

Patterned Defect Structures Predicted for Graphene Are Observed on Single-Layer Silica Films

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Supporting Information

ABSTRACT: Topological defects in two-dimensional materials such as graphene are considered as a tool for tailoring their physical properties. Here, we studied defect structures on a single-layer silica (silicatene) supported on Ru(0001) using a low energy electron diffraction, scanning tunneling microscopy, infrared reflection—absorption spectroscopy, and photoelectron spectroscopy. The results revealed easy formation of periodic defect structures, which were previously predicted for graphene on a theoretical ground, yet experimentally unrealized. The structural similarities between single-layer materials (graphene, silicene, silicatene) open a new playground for deeper understanding and tailoring



structural, electronic, and chemical properties of the truly two-dimensional systems.

KEYWORDS: Ultrathin oxide films, silica, silicatene, topological defects, graphene

wo-dimensional (2D) materials remain very attractive objects in materials science. In particular, graphene has received enormous attention owing to its possible application in electronic devices.¹ Structural imperfections (defects) are believed to play a key role in tailoring the physical and chemical properties of graphene and related materials. Various types of defects on graphene and other carbon nanomaterials have been addressed both experimentally and theoretically and can now be imaged with atomic resolution (see ref 2 and references therein). The defects are commonly described in terms of the Stone-Thrower-Wales³ (STW) defects (where four hexagons are converted into pentagon-heptagon pairs) that together with the so-called inverse STW defects are considered as building blocks for a wide range of defect structures.⁴ On the basis of density functional theory (DFT) simulations, Lusk and Carr^{4b} have recently suggested "defect engineering" via patterning the defects in the periodic 2D arrays as a tool to create artificial materials that might exhibit entirely new properties. They demonstrated this approach by constructing 2D carbon allotropes referred to as Haeckelite^{4a-c} after Terrones et al.,⁵ who predicted a high stability of ordered arrangements of pentagons, hexagons, and heptagons. However, to the best of our knowledge such materials have not yet been realized in practice.

Other interesting 2D materials, still awaiting investigations of technologically important properties, are ultrathin silica films grown on metal substrates (see ref 6 and references therein). The monolayer silica films, which were identified on $Mo(112)^7$ and $Ru(0001)^8$ as well as on SiC(0001)⁹ substrates, consist of a single-layer network of corner-sharing [SiO₄] tetrahedra forming a honeycomb-like structure as shown in Figure 1a. There is obvious similarity between structures of graphene and of monolayer silica, although the silica sheet needs a support to bind one of the four apical O atoms in the [SiO₄] tetrahedron,



Figure 1. (a) Atomic structure of a monolayer silica film on Mo(112). (Si, large yellow; O, small red). (b) Typical STM image showing a honeycomb-like structure of the film. Marked by the arrows are the line defects, consisting of alternating octagons and tetragons, zoomed in the inset.

otherwise uncoordinated. Analysis of structural defects on monolayer silica films grown on Mo(112) revealed that the most abundant defects are antiphase domain boundaries,^{7,10} which form a line of alternating octagons and tetragons (in other notation, 8- and 4-membered rings, respectively) (see Figure 1b) as a result of a lateral shift, by half of the unit cell, between the perfect hexagonal (6-membered rings) domains. It was suggested that the good crystallinity of the silica film on Mo(112) is primarily due to its very strong bonding to the metal surface through the Si–O–Mo linkages¹¹ that drives formation of extended terraces following basically the topography of Mo(112) underneath.

In this work, we address defect structures of a monolayer silica film that is supported by Ru(0001) via much weaker

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Received:June 20, 2013Revised:August 8, 2013Published:August 12, 2013
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SiO-Ru bonds.⁸ The results obtained by a low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), infrared reflection-absorption spectroscopy (IRAS), and scanning tunneling microscopy (STM) show easy formation of various defects in the silica layer. The periodic defect structures reveal interesting similarities to the topological structures theoretically predicted, yet unrealized on graphene. Those structures are reversibly formed on silica films by thermal treatment and therefore do not need sophisticated techniques like electron or ion irradiation for defect creation. We believe that the results may have a strong impact on tailoring structural, electronic, and chemical properties of the truly two-dimensional systems.

The "as prepared" monolayer silica films on Ru(0001) are characterized by (i) a (2×2) -Ru(0001) LEED pattern corresponding to the 5.42 Å lattice constant of the silica overlayer; (ii) a principal, very strong IRAS band at 1134 cm⁻¹, assigned to asymmetric stretching vibration of the O–Si–Ru linkage; (iii) a variety of O coordinating bonds such as Si–O– Si, Si–O–Ru, and O–Ru, as judged by XPS.⁸ The honeycomblike structure of the silica monolayer with a ~ 5.4 Å periodicity is clearly seen in STM images, although silica nanoparticles as well as "holes" may also be present in small amounts (Figure 2a). In addition, the films contain interfacial oxygen which



Figure 2. (a) Typical STM image of a monolayer silica film grown on Ru(0001) showing a mosaic-like structure. Marked in (b) and (c) are structural defects, such as a "blister defect" (b) and domain boundary defects (c). Tunneling conditions: sample bias 2 V and current 0.1 nA (a); 1.2 V and 0.15 nA (b,c).

adsorbed directly on a metal surface.^{8,10} Compared to the silica films on Mo(112),⁷ the silica film on Ru(0001) is not perfectly ordered on a large scale and form a mosaic-like structure, although each domain is well-aligned with principal crystallographic directions of the Ru(0001) surface.

Since the STM contrast often depends on tunneling parameters and tip conditions, precise atom mapping in the high-resolution images is not straightforward. Therefore, we applied here a simplified analysis of the defect structures that is based on the fact that regardless of the nature of protrusions in these images the midpoint of a triangle, connecting centers of three neighboring hexagons, coincides with the position of Si atoms (Figure 1a). In addition, the size (N) of a ring, that is, whether it is pentagon (N = 5) or heptagon (N = 7), can easily be determined by counting the number of the nearest neighbors rings. Following this approach, the defect marked in Figure 2b consists of a hexagon surrounded by three 5- and three 7-membered rings. In the case of graphene, such a defect with a 3-fold symmetry was referred to as a single blister.^{4b}

One-dimensional (or line) defects forming a network of domain boundaries, imaged as protruding lines in Figure 2a, are more complex. A closer look at Figure 2a shows that most of the boundaries are imaged as zigzag lines formed by relatively large depressions. This is better seen in Figure 2c showing the STM image of the surface area consisting of several hexagonal domains. In the right portion of the image, domain boundary formed by STW (7,5-5,7) defects is identified. It is noteworthy that such an extended defect is different from the grain boundaries observed on a metal supported graphene,¹² where STW defects are lined up along the 7-7 axis. Also, the grain boundaries between rotational domains of the graphene showed curved lines of alternating 5 and 7 rings in an "endon" arrangement,^{2c,13} which are, again, different from the line defects observed here for silica. Interestingly, when three such line defects intersect they form a blister defect (see the bottom portion of Figure 2c).

Thin oxide films commonly exhibit better long-range ordering when prepared at high temperatures. Therefore, the silica films were further annealed in UHV at higher temperatures. In addition, it was expected that vacuum annealing will deplete interfacial oxygen present in these "O-rich" films. Indeed, after annealing to 1070 K, the intensity of the O1s signal in XP spectra at ~530 eV, which is assigned to O-Ru species, is reduced by \sim 9%, and the binding energies of Si2p (~102.5 eV) and O1s (~531.5 eV) core levels, related to the Si-O bonds, both shift by ~0.5 eV (not shown here). On the basis of our previous study,¹⁴ these effects are assigned to the work function changes that accompany desorption of O adatoms from the Ru surface. It has turned out, however, that this treatment causes more dramatic structural changes, which are immediately seen in LEED pattern depicted in Figure 3a. It is clear that the unit cell of the silica layer is now rotated by 30° with respect to Ru(0001), and the lattice constant is shortened to about 5.23 Å (cf 5.42 Å in the original film). In addition, satellite spots appear around the integer spots, thus indicating the Moiré-like superstructure commonly observed for ultrathin oxide films on metals exhibiting a small lattice mismatch.

In the IRA-spectra (Figure 3b), the principal phonon at 1134 $\rm cm^{-1}$ redshifts to 1037 $\rm cm^{-1}$, which is still in the range of frequencies characteristic for Si–O-metal linkages,⁶ thus suggesting that the monolayer nature of the silica film is maintained upon vacuum annealing. However, the peak at 790 $\rm cm^{-1}$ apparently disappears, whereas the signal at 687 $\rm cm^{-1}$ survives upon annealing. Broadening of the 1037 $\rm cm^{-1}$ band implies some structural disordering.

Solely on the basis of those results, one may suggest a tentative structural model, where a silica honeycomb network with a 5.23 Å periodicity is rotated by 30° with respect to Ru(0001). Accordingly, a coincidence superstructure is formed, as shown in Figure 3d, with a periodicity equal to the ten



Figure 3. (a) LEED pattern of a monolayer silica film on Ru(0001) annealed to 1070 K in UHV. Two coexisting unit cells are indicated, one of which (as dash line) being the same as in the original film. (b) IRA-spectra of the "as prepared" and annealed films. (c) Structural model for the pristine film (the top view) showing a (2×2) -Ru(0001) structure with the 5.42 Å lattice constant as indicated. Nodes of the hexagons show the position of the Si cations in [SiO₄] tetrahedra; oxygen ions are not shown for clarity. (d) The LEED-derived model for the annealed silica film with a 5.23 Å lattice constant rotated by 30° with respect to Ru(0001). The unit cell of a silica overlayer and a coincidence superstructure are indicated.

Ru(0001) cells along the surface lattice directions. (The rotation of the silica layer without any change of the lattice constant, i.e. 5.42 Å, would result in the Ru(0001)-(7 \times 7) structure).

To rationalize the spectral changes caused by annealing, we first recall that in the pristine films the silica sheet forms a $(2 \times$ 2)-Ru(0001) structure, depicted in Figure 3c, where the Rubonded apical oxygen ions in [SiO₄] equally occupy atop and hollow sites. The DFT simulation⁸ showed that the main peak at 1134 \mbox{cm}^{-1} corresponds to in-phase asymmetric stretching vibrations of Si-O-Ru linkages, with the main contribution coming from atop sites. The weaker phonon band at 790 cm⁻¹ corresponds to out-of-phase asymmetric stretching vibrations of the two Si-O-Ru linkages in atop and hollow sites, respectively. Finally, the $\sim 690 \text{ cm}^{-1}$ band corresponds to the "umbrella" mode that includes the vertical motion of the topmost O atoms. Certainly, in the 30°-rotated film, a variety of Si-O-Ru coordinations exist (Figure 3d), which may influence the principal phonon frequency and also cause signal broadening. In contrast, the film rotation should not affect the umbrella mode involving the topmost oxygen atoms. All these effects are, indeed, consistent with the IRAS data for the annealed films as shown in Figure 3b. In principle, such a sensitivity of the vibrational frequencies to the film/support registry is not surprising and has already been shown by DFT for the silica film on Mo(112),^{7,10} where the calculated frequencies of the principal mode shifted by $\sim 150 \text{ cm}^{-1}$ upon lateral shift of the silica layer with respect to the Mo(112)surface underneath.

The Moiré-like superstructure inferred by LEED for the annealed films is also observed by STM. Figure 4a shows a weak long-range modulation of the STM contrast with a ~ 24 Å periodicity, which, at first glance, justifies the coincidence structure depicted in Figure 3d. However, a closer STM inspection revealed much more complex and intriguing structures than predicted from the tentative model shown in Figure 3d, which included rotation of the silica overlayer only. High-resolution STM images, displayed in Figure 4b,c, show that the film is no longer represented by hexagons exclusively, as in the original film. Instead, the surface is formed by a 2D array of structural defects, marked as triangles (T) and rectangles (R) in Figure 4b, which are embedded into the hexagonal network. The polygonal representation of these defects deduced from the STM images (Figure 4c) revealed that the T-defects are, in fact, the blister defects with 3-fold symmetry (see also Figure 2b). The R-defects, never reported before, constitutes an octagon surrounded by two pentagons, two tetragons, and four heptagons, thus exhibiting the 2-fold symmetry.

Both the T- and R-defects outlined in Figure 4c are surrounded by hexagons (see also Figure S1 in the Supporting Information). It is noteworthy that the defects in the periodic structure are not isolated and in fact are very close to each other that may in turn affect structural identification of the previously unknown R-defect. Yet we have not observed an isolated Rdefect in our samples, a schematic representation in Figure 4d illustrates how the R-defect could fit within a hexagonal lattice. Certainly, the proposed structure needs to be further analyzed



Figure 4. (a-c) STM images of the annealed films. In the large-scale image (a), the film initially contained many holes exposing a Ru substrate. A periodic contrast modulation of the film surface is clearly observed. High-resolution image (b) shows a two-dimensional array of structural defects, marked as T and R. The image (c) is superimposed with the polygonal representation of the defects. The R-defect (marked in red) and T-defect (in green) are surrounded by hexagons (in yellow). (d) A schematic representation of isolated R- and T-defects imbedded into a hexagonal matrix. (The images (b,c) were corrected to compensate distortions caused by the thermal drift of a microscope. Tunneling conditions for all images: bias 1.2 V and current 0.15 nA).

and optimized by DFT. It appears, however, that the hexagons surrounding the R-defect are distorted owing to a relatively high flexibility of the Si–O bonds.

In addition, Figure 4b revealed two isomorphs for both Tand R-defects, which are rotated by 60° with respect to each other. The T- and R-defects were almost equally present at random on the entire surface. However, the T-defects start to dominate after prolonged annealing, thus indicating that Tdefects seem to be energetically more favorable than R-defects. Indeed, the comparison of the T- and R-structures in Figure 4d, although simplified, suggests that the T-defects seem to be easier accommodated by the hexagonal matrix than the Rdefects.

Finally, it has turned out that reoxidation of the film in 10^{-6} mbar O₂ at 1100 K recovers the original structure of the film. Again, the film shows a (2 × 2)-Ru(0001) LEED pattern, and the principal IRAS band shifts back to 1134 cm⁻¹. Therefore, the formation of the patterned defect structure is not a kinetically limited but thermodynamically driven process.

Creation of allotropes composed of patterned defects has long been considered for graphene and related carbon nanomaterials on theoretical grounds. In particular, Haeckelites,⁵ that is a family of layered carbon materials consisting of ordered arrangements of pentagons, hexagons, and heptagons, were suggested as thermodynamically stable "metacrystals".^{4b,15} However, to the best of our knowledge no experimental evidence for such materials has yet been reported. Surprisingly, a silica monolayer film on Ru(0001) studied here can readily form haeckelite-type structures upon heating to elevated temperatures in UHV. Furthermore, the R-defect may be suggested as another building block in such architectures. Although several types of octagonal defects have theoretically been predicted for graphene,¹⁶ the R-defect identified here was never reported.

Obviously, a single silica layer may be considered as a graphene composed of $[SiO_4]$ entities instead of the C atoms and henceforth referred to as silicatene to distinguish it from the silicon equivalent of graphene called silicene.¹⁷ The latter has recently received much attention, in particular for Si-based electronic applications. Similar to a single silica layer, silicene does not exist as a free-standing sheet and needs a support. The results reported so far (primarily on noble metal supports) showed formation of almost perfect honeycomb-like, albeit buckled silicene structures with a low density of defects. In contrast, the silicatene layers on Ru(0001) studied here show a variety of defect structures, which under some conditions can form a periodic 2D-pattern. It seems plausible that such a difference between homoelemental (graphene, silicene) and heteroelemental (silicatene) layers results from the relatively high flexibility of the Si–O bonds constituting a $[SiO_4]$ unit, thus providing additional degree of freedom while adopting the most stable structure. On the other hand, haeckelite-like structures were never observed for the silicatene layer on Mo(112), most likely due to a strong SiO-Mo bond that dictates a perfect registry of a layer to a single crystal support underneath. Apparently, the same holds true for silicene layers on metals. It therefore appears that a much weaker SiO-Ru bond allows the silicatene layer to reconstruct into a presumably more stable haeckelite-type structure, yet awaiting theoretical proof.

Interestingly, in the course of this reconstruction the entire silicatene layer rotates by 30°. The rotation is identified by LEED as well as by STM (see Supporting Information Figure S2). In attempts to rationalize this effect, we recall that the previous DFT calculations⁸ showed that a silicatene layer on Ru(0001) in a (2×2) -registry is stable only in the presence of additional oxygen atoms bonded to Ru. These atoms are sitting in the hollow sites and form the (2×2) sublattice. Heating to elevated temperatures in UHV results in desorption of the O atoms, as judged by XPS, and 30°-rotation of the silica overlayer. As mentioned above, reoxidation leads back to the unreconstructed (2×2) -structure. Therefore, one may link the presence of O ad-atoms on Ru to the structural stability of the silicatene layer such that the $O(2 \times 2)$ -surface provide a template for the (2×2) -structure, whereas in the absence of the interfacial O atoms the silica layer reconstructs into the most stable haeckelite structure. In principle, solely the lattice constant considerations favor this reconstruction. Indeed, assuming that a hypothetical free-standing silicatene has the same lattice constant as computed for an unsupported bilayer silica film, that is, in the range of 5.24–5.32 \AA^{18} formation of the (2×2) -Ru(0001) structure with the 5.42 Å lattice constant implies a substantial stretching of the silica layer. In the reconstructed, 30°-rotated silicatene layer, however, the lattice constant is reduced to 5.23 Å, as measured by LEED, which fits better free-standing geometry and hence unstrained structure.

On a more noble Pt(111) support, only bilayer silica films were observed.¹¹ Interestingly, such bilayer films, grown on Ru(0001) and Pt(111), did not show any reconstruction upon UHV annealing: only interfacial O-atoms between the silica sheet and a metal substrate desorb at high temperatures.¹⁴ These findings, therefore, suggest that the support plays a substantial role in the structural stabilization of the silicatene.

In summary, we studied defect structures on a single-layer silica sheet (silicatene) supported by Ru(0001). The results

show that high-temperature annealing in UHV causes the formation of a two-dimensional array of topological defects that are very similar to haeckelite-based structures predicted, yet unrealized for graphene. Two types of defects were observed. The T-defects are in essence the blister defects with a 3-fold symmetry theoretically predicted for graphene. The R-defects constitutes an octagon surrounded by two pentagons, two tetragons, and four heptagons, thus exhibiting the 2-fold symmetry. In addition, two isomorphs for both T- and R-defects were found, which are rotated by 60° with respect to each other. The T-defects and they dominate the structure after prolonged annealing.

Comparison of homoelemental (graphene, silicene) and heteroelemental (silicatene) single layers suggests that the relatively high flexibility of the Si–O bonds in silica provides an additional degree of freedom while adopting the most stable structure, and as such may result in a variety of yet unexplored defect structures. The results also indicate that certain fundamental defect building blocks seem to be related to crystalline symmetry of these 2D-systems and not material details. As such, studying defects in silicatene may aid in better understanding of defect structures in graphene and vice versa. The structural similarities between single-layer materials open a new playground for tailoring structural, electronic, and chemical properties of the truly two-dimensional systems.

Methods. The experiments were carried out in an UHV chamber (base pressure 5×10^{-10} mbar) equipped with LEED (from Omicron), XPS with Scienta SES 200 hemispherical analyzer, IRAS (Bruker IFS 66v), and STM (from Omicron). The Ru(0001) crystal (from MaTeck GmbH) was mounted on the Omicron sample holder. The crystal could be heated by ebeam from the backside of the crystal using a tungsten filament. The temperature was measured by a Type K thermocouple spot-welded to the edge of the crystal.

The clean Ru(0001) surface was obtained by cycles of Ar⁺sputtering and annealing to 1300 K in UHV. The $3O(2 \times 2)$ -Ru(0001) surface was prepared by exposing the clean surface to 3×10^{-6} mbar O₂ at 1100 K for 5 min and cooling to 500 K before oxygen was pumped out. Silicon (99.99%) was deposited onto the $3O(2 \times 2)$ -Ru(0001) surface at 100 K in 2×10^{-7} mbar O₂ using e-beam assisted evaporator (EMT3, Omicron). Final oxidation was performed in 3×10^{-6} mbar O₂ at ~1100 K. The amount of Si at the surface was monitored by XPS using the well-established structure of silica film on Mo(112) as a reference.⁷

The XP-spectra were referenced by setting the Au $4f_{7/2}$ level to 84.0 eV measured on a clean gold foil. The IRA-spectra were recorded using p-polarized light at 84° grazing angle of incidence (resolution 4 cm⁻¹). All STM images were obtained at room temperature using Pt–Ir tips. Typical bias voltages and tunneling currents are in the range of 1–2 V and 0.2 nA.

ASSOCIATED CONTENT

S Supporting Information

Additional high-resolution STM images of the T- and Rdefects. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft through CoE "UniCat". J.A.B. thanks the Alexander von Humboldt Foundation for the fellowship. X.Y. acknowledges the International Max-Planck Research School "Complex surfaces in materials science".

REFERENCES

(1) (a) Geim, A. K.; Novoselov, K. S. The rise of graphene. *Nat. Mater.* **2007**, *6* (3), 183–191. (b) Weiss, N. O.; Zhou, H.; Liao, L.; Liu, Y.; Jiang, S.; Huang, Y.; Duan, X. Graphene: An Emerging Electronic Material. *Adv. Mater.* **2012**, *24* (43), 5782–5825.

(2) (a) Batzill, M. The surface science of graphene: Metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects. *Surf. Sci. Rep.* **2012**, 67 (3–4), 83–115. (b) Suenaga, K.; Wakabayashi, H.; Koshino, M.; Sato, Y.; Urita, K.; Iijima, S. Imaging active topological defects in carbon nanotubes. *Nat. Nanotechnol.* **2007**, *2* (6), 358–360. (c) Banhart, F.; Kotakoski, J.; Krasheninnikov, A. V. Structural Defects in Graphene. *ACS Nano* **2010**, *5* (1), 26–41.

(3) (a) Stone, A. J.; Wales, D. J. Theoretical studies of icosahedral C60 and some related species. *Chem. Phys. Lett.* **1986**, 128 (5–6), 501–503. (b) Thrower, P. A. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Dekker: New York, 1969; Vol. 5, p 262.

(4) (a) Lusk, M. T.; Wu, D. T.; Carr, L. D. Graphene nanoengineering and the inverse Stone-Thrower-Wales defect. *Phys. Rev. B* **2010**, *81* (15), 155444. (b) Lusk, M. T.; Carr, L. D. Nanoengineering Defect Structures on Graphene. *Phys. Rev. Lett.* **2008**, *100* (17), 175503. (c) Lusk, M. T.; Carr, L. D. Creation of graphene allotropes using patterned defects. *Carbon* **2009**, *47* (9), 2226–2232. (d) Ma, J.; Alfe, D.; Michaelides, A.; Wang, E. Stone-Wales defects in graphene and other planar sp̂{2}-bonded materials. *Phys. Rev. B* **2009**, *80* (3), 033407.

(5) Terrones, H.; Terrones, M.; Hernández, E.; Grobert, N.; Charlier, J. C.; Ajayan, P. M. New Metallic Allotropes of Planar and Tubular Carbon. *Phys. Rev. Lett.* **2000**, *84* (8), 1716–1719.

(6) Shaikhutdinov, S.; Freund, H.-J. Ultrathin Silica Films on Metals: The Long and Winding Road to Understanding the Atomic Structure. *Adv. Mater.* **2012**, *25* (1), 49–67.

(7) Weissenrieder, J.; Kaya, S.; Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J.; Sierka, M.; Todorova, T. K.; Sauer, J. Atomic Structure of a Thin Silica Film on a Mo(112) Substrate: A Two-Dimensional Network of SiO₄ Tetrahedra. *Phys. Rev. Lett.* **2005**, *95* (7), 076103.

(8) Yang, B.; Kaden, W. E.; Yu, X.; Boscoboinik, J. A.; Martynova, Y.; Lichtenstein, L.; Heyde, M.; Sterrer, M.; Wlodarczyk, R.; Sierka, M.; Sauer, J.; Shaikhutdinov, S.; Freund, H.-J. Thin silica films on Ru(0001): monolayer, bilayer and three-dimensional networks of [SiO₄] tetrahedra. *Phys. Chem. Chem. Phys.* **2012**, *14* (32), 11344.

(9) Bernhardt, J.; Schardt, J.; Starke, U.; Heinz, K. Epitaxially ideal oxide-semiconductor interfaces: Silicate adlayers on hexagonal (0001) and (0001) SiC surfaces. *Appl. Phys. Lett.* **1999**, 74 (8), 1084–1086.

(10) Todorova, T. K.; Sierka, M.; Sauer, J.; Kaya, S.; Weissenrieder, J.; Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J. Atomic structure of a thin silica film on a Mo(112) substrate: A combined experimental and theoretical study. *Phys. Rev. B* **2006**, *73* (16), 165414.

(11) Yu, X.; Yang, B.; Boscoboinik, J. A.; Shaikhutdinov, S.; Freund, H.-J. Support effects on the atomic structure of ultrathin silica films on metals. *Appl. Phys. Lett.* **2012**, *100* (15), 151608–4.

(12) Lahiri, J.; Lin, Y.; Bozkurt, P.; Oleynik, I. I.; Batzill, M. An extended defect in graphene as a metallic wire. *Nat. Nanotechnol.* **2010**, *5* (5), 326–329.

(13) Huang, P. Y.; Ruiz-Vargas, C. S.; van der Zande, A. M.; Whitney, W. S.; Levendorf, M. P.; Kevek, J. W.; Garg, S.; Alden, J. S.; Hustedt, C. J.; Zhu, Y.; Park, J.; McEuen, P. L.; Muller, D. A. Grains and grain

Nano Letters

boundaries in single-layer graphene atomic patchwork quilts. *Nature* **2011**, *469* (7330), 389–392.

(14) Wlodarczyk, R.; Sierka, M.; Sauer, J.; Löffler, D.; Uhlrich, J. J.; Yu, X.; Yang, B.; Groot, I. M. N.; Shaikhutdinov, S.; Freund, H. J. Tuning the Electronic Structure of Ultrathin Crystalline Silica Films on Ru(0001). *Phys. Rev. B* **2012**, *85*, 085403.

(15) Carr, L. D.; Lusk, M. T. Defect engineering: Graphene gets designer defects. *Nat. Nanotechnol.* **2010**, 5 (5), 316–317.

(16) (a) Appelhans, D. J.; Lin, Z.; Lusk, M. T. Two-dimensional carbon semiconductor: Density functional theory calculations. *Phys. Rev. B* **2010**, *82* (7), 073410. (b) Appelhans, D. J.; Carr, L. D.; Lusk, M. T. Embedded ribbons of graphene allotropes: an extended defect perspective. *New J. Phys.* **2010**, *12* (12), 125006.

(17) (a) Guzmán-Verri, G. G.; Lew Yan Voon, L. C. Electronic structure of silicon-based nanostructures. Phys. Rev. B 2007, 76 (7), 075131. (b) Takeda, K.; Shiraishi, K. Theoretical possibility of stage corrugation in Si and Ge analogs of graphite. Phys. Rev. B 1994, 50 (20), 14916-14922. (c) Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M. C.; Resta, A.; Ealet, B.; Le Lay, G. Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. Phys. Rev. Lett. 2012, 108 (15), 155501. (d) Lalmi, B.; Oughaddou, H.; Enriquez, H.; Kara, A.; Vizzini, S.; Ealet, B.; Aufray, B. Epitaxial growth of a silicene sheet. Appl. Phys. Lett. 2010, 97 (22), 223109-2. (e) Lay, G. L.; Padova, P. D.; Resta, A.; Bruhn, T.; Vogt, P. Epitaxial silicene: can it be strongly strained? J. Phys. D: Appl. Phys. 2012, 45 (39), 392001. (f) Arafune, R.; Lin, C.-L.; Kawahara, K.; Tsukahara, N.; Minamitani, E.; Kim, Y.; Takagi, N.; Kawai, M. Structural transition of silicene on Ag(111). Surf. Sci. 2013, 608 (0), 297-300. (g) Meng, L.; Wang, Y.; Zhang, L.; Du, S.; Wu, R.; Li, L.; Zhang, Y.; Li, G.; Zhou, H.; Hofer, W. A.; Gao, H.-J. Buckled Silicene Formation on Ir(111). Nano Lett. 2013, 13 (2), 685-690.

(18) (a) Giordano, L.; Ricci, D.; Pacchioni, G.; Ugliengo, P. Structure and vibrational spectra of crystalline SiO₂ ultra-thin films on Mo(112). *Surf. Sci.* **2005**, *584* (2–3), 225–236. (b) Freysoldt, C.; Rinke, P.; Scheffler, M. Ultrathin Oxides: Bulk-Oxide-Like Model Surfaces or Unique Films? *Phys. Rev. Lett.* **2007**, *99* (8), 086101.