Epitaxial growth of silicene on ultra-thin Ag(111) films

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Abstract
Epitaxial growth of silicene on atomically flat ultra-thin Ag(111) films was investigated using scanning tunneling microscopy. The Ag films were prepared by low-temperature deposition of Ag on Si substrates, followed by soft annealing at room temperature. Patchy \(4 \times 4\), \(\sqrt{13} \times \sqrt{13}\), \(\sqrt{7} \times \sqrt{7}\), and \(2\sqrt{3} \times 2\sqrt{3}\) silicene domains were nucleated on regions that were one mono-layer lower than the pristine Ag surface after the initial morphological change had been completed. On the first-layer silicene containing the above domains, two types of \(\sqrt{3} \times \sqrt{3}\) silicene domains (\(\sqrt{3} \times \sqrt{3} - \alpha\) and \(\beta\)) were formed in the second layer. A bias voltage-independent Moiré pattern was observed for the \(\sqrt{3} \times \sqrt{3} - \alpha\) silicene, and a bias voltage-dependent standing wave pattern for the \(\sqrt{3} \times \sqrt{3} - \beta\) silicene. The \(\sqrt{3} \times \sqrt{3} - \beta\) silicene had a dispersion relation that could be fitted using a linear function, although the resulting Fermi velocity was twice as large as the expected value.

Keywords: silicene, growth, STM, Ag ultra-thin films

1. Introduction
Silicene is a two-dimensional (2D) Si crystal one atomic layer thick. In 1994, Takeda and Shiraishi provided theoretical evidence that silicene is a stable allotrope of crystalline Si [1]. Silicene should, in principle, have a Dirac dispersion similar to that for graphene because of the
2D hexagonal lattice structure. However, the Si atoms are expected to be slightly buckled in the silicene plane due to mixing of sp³ hybridized orbitals and sp² planar bonds [2]. This could lead to the appearance of a band gap, which is a requirement for electronic device applications. It has also been predicted that this band gap could be tailored using an external electric field [3]. Furthermore, silicene is expected to have 2D topological insulating characteristics, according to recent theoretical studies [4]. It is also compatible with conventional semiconductor device fabrication processes, since it is essentially Si. For all of these reasons, silicene is regarded as a promising material for next-generation electronic devices.

However, since a graphite-like layered form of Si does not exist in nature, silicene cannot be produced by conventional exfoliation processes. Epitaxial growth has thus been proposed as a means of forming silicene on substrates. In particular, honeycomb Si nanostructures have been experimentally observed following deposition of Si on Ag(001) and (110) substrates [5–7]. The first successful synthesis of silicene was reported on Ag(111) and ZrB₂(0001) surfaces in 2012 [8, 9], and later on Ir(111) surfaces [10].

Most experimental studies have involved epitaxial growth of silicene on the (111) surface of bulk crystalline Ag. Vogt et al first reported the growth of 4 × 4 commensurate silicene domains on a Ag(111) 1 × 1 substrate [8]. Subsequently, \(\sqrt{13} \times \sqrt{13}\), \(2\sqrt{3} \times 2\sqrt{3}\), and \(\sqrt{7} \times \sqrt{7}\) commensurate silicene regions were identified in the first silicene layer on Ag(111) surfaces [11–13]. However, epitaxial silicene is expected to interact with the Ag substrate and reduce the intrinsic Dirac dispersion, and as such, the existence of Dirac dispersion is controversial. Density functional theory (DFT) calculations and Landau level spectroscopy measurements have suggested the destruction of Dirac dispersion [14–16], while a Dirac-like linear dispersion was reported for the first-layer silicene on a Ag(111) substrate based on angle-resolved photoemission spectroscopy (ARPES) measurements [17]. In contrast, the substrate effect is expected to be negligible for the second-layer silicene, for which \(\sqrt{3} \times \sqrt{3}\) (with respect to the silicene 1 × 1 lattice) silicene domains were observed on a Ag(111) substrate [18, 19]. A linear dispersion in the second-layer \(\sqrt{3} \times \sqrt{3}\) silicene was reported based on scanning tunneling microscopy (STM) and ARPES studies [18, 20]. However, the linearity was called into question by another STM study [21].

One of the origins of such confusion is the difficulty in obtaining a wide, single-phase silicene domain by epitaxial growth. However, the growth of silicene is too complicated to be understood in the simple framework of conventional layer-by-layer growth. A very recent \(\mu\)-low-energy electron diffraction (\(\mu\)-LEED)/low-energy electron microscopy (LEEM) study reported that the growth was surprisingly self-destructive [22]. Thus, it is crucial to understand in more detail the epitaxial growth process for silicene on Ag(111) substrates. In this study, we investigated the epitaxial growth of silicene on ultra-thin Ag(111) films on Si(111) 7 × 7 substrates. It is possible to produce such films on wafer-scale Si substrates, whereas commercially available bulk Ag(111) substrates have maximum sizes of only 10 mm. In this respect, ultra-thin Ag films offer advantages for the synthesis of large-scale epitaxial silicene. The silicene growth process was examined in detail as a function of temperature (\(T\)) and Si coverage (\(\theta_{Si}\)) using STM.
2. Experimental

Experiments were conducted in an ultra-high vacuum (UHV) apparatus with a liquid nitrogen sample cooling system, a Ag Knudsen cell, a Si evaporation source, and a low-temperature STM unit. Si(111) substrates were cleaned by conventional thermal flashing under UHV. Seven to twenty monolayer (ML) thick Ag films were deposited on the substrates at liquid nitrogen temperature. The films were then heated to room temperature overnight. This two-step growth method led to the formation of atomically flat Ag(111) films over the entire substrate [23].

Silicene was grown on the Ag films by the deposition of Si atoms at temperatures of 500–640 K. The temperature was controlled by resistive heating and was monitored using an optical pyrometer with an emissivity of 0.1 [24]. Si atoms were deposited from Si wafers that were resistively heated above 1400 K. The Si deposition rate was adjusted in the range 0.005 to 0.08 ML min\(^{-1}\), depending on the substrate temperature.

As will be described later, the morphology of the Ag films initially changed drastically at the silicene growth temperature. Therefore, the Ag films were annealed at the growth temperature for 15 min to settle the morphological change prior to the deposition of Si atoms. In most cases, silicene was grown on the pre-annealed Ag films in this study.

The Si atoms nucleated into silicene domains on the pre-annealed Ag film surfaces. The Si coverage was evaluated based on the area of these domains in STM images, which was found to increase linearly with deposition time. At the end of the first-layer growth, the surface was fully covered by silicene domains with mainly 4\(\times\)4 and \(\sqrt{13}\times\sqrt{13}\) reconstructions. Since the Si atom concentration in 4\(\times\)4 and \(\sqrt{13}\times\sqrt{13}\) silicene is \(1.56\times10^{15}\) and \(1.49\times10^{15}\) cm\(^{-2}\), respectively,\(^1\) 1 ML is regarded as corresponding to a Si atom concentration of \(1.5\times10^{15}\) cm\(^{-2}\) in the present study. From the linear increase in the silicene area, the Si deposition rate was determined to be 0.02 ML min\(^{-1}\) at 500 K with the Si source at 1463 K. However, for the same amount of Si deposition, no silicene growth was evident at 600 K. Thus, the Si source temperature was raised in order to increase the Si deposition rate for the successful growth of silicene at 600 K. The required deposition rate was estimated to be 0.08 ML min\(^{-1}\) from the temperature dependence of the Si vapor pressure [24].

The silicene growth processes were investigated by repeating a deposition of a small amount of Si and subsequent STM observation. The STM images were taken at room temperature. The electronic structure was investigated from differential conductance maps (d\(I/dV\) images) and scanning tunneling spectroscopy (STS) measurements at liquid nitrogen temperature. The d\(I/dV\) images and STS spectra were acquired using the conventional lock-in technique [25]. A bias voltage (\(V_s\)) was applied to the sample during the STM measurements.

3. Results and discussion

3.1. Morphological change of Ag films and its effect on silicene growth

An STM image of a Ag film with a thickness of 11.9 ML is shown in figure 1(a). A patchwork of bright and dark regions appear, which correspond to high and low terraces, respectively, with a height difference of 1 ML between them. The pristine Ag films were thus atomically flat [23].

\(^1\) We deduced the density of the Si atoms was from the structural model of 4\(\times\)4 and \(\sqrt{13}\times\sqrt{13}\) silicene in [12].
The surface morphology of the Ag films was significantly modified by annealing at typical silicene growth temperatures. Figure 1(b) shows the surface of the same film seen in figure 1(a), following annealing at 570 K for 10 min. It can be seen that step movement has occurred, leading to a large increase in the terrace area. However, the Shockley surface state dispersion determined from STS and dI/dV images (data not shown) confirmed that the terraces still had the intrinsic nature of Ag(111) surfaces, even after annealing.

The above change in morphology occurred mainly during the initial 10 min of annealing, and after 15 min no further changes were seen. Once the Ag films obtained such a simple wide terrace and relatively straight step structure as in figure 1(b), the drastic change of the Ag film morphology was subsided. No further drastic change was noticed to happen for the terrace and step structure in further annealing. Even if Si atoms were deposited on the Ag films, no silicene nucleation was observed during the initial period in which the drastic change in Ag film morphology occurred. Therefore, prior to Si deposition, the Ag films were intentionally annealed at the silicene growth temperature for 15 min in order to stabilize the Ag surface morphology. Silicene domain growth then successfully occurred on these pre-annealed Ag films.

3.2. Growth of the first-layer silicene

3.2.1. Growth process. Epitaxial growth of silicene was conducted on pre-annealed Ag films at low (ca. 500 K) and high (ca. 600 K) temperatures. Figure 2 shows STM images of silicene growth at $T=500$ K for $\theta_{\text{Si}}=0.19$, 0.57, and 1.14 ML. As seen in figure 2(a), initial nucleation of Si atoms occurred at random in small dark regions in the bright areas. These regions expanded with deposition time (figure 2(b)) until the Ag film surface was finally completely covered. For a coverage of greater than 1 ML, nucleation of three-dimensional (3D) islands occurred on the first layer (figure 2(c)).

As shown in the zoomed STM images in figures 2(d)–(f), the protrusions were sparsely distributed in the dark regions in the initial stage (e.g., figure 2(d) at 0.19 ML). However, the density of protrusions increased with coverage (e.g., figure 1(e) at 0.57 ML). At the same time, a triangular arrangement of protrusions appeared locally. The Ag film surface was entirely covered by a close-packed arrangement of protrusions with further Si deposition (figure 2(f)).
although several point defects remained. Silicene can assume several commensurate structures by rotation of the lattice on the Ag(111) surface [11, 12, 26]. A 4 × 4 structure, a $\sqrt{13} \times \sqrt{13}$ (type I) structure with a triangular lattice, a $\sqrt{13} \times \sqrt{13}$ (type II) structure with a hexagonal lattice, and a $2\sqrt{3} \times 2\sqrt{3}$ structure have all been identified on the surface of bulk Ag(111) substrates [11, 12]. The protrusions in the present study were identical in appearance, periodicity and rotation angle relative to the Ag(111) 1 × 1 lattice to those reported on bulk Ag(111) substrates. Thus, on ultra-thin Ag films, silicene is considered to form the same commensurate structures as on bulk Ag(111) substrates. The triangular arrangement of protrusions that appear at 0.57 ML (figure 2(e)) is mainly assigned to $\sqrt{13} \times \sqrt{13}$ (type I) silicene. At a coverage of 1 ML, a 4 × 4 structure with a honeycomb lattice became predominant [8], as seen for example in the lower left region of figure 2(f). At this stage, the $\sqrt{13} \times \sqrt{13}$ type I structure was the second most common.

However, when growth was carried out at 600 K, no silicene formation was evident although the Si deposition rate was the same as that for growth at 500 K. Figures 3(a) and (b) show STM images of the Ag films after 60 min Si deposition at a rate of 0.02 ML min$^{-1}$ at 550 and 600 K, respectively. At 550 K, the Ag surface is entirely covered by the first-layer silicene, made up of 4 × 4 and $\sqrt{13} \times \sqrt{13}$ domains. In contrast, at 600 K, a large proportion of the Ag surface remains uncovered, as indicated by the bright featureless region in the upper half in

Figure 2. STM images of silicene growth on ultra-thin (18.0 ML thick) Ag film at a temperature $T$, of ca. 500 K. The Si coverage ($\theta_{Si}$) was 0.19 ML in (a) and (d), 0.57 ML in (b) and (e), 1.14 ML in (c) and (f). The image size is 40 × 40 nm$^2$ in (a)–(c), and 16 × 16 nm$^2$ in (d)–(f). $V_s = +2.0$ V and $I = 0.1$ nA. The image (c) was high-pass filtered to enhance the contrast of both the 3D islands and the underlying first layer silicene. The black arrows indicate the Ag[110] direction.
Figure 3(b). The deposited Si atoms diffuse along the surface and form 3D islands in the gaps between the step edges. Based on LEEM observations of bulk Ag(111), Moras et al. reported that most of the Ag surface remained uncovered following 0.6 ML Si deposition at 588 K, whereas silicene grew normally at lower temperatures [27]. The Si atoms were assumed to form small 3D Si islands with high aspect ratios. A high Si deposition rate was necessary to enable silicene growth at 600 K. The first-layer silicene was successfully grown on the Ag islands by increasing the Si deposition rate to 0.08 ML min$^{-1}$, as seen in figure 3(c), and consisted of $4 \times 4$ and $\sqrt{13} \times \sqrt{13}$ domains as in the case of growth at 500 K. However, at 600 K, the domains were larger (greater than $20 \times 20$ nm$^2$ on average), and defect areas with vacancies were decreased. A similar increase in domain size with growth temperature was also reported for bulk Ag(111) substrates, based on an increase in the LEED spot intensity [27].

At a coverage of about 1 ML, in addition to the hexagonal $4 \times 4$ and triangular $\sqrt{13} \times \sqrt{13}$ type I silicene lattices, the hexagonal $\sqrt{13} \times \sqrt{13}$ type II and $2\sqrt{3} \times 2\sqrt{3}$ lattices were also observed as minor domains. Resta et al. reported that the two types of $\sqrt{13} \times \sqrt{13}$ structures correspond to different forms of stacking of the $\sqrt{7} \times \sqrt{7}$ lattice on the Ag(111) $\sqrt{13} \times \sqrt{13}$ supercell, based on an STM image in which all four $\sqrt{13} \times \sqrt{13}$ silicene domains coexisted [28]. However, the plausibility of this model can not be discussed based on the results obtained in the present study, because $\sqrt{13} \times \sqrt{13}$ type II silicene domains were only occasionally observed locally in STM images.

3.2.2. Ag–Si exchange during first-layer silicene growth. As seen in figures 2(a)–(c), the first-layer silicene seems to form via conventional 2D nucleation and growth. However, the silicene was observed to always nucleate in the dark regions in the featureless bright areas of the STM images. These dark regions were found to be lower than the bright regions by about 0.18 nm. Although the contrast in STM images is known to be influenced by both the topography and the electronic density of states at the surface, this same height difference was obtained for both positive and negative bias voltages. Since this is close to the step height for an Ag(111) monolayer (0.24 nm), the dark regions are considered to be 1 ML lower than the bright
featureless regions. In addition, the protrusions in the dark regions were observed to be 0.03 nm lower for a positive bias voltage, and 0.03 nm higher for a negative bias voltage, than the remaining featureless area. This small discrepancy is tentatively attributed to the bias voltage-dependence of the electron density of states. However, it is negligible in comparison to the thickness of a silicene layer (0.21 nm) [29]. The surface of a silicene layer formed in such a recessed region would be expected to be almost level with the non-recessed Ag surface. Thus, it is reasonable to assume that silicene is selectively nucleated in such recessed regions of the Ag surface.

It is unlikely that the dark regions in the STM images are simply tip-induced artifacts because they did not change in number or shape under repeated STM scans. It is therefore reasonable to conclude that they are naturally formed on the Ag surface during silicene growth.

Similar bright and dark regions were observed in STM images of silicene on bulk Ag(111) surfaces [11]. However, the featureless bright areas were tentatively attributed to flat 2D Si layers. It was speculated that the deposited Si atoms formed both the bright-contrast, featureless flat 2D Si layers and the dark regions with Si protrusions on the Ag surface.

In the present study, STS and dI/dV imaging was performed to clarify whether the bright regions were 2D Si layers or not. Figure 4(a) shows an STM image obtained during growth of the first-layer silicene. Both featureless bright areas and dark areas with protrusions are evident. In the corresponding empty state dI/dV image (figure 4(b)), periodic standing waves appear only
for the featureless bright regions. The bias voltage-dependence of the wavelength reproduced the intrinsic Ag(111) surface Shockley state dispersion [30]. Furthermore, the characteristic step-like onset of the Shockley state was clearly detected in STS spectra for the bright area (red line in figure 4(c)) [31]. In contrast, no significant features appeared in the corresponding dI/dV images or the STS spectra (the black line in figure 4(c)) for the regions where protrusions appeared in the STM image. These results indicate unambiguously that the featureless bright areas in the STM image are not flat Si regions, but uncovered regions of the Ag surface.

The present results suggest that one Ag layer was removed from the Ag surface to form the dark regions. Silicene was then selectively nucleated in these recessed regions (figure 4(d)). This implies that that Si atoms exchange with Ag atoms to produce the 1 ML-deep dark regions, and preferential nucleation occurs here. Silicene nucleation in such dark areas was commonly observed both for the present ultra-thin Ag films and on bulk Ag(111) surfaces [11, 28], and can therefore be regarded as a normal part of first-layer silicene growth.

3.2.3. Silicene nucleation in dark regions. The nucleation of silicene was observed to occur selectively in the 1 ML-deep recessed regions. This is considered to be due to the fact that the Si atoms, which exchanged with Ag atoms, were then effectively trapped in the resulting recessed regions. The stability of the $4 \times 4$, $\sqrt{13} \times \sqrt{13}$, $\sqrt{7} \times \sqrt{7}$ and $2\sqrt{3} \times 2\sqrt{3}$ silicene structures has been theoretically calculated as a function of the Si concentration on the Ag(111) surface [32]. The results indicated that these silicene structures were metastable at a Si coverage of about 1 ML. Therefore, it is necessary for the Si coverage to be sufficiently high in the recessed regions, even if the overall Si coverage is still in the submonolayer range. This suggests that migrating Si atoms are trapped in the recessed regions for a long time, allowing their local coverage to increase.

In the dark regions, $\sqrt{13} \times \sqrt{13}$ type I domains were dominant at a low Si coverage of 0.57 ML (figures 2(b) and (e)). However, as described earlier, the dominant phase changed to $4 \times 4$ silicene with increasing Si coverage. The same trend was observed with regard to the dependence of the silicene LEED spot intensity on the coverage during growth on bulk Ag(111) surfaces at a relatively low (491 K) temperature [27]. The coverage dependence of the preferred silicene structure can be reasonably well explained by the results of the theoretical calculations of Pflugradt et al [32]. They revealed that $\sqrt{13} \times \sqrt{13}$ silicene is stable under Si-poor conditions, while $4 \times 4$ silicene becomes stable under Si-rich conditions at a coverage of approximately 1 ML [32]. In the recessed regions, the Si concentration is locally high, and increases with further Si deposition. Thus, $\sqrt{13} \times \sqrt{13}$ silicene, which is stable at a relatively low Si concentration, is nucleated first, followed by $4 \times 4$ silicene, which is stable at a higher Si concentration.

The need for a locally high Si concentration also explains why no silicene nucleation occurred during the early stages of Si deposition on unannealed samples, when the morphology of Ag film changed drastically. During this period, active migration of Ag atoms occurs and the step and terrace structure is transformed. In such a situation, stable recessed regions cannot exist, and the local Si concentration cannot build up sufficiently to initiate the formation of silicene domains.
3.3. Growth of second-layer silicene

3.3.1. Low growth temperature (ca. 500 K). An overlayer began to nucleate after the Ag film surface was almost completely covered by the first-layer silicene. Nucleation of 3D islands was dominant at a temperature of approximately 500 K, as shown in figure 2(c). However, nucleation of small 2D islands was occasionally observed at some locations on the surface. The 2D islands appeared after the Ag film surface was fully covered by the first-layer silicene; therefore, these island domains are considered to be the second-layer silicene. A typical STM image of such an island is shown in figure 5(a). The bright protrusions in the island are arranged in a triangular lattice, whereas 4 × 4 and $\sqrt{13} \times \sqrt{13}$ silicene domains appear in the first layer. The triangular lattice for the second layer has a periodicity of 0.63 nm, which is identical to the $\sqrt{3} \times \sqrt{3}$ unit cell size on the underlying silicene 1 × 1 lattice. Thus, this second-layer silicene is referred to as the $\sqrt{3} \times \sqrt{3} - \alpha$ phase hereafter.

![Figure 5](image_url)
The second-layer silicene is in principle expected to be free from the influence of the Ag substrate, and the intrinsic Dirac dispersion associated with free-standing silicene may be realized. This possibility was examined by dI/dV imaging of second-layer $\sqrt{3}\times\sqrt{3}$-$\alpha$ silicene and typical results are presented in figure 5(b) ($V_s = +1.0$ V) and (c) ($V_s = +0.8$ V). No periodic pattern was evident in the first-layer silicene domains. However, a standing wave-like pattern was observed in the second-layer $\sqrt{3}\times\sqrt{3}$-$\alpha$ islands within the limited $V_s$ range from +0.8 to +1.2 V. The lack of a periodic pattern in the first layer is consistent with recent theoretical calculations and Landau level spectroscopy measurements that indicated the destruction of Dirac dispersion in the first-layer silicene by mixing with the sp electron bands of the Ag(111) substrate [14–16]. In contrast, the periodic pattern suggests the existence of a Dirac dispersion in this second-layer silicene island. However, the pattern did not exhibit the bias voltage-dependence that was expected for Dirac dispersion. The bright spots always appear at the same sites with the same periodicity (almost $2\times2$ periodicity with respect to the $\sqrt{3}\times\sqrt{3}$ silicon lattice), despite changes in the bias voltage. Therefore, Dirac dispersion was not realized in the second-layer $\sqrt{3}\times\sqrt{3}$-$\alpha$ silicene.

Alternatively, the periodic pattern could be reasonably interpreted as a Moiré pattern due to interference between the second-layer $\sqrt{3}\times\sqrt{3}$-$\alpha$ silicene and the underlayers. Figure 5(d) depicts the corresponding structural model, in which the second-layer $\sqrt{3}\times\sqrt{3}$ (with respect to the silicene 1×1 lattice) silicene lattice (red mesh) is overlaid so as to be commensurate with the first-layer $\sqrt{7}\times\sqrt{7}$ (with respect to the Ag(111) 1×1 lattice) silicene lattice (blue mesh). As depicted, the first-layer $\sqrt{7}\times\sqrt{7}$ silicene becomes commensurate with the second-layer $\sqrt{3}\times\sqrt{3}$ silicene with a $2\times2$ periodicity (with respect to the silicene $\sqrt{3}\times\sqrt{3}$ lattice), as indicated by the black rhombus. The periodicity and direction are consistent with the results obtained from the dI/dV images.

### 3.3.2. High growth temperature (ca. 600 K)

Two types of $\sqrt{3}\times\sqrt{3}$ silicene were observed in the second layer in the case of higher-temperature growth. As shown in figures 6(a) and (b), small $\sqrt{3}\times\sqrt{3}$-$\alpha$ silicene domains were nucleated during the initial stage of second-layer growth, which was also the case for growth at the lower temperature. In addition, a second layer with a new hexagonal lattice appeared with further Si deposition during growth (figure 6(c)). The new lattice also has a $\sqrt{3}\times\sqrt{3}$ periodicity with respect to the silicene 1×1 lattice, and is hereafter referred to as $\sqrt{3}\times\sqrt{3}$-$\beta$ silicene. The $\sqrt{3}\times\sqrt{3}$-$\alpha$ and $\sqrt{3}\times\sqrt{3}$-$\beta$ silicene showed different STM patterns even at the same bias voltage, as shown in the insets in figures 6(b) and (d). These patterns were observed reproducibly for the $\sqrt{3}\times\sqrt{3}$-$\alpha$ and $\sqrt{3}\times\sqrt{3}$-$\beta$ silicene islands. Thus, the $\sqrt{3}\times\sqrt{3}$-$\alpha$ and $\sqrt{3}\times\sqrt{3}$-$\beta$ silicene can be safely regarded as having different structures, and the difference in the patterns was not a tip-induced artifact or a bias-voltage effect.

Salomon et al pointed out that $\sqrt{3}\times\sqrt{3}$ silicene can have rotationally different domains involving combinations of the second-layer $\sqrt{3}\times\sqrt{3}$ lattice with the 4×4 and $\sqrt{13}\times\sqrt{13}$ lattices of the first-layer silicene domains [33]. In this respect, the $\sqrt{3}\times\sqrt{3}$-$\alpha$ and -$\beta$ silicene could be the result of two different combinations of the first-layer and second-layer silicene lattices. The $\sqrt{3}\times\sqrt{3}$ silicene is expected to have five possible rotation angles of $-30$, $24.8$, $30$, $35.2$ and $63.0^\circ$ with respect to the Ag[110] direction [33]. In the present study, $\sqrt{3}\times\sqrt{3}$-$\alpha$ domains were observed with rotation angles of $30$, $-3$, and $11^\circ$ on the first-layer 4×4, $\sqrt{13}\times\sqrt{13}$-I, and $\sqrt{7}\times\sqrt{7}$ domains, respectively. However, the $\sqrt{3}\times\sqrt{3}$-$\beta$ silicene was always observed to have a $30^\circ$ rotation angle. Therefore, two types of $\sqrt{3}\times\sqrt{3}$ lattices could
have the same rotation angle of 30°. Thus, the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) and \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene could not be attributed to a difference in the rotational stacking of the second-layer \( \sqrt{3} \times \sqrt{3} \) lattice on the first-layer silicene domains.

Height profiles obtained from the STM images indicate that the height of the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene on the first layer (0.21 nm) was almost the same as that of the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene. However, the \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene tended to have larger domains, with an average domain size of about 30 \( \times \) 30 nm\(^2\). Furthermore, the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene disappeared at the stage when the \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene appeared, which suggests that the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene is transformed to the \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene during second-layer silicene growth at a higher temperature.

Two different growth modes were reported for the second-layer silicene on bulk Ag(111) substrates. Several studies found that \( \sqrt{3} \times \sqrt{3} \) silicene nucleated in the second and higher layers with increasing coverage [18, 20, 33, 34]. We also observed that \( \sqrt{3} \times \sqrt{3} \) silicene grew with increasing coverage at a high deposition rate at 600 K on the ultra-thin Ag films. In two recent LEEM studies, silicene was found to reduce its area during second-layer growth [28, 22], and this was attributed to a tendency to form an \( \text{sp}^3 \)-like silicon structure [22]. The reduction in

**Figure 6.** STM images of two types of second-layer silicene. (a) STM image of second-layer \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene which appeared at \( \theta_{\text{Si}} = 1.2 \) ML during growth at 570 K. The image size is 16 \( \times \) 16 nm\(^2\). \( V_s = -2.0 \) V, \( I = 0.1 \) nA. (b) Magnified image of the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene in (a). The image size is 8 \( \times \) 8 nm\(^2\). \( V_s = -2.0 \) V, \( I = 0.1 \) nA. The inset shows an image of the \( \sqrt{3} \times \sqrt{3} \)-\( \alpha \) silicene taken at \( V_s = +2.0 \) V, \( I = 0.1 \) nA. (c) STM image of the second-layer \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene at 620 K, which appeared at \( \theta_{\text{Si}} = 2.0 \) ML. The image size is 16 \( \times \) 16 nm\(^2\). \( V_s = +2.0 \) V, \( I = 0.1 \) nA. (d) Magnified image of \( \sqrt{3} \times \sqrt{3} \)-\( \beta \) silicene in (c). \( V_s = -2.0 \) V, \( I = 0.1 \) nA. The image size is 8 \( \times \) 8 nm\(^2\). The black arrows indicate the Ag[110] direction.
area was reported to become more pronounced at higher temperature [28]. It is also expected to be influenced by the Si deposition rate, given the difficulty in first-layer silicene nucleation at a low deposition rate and a high growth temperature observed in the present study. The temperature controls the Si adatom spreading pressure at the substrate [22]. The deposition rate determines the supersaturation of the Si adatoms. The growth mode will then be governed by a combination of these two factors. In the present study, it was found that even for the same Si deposition rate, raising the substrate temperature from 600 to 630 K caused a large fraction of the Ag surface to be exposed, and $\sqrt{3} \times \sqrt{3}$ silicene was nucleated only in the narrow regions at the foot of the Ag islands.

3.3.3. Dispersion for $\sqrt{3} \times \sqrt{3}$-β silicene. In contrast to the $\sqrt{3} \times \sqrt{3}$-α silicene, energy-dependent electron standing waves were successfully observed for the $\sqrt{3} \times \sqrt{3}$-β silicene in dI/dV images obtained at liquid nitrogen temperature. Figure 7 shows STM and dI/dV images for $\sqrt{3} \times \sqrt{3}$-β silicene. In the STM image in figure 7(a), it can be seen that the terraces on the Ag film are completely covered by the second-layer silicene. The second layer of the $\sqrt{3} \times \sqrt{3}$-

Figure 7. (a) STM image of the second layer $\sqrt{3} \times \sqrt{3}$-β silicene. $V_s = +0.1 \, \text{V}$ and $I = 0.3 \, \text{nA}$. The image size is $28 \times 28 \, \text{nm}^2$. (b) Energy dispersion from the series of dI/dV images for the second layer $\sqrt{3} \times \sqrt{3}$-β. The blue solid line and red dashed line indicate the linear and parabola fitting of the data, respectively. (c, d) dI/dV images of the area in (a). $V_s = +0.3 \, \text{V}$ (c), and $+0.8 \, \text{V}$ (d). $I = 0.3 \, \text{nA}$. The image size is $28 \times 28 \, \text{nm}^2$. $\theta_{\text{Si}} = 1.8 \, \text{ML}$. The black lines in (a), (c) and (d) indicate the step edges. All the STM and dI/dV images were acquired at liquid nitrogen temperature.

2 Details will be published elsewhere.
structure is shown in the inset. In the corresponding $dI/dV$ images in figures 7(c) and (d), standing waves are seen to extend from the steps toward the inner regions of the terraces; they were clearly observed over a wide energy range from $V_s = +0.1$ to $+1.2$ eV. The wavelength of the standing waves decreased with increasing bias voltage, as shown in figures 7(c) and (d). The dispersion relation was obtained from the series of $dI/dV$ images and is shown in figure 7(b).

The results in figure 7(b) could be roughly fitted using a Dirac electron-like linear dispersion relation, although there were some deviations. The Fermi velocity and the Dirac point were estimated to be $1.1 \times 10^6$ m s$^{-1}$ and 0.3 eV below the Fermi level, respectively, from the linear fitting line. In terms of the appearance of the STM images, the existence of standing waves, and the Fermi velocity and Dirac point, the present $\sqrt{3} \times \sqrt{3}-\beta$ silicene closely resembles the $\sqrt{3} \times \sqrt{3}$ silicene reported on a bulk Ag(111) surface by Chen et al [18], and is therefore likely to be the same.

The above results could be regarded as evidence of Dirac dispersion in the second-layer $\sqrt{3} \times \sqrt{3}-\beta$ silicene. However, questions remain regarding the linearity and the large Fermi velocity, although the downward shift of the Dirac point could be explained by electron doping from the weakly interacting Ag substrate. In the case of $\sqrt{3} \times \sqrt{3}$ silicene on bulk Ag(111) surfaces, standing waves were observed in the energy range from +0.4 to +1.1 eV [18]. Although the data could be well fitted using a linear dispersion relation, the linearity was questioned by another group due to the lower energy; it was claimed that the data below 0.4 eV at 6 K could be better fitted using a parabolic relation [21]. However, $\sqrt{3} \times \sqrt{3}$ silicene has been reported to undergo a phase transition with the introduction of many domain boundaries below 40 K [35]. The scattering between such narrow boundaries could result in modification of the dispersion relation [36]; therefore, it is at present inconclusive as to whether the dispersion is linear or parabolic [18, 21]. The present data span a wide energy range from +0.1 to +1.2 eV for the $\sqrt{3} \times \sqrt{3}$ silicene at liquid nitrogen temperatures. As indicated by the red broken line in figure 7(b), the data could also be fitted using a parabolic dispersion relation. Here, the deviation from linearity below 0.4 eV was not as significant as that reported for the study conducted at 6 K [21]. However, given the amount of scatter in the present data, the possibility that the dispersion is not exactly linear cannot be unambiguously ruled out.

It should be noted that the Fermi velocity ($1.1 \times 10^6$ m s$^{-1}$) obtained was almost the same as that for graphene ($1.0 \times 10^6$ m s$^{-1}$ [37]). The Fermi velocity is, in principle, proportional to the nearest-neighbor (NN) hopping integral for the electrons in the hexagonal lattice. The integral is sensitive to the NN distance. Thus, the Fermi velocity for silicene with a larger NN distance is expected to be smaller than that for graphene with a shorter NN distance. In addition, the theoretically predicted Fermi velocity for silicene is $0.5 \times 10^6$ m s$^{-1}$ [32]. A linear dispersion with a Fermi velocity of $0.3 \times 10^6$ m s$^{-1}$ was also recently obtained for occupied states for the second and higher $\sqrt{3} \times \sqrt{3}$ silicene layers on a bulk Ag(111) substrate using ARPES [20]. The linear dispersion for empty states should have a similar Fermi velocity, if it corresponds to the upper branch of the Dirac dispersion. Therefore, we suggest that the observed dispersion in the empty-state $dI/dV$ images is not related to the Dirac dispersion, but to a Si–Ag hybridized state, as was reported for the first-layer $4 \times 4$ silicene on a bulk Ag(111) surface [14, 15].

4. Summary

Epitaxial growth of silicene on ultra-thin Ag(111) films was investigated using STM. During the early stages, the changing morphology of the Ag surface hindered the growth of silicene.
The results indicate that silicene domains could not be nucleated when there was excessive migration of Ag atoms. However, the morphological change subsided after pre-annealing at the growth temperature for 10 min, and silicene domains were successfully nucleated. The first-layer silicene domains were nucleated in recessed regions that were 1 ML lower than the original Ag surface. This implies that Ag–Si exchange and the resulting formation of the recessed regions are crucial for the nucleation of silicene domains.

A $\sqrt{13} \times \sqrt{13}$ commensurate structure was preferentially formed during the initial stage of first-layer silicene growth, while the $4 \times 4$ structure became dominant in the later stage. This is consistent with the results of a recent theoretical study, which indicated that $\sqrt{13} \times \sqrt{13}$ and $4 \times 4$ silicene are Si-poor and Si-rich phases, respectively, and a Si coverage of approximately 1 ML is required to form these phases [31]. Thus, the present results indicate that Si atoms were preferentially trapped in the recessed regions until their concentration became sufficient for the nucleation of silicene. The change from the $\sqrt{13} \times \sqrt{13}$ to the $4 \times 4$ silicene phase is therefore reasonable given the increase in the local Si concentration as growth proceeded.

The completed first layer consisted of a patchwork of silicene domains, vacancies and locally disordered regions. As the growth temperature was increased, the number of such defects decreased and the silicene domain size became larger. However, a higher Si deposition rate was necessary for the growth of silicene at a higher temperature.

As growth proceeded further, 2D and 3D islands were nucleated on the first layer, the latter of which were dominant during growth at a lower temperature. In this case, $\sqrt{3} \times \sqrt{3}$-α silicene was nucleated as small 2D islands. Higher temperatures also led to the growth of larger 2D second-layer silicene islands. At a higher temperature, small $\sqrt{3} \times \sqrt{3}$-α silicene islands were transformed to larger $\sqrt{3} \times \sqrt{3}$-β silicene islands during the later stage. The $\sqrt{3} \times \sqrt{3}$-α silicene exhibited a Moiré pattern, while the $\sqrt{3} \times \sqrt{3}$-β silicene exhibited electron standing waves. No interference pattern was observed for the first layer silicene. The energy dependence of the standing waves revealed a dispersion that was linear, although the resulting Fermi velocity was twice as large as that expected for free-standing silicene.

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