

Title	Insights into the spontaneous formation of silicene sheet on diboride thin films
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Citation	Applied Physics Letters, 110(4): 041601-1-041601-4
Issue Date	2017-01-23
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/14720
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Description	

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Citation: *Appl. Phys. Lett.* **110**, 041601 (2017); doi: 10.1063/1.4974467

View online: <http://dx.doi.org/10.1063/1.4974467>

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Insights into the spontaneous formation of silicene sheet on diboride thin films

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(Received 20 October 2016; accepted 8 January 2017; published online 23 January 2017)

The realization of silicene-free $\text{ZrB}_2(0001)$ thin films grown on Si(111) by Ar^+ ion bombardment allowed for studying the spontaneous formation of silicene on their surfaces. Imaging the bare $\text{ZrB}_2(0001)$ surface by STM revealed the structures of Zr-terminated and B-terminated $\text{ZrB}_2(0001)$ created by the bombardment. The spontaneous formation of a continuous silicene sheet on a sputtering-induced disordered ZrB_2 surface demonstrates that silicene does not require an atomically-flat crystalline template to be stabilized. This opens the way to the fabrication of large scale single-crystal sheets and points out the potential of silicene to be used in the next generation silicon-based technologies. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4974467>]

The emergence of silicene, the graphene-like allotrope of silicon which happened a few years ago, opened perspectives for silicon-based nanotechnologies¹ owing to its ultimate flatness, its flexibility, and the particularity of its electronic, physical, and chemical properties.^{2–4} Those expectations derived from its structure predicted to adopt a low-buckled honeycomb structure in the hypothetical free-standing form originating from the intermediate sp^2/sp^3 hybridization of the Si atom orbitals required to sustain the cohesion of silicene.⁵ Using silicene routinely in large-scale processes requires the fabrication of wide scale monocrystalline sheet similar to graphene sheet synthesized on Cu foil⁶ that can be employed in industrial processes.⁷ Up to now, silicene was only observed in epitaxial forms on a limited number of monocrystalline substrates,^{8–18} which suggests that a template is required to fabricate it. Among them, a unique form of silicene crystallizes spontaneously in a reproducible and self-terminating way on the (0001) surface of zirconium diboride (ZrB_2) thin films grown on Si(111).¹⁷ The resulting silicene sheet fully covers atomically-flat $\text{ZrB}_2(0001)$ terraces and has a single crystal orientation with respect to the substrate. The objective of the investigations presented in this report, was to get insights into the formation of silicene during the annealing required to remove the native oxide.¹⁷ For this purpose, silicene-terminated $\text{ZrB}_2(0001)$ thin film surfaces were bombarded with Ar^+ ions. This allowed for giving access to the bare $\text{ZrB}_2(0001)$ surface on which silicene crystallizes and for getting insights into the formation process. These experiments also determined the influence of the surface disorder caused by the sputtering on the crystallization of silicene sheet on $\text{ZrB}_2(0001)$.

The growth of ZrB_2 thin films on Si(111) by chemical vapor epitaxy is detailed elsewhere.¹⁹ Samples were then transferred in air to the UHV setup in which these investigations were carried out. The spontaneous and self-terminating formation of silicene is first generated by annealing at temperature up to 800 °C. The silicene layer was then removed

by an Ar^+ bombardment with an energy of 200 eV and a partial Ar pressure of 1.9×10^{-5} mbar.

Fig. 1(a) compares the AES spectra recorded before and after the oxide removal. In agreement with the previous report,²⁰ annealing at 750 °C gives rise to an oxide-free ZrB_2 surface. The segregation of silicon atoms in the form of a silicene sheet¹⁷ is reflected by an intense peak in the Si KLL region. In STM images, silicene is identified as a $\text{ZrB}_2(0001)$ - (2×2) reconstruction, due to the matching of this unit cell with that of the $(\sqrt{3} \times \sqrt{3})$ unit cell of epitaxial silicene.^{17,21} As shown in the large scale STM image of Fig. 1(b), a highly ordered one-dimensional periodic domain-structure^{17,22} forms spontaneously with three equivalent orientations to account for the 6-fold symmetry of the $\text{ZrB}_2(0001)$ surface.

The AES spectra of Fig. 2(a) shows the evolution of the amount of silicon upon a sputtering of a few seconds and subsequent annealings. Approximately one third of the silicon atoms was removed from the surface. The as-bombarded surface appears disordered in the STM image of Fig. 2(b). As shown in Fig. 2(c), annealing the sample at 450 °C leads to the recrystallization of the silicon atoms giving rise to (2×2) -reconstructed silicene islands (Fig. 2(b)). This temperature is

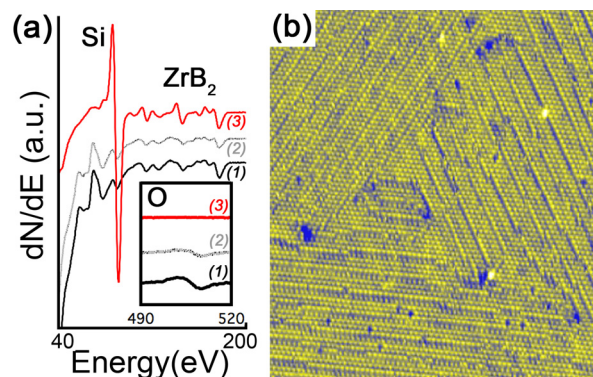


FIG. 1. Silicene on $\text{ZrB}_2(0001)$. (a): AES spectra recorded for (1) the as-loaded sample, (2) after annealing 160 min at 660 °C and (3) after annealing 30 min at 750 °C. (b): STM image ($44 \text{ nm} \times 50 \text{ nm}$, $V = 0.4 \text{ V}$, $I = 500 \text{ pA}$) of the spontaneously formed silicene on $\text{ZrB}_2(0001)$. Three equivalent orientations of the domain structure are visible.

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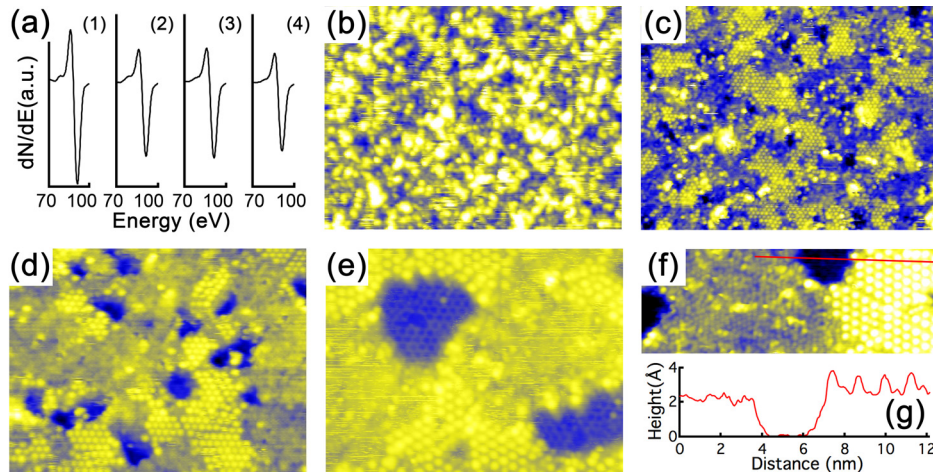


FIG. 2. Sputtered silicene on $\text{ZrB}_2(0001)$. (a): AES spectra of the Si KLL region: (1): Before sputtering, (2): After Ar^+ bombardment, (3): After annealing 15 min at 450°C and (4) few seconds at 620°C . (b)–(d): STM images ($50\text{ nm} \times 38\text{ nm}$, $V = 1.0\text{ V}$, $I = 200\text{ pA}$, $50\text{ nm} \times 38\text{ nm}$, $V = 0.6\text{ V}$, $I = 100\text{ pA}$, $30\text{ nm} \times 23\text{ nm}$, $V = 1.2\text{ V}$, $I = 500\text{ pA}$) corresponding to the AES spectra (2), (3), and (4) respectively. (e) and (f): STM images of the atomic structure ($20\text{ nm} \times 15\text{ nm}$, $V = -0.3\text{ V}$, $I = 500\text{ pA}$ and $20\text{ nm} \times 7\text{ nm}$, $V = -0.3\text{ V}$, $I = 500\text{ pA}$). (g): Profile along the red line in Fig. (f).

therefore above that required for the diffusion of the Si atoms on the $\text{ZrB}_2(0001)$ surface and the crystallization of silicene. This is in agreement with the reported formation of silicene by Si deposition on bulk $\text{ZrB}_2(0001)$ at 350°C .¹⁶ Annealing for a few seconds at temperature as high as 620°C , leaves the surface almost unchanged with a same amount of silicon atoms on the surface (See Fig. 2(a)), but the atomic structure of the bare $\text{ZrB}_2(0001)$ areas is better resolved by STM. The resolution of the atomic structure of the bare $\text{ZrB}_2(0001)$ surface reveals the existence of two different types of terraces with different surface structures. The topmost terraces of the silicene-free areas are made of a few nm wide domains consisting of arrays of protrusions and with the same periodicity as $\text{ZrB}_2(0001)$. The fact that a single protrusion per unit cell is observed indicates that this $\text{ZrB}_2(0001)$ surface is an unreconstructed Zr-terminated $\text{ZrB}_2(0001)$ as expected for bulk ZrB_2 .²³ It thus confirms that silicene crystallizes on a bulk-like surface in agreement with the observation of Zr-related surface states in the band structure of epitaxial silicene on $\text{ZrB}_2(0001)$.^{17,19,24} As pointed out by the profile plotted in Fig. 2(g), the apparent difference of height

between the Zr-terminated $\text{ZrB}_2(0001)$ and silicene is 1.8 \AA . This value is significantly smaller than that given by ab-initio calculation²¹ but this difference is in agreement with the difference of local density of states between semiconducting silicene^{24,25} and conductive ZrB_2 . The sputtered, silicene-free $\text{ZrB}_2(0001)$ surface is not atomically flat as for the pristine sample, and several holes are visible. The apparent depth of these holes with respect to Zr-terminated surface is approximately 2 \AA , which can be compared to the distance between Zr and B layers along $\text{ZrB}_2[0001]$ (1.78 \AA). It suggests that the topmost Zr atoms of the thin film were sputtered, and the terraces in the holes are B-terminated. STM images reveal that the B-terminated surface is $(\sqrt{3} \times \sqrt{3})$ -reconstructed in agreement with predictions from ab-initio calculation.²⁶ However, the exact structure of the reconstruction cannot be determined. The adsorption of Si or C atoms cannot be excluded as AES spectroscopy points to the trace of carbon on the sputtered surface.

As shown in Fig. 3, sputtering further the surface by means of a longer Ar^+ bombardment in the same conditions leads to an increase of the roughness of the surface, that is

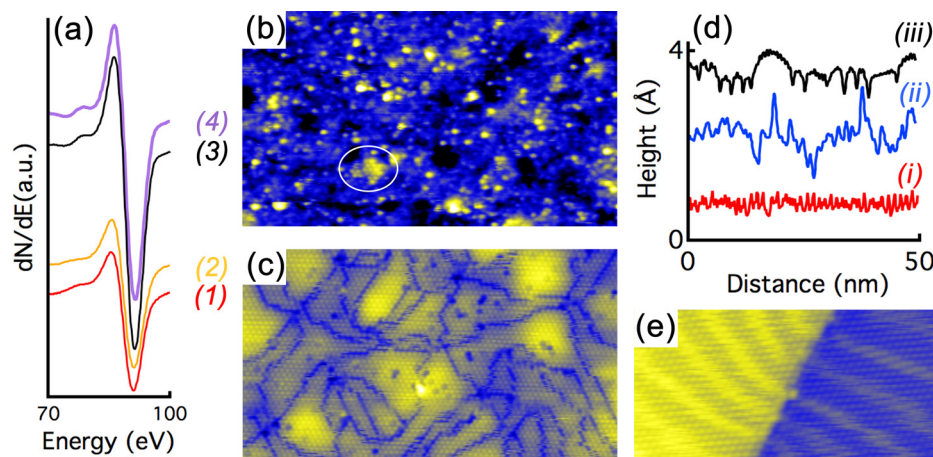


FIG. 3. Silicene formation on sputtered $\text{ZrB}_2(0001)$. (a): AES spectra in the Si KLL region after (1) Ar^+ bombardment, (2) annealing few seconds and (3) annealing 15 min at 645°C . (4) AES spectrum recorded on pristine silicene. (b): STM image ($50\text{ nm} \times 28\text{ nm}$, $V = 1.0\text{ V}$, $I = 100\text{ pA}$) corresponding to the spectrum (2). The white circle indicates a small (2×2) -reconstructed island. (c): STM image ($50\text{ nm} \times 28\text{ nm}$, $V = 2.5\text{ V}$, $I = 500\text{ pA}$) corresponding to the spectrum (3). (d): Typical profiles measured on the STM images of (i) Fig. 1(b), (ii) Fig. 3(b), and (iii) Fig. 3(c). (e): STM image ($25\text{ nm} \times 12\text{ nm}$, $V = 0.3\text{ V}$, $I = 22\text{ pA}$) of a 1.7 \AA -high step observed on the pristine sample.

visible in the STM image of Fig. 3(b) recorded after a few seconds annealing at 645 °C. Atomically-flat terraces are not visible anymore and the single ordered structures observed on the surface are sparse (2×2)-reconstructed islands. It is thus suggested that it is not possible to realize an atomically flat bare surface by sputtering ZrB_2 thin films even with very soft conditions. Whereas annealing at 645 °C for few seconds does not change significantly the amount of silicon atoms on the surface (Fig. 3(a)), annealing at the same temperature for 15 min gives rise to a (2×2)-reconstructed layer covering the entire surface. The reformation of silicene is confirmed by the AES spectrum of Fig. 3(a) which indicates that the amount of Si atoms returned to a value close to that of the pristine silicene. One can deduce that this temperature is above the one needed to promote the surface segregation of the Si atoms from the silicon substrate. The formation of silicene is possibly accompanied by the recrystallization of Zr and B atoms of the thin film but it does not affect significantly the morphology of the ZrB_2 surface. This temperature is lower than the one required to remove the oxide layer formed on top of the ZrB_2 thin film as evidenced by the AES spectrum of Fig. 1(a) measured after annealing at 660 °C. Therefore, this result suggests that the silicon atoms segregate on top of the $ZrB_2(0001)$ surface immediately after the oxide layer has been removed.

The comparison of typical profiles measured on STM images of silicene layers formed on atomically flat and sputtered $ZrB_2(0001)$ surfaces (Fig. 3(d)) demonstrate that the crystallization of silicene is not hindered by the apparent disorder and the roughness of the $ZrB_2(0001)$ surface induced by the bombardment. The amplitude of the corrugation is in the order of 1 Å and is much smaller than that of an atomic step in $ZrB_2(0001)$. The fact that the amplitude of the surface corrugation before and after the formation of silicene is similar suggests that the silicene sheet can carpet over such disordered surface. It therefore suggests that in agreement with a recent report,²⁷ silicene does not need a perfectly ordered substrate to be stabilized. The STM of Fig. 3(e) shows an atomic step observed on a pristine sample. The fact that the step height is 1.7 Å indicates that sparse B-terminated terraces may also have been created during the oxide removal. The observation of the same atomic structure on both terraces and the fact that the domain boundaries are crossing the step gives an indication that silicene can form on both Zr- and B-terminated $ZrB_2(0001)$ terraces and can grow over atomic steps.

Note that, even though the ZrB_2 surface deviates significantly from an atomically flat (0001) surface, silicene seems to preserve its ($\sqrt{3} \times \sqrt{3}$)-reconstructed structure. The silicene sheet visible in the STM image of Fig. 3(c) is textured into domain boundaries, but no periodic domain structures are visible anymore. The recovering of the large-scale ordering is not possible, even upon annealing at higher temperature, most likely because the mobility of the boundaries is hindered by the roughness of the surface. The fact that domain boundaries are systematically observed even in small islands with dimensions of the same order of magnitude as the typical distance between two boundaries in pristine silicene (approximately 3 nm) gives confirmation that even though a single-domain silicene can be formed on

$ZrB_2(0001)$,²⁸ the domain boundaries release the epitaxial strain due to the epitaxial relationship between $ZrB_2(0001)$ and silicene.

In conclusion, we demonstrated that a soft Ar^+ bombardment is capable of sputtering the silicene layer spontaneously formed on $ZrB_2(0001)$ thin film grown on Si(111). The structure of the Zr- and B-terminated surfaces of the so-created bare surface could be imaged by STM. Moreover, the realization of silicene-free $ZrB_2(0001)$ thin films on Si(111) allowed for determining the temperature at which silicon atoms diffuse out of the substrate to segregate and crystallize forming a silicene sheet. We could also establish that the spontaneous formation of silicene on $ZrB_2(0001)$ surface is not hindered by the roughness of the $ZrB_2(0001)$ surface. These findings indicate that silicene can be considered as a truly two-dimensional material rather than a simple ad-atom reconstruction, which has the potential to be used in the fabrication of next generation Si-based devices.

A.F. acknowledges the financial support from JSPS KAKENHI Grant No. JP26790005.

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