Combined AFM and STM measurements of a silicene sheet grown on the Ag(111) surface

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Abstract
In this paper, we present the first non-contact atomic force microscopy (nc-AFM) of a silicene on a silver (Ag) surface, obtained by combining non-contact atomic force microscopy and scanning tunneling microscopy (STM). STM images over large areas of silicene grown on the Ag(111) surface show both (√13 × √13)R13.9° and (4 × 4) superstructures. For the widely observed (4 × 4) structure, the observed nc-AFM image is very similar to the one recorded by STM. The structure resolved by nc-AFM is compatible with only one out of two silicon atoms being visible. This indicates unambiguously a strong buckling of the silicene honeycomb layer.

1. Introduction
Advances in nanoscience involving low-dimensional carbon-based structures such as carbon nanotubes and graphene are attractive because of their interesting electronic properties [1, 2]. Recently, much attention has been turned to the question of whether the silicon counterpart, namely silicene, can be fabricated and whether it will exhibit similar interesting properties. The main difference is that for carbon sp² hybridization is stable, while silicon tends to prefer sp³ hybridization. Theoretical investigations have shown that slightly buckled silicene has an intrinsic stability and presents electronic properties similar to those of graphene [3–6]. Experimentally, we have succeeded in synthesizing silicene on both Ag(110) and Ag(111) substrates [7–10]. On the Ag(110) surface, massively parallel silicene nano-ribbons (NRs) of 1.6 nm in width were obtained [7, 10]. We have shown that their reactivity towards molecular oxygen is substantially less than that of silicon [11]. In addition, angle-resolved photoelectron spectroscopy (ARPES) measurements showed quantum confined electronic states of a one-dimensional character with a dispersion along the length of the NRs in the vicinity of the X-point of the Brillouin zone suggesting a behavior analogous to the Dirac cones of graphene [12]. On the Ag(111) surface, a continuous two-dimensional (2D) sheet of silicene, presenting a (2√3 × 2√3)R30° superstructure, has been observed by scanning tunneling microscopy (STM) [9]. Following our pioneering work, several groups have successfully grown silicene on Ag(111) and reported the existence of different ordered phases ([13–16], (4 × 4), and (√13 × √13)R13.9°). These ordered phases, obtained by varying the substrate temperature during the silicon growth, correspond simply to different orientations of the silicene sheet relative to the Ag(111) surface [8, 16]. Recently ARPES measurements performed on a silicene sheet on the (4 × 4) superstructure have reported a linear dispersion (Dirac cone) around the K-point of the Brillouin zone [15].

So far STM images, which are dominated by electronic contrast, have formed the basis for the reported atomic models
of silicene on Ag(111) [9, 13–16]. However, the atomic structure is still under intense debate. Non-contact atomic force microscopy (nc-AFM) measurements should permit us to discriminate between the electronic and geometric contributions and provide additional information enabling the construction of a realistic model for the structure of silicene adsorbed on Ag(111).

In this paper, we present combined nc-AFM/STM measurements using a qPlus sensor of the 4 × 4 superstructure of silicene grown on the Ag(111) surface at room temperature (RT). We observe that constant height nc-AFM images show very similar atomic contrast to the STM topography. This similarity indicates that the observed atomic scale contrast is mainly a topographic effect instead of an electronic effect. This is unambiguous evidence that the investigated (4 × 4) silicene superstructure has a strongly buckled honeycomb structure.

2. Experimental details

All experiments and procedures were performed in an ultra-high vacuum (UHV) chamber of a modified variable temperature scanning probe microscope (Omicron VT XA qPlus nc-AFM/STM), which is capable of simultaneous measurements of the tunneling current and interaction forces. The heart of the microscope is the mechanically resonated qPlus sensor with a tungsten tip mounted at the extremity of the free prong [17]. This particular sensor has a resonant frequency of 51 264 Hz and a stiffness of 2975 N m⁻¹, which was determined from a thermal noise analysis of the sensor [18]. The internal wiring of the microscope was modified in order to eliminate any cross-talk phenomena, which can occur between the deflection channel and the tunneling current [19]. A Specs-Nanonis OC4 PLL controller was used for the frequency demodulation and the Omicron MATRIX control system for the data acquisition. The base pressure of the chamber was always below 1 × 10⁻¹⁰ mbar during data acquisition and all results were recorded at room temperature.

The Ag(111) single crystal was cleaned in UHV by ion sputtering (Ar⁺ 500 eV) and annealing to 700 K. Evaporation of silicon was achieved by passing a direct current through a 10 × 4 × 0.5 mm³ piece from a silicon wafer. A reasonably stable Si flux, approximately 0.5 monolayer (ML) per minute, was achieved in this way. Si was deposited onto the clean Ag(111) surface held at 500 K. After Si deposition, the sample was transferred to the microscope in the same UHV chamber for characterization with nc-AFM/STM. Constant current operation was chosen for STM imaging. On the other hand the nc-AFM measurements were performed using a slow feedback on the frequency shift signal to compensate the tilt between the plane of the surface and the scanning plane. This procedure allows the drift in the Z direction to be eliminated, which can be quite significant and nonlinear at room temperature. The constant separation between the tip and the sample was maintained by this semi-constant height mode and no atomic corrugation was apparent in the topographic (Z) channel.

3. Results and discussion

Figure 1(a) shows the atomically resolved STM topography of a selected area on the sample, containing two known reconstructions [13–16]; the (√13 × √13)R13.9° and the
(4 × 4). As a result of the sample preparation, the entire sample is covered by large areas of the (4 × 4) structure and only small areas of the (√13 × √13)R13.9° were obtained, so we focused on the (4 × 4) structure to obtain atomically resolved AFM images using the constant height nc-AFM mode. Interpreting the nc-AFM images is quite challenging since the presence of the tunneling current can alter the observed frequency shift. Recent studies have shown that the nc-AFM contrast is bias dependent, especially at high bias voltages, where it is governed by the sample resistance and tunneling current [20] or so-called cross-talk phenomena [19]. Consequently, we chose to record all images at zero bias voltage, where the tunnel current is negligible. Consequently the observed atomic contrast is interpreted as a direct consequence of the short-range chemical interactions between the tip and the sample.

In order to align the STM and AFM images, the operation mode was changed during the scanning. This allows the atomic positions to be well matched. The resulting STM topography and nc-AFM images of the same area are shown on figures 1(b) and (c), respectively. The nc-AFM image, figure 1(c), was taken in the Z height where the repulsive force over the imaged Si atoms prevails (see discussion below). Therefore, the bright protrusions in the image correspond to sites that have a greater repulsive action on the tip apex. The STM and nc-AFM images in figures 1(b) and (c) are remarkably similar, showing protrusions at identical locations in the unit cell. Each triangle represents one half of the elementary surface unit cell.

Before we analyze the atomic contrast of silicene observed in the nc-AFM experiment, we will discuss some details of the atomic contrast variation of graphene, which has a very similar 2D structure. Recently it has been shown, both theoretically [23] and experimentally [24], that the short-range force drives the atomic contrast of graphene in nc-AFM experiments and that it depends on the tip structure and the tip–sample distance. We should also note that a similar tendency has also been observed on metal surfaces [25, 26].

In particular, the inversion of atomic contrast of graphene during the tip–approach step has been attributed to the different response of the short-range force over an atom or a hollow site. The short-range force acting between the apex atoms of the tip and the sample usually decays exponentially with the tip–sample distance. Therefore only the atoms which are the nearest contribute significantly to the atomic contrast in both the attractive and repulsive regimes. Consequently, in the case of the atom site, the resulting short-range force is determined mainly by interaction between the specific surface atom and the tip apex atom. On the other hand, the interaction over the hollow site is driven by a net force, which is the sum of the short-range forces acting between the tip apex and the nearest surface atoms.

This tendency usually leads to the following behavior (for chemically active tips): (i) in the regime where the tip is close to the surface, the Pauli repulsion dominates the short-range force over the atom site, and so the hollow sites show a more attractive signal.

In our case the whole picture is slightly more complicated, because the proposed silicene (4 × 4) structure possesses two different hollow sites. One is located in the center of the unit cell with four neighboring protruding Si atoms (see figure 1(d)). The second hollow site is located on the edge of the 4 × 4 unit cell and surrounded by six Si atoms. The important difference is that the four Si atoms forming the center hollow site are positioned higher than the six Si atoms forming the corner hollow site. Taking into account the exponential dependence of the force on distance, the center hollow site will provide a larger attractive net force than the edge hollow site.

We can now compare the observed variation of the atomic contrast as a function of the tip–sample distance with our prediction. First, the tip was positioned far from the sample with a constant distance corresponding to a feedback set point of $\sim 10.5$ Hz. At this distance only the contour of the unit cells was resolved, as shown in figure 2(a). The internal part of the unit cell is more attractive than the corners of the unit cell (corner hollow). This indicates that the center hollow site is more attractive than the corner hollow, in good agreement with our prediction made above. However, we are unable to achieve atomic resolution within the (4 × 4) unit cell. We attribute the absence of the atomic contrast due to a negligible difference of the attractive short-range interactions between the atom and the center hollow site.

To enhance the atomic contrast, we reduced the tip–sample separation by changing the set point to $\sim 14$ Hz. As figure 2(b) shows; we can distinguish six bright protrusions forming two characteristic edge-to-edge triangles, as observed in the STM mode. Therefore we attribute the protrusions to the center atoms of the (4 × 4) phase. The tip feels the most attractive interaction in the middle of the (4 × 4) unit cell while the corner hollow and six center atoms show a very similar magnitude of the frequency shift. This can be explained by the fact that the short-range attractive force over each atom site is no longer at a minimum and its magnitude is similar to the net force acting over the corner hollow sites.

Finally, at the closest tip–sample distance with a set point of $\sim 17$ Hz, the topmost six center Si atoms of the (4 × 4) structure are clearly resolved, as shown in figure 2(c). Now, figure 2(d) shows a cross sectional cut of the frequency shift image in figure 2(c) along the long diagonal of the unit cell (the arrow indicates the position and direction of the line profile). We see that the frequency shift over the topmost Si atoms is $\sim 16.5$ Hz. In fact, this is about 1 Hz larger than the average shift over corner hollow sites. Consequently, the topmost Si atoms are less attractive than hollow sites. This observation can be only interpreted by the presence of the repulsive short-range interactions over the topmost Si atoms. Our experiment provides clear evidence of the presence of the weak attractive short-range force compared to bare Si-based surfaces [21, 22], where the maximal attractive force is $\sim 2$ nN. This indicates that either our tip apex was not chemically active or the silicene (4 × 4) structure is chemically...
Figure 2. Constant height, nc-AFM, which was maintained by a slow feedback regulated on $\Delta f$, scans of the same area. The tip–sample separation was gradually decreased by adjusting the $f_{\text{set}}$ to: $-10.5$ (a), $-14.0$ (b) and $-17$ Hz (c). The color scale is presented relative to $f_{\text{set}}$, therefore the total frequency shift is: $\Delta f = \Delta f_{\text{set}} + \Delta f^*$. The size of images is $3 \times 2.6$ nm$^2$ and they are collected with $U_{\text{BIAS}} = 0.0$ V and $a_{\text{osc}} = 220$ pm. Figure (d) shows the line profile of the frequency shift $\Delta f$ obtained along the direction indicated by the arrow shown on image (c).

inert. The latter could explain the low reactivity towards molecular oxygen [11]. We should note that approaching the tip closer towards the surface leads to unstable scanning conditions.

The atomic contrast acquired by nc-AFM and STM consists of six characteristic protrusions arranged in two triangles within the unit cell. The observation coincides very well with the proposed $(4 \times 4)$ model structure, as can be seen directly in figure 1(d) [8, 16]. In particular, the $(4 \times 4)$ model structure shows clearly that the Si atoms are relaxed out of the surface plane, forming pyramids whose apices are located at the positions where both the STM and AFM show bright protrusions. This structural relaxation breaks the symmetry of the honeycomb structure over a distance corresponding to three honeycomb unit cells.

4. Conclusion

In summary, we have investigated the electronic and topographic landscape of a silicene sheet grown on the Ag(111) surface by means of simultaneous STM and nc-AFM techniques. The nc-AFM images are identical to the STM images, but only when the tip is relatively close to the surface. This is explained by the contribution of repulsive short-range forces which are strongest at the atomic positions of the Si atoms that are nearest to the tip. For the $(4 \times 4)$ superstructure of silicene on Ag(111), the nc-AFM measurements clearly indicate a strong buckling of the Si honeycomb layer.

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