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## 科学研究費助成事業 研究成果報告書

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研究成果の概要(和文)：本研究では、ケイ素版グラフェンといえる新しい二次元材料「シリセン」の結晶・電子構造を原子や分子の吸着・反応により制御するための指導原理を実験的に得ることを目的とした。二ホウ化ジルコニウム薄膜上に形成されたエピタキシャルシリセンにカリウムを蒸着したところ、構造の変化は認められなかったが、カリウム原子からシリセンへと電子が供与され、基板である二ホウ化物の表面電子状態とシリセンのパイ電子状態との間の混成が強まるのが観測された。また、水素化を試みたところ、シリセンの内部構造を大きく変えることなくキャッピング層が形成されることが示唆された。

研究成果の概要(英文)：Silicene on ZrB<sub>2</sub>(0001) thin films grown on Si(111) is a perfect test bench for the study of this two-dimensional material, which only exists in epitaxial forms. We particularly investigated (i) the local origin of the electronic states of silicene and (ii) how the properties of silicene can be tuned upon adsorption of foreign atoms. Our study revealed the microscopic origin of the previously resolved pi states and pointed out a clear correlation between the local conformation of the Si atoms and the contribution of their pz orbital to those states. Upon adsorption of potassium atoms, we found out that there is no change in the silicene structure and that an electron donation to silicene occurs. It also causes the hybridization between ZrB<sub>2</sub>(0001) surface state and silicene pi states, which are decoupled in the pristine case. The investigation of the hydrogenation of silicene suggests that a capping layer forms without affecting significantly the internal structure of silicene.

研究分野：ナノマテリアル

科研費の分科・細目：ナノ・マイクロ科学、ナノ構造科学

キーワード：シリセン 二次元物質 走査トンネル顕微鏡 局所状態密度 バンドエンジニアリング 表面・界面物性 電子・電気材料 ナノ材料

## 1. 研究開始当初の背景

Due to their flexibility, their smoothness and their ultimate thinness, two-dimensional materials are expected to improve significantly the speed, the scalability and the energy efficiency of microelectronics devices.

The development of devices based on graphene, the most appealing 2D material, is hindered by its difficult integration with existing silicon-based technologies and the absence of a gap at Fermi level. A possible alternative to graphene is silicene, whose existence has been verified experimentally recently [1-3]. Silicene is an atom-thick honeycomb lattice made of silicon atoms, which is predicted to be stable in the free-standing form in a slightly-buckled conformation [4]. The computed band structure is similar to that of graphene with Dirac cones at  $K_{Si}$ , the K point of the Brillouin zone of silicene [4]. Nevertheless, as a consequence of the staggered structure, the band structure is predicted to be tunable by a vertical electric field, in such a way that a spin/valley polarization of the charge carriers is achievable [5].

So far, silicene only exists in epitaxial forms on conductive substrates like Ag(110) [1], Ag(111) [2] or as we demonstrated, on the (0001) surface of zirconium diboride ( $ZrB_2$ ) thin films grown on Si(111) [3]. Using scanning tunneling microscopy (STM) and core-level photoelectron spectroscopy (PES) recorded in a surface sensitive mode, we demonstrated that a single layer of silicon atoms segregating spontaneously on the diboride surface crystallizes in the form of a ( $3 \times 3$ )-reconstructed honeycomb structure. Core-level Si 2p photoelectron diffraction together with density functional theory (DFT) calculations pointed out that it adopts a specific buckling, shown in Figure 1.(a), imposed by the epitaxial conditions. Strong evidence for the silicene nature of this silicon monolayer was found in the observation by angle-resolved ultraviolet photoemission spectroscopy (ARUPS) of a  $\pi$ -electronic band centered on  $K_{Si}$ . DFT calculations suggest that the opening of this gap in the Dirac cone is a result of the specific imprinted buckling. It demonstrates that the electronic properties of silicene can be tuned, owing to the interplay between structure and the electronic band structure, in such a way

that it becomes semiconducting with a suitable electronic band gap [3].

The experimental demonstration of the stability of silicene in epitaxy on different substrates, evidences that crystalline silicon can possess a much wider range of physical and chemical properties than believed so far. However, the promising properties of silicene are far from being fully explored. In absence of a free-standing form of silicene, epitaxial silicene on  $ZrB_2/Si(111)$ , that we are today the single group in the world able to produce, is an ideal test bench to investigate the chemical, electronic and structural properties of silicene. Epitaxial silicene on  $ZrB_2$  thin films has the advantage with respect to silicene on Ag(111) to be easy to prepare and to be perfectly reproducible. The so-obtained silicene sheet can therefore be used to investigate the intimate relation between the structure and the electronic properties of silicene and how these properties can be tuned upon adsorption of foreign atoms.

## 2. 研究の目的

The objective of this research project was two-fold.

(1) First, we wanted to get a better understanding of how the internal structure of epitaxial silicene and its electronic properties are interplaying with each other. For this purpose, a STM tip is a perfect tool since it can probe the local density of state (LDOS) and give precious insights on the spatial origin of the electronic states resolved by ARUPS.

On the other hand, we wanted to determine in what extent the physical and chemical properties of silicene are tunable through the adsorption of foreign atoms. In particular the project was aimed at:

(2) determining what is the effect of the deposition of an alkali metal like potassium on silicene and to verify whether electron donation occurs as predicted [7].

(3) verifying the feasibility of the silicene hydrogenation and to investigate experimentally its consequence on the chemical and electronic properties of silicene. As predicted by calculations [8], the hydrogenation may result in a change in the buckling, and thus it may cause a transformation of the band structure. The possible passivation of silicene resulting from the hydrogenation would be a major step towards the realization of

devices based on silicene.

### 3. 研究の方法

Samples were prepared following a reproducible and well-established procedure [6]. Silicon (111) substrates are first cleaned in the ultrahigh-vacuum (UHV) chamber dedicated to chemical vapor epitaxy (UHV-CVE). A Si surface exhibiting the (7×7) reconstruction is obtained by heating the substrate at approximately 1200 °C. An epitaxial, single crystalline, (0001)-oriented ZrB<sub>2</sub> thin film is then grown by UHV-CVE through the thermal decomposition of the single precursor Zr(BH<sub>4</sub>)<sub>4</sub> into solid crystalline ZrB<sub>2</sub> and gaseous byproducts at the surface of the substrate heated at temperature, typically around 900 °C.

When taken out of the chamber, the surface of the ZrB<sub>2</sub> is getting oxidized providing a protection cap to the thin film. The sample can then be transferred to any UHV systems. In each of the setups used for these experiments, the native oxide layer is removed by annealing at 800 °C. Concomitantly a silicene sheet forms spontaneously by the self-terminating segregation of Si atoms on the top of the clean ZrB<sub>2</sub> thin film.

Low-temperature STM and scanning tunneling spectroscopy (STS) experiments were carried out at the institute of solid state physics (ISSP, The University of Tokyo, Kashiwa, Japan) in a dedicated low-noise setup cooled down to 5.5 K. The tunneling conductance dI/dV spectra were recorded by means of a lock-in detection method.

The adsorption of potassium on epitaxial silicene were studied at the beam line 18-A of photon factory (PF, KEK, Tsukuba, Japan) and at the beam line BL U5UA of the national synchrotron light source (NSLS, Brookhaven National Laboratory, Upton, NY, USA). After preparation of silicene, the samples were exposed to K vapor from well-degassed getter sources with the substrates held at room temperature. For the calibration of the flux, the change of the work function as a function of the amount of potassium  $x$  was measured following the stepwise deposition of K atoms onto the Si(111)-(7 × 7) surface [9]. Adsorption of potassium on the samples was studied by low-energy electron microscopy (LEEM) and low-energy electron diffraction (LEED) at NSLS. ARUPS experiments were done at PF.

Hydrogenation of epitaxial silicene was

realized at NSLS by means of an atomic hydrogen source. In our home setup, the hydrogenation is achieved by cracking H<sub>2</sub> molecules with a hot filament located in front of the sample. The H flux is calibrated through the hydrogenation of a clean Si(111) surface [10].

### 4. 研究成果

#### (1) Determination of the origin of the states in epitaxial silicene

To understand how the deviation of the buckling from that of free-standing silicene affects its electronic properties, we carried out in collaboration with the group of Prof. Y. Hasegawa from the ISSP of the University of Tokyo, a mapping of the LDOS aimed at determining the microscopic origin of the electronic states of silicene [11]. The mapping of the LDOS consists of 64 × 64 tunneling conductance dI/dV spectra recorded in the 2 nm × 2 nm square shown in Figure 1.(b). Figure 1.(c) shows the spectra taken at the positions labeled (1) to (9) in Figure 1.(b).

Spectra point out the existence of a 350 meV gap in the density of state (DOS). Several spectral features, labeled (i) to (vi) were identified. For the filled states, two features labeled (i) and (ii), are observed. The former is in the vicinity of the lower limit of the bias voltage range, and the latter, centered on  $V = -0.36$  V, extends up to the gap edge at  $-0.23$  V. Thus, it coincides with the maxima of the parabolic valence band observed at  $K_{Si}$  [3]. Whereas feature (i) was found to be located around positions (2), (3), and (5), feature (ii) appeared centered on position (1) with some extension to the positions (4), (5), and (6). Within the gap, two low-intensity features labeled (iii) and (iv) can be attributed to the metallic ZrB<sub>2</sub>(0001) surface states. In the empty states, two features labeled (v) and (vi) both centered on position (7) and extending to neighboring positions are observed around  $V = 0.20$  V and  $V = 0.36$  V. The first one, which extends down to the energy gap at 0.10 V above the Fermi level can be associated to the conduction band predicted to exist in the middle between  $K_{Si}$  and  $K_{Si}$  points [12].

The comparison of experimental data with calculated LDOS shows very good agreements between the energies of the spectral features labeled (i) to (vi) for the measured ones and (a) to (f) for the calculated ones. It also allows the

assignment of the positions (1) to atoms C, positions (2)-(3) to atoms A, positions (4)-(6) to atoms B and positions (7)-(9) to the center of the hexagons of the honeycomb lattice. Thus, the silicene structure coincides with the green honeycomb plotted in Figure 1.(b).

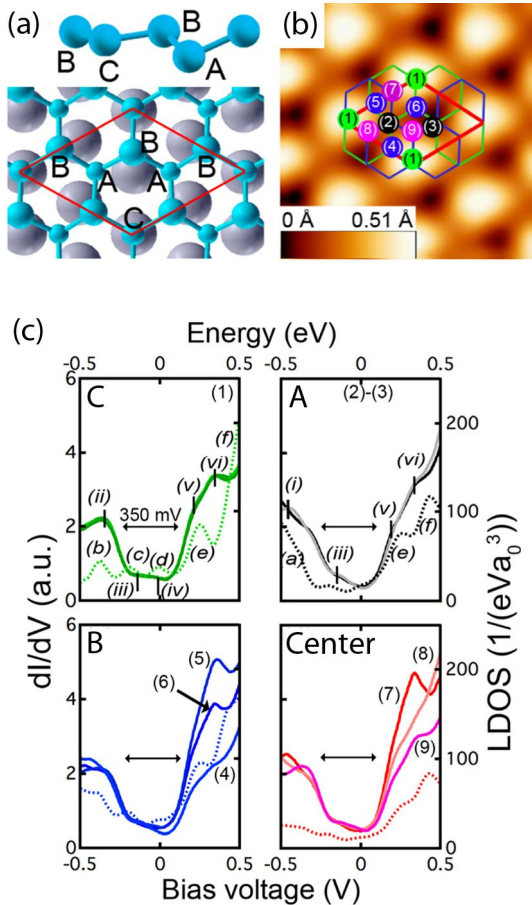


Figure.1. (a): Structure of epitaxial silicene on  $ZrB_2(0001)$  derived from DFT calculations. Si and Zr atoms are respectively colored in blue and grey. (b): STM image ( $2\text{ nm} \times 2\text{ nm}$ ,  $V = -0.50\text{ V}$ , and  $= 500\text{ pA}$ ) recorded at  $5.5\text{ K}$  in the current-constant mode. The green and blue honeycombs show the two possible positions of the Si lattice. (c): LDOS of epitaxial silicene on  $ZrB_2(0001)$ . Solid curves represent the  $dI/dV$  tunneling conductance spectra recorded at positions (1) to (9) as indicated in Figure (b). Dashed curves represent the computed LDOS above the A, B and C atoms, and the center of the hexagons of the honeycomb lattice, as also indicated. Spectral features in the tunneling conductance and in the calculated LDOS are denoted (i) to (vi) and (a) to (f), respectively.

To determine the origin of the spectral features, we calculated the DOS of the  $p_z$  orbitals of the different Si atoms. While the LDOS can be compared with the STS data, the DOS per atomic orbital is also

informative since it provides indications on the atomic origin of the spectral features. In particular, the weight of the respective contributions of the s,  $p_x$ ,  $p_y$ , and  $p_z$  orbitals to the electronic states can tell us the degree of hybridization of the orbitals between  $sp^2$  and  $sp^3$ . The hybridization indicates how much the  $p_z$  orbital merges with the s,  $p_x$ , and  $p_y$  orbitals, which in a purely  $sp^2$ -hybridized system form three equivalent bonds with the nearest neighbors. The bonding between  $p_z$  orbitals gives rise to the states. As the features right above and below the band gap correspond to strong peaks in the DOS of the  $p_z$  orbitals, it may be concluded that these spectral features correspond to  $\pi$  and  $\pi^*$  states. In particular, Si atoms sitting on top of Zr atoms (C atoms) seem to contribute predominantly to those bands, in good agreement with the fact that they have the conformation the closest to that of  $sp^2$  hybridized atoms.

This study allows the determination of the local origin of the previously resolved states, which are attributed to originate predominantly from the  $p_z$  orbitals of the Si atoms sitting on top of Zr atoms. A clear correlation between the buckling of the Si atoms and the contribution of their  $p_z$  orbitals to the  $\pi$  states was found.

## (2) Tuning of the electronic properties of epitaxial silicene

The adsorption of K studied by LEEM, LEED at Brookhaven National Laboratory and ARUPS at KEK has demonstrated that the electronic structure of silicene can be tuned upon adsorption of foreign atoms [13].

In Figures 2.(a) to 2.(c), LEED patterns for different values of x the K coverage are shown. The  $(3 \times 3)$  pattern of pristine silicene on  $ZrB_2(0001)$  thin films shown in Figure 2.(a) is consistent with the reflection high-energy electron diffraction data reported previously [6]. The reconstruction of the surface does not change upon exposure to potassium atoms up to a level of  $x = 0.16$ , which indicates that the silicene layer remains structurally intact maintaining the epitaxial relation.

The Figures 2.(d) and 2.(e) show ARUPS spectra taken at  $x=0$  and  $x=0.18$ . The presence of two upwards-curved electronic features centered on  $K_{Si}$  is consistent with the prediction for two bands in  $(3 \times 3)$ -reconstructed

silicene. As shown in Figure 2.(e), upon deposition of K atoms, the two bands shift towards higher binding energy by about 100 meV, giving a clear evidence for the electron donation from K atoms to silicene.

The Figure 2.(f) shows the spectra in the vicinity of the M point of the reconstructed Brillouin zone with  $x=0.18$ . The electron donation to the silicene sheet results in the occupation of a formerly unoccupied (likely to be  $\pi^*$ -derived) band, denoted "X<sub>5</sub>". It also induces the hybridization between "S<sub>1</sub>" and "X<sub>4</sub>", two bands observed in the pristine system and whose positions are indicated by dashed lines. They are respectively a surface state of ZrB<sub>2</sub>(0001) and a  $\pi$ -derived electronic band of pristine silicene. Whereas "S<sub>2</sub>", another surface state, remains intact upon adsorption of potassium atoms, "S<sub>1</sub>" hybridizes with "X<sub>4</sub>" and forms a new band "SX". If electron donation results in stronger interactions at the interface between silicene and the thin film surface, it is expected that electron withdrawal by acceptors, e.g., iodine molecules, may lead to the opposite. With the synthesis of free-standing silicene remaining a major challenge, the tuning of electronic properties of epitaxial silicene with foreign atoms then promises an alternative way to realize the exciting properties predicted for free-standing silicene.

### (3) Hydrogenation of epitaxial silicene

The study of the hydrogenation of epitaxial silicene has been carried out by STM in our setup and by LEEM, LEED and ARUPS at NSLS. The latter experiments did not reveal any significant change in the atomic structure or in the electronic band structure. The preliminary characterization by STM pointed out a strong decrease of the tunneling conductivity, suggesting that the hydrogen atoms form an insulating capping layer weakly interacting with the silicene layer. However, we observed that upon exposure to ambient air, hydrogenated silicene tends to get oxidized.

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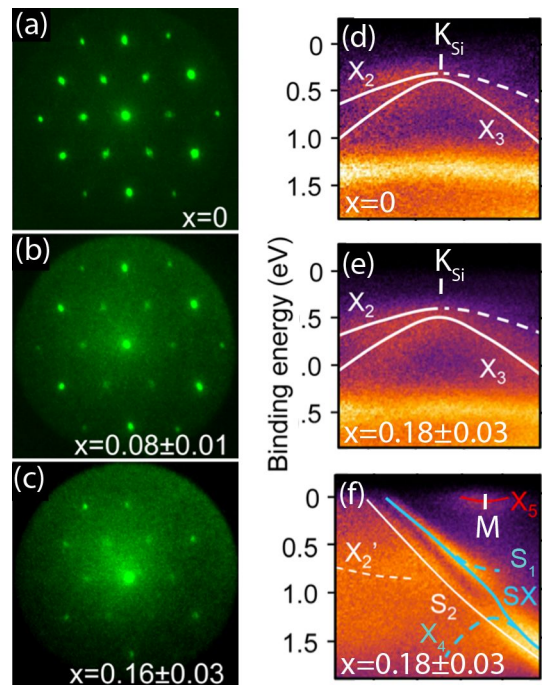


Figure 2. (a)-(c): LEED patterns recorded with an electron energy of 30 eV, corresponding to different coverages of potassium. (d)-(e): ARUPS spectra of epitaxial silicene on ZrB<sub>2</sub>(0001) along the  $\bar{M}$  direction, in the vicinity of  $K_{Si}$ . (f): ARUPS spectrum along the  $\bar{M}$  direction, in the vicinity of the M point of the  $(\sqrt{3} \times \sqrt{3})$  reconstruction for a coverage of  $x=0.18$ . ARUPS spectra were recorded at PF with a photon energy of  $h\nu=43$  eV.

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#### 5. 主な発表論文等

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[図書](計0件)

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出願状況(計0件)

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#### 6. 研究組織

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