SILICENE, A PROMISING NEW 2D MATERIAL

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Abstract:

Silicene is emerging as a two-dimensional material with very attractive electronic properties for a wide range of applications; it is a particularly promising material for nano-electronics in silicon-based technology. Over the last decade, the existence and stability of silicene has been the subject of much debate. Theoretical studies were the first to predict a puckered honeycomb structure with electronic properties resembling those of graphene. Though these studies were for free-standing silicene, experimental fabrication of silicene has been achieved so far only through epitaxial growth on crystalline surfaces. Indeed, it was only in 2010 that researchers presented the first experimental evidence of the formation of silicene on Ag(110) and Ag(111), which has launched silicene in a similar way to graphene. This very active field has naturally led to the recent growth of silicene on Ir(111), ZrB₂(0001) and Au(110) substrates. However, the electronic properties of epitaxially grown silicene on metal surfaces are influenced by the strong silicene-metal interactions. This has prompted experimental studies of the growth of multi-layer silicene, though the nature of its “silicene” structure remains questionable. Of course, like graphene, synthesizing free-standing silicene represents the ultimate challenge. A first step towards this has been reported recently through chemical exfoliation from calcium disilicide (CaSi₂). In this review, we discuss the experimental and theoretical studies of silicene performed to date. Special attention is given to different experimental studies of the electronic properties of silicene on metal substrates. New avenues for the growth of silicene on other substrates with different chemical characteristics are presented along with foreseeable applications such as nano-devices and novel batteries.

48	<u>Outline</u>
49	
50	1-Introduction
51	2-Silicene growth on Ag(110)
52	2.1 Formation of Silicene nanoribbons on the clean Ag(110) surface
53	2.2 Calculations of Silicene nanoribbon structures on the clean Ag(110) surface
54	3-Silicene growth on Ag(111)
55	3.1 Experimental observations of Silicene on Ag(111).
56	3.2 Calculations of the different Silicene structures on Ag(111).
57	4-Silicene growth on other surfaces
58	4.1 Silicene on Au(110)
59	4.2 Silicene on Ir(111)
60	4.3 Silicene on other metals - Pt(111)
61	4.4 Silicene on ZrB ₂ (0001)
62	4.5 Silicene on an insulator - LaAlO ₃ (111)
63	5-Chemical synthesis of Silicene
64	6-Future directions:
65	6.1 Silicene for Li-ion Batteries
66	6.2 Silicene for devices
67	7-Conclusion

1-Introduction

The discovery of the exotic nature of graphene in 2004 [1-4] has stimulated a growing interest in the silicon and germanium counterparts, namely silicene and germanene. The obvious question was whether silicene and germanene could be fabricated and would they exhibit similar properties to those of graphene [5-7]. The main difference between carbon and silicon or germanium is the tendency to form sp^2 hybridization for the former and sp^3 for silicon and germanium, as is reflected by the fact that Si/Ge bulk presents a diamond structure while carbon is more often present in a graphitic structure.

Theoretical investigations of free-standing silicene and germanene showed that these 2D systems had the potential to be stable with properties similar to those of graphene, provided that they could be fabricated [5-6]. These calculations suggested that free-standing silicene presents a linear dispersion with a Dirac cone at the Brillouin zone corners and consequently, as in graphene, its charge carriers behave as massless relativistic particles. However, early calculations of free-standing germanene indicated that the K-points were above the Fermi level so that the germanene layer behaved as a poor metal [8]. Nevertheless, all expectations held for graphene, such as high-speed electronic nanometric devices based on ballistic transport at room temperature (RT), could be applied to these new materials with the advantage of being directly compatible with existing semiconductor technologies. Over the last couple of years, a number of theoretical calculations have been made to study the electronic, structural and magnetic properties of silicene and other 2D materials. Silicene and germanene have a larger spin-orbit coupling strength than graphene [9]. Recent calculations have shown that the spin-valley electronics structure of silicene leads to exotic effects; namely, it has potential giant magneto-resistance and acts as a spin filter [10], it is also a topological insulator [11]. Both of these properties imply a quantum spin Hall effect which should be detectable by optical adsorption measurements. Other calculations have

shown that defects have smaller energy barrier to formation than their equivalent on graphene but they do not self-heal because the buckling stabilizes the defect [12]. Calculations have also shown that the electronic and magnetic properties of silicene are in controllable under an external electric field [9] and the charge transport characteristics in a gate-controlled device can be modulated as a function of the doping [13]. Indeed, calculations showed that the adsorption of B, N and P atoms induce p-type doping while Al induces n-type doping [14].

Experimentally, only a few studies have been performed on the Ge/Ag [15-18] and Si/Ag systems [7,19-22]. However, clear evidence for the formation of 2D silicene honeycomb structures for the Si/Ag system has only been shown recently [7,19-21]. Silicene can form either an assembled parallel array of 1D nano-ribbons (NRs) on Ag(110) [7,19,22] or a highly ordered sheet on Ag(111) [7,23-31]. Successful formation of silicene has been also reported on other surfaces including ZrB₂(0001) [32], Ir(111) [33] and very recently on Au(110) surfaces [34].

The majority of studies were performed under ultra-high vacuum (UHV) because both the metal surface and the silicon deposition require atomically clean conditions. This is a time-consuming and expensive process. Hence, the biggest challenge is the chemical synthesis of silicene. The chemical processes should provide an alternative route to large-scale synthesis of 2D silicon nanomaterials under production conditions. Only a few studies have investigated the synthesis of 2D silicon structures [35-37]. The starting point is the inorganic solid CaSi₂ which has a structure of interconnected Si₆ rings forming hexagonal 2D silicon sheets held together in planar monolayers by Ca²⁺ ions [35-37].

In this review paper, we will present the current state of the art of silicene. We will present new avenues for the growth of silicene along with foreseeable potential applications of silicene.

2-Silicene growth on Ag(110)

2.1 Formation of Silicene nanoribbons on the clean Ag(110)

A sub-monolayer deposition of silicon on Ag(110) at room temperature (RT) results in the formation of one-dimensional silicene structures [38]. The STM images clearly show isolated ribbons all oriented along the (-110) direction [38-40]. It is remarkable to observe that the ribbons all have exactly the same width of 1.6 nm as shown in Figs. 2.1(a) and (b). The higher resolution STM image in Fig. 2.1(b) shows that the isolated Si nanoribbons (NRs) have an internal structure composed of six-atom blocks aligned along the nanowires. Each block has the form of a square joined to a parallelogram with a ridged profile (Fig. 2.1c). From a visual inspection of the STM images, a hexagonal structure is not visible. In fact, DFT structure calculations were necessary to reveal the hexagonal structure of the Si nanowires [41]. These calculations showed that the interaction between the Density of States (DOS) of the Ag atoms and a buckled Si NRs could explain the structure observed in the STM images [19].

Fig. 2.1: Topographic images ($V = -1.7$ V and $I = 1.1$ nA) of 0.25 Si ML deposited on Ag(110) at room temperature showing Si NRs : (a) 42×42 nm², (b) 12.1×12.1 nm². (c) Line profile along the black line drawn in (b) (reproduced from [38]).

The electronic properties of silicene NRs grown on Ag(110) have been investigated by a number of different experimental techniques including valence band and core-level photoemission spectroscopy [38]. The metallic character of the silicene NRs is indicated by an increase of the Density of States at the Fermi level compared to that of the bare silver surface (Fig. 2.2) [38]. Discrete electronic states appear in the valence band, dispersing along the (-110) direction while being confined along the (100) direction indicating that the Si-NRs host a quantum confinement of the electronic states [38,42].

Fig. 2.2: Normal incidence valence band angle integrated spectra measured at $h\nu = 74$ eV for the initial pristine Ag(110) surface (bottom curve) and after 0.25 monolayer of silicon deposited at room temperature (top curve) (reproduced from [38]).

The Si $2p$ core-levels were also studied by photoemission spectroscopy and the spectra were fitted with two narrow spin-orbit split components (Fig. 2.3), these components are a signature of

an ordered silicene structure [38]. The spectra present an asymmetric line shape which indicates that silicene NRs have a metallic character. Angle resolved photoemission spectroscopy (AR-PES) measurements have been also performed in normal incidence. After growing silicene NRs on Ag(110), the presence of a linear dispersion along the (-110) direction was observed, which was interpreted as a Dirac cone [43-44].

Fig. 2.3: Si 2p core level spectrum and its deconvolution in two asymmetric components (bottom curves). The spectrum was recorded at normal incidence and at $h\nu = 140$ eV; the emission angle was 45° . (reproduced from [38]).

The structural ordering of the Si NRs could be improved by adjusting the temperature of the substrate and silicon coverage. Indeed, if the deposition of one silicon monolayer is made under ideal conditions with the Ag(110) substrate at 230°C [22, 45], a self-assembled array of silicene NRs can be grown as Figure 2.4a shows. Along the [-110] direction, the Si-NR array shows a (x2) periodicity (Fig. 2.4c), whereas across the NR the periodicity is 2 nm corresponding to x5 or $\sim 5 a_{\text{Ag}}$ (Fig. 2.4b). In addition, the temperature of Ag(110) substrate was shown to be a critical

parameter, for the width of the NRs [46]. Depending on the substrate temperature, NRs with different widths were obtained (0.8 nm, 1.6 nm) and correlatively a (3x2) grating of 0.8 nm wide NRs was also observed [46]. It was also previously observed that a post-deposition annealing leads to a significant elongation of the NRs [38]. This indicates that the basic building blocks of Si clusters that form the wires can diffuse across the metal surface. The formation of these NRs is the result of anisotropic diffusion combined with a higher reactivity of the ends of the NRs [22,38].

Fig. 2.4: (a) STM image of Silicene NRs grown at 230°C on a Ag(110) surface ($15 \times 15 \text{ nm}^2$, $V = -80 \text{ mV}$, $I = 2.2 \text{ nA}$), (b) line scan across the NR showing the x5 periodicity, (c) line scan along the NR showing the x2 periodicity. (reproduced from [22]).

Fig. 2.5: High resolution filled state STM image revealing the honeycomb arrangement (reproduced from [19]).

By reducing the bias voltage and increasing the current we can modify the observable internal structure of the NRs as Figure 2.5 shows [19,22]. This can be seen in detail in Figure 2.6a which displays an atomic resolved STM image of silicene NRs showing clearly a honeycomb arrangement highlighted by the red hexagons. The STM images recorded at both positive and negative bias voltage show the same features which indicate that they show mainly the surface morphology. The distance between the first nearest protrusions of this honeycomb structure is equal to 0.335 nm. This distance is larger than the expected Si-Si distance of 0.235 nm, indicating that the protrusions observed in the STM image in Figure 2.6a do not correspond to first neighbour Si atoms. Based on these experimental observations, we derive a structural model which is displayed in Figure 2.6b. In this model we assign the protrusions observed in STM to the two second nearest neighbour silicon atoms of an armchair-edge terminated silicene NR. Thus the protrusions in the STM image (red hexagons) have a $\sqrt{3}$ periodicity with respect to the honeycomb lattice of the silicene NR. The periodicity of the armchair edge of the NR fits the x2 periodicity along the Ag $[\bar{1}10]$ direction if we set the lateral in-plane Si-Si distance to 0.193 nm. This gives a distance of 0.335 nm for the $\sqrt{3}$ structure between the two second nearest silicon atoms in agreement with that measured from the STM image (Figure 2.6a). Hence we conclude that all Si atoms are not resolved by the STM topography. This is consistent with a buckled NR.

Fig. 2.6: (a) Atomically resolved filled-states STM image of silicene NRs grown at 230°C on a Ag(110) surface ($8 \times 8 \text{ nm}^2$, $V = -0.2 \text{ V}$, $I = 1.9 \text{ nA}$). (b) Proposed model showing that silicene NRs are buckled. Green and gold atoms correspond to the first and the second silver layer respectively. The blue honeycomb structure corresponds to the internal structure of silicene NRs while the red one corresponds to the one observed on the STM image (reproduced from [22]).

This nearest neighbour Si-Si distance of 0.193 nm is close to the one reported for the silicene sheet on Ag(111) [21]. This model is also supported by recent studies reporting corrugated silicene [20,25,41] with a buckling of between 0.04 and 0.12 nm. By projection, this would explain why even with a Si-Si bond length of 0.235 nm, such relatively small in-plane distance of 0.193 nm is observed. This first neighbour Si-Si distance is close to those reported for silicene sheets (0.20, 0.22, 0.25 nm) [7,20-21]. The experiments did not reveal any reconstruction of silicon atoms at the edge of the NR. However, theoretical studies have explored the structural stability of freestanding silicene NRs with zigzag, Klein and pentagon-heptagon edges reconstructions [47].

It has been argued recently that an anomalous tip effect could also lead to a misleading honeycomb-structure in STM topography [46]. However, in this study a huge tunnelling current of 50 nA was used. Under these conditions, the proximity of the tip to the surface and the high

current density will inevitably induce strong tip instabilities and an anomalous tip effect. Even if the imaging of the honeycomb structure of the NRs is not straightforward, similar difficulties have been encountered on other well-known systems such as graphite. This phenomenon caused controversial theories in the case of graphite [48]. For silicene NRs, a number of points remain to be clarified, including their atomic structure. Here, surface X-Ray diffraction should remove any remaining doubts as to their true atomic structure.

Very recently, it was claimed that “thick multilayers of silicene” having a “graphite-like” structure were synthesized on Si/Ag(110). The silicene multilayers display a pyramidal cross-section in STM topography [49]. However, it turned out that these new nanostructures can be obtained on Ag(110) even at low silicon coverage if the temperature of the substrate is beyond 490K [46, 50] which contradicts the previous results [49]. Indeed, a very detailed study based on STM and LEED measurements describe these structures as “nanodikes” and “nanotrenches” resulting from the faceting of the silver substrate induced at high temperature by silicon deposition [50]. The lateral facets of these nano-pyramids present a stepped structure with a vertical periodicity of 0.3 nm (consistent with the $a_{\text{Ag}[110]}$ interlayer distance) and a well-defined average slope of $\pm 19.5^\circ$ corresponding to the (221) and (22-1) crystallographic faces of silver. According to the STM images, NRS identical to the ones grown on the flat Ag(110) surface are formed on the top of these “nanodikes”, or on the base of the “nanotrenches”, whereas the silver facets present a (1x2) reconstruction displaying the same (x2) periodicity as the NRs along the [-110] direction [50]. This study rules out the formation of multilayers of silicene on Ag (110).

Recently, a study based on GIXRD measurements concluded that the silver substrate undergoes a missing-row reconstruction when it is covered by silicene NRs [51]. However, no structural model of the NRs was derived from these latter GIXRD measurements. The interaction between

the silver and silicon atoms was considered in the first studies which described the NRs as asymmetric structures inducing significant displacements of the silver atom chain on one side of each NR [19, 41, 52]. The discrete electronic states near the Fermi level observed in valence-band photoemission measurements [38, 43] were also attributed to the confinement of hybridized Ag and Si electronic states [41].

The oxidation process of the Si NRs was also studied by STM and PES [53]. Molecular oxygen exposition of the surface was performed at RT at several doses. STM images demonstrated that only the ends of the ribbons are reactive to oxidation. The oxidation process starts propagating along the $[-110]$ direction when the oxygen dose is increased.

The atomic structure of the NRs is still puzzling. The lack of a clear structural model for the NRs is detrimental to our understanding the electronic properties of this system. The formation of the discrete electronic states is not yet completely understood, and the discussion about Dirac cones remains highly controversial.

2.2 Calculations of Silicene nanoribbon structures on the clean Ag(110) surface

In the previous section, we have shown that silicene NRs grown on Ag(110) usually have a width of $16\text{\AA}$ which gives a 2×5 superstructure with respect to the underlying Ag surface. The first theoretical attempt to study these nano-ribbons was performed by Guo-Min He using density-functional theory [54]. In this study, it was proposed that silicon dimers form the building blocks of the Si NRs. However, this was constructed on a constrained 2×5 rectangular motif, which is not compatible with the experimental observation. Another structure was needed to match the observed STM image; a structure that would reproduce the detailed features.

Subsequently, we started a comprehensive study of the energetics and electronic structure of these SiNRs. This study used density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [55-57]. Exchange-correlation interactions were included within the generalized gradient approximation (GGA) in the Perdew-Burker-Ernzerhof (PBE0) form [58]. The electron-ion interaction was described by the projector augmented wave method [59-60]. A cut-off of 250 eV for the plane-wave energy was used for all calculations and it was enough to capture the edge reconstruction of the Ag substrate as can be seen clearly in figure 2.7 (right).

The bulk lattice constant for Ag was found to be 4.175 Å using a k-point mesh of 10×10×10. The slab supercell approach with periodic boundaries was used to model the surface; this consists of 5 layers of Ag(110) each containing 24 atoms (4×6). The Brillouin zone sampling by a (3×2×1) k-points mesh, is based on the technique introduced by Monkhorst and Pack [61]. The whole system was allowed to relax to the optimum configuration (with forces on every atoms less than 0.01 eV/Å), with the bottom layer atoms kept fixed.

In order to determine the exact atomic structure of the SiNRs on Ag(110), one needs atomically resolved STM images. These were not available in the early experimental studies. It was not possible either to screen tens (or hundreds) configurations as the system is relatively large. Hence, a different approach was adopted where the starting point, was the periodicity of the system and the fact that silicon atoms would form a honeycomb. A few configurations containing between 27 and 36 Si atoms per unit cell were studied, using DFT. The resulting STM images were compared in great detail with the observed one. As a criterion of selection, we had to use the presence of the observed prominent STM features mentioned, and found out that only the Si₃₀ (the Si₃₀ configuration consists of 4 hexagons) provided the most clear and unambiguous STM image. In Fig. 2.7 (left), we show the charge density in a plane just above the highest Si

atoms. This charge density presents the same characteristics as those in the observed STM images. The protrusions seen in the observed STM images are actually formed by 9 Si atoms out of 30, sitting at a higher position than the other Si atoms. This shows how a corrugated honeycomb structure may appear give a square symmetry.

Fig. 2.7: Charge density (left) in a plane parallel to (110) containing the topmost Si atoms, shown in the top view (right) as yellow with the other Si atoms shown as red. The Ag(110) surface layer atoms are shown as dark blue (reproduced from [40]).

If the Si NRs maintain their honeycomb structure after full relaxation, their atomic position, especially the vertical one, experienced substantial change. A side view (Fig 2.8) shows that Si NRs present a curved shape with the substrate layers experiencing buckling. The substrate surface atoms are more affected on one side than the other. As can be seen on figure 2.7 (right), the Ag edge atoms on the left side of the NR are not aligned, as they would be in the clean surface, but rather show a reconstruction, giving the Si-NRs an asymmetric shape.

This asymmetry is also reflected in the electronic structure of the system, as shown in Fig. 2.8, where the charge density, in a plane through the SiNR (perpendicular to the (110) plane) is plotted. This “arch-shaped” configuration explains the “bump” seen in the measured STM images [38].

Fig. 2.8: Charge density (top) in a plane perpendicular to the (110) plane cutting the ribbon across the width and containing some top most Si atoms. A side view (bottom) shows the curved shape of the nanoribbon (Si atoms are coloured red and Ag(110) surface atoms are coloured dark blue). (reproduced from [19]).

The electronic structure of these SiNRs adsorbed on Ag(110) also show interesting features. As we have shown, the atomic structure of both the Si NRs and the substrate are substantially altered, which in turn induces changes in the electronic structure of the system. Because of this strong interaction, the Si NRs are metallic, in accord with a recent study [62]. These Si NRs also induce the appearance of new states near the Fermi energy, revealing a strong hybridization between the states of the substrate atoms and the Si NRs atoms. When comparing the positions of these new interface states with the free standing Si NR, we found that they coincide at the same energies, which allows us to conclude that the observed new interface states close to the Fermi energy are due to a tandem of confinement-hybridization.

3-Silicene growth on Ag(111)

3.1 Experimental observations of Silicene on Ag(111).

The (111) face of transition metals is usually composed of a hexagonal close packed (*hcp*) array of atoms. This dense phase is isotropic with a smooth surface potential and such surfaces are ideal for the formation of two dimensional sheets or thin films [63-64]. The clean Ag(111)

surface forms this dense hexagonal surface as the STM image in Figure 3.1a shows. The deposition of one monolayer (ML) of silicon on the bare Ag(111) substrate leads to the formation of a $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ superstructure visible in the LEED (not shown). The first STM observations revealed, a continuous, almost defect free, two dimensional (2D) sheet of silicene, formed over large areas in a $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ registry with the underlying Ag(111) surface [21]. Figure 3.1b shows the atomic resolved STM image of this highly ordered honeycomb lattice silicon structure.

Fig. 3.1: (a) Filled-state atomically resolved STM image of the clean Ag(111) surface. (b) Filled-state atomically resolved STM image of the same sample (without any rotation) after deposition of one silicon monolayer. (c) Line-profile joining neighbouring Si atoms along the direction (A) indicated in Fig. 3.1-a. (reproduced from [29]).

In a subsequent study, Le Lay et al. claimed that the STM image of the honeycomb $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ structure did not correspond to a silicene layer but instead to the bare Ag(111) surface [65]. They argued that the observed honeycomb structure was due to a contrast inversion, in other words to a graphically inverted image or to a tip effect. A careful inspection of the experimental observations shows the following: First, the basal chains of the honeycomb silicene sheet are clearly rotated by an angle of $(30-19.1)^\circ = 10.9^\circ$ with respect to the axes of the Ag(111), exactly matching the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ superstructure. In the case of an inversion of contrast of the

STM image of the bare silver surface, the angle between the observed honeycomb structure and that of the bare Ag(111) would be 0° and not 10.9° . Second, the line profile along line (A) gives a projected Si-Si lateral distance of 0.2 nm due to the buckling of the Si-Si bonds (Figure 3.1c). Third, the height difference between the up and down Si atoms of each Si-Si bond is 0.02 nm. The (111) surface of silver has a smooth density of states which gives a small corrugation of 0.02 nm and a perceived buckling of 0.002 nm [65]. This is 10 times smaller than the corrugation and buckling observed in the STM images of the honeycomb $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ superstructure [21]. It is clear that the arguments of Le Lay et al. simply don't stand up to a rigorous analysis. In any case, the existence of the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ superstructure has been also confirmed by several authors using STM [26] and LEED [66-67]

Following the pioneering work of reference [21], studies of the growth of silicene on Ag(111) surface revealed the existence of further ordered phases with respect to the Ag(111) unit cell; in addition of the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ described above, the (4×4) and $(\sqrt{13}\times \sqrt{13})R13.9^\circ$ superstructures have also been found [23,25-26,31,66-71]. These ordered phases can be obtained by varying the substrate temperature during the silicon growth and a detailed study has shown that they correspond to different orientations of the silicene sheet relative to the Ag(111) surface [20,30-31]. The observed silicene periodic structures are most often, as in the present paper, referred with respect to the substrate Ag(111) unit cell. However, from time to time, they are also referenced with respect to the hexagonal silicene structure. Therefore, it is useful to recall here the correspondence between the two sets of silicene superstructures: The (4×4) supercell relative to the Ag(111) surface is equivalent to the (3×3) relative to the silicene sheet, the $(\sqrt{13}\times \sqrt{13})R13.9^\circ$ supercell relative to the Ag(111) surface is equivalent to the $(\sqrt{7}\times \sqrt{7})R19.1^\circ$ of

the silicene sheet, and the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ supercell relative to the Ag(111) surface is equivalent to the $(\sqrt{7}\times\sqrt{7})R19.1^\circ$ of the silicene sheet.

One of the properties of silicene that has prompted a great deal of interest and discussion is the presence of a Dirac cone at the crossing points of the surface states in the Brillouin zone as is observed in graphene. Early calculations predicted that free-standing silicene would have a Dirac cone [5-7], so it has been a logical question since as to whether the Dirac cone is preserved or not when silicene is grown on a supporting substrate. Two groups have tried to show the existence of Dirac fermions in silicene on the Ag(111) surface [24,71]. Vogt et al. studied the electronic structure of (4×4) silicene structure by angular-resolved photoemission spectroscopy (ARPES) [24]. They found a linear dispersion near the K point of Brillouin zone of silicene. They attributed this linear dispersion to silicene with a Dirac point at 0.3 eV below the Fermi level. From the dispersion, the Fermi velocity was estimated to be $1.3 \times 10^6 \text{ ms}^{-1}$ which is even higher than the value reported for graphene. However, they did not show the expected *sp* band of the bare Ag(111) surface, which raised doubts about their result. The second investigation of the existence of Dirac fermions in silicene on Ag(111) surface was reported by Chen et al. [71]. They studied the silicene structure using scanning tunnelling spectroscopy (STS). Quasi-particle interference (QPI) patterns at the surface of silicene were observed and the Dirac cone was deduced from the linear dispersion curve obtained from the STS curves [71]. However, more complete experiments [72] revealed that the limited energy range in STS measurements of reference [71] led to a wrong conclusion concerning the band dispersion. Furthermore, STM measurements recorded under high magnetic field by Lin et al. found that the discrete Landau levels expected in the case of massless carriers were absent [73]. Hence, the authors concluded that the carriers in the (4×4) silicene do not show a Dirac cone. The interpretation of the single-layer silicene photoemission

data presented by Vogt et al. has been also questioned on the basis of band structure calculations [74]. Indeed, these theoretical analyses propose that the experimentally reported bands should in fact be attributed to the Ag *sp* states. The calculations revealed that the Dirac cone in the (4x4) silicene phase is destroyed as a result of the strong band hybridization between silicene and the Ag surface. Very recently, Mahatha et al. [75] performed the same experiment as Vogt et al. [24] in order to prove or disprove the presence of the Dirac cone. They performed a detailed ARPES study coupled with density-functional theory calculations of the (4x4) silicene structure. They found that silicene on Ag(111) does not retain the Dirac cone at all due to the hybridization of silicene and silver states. Their result contradicts completely the linear dispersion observed by Vogt et al. [24] and Chen et al. [71]. The current understanding of the absence of the linear dispersion of silicene is that the bare Ag(111) shows the *sp* branch in the ARPES measurements as a linear dispersion near the K point of (4x4) silicene. The *sp* states are still observed even after the growth of the (4x4) silicene sheet indicating that the linear dispersion observed by Vogt et al. corresponds simply to the *sp* branch of silver.

As a result of these studies, our understanding of the importance of the silicene-substrate interaction has been made clear. To overcome this obstacle, one possible avenue is to deposit a more silicon to make multilayer silicene. Again, graphene has provided inspiration in that multilayer graphene is decoupled electronically from the substrate. We could reasonably expect the silicene-substrate interaction to decrease as the thickness of silicene increases. In addition, if we succeed in growing silicene multilayers, this will have a very high impact in the integration of this 2D atomic material into electronic devices.

Vogt et al. have pursued this avenue with the study of the epitaxial growth of multilayer silicene on the Ag(111) [76]. Based only on STM and LEED measurements, they claim to have grown

silicene stacks, consisting of a number of atomic layers, where the lowest one has the (4x4) structure and the subsequent layers have the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure [76]. Acun et al. came to a very different conclusion based on their LEEM and micro-LEED experiments [67]. They studied the formation and the stability of silicene layers on a Ag(111) substrate and found that silicene layers are intrinsically unstable with respect to the formation of an “sp³-like” hybridized, bulk-like silicon structure. This diamond-like structure of the multilayers is reported in another study by A. Shirai et al. who observed the multilayers by low-energy electron diffraction [77]. Their data are consistent with silicon multilayers on Ag(111) with diamond-like silicon termination close to the Si(111)- $(\sqrt{3}\times\sqrt{3})R30^\circ$ -Ag surface. They concluded that the $(\sqrt{3}\times\sqrt{3})R30^\circ$ observed by Vogt et al. [76] is the result of segregation of Ag atoms to the top of the bulk-like multilayer silicon. This has been also recently confirmed by A.J. Mamix et al [76]. The model is similar to the one previously observed in the case of the Ag on Si(111) surface [79-80]. At this time, more experimental and theoretical studies are needed before reaching a conclusion on the evidence of silicene multilayers.

3.2 Calculations of the different Silicene structures on Ag(111).

Since the first experimental evidence of the synthesis of silicene on Ag(111) [21], several theoretical investigations of the different structures of silicene on Ag(111) have been performed [6,70,75,81-93]. All these studies point to the fact that as silicene is slightly incommensurable with the Ag(111) substrate, several stable configurations co-exist. The consequence of this is a strongly corrugated silicene layer by as much as 1 Å, much larger than the intrinsic buckling of 0.4 Å of the free-standing silicene. In turn, the electronic structure of silicene is strongly altered compared to that of free-standing silicene. It was found in most cases that the adsorbed silicene is metallic and the Dirac cone is absent. The calculations also show that the reported linear

dispersion is actually a feature of the Ag(111) electronic structure. Here, we will briefly describe some the calculated characteristics of these silicene on Ag(111) configurations; namely the (4x4), the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ I and II, the $(\sqrt{13}\times\sqrt{13})13.9^\circ$ I and II and the $(\sqrt{7}\times\sqrt{7})R9.1^\circ$.

The computational details are similar to those described for the Si NRs on Ag(110). The Brillouin zone sampling was performed with a $(3\times 2\times 1)$ mesh of k points. The slab comprised 5 layers of Ag(111). A hexagonal 2D sheet of silicene is adsorbed for each configuration as shown in the respective figure. The coordinates of all atoms were allowed to relax to the optimum configuration until the forces on every atom were < 0.01 eV/Å. The Tersoff-Hamann model [94] was used to simulate the scanning tunnelling microscopy (STM) images. We start with the (4x4) as shown in Figures 3.2a (top view) and 3.2b (side view).

Fig. 3.2: the top (a) and side (b) view corresponding to the (4x4) structure and (c) the calculated STM image (reproduced from [20]).

We note here that the silicon atoms lie on the silver surface at different heights ranging from 2.2 Å to 3.0 Å. The substrate surface atoms also experience modifications in their positions resulting in a buckling of the top Ag layer of 0.4 Å. The nearest neighbour Si-Si distance in this structure is

2.35 Å, with a lateral distance of 2.23 Å which would be measured in an STM image. For this configuration, the average binding energy per silicon atom is 0.46 eV. The Si atoms closest to the substrate bind more strongly than those Si atoms further away from the substrate. The corresponding STM image, shown in Fig. 3.2c, is in very good agreement with that observed experimentally.

Fig. 3.3: the top (a) and side (b) view corresponding to the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ -I structure, (c) STM image (reproduced from [20]).

The second configuration we have studied is the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ -I that we show in Fig. 3.3a (top) and Fig. 3.3b (side). For this configuration, the buckling of the silicene sheet is significantly higher at about 1.5 Å. Again the large distortion of the silicene sheet induces changes in the electronic structure in such a way that the system is metallic. The nearest neighbour Si-Si distance in this model is the largest at 2.51 Å, but due to the large buckling the observable lateral distance will only be 1.99 Å comparable to that observed by Lalmi et al. [21]. As the buckling in the silicene sheet is large, the calculated STM image (Fig. 3.3c) shows protrusions that correspond to the highest silicon atoms. However, the calculated does not match the observed STM image so well.

The third superstructure we present here is the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ\text{-II}$ where the silicon atoms are translated with respect to the Ag(111) surface compared to the previous model as shown in figures 3.4a (top view) and 3.4b (side view). In this configuration, the silicon hexagons surround either bridge or on top sites.

Fig. 3.4: the top (a) and side (b) view corresponding to the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ\text{-II}$ structure and (c) the corresponding STM image (reproduced from [20]).

The buckling in this configuration of $1.0 \text{ \AA}$ is smaller than the first $(2\sqrt{3}\times 2\sqrt{3})R30^\circ\text{-I}$ structure ($1.5 \text{ \AA}$). This smaller buckling is reflected in the corresponding STM image that compares very well with the measured one. The nearest neighbour Si-Si distance varies between $2.28 \text{ \AA}$ and $2.37 \text{ \AA}$; with a projected lateral distance of $2.0 \text{ \AA}$, in good agreement with the one observed by Lalmi et al. [16]. In summary, these two $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ configurations show the same LEED pattern but very different STM images pointing to the necessity to use multiple tools to study silicene on Ag(111). Hence several configurations yielding the same LEED pattern may show different STM images because a slight translation of the silicene on top of Ag(111) induces dramatic changes in the STM images.

Fig. 3.5: the top (a) and side (b) view corresponding to the $(\sqrt{13}\times\sqrt{13})13.9^\circ$ -I structure, and (c) the corresponding STM image (reproduced from [20]).

We continue with the study of the observed superstructures of silicene on Ag(111) and this time we turn our attention to the $(\sqrt{13}\times\sqrt{13})R13.9^\circ$. As for the $(2\sqrt{3}\times2\sqrt{3})R13.9^\circ$, there are two observed structures that differ by a simple translation. The top and the side views of the $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ -I are shown in Fig. 3.5a and Fig. 3.5b. It is obvious from Figure 3.5b that the silicene sheet is substantially buckled, with a buckling of about 1.2 Å. The nearest neighbour silicon-silicon distance is either 2.35 Å or 2.43 Å in this structure; and the projected lateral distance is 2.34 Å. In figure 3.5c, we show the corresponding calculated STM image, and again we notice the remarkable agreement with the experimentally determined images [30].

We proceed with a comparison of this first $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ -I structure with the topologically similar structure, which differs by a translation of the silicene sheet as shown in figures 3.6a (top view) and 3.6b (side view). This is the $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ -II structure.

Figure 3.6: the top (a) and side (b) view corresponding to the $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ -II structure, and (c) the corresponding STM image (reproduced from [20]).

This configuration shows the lowest buckling in the silicene sheet of $0.7 \text{ \AA}$, however the buckling in the silver top layer is $0.4 \text{ \AA}$. The nearest neighbour distance in this configuration varies between $2.35 \text{ \AA}$ and $2.40 \text{ \AA}$, with the smallest projected lateral distance being $1.89 \text{ \AA}$. For this configuration, the work function was found to be unchanged.

The last configuration of interest here is the $(\sqrt{7}\times\sqrt{7})R19.1^\circ$ that we show in figures 3.7a (top view) and 3.7b (side view). This has the smallest unit cell of all those presented here. This is the second configuration with a relatively small buckling of only $0.7 \text{ \AA}$. There are three out of eight silicon atoms occupying the highest plane. The nearest neighbour Si-Si distance in this case was found to be between $2.32 \text{ \AA}$ and $2.34 \text{ \AA}$, while the projected lateral distance is $2.2 \text{ \AA}$.

Figure 3.7: the top (a) and side (b) view corresponding to the $(\sqrt{7} \times \sqrt{7})$ R19.1 structure, and (c) the corresponding STM image (reproduced from [20]).

In summary, the theoretically determined silicene configurations on Ag(111) were found to have a remarkably good agreement between the calculated STM images and those obtained experimentally

4-Silicene growth on other surfaces

Silicene research has evolved in the search for other substrates since the original experiments of on silver surfaces. Given the perceived instability of free-standing silicene, the first selection criterion is that of the unit cell size. This has led to number of studies on metal and even insulating surfaces with similar unit cell sizes to that of silver. Energetically, if the difference between the unit cell of the silicene and that of the supporting surface is small, then the in plane stress or strain will be at a minimum which should favour the stability of the silicene layer. In this chapter, we will review the different surfaces that have been considered and studied as a support for silicene.

4.1 Silicene on Au(110)

511 Considering that the discovery of silicene was made on silver surfaces initially, it was logical that
512 silicene could be grown on gold surfaces as well. Physically, gold behaves the same towards
513 silicon. Firstly, alloy formation is not favourable [95] so that silicon should segregate to the
514 surface, so that the formation of a silicon layer should be energetically stable. Secondly, gold has
515 the same unit cell dimension as silver (4.09 Å) [95]. Given that silicene formation on silver is in
516 part determined by the presence of the metal and that the commensurability of the hexagonal
517 silicene lattice with the surface leads to a low strain field and stable formation of silicene. The
518 same should true for silicene on gold.

519 With this in mind, we performed LEED, STM, Auger and photoemission studies of the growth of
520 sub-monolayer coverages of silicon the Au(110)-2x1 surface.

521 In our first study [96], the Au(110) substrate was held at 400°C for the deposition of silicon. As
522 the deposition progressed, the 2x1 reconstruction was replaced by a complex superstructure (Fig.
523 4.1a) which completely covers the surface after the deposition equivalent to 0.2 monolayer.
524 Atomically resolved STM images taken during the formation (equivalent to 0.1 monolayer) show
525 the new superstructure is composed of two domains whose oblique unit cells are rotated with
526 respect to the [-110] direction (Fig. 4.1b). A zoom in Fig. 4.1c shows the complex pattern in the
527 surface density of states. To understand the atomic structure, we performed DFT calculations of
528 the atomic structure using a 5-layer thick slab. A PBE potential was used and the top 3 layers
529 relaxed [59-60]. Given the 4-fold symmetry of the unit cell, 8 or 12 Si adatoms were added. After
530 relaxation, simulated STM images were calculated using the Tersoff-Hamann method with an *s*-
531 like tip [94]. However, the images obtained with only Si adatoms did not agree with the STM
532 images. Now at 400°C, the Au surface is mobile and atom exchange can occur between the Si
533 adatom and an Au atom underneath so that the Au atom migrates to the top. The best agreement

was obtained with 8 Si adatoms and 4 Au adatoms on top of Si atoms after exchange (Fig. 4.1d). This means that the observed superstructure is in fact a 2D surface alloy with a stoichiometry close to Au_3Si .

Fig. 4.1: Silicon-Gold surface alloy on Au(110). (a) LEED pattern corresponding to the superstructure obtained after the deposition of 0.2 Si ML on Au(110) kept at 400°C. Unit cell vectors corresponding to two mirror-symmetric domains of the surface alloy are indicated by the blue and red arrows, and the rectangular $p(1 \times 1)$ unit cell of the Au(110) substrate is drawn in black ($E_p = 55$ eV). (b) Atomically resolved filled-states STM image recorded after the first stage of Si adsorption (<0.1 Si ML), (60×60 nm, $V = -1.5$ V and $I = 1.7$ nA). The unit cells of the two mirror-symmetric domains are indicated in blue lines. (c) Atomically resolved filled-states STM image recorded at 0.2 Si ML showing the superstructure (11.5×11.5 nm, $V = -1.4$ V and $I = 2.3$ nA). The unit cell and the two-fold symmetry are indicated. (d) Top view of the proposed model where 8 silicon atoms occupy 4-fold sites and 4 silicon atoms are sitting just below 4 gold atoms. The Au atoms of the 1st and the 2nd monolayers are coloured in gold and grey, respectively. Si atoms are in blue. The Au atoms located on top of Si atoms are coloured in pink. The unit cell is indicated with black lines (reproduced from [96]).

In the second experiment [34], we continued the silicon growth on the Au(110) surface beyond the 0.2 monolayer coverage. The Au surface was held at 400°C during the deposition. The LEED pattern evolved further to form a sharp $\sqrt{6}$ pattern at 0.3 monolayers (Fig. 4.2a). The STM image in Fig. 4.2b reveals a network of ribbons roughly equidistant and all aligned parallel to the $[-110]$

direction. A more detailed STM image shows a relatively complicated internal structure within an asymmetric electron density (Fig. 4.2c). Each nanoribbon is 1.6 nm wide corresponding to 4x the Au lattice spacing. However, the periodicity along the length of the ribbon is (x6) the Au periodicity.

Fig. 4.2: Silicene NRs on the Au(110) surface. (a) LEED pattern recorded at $E_p = 40$ eV corresponding to the x6 superstructure is visible inside the 2×1 rectangle after the deposition of 0.3 Si ML on Au(110) held at 400°C . (b) STM image of the surface at 0.3 Si ML coverage showing the silicene NRs oriented along the $[-110]$ direction (60×50 nm, $V = -0.2$ V, and $I = 1.9$ nA). (c) High resolution STM image showing the structure of the 1.6 nm wide Si NRs. (8×8 nm, $V = -64$ mV, and $I = 3.5$ nA). (d) STM image of a Si NR showing the internal order with the asymmetry across its width (left panel). Proposed model based on the STM image and the LEED pattern (right panel). The Si NR with zig-zag edges is presented by a black honeycomb lattice. The atoms of the 1st and the 2nd Au layer are in light grey and dark grey, respectively. The asymmetry across the width of the NR is highlighted. The Au atoms corresponding to the corners of the lozenge are in blue (reproduced from [34]).

In the STM image, the surface alloy we observed previously is no longer visible between the NRs just as it is no longer visible in the LEED pattern. It would appear that the silicon adatoms and subsurface Si atoms are all integrated into these NRs. This is indeed confirmed by valence band photoemission experiments on these NRs, performed on the TEMPO beamline at the SOLEIL

synchrotron facility. The Au $4f$ spectra show two components; one corresponding to the bulk environment and the other to the surface [34]. The bulk component does not move when the Si NRs are present but the surface one does. This indicates that the shift in the surface component is due to the addition of the silicon and that it is confined to the surface. The Si $2p$ spectra also show two components indicating that the Silicon atoms have two environments. These can be equated to the edge and centre Si atoms of the NRs.

With this information, we proposed a model structure for the NRs composed of a hexagonal silicene lattice (Fig. 4.2d). With a lattice unit dimension of 0.346 nm, 5 silicene hexagons correspond to a periodicity of (x6) Au. However, the internal structure visible in the STM image (Figs. 4.2c and 4.2d) has a larger periodicity by a factor $\sqrt{3}$. This could be due to the formation of quantum interference patterns generated by electron scattering from the edges of the NRs. This Quasi Particle Interference (QPI) behaviour has been observed on graphene surfaces both at edges [97-98] and at point defects [99-100]. Recently, this has also been observed at the edges of bilayer silicene islands on Ag(111) showing a periodicity close to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern [71]. The small difference of 0.64 nm compared to 0.67 nm can be explained by the mismatch between the interference wavelength and the Fermi wavelength at the K-point as we explained for graphene [97]. Now this may not be the only explanation as interfaces states between the metal atoms underneath the nanoribbon and the silicene lattice can generate patterns with periodicities larger than the unit lattice dimensions. Nevertheless, the edge structure of the Si NRs is important; as recent theoretical calculations predict that by creating different edge structures [47] or applying an inhomogeneous electric field to such NRs will lift the spin degeneracy and allow the conduction channels to be localized within the NRs [101]. Of course this requires the formation of NRs on the appropriate substrate.

4.2 Silicene on Ir(111)

Another metal substrate for silicene growth that has received much attention recently is Iridium. The first study of silicon on the Ir(111) surface revealed the formation of a $(\sqrt{7} \times \sqrt{7})19^\circ$ superstructure following the deposition and annealing of 1 monolayer of silicon on top of the Ir(111) surface [33]. The $(\sqrt{7} \times \sqrt{7})19^\circ$ superstructure is clearly seen in both the LEED pattern and the STM images. The STM images show a regular hexagonal structure with a spacing of $7.2\text{\AA}$ and a height corrugation of $0.7\text{\AA}$. Detailed DFT calculations and simulated STM images using the Tersoff and Hamann approach were then performed to try to understand the structure of the silicon layer. The most stable configuration that matched best the STM images is a buckled silicon layer composed of an irregular hexagonal lattice of Si atoms. (Fig.4.3)

Fig.4.3: Silicene on Ir(111). (a) Zoomed-in STM image of the silicon layer. Besides the brightest protrusions, two other regions showing different contrast are indicated by the upward and downward triangles. The honeycomb feature is indicated by the black hexagon. (b) Simulated STM image, showing features identical with the experimental results in the same triangles and hexagons. (c) Top view of the relaxed atomic model of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -silicene/ $(\sqrt{7} \times \sqrt{7})R19^\circ$ -Ir(111) configuration (reproduced from [33]).

The rhombohedral unit cell contains 6 Si atoms. Those at the corners (with $\sqrt{3}$ periodicity) are raised above the plane of the Si lattice because they are positioned on top of an underlying Ir atom. The other Si atoms within the unit cell are in bridge or hollow sites. The Si atom in the *fcc* hollow site generates a small contribution to the STM image which can be seen in the detailed STM image. A final calculation of the electron localisation function [102-103] shows that the Si-Si bonding is strong and that there are no covalent bonds to the Ir atoms of the substrate. This provides clear evidence of the formation of a buckled silicene sheet on the Ir surface and has been compared with the adsorption of graphene on Pt(111) [104] as well as Hafnene on Ir(111) [105] in a recent review [106].

4.3 Silicene on other metals - Pt(111)

So far there have been very few studies on other metals. Two theory papers have investigated the adsorption of different metal atoms on a free-standing silicene sheet [107-108]. The first study investigated the adsorption of Be, Mg and Ca adatoms, finding that silicene became a narrow gap semiconductor while the adsorption of atoms such as Ti, V, Cr, Mn, Fe, Co, Mo and W resulted in the transfer of charge from the adsorbate to the silicene [107]. In the second study, adsorption of adatoms of Cu, Ag, Au, Pt and Ir were investigated as a function of adatom density [108]. The interesting result here is that adatoms of Cu, Ag and Au all induce n-type doping, while Pt is intrinsic (neutral) and Ir is p-type. A silicene field effect transistor using a p-i-n configuration of doping atoms was shown to be feasible. Another study by the same group calculated the adsorption configurations of silicene on the five full metal substrates mentioned above including Al and Mg [86]. They found two different interface structures. On the Ir, Mg, Cu and Ag substrates, the Si adatoms were distributed over several heights with significant buckling of around 1 Å or more. In the supercell commensurate with the underlying metal substrate, only one

638 Si atom is located directly on top of a substrate metal atom. Silicene forms a second type of
639 interface on Pt, Al, and Au substrates with a much smaller buckling of around 0.3 Å, which is
640 slightly less than that of free-standing silicene. This may be related to the larger mismatch on
641 these metals than for the others. The study then goes on to calculate the effect of intercalating
642 alkali metal atoms between the silicene and the transition metal substrate. The band structure
643 shows that alkali metal enable the silicene to recover the Dirac cone with the Dirac point being
644 some 0.5 eV below the Fermi level and centred on the Γ -point.

645 In this context, early studies of Si adsorption on Pt(111) found that a thin layer silicide was
646 formed [109-110]. However, the precise atomic structure could not be determined at the time. A
647 recent study using STM, AFM, photoemission and DFT calculations has shed more light on this
648 system [111]. The STM images reveal a well-ordered hexagonal structure covering most of the
649 surface. Two domains are observed, rotated with respect to each by 13°. The superstructure has a
650 $(\sqrt{19} \times \sqrt{19})$ periodicity with the atoms of the Pt(111) substrate. A detailed STM image shows
651 that the bright protrusions have a pyramidal structure, with dark triangular structures in between
652 that form a Kigome pattern (Fig. 4.4).

Fig.4.4: Characterization of the $\text{Si-(}\sqrt{19}\times\sqrt{19}\text{)R23.4/Pt(111)}$ surface structure. (a) STM image of two terraces divided by a step, each hosting one of the two domain orientations of the structure. Yellow lines denote the mutual orientation between the domains. (b) Atomically resolved STM topography of a Pt(111) region (5×7.2 nm) mostly covered with $\text{Si-(}\sqrt{19}\times\sqrt{19}\text{)R23.4}^\circ$ structure, filled states, -50 mV, 7 nA. The triangular inset shows the Δf signal obtained by a simultaneous STM/dAFM measurement in the constant height and repulsive mode. (c) The grid corresponding to the Pt atom positions on the (1×1) lattice superimposed onto the STM image. Surface lattice vectors are determined from the orientation of the main surface crystallographic axes and the periodicity of the (1×1) . (d) A blend of a high-resolution STM topography (left), a simulated STM image (centre, both at -20 mV), and the model (right) [111] (reproduced from [111]).

The ARUPS data shows Si $2p$ doublet with an energy characteristic of a silicide and the formation of strong Pt-Si bonds. The atomistic model generated from DFT calculations that fits best the STM images is a surface alloy composed of Si_3Pt tetramers. If the top Pt atom is above a Pt atom in the bulk, then it protrudes giving a bright feature in the STM image, while a top Pt atom over a 3-fold hollow site gives a darker feature. The formation of an ordered surface alloy is very similar to the Au_3Si alloy observed on the Au(110) surface [96].

670 4.4 Silicene on ZrB_2

671 In this review, we have looked so far only at metal surfaces as suitable substrates for the growth
672 of silicene layers or nano ribbons. We now discuss the first of two non-metallic crystalline
673 materials on which silicene or a silicon layer has been grown.

674 Zirconium diboride can be grown in a crystalline form by epitaxy. Thin films of ZrB_2 with a
675 (0001) surface orientation can be grown on a Si(111) substrate [112]. During the growth process,
676 silicon is segregated from the substrate to form a single Si adlayer. Synchrotron radiation
677 measurements show that this is indeed a single Si layer covering the surface [32]. Detailed STM
678 measurements show that this Si covered surface is composed of a compact layer of Si ribbons
679 each roughly 10 nm wide, caused by the stress induced mismatch between the equilibrium Si-Si
680 distances and the ZrB_2 film. This layer has a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity with respect to the (2×2)
681 lattice of the ZrB_2 substrate. By changing the scanning conditions, a hexagonal structure is
682 revealed (Fig.4.5)

Fig. 4.5: STM images of the (2 x 2)-reconstructed $\text{ZrB}_2(0001)$ surface with different length scales: (a) 20 nm x 9.5 nm, $I = 55$ pA, $V_s = 700$ mV, (b) 4.2 nm x 2 nm, $I = 600$ pA, $V_s = 100$ mV. The white lines emphasize the direction of offsets between successive domains. The (2 x 2) unit cell and the honeycomb mesh are emphasized by green and blue solid lines, respectively (reproduced from [32]).

From the photoemission spectra of the Si $2p$ valence band, it has been found that the silicon atoms occupy one of three different sites that are chemically distinct, thus the layer is buckled with the Si atoms on top of the Zr sites forming the 2 x 2 pattern. At this point, the hexagonal Si structure can be considered to be an epitaxial grown overlayer [32].

Since this initial experiment, a number of other articles have followed describing different aspects of silicene adsorption on ZrB_2 thin films. A detailed STM, STS and DFT study of the atomic structure of the silicene layer showed that the 6 silicon atoms in the silicene unit cell are in 3 different positions on top of a Zr atom, in a bridge site or in a hollow site [113]. The Si atoms sitting on top of a Zr atom show the strongest sp^2 character and so the p_z orbital contributes to the

π and π^* states. Photoemission experiments of the Si 2p valence bands also show that the silicon atoms are in several environments [114]. The study of this system has been extended to the study of the intercalation of Potassium and its effect on the band structure [115]. K adsorption results in charge transfer to the silicene layer populating the π^* states while there is increased hybridisation between the Zr d -states and Si π states. So far, there has been only one theory paper on the electronic structure and properties of this Si overlayer [116]. The particular almost planar form of silicene on ZrB_2 with only one Si per unit cell out of plane is shown to be stable due to the interplay between the Zr-Si interactions normal to the surface and the in-plane Si-Si interactions.

4.5 Silicene on an insulator - LaAlO_3

One of the key challenges standing in the way of silicene applications is the fabrication of silicene on insulating surfaces. This would enable the silicene to retain its intrinsic properties without them being strongly coupled as they are currently on any metal surface.

One promising insulating surface is lanthanum aluminate LaAlO_3 (LAO). This oxide is crystalline, has a high dielectric constant $\kappa = 24$, and is thermodynamically stable with respect to Si [117]. On the (100) face, Si grows in the form of nanoislands. These are crystalline and Si 2s photoemission measurements show that the interface with the LAO is abrupt [118]. Recent investigations of the $\text{LaAlO}_3(111)$ surface using RHEED and XPS show that a 2D silicon layer forms by epitaxy [119]. The presence of Kikuchi lines in the RHEED patterns during growth indicates that the surface remains flat, and the persistence of the integral lines indicates the formation of a 2D layer of silicon. The experiments were performed at two different surface temperatures: 300°C and 500°C. XPS spectra of the O 1s and Al 2p peaks show no evolution implying that the crystalline structure of the LAO is not modified. This is indirectly supported by

a study of Al and Si contacts on La_2O_3 which shows a mutual repulsion between the Al and Si with the Al diffusing into the substrate and the Si out of the substrate [120]. On the other hand, the Si 2s core levels presents two peaks of which one changes as a function of the substrate temperature during growth. The higher binding peak at 153.2 eV does not change and is consistent with the formation of SiO bonds. The lower energy peak at 150.5 eV does change; this is consistent with Si-Si bonds and its behaviour suggests that the silicon layer is more complete at 500°C.

These studies on LAO hold much promise for growing ordered 2D silicon layers on insulating surfaces. However, further studies especially with STM and AFM will be required before we can be sure that this epitaxial Si layer has the hexagonal structure of silicene.

5-Chemical synthesis on Silicene

Techniques for the exfoliation of layered compounds are widely used to fabricate nanometer-thick materials, such as oxides [121-122], niobates [123], chalcogenides [124], phosphates [125], and the recently discovered graphene [1-4]. Although a variety of nanosheets have been synthesized, there have been few reports of silicon nanosheets (SiNSs). Mass production of silicon nanosheets (SiNSs) without conventional vacuum processes and vapor deposition can be achieved using low cost top-down approach starting from materials that comprise a 2D sheet structure as a fundamental unit. Recently, we have developed a soft synthetic method for fabricating silicon sheets, with hexagonal graphitic-like structure resembling that of silicene, in gram-scale quantities by redox-assisted chemical exfoliation (RACE) of calcium disilicide (CaSi_2) [35, 126].

Chemical processes provide an alternative route to large-scale synthesis of 2D silicon nanomaterials under production conditions. To date, all attempts to obtain such sheet polymers by polymerization through “bottom-up process” have only led to the formation of statistical network polymers, which on average, do exhibit a three-fold coordination, but form a 3D amorphous structure rather than stacked layers [127-128]. Thus, only the topochemical transformation of layered Zintl phases including a 2D sheet structure can be used to obtain sheet polymers.

Alkali and alkaline earth silicides belong to the family of Zintl phases, in which polyanionic species formed by the tetravalent (or tetrelide) atoms [129] counter balance the electropositive metal cations [127-130]. These compounds are interesting because the Si atoms are in low coordination sites with negative oxidation states, and they form unusual low-dimensional structures such as sheets, chains or isolated polyhedra. Among the Zintl silicides, only calcium disilicide (CaSi_2) has a structure of interconnected Si_6 rings forming anionic puckered 2D silicon sheets $(\text{Si}_2)_\infty^{2-}$ held together by Ca^{2+} cations in planar monolayers (Figure 5.1). The covalent structure of the silicide layers is stable and remarkably flexible [131-133] and can be chemically modified by oxidation, leading to removal of the intercalated metal ions.

Fig. 5.1: (a) Crystal structure of CaSi_2 (cell parameters: $a = 3.855 \text{ \AA}$ and $c = 30.60 \text{ \AA}$ with space group R-3m). The large circles represent Ca atoms and the small circles represent Si atoms. (b) Silicon sheet in CaSi_2 crystal structure. (c) Weiss siloxene $\text{Si}_6\text{H}_3(\text{OH})_3$. All OH groups are replaced to H atoms in layered polysilane Si_6H_6 .

Removal of Ca^{2+} from CaSi_2 was first achieved by Bonitz et al. [134] by the treatment of a suspension of CaSi_2 in CCl_4 with gaseous Cl_2 . However, the 2D silicon sheets obtained with this method are unstable, highly reactive, and cannot be handled and characterized easily [135-136]. The synthesis of a stable siloxene sheet polymer ($\text{Si}_6\text{H}_3(\text{OH})_3$) was reported for the first time by Wöhler by the treatment of CaSi_2 in an ice-cold aqueous HCl solution [137]. During this transformation, Ca^{2+} ions are removed without destroying the polyanion layers, which then forms the backbone of the resulting sheet polymer. This material is of considerable interest due to its intense luminescence and the possibility of shifting the luminescence wavelength through substitution [138-139]. The use of a solution of HCl in methanol or ethanol instead of an aqueous solution enables the preparation of alkoxide-terminated siloxenes ($\text{Si}_6\text{H}_3(\text{OCH}_3)_3$ or $\text{Si}_6\text{H}_3(\text{OC}_2\text{H}_5)_3$) [140].

Weiss et al. in 1979 [133], proposed that the crystalline sheet polymer structure was a puckered 2D Silicon layer similar to a crystalline Si(111) layer stabilized through termination of hydrogen or hydroxide groups orientated normal the layer plane. This suggestion was later confirmed by Dahn et al. (Figure 5.1c) [141] and more recently by Nakano et al. [142] when they were able to exfoliate layered siloxene $\text{Si}_6\text{H}_3(\text{OH})_3$ into individual nanosheets with a thickness of 0.7 nm and dimensions in the range 100–200 nm by using sodium dodecyl sulfate as a dispersing agent (Figure 5.1c). This is a convenient method to synthesize $\text{Si}_6\text{H}_3(\text{OH})_3$ nanosheets, however, the silicon skeleton remains partially oxidized.

Applying the treatment at temperatures below -30°C resulted in non-oxidized silicon sheet polymer; a layered polysilane (Si_6H_6), with similar structure to $\text{Si}_6\text{H}_3(\text{OH})_3$ in which the Si atoms are terminated by hydrogen (Figure 5.1c) [143-144]. Performing the reaction at 0°C , Dahn et al. obtained the same layered polysilane Si_6H_6 [141]. However, Yamanaka *et al.* reported the formation of $\text{Si}_6\text{H}_3(\text{OH})_3$ as a by-product which was then removed by washing with a solution of HF [142].

Layered polysilane Si_6H_6 has been used for the preparation of non-oxidative silicon nanosheets by organic modification and exfoliation. The introduction of organic groups to the Si_6H_6 ring through Si-C or Si-N bonds is a plausible method to obtain SiNSs capped with organic moieties. This generates SiNSs that present a high dispersion in organic solvents and a high stability with respect to oxidation and/or hydrolysis due to formation of a hydrophobic termination of the silicon surface. In contrast to carbon, silicon ($\chi=1.90$) is less electronegative than hydrogen ($\chi=2.20$); hence Si-H bonds are polarized in the opposite sense, as $\text{Si}^{\delta+}-\text{H}^{\delta-}$. This implies that nucleophilic attacks on silanes usually occur at the silicon centers. Based on this characteristic, Nakano et al. [145] have functionalized Si_6H_6 with hexyl chains using a Pt-catalyzed hydrosilylation reaction with 1-hexene to produce a stable colloidal suspension (Figure 5.2a). The obtained product was soluble in typical organic solvents, such as hexane, chloroform, acetone, and ether, and insoluble in water and ethanol. FTIR and Si K-edge X-ray absorption near-edge structure (XANES) analyses revealed that the 1-hexene does not merely attach to Si_6H_6 , but reacts with it to form Si-C linkages.

Another method for the formation of Si-C bonds in layered polysilane Si_6H_6 was recently reported by Sugiyama *et al.* [146] The authors reported the synthesis of oxygen free, phenyl-

modified organo-silicon nanosheets with atomic thickness by the reaction of layered polysilane (Si_6H_6) with phenyl magnesium bromide (PhMgBr) (Figure 5.2b). The authors suggested that the phenyl group was successfully bonded to the silicon sub-lattice based on the fact that the material obtained as a colourless paste was soluble in typical organic solvents such as hexane, chloroform, acetone, or ether. FTIR, ^1H NMR spectroscopy, Si K-edge X-ray absorption near-edge structure (XANES) and XRD analyses have confirmed the assignment that the SiNSs are composed from $\text{Si}_6\text{H}_4\text{Ph}_2$.

Si atoms can easily accept nucleophilic attack of a lone pair from the N atoms of amine groups because the Si-H bonds in Si_6H_6 are similar to those in silyl hydride, where the bonds are polarized as $\text{Si}^{\delta+}\text{-H}^{\delta-}$. It is known that ammonia adsorbs on a Si surface by reaction with dangling bond sites without major disruption to the Si surface structure [147]. The formation of Si-N bonds upon reaction of n-alkylamines with chlorinated or hydrogenated Si surface has been reported [148-150]. Okamoto *et al.* [151] have recently reported an approach to the synthesis of oxygen-free silicon nanosheets covered with amines by reaction of Si_6H_6 with n-decylamine in chloroform at 60°C under a nitrogen atmosphere (Figure 5). Reaction progress is evidenced by a change in colour and the flotation of the Si_6H_6 . A similar change was observed when n-butylamine was used instead of n-decylamine, but not for di- or tri-n-butylamine [151]. Bubble formation observed just after pouring the amine onto Si_6H_6 implies that hydrogen is generated as a result of the reaction. IR spectroscopy, Si K-edge X-ray absorption near-edge structure (XANES) and XRD analyses permitted the authors to suggest that the binding mode in this surface modification is the reaction of the amine with Si_6H_6 [151-152]. Some Si-H bonds react with amine molecules to form Si-NH-R linkages (R: decyl group) which subsequently react through its N-H bond with another Si-H bond on Si_6H_6 to form a Si-NR-Si linkage. The final

product contains both Si-NH-R (Figure 5.2c) and Si-NR-Si linkages (Figure 5.2d) in variable proportions, depending on the reaction conditions.

Fig. 5.2: (a) Model structure of $\text{Si}_6\text{H}_3\text{C}_6\text{H}_{13}$ obtained by Pt-catalyzed hydrosilylation reaction of Si_6H_6 with 1-Hexene. b) Model structure of $\text{Si}_6\text{H}_4\text{Ph}_2$ prepared by the reaction of layered polysilane (Si_6H_6) with phenyl magnesium bromide (PhMgBr). c) and d) Optimized structure of monolayer with methylamine residue(s) that form -NR- bridge(s) between alternately adjacent Si atoms, of silicon nanosheets obtained by reaction of Si_6H_6 with amines (c) a single bridge and (d) double bridges on both sides. Methylamine was used instead of n-decylamine to simplify the calculation.

The silicon sheets prepared by hydrosilylation, the Grignard reaction or amination of Si_6H_6 were stabilized though the termination of organic groups normal to the layer plane with (111) plane structure of bulk silicon since they were prepared from layered polysilane (Si_6H_6).

The most important technique to exfoliate single layers from the parent layered silicide compound is through the adjustment of the charge on the silicon layer. Recently, this method was applied to CaSi_2 by Nakano *et al.* [36-37] who used Magnesium (Mg^{2+}) as electro-positive

element to weaken the electrostatic interaction between the Ca^{2+} and $(\text{Si}_2)_{\infty}^{2-}$ layers and to reduce the silicon charge in CaSi_2 . Mg-doped CaSi_2 , ($\text{CaSi}_{1.85}\text{Mg}_{0.15}$) was prepared by melting a mixture of CaSi , Si , and Mg and used as a precursor for the chemical synthesis of silicon sheets. The prepared $\text{CaSi}_{1.85}\text{Mg}_{0.15}$ was treated in a solution of propylamine hydrochloride ($\text{PA}\cdot\text{HCl}$), resulting in the de-intercalation of Ca^{2+} ions and the formation a light-brown suspension containing silicon nanosheets (SiNSs).

The TEM image shown in Figure 5.3, revealed a 2D structure with lateral dimensions in the range of 200 to 500 nm. The composition of the obtained monolayer SiNSs was determined by X-ray photoelectron spectroscopy (XPS) and found to be $\text{Si/Mg/O}=7.0:1.3:7.5$. Monolayer and ultrathin sheets were examined by Atomic Force Microscopy (AFM) (not shown) from which an average thickness of 0.37 nm was measured at intervals between the sheets and the substrate surface.

The Electron Diffraction pattern (Figure 5.3) confirmed that the sheet was single crystalline and the diffraction spots could be indexed as hk reflections of a hexagonal lattice with $a = 0.82$ nm, which corresponds to approximately twice of the interplanar distance of the (111) planes of bulk silicon (0.38 nm). Therefore, the exfoliation of Mg-doped CaSi_2 using $\text{PA}\cdot\text{HCl}$ produces less than 1% of surface-oxidized silicon nanosheets (SiNSs). This oxygen capping is inherent to the process, because the capping is thought to promote exfoliation when the layered silicon becomes a stable colloidal suspension by reaction with the aqueous propylamine solution. Despite these studies, the chemical synthesis of pure silicon sheets has not yet been reported.

Fig. 5.3: (a) TEM image of the sheet. (b) ED pattern recorded along the [001] zone axis perpendicular to the surface of the sheet. Reproduced from reference (reproduced from [36]).

We have recently reported the direct chemical synthesis of pure silicon sheets in gram-scale quantities using redox-assisted chemical exfoliation (RACE) of potassium modified calcium disilicide (CaSi_2) [35,126]. Let us recall that CaSi_2 is an ionic ($\text{Ca}^{2+}(\text{Si}_2)^{2-}$) material, and the reduction of the charge on the (negatively charged) silicon layers is an important step in order to weaken the electrostatic interaction between the Ca^{2+} and $(\text{Si}_2)_\infty^{2-}$ layers [36-37]. For that, we chose potassium (K) as doping element with low melting point (63.2°C), high reactivity and lower electronegativity. We proposed the following mechanism for the exfoliation process:

- (1) Diffusion of potassium (K) in CaSi_2 at 160°C , leads to the formation of a $\text{K}_{2x}\text{Ca}_{1-x}\text{Si}_{2-x}$ phase and a small amount of KSi and Ca metal driven by the reduction of some Ca^{2+} by K, as shown in the following chemical equation (5) :

(2) The obtained mixture was then treated with a degassed solution of isopropylamine hydrochloride (*i*-PA·HCl) in ethanol at room temperature for 24 hours under nitrogen. The calcium ions are de-intercalated accompanied by the evolution of hydrogen (eq. (6)) and a greenish-brown suspension was formed accompanied with an insoluble black solid which was assigned to the unreacted CaSi₂ after analysis by XRD. The SiNSs was obtained after filtration of the greenish-brown suspension with a 20% yield. These steps can be summarized by the following three chemical equations:

It is important to note that when adding the iPA.HCl solution, a strong evolution of hydrogen is observed which may be due to excess potassium oxidation (eq. (8)). The rate of hydrogen evolution involving the oxidation of de-intercalated calcium (eq. (7)) accompanied by liberation of nanosheets of silicon, decreases significantly after a few minutes.

The excess potassium reacts with iPA.HCl to release H₂ as follows:

The synthesized sheets were analysed by energy dispersive X-ray spectroscopy (EDX), X-ray photoemission spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM).

Fig. 5.4: EDX spectra of selected area of grains: (a) starting material (CaSi_2); (b) and (c) of the prepared sample by the RACE method (reproduced from [35]).

To check the degree of oxidation in the silicon sheets we performed Energy-dispersive X-ray spectroscopy (EDX) experiments. These spectra show a small trace of oxygen which is most probably due to exposure of the powder to air (Figure 5.4).

XPS measurements display a Si $2p$ peak with a binding energy of ~ 100 eV (Figure 5.5a). This is different from that of SiO_2 (104 eV) which indicates that the synthesized sheets contain almost exclusively Si atoms. HR-TEM experiments (Figure 5.5b) reveal that the synthesized silicon product is composed of highly ordered stacked silicon sheets. The electron diffraction pattern (Figure 5.5d) shows a hexagonal periodicity which is consistent with well-ordered and crystalline silicon sheets. This hexagonal pattern originates from a quasi-two dimensional hexagonal lattice, with the observed spots corresponding to the four (100) and the two (110) reflections. From the interplanar distance d_{100} (or d_{110}) we extracted the 2D hexagonal lattice constant a_{hex} of 0.330 ± 0.018 nm. This is smaller than the (111) plane structure of bulk silicon which is 0.38 nm. The evidence points to these silicon sheets corresponding to a 2D honeycomb Si lattice stacked in planes with a surface lattice constant $a_{\text{hex}} = 0.330 \pm 0.018$ nm. This lattice constant would imply a distance between the nearest neighbour Si atoms of 0.19 nm. Previous studies reported that silicene is corrugated [6-7,20-21,26,33,68] with a buckling between 0.04 and 0.12 nm [20,66], resulting in a projected distance (in the plane of the hexagons) as low as 0.19 nm. The data clearly show that the synthesized Si sheets do not correspond to a (111) layer of Si with a

917 diamond structure; instead they have a hexagonal honeycomb structure resembling that of
918 silicene.

919
920 Fig. 5.5: (a) XPS spectrum of the synthesized Si sheets, the Si 2p core level is shown, (b) TEM
921 image showing a stack of silicon sheets, (c) TEM image showing a highly oriented crystalline
922 silicon sheet, (d) ED pattern recorded perpendicular to the surface of the sheet (reproduced from
923 [35]).

924 6-Future directions

925 6.1 Silicene for Li-ion Batteries

926 The areas of application for silicene will be further extended beyond those discussed above when
927 free-standing silicene layers can be isolated from the substrates on which it is grown. Among
928 these applications, one area that shows high promise is the utilization of silicene as an electrode
929 for Li-ion batteries (LIBs). To date, the LIBs are seen as a promising energy storage technology
930 for portable, automotive, and grid applications. One of the targets of the highly active research in
931 energy storage is to increase the capacity of LIBs [153-154].

932 The energy density of LIBs depends strongly on the specific capacity of the electrodes [153,155].
933 Of the different possible types of electrodes, Si-based anodes have attracted much attention as a
934 promising alternative anode material to the conventional graphite due to their high theoretical
935 capacity of 4200 mAh/g, compared to 372 mAh/g for graphite [155-161]. However, Si-based
936 anodes present significant challenges for the commercialization of this technology [162-165].
937 Among the issues limiting their commercial applications are the swelling of Si anodes upon
938 lithiation [156] which leads to fracture and subsequent reduction in charge rate, as well as
939 overgrowth of solid electrolyte interface (SEI) resulting from the interaction between Si and the
940 decomposed electrolyte species [166].

941 Motivated by the desire to find alternatives to Si anodes, nanomaterials are considered to hold
942 great promise due to their high surface-to-mass ratio. In particular, there has been a growing
943 interest in two-dimensional layered materials [1-4,167-168]. Among these, graphene in both its
944 single-layer and few-layer forms has attracted much attention as an anode alternative [169-171]
945 as well as a conducting additive to active materials in electrodes [172-175]. Given the similarity
946 to graphene, it is natural to consider silicene as a potential material for applications in LIBs.
947 Silicene is the analogue to graphene, composed of a silicon honeycomb lattice of one-atom thick.
948 The large surface area of this nanomaterial could serve as a potential high-capacity host of Li in
949 LIBs. Additionally, research in this direction will contribute to a better understanding of the
950 properties of low-dimensional Si [6,176-179].

951 It was suggested by an earlier first principles calculation that lithiation could provide a unique
952 way of isolating silicene while inducing and tuning its band gap [180]. At the moment, silicene
953 monolayers are grown on metal substrates such as Ag, and they have yet to be isolated. Previous
954 calculations based on cohesive energies have shown that silicene is less stable than bulk silicon;

therefore, it is unlikely to grow naturally like graphene [181]. To date, only a limited number of theoretical studies have been reported exploring the nature of Li interaction with silicene (single layer and bi-layers), and comparing Li storage metrics with those established for silicon (bulk and nanostructures), graphene, and graphite [180,182-183].

A recent first principles density functional theory (DFT) study and molecular dynamics (MD) simulation reported by Osborn et al. [180], explored the ways of creating a stable semiconducting material based on silicene. They studied the nature of the Li interaction with a single layer of silicene, and assessed the energetics, and the stability of the lithiated silicene. For the $\text{Li}_x\text{Si}_{1-x}$ compounds considered, the Li-Si bond strength was evaluated based on the adsorption energies. The Gibbs free energy of formation was used to evaluate the stability of a $\text{Li}_x\text{Si}_{1-x}$ compound with respect to the Li and Si bulk. By varying Li content ($x= 0.11, 0.2, 0.3$, and 0.5), several different $\text{Li}_x\text{Si}_{1-x}$ compounds were optimized; here the fully lithiated sheet ($\text{Li}_{0.5}\text{Si}_{0.5}$) corresponds to eight Li atoms ($x = 0.5$) adsorbed on both sides of the silicene layer. The adsorption energies vary from 2.21 to 2.52 eV/Li suggesting that Li is strongly chemisorbed on the silicene. The changes in the Gibbs free energies of the lithiated silicene compounds showed that as the Li content increases, the structures approach the stability of bulk compounds of the same ratio. The most stable Li-Si compound reported was the fully lithiated case, named as silicel, that has almost the same Gibbs free energy as that of the bulk with the same Li content. Comparison of the energies correspond to the hydrogenated silicene and silicel with that of the pristine silicene, led to the conclusion that both hydrogenated silicene and silicel are more stable, relative to their bulk counterparts, than pristine silicene. They suggest that this may provide a feasible way for isolating a silicene-based nanosheet. The stability of Li in the presence of oxygen was also evaluated, and it was found that Li binds strongly, 3.25 eV/Li, with the hydroxyl group, which is much higher than the Li-Si bond

energy. This indicates that Li desorption in an oxygen environment may be possible which is a potential concern for LIB environments. The authors also evaluated the structural stability of silicel using MD simulations and the phonon frequencies. They showed that silicel is stable between 300K and 900K, and structural deformation is observed at 1500K. The phonon band structure of the fully lithiated silicel showed stability based on the absence of imaginary phonon eigen-frequencies. The electronic band structure of the fully lithiated silicene showed that the band structure transforms from a zero-gap semiconductor to a semiconductor with 0.37 eV band gap. This is in contrast with graphene, which upon lithiation behaves as a metal [184].

A DFT study by Tritsarlis *et al.* [183], assessed the suitability of silicene for LIBs by studying the Li interaction with free-standing single-layer and double-layer silicene. For the description of exchange and correlation, the PBE functional was used. Their study explored the Li binding sites and diffusion barriers in these model electrode structures. For single-layer silicene, the binding energy of Li was found to vary little from 2.08 eV ($\text{Li}_{0.11}\text{Si}_{0.89}$) to 2.28 eV ($\text{Li}_{0.50}\text{Si}_{0.50}$) over a relatively large range of Li content. However, for $x > 0.50$ the binding of Li was reported to be significantly weaker. Similar to the earlier study [180], they concluded that $\text{Li}_{0.50}\text{Si}_{0.50}$ represents the fully lithiated configuration of single-layer silicene. Using MD simulations to calculate the energy necessary to separate the silicene sheets, they showed that free-standing double layer silicene is stable. Li adsorption energies were found to vary little (from 2.08 to 2.23 eV) with increasing Li content, and were very similar to those of the single-layer silicene. The comparison of the Li binding energies showed that the Li binding to silicene is stronger than those in bulk Si and thin Si nanowires (typically less than 1.64 eV). The theoretical specific charge capacity of silicene was reported to be 954 and 715 mAh/g for single-layer and double-layer, respectively. These capacities are much higher than the theoretical capacity (372 mAh/g) of the most common

1001 electrode material, graphite.

1002 One of the major challenges in bulk crystalline Si anodes is the very large volume change (400%)
1003 upon full lithiation. The analysis of the change in the volume of the silicene showed increases of
1004 13% and 24% for the single-layer and double-layer, respectively. Furthermore, after complete
1005 delithiation, silicene is restored to pristine silicene in contrast to crystalline Si, which experiences
1006 significant structural changes [185-186]. The electronic band structure analysis, similar to the
1007 earlier finding [180], showed that upon full lithiation the band gap of the initially pristine silicene
1008 changes from zero to 0.32 eV, which is half of the band gap of bulk crystalline Si. The Li
1009 diffusion energetics calculated in both single-layer and double-layer silicene structures show that
1010 they are lower or comparable to those in bulk Si and thin Si nanowires [187].

1011 Based on the available reports so far regarding the potential of silicene for applications in LIBs,
1012 one can draw the several promising conclusions, however, with the caveat that care must be taken
1013 as there is a need for more input for accurately assessing the potential of this system for LIB
1014 applications. One of the promising findings of these studies is that silicene does not undergo
1015 significant volume change unlike crystalline Si during lithiation and delithiation cycles. Thus, for
1016 Si, the observed significant reduction in the capacity related to this large volume change is not
1017 observed for silicene. As the diffusion barriers for Li in silicene are found to be smaller than or
1018 comparable to those for diffusion in bulk Si and thin Si nanowires, one does not necessarily
1019 expect kinetic limitations for the lithiation of silicene. In contrast to graphene, increasing the
1020 number of silicene layers does not result in any significant effect on the energetics for Li
1021 adsorption. The theoretical capacity reported for silicene is much higher than that of graphite. In
1022 addition, low diffusion barriers for Li, as well as a small volume change with lithiation and
1023 delithiation, are useful metrics for the application of silicene in LIBs. These could potentially

1024 impact the energy density as well as improve cycle life. However, these features are not sufficient
1025 enough for designing electrode materials based on silicene. It is clear that further investigations
1026 are necessary for determining whether free-standing silicene can be stable in a LIB environment,
1027 and how the possible SEI formation can be efficiently controlled.

1028 *6.2 Silicene for devices*

1029 Research on silicene has progressed at a rapid rate to the extent that the first steps towards
1030 chemical synthesis of silicene [35,126] or the premise of a 2D silicon layer on an insulating
1031 substrate have been achieved [119]. Now is a good time to consider the integration of silicene
1032 into future devices. Indeed, two reviews on 2D materials for electronics [188] and even graphene
1033 spintronics [189] mention silicene and germanene as potential candidates. So far, a few
1034 theoretical investigations have considered the potential of silicene in future devices [10-13].
1035 Another by Ezawa has shown a pronounced response of silicene to an external electromagnetic
1036 field [190]. This implies that controlling the electronic and magnetic properties of silicene will be
1037 easier because the ratio between the on and off states will be sufficiently large.

1038 A second property of silicene that is particularly interesting is the formation of spin states [10-
1039 11]. Recent calculations have shown that the electronic properties of the silicene NRs change as a
1040 function of the different edge structures [47], and that the conduction channels of the NRs can be
1041 controlled by applying an inhomogeneous electric field to lift the spin degeneracy [101, 191-
1042 192]. Spin also plays a role in generating the thermoelectric effect in hydrogenated silicene NRs
1043 as recent calculations have suggested [193]. Another theoretical study by Fang et al. [194] has
1044 calculated the effects of doping hydrogenated silicene NRs with nitrogen and phosphorus atoms.
1045 They find that the dopant atoms induce magnetism in the semiconducting nanoribbon which

becomes metallic under a transverse electric field. The spin properties of silicene have been considered from a more general point of view by Tsai et al. [195]. They showed that the buckling of silicene could generate a band gap and polarized spin-states that can be controlled with a perpendicular electric field. Using first-principles calculations they showed that field-gated silicene possesses two gapped Dirac cones situated at the corners of the Brillouin zone, exhibiting nearly 100% spin-polarization. They also proposed a design for a silicene-based spin-filter which when considered within the context of spintronics means that the prospect for silicene in devices is bright.

The functionalization of silicene with molecules or metals [19] is the third aspect that should be considered for the fabrication of silicene based devices as is the case for graphene [196]. The idea behind this avenue of research is to control the band gap and conduction properties of silicene. However, the reactivity of silicene has received only little attention so far because the focus has been on controlling and understanding the elementary growth mechanisms of silicene. Nevertheless, silicon chemistry is vast and we would be wise to take inspiration from the wealth of studies on the reactivity of silicon surfaces. For example, there have been a number of reviews on the adsorption of small molecules including hydrogen, oxygen, or larger molecules on silicon surfaces and these have discussed at length the effects of atomic and molecular adsorption on the electronic properties of the silicon surfaces [147, 197-198]. While many more detailed experimental and theoretical studies are required before the chemical properties of silicene can be put to full use, we can give a few pointers.

In this context, hydrogen is the simplest reactant. In the case of graphene, hydrogenation leads to the formation of graphane, where hydrogen is attached to most of the carbon atoms. There are several recent articles and reviews on the subject which indicate that hydrogenation modifies the

electronic properties and the structure so that fully hydrogenated graphane forms a buckled sheet like silicene [199-200]. Graphane can be produced by chemical methods which is encouraging in that the silicene produced by the RACE method [35,126] also contains Si-H bonds. If we now consider silicon surfaces, we find that the reaction of hydrogen results in a passivated surface with a band gap of around 2 eV [201]. These passivated surfaces can be used to decouple molecules electronically [202], templated with atomic scale structures by removing selectively hydrogen atoms with electrons from the STM [203-205] and the templates used to selectively chemisorb molecules [206].

The reactivity of silicene NRs on Ag(110) [53] and silicene sheets on Ag(111) to oxidation has been analysed qualitatively using STM and photoemission experiments. A recent preliminary analysis has revealed that silicene is inert to high doses molecular oxygen and is slow to react even to atomic oxygen. However, the precise mechanism for oxidation remains elusive for the moment. Again, graphene sets a good precedent in that graphene oxide can be formed by chemical methods [207-208]. Oxidation of silicon surfaces has been studied for years as it is the basis of the early CMOS devices. However, at the atomic scale, the oxidation processes are complex and depend on the reconstruction of the silicon surface; for example, Si(111) surfaces while being relatively slow to react, form SiO₄ units easily [209-211], while Si(100) surfaces react more quickly because the oxidation reaction has a zero energy barrier in the precursor state which propagates easily across the surface [212]. However, the silicon atoms are found in all oxidation states which give rise to an inhomogeneous oxide.

A theoretical study by Ni et al. [108] has calculated the adsorption energies of single metal atoms on silicene. However, there has been only one experimental study of the adsorption of Mn on silicene NRs [213]. The Mn atoms adsorb in rows along the silicene NRs and photoemission

measurements show that the Mn atoms bind strongly to the silicon to form a silicide. Again, we can consider how metals adsorb on graphene. Two examples are worth mentioning. Gold intercalates under the top graphene layer to form a pseudo ordered array of small Au clusters [214]. These clusters have a profound effect on the Fermi surface of the graphene by inducing trigonal warping of the K-points. The second example is the adsorption of Cobalt on graphene on Iridium(111) where the deposition conditions influence the adsorption sites of the Co atoms under the graphene [215]. The key considerations that need to be made for silicene concerns the type of metal and how it reacts; does it adsorb on the nanoribbons or sheets or does it intercalate. The physical properties of the metal-silicene system will determine what type of device can be built.

Another aspect concerns the adsorption of an organic molecule on silicone. So far, there has only been one experimental study of molecular adsorption on the isolated Si nanowires formed on the Ag(110) surface [216]. The molecules were found to adsorb preferentially on the Si nanowires. Other molecules that are very interesting for their optical properties are the porphyrines and phthalocyanines. These are known to adsorb easily on structured semiconductor surfaces [217-218]. Molecular adsorption on graphene has also had a major impact on research and devices. Molecules form ordered layers [219], where the interaction between the molecules and the graphene modifies both the molecular properties and the graphene – molecular orbitals cannot be seen and a band gap can be opened in the graphene [220]. This can be taken further by using free-standing graphene where molecular adsorption of electron acceptors and donors on either side of a single graphene sheet can open a considerable band gap of 1.8 eV [221]. This should be considered as a key avenue of research particular from the chemical synthesis of silicene for two

1114 reasons: first it should be possible to stabilize the silicene sheet with molecules on either side and
1115 second it will enable the electronic properties to be modified in a controlled way.

1116 Finally, the optical properties of silicene need to be considered in the context of potential future
1117 applications. There have been only a few theoretical studies all of them indicating that silicene
1118 behaves like a group IV material, though the precise properties depend on the electronic structure
1119 (gap or no gap, doping or passivation) [222-224]. Another study of the valley spin polarization
1120 mentions clearly the potential for silicene to be optically active in the infrared and THz ranges
1121 [225].

1122 **7-Conclusions**

1123 The field of *Silicene* has grown very rapidly and it is important to have milestones summarizing
1124 the progress of different aspects of silicene. When we wrote the first review on silicene [7], only
1125 about forty-five papers had been published on the subject. Now, there are close to five hundred,
1126 though most of these papers are either theoretical or computational studies on free-standing
1127 silicene, there are a few reviews on specific aspects of silicene formation [86,106,225]. These
1128 theoretical and computational studies predicted that silicene should have many chemical and
1129 physical properties, and functionalities similar to graphene. For silicene on substrates, many
1130 advances both experimentally and theoretically have been achieved and we have summarized a
1131 number of them here.

1132 The variety of different silicene structures makes it complicated to discern their physical
1133 characteristics. Consequently, a number of debates have arisen over the silicene structures and
1134 properties. The first concerned the nearest-neighbour distance (NND) or bond length in the
1135 honeycomb lattice of silicene adsorbed on Ag surfaces. STM images revealed distances 1.9 Å to

1136 2.2 Å, whereas distances of around 2.25-2.35 Å were expected from theory. Careful analysis of
1137 the STM images concluded that the observed short distances were in fact projected lateral
1138 distances caused by the large buckling of the adsorbed silicene layer. Though very precise SXRD
1139 measurements are still to be obtained, the consensus is that the NND in adsorbed silicene is
1140 around 2.3 Å.

1141 The second aspect over which there has been much debate is electronic in nature. A linear
1142 dispersion in the electronic band structure of silicene adsorbed on Ag(111) had been reported
1143 [19]. This interpretation proved to be incorrect as subsequent experimental and theoretical studies
1144 provided further information. It was found that the observed linear dispersion is an intrinsic
1145 electronic property of the Ag substrate. This finding actually should not be a surprise since
1146 silicene strongly interacts with the Ag substrate. The consequences are multiple; strong buckling,
1147 the appearance of interface states, changes in the electronic character of silicene from a
1148 semiconductor to a metal, to name but a few.

1149 The growth of multi-layer silicene, containing up to 40 layers, has been claimed. For this to
1150 remain silicene the interaction between the layers would have to be van der Waals. However,
1151 very recent experimental studies present evidence that despite layer-by-layer growth of silicon
1152 beyond the second layer, it has a diamond-like bulk silicon structure with sp^3 bonding.

1153 Finally, the production of silicene via chemical methods and the growth of silicene on insulating
1154 substrates are important prerequisites for the development of electronic devices.

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