Buckling of epitaxial silicene
from Si 2p photoelectron diffraction experiments

Rainer Friedlein, Ying Wang, Antoine Fleurence, Yukiko Yamada-Takamura

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST)

As the counterpart of graphene, silicene is an atom-thick honeycomb layer of silicon. Different to graphene, however, it is considered to be stable in its slightly buckled form [1,2]. While two-dimensional silicene is discussed only theoretically, previously, silicene ribbons formed on the Ag(110) surface have been well characterized by surface science techniques [3,4]. In yet unpublished work, we demonstrate that two-dimensional silicene forms spontaneously on the surface of zirconium diboride, ZrB$_2$(0001), grown on Si (111) wafers [5]. Determined by the epitaxial relation with the substrate, scanning tunnelling microscopy (STM) images reveal the $\sqrt{3} \times \sqrt{3}$ structural motif.

Surface-sensitive Si 2p core-level photoelectron spectroscopy has been performed at BL18A using a photon energy of 130 eV. A high resolution of better than 130 meV is obtained by employing third-order light. Samples are prepared by annealing at a temperature of about 800 °C in situ such that the native oxide is removed.

The Si 2p spectrum obtained at normal emission is shown in Fig. 1. As quantified by a peak fitting procedure, the spectrum is composed of three components in a ratio of about 2:3:1, labeled A, B and C that proof the existence of Si ad-atoms in three distinct chemical states. This ratio is consistent with a structure model derived from the STM images where Si$_A$ atoms are located at hollow sites of the hexagonal Zr lattice, Si$_B$ atoms at intermediate positions between top and bridge sites, and Si$_C$ atoms on top of Zr atoms. When varying the polar photoelectron emission angle $\theta$ with respect to normal, perpendicular to the Si-Si nearest-neighbor direction, the intensity ratios A/B and C/B remain constant up to $\theta$=60° (Fig. 1(B)), while along the nearest-neighbor direction, A/B decreases by about 30 % indicating diffraction of Si$_A$ photoelectrons on Si$_B$ atoms. This shows that electron-rich Si$_A$ atoms are

![Figure 1: Si 2p photoelectron spectrum in normal emission. The inset shows a table containing the intensities of three chemical states obtained by a peak fitting procedure.](image1)

![Figure 2: Intensity ratios A/B and C/B as a function of the polar photoelectron emission angle $\theta$, along the two high-symmetry directions.](image2)
in a lower position than Si\textsubscript{B} atoms providing decisive experimental evidence for an atomic scale buckling of the silicene layer. It also confirms a charge density modulation connected to the particular internal silicene structure imprinted by interactions with the diboride substrate.

We thank K. Yaji and A. Harasawa (ISSP) for experimental help. Support from Special Coordination Funds for Promoting Science and Technology, commissioned by MEXT, Japan, by a Grant-in-Aid for Scientific research (KAKENHI nos. 22560006 and 22015008) and by the MAZDA Foundation is acknowledged. A.F. is supported by a JSPS through a postdoctoral fellowship.

References