Structure of Silicene on a Ag(111) Surface Studied by TRHEPD

The structure of silicene, which consists of a single layer of silicon deposited on a single-crystal silver Ag(111) surface, was experimentally determined for the first time using total-reflection high-energy positron diffraction (TRHEPD) [1]. It was confirmed that silicene has a buckling structure unlike graphene, which consists of a flat single layer of carbon atoms.

The Slow Positron Facility (SPF) of the Institute of Materials Structure Science (IMSS), KEK increased the intensity of the slow positron beam ten-fold in 2010 [2] to create one of the world's highest-intensity slow positron beams. The beam is about 1000 times stronger than a beam obtained by using a commercially-available positron source of radioisotope ^{22}Na. TRHEPD, formerly called reflection high-energy positron diffraction (RHEPD), can accurately determine atomic positions on the topmost surface and immediate subsurface of a crystal. TRHEPD was first developed and applied to surface science by the Japan Atomic Energy Agency (JAEA) [3]. In order to improve this method further, KEK and JAEA installed a TRHEPD station at SPF, KEK in 2011 [2]. Later, the brightness of the beam was enhanced by using a method characteristic to a positron beam, the remission of thermalized positrons.

Since the discovery of a method to isolate a single sheet of carbon (C) atoms in a hexagonal honeycomb lattice structure, graphene, in 2004, the fundamental properties of graphene have been extensively studied as well as its potential application to high carrier-mobility electronic devices. Stimulated by this, extensive efforts to create a similar structure of silicon (Si) atoms have been made, along with theoretical investigations. Theories predict that, unlike carbon which has a layer structure as in graphite as well as diamond structures, silicene would have a buckling structure as shown in Fig. 1 since Si has a diamond structure alone.

In 2012 a number of different procedures were successfully developed for the synthesis of silicene, including one on a Ag(111) surface.

While the theoretically predicted two-dimensional (4×4) symmetry of silicene grown in this way was verified by scanning tunneling microscopy (STM) observations, a buckled structure due to the strong sp^3 bonding character also predicted by the theories was not confirmed. It is also predicted that the Dirac cone of the energy dispersion in silicene depends on the magnitude of the buckling as well as on interactions with the Ag(111) substrate. Thus, the amount of the buckling (spacing between the top and bottom Si layers in silicene, Δ) and the spacing between the bottom Si layer and the top Ag layer, d, are important factors in understanding its electronic properties.

A collaboration of researchers from JAEA, KEK, University of Tokyo and Nagoya University used KEK's high-intensity, high-brightness positron beam with an energy of 10 keV (wavelength of 0.12 Å) to measure the TRHEPD pattern of silicene while varying the glancing angle (θ = 0°–6°) of the incident positron beam. Then rocking curves, i.e., plots of the glancing angle dependence of the diffraction spot intensity, for the specular diffraction spot were extracted. By analyzing the rocking curves the detailed structure of the silicene was successfully determined.

A single-crystal Ag(111) film comprising 20 atomic layers was grown on a Si (111) surface, subsequent to which Si was vapor-deposited onto the surface of the Ag film to form silicene. The expected symmetry of (4×4) was confirmed using reflection high-energy electron diffraction (RHEED). It is worth noting that the symmetry of the surface atomic configuration can be easily identified by using various surface-sensitive methods such as RHEED, but it is not easy to determine the accurate position of each surface atom by analyzing the data in detail.

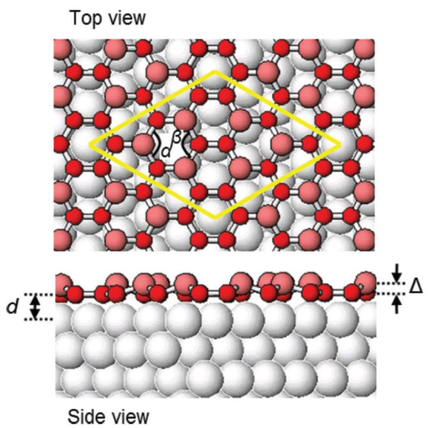

Figure 1: Top and side views of proposed silicene on Ag(111) surface. Large and small red spheres are the top and bottom Si atoms, respectively. The gray spheres are the underlying Ag atoms of the substrate. The spacing between the top and bottom Si layers is denoted by Δ. The distance between the bottom layer of silicene and the underlying first Ag layer is denoted by d. The bond angles are labeled as α and β.

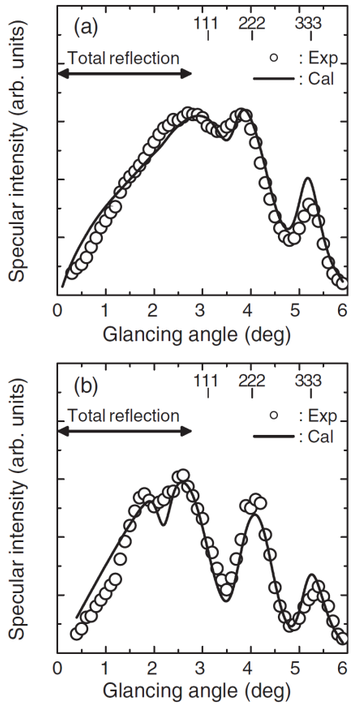

Figure 2: TRHEPD rocking curves for (a) Ag(111)-(1×1) surface before the Si deposition and (b) silicene on an Ag(111) surface in the one-beam condition at room temperature. Circles are the experimental data. Solid curves indicate the results calculated with the optimum values for the adjustable parameters.

The rocking curve measurements were conducted with the beam azimuths 13° off the [11$\bar{2}$] direction (one-beam condition) and along the [11$\bar{2}$] direction (many-beam condition). When viewed from the beam direction in the one-beam condition, the in-plane atoms are randomly distributed, and hence, the specular reflection intensity depends exclusively on the vertical coordinates of the atomic positions. In the many-beam condition, the specular intensity depends not only on the vertical coordinates but also on the in-plane coordinates owing to the in-plane multiple scattering.

First, the vertical structure configuration was determined by analyzing the rocking curve in the one-beam condition. The circles in Fig. 2(a) show experimental rocking curve in the one beam condition for Ag(111)-(1×1) surface before the Si deposition. The solid curve shows the optimized calculated curve. Fig. 2(b) shows the experimental and calculated rocking curves after silicene was grown on the Ag(111) surface, also in the one-beam condition at room temperature. Significant difference between the figures (a) and (b) indicates

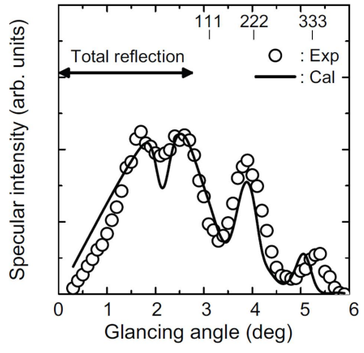

Figure 3: TRHEPD rocking curve for silicene on an Ag(111) surface in the many-beam condition at room temperature. Circles indicate the experimental data. The solid line indicates the calculated curve using the optimum parameters.

the very high sensitivity of TRHEPD on the topmost surfaces. The optimized curve in Fig. 2 (b) corresponds to the structure where the bucking distance Δ is 0.83 Å and the Si-Ag layer distance d is 2.14 Å. Next, the rocking curve shown in Fig. 3, measured under the many-beam condition, was analyzed with the vertical positions already determined fixed. The two Si–Si bond angles (see Fig. 1) were determined to be α = 112° and β = 119°, confirming the buckling structure which leads to (4×4) symmetry. These results agree well with the theoretical predictions (Δ = 0.78 Å, d = 2.17 Å, α = 110°, and β = 118°) [4].

These experimental results highlight the fact that TRHEPD with the high-brightness, high-intensity variable-energy positron beam at KEK is very useful for determining the atomic arrangement of a surface. This method is expected to become a standard method for surface structure determination, as X-ray and neutron diffraction is the standard method for structural determination of bulk structures.

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