Structure of silicene on a Ag(111) surface studied by reflection high-energy positron diffraction

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The structure of silicene fabricated on a Ag(111) surface was determined using reflection high-energy positron diffraction with a linac-based brightness-enhanced intense positron beam. From the rocking curve analysis, the silicene was verified to have a buckled structure with a spacing of 0.83 Å between the top and the bottom Si layers. The distance between the bottom Si layer in the silicene and the first Ag layer was determined to be 2.14 Å. These results agree with the theoretically predicted values from a previous study [Phys. Rev. Lett. **108**, 155501 (2012)] within an error of ±0.05 Å.

Two-dimensional systems suspended on a crystal surface, such as graphene,[1] have attracted increasing attention because of the interest in their fundamental properties and their potential applications in the technology of high carrier-mobility electronic devices. Silicene, which is a two-dimensional sheet composed of silicon, is an example of an analog of graphene. Since the first theoretical discussion on the structural and electronic properties of free-standing silicene,[2] the synthesis of silicene has been extensively attempted by many researchers. In particular, various phases of Si layers were reported to form on a Ag(111) surface; the resulting phase was dependent on the amount of Si coverage and the substrate temperature.[3,4] Recently, the synthesis of silicene on a Ag(111) surface, finally, was successfully performed.[5,6] Silicene has also been formed on a zirconium diboride thin film grown on a Si(111) surface.[7]

Two-dimensional symmetry of silicene on a Ag(111) surface, predicted by the theoretical calculations, was verified by scanning tunneling microscopy observations.[5,6] However, a buckled structure due to the strong sp^3-bonding character predicted by the theories,[5,6] as shown in Fig. 1, has not been confirmed. The buckling feature is in sharp contrast to the case of graphene, which is a flat sheet. The calculated shape of the Dirac cone of the energy dispersion in silicene is modulated by the magnitude of buckling in the silicene sheet[8] as well as by interactions with the Ag(111) surface.[9] Thus, the spacing between the top and the bottom Si layers in silicene and that between the bottom Si and the top Ag layers are important factors in understanding its electronic properties.

In this paper, we determined the detailed structure of silicene on a Ag(111) surface using reflection high-energy positron diffraction (RHEPD) with a brightness-enhanced intense positron beam. Recently, RHEPD has been shown to be a powerful tool in determining the structure of the topmost surface layer.[10] When incident on a surface at an angle smaller than a certain critical angle, positrons are totally reflected at the first surface layer, owing to the positive potential barriers of materials to positrons. Under the total reflection condition, the penetration of the positron wave into the crystal is negligibly small, and hence, the diffraction intensity depends almost exclusively on the structure and the thermal vibration of the first surface layer. Since the first observation of RHEPD using a ^{22}Na-based positron beam,[11] this method has been

applied to the structural analysis of various surface systems.[12] Developments incorporating the positron beam at the Slow Positron Facility of the Institute of Materials Structure Science, KEK,[13] which is nearly 100 times more intense than the ^{22}Na-based positron beam, has allowed measurements of greatly increased precision and, consequently, a more efficient structural analysis of the topmost surface layer.

The present study, carried out at the Slow Positron Facility at KEK,[13] used a pulsed 50-Hz electron beam from a dedicated 55-MeV linac to produce positrons from pair creation through bremsstrahlung radiation in a Ta convertor. The positrons were then injected into 25-μm W foils, moderated to thermal energy, and a fraction were spontaneously reemitted from the foil surfaces with an energy of 3 eV due to the negative work function. The positron convertor/moderator assembly was held at an electrostatic voltage of 15 kV. The monoenergetic positrons emitted were, thus, accelerated to 15 keV as they entered the grounded beamline and were magnetically transported to the experimental hall. The beam was then released into a nonmagnetic region and was focused with a magnetic lens on a transmission type remoderator (100-nm W film)[14,15] electrostatically floated to 10 kV. The remoderated positrons were reemitted from the other side of the film with a brightness enhanced by about 5×10^5 times over the initial magnetically guided beam and were further transported to the grounded RHEPD chamber with an energy of 10 keV. The final beam intensity at the sample was estimated to be approximately 1×10^6 slow e^+/s with a beam diameter of 0.5 mm. The diffracted positrons were observed with a microchannel plate and a charge-coupled device camera. The reflection high-energy electron diffraction (RHEED) was used to monitor the Ag thickness and to check the formation of the silicene through the symmetry of the pattern *in situ* as in surface experiments with other techniques.

The fabrication procedure of silicene was as follows.[5,6] A Si substrate was cut from an n-type mirror polished Si(111) wafer. This sample was held at 700 K overnight, then was taken up to 1473 K for a few seconds several times in ultrahigh vacuum—a clean 7×7 reconstructed structure was, thus, formed on the Si(111) surface. By depositing Ag atoms onto the Si(111)-7×7 surface at 130 K (Ref. 16) and subsequently annealing it by heating up to room temperature, a crystalline Ag(111) thin film
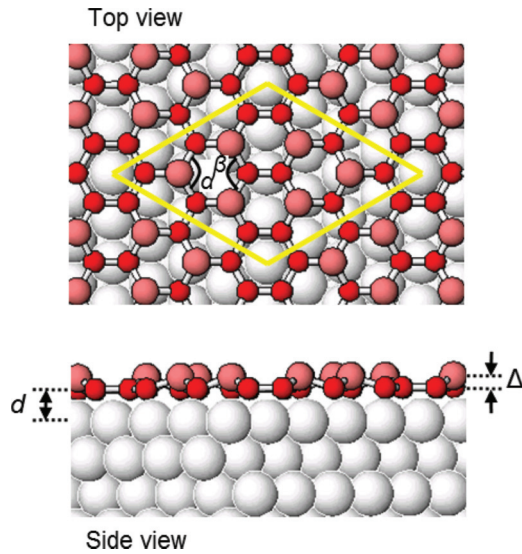
FIG. 1. (Color online) Schematic of proposed silicene on a Ag(111) surface.[5,6] Light- and deep-red circles are the Si atoms, and the gray circles are the Ag atoms of the substrate. The spacing between the top (denoted by large light-red circles) and the bottom (denoted by small deep-red circles) Si 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 α and β.

with a thickness of 20 monolayers (MLs) was formed. After depositing 1 ML of Si atoms at 520 K, the formation of a 4×4 structure was confirmed by the RHEED pattern obtained where 1 ML is defined as 1.38×10^{15} cm^{-2}. Weak spots showing the formation of a small fraction of $\sqrt{13} \times \sqrt{13}$ domains were also observed, indicating that the control within the narrow temperature range during the deposition was not perfect.[3] The coverage of the $\sqrt{13} \times \sqrt{13}$ domains is estimated to be less than 5% from the spot intensity relative to that of the 4×4 domains. Thus, the effect of the $\sqrt{13} \times \sqrt{13}$ domains on the rocking curve for the specular spot is negligibly small.

The critical angle for the total reflection of a positron beam from a surface θ_c is given by $\theta_c = \arcsin(eV/E)^{1/2}$, where eV and E are the mean potential energy of the positrons in the crystal and the kinetic energy of the incident positron beam.[10] For a positron beam of $E = 10$ keV, θ_c is estimated to be $2.0°$ for Si ($eV = 12$ eV) and $2.8°$ for Ag ($eV = 23$ eV).

RHEPD rocking curves of the specular spot were measured in two different incidence directions. The first was in the one-beam condition where the incident azimuth was $13°$ off the $[11\bar{2}]$ direction. Under this condition, the intensity of the specular spot depends mainly on the vertical components of the atomic positions and the number density of atoms in each layer for atoms in plane are randomly distributed when viewed with a small glancing angle along this particular incidence direction.[17] The other was in the many-beam condition where the incident azimuth was along the $[11\bar{2}]$ direction. Under this condition, the intensity of each spot depends on the in-plane as well as the vertical components of the atomic positions. By using rocking curve analyses in both conditions, it is possible to make a reliable determination of the structure. First, the vertical features of the structure can be elucidated by using the data from the one-beam condition without being hindered
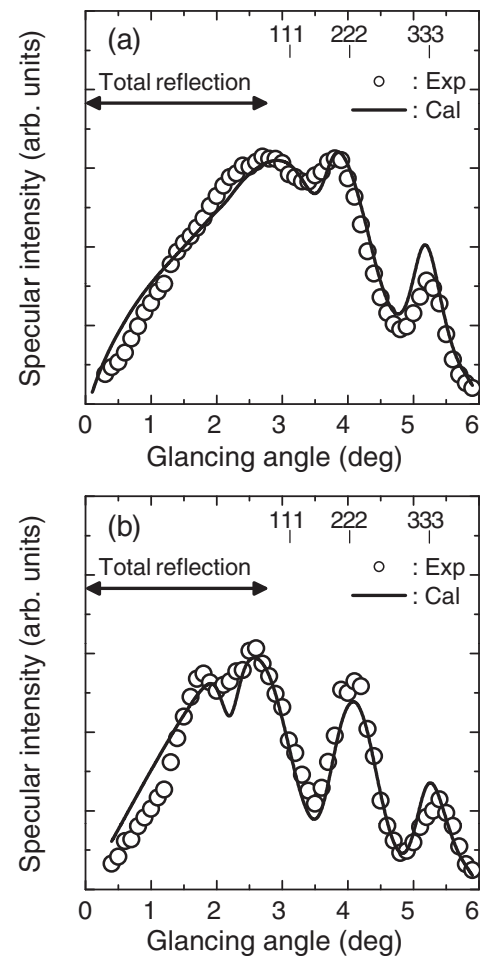

FIG. 2. RHEPD rocking curves for (a) the Ag(111)-1 × 1 surface and (b) silicene on a Ag(111) surface in the one-beam condition at room temperature. Circles are the experimental data. Solid lines indicate the calculated curves using optimum values for the adjustable parameters. The incident positron energy is 10 keV. The angle range for total reflection for the Ag crystal is shown by a double-headed arrow.

by the uncertainty in the in-plane location of atoms. Then, the in-plane positions can be found by using the data from the many-beam condition taking into account the information on the vertical features already known.

After deposition of Ag atoms on the Si(111)-7 × 7 surface, the formation of the Ag(111)-1 × 1 surface was confirmed from observations of the RHEED pattern. Then the interlayer distance between the first and the second Ag layers was determined by the rocking curve of RHEPD in the one-beam condition at room temperature. The circles in Fig. 2(a) show the results obtained, and the solid line shows the best-fit rocking curve calculated with the dynamical diffraction theory.[18] The thermal vibrational amplitude for the Ag layers was assumed to be 9.64×10^{-2} Å.[19] The absorption potential due to electronic excitations was taken to be 1.68 eV for Ag layers.[20] The interlayer distance between the first and the second Ag layers was varied so as to minimize the difference between the measured and the calculated rocking curves. The goodness of fit was judged using a reliability factor R.[21] The optimum interlayer distance was, thus, determined to be 2.34 Å, which

is close to that of 2.36 Å in the bulk. Therefore, the first Ag layer of the Ag(111) thin-film surface was found to have no significant relaxations in the lattice.

The circles in Fig. 2(b) show the RHEPD rocking curve for the 4×4 reconstructed structure of silicene on the Ag(111) surface measured in the one-beam condition at room temperature. It is significantly different from the curve before deposition [Fig. 2(a)]. Using these data, the interlayer distances and the number density in each layer in the silicene were determined. The thermal vibrational amplitude and the absorption potential for silicene were assumed to be 7.84×10^{-2} Å (Ref. 19) and 0 eV,[21] respectively. The rocking curve was calculated as a function of the distance between the top and the bottom Si layers Δ and the distance between the bottom Si layer and the top Ag layer d (see Fig. 1) and the number densities of the top and bottom layers of atoms in silicene ρ_{top} and ρ_{bottom}, respectively. These parameters were simultaneously varied with the constraint that $\rho_{top} + \rho_{bottom} = 18$ so as to minimize the factor R. The solid line in Fig. 2(b) is the result; it can be seen that the experimental result is reproduced very well by the calculation. The optimized values thus obtained are $d = 2.14$, $\Delta = 0.83$ Å, $\rho_{top} = 5.9$, and $\rho_{bottom} = 12.1$. These values are in good agreement with the theoretical predictions of Ref. 5 ($d = 2.17$, $\Delta = 0.78$ Å, $\rho_{top} = 6$, and $\rho_{bottom} = 12$). The value of Δ reported in Ref. 6 is slightly smaller than our result. Thus, it is certain that silicene has some buckled structure as predicted and does not have a flat structure as in graphene.

Figures 3(a) and 3(b) show the dependence of the calculated rocking curves on d and Δ, respectively. The value of Δ is fixed at 0 Å in (a) and that of d is fixed at 2.2 Å in (b). The sensitivity to these parameters of both the overall shape and the peak positions are illustrated in these figures. In Fig. 3(a), it can be seen that the peak positions gradually shift towards lower angles with increasing d. The same tendency is observed for Δ up to 0.6 Å as shown in Fig. 3(b). When the value of Δ

FIG. 4. (a) RHEPD rocking curve for silicene on a 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. (b) Calculated rocking curves for silicene on a Ag(111) surface in the many-beam condition for various values of α with β fixed at 110°.

increases from 0.6 to 0.8 Å, there appears to be a sudden shift towards higher angles of the peak positions of the 222 and 333 Bragg reflections.

The circles in Fig. 4(a) show the RHEPD rocking curve measured in the many-beam condition. Using these data, the in-plane components of the atomic positions were determined. The rocking curves under this condition were calculated for various bond angles α and β (see Fig. 1) within the framework of the model given in Ref. 5 and using the values for d and Δ obtained from the analysis of the rocking curve in the one-beam condition. Figure 4(b) shows the sensitivity of the curve to the value of α with β fixed at 110°. The width of the peak at 2.5° broadens, and the dip at around 3.5° shifts towards higher angles with increasing α. The same tendency was found for β with α fixed. The values of α and β were simultaneously varied with the constraint of $d = 2.14$ and $\Delta = 0.83$ Å so as to minimize the R factor. The solid line in Fig. 4(a) shows the best-fit result. The optimum bond angles thus determined are $\alpha = 112°$ and $\beta = 119°$, which are close to those expected from the theoretical calculations.[5] This indicates that six Si atoms at on-top sites in the unit cell
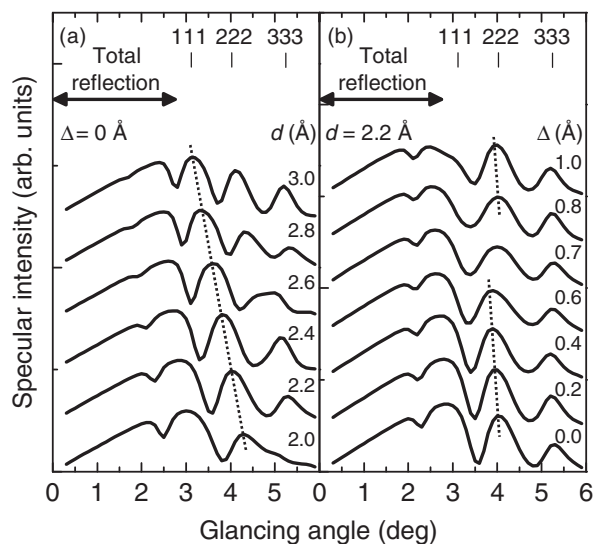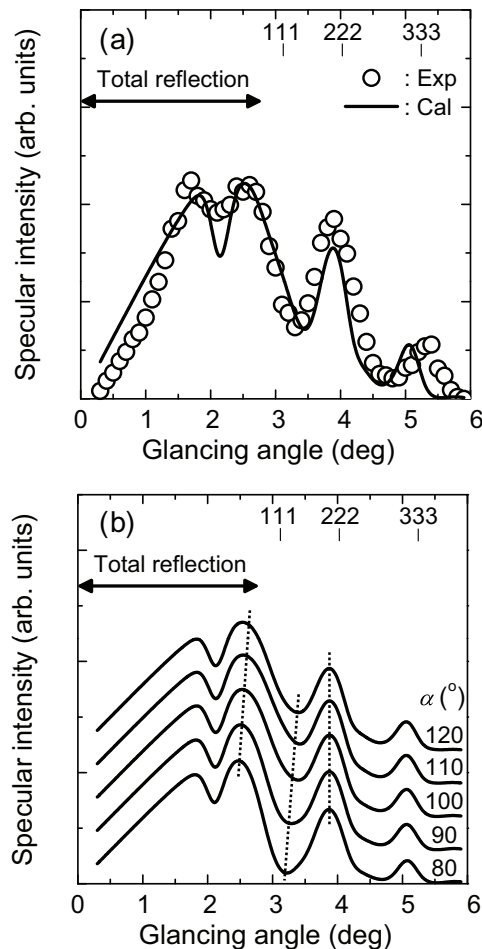

FIG. 3. Calculated RHEPD rocking curves for silicene on a Ag(111) surface in the one-beam condition (a) for various d's with a fixed Δ and (b) for various Δ's with a fixed d. Dotted lines are a visual guide.

TABLE I. Structure parameters for silicene on a Ag(111) surface.

	Δ (Å)	d (Å)	α (°)	β (°)
This study	0.83	2.14	112	119
Theory[5]	0.78	2.17	110	118
Theory[6]	0.7			

are displaced upward. The present study, thus, confirms that the 4×4 model predicted by the theoretical calculations[5,6] is valid for the atomic configuration of silicene on a Ag(111) surface. Table I summarizes these results.

The atomic arrangement of silicene on a Ag(111) surface, theoretically proposed[5,6] to have a buckled configuration, was confirmed experimentally by this study using RHEPD. The magnitude of the buckling and the interlayer distance between the silicene and the underlying Ag layer concur with those reported previously by theoretical calculations[5] within an error of ± 0.05 Å.

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