

Buckling-Induced π -Band Gap Opening in Epitaxial Silicene

Rainer FRIEDLEIN, Antoine FLEURENCE, Yukiko YAMADA-TAKAMURA
School of Materials Science, Japan Advanced Institute of Science and Technology

Abstract

A two-dimensional, atom-thick honeycomb layer composed of silicon atoms forms through surface segregation on zirconium diboride thin films on Si wafers. Surface-sensitive Si $2p$ photoelectron diffraction and spectroscopy performed at BL-18A provide among other well-established surface science techniques essential evidence for a particular buckling of this layer induced by the epitaxial relationship with the substrate. This associated reconstruction causes a back-folding of silicene π bands into the reduced Brillouin zone and an opening of a direct band gap. The results imply that silicene is less rigid than graphene which may allow the tuning of the electronic properties.

1. Introduction

While the Nobel-Prize awarded creation of graphene opened the hottest playground for physics and nanotechnology so far, until recently, it was thought to be impossible to form similar sheets made of Si atoms. This is because the four valence electrons prefer to hybridize in a different way than C atoms, in the so-called sp^3 hybridization instead of the sp^2 hybridization. The creation of “silicene”, as the new material was baptized [1], by various groups as epitaxial Si monolayers on the Ag(111) surface [2-4] and independently on the metallic ceramics called zirconium diboride by ourselves [5] therefore came as a surprise. However, even with the limited available experimental evidence so far, it became already clear that epitaxial silicene has properties that differ from those of graphene such that it is a complex matter even to define silicene.

Honeycomb-like Si monolayer structures occur in the bulk and at the surface of disilicides in which the Si atoms are strongly hybridized with the metal interlayers [6]. In order to call a honeycomb Si monolayer “epitaxial silicene”, interactions with the substrate surface shall be sufficiently weak such that sp^2 hybridization between the Si atoms does prevail. Accordingly, its classification and any characterization shall include both structural and electronic properties: silicene may be defined as an at least partially sp^2 -hybridized, atom-thick honeycomb layer of Si that possesses π -electronic bands [5].

For the yet hypothetical freestanding silicene, astonishing electronic and transport properties similar to those of graphene like *e.g.* the presence of very light an mobile charge carriers are predicted to prevail even in its slightly-buckled form where Si atoms are displaced out of plane [1,7]. Different to graphene, especially under epitaxial conditions, silicene may exist with a variety of lattice constants, atomistic structures and with a varying sp^2/sp^3 ratio. This structural flexibility may give rise to

altered electronic properties related to the different degree of buckling.

In our recent work, a comprehensive study using a number of well-established surface science techniques and first-principles calculations [5], we provided evidence for the spontaneous formation of epitaxial silicene under ultra-high vacuum conditions and at high temperatures on the (0001) surface of thin films of a metallic ceramics called zirconium diboride. In particular, conclusive evidence for the presence of a Si honeycomb lattice and for atomic-scale buckling comes from the Si $2p$ core-level chemical shifts and intensity ratios related to three atomic sites within the Si layer and from the diffraction of those photoelectrons [5]. These essential data were obtained at beamline (BL) 18A of the KEK-Photon Factory synchrotron radiation facility, managed by the Institute of Solid State Physics (ISSP) of the University of Tokyo.

2. Experimental

Thin ZrB_2 films are grown by ultrahigh vacuum (UHV) chemical vapor epitaxy on Si(111) wafers [8]. Prior to the experiments in different UHV set-ups, the samples were annealed at 750 to 800 °C in order to remove the native oxides. Below 650 °C, the oxide-free single-crystalline $ZrB_2(0001)$ surface is (2×2) reconstructed [8].

Scanning tunneling microscopy was performed in a home-based set-up using chemically-etched Pt-Ir tips. Si $2p$ core level spectra were recorded with the SES-100 hemispherical analyzer of BL-18A, using third-order light ($h\nu=130$ eV, resolution ~ 130 meV). Angle-resolved ultraviolet photoelectron (ARUPS) spectra were measured in a home-based set-up ($h\nu=21.2$ eV, resolution ~ 30 meV), with the samples held at 140 K.

3. Results and Discussion

As shown in Fig. 1a, the large-scale scanning tunneling microscopy (STM) image reveals stripe-like domains that are offset with respect to each other. The formation of these domains is related to the release of stress within a two-dimensional layer of ad-atoms. A fine structure observed in the high-resolution STM image recorded in the constant-current mode, shown in Fig 1b, is consistent with a honeycomb mesh with a lattice constant of about 3.65 Å.

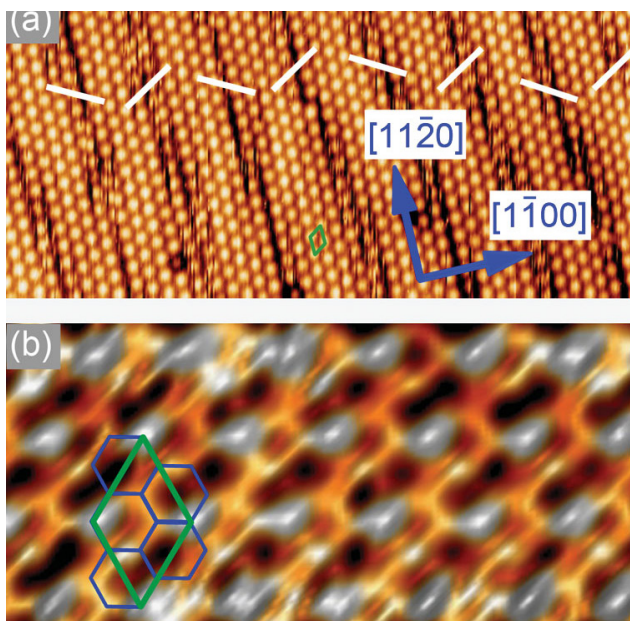


Figure 1 STM images of the (2×2) -reconstructed $ZrB_2(0001)$ surface with different length scales: (a) $20 \text{ nm} \times 9.5 \text{ nm}$, (b) $4.2 \text{ nm} \times 2 \text{ nm}$. The white lines indicate the direction of offsets of neighboring domains. The (2×2) unit cell and the silicene honeycomb mesh are drawn by green and blue solid lines, respectively (all figures adapted from “Experimental Evidence for Epitaxial Silicene on Diboride Thin Films”, Phys. Rev. Lett. 108 (2012) 245501, DOI: 10.1103/PhysRevLett.108.245501, ref. [5]).

The surface-sensitive Si $2p$ spectrum obtained at normal emission, shown in Fig. 2a indicates the presence of Si atoms at the surface. The line shape of the doublet is very different from reconstructed Si(111)- 7×7 surfaces [9] and can, within the error bars of a peak fitting procedure, be understood by just three components with an intensity ratio of about 2:3:1, labeled “A”, “B” and “C”. Components “C” and “A” exhibit chemical shifts of about 140 and 260 meV towards lower binding energy with respect to the main peaks that have major contributions from “B”. The existence of three well-defined chemical environments of Si atoms agree with the in-plane position of a Si honeycomb mesh laid over the STM image in Fig. 1b which allows a unique assignment of in-plane positions within the $ZrB_2(2 \times 2)$ unit cell: two “A” atoms are on hollow sites of the Zr lattice, three “B” atoms are located at intermediate positions between top and bridge sites, and the single “C” atom is on top of a Zr atom. The corresponding structure model is sketched in Fig. 2b.

In Fig. 2c is shown the dependence of intensity ratios “A”/“B” and “C”/“B” as a function of the polar photoelectron emission angle. While “C”/“B” does not change along the $[-1100]$ and $[11-20]$ high-symmetry directions of the $ZrB_2(0001)$ film, the intensity of “A” is reduced exclusively along the $[11-20]$ directions. This reduction is attributed to diffraction of Si $2p$ photoelectrons originating at “A” atoms on “B” atoms in this direction. The occurrence of photoelectron diffraction is strong evidence for atomic-scale buckling and, in particular, may indicate a lower position of “A” with respect to “B” atoms. In this structure model, the matching of the $ZrB_2(0001)-(2 \times 2)$ unit cell with that of the Si overlayer provides a $(\sqrt{3} \times \sqrt{3})$ reconstruction of silicene with a yet unpredicted buckling.

The Brillouin zones (BZs) of the (2×2) -reconstructed $ZrB_2(0001)$ surface and of unreconstructed silicene are shown in Fig. 3a. Note that, importantly, the $\bar{\Gamma}$ and \bar{M} high symmetry points coincide with the K_{Si} and M_{Si} points, respectively.

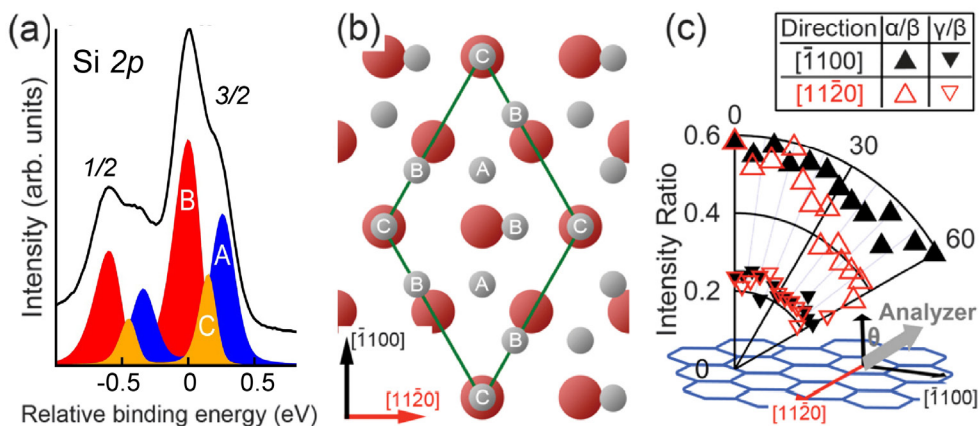


Figure 2 (a) Surface-sensitive Si $2p$ core level spectrum recorded at normal emission. Chemical states “A”, “B” and “C” as identified by peak fitting are indicated. (b) Model of the silicene structure on $ZrB_2(0001)$. (c) Intensity ratios “A”/“B” and “C”/“B” as a function of the polar photoelectron emission angle, along the high-symmetry directions of the surface (adapted from ref. [5]).

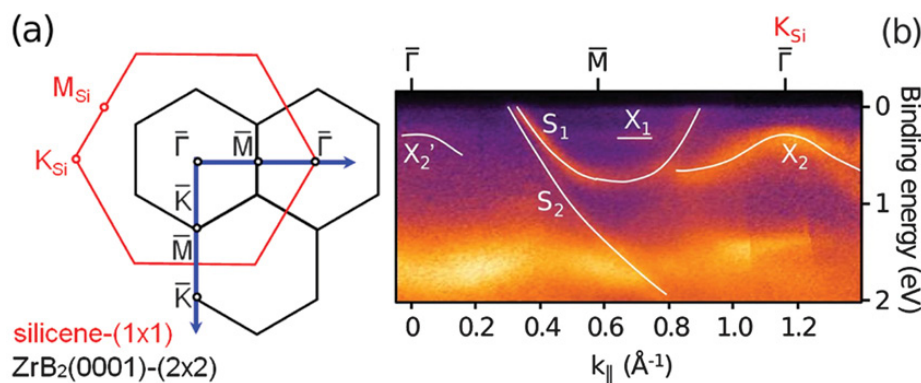


Figure 3 BZs of the (2×2) -reconstructed $\text{ZrB}_2(0001)$ surface and of an unreconstructed silicene layer, (B) ARUPS spectrum along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction (adapted from ref. [5]).

ARUPS spectra taken along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction of the (2×2) -reconstructed $\text{ZrB}_2(0001)$ surface, plotted in Fig. 3b, show among others two spectral features “ S_1 ” and “ X_2 ” that can be assigned to relate to a Zr-derived surface state and silicene-derived π -electronic bands [5]. Since the surface state “ S_1 ” is robust, it is concluded that the outermost Zr layer is structurally intact and only to a minor degree hybridized with silicene states. The intense feature “ X_2 ”, is mirrored with weaker intensity as “ X_2' ” at the $\bar{\Gamma}$ point of the first BZ. It approaches the Fermi level by up to 250 meV and is curved upwards. This is reminiscent of the predicted Dirac cone of π bands of freestanding, non-reconstructed silicene at its K point, but with a gap opened due to the back-folding of bands into the reduced 1st BZ.

4. Conclusions

The experimental data obtained at the home labs and the Photon Factory BL-18A provide clear proof for the presence of two-dimensional, epitaxial silicene exhibiting a single orientation with respect to the substrate. The particular buckling imposed by epitaxial conditions leads to a direct band gap for silicene-derived π -electronic states. This implies that the atomistic structure and thus the electronic properties of silicene may be changed by the choice of appropriate substrate with selected lattice parameters, something that is (almost) impossible for the rather rigid graphene. The creation of a band gap by the control of the internal structural is likely to be fundamentally relevant for the future use of silicene in devices that perform logical operations.

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著者紹介

Rainer FRIEDLEIN

北陸先端科学技術大学院大学マテリアルサイエンス研究科
准教授

〒923-1292 石川県能美市旭台 1-1

TEL: 0761-51-1580 FAX: 0761-51-1149

e-mail: friedl@jaist.ac.jp

略歴：2000年ドレスデン工科大学博士課程修了。Dr. rer. nat. リンショッピン大学研究員，北陸先端科学技術大学院大学マテリアルサイエンス研究科講師を経て2011年より

現職。

最近の研究：角度分解紫外光電子分光を用いた有機半導体薄膜、及び、エピタキシャルシリセンの電子状態研究。

趣味：釣り、ハイキング、旅行、ダンス。

Antoine FLEURENCE

北陸先端科学技術大学院大学マテリアルサイエンス研究科助教

〒 923-1292 石川県能美市旭台 1-1

TEL: 0761-51-1572 FAX: 0761-51-1149

e-mail: antoine@jaist.ac.jp

略歴：2007年パリ南大学博士課程修了。博士（物理学）。日本学術振興会外国人特別研究員などを経て2012年より現職。

最近の研究：走査トンネル顕微鏡を用いたエピタキシャルシリセンの構造と電子状態の研究。

趣味：ピアノ、テニス、水泳、ハイキング、旅行。

高村（山田）由起子 Yukiko YAMADA-TAKAMURA

北陸先端科学技術大学院大学マテリアルサイエンス研究科准教授

〒 923-1292 石川県能美市旭台 1-1

TEL: 0761-51-1570 FAX: 0761-51-1149

e-mail: yukikoyt@jaist.ac.jp

略歴：1998年東京大学大学院工学系研究科金属工学専攻博士課程修了。博士（工学）。日本学術振興会特別研究員、東北大学金属材料研究所助手、北陸先端科学技術大学院大学マテリアルサイエンス研究科講師を経て2011年より現職。

最近の研究：二ホウ化物薄膜のエピタキシャル成長。エピタキシャルシリセンの研究。

趣味：読書。