Phonon dispersion of silicene on ZrB$_2$(0 0 0 1)

T Aizawa, S Suehara and S Otani

National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

E-mail: AIZAWA.Takashi@nims.go.jp

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Abstract

We measured the phonon dispersion of silicene (monolayer Si with a honeycomb lattice) on ZrB$_2$(0 0 0 1) using high-resolution electron energy loss spectroscopy. The measured phonon dispersion was compared with ab initio density functional theory calculations for a silicene model with $2 \times 2$ periodicity of the substrate. The most stable $\sqrt{3} \times \sqrt{3}$ silicene structure, which is similar to the so-called ‘planar-like’ model (Lee C C et al 2013 Phys. Rev. B 88 165404) reproduced the observed phonon modes very well. The recently reported soft phonon around the $\overline{M}$ point (Lee C C et al 2014 Phys. Rev. B 90 241402(R)) was not reproduced, either experimentally or theoretically. The calculated electronic structure revealed that the silicene was metallic on ZrB$_2$(0 0 0 1) and semiconducting on ZrC(1 1 1).

Keywords: Silicene, Phonon dispersion, ZrB$_2$

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last few years, a two-dimensional honeycomb layer of silicon called ‘silicene’ has attracted considerable attention because of its promising versatility [1]. Recently, we investigated the Si/ZrC(1 1 1) system [2] and concluded that Si can form a distorted $\sqrt{3} \times \sqrt{3}$ silicene layer (hereafter referred to as $\sqrt{3}$-silicene). One Si atom in the unit cell protrudes significantly from the others, which make a flat layer. On ZrC(1 1 1), $\sqrt{3}$-silicene coincides with the $2 \times 2$ unit of the substrate, forming a commensurate overlayer. Similar $\sqrt{3}$-silicene models were proposed for silicene on Ag(1 1 1) [3], Ir(1 1 1) [4], and ZrB$_2$(0 0 0 1) [5]. In theoretical calculations, the $\sqrt{3}$-silicene structure seems commonly stable on many metallic substrates.

ZrB$_2$(0 0 0 1) has been studied by several groups as a promising substrate for GaN epitaxy because of lattice and thermal-expansion matching [6, 7]. However, its high melting point of 3493 K makes it difficult to obtain a large single crystal. Instead of preparing single crystals, epitaxial growth of a thin ZrB$_2$(0 0 0 1) film on a Si(1 1 1) substrate by chemical vapor deposition (CVD) has been proposed, and the successful growth of GaN using this method was reported [8–10]. A $2 \times 2$ surface structure was observed [11] on the CVD-grown ZrB$_2$ film, and it was concluded by Fleurence et al [12] that this structure was a silicene layer made up of diffused Si atoms from the Si substrate. Clean ZrB$_2$(0 0 0 1) is, similarly to ZrC(1 1 1), terminated with a metal layer [13–15]. Lee et al calculated two structure models using first-principles density functional theory (DFT) for Si/ZrB$_2$(0 0 0 1): the most stable $\sqrt{3}$-silicene structure (called ‘planar-like’) and a metastable ‘buckled’ structure [5]. The energy difference between the two models is fairly large: $-0.28$ eV per Si atom, but they are divided by a very low energy barrier, suggesting that the metastable structure is improbable.

In this paper, we investigated the phonon dispersion of silicene on a ZrB$_2$(0 0 0 1) single crystal surface using high-resolution electron energy loss spectroscopy (HREELS). The experimental results were compared with first-principles DFT calculations. The $\sqrt{3}$-silicene model was able to reproduce the measured phonon dispersion very well.

2. Methods

2.1. Experiment

The experiment was performed in an ultra-high vacuum (UHV) surface analysis system consisting of two chambers. The first chamber was made of a high-permeability alloy for HREELS, and maintained an UHV of approximately $10^{-9}$ Pa. This chamber was equipped with an HREEL spectrometer
(Delta 0.5, SPECS GmbH) and low-energy electron diffraction (LEED) optics for setting the sample azimuth. An HREELS resolution of approximately 2 meV in full-width at half-maximum (FWHM) was used in order to obtain a good signal-to-noise ratio. The second chamber was a stainless steel sample preparation chamber with an UHV of 1–2 × 10⁻⁸ Pa. A reflection high-energy electron diffraction (RHEED) system, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a silicon evaporator, and a load-lock system were mounted on this chamber. A transfer tube between the two chambers enabled UHV sample transfer.

A ZrB₂ single-crystal rod was grown using a radio-frequency heated floating zone method [16, 17]. A ZrB₂(0 0 0 1) sample disk 7–9 mm in diameter and 1–1.5 mm thick was cut from the crystal rod using spark erosion after x-ray back Laue orientation. One face of the sample was mirror-polished using B₂C and diamond pastes. After ultrasonic washing in acetone, the sample was placed in vacuum and heated with electron-bombardment from the backside for cleaning. Degas heating at 1500 K followed by several repeated flash heating steps to ≥2500 K in UHV cleaned the surface, which then produced a sharp 1×1 RHEED pattern with no impurities detected by AES [13]. The sample temperature was measured using optical pyrometers (infrared: 570–1870 K, and two-color: 1070–1870 K, λ = 0.85/1.0 μm) without calibration. Si was evaporated from a DC-heated Si wafer placed in front of the substrate (30–40 mm apart).

2.2. Calculation

The calculation method was similar to that described previously [15]. We adopted QUANTUM ESPRESSO 5.1.1 code [18], the Perdew–Burke–Ernzerhof functional [19] for the exchange correlation, and the GBRV ultrasoft pseudopotentials [20]. The bulk ZrB₂ was initially optimized to achieve a residual stress of less than 0.5 kbar. We employed a cut-off energy of 35 Ry and k-points of 10×10×9 in the Monkhost–Pack scheme after checking for convergence of these parameters. The surface was modeled with a ZrB₂(0 0 0 1) 2×2-unit 13-layer (2Si₆ + 6Zr₄ + 5B₈) slab supercell divided by an approximately 1.3 nm-thick vacuum layer. Both sides of the slab were covered by the silicon layer. The k-point number for the slab calculation was 6×6×1. Structural optimization with no symmetry assumption was performed to achieve residual forces of less than 0.01 mRy/bohr. Self-consistent electronic ground-state calculations established a convergence error of less than 10⁻¹¹ Ry/cell. Phonon-dispersion calculations were performed using density functional perturbation theory (DFPT) [21]. The phonons of Γ and M were solved for using DFPT, and the other phonons in the Brillouin zone were calculated by interpolation from the calculated force constants [22].

3. Results and discussion

3.1. Si deposition on ZrB₂(0 0 0 1)

Figure 1 shows the observed RHEED evolution during Si deposition. The Si deposition was initiated 15 min after the flash heating for sample cleaning, and the sample temperature was below the measurement range of the pyrometer (570 K). The 1×1 pattern (a) of the clean ZrB₂(0 0 0 1) changed gradually to a 3×3 pattern at first (b)–(e), eventually disappearing (g) before a 2×2 pattern emerged (h)–(i). Further deposition at this temperature caused the RHEED pattern to diffuse, indicating amorphous Si growth. At higher temperatures, Si was almost saturated at the coverage for the 2×2 completion, suggesting a steep decrease of the sticking probability at this coverage, which was defined here as the saturation coverage. In fact, after exposure to Si molecular beam of over 40 double layers of Si(1 1 1) at 1300 K in another molecular-beam epitaxy apparatus, AES revealed that little more than the saturation coverage of Si remained on the surface. Moreover, any excess Si beyond the saturation coverage deposited at room temperature was easily desorbed during subsequent heating to 1100–1300 K.

The 2×2 RHEED pattern changed reversibly to 1×1 at approximately 870 K. In the case of Si/ZrC(1 1 1), a similar 2×2 ↔ 1×1 phase transition occurs at 1000 K, about 100 K higher than on ZrB₂(0 0 0 1). This transition has been considered an order–disorder transition. In the disordered (1×1) phase, the silicon layer frequently changes its registry to the substrate, disrupting the long-range 2×2 ordering. The lower transition temperature suggests a lower potential barrier for the registry change.

Scanning tunneling microscopy (STM) indicated that the ZrB₂(0 0 0 1) 2×2-Si phase consisted of many striped domains [12]. In fact, the ‘2×2’ RHEED pattern was not a simple 2×2, because the 1/2-order diffraction spots were split. This splitting became clearer after annealing at 1100 K, as shown in figure 2(a). The same spot splitting was observed in a LEED pattern found in the literature: figure 2(a) in [23]. This spot splitting may correspond to the striped-domain structure. Note that no splitting was observed on Si/ZrC(1 1 1), as shown in figure 2(b). On ZrC(1 1 1), the lattice constant a_{ZrC} = 332 pm was larger than that of ZrB₂(0 0 0 1) (a_{ZrB₂} = 317 pm), where 2a_{ZrC}/√3 = 383 pm coincides very well with the Si(1 1 1) lattice, resulting in
insufficient stress to form the striped domain. AES results indicated comparable Si coverages on both ZrB$_2$ and ZrC substrates.

Si at the saturation coverage survived heating to 1300 K. Above 1500 K, Si desorbed gradually and $\sqrt{3} \times \sqrt{7}$ and $2\sqrt{3} \times 2\sqrt{3}$ phases appeared. The $\sqrt{3} \times \sqrt{7}$ structure is probably identical to the Si dimer structure reported on HfB$_2$(0 0 0 1) [24].

3.2. Phonon dispersion measurement

The phonon dispersion was measured using HREELS on the sample shown in figure 2(a). Figure 3 shows an example of the measured off-specular HREELS series. In order to detect as many phonon modes as possible, several series were obtained at various primary electron energies (9 eV, 14 eV, 21 eV, and 27 eV). Azimuths were measured along both $\Gamma - \mathbf{K}$ and $\Gamma - \mathbf{M}$. The resultant phonon dispersion relationships are plotted in figure 4. In the obtained data, the highest frequency modes in the 90–100 meV range and modes lying in the 60–70 meV range were assignable to the substrate boron modes from comparison with the substrate phonon dispersion [13]. The modes between 43 meV and 60 meV, within the energy gap of the ZrB$_2$(0 0 0 1) substrate, were silicene phonon modes. The surface acoustic phonon, the lowest frequency mode that exhibits a large dispersion near the $\Gamma$ point, is almost identical to that on the clean ZrB$_2$(0 0 0 1) substrate.

3.3. Calculated phonons

The optimum bulk ZrB$_2$ lattice parameters were calculated to be $a = 317.2$ pm and $c = 354.0$ pm. Structural optimization of the slab model gave a similar $\sqrt{3}$-silicene structure to what was proposed by Lee et al [5] as a ‘planar-like’ structure or to the $\sqrt{3}$-silicene on ZrC(1 1 1) that we proposed [2]. The obtained Si heights from the substrate’s outermost Zr layer are listed in table 1. In the silicene layer, only atop Si (SiA) protrudes significantly from the flat others (bridge-site Si; SiB and hollow-site Si; SiH) by about 160 pm. This protrusion is slightly larger than that on ZrC(1 1 1) (135 pm). The smaller lattice of ZrB$_2$ probably induces compressive stress in the silicene layer, which makes the protrusion larger.

In figure 5, the calculated phonon results are compared with the measured data. The phonon partial density of states (PDOS) in the silicene layer is indicated by blue (vertical component) and green (longitudinal component) markers.
The vertical modes have frequencies from 15 meV to 30 meV, and the longitudinal modes lie between 45 meV and 60 meV. Furthermore, a mixed (longitudinal and vertical) mode exists near 10 meV. The rest of the modes (shown as gray lines) correspond to substrate ZrB₂ phonons, some of which were observed experimentally. As the calculations contained no parameters fitted to the experiment, the observed agreement between the calculation and the experiment seems surprising.

Our calculated phonon dispersion also agrees with that previously reported by Lee et al [25] to within a few meV, except for the lowest frequency mode around the $\overline{M}$ point. This longitudinal-vertical mixed mode was reported to soften deeply, down to almost zero frequency, in their calculations. However, we calculated a finite energy of approximately 7 meV, which was actually observed in the HREELs, although the signal was weak.

Table 1. Calculated height in pm from the substrate Zr layer.

|       | $\text{Si}_A$ | $\text{Si}_B$ | $\text{Si}_H$ | $\text{Zr}_A$ |
|-------|---------------|---------------|---------------|---------------|
| This work | 394           | 234           | 232           | 3             |
| Lee et al [5] | 389           | 231           | 230           | 5             |

Note: $\text{Si}_A$, $\text{Si}_B$, and $\text{Si}_H$ denote atop Si, bridge-site Si, and hollow-site Si, respectively. $\text{Zr}_A$ means the outward relaxation of Zr below $\text{Si}_A$.

The vertical modes have frequencies from 15 meV to 30 meV, and the longitudinal modes lie between 45 meV and 60 meV. Furthermore, a mixed (longitudinal and vertical) mode exists near 10 meV. The rest of the modes (shown as gray lines) correspond to substrate ZrB₂ phonons, some of which were observed experimentally. As the calculations contained no parameters fitted to the experiment, the observed agreement between the calculation and the experiment seems surprising.

Figure 4. Measured phonon dispersion relationships of ZrB₂(0001) 2×2-silicene. The primary electron energy $E_0$ was 9 eV (blue circles), 14 eV (green pentagons), 21 eV (brown diamonds), or 27 eV (red squares).

Figure 5. Calculated phonon dispersion relationships of ZrB₂(0001) 2×2-silicene (gray lines) compared with measured data (red dots). The phonon partial DOS of the vertical/longitudinal component of silicene is indicated by the blue/green markers, respectively. Marker sizes (areas) are proportional to the partial DOS.

3.4. Calculated electronic structure of silicene

Figure 6 shows the calculated electronic PDOS of the silicene layer compared with that on ZrC(1 1 1). On both substrates, silicene has similar Si $\sigma$ bands between $-10$ eV and $-5$ eV. In the energy range from $-5$ eV to the Fermi energy ($E_F \equiv 0$ eV), mixed bands of Si $\pi$ and Zr d appeared. The large modification of C $\pi$ band was also reported in graphene on ZrC(1 1 1) system [26]. At the $\overline{K}$ point, where the $\overline{K}$ point of the silicene is folded back in the $\sqrt{3} \times \sqrt{3}$ periodicity, the Dirac cone seems to be broken, and instead a parabolic band is formed around $E_F$. Note that this Si $\pi$ band crosses $E_F$ in Si/ZrB₂(0 0 0 1) but not in Si/ZrC(1 1 1), as shown in figures 6(c) and (d), respectively. In other words, silicene is metallic on ZrB₂ and semiconducting on ZrC.

In figure 7, the specular HREEL spectra of silicene on ZrB₂(0 0 0 1) and on ZrC(1 1 1) are compared. The spectra are normalized with respect to the elastic peak intensity, so that the relative intensity of both spectra can be compared directly. The background intensity on ZrC was much higher than on ZrB₂, although FWHM of the elastic peak did not largely vary: 1.5 meV and 1.6 meV for figure 7(a) and (b), respectively. The high background was due to ZrC(1 1 1) substrate, which had been observed on some transition-metal carbide (1 1 1) surfaces [27].
clear loss peak appeared at 53 meV on Si/ZrC, which was assigned as a SiA (the protruding Si) vertical vibration. A similar vibrational mode also exists on Si/ZrB$_2$(0 0 0 1) at a slightly higher frequency of 57 meV, but its loss peak intensity in HREELS was very low. The induced dipole (between SiA and Si B) was probably shielded by electron redistribution within the metallic silicene layer. On the other hand, the dipole activity survived in the semiconducting silicene on ZrC. The large loss peaks observed below 35 meV on ZrB$_2$ correspond to vibrations between silicene and substrate Zr, which cannot be shielded by electron redistribution within the silicene layer. The variation in the specular HREELS was consistent with the electronic structure of the silicene.

4. Summary

In summary, a silicene overlayer was deposited on a ZrB$_2$(0 0 0 1) single crystal surface, and its phonon structure was measured using HREELS. *Ab initio* DFT calculations revealed that the most stable model is $\sqrt{3}$-silicene in a 2 × 2 ZrB$_2$(0 0 0 1) unit cell. The calculated phonon dispersion relations were in excellent agreement with the measured phonon dispersion. In the calculated electronic PDOS band of silicene, the Dirac cone was modified by mixing with the substrate Zr d band into a parabolic state. The calculated silicene $\pi$ band was metallic on ZrB$_2$(0 0 0 1) and semiconducting on ZrC(1 1 1).

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References

[1] Kara A, Enriquez H, Seitsonen A P, Lew Yan Voon L C, Vizzini S, Auftray B and Oughaddou H 2012 Surf. Sci. Rep. 67 1
[2] Aizawa T, Suehara S and Otani S 2014 J. Phys. Chem. C 118 23049
[3] Chen L, Li H, Feng B, Ding Z, Qiu J, Cheng P, Wu K and Meng S 2013 Phys. Rev. Lett. 110 085504
[4] Meng L et al. 2013 Nano Lett. 13 685
[5] Lee C C, Flurence A, Friedlein R, Yamada-Takamura Y and Ozaki T 2013 Phys. Rev. B 88 165404
[6] Kinoshita H, Otani S, Kamiyama S, Amano H, Akasaki I, Suda J and Matsunami H 2003 Japan J. Appl. Phys. 42 2260
[7] Tomida Y, Nitta S, Kamiyama S, Amano H, Akasaki I, Otani S, Kinoshita H, Liu R, Bell A and Ponce F A 2003 Appl. Surf. Sci. 216 502
[8] Tolle J, Roucka R, Tsong T S T, Ritter C, Crozier P A, Chizmeshya A V G and Kouvetakis J 2003 Appl. Phys. Lett. 82 2398
[9] Hu C W, Chizmeshya A V G, Tolle J, Kouvetakis J and Tsong I S T 2004 J. Cryst. Growth 267 554
[10] Tolle J, Kouvetakis J, Kim D W, Mahajan S, Bell A, Ponce F A, Tsong I S T, Kottke M L and Chen Z D 2004 Appl. Phys. Lett. 84 3510
[11] Yamada-Takamura Y, Wang Z T, Fujikawa Y, Sakurai T, Xue Q K, Tolle J, Liu P L, Chizmeshya A V G, Kouvetakis J and Tsong I S T 2005 Phys. Rev. Lett. 95 266105
[12] Flurence A, Friedlein R, Ozaki T, Kawai H, Wang Y and Yamada-Takamura Y 2012 Phys. Rev. Lett. 108 245501
[13] Aizawa T, Hayami W and Otani S 2001 Phys. Rev. B 65 024303
[14] Aizawa T, Suehara S, Hishita S, Otani S and Arai M 2005 Phys. Rev. B 71 165405
[15] Suehara S, Aizawa T and Sasaki T 2010 Phys. Rev. B 81 085423
[16] Otani S and Ishizawa Y 1996 J. Cryst. Growth 165 319
[17] Otani S, Korsukova M M and Mitsuhashi T 1998 J. Cryst. Growth 186 582
[18] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[19] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[20] Garrity K F, Bennett J W, Rabe K M and Vanderbilt D 2014 Comput. Mater. Sci. 81 446
[21] Baroni S, de Gironcoli S, Corso A D and Giannozzi P 2001 Rev. Mod. Phys. 73 515
[22] Gonze X and Lee C 1997 Phys. Rev. B 55 10355
[23] Friedlein R, Fleurence A, Sadowski J T and Yamada-Takamura Y 2013 Appl. Phys. Lett. 102 221603
[24] Singh R, Trenary M, Tanaka T, Sen P and Batra I P 2002 Phys. Rev. B 66 155416
[25] Lee C C, Fleurence A, Friedlein R, Yamada-Takamura Y and Ozaki T 2014 Phys. Rev. B 90 241402
[26] Hwang Y, Aizawa T, Hayami W, Otani S, Ishizawa Y and Park S J 1992 Surf. Sci. 271 299
[27] Aizawa T, Hayami W, Souda R, Otani S and Ishizawa Y 1997 Surf. Sci. 381 157