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研究課題名（和文）エピタキシャルシリセンの形成機構解明

研究課題名（英文）Elucidation of the formation mechanisms of epitaxial silicene

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研究成果の概要（和文）：二次元材料はその柔軟さと素子の小型化を可能にする低次元性から、電子工学分野への応用に高い関心が寄せられている。シリセンは最近発見された二次元状Siであり、その座屈した蜂の巣構造に由来する電子的性質から大いに期待されている。だが、極限られた導電性基板上にしか形成されていないことがシリセンの応用を阻んでいる。絶縁性基板上に形成するために必要な表面の性質を知るために、Si基板上二ホウ化ジルコニウム薄膜上へのシリセンの自発形成過程について調べた。この系はまた、熱的安定性を調べるのに適しており、シリセンの構造の温度依存性を明らかにする実験から、座屈構造に由来する機械的性質について貴重な知見が得られた。

研究成果の概要（英文）：In reason of their flexibility and their low-dimensionality that allows for the miniaturization of the devices, two-dimensional materials are of high interest for applications in electronics. Silicene is a recently discovered two-dimensional form of silicon with great expectation for applications owing to the electronic properties originating from its buckled structure. However, silicene needs to be stabilized by a substrate and was observed only on top of a very few number of conductive materials, that hinders its use in electronic devices. The spontaneous formation of silicene on top of Zr diboride thin films grown on Si(111) was investigated in order to get hints on the surface properties required to synthetize silicene on insulating substrates. This form of silicene is also a perfect template to study the thermal stability of silicene. The temperature dependence of its structure gave very insightful information on the mechanical properties of silicene deriving from the buckling.

研究分野：ナノマテリアル

キーワード：シリセン

１．研究開始当初の背景

Silicene is the graphene-like two-dimensional allotrope of silicon made of atoms arranged in a one atom-thick honeycomb structure. Free-standing silicene is predicted to deviate from graphene by the buckling of its structure [1]: the atoms belonging to the two different sub-lattices are vertically shifted with respect to each other as a result of the intermediate sp^2/sp^3 hybridization of the Si atoms. In spite of this buckling, the band structure of free-standing silicene is predicted to features π-bands forming Dirac cones [1] similar to those of graphene, making silicene a promising two-dimensional material with a high mobility of the charge carriers. Nevertheless, the buckling of its structure gives silicene particular physical and chemical properties including predicted tunable quantum spin Hall effect [2] and gate-controlled spin-valley polarization of the charge carriers [3] or a reactivity to oxygen significantly reduced compared to bulk silicon [4].

Silicene was found to be stable only in epitaxy on a limited number of conductive substrates, with structural and electronic properties different from those expected for free-standing silicene. Among them, our research group demonstrated that (0001)-oriented zirconium diboride (ZrB_2) thin films grown on Si(111) have the unique faculty of promoting the spontaneous and self-terminating growth of an homogeneous sheet of silicene on their surface [5]. As shown in Fig. 1, the epitaxial relationship with the ZrB_2(0001) surface forces silicene to adopt a(√3×√3)-reconstructed structure that fits with the (2×2) unit cell of ZrB_2(0001). The buckling is different from that of free-standing silicene, that results in a gap opening in the Dirac cones [5,6]. In addition, the silicene sheet is textured by a highly ordered periodic domain structure made of stripe-shaped domains separated by domain boundaries [5].

２．研究の目的

The absence of a form of silicene decoupled from a conductive substrate hinders its use in electronic devices. As the unique example of silicene which does not require any silicon deposition, silicene on ZrB_2(0001) may reveal key features that a insulating substrate needs to possess to host silicene on its surface.

The first objective of the present research was to study the process of formation of silicene on ZrB_2(0001) and to determine the driving force promoting the spontaneous segregation of Si atoms and the crystallization of silicene. Nevertheless, silicene on ZrB_2(0001) is a perfect template for the investigation of the temperature-dependence of the structural properties of silicene on ZrB_2(0001). On the one hand, it is aimed at probing the thermal stability of silicene which is of crucial importance in the perspective of using silicene in devices. On the other hand, as the periodic structure is likely to originate from the release of the epitaxial stress [7], the evolution with the temperature of the silicene structure can give hints on the mechanical properties resulting from the buckled structure of silicene.

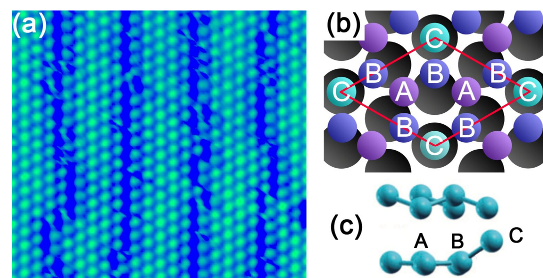

Fig. 1: (a): STM image (14 nm×13 nm, V=1.0 V, I=50 pA) of silicene on ZrB_2(0001). The (√3×√3)-reconstruction and the periodic domain structure are visible. (b): Model of the (√3×√3)-reconstructed unit cell of epitaxial silicene on ZrB_2(0001). A, B and C denote the Si atoms sitting respectively on the hollow, bridge and on-top sites of the Zr-terminated ZrB_2(0001) surface. Zr atoms are in black. (c): Side-views of the structures of free-standing silicene (top) and of epitaxial silicene on ZrB_2(0001) (bottom) [6]. C atoms correspond to the protrusions visible on the STM images.

３．研究の方法

ZrB_2(0001) thin films were grown on Si(111) in an ultra-high vacuum (UHV) chamber dedicated to the deposition of diboride thin films by chemical vapor epitaxy.

The native oxide formed on top of ZrB_2 thin films during the transfer to air is removed by annealing by direct current heating in the UHV chamber used for the characterizations. A silicene sheet crystallizes on the oxide-free ZrB_2(0001)

surface during the cooling to room temperature.

The UHV chamber is equipped to characterize the samples by scanning tunneling microscopy (STM) at variable temperature, low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES).

In order to study the formation of silicene on a bare surface, $ZrB_2(0001)$ thin films were sputtered by means of an Ar^+ ion gun. The temperature dependence of the silicene structure was thoroughly investigated by LEED, AES and variable-temperature STM. A silicon source was also implemented and calibrated.

４．研究成果

(1) Sputtering of $ZrB_2(0001)$ thin films on Si(111)

Efforts were first dedicated to finding the sputtering conditions capable of giving rise to an atomically smooth bare $ZrB_2(0001)$ surface. Oxidized and silicene-covered $ZrB_2(0001)$ thin films were both sputtered with different sputtering times and beam energies. Preliminary results pointed out that gentle sputterings of silicene-covered $ZrB_2(0001)$ with low acceleration energy and very short time (less than 1 minute) are required in order not to damage the ZrB_2 thin films.

Silicene-covered $ZrB_2(0001)$ thin films were sputtered for few seconds with a beam energy of 200 eV. After sputtering, the samples were annealed at increasing temperatures.

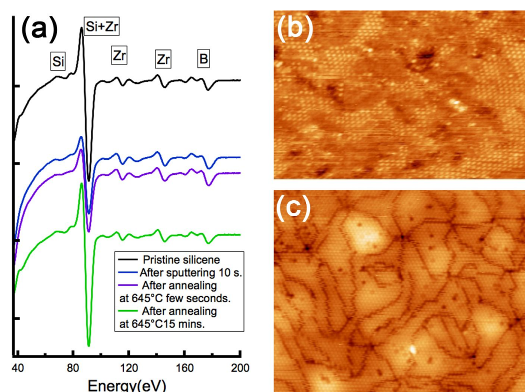

Fig. 2. (a): AES spectra recorded with E_b=1500 eV before and after sputtering 10 s a silicene-covered $ZrB_2(0001)$thin film and after annealing. (b): STM image (35 nm × 23 nm, V=1.0 V, I=500 pA) after sputtering 5 s a silicene-covered $ZrB_2(0001)$thin film and after annealing 15 min. at 450°C. (c): STM image (50 nm × 41 nm, V=2.5 V, I=500 pA) after sputtering 10 s and annealing 15 min. at 645°C.

As shown on Fig. 2.(a), The comparison of AES spectra recorded before and after a 10 s sputtering reveals a decrease of the intensity of the Si-related peaks and a slight increase of that of the Zr- and B-related peaks. Sputtering with a shorter time (5 s) leaves a significant amount of Si atoms on the surface which forms a disordered layer. Annealing the sample at 450°C leads to the recrystallization of the silicon atoms in the form of small silicene islands (Fig. 2.(b)). This temperature is therefore above that required for the diffusion of the Si atoms on the $ZrB_2(0001)$ surface and the crystallization of silicene. However, one can observe that holes caused by the sputtering are found at several places. The number of these holes increases with the duration of sputtering in such a way that for the sputtering duration required to remove all the silicon (approximately 10 s), the surface appears to be significantly degraded. It is thus suggested that it is not possible to realize an atomically smooth bare surface by simply sputtering ZrB_2 thin films. However, the obtained silicene-free $ZrB_2(0001)$ thin film surface allows for determining whether silicene can form on a rough $ZrB_2(0001)$ surface. Whereas annealing at 645°C for few seconds does not change significantly the amount of silicon atoms on the surface, annealing at the same temperature for 15 min. gives rise to a silicene sheet covering the whole surface with an amount of Si atoms similar to that of the pristine silicene (See Figs. 2.(a) and 2.(c)). One can deduce that this temperature is slightly above the one needed to promote the diffusion of the Si atoms out of the silicon substrate. It also demonstrates that the crystallization of silicene is not hindered by the roughness of the $ZrB_2(0001)$ surface. The resulting silicene sheet is textured by a disordered domain structure with a density of boundary similar to that of the pristine silicene sheet. The recovering of the large-scale ordering is not possible, even upon annealing at higher temperature, most likely because the boundaries are pinned by the defects caused by the sputtering. The impossibility of preparing a smooth surface hindered the study of the formation of silicene by silicon deposition on bare $ZrB_2(0001)$. This was

however experimentally realized by an other group which performed the deposition of silicon on the (0001) surface of bulk ZrB_2. The resulting silicene layer features properties very similar to those of silicene that forms spontaneously on ZrB_2 thin films grown on Si(111) [8].

(2) Single-domain silicene on ZrB_2(0001)

Interestingly, domains are systematically observed in silicene on ZrB_2(0001) including in islands resulting from sputtering and having a size similar to the typical width of the domains. It was thus considered that the formation of the domain structure plays an important role in the stability of silicene on ZrB_2(0001).
To determine whether a boundary-free silicene sheet could exist on ZrB_2(0001), we investigated the effect of the deposition of a small amount of silicon on pristine silicene. This work was done in collaboration with C. Hirjibehedin and T. Gill from UCL (United Kingdom), J. Sadowski from BNL (U.S.A.) and R. Tromp and M. Copel from IBM (U.S.A.). The periodic domain structure is reflected in LEED patterns by the splitting of the diffraction spots related to the($\sqrt{3}\times\sqrt{3}$)-reconstruction. The merging of the split spots and the vanishing of the domain boundaries in STM images upon deposition of 0.04 monolayer (ML) of Si (Fig. 3.(a)) show that the domain structure has turned into single-domains. As exemplified by the core-level spectra of Fig. 3.(b), single-domain silicene features

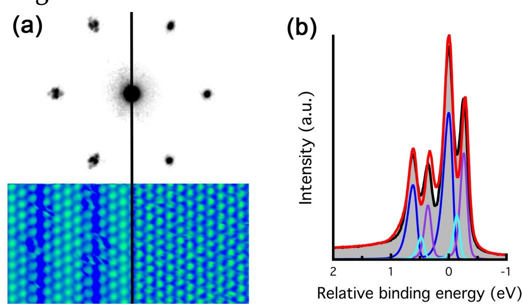

Fig. 3: (a): LEED patterns (E_b=30 eV) and STM images (7 nm × 7 nm, V=1.0 V, I=50 pA) before (left) and after (right) the deposition of 0.04 ML Si on the domain structure. (b): Si 2p core-level photoemission spectra recorded with a photon energy of 130 eV before (black) and after (red) the Si deposition. The spin-split doublets colored in purple, dark blue and light blue are the components corresponding respectively to the A, B and C atoms of the pristine silicene.

structural and electronic properties very similar to those of the pristine silicene on ZrB_2(0001).
Even though the periodic domain structure is the ground-state of silicene on ZrB_2(0001), the formation of single-domains demonstrates that it is not a requisite to stabilize silicene on ZrB_2(0001).

(3) Temperature-dependence of silicene on ZrB_2(0001)

LEED patterns and STM images recorded at different temperatures ranging from room temperature to 650 °C reveal that silicene undergoes two reversible phase transitions in this temperature range. The fact that the amount of silicon on the surface, derived from AES spectra, remains constant points out that these transitions relate only to the arrangement of the Si atoms on the surface.
A periodic domain structures is systematically observed for temperature up to 400 °C. The measure of the lattice constant in the direction perpendicular to the domains, indicates that the silicene lattice expands with the temperature in this direction. This is reflected by the

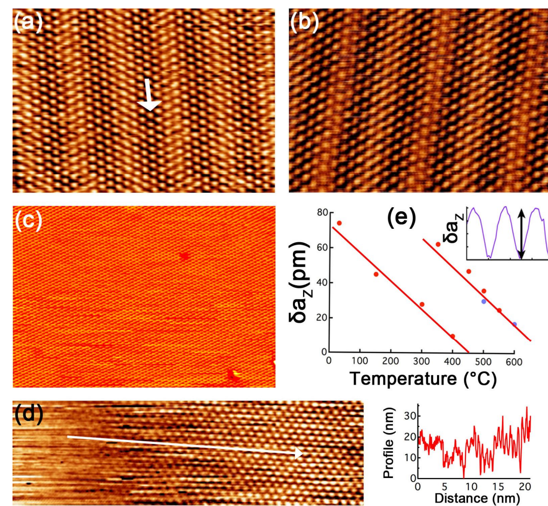

Fig. 4. (a)-(d): STM images recorded respectively at 300 °C, 400 °C, 500 °C and 650 °C ((a) and (b): 20 nm × 14 nm, (c): 50 nm × 34 nm, (d): 30 nm × 9 nm, (a)-(d): V=-0.5 V, I=500 pA). The profile shows the interface between ordered and disordered domains. (e): Atomic corrugation measured on STM images recorded with V=-0.5 V and I=500 pA, plotted as a function of the temperature. The profile in the inset was measured in the image of Fig. (a). Red and blue dots correspond respectively to measures in domain-structure and single-domain areas.

difference between the domain boundaries in the STM image of Fig. 1.(a) recorded at room temperature and those in the STM images of the Figs. 4. (a) and (b), respectively recorded at 300 ° C and 400 ° C. The gap observed between the domains in the former is not visible anymore in the latter two.

Above 400 ° C, the periodic domain structure turns progressively into wide (√3×√3)-reconstructed single domains such as the one seen in the STM image of Fig. 4.(c).

At temperature higher than 550 ° C, the intensity of the spots related to the (√3×√3)-reconstruction in LEED patterns steadily decays and at 650 ° C, only the diffraction spots of ZrB_2(0001)-(1×1) are observed. The STM image of Fig. 4.(d) recorded at a temperature slightly below the transition temperature shows that (√3 × √3)-reconstructed domains coexist with featureless domains assigned to disordered areas. This observation indicates that the melting of silicene is a first-order phase transition. The coexistence of ordered and disordered areas is most likely due to their different surface strains [9]. The linear decrease of the atomic corrugation at the interface is in striking contrast to the abrupt interface between (7 × 7)-reconstructed and unreconstructed domains on Si(111) [9].

Fig. 4.(e) shows the temperature dependence of the atomic corrugation of the silicene structure. Whereas the monotonous decrease of the protrusion height with the temperature below and above 350-400 ° C can be explained by the increase of the vibration of the silicene lattice, the step in this temperature range is associated with a transition between two different phases of silicene with different atomic structures. The fact that the domain structure starts to vanish at approximately the same temperature suggests that the high-temperature phase can exist without forming a periodic domain structure to accommodate the epitaxial strain. The experimental data suggests that it has a smaller lattice parameter and a larger bucking than the low-temperature phase.

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