Buckling of epitaxial silicene

from Si *2p* photoelectron diffraction experiments

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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 In yet unpublished work, we demonstrate that two-dimensional silicene forms spontaneously on the surface of zirconium diboride, $ZrB_2(0001)$, grown on Si (111) wafers [5].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.

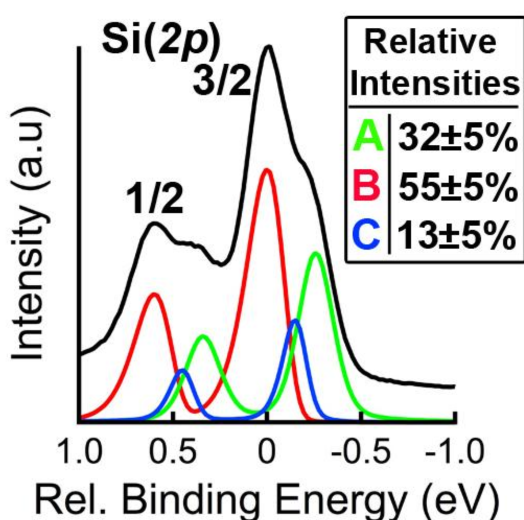

Figure 1: Si *2p* photoelectron spectrum in normal emission. The inset shows a table containing the intensities of three chemical states obtained by a peak fitting procedure.

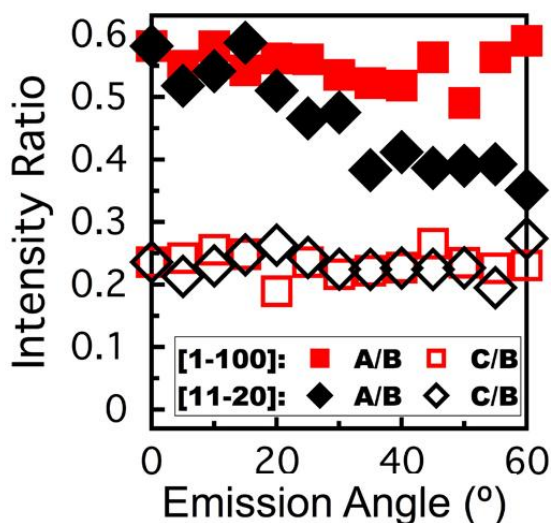

Figure 2: Intensity ratios A/B and C/B as a function of the polar photoelectron emission angle θ, along the two high-symmetry directions.

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 θ with respect to normal, perpendicular to the Si-Si nearest-neighbor direction, the intensity ratios A/B and C/B remain constant up to θ=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

in a lower position than Si_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.

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