Adatom-induced dislocation annihilation in epitaxial silicene

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Abstract
The transformation of the stripe domain structure of spontaneously-formed epitaxial silicene on ZrB$_2$ thin films into a single-domain driven by the adsorption of a fraction of a monolayer of silicon was used to investigate how dislocations react and eventually annihilate in a two-dimensional honeycomb structure. The in-situ real time scanning tunneling microscopy monitoring of the evolution of the domain structure after Si deposition revealed the mechanisms leading to the nucleation of a single-domain island into a domain structure through a stepwise reaction of partial dislocations. After its nucleation, the single-domain island extends by the propagation of edge dislocations at its frontiers. The identification of this particular nucleation-propagation formation of dislocation-free silicene sheet provides insights into how crystallographic defects can be healed in two-dimensional materials.

1. Introduction
Dislocations are linear irregularities in the ordering of crystals, which strongly influence their optical, electrical, chemical and mechanical properties. Although their presence can result from an imperfect crystallization, they also appear to reduce the strain in the crystals at their surfaces [1] or in epilayers [2–6]. Dislocations are carrying a topological charge, the Burgers vector, which is conserved upon their migration or reaction. Such a reaction can be for instance the spontaneous decomposition of a normal dislocation, i.e. with a Burgers vector equal to a lattice vector, into partial dislocations, i.e. with Burgers vectors whose sum is equal to the Burgers vector of the normal dislocation. Dislocation reactions can also be induced by applying external strain [7–9] or by depositing adatoms [10, 11].

Silicene is a graphene-like two-dimensional material made of silicon atoms, which has been observed experimentally on a limited number of substrates [12–16]. In contrast to graphene for which the robust sp$^2$ hybridization of the orbitals in C atoms forces the covalent bonds to remain in the basal plane, the intermediate sp$^3$/sp$^3$ hybridization of the orbitals in Si atoms [17] makes the atomic structure of silicene buckled and highly flexible. The stripe domain structure consisting of an array of partial dislocations and texturing the epitaxial silicene sheet spontaneously forming on top of zirconium diboride (ZrB$_2$) thin film grown on Si(111) [12, 18] is a perfect test bench to study how dislocation reaction occurs in honeycomb structures. Such a reaction can be induced by the deposition of a fraction of monolayer (ML) of Si atoms which turns the domain structure into a single-domain [19].

In this publication, we report the results of a real-time scanning tunneling microscopy (STM) monitoring of the evolution of this partial dislocation network after deposition of Si atoms. With the support of density functional theory (DFT) calculations, it revealed the non-trivial reaction path which, in contrast to previously reported adatom-induced reactions of partial dislocations [10, 11], leads to their annihilation and to the formation of a dislocation-free two-dimensional crystal.

2. Experimental and computational details
ZrB$_2$(0001) thin films were grown on Si(111) by chemical vapor epitaxy in ultrahigh vacuum (UHV) [20]. The silicene layer was generated by annealing the sample in a separate UHV system at 800 °C for 30 min which removes the natural oxide layer formed on the

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ZrB$_2$ thin film upon transfer in air and induces the segregation of Si atoms on its surface [12]. Silicon was evaporated with a rate of 0.030 ML silicon per min (1 ML silicon corresponds to $1.73 \times 10^{15}$ at cm$^{-2}$) by direct current heating a silicon piece. Room temperature (RT) STM observations were realized with a UHV-STM system (JSPM-4500A, JEOL) and STM images at higher temperature were acquired with an OMICRON UHV variable temperature STM. Pt-Ir and W tips were used respectively for the former and latter systems. Otherwise specified, constant-current STM images were recorded with a sample bias voltage of 500 mV and a tunnel current of 500 pA.

DFT calculations within a generalized gradient approximation [21, 22] were performed using the OPENMX code [23, 24] based on norm-conserving pseudopotentials generated with multireference energies [22] and optimized pseudotatomic basis functions. The domain structures of epitaxial silicene on ZrB$_2$(0001) thin film were modeled by ZrB$_2$ slabs consisting of two Zr, one B, and one silicene layers. A 32 Å-thick vacuum space was used. The structure of silicene was compared to that of a silicene layer put in contact with a thicker ZrB$_2$ slab, to make sure that the effect of the slab ultimate thickness is not significant. A ZrB$_2$ slab without silicene was also considered, as reference. For Zr atoms, three, two, and two optimized radial functions were allocated for the s, p, and d orbitals, respectively, as denoted by s3p2d2. For both Si and B atoms, s2p2d1 basis functions were adopted. A cutoff radius of 7 Bohr was chosen for all the basis functions. A regular mesh of 150 Ry in real space was used for the numerical integration and for the solution of the Poisson equation together with a (1 × 3 × 1) mesh of the reciprocal space. For the geometrical optimization, the bottom Zr layer is fixed and the other atoms can relax freely. The force on each atom was relaxed to be less than 0.0001 Hartree/Bohr. Calculations were performed in the 'four domains supercell' to account for the domain structure of the silicene sheet. Details of the structures considered for this study can be found in the supplementary materials [25] (available online at stacks.iop.org/2DM/8/045011/mmedia). The nudged elastic band (NEB) method was used to estimate the energy barrier between two neighboring equilibrium positions for the partial dislocations.

3. Partial dislocations in epitaxial silicene on ZrB$_2$(0001)

The differentiated large-scale STM image of figure 1(a) shows the silicene sheet spontaneously crystallized on ZrB$_2$(0001), which is textured by one-dimensional periodic stripe domain structures having a pitch of 2.7 nm along $<1100>$ directions of ZrB$_2$. The spontaneous formation of the domain structure is the result of the 5% compressive epitaxial strain which forces the silicene structure to adopt a lattice parameter $a_{Si}$ of 3.65 Å inside the domains to make the $(\sqrt{3} \times \sqrt{3})$ unit cell of silicene fit the $(2 \times 2)$ unit cell of ZrB$_2$(0001). As shown in figure 1(c), epitaxial silicene crystallizes in the domains in the planar-like structure in which five out of the six Si
4. Nucleation of a single-domain island by Si adatoms-induced reaction of partial dislocations

As depicted in figure 2(a), the transformation of the abcdab domain sequence of the pristine silicene layer into a single-domain needs the reaction of four partial dislocations giving rise to a normal dislocation (with a perfect Burgers vector of $2\mathbf{b}_a + 2\mathbf{b}_c = a_S\mathbf{u}_x$) permitting the integration of silicon atoms into the silicene lattice. According to DFT calculations, the creation of such a normal dislocation would represent a cost of energy of about 16 meV per Si atom of the four domains supercell (see table 1 and figure S1 in supplementary materials [25]). It would involve the unlikely coherent motion of a large number of Si atoms that would need to overcome the repulsion between domain boundaries. The collective motion of the domain boundaries pointed out by arrows in the STM image of figure 2(d) recorded at 300 °C shows that this interaction is also effective in the substrate temperature range (300 °C–350 °C) at which the formation of single-domain can be realized by Si deposition [19]. Intriguingly, as reported in table 1, the formation of single-domain corresponds to an even higher increase of energy (30 meV per Si atom of the four domains supercell), which points out that the adsorption of Si atoms on silicene sheet must represent a cost of energy even higher to make the reduction of the number of Si adatoms a driving force for the transformation of the stripe domain structure into a single-domain. This gain of energy was evaluated by considering stripe domain structures on which Si individual adatoms were adsorbed above the center of the domains and above the center of the boundaries, respectively. The formation of a single-domain from each of these structures corresponds respectively to a reduction of energy of 24.5 meV and...
of 26.4 meV per Si atom of the four domains supercell (see table 1 and figure S1 of the supplementary materials [25]).

As the time scale of the formation of single-domain silicene upon deposition on heated samples is not suitable for real-time STM observations [19], a different approach was considered to identify the nontrivial dislocation dynamics process leading to the silicene sheet transformation. To determine how the partial dislocations react to eventually incorporate the Si adatoms in the silicene lattice, a small amount of Si atoms (0.015 ML) corresponding coarsely to half of the coverage required to turn the stripe domain structure of pristine silicene into a single-domain [19] was deposited on epitaxial silicene at RT, and the evolution of the silicene sheet was monitored by STM during several hours after this deposition while the sample and the tip are kept at RT.

The flexibility of the atomic structure of silicene is exemplified by the fluctuation of the domain boundaries by $\sqrt{3}a_{ZrB_2}$ observed in STM images recorded at RT such as that of figure 1(b). As shown in figure S2(b) of supplementary materials [25], this motion of the boundaries is the consequence of the displacement of a pair of atoms by a distance corresponding to the Burgers vector of the dislocation. The energy barrier between the two equilibrium positions of these pair of atoms is 0.17 meV Å$^{-1}$ as estimated by DFT calculations (However, this calculation does not take into account the energy cost represented by the formation of a pair of kinks) [25]. The energy of the barrier is shallow enough to allow for the thermal activation of the free motion of the dislocations at RT in silicene. This is strikingly different from graphene whose robust bonding requires a much higher temperature [31] or irradiation [32]. The reaction of the dislocations is therefore only limited by the repulsive interaction between the domain boundaries.

The STM images of figures 3(a) and (e) compare the domain structures of silicene after 0.015 ML Si depositions at 350 °C and at RT. In the former case, the density of domain boundaries is reduced by half while their ordering is locally preserved which suggests that the interaction between them is still acting for such larger periodocities. In contrast to the case of heated samples, the deposition at RT did not cause the vanishing of domain structures except at sparse locations, but the Si adatoms form clusters with an apparent height of 1 Å, an apparent size of 2–3 nm, an estimated density of $10^4$ μm$^{-2}$ and a first neighbor distance of 6 nm. The clusters are sitting systematically at the domain boundaries which is in contradiction with DFT calculations that predicted an adsorption energy lower in the center of the domains than in the center of the boundaries. This difference may be explained by a possible better mismatch between the clusters and the silicene atomic structures which may turn the domain boundaries into more stable sites for the clusters. Please note that the formation of clusters must represent a significant gain of energy in comparison with isolated adatoms, owing to a reduced number of dangling bonds.

The sequence of STM images shown in figures 3(a)–(e) presents the evolution of the silicene sheet in the presence of these Si clusters. The figure 3(a) depicts a $abcda$ domain sequence similar to that of the pristine domain structure. The STM image of figure 3(b) recorded 257 min after that of figure 3(a), shows that along a distance of 20 nm a pair of domain boundaries $ab/c$ disappeared together with the domain $b$. The so created $alc$ boundary, which sits near the location of the $b/c$ boundary, consists of a straight 11 Å-wide gap between the protrusions rows of the $a$ and $c$ domains. This feature is consistent with the $(2\sqrt{3}a_{ZrB_2})$-wide dislocation having a Burgers vector of $\vec{b}_{alc} = \frac{\sqrt{3}}{2} \vec{u}_a$, whose optimized structure is shown in figure 2(e). Since $\vec{b}_{alc} = \vec{b}_b + \vec{b}_c$, this $alc$ boundary can be identified as the result of the reaction of partial dislocations $a/b + b/c \rightarrow a/c$. The fact that this type of partial dislocation is never observed in the domain structure of pristine silicene is consistent with the fact that this reaction is in violation of the Frank criterion which predicts that such $alc$ dislocation must decompose into $ab/c$ and $b/c$ dislocations as $||\vec{b}_{alc}||^2 > ||\vec{b}_{a/b}||^2 + ||\vec{b}_{b/c}||^2$. DFT calculations confirm that such a reaction represents an increase in energy of the silicene sheet by about 4 meV per Si atom of the four domains supercell (see table 1). As the reaction does not involve the incorporation of any Si atoms in the silicene sheet, its spontaneous evolution towards a metastable structure in spite of the repulsion between domain boundaries can only be explained by the modification of the stress field caused by the clusters. One can observe that the

| Domains sequence | Burgers vectors | $N_{Si}$ | $E$ (meV) |
|------------------|----------------|---------|-----------|
| $abcd a$ | $b_c \times 2, b_\perp \times 2$ | 104 | 0 |
| $abcd a$, Adatoms above the boundaries | $b_c \times 2, b_\perp \times 2$ | 108 | 66.9 |
| $abcd a$, Adatoms above the domains | $b_c \times 2, b_\perp \times 2$ | 108 | 65.0 |
| $abcda$ | None | 108 | 30.5 |
| $a a$ | $2(b_+ + b_-)$ | 104 | 15.8 |
| $aca d$ | $b_+ + b_- + b_{x}$ | 104 | 3.8 |
| $ada d$ | $2b_+ + b_\perp$ | 104 | 7.9 |
| $ada d$ | $-b_+ + b_\perp$ | 108 | 39.7 |
position of this a/c boundary does not fluctuate much in comparison with the partial dislocations with \( \vec{b}_{ac} \). Burgers vectors in spite of the fact that the energy barrier is lower (see figure S2(b) of supplemental materials). This can be explained by the fact that the shift of this boundary by a distance of \( \sqrt{3}a_{ZrB_2} \) needs the motion of three atoms instead of two in the case of dislocations with \( \vec{b}_{ac} \) Burgers vectors [25].

The stripe domain structure continues to evolve after this first reaction as around 27 min after the moment the image of figure 3(b) was recorded, the acda domains sequence turned into a ada sequence (figure 3(c)). The ada domain boundary appears in the STM image as a narrow and fuzzy 9 Å-wide feature. A simple \( a/c + c/d \rightarrow a/d \) reaction would give rise to a dislocation with a Burgers vector of \( \vec{b}_{ad} = \vec{b}_{ac} + \vec{b}_{cd} - 2\vec{b}_{d} = 2\vec{u}_x (3\vec{u}_x - \sqrt{3}\sqrt{2}\vec{u}_y) \). This possibility was evaluated in DFT calculations by considering a dislocation spanning a width of \( \frac{1}{2}\sqrt{3}a_{ZrB_2} \). Upon geometrical optimization, this dislocation decomposed in a pair of a/c and c/d dislocations sitting side-by-side (figure 3(g)) resulting in an overall width of the a/d boundary inconsistent with that observed in STM image of figure 3(c). It has to be noted that the comparison of the energies (table 1) of the structures of figures 3(f) and (g) indicates that the closer proximity of these two dislocations represents an increase of energy which reflects the repulsive interaction between boundaries.

The comparison of the images of figures 3(b) and (c) indicates that the dislocation reaction is accompanied by the vanishing of the Si cluster marked by a white circle. One can deduce that silicon atoms were incorporated in the silicene lattice at this stage of the silicene sheet transformation. To verify this hypothesis, a four domain supercell in which a row of Si atoms was added between the domains a and d was considered. This domain boundary is therefore a dislocation with a Burgers vector of \( \vec{b}_{ad} = \vec{b}_{ac} + \vec{b}_{cd} - a_S \vec{u}_x = -\frac{a_S}{4}(\vec{u}_x + \frac{1}{\sqrt{3}}\vec{u}_y) = -\vec{b}_{ac} \). The optimized structure visible in figure 3(h) suggests that this boundary is made of highly compressed hexagon rings along which protruding atoms are separated by a single row of Zr atoms. In contrast to the structure of figure 3(g), this structure is consistent with the boundary observed in the STM image shown in figure 3(c). The apparent width of the boundary can be explained by the fluctuation of the pair of Si atoms marked by a circle in figure S2(c) of supplementary materials [25] allowed by an energy barrier even shallower (0.07 meV Å\(^{-1}\)) than for the boundaries with Burgers vectors of \( \vec{b}_{ac} \).

According to DFT calculations, the formation of the ada sequence with the incorporation of Si atoms, represents a much higher cost of energy than the simple \( a/c + c/d \rightarrow a/d \) reaction. The silicene sheet must transit by the structure shown on figure 3(f), which may explain the position of the ada boundary slightly on the side of the position of the a/c boundary.

However, one may conceive the following explanation based on the fact that the position of the a/d dislocation is the same as that of the a/c dislocation. The tension at the a/c boundary weakens the silicon bonds and the honeycomb lattice eventually cracks. As a consequence of it, the domain c is pulled to the left to annihilate the c/d dislocation. On the other side, the so-created empty space separating dangling bonds can be filled by Si atoms which can crystallise in the
form of an honeycomb structure in spite of the compressive strain exerted on it.

After the record of the STM image in figure 3(c), no further evolution of the surface was observed until the tip eventually degraded. One can easily conceive that the ada domain sequence could have evolved into a single a domain (or a single d domain) by reaction of the a/d dislocation with the d/a dislocation on its right (or the d/a dislocation on its left). Their annihilation \((\vec{b}_{a/d} + \vec{b}_{d/a} = 0)\) would reduce the energy of the silicene sheet by 9 meV per Si atom of the four domains supercell (table 1) and would lead to the nucleation of a single-domain island as the one whose optimized structure is shown in figure 3(i) and observed experimentally in figure 4. Please note that the single-domain imaged in this figure nucleated before the dislocations reaction shown in figure 3, which indicates that single-domain islands keep nucleating while already formed single-domain islands expand.

5. Propagation of a single-domain island

As depicted in figure 4(a), the nucleation of a five domains-wide single-domain island in the domain structure results in interfaces with the stripe domain structure where dislocations merge into normal edge dislocations. Note that such edge dislocations are also observed in the pristine silicene sheet at the frontiers between domain structures with different orientations [28]. However, in contrast to pristine silicene, the edge dislocations formed by the nucleation of a single-domain island within a domain structure propagate in such a way that the single-domain island extends, as shown in the STM images of figures 4(b)–(e) recorded at different times after the Si deposition. Please note that this island nucleated in a region which was not scanned, which demonstrates that the effect of the STM tip is negligible. Although this propagation is limited by its highly anisotropic character, it allows for enlarging the single-domain island much more rapidly than by the nucleation of new single-domain islands. This is exemplified in the STM images of figures 4(b)–(d) in which dislocations started reacting but the passage of the edge dislocation occurs before completion of the nucleation of a new single-domain island. The migration of the edge dislocation occurs mostly by climb steps resulting from the integration of Si adatoms into the silicene sheet. This is in contrast with previous observation of the diffusion of dislocations in graphene for which the climbs are mostly the result of the evaporation of atoms [31–33]. It has to be noted that the extension of the single-domain island is made possible by a diffusion length at RT large enough to allow for the Si adatoms from the surrounding clusters to reach the edge dislocation. The propagation of the single-domain island gives rise to the vanishing of all Si clusters on the passage of the interface between single-domain and the stripe domain structure. The comparison of the clusters surrounding the single domain island in figures 4(b) and (e) points out a slight increase of the size of some of them and the apparition of new clusters. This can be explained by Si atoms which were not incorporated into the single domain island, diffuse on the surface and eventually reach already existing Si clusters or give rise to new clusters. These enlarged Si clusters may lose their mobility and therefore hinder the nucleation of new single-domain islands. This may explain why the surface stops evolving toward larger single-domain area. At temperatures as high as 300 ◦C [19], this effect may not occur and the silicene sheet fully transforms into a single-domain.

6. Conclusions

By means of a real-time STM monitoring, we experimentally determined the complex nucleation-propagation process through which an array of partial dislocations in epitaxial silicene on ZrB$_2$(0001) turns into a single-domain in presence of Si adatoms. This transformation involves first the nucleation of a single-domain island through a sequence of reaction of partial dislocations and incorporation of adatoms into the silicene sheet. Noteworthy, the presence of adatoms on top of silicene initiates the reaction of dislocations even before they get integrated into
the silicene sheet. The single-domain island then extends anisotropically by the motion of edge dislocations leading to further incorporation of Si adatoms. Beyond insightful information on the dynamics of dislocations in two-dimensional honeycomb structures, these experimental observations indicate how dislocations can be removed from crystals in spite of their stability. It may thus help finding solution to heal crystallographic defects in surfaces, interfaces, 2D materials, or any kind of nanomaterials.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

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**Conflict of interest**

The authors declare no competing interests.

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