatures [8, 38], a number of epitaxial Si-related structures form on Ag(1 1 1) in a typical substrate temperature range between 250 and 300 $^\circ$C, depending on the amount of Si atoms and the temperature during deposition. These phases manifest themselves as (\sqrt{3} \times 2 \sqrt{3}) [46] and (4 \times 4) [34–36] reconstructions of the Ag(1 1 1) surface, and as a reconstruction corresponding to a (\sqrt{3} \times \sqrt{3})-reconstructed silicene lattice [37, 41, 61], and may represent various phases of epitaxial silicene or Si networks that consist of incomplete honeycombs [37], possibly bilayers [62] or honeycomb dumbbell [26] structures.

The electronic structure of the (4 x 4)-reconstructed Ag(1 1 1) surface (which corresponds to (3 x 3)-reconstructed silicene) has been studied in detail by ARPES [36, 48, 50]. A linearly dispersing state observed at the $K_S(1 \times 1)$ point [36] has later been found to be repeated at $\Gamma(3 \times 3)$ points. These states appear with cone-like dispersion with a peak at 0.3 eV below $E_F$ [48, 50].

More recent reports describe the preparation of epitaxial silicene on Ir(1 1 1) [45] and ZrC(1 1 1) [42] surfaces by deposition of Si atoms but without details of their electronic structures. While the formation process of epitaxial Si surface layers is not yet fully understood, it seems so far that in particular d electronic states of the metal substrates play a certain role in the stabilization of such structures. Although free-standing silicene-like properties may not be realized in this way, it is now certain that a number of Si surface systems characterized by a varying degree of interaction strength do exist.

3.2. Epitaxial silicene on ZrB$_2$(0 0 0 1) thin film surfaces

Epitaxial silicene is found to form spontaneously on the surfaces of oxide-free ZrB$_2$(0 0 0 1) thin films grown on Si(1 1 1) wafers via segregation of the substrate material [38]. Thin films of ZrB$_2$ are grown in a UHV chamber through the thermal decomposition of highly pure Zr(BH$_4$)$_4$ gas at the substrate surfaces kept at temperatures between 900 and 1000 $^\circ$C [43]. During the growth, the thin film surface is monitored in situ by reflection high-energy electron diffraction (RHEED). After the growth, upon cooling down to temperatures below 650 $^\circ$C, one can observe that silicene crystallizes epitaxially on atomically flat ZrB$_2$(0 0 0 1) terraces, manifesting itself as the (2 x 2) reconstruction of the ZrB$_2$(0 0 0 1) surface [38].

Once removed from the UHV chamber, the thin film surface including silicene is readily oxidized. However, silicene forms again upon renewed annealing in UHV. Under optimal conditions, this procedure reproducibly leads to samples with more than 99.5% of the surface covered with single-crystalline-like silicene [43, 63].
Figure 6. STM images and in-plane structural model of the (2 × 2)-reconstructed ZrB$_2$(0001) surface with different length scales: (a) 20 nm × 9.5 nm, (b) 1.7 nm × 2.4 nm. The white lines emphasize the direction of offsets between successive domains. The (2 × 2) unit cell and the honeycomb mesh are emphasized by green and blue solid lines, respectively. (c) Model of the Si honeycomb structure on the topmost Zr layer of ZrB$_2$(0001). Chemically different types of Si atoms ‘A’, ’B’ and ‘C’ are indicated. Reproduced from [38]. Article published under a Creative Commons Attribution 3.0 Unported (CC BY 3.0) License.

A typical large-scale STM image of epitaxial silicene on ZrB$_2$(0001) thin films prepared on Si(1 1 1) wafers is shown in figure 6(a). With respect to the ZrB$_2$ film, the surface is (2 × 2) reconstructed. Apart from the surface reconstruction, stripe domains which are running parallel along the ZrB$_2$[1 1 2 0] direction with alternating regular offsets corresponding to the lattice constant a of ZrB$_2$(0001) towards the other two ZrB$_2$[1 1 2 0] directions form large-scale structures that cover terraces completely [38]. These stripes represent stress domains of a single continuous 2D layer of adatoms and result from large-scale interactions within the layer [38, 40] and local interactions between Si atoms and the Zr atoms of the uppermost layer of the substrate [40]. As we have recently suggested by first-principles calculations, the formation of the striped phase offers a way to lower both the atomic surface density and the total energy of silicene on the particular surface [40]. As discussed in detail in the reference, this releases epitaxial strain and avoids some unfavorable on-top positions of Si atoms.

Within the center of stripe domains, fine details can be recognized in the constant-current STM image shown in figure 6(b) obtained under good experimental conditions [38]. A honeycomb mesh with the in-plane lattice constant of about 3.65 Å can be superimposed in a way in which the (√3 × √3) unit cell of the Si adlayer fits with the ZrB$_2$(0001)-(2 × 2) unit cell. This leads to the in-plane structural model shown in figure 6(c) that has been derived for the center of the stripe domains [38]. In this model, two ‘A’ Si atoms per unit cell are located on hollow sites of the Zr lattice, three ‘B’ Si atoms sit at intermediate positions between top and bridge sites, or so-called ‘near-bridge’ sites, and one ‘C’ Si atom is on top of a Zr atom.

4. Core levels of epitaxial silicene

4.1. Varying sp$^3$/sp$^2$ ratio in epitaxial silicene

The elemental nature and the chemical environment of surface adatoms are best probed using high-resolution core-level spectroscopy performed at a tunable light source that is a synchrotron radiation light source [38, 49]. Si 2p spectra have been acquired with the photon energies $h\nu = 130$ eV (figure 7(a)), $h\nu = 340$ eV (figure 7(b)) and $h\nu = 700$ eV (figure 7(c)) in the normal emission geometry, in order to provide a high-resolution and surface sensitivity or bulk sensitivity, for low and high photon energies, respectively [49]. Each line of the Si 2p doublet consists of two peaks that are well separated from each other [38].

The spectra are compared to a bulk-sensitive spectrum of the clean Si(1 1 1)-(7 × 7) surface ($h\nu = 268$ eV, figure 7(e)) for which the bulk 2p$_{3/2}$ component at the binding energy of about $E_B = 99.43$ eV [64, 65] is indicated by a vertical line. The silicene peaks associated with the same line appear at $E_B = 98.98–98.72$ eV and thus at 450–710 meV lower binding energies [49]. Since similar low binding energies are observed for a silicene phase on Ag(1 1 1) [66], they must be considered to reflect the particular local valence electron densities and core-hole screening capability of epitaxial silicene phases. Instead of being close to the binding energy of sp$^3$-hybridized Si bulk atoms, the low binding energies are in the range of those attributed to surface atoms with dangling bonds on reconstructed Si(1 1 1)-(7 × 7) and Si(1 0 0)-(2 × 1) single-crystal surfaces [65, 67, 68].

In this context, a direct comparison to carbon materials can be made: the observed binding energy differences are similar to that of about 0.8 eV in between the C 1s lines of diamond [69] and graphene [70]. This suggests that the low Si 2p binding energy is related to the higher degree of sp$^2$ hybridization for all of the Si atoms of epitaxial silicene [49]. The spread of binding energies for epitaxial silicene on ZrB$_2$(0001) thin films derives then primarily from the varying sp$^2$/sp$^3$ ratio caused by the buckling [49].

4.2. π* resonances in core-level excitations

Low core-level binding energies are also expected to contribute to a low-energy onset in the x-ray absorption. The near-edge x-ray absorption fine structure (NEXAFS) spectra of epitaxial silicene on ZrB$_2$(0001) thin films for the three angles $\theta = 20^\circ$, 50° and 90° are shown in figure 8 together with the corresponding spectrum of the Si(1 1 1)-(7 × 7) surface at $\theta = 50^\circ$ [49]. Here, $\theta$ is the angle between the electric field vector of the light and the normal of the sample.

Following a sharp onset of absorption at $h\nu = 98.7$ eV, the silicene spectra increase steadily until about 102.2 eV.
Resonances (1)–(4) do not show any angular dependence while feature (5) increases and feature (6) and (7) decrease with θ. While p–p transitions are dipole forbidden [71], transitions from the Si 2p level into π* electronic states will occur with a minor intensity since π* orbitals have a partial s character [72]. Additionally, transitions from core orbitals with p symmetry into orbitals with a partial s character exhibit a vanishing angular dependence. It has therefore been concluded that weak features (1)–(4) with a vanishing dependence on θ correspond to π* resonances, providing evidence for low-energy unoccupied π* electronic states.

For the Si(1 1 1)-(7 × 7) surface, on the other hand, bulk-related absorption with σ* character starts at 99.6 eV [73] which is only 0.9 eV higher than the onset for silicene. Since the energy difference between the onsets of bulk-related absorption in silicon and of the absorption in silicene corresponds just to the core-level binding energy difference, and since π* electronic states in silicene are predicted to be closer to E_F than σ states in silicon, it can be concluded that excitations from core into π* valence states in silicene are much less excitonic than the core-level-σ* excitations in sp³ hybridized silicon. This may be expected since σ* states are highly localized.

4.3. Chemical environment of the Si atoms: a fingerprint of the structure of epitaxial silicene

In our original work describing the properties of silicene on ZrB₂(0 0 0 1) thin films, three components labeled α, β and γ in figure 9(a) have been identified by a peak fitting procedure in a surface-sensitive Si 2p spectrum obtained with hν = 130 eV. From this spectrum taken with a relatively low experimental resolution [38], the intensity ratio between the three components follows roughly the atomic ratio of 2:3:1 characteristic of the three chemical environments of Si adatoms ‘A’, ‘B’ and ‘C’ within the center of stripes. This agreement is confirmation of the in-plane structural model in which the (√3 × √3)-reconstructed Si honeycomb lattice matches the (2 × 2) unit cell of the ZrB₂(0 0 0 1) thin film surface.

In later work, we have obtained spectra with a higher experimental resolution and in a wide range of photon energies [49]. As shown in figure 9(b), the intensities of the α, β and γ components show strong photon-energy-dependent intensity variations [49]. These oscillations as well as a strong dependence on the photoelectron emission angle [38] derive from photoelectron diffraction effects. Due to the strong component-dependent intensity variations, the atomic ratios derived from spectra obtained with just a few photon energies cannot provide the atomic ratio in a reliable manner.

In the inset of figure 9(b), the intensities averaged over the photon-energy range of up to about hν = 255 eV and
Figure 9. (a) Surface-sensitive Si 2p photoelectron spectrum of silicene on a thin ZrB$_2$(0001) film recorded at normal emission, using a photon energy of $h\nu = 130$ eV. (•). Chemical states $\alpha$, $\beta$, and $\gamma$ are identified by a peak fitting procedure and relate to the three distinct atomic sites within the ($\sqrt{3} \times \sqrt{3}$)-reconstructed and buckled honeycomb lattice. The full line (——) is the sum of the three components. (b) Spectral intensities of the $\alpha$ (■), $\beta$ (●) and $\gamma$ (○) components as a function of the photon energy, as normalized to the photon flux. The inset shows the relative intensities of the $\alpha$, $\beta$, and $\gamma$ components as normalized to the total Si 2p intensity. Averaged intensities are shown by dotted lines. Reproduced with permission from [49]. Copyright 2014, AIP Publishing LLC.

normalized to the total Si 2p intensity provide, within the restraints of the applied fitting procedure, more reliable values for the atomic ratio. The as-derived ratio of $2.3 : 3.4 : 0.3$ indicates a deviation from the model ratio especially for the ‘C’ but also ‘B’ atoms. It has therefore been suggested that additional chemical states must be present that cannot be properly resolved [49]. In particular, some of the ‘C’ atoms must be in chemical states that are close to those of ‘B’ atoms: that is, not in ‘on-top’ positions any more. These atoms might well be located in extended boundary regions that separate stripe domains.

This picture is also supported by first-principles calculations that reveal the origin of the stripe pattern [40]. In short, the ‘striped’ phase with a specific buckling is formed under epitaxial strain in order to avoid energetically unfavorable ‘on-top’ positions that are also associated with a characteristic phonon instability at the high-symmetry $M$ point. On the other hand, in order to fulfill epitaxial conditions, the majority of ‘C’ atoms in the center of stripes sit on top of Zr atoms and are in the $\gamma$ chemical state. The corresponding structural model is displayed in figure 10 [40].

This demonstrates that high-resolution Si 2p core-level spectra are highly sensitive to details of the structural configuration of epitaxial silicene layer and can be used to confirm the validity of in-plane structural models derived from STM images.

5. The valence electronic properties of epitaxial silicene

5.1. The valence electronic structure of epitaxial silicene

While chemical shifts measured by core-level photoelectron spectroscopy contain a wealth of chemical and indirectly structural information associated with individual atomic sites, the electronic band structure of a 2D material or of a surface layer is an even more precise fingerprint of a low-dimensional, epitaxial material that derives from both the particular structural configuration of the layer and its interactions with the substrate.

The ARPES spectra measured along the $\Gamma$–$K_{Si}$ direction of epitaxial silicene on ZrB$_2$ thin films as a function of the in-plane wave number $k_{||}$ [25] are shown in figures 11(a) and (b). Features denoted ‘S$_1$’ and ‘S$_2$’ resemble [43] characteristic surface states of the unreconstructed Zr-terminated ZrB$_2$(0001) surface [74]. It has therefore been concluded that the outermost Zr layer must be considered structurally intact [38] and that the interactions between silicene and the outermost Zr layer must be non-local [25]. Features ‘X$_1$', ‘X$_2$', ‘X$_3$' and ‘X$_4$’ are related to the presence of silicene [38] since they do not have a counterpart [25] in the calculations for the unreconstructed Zr-terminated ZrB$_2$(0001) surface [74]. Of highest interest are certainly the intense, upward curved features X$_1$ and X$_2$ that approach $E_F$ by up to about 250 meV at the $K_{Si}$ point. They resemble the predicted Dirac cone of $\pi$ bands of free-standing, unreconstructed silicene at $K_{Si}$ [38] which can be seen in figure 3(b).

Note that a similar feature X$_3'$ appears with weak intensity in the vicinity of the $\Gamma$ point in the first BZ as well [25, 38]. This is a direct consequence of the ($\sqrt{3} \times \sqrt{3}$) reconstruction of the Si honeycomb layer because, as we have derived in section 2.3, the $K_{Si}$ point of unreconstructed, hypothetical, free-standing silicene (with a unit cell containing two Si atoms) coincides with the $\Gamma$ point of the repeated BZ of the reconstructed surface (figure 4).
While in earlier attempts to understand silicene on ZrB$_2$(0001), our preliminary interpretation leaned towards the metastable phase resembling regularly buckled silicene [38], in our recent results, density functional theory (DFT) calculations and ARPES data obtained in a wide energy range converged into the planar-like phase shown in figure 10.

That is, using variations of structural parameters within an assumed in-plane structural model as input, the combination of ARPES and first-principles calculations provided the most conclusive information on details of the out-of-plane buckling so far [25]. In addition to the agreement between features in the ARPES spectra and the calculated dispersion of bands, as shown in figure 11, it is even found that by representing the band structure in a large BZ associated with a single Si atom, the imaginary part of the one-particle Green’s function follows the spectral weight observed in the ARPES spectra. This indicates that the degree of translational symmetry breaking due to the (√3 × √3) reconstruction might not be strong enough to allow ARPES experiments to observe the spectral weight calculated in the corresponding crystallographic unit.
Figure 12. The (a) Si $s + p_x + p_y$, (b) Si $p_z$, and (c) Zr $d$ orbital character of the electronic bands of the planar-like phase along the $\bar{\Gamma} - K_{Si}$ direction, as calculated for the $(2 \times 2)$ lattice constant of $a = 6.480$ Å. Zr $d$ denotes the contribution from the terminating layer that more strongly interacts with silicene. Reproduced from [25]. Copyright 2014 by the American Physical Society.

5.2. The orbital character of valence electronic states and interactions with the substrate

Some experimental evidence for the nature of electronic states in the vicinity of $E_F$ can be obtained in experiments in which the surface is doped by adsorbed (or intercalated) foreign atoms. For instance, like for graphene [75, 76], in a rigid band picture, the adsorption of strong donors like alkali metal atoms may lead to a (partial) charge transfer into formerly unoccupied states of silicene, thus shifting the Fermi level upwards with respect to $\pi$ electronic bands.

As was found in our recent experiment [24], potassium (K) atoms donate charge into feature ‘X5’. This feature barely touches $E_F$ and provides electronic states above $E_F$ [25] that can readily be filled. Upon n-type doping, occupied features X$_2$ and X$_3$ shift towards higher binding energy. This is consistent with a rigid band picture in which all of these states have strong contributions at silicene [24]. On the other hand, the diboride-derived surface state S$_1$ is found to hybridize with feature ‘X4’ which indicates (1) that X$_4$ has strong contributions from silicene as well, and (2) that the interactions between silicene and the diboride substrate are enhanced upon K adsorption [24].

While doping experiments can go so far, a very much deeper insight into the nature and orbital character of the electronic states at the silicene/ZrB$_2$(0001) interface has only been obtained once it was possible to achieve a credible agreement between the results of DFT calculations and the ARPES data [25]. This agreement itself is astonishing since the stripe character of the Si layer is not accounted for in the calculations.

The orbital character of electronic states in terms of Si $s + p_x + p_y$, Si $p_z$, and Zr $d$ contributions is shown in figures 12(a), (b) and (c), respectively. It turns out that all silicene-derived bands are hybridized to some extent with Zr $d$ electronic states. This is consistent with non-negligible interactions at the interface. While $p_2$ and $p_3$ (that correspond to features X$_2$ and X$_3$) are of partial $\pi$ character indeed, they are actually formed by a hybridization of Si $s$, $p_x$, $p_y$, and Zr $d$ orbitals. This hybridization reflects the intermediate $sp^2/sp^3$ hybridization of epitaxial silicene and its interactions with the metallic substrate [25].

Band edges of the occupied, upward curved $p_2$ and $p_3$ bands, on one side, and of the downward curved band $p_5$, on the other, provide a high density of states seen as well as peaks in scanning tunneling spectroscopy performed at temperatures as low as 5.5 K (revealing a 350 meV gap) [47]. These band edges have strong contributions within the silicene layer, thus confirming our previous experimentally derived conclusions about the nature of these electronic states.

5.3. Interband transitions in epitaxial silicene

For ultrathin materials on metallic substrates, the dielectric and optical response is obviously determined by the substrate. It therefore represents a challenging task to experimentally determine the nature of interband transitions in an epitaxial 2D system like silicene on ZrB$_2$(0001) thin films. Strictly speaking, due to the hybrid nature of the electronic structure at the surface, it also makes sense only to talk about excitations that have a certain probability at Si sites. However, it is of great interest to study these valence excitations in order to verify if they follow theoretical predictions for silicene phases.

A high selectivity to atomic sites is provided by spectroscopic techniques that involve core holes or (resonant) core-level excitations [77–79]. As such, satellite features in x-ray photoelectron (XPS) spectra are typically associated with either shake-ups or plasmon excitations. In spectroscopic terms, they can be distinguished from chemical states since, as dynamical processes, they depend strongly on the excitation energy [77, 78].

For the Si 2p spectra in figure 7 obtained with $h\nu = 130$, 340 and 700 eV, at the high-energy side of the spectrum, a tail is observed that is enhanced with increasing $h\nu$. For
$h\nu = 700$ eV, the tail becomes even structured, showing two groups of features that are split by 0.6–0.7 eV. Since this splitting likely derives from the SOC, these satellite features may be related to either shake-up or plasmon excitations associated with the $2p_{3/2}$ and $2p_{1/2}$ main lines, respectively. These satellites, denoted as $s_1$, $s_2$, $s_3$ and $s_4$, are located at 1.95 ± 0.10 eV deeper than the four main peaks.

Looking at the band structure related to Si-derived orbitals shown in figure 12, this particular energy could correspond to the transition between the edges of bands at the $K_S$($1 \times 1$) point that corresponds to the $\Gamma$ point of the ($\sqrt{3} \times \sqrt{3}$)-reconstructed honeycomb lattice (as illustrated in figure 4), and in particular to the energetic separation of about 2.0–2.1 eV between the $p_6$ band and the band edge visible at about 0.85 eV above $E_F$. Note in this context that shake-up energies are, like all e–h excitations, excitonic in nature such that their energies are expected to be smaller than the corresponding maximum in the joint density of states. Both bands have dominant contributions from Si $p_z$ orbitals.

Looking at a more general picture, the energy of 1.95 ± 0.10 eV is also close to the prominent peak at 1.7 eV in the calculated optical absorbance of unreconstructed, free-standing silicene [80]. Here, this maximum is related to the predicted high optical transition strength between $\pi$ bands at the $M$ point.

6. Conclusions and perspectives for applications of epitaxial silicene

Only about two years after the experimental verification of epitaxial 2D Si honeycomb lattices on silver and zirconium diboride substrates, the concerted effort by both experimentalists and theorists is now leading to a comprehensive understanding of the nature of these exciting epitaxial systems and their relation to properties predicted for phases of free-standing silicene and related 2D Si structures.

As we have attempted to show in this review, the thinnest crystalline form made of Si atoms has electronic properties dramatically different from those of silicon used in the semiconductor industry, both from those in the bulk and at the surfaces. However, since free-standing silicene is predicted not to be the lowest energy configuration of a 2D Si lattice [3] and because silicene exhibits a certain reactivity towards compounds with heteroatoms [49, 66, 81], it may be difficult to form silicene with properties resembling those of graphene.

Instead, Si honeycomb lattices can now be grown epitaxially on a number of single-crystal surfaces. Their properties are, however, to a varying degree but substantially affected by interactions with the corresponding substrates, and as it turns out, in particular with the d electrons of the uppermost metal atom layers.

Also from a practical point of view, an atom-thick material is easier to handle with a substrate as support. If epitaxial silicene should then be applied and integrated in thin film devices, it is important to consider how for this purpose the desired electronic properties can be realized.

As we have shown, the key to this engineering is naturally the interaction between silicene and its surrounding materials. For electronic or optoelectronic device applications, these materials must be (1) insulating and (2) protect the layer from environmental conditions. With regard to (1), based on a relatively large number of theoretical studies, silicene has been proposed to exhibit epitaxial relationships with a number of surfaces of insulating substrate materials such as H- and Cl-passivated Si(1 1 1) [82, 83], CaF$_2$(1 1 1) [88] and hexagonal-BN [82].

Although, unlike both Si(1 1 1) and Si(0 0 1) surfaces, silicene sheets on Ag(1 1 1) [66] and ZrB$_2$(0 0 0 1) [84] resist oxidation to some extent, epitaxial silicene is immediately oxidized once removed from the UHV environment. Our attempts to form capping layers on epitaxial silicene on ZrB$_2$(0 0 0 1) thin films suggest that neither aluminum oxide (Al$_2$O$_3$) prepared by deposition of Al atoms and subsequent exposure to O$_2$ gas [49] nor aluminum nitride (AlN) deposited at elevated temperatures using trimethylaluminum and ammonia precursors [81] are suitable for encapsulation of silicene.

In contrast, the structural integrity of epitaxial silicene is not destroyed upon deposition of either K or Al atoms [24, 49]. K adsorption has been found to lead to charge donation to the silicene lattice and an increase of the hybridization between the silicene- and diboride-related electronic states [24]. Since charge donation leads to stronger interactions at the interface, it is anticipated that charge withdrawal will result in the weakening of the interactions, which may lead to epitaxial silicene with free-standing silicene-like properties.

Silicene may also be applied in order to integrate silicon-based semiconductor and organic electronics. For hybrid organic/semiconductor junctions, interfaces should ideally be well defined in a way in which two crystalline materials can epitaxially be combined. In our yet unpublished work [85], epitaxial silicene on diboride thin films has been demonstrated to serve as a template for the epitaxial growth of thin crystalline films of the small organic molecule anthracene. While due to the site-specific charge distribution associated with the buckling of silicene, the interactions between anthracene and silicene are enhanced [85] with regard to graphite (0 0 0 1) [86], epitaxial silicene is much less reactive than silicon surfaces with dangling bonds [85].

While the science and technological progress of 2D Si materials remains challenging, their unique properties provide opportunities for further engineering. For instance, a variation of the band gap could be achieved through the modification of the buckling, either through external applied mechanical stress or through epitaxial growth on appropriate substrates with selected lattice parameters [38]. The existence of a band gap is important for electronic devices that perform logical operations or emit light.

Since Si-based technologies are restricted by top-down approaches, the use of ultimately thin Si structures provides not only an alternative way to achieve the future miniaturization of existing technologies but also completely new quantum-physical effects to be used in nanoscale devices with novel functions.
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