Structure Analysis of Two-Dimensional Atomic Sheets by Total-Reflection High-Energy Positron Diffraction

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Recently, two-dimensional atomic sheets composed of group-IV elements, which are expected to possess intriguing properties in terms of electronic and spin-related phenomena, have been fabricated on various substrate surfaces. The atomic configurations of atomic sheets are varied depending on the bonding character of the elements and the interaction with substrates. In particular, the magnitude of buckling and the spacing between the atomic sheet and the substrate are crucial to elucidate the origin of its properties. In this review, we report the structure determinations of graphene, silicene, and germanene on the particular substrate surfaces by using total-reflection high-energy positron diffraction (TRHEPD) technique. [DOI: 10.1380/ ejssnt.2018.111]

Keywords: Graphene; Silicene; Germanene; Surface structure; Positron diffraction

I. INTRODUCTION

Since the successful isolation of graphene from graphite [1], there has been growing progress in the research on two-dimensional (2D) atomic sheets that consist of single atomic layer or one unit cell. Graphene, a major type of 2D atomic sheets, possesses an extremely high carrier mobility, which is derived from the so-called Dirac cone, and many other promising features such as high thermal conductivity and robust mechanical property. Recently, efforts are devoted to make a novel single-element 2D atomic sheet that is composed of other group-IV elements with keeping the honeycomb framework of graphene [2]. For example, Si and Ge counterparts of graphene are respectively named as silicene and germanene, which have a good affinity to current Si-based technology, in addition to the above-mentioned fascinating properties. Furthermore, on the basis of the larger spin-orbit interaction in the relatively heavier atom and the expected buckled configuration due to the strong sp3 bonding character, silicene and germanene are expected to provide a new spin-related phenomenon such as 2D topological insulator [3, 4].

Silicene and germanene do not exist in nature, unlike a graphene. Hence, since the first theoretical work in 1994 [5], there had been no significant progress in the experimental works on silicene and germanene. In 2012, eventually, silicene has been successfully fabricated on Ag(111) [6, 7] and ZrB2(0001) thin film surfaces [8]. In 2014, germanene also fabricated on Au(111) [9] and Pt(111) substrates [10], and subsequently on Al(111) [11] and MoS2 substrates [12]. In this review, we report the recent results on the structure determination of 2D atomic sheets, graphene [13], silicene [14], and germanene [15], on the particular substrates by using total-reflection high-energy positron diffraction (TRHEPD) technique.

II. POSITRON DIFFRACTION

Experimental setup of TRHEPD method is depicted in Fig. 1. TRHEPD is the positron counterpart of reflection high-energy electron diffraction (RHEED) [16, 17]. The positron beam accelerated at ~10 kV is incident on a sample surface at a glancing angle (θ) and the diffraction pattern is observed on a screen.

FIG. 1. Experimental setup of total-reflection high-energy positron diffraction (TRHEPD). The positron beam with an energy of 10 keV is incident on a sample surface at a glancing angle (θ) and the diffraction pattern is observed on a screen.

The advantage of the TRHEPD method relies on the positive potential energy of materials for positrons. The positron is the antiparticle of the electron and has the same mass and spin as the electron. Opposite to the electron, however, the electric charge for the positron is positive. Therefore, the crystal potential for the positron beam acts as a barrier at incidence on a material surface. Figure 2(a) illustrates the refraction of a positron beam at crystal surface. The refractive index (n) can be approximately expressed by $n = 1 - \delta$. Here, $\delta = qV/E$, where $q$ is the momentum of the positron.
where $qV$ is the inner potential energy of crystal and $E$ is the incident beam energy. The sign of $\delta$ for positrons and electrons are always positive and negative, respectively. Thus, the value of $n$ for positrons and electrons are less and greater than unity, respectively. This indicates that the total reflection takes place for positrons, the critical angle ($\theta_c$) of which can be obtained in the form of $\theta_c = \sqrt{2\delta}$.

Figure 2(b) represents the penetration depths of positron beam into the ideal Si(111) surface with a step-like potential as a function of $\theta$. When $E = 10$ keV and $qV = 12$ eV, $\theta_c$ is estimated to be $2.0^\circ$ using the above equation. Under the total reflection region except for vicinity of $\theta_c$, the penetration depth is less than $\sim 1 \text{Å}$, which corresponds to the thickness of one atomic layer. Over $\theta_c$, the penetration depth gradually increases with increasing $\theta$. Therefore, the diffraction intensity at low $\theta$ carries information on only the atomic sheet and at high $\theta$ includes on the interface between the atomic sheet and the substrate without effects from the deeper layers.

Experiments were performed at the Slow Positron Facility, KEK, Japan. Recently, we developed a TRHEPD apparatus using a linear electron accelerator (linac) [19]. The positron is produced through the positron and electron pair creation via bremsstrahlung radiation of high-energy x-rays in a converter and moderator unit, and then is magnetically transported to the TRHEPD station. After the energy monochromatization, the beam flux reaches $5 \times 10^5$ positron/s, which is about 100 times larger than the previous isotope-based beam. The newly developed apparatus dramatically improved the data quality and make it possible to observe weak fractional-order spots in higher Laue zones for surface superstructures [20].

FIG. 2. (a) Refraction of a positron beam at an ideal surface. The glancing angles before and after refraction are denoted by $\theta$ and $\theta'$, respectively and the wavenumbers are $k$ and $k'$. (c) Penetration depth of a positron beam into a crystal (Si) as a function of $\theta$.

III. SAMPLE PREPARATIONS

Single-layer graphene was synthesized on the surfaces of crystalline Co(0001) and Cu(111) thin films grown on a Al$_2$O$_3$(0001) substrate by an exposure to acetylene and gas mixture (Ar, H$_2$, and CH$_4$), respectively. The 3 × 4 structure of silicene was fabricated on the surface of crystalline Ag(111) thin film grown on a Si(111) substrate. The 3 × 3 structure of germanene was fabricated on an Al(111) single crystal surface. The details of the sample preparations were described elsewhere [13–15].

IV. RESULTS

A. Graphene/Co(0001) and Cu(111)

The contact of single-layer graphene with other materials brings about a significant change in its property. The calculated electronic structures exhibit, for instance, the existence of the Dirac cone for Al(111) and Pt(111) substrates whilst not for Co(0001) substrate [21]. In addition, the spacing between the graphene and the substrate can be classified into two groups, depending on the strength of the interaction between them [22]. There is a one-to-one correspondence between the electronic state and the spacing between the graphene and the substrate. Therefore, the determination of the spacing between the graphene and the substrate is crucial to elucidate the origin of the electronic property of graphene adsorbed on the particular substrate. However, the spacing had not been investigated experimentally, except for a Ni(111) case [23]. We then determined the spacing between the graphene and the substrates of Co(0001) and Cu(111) using the TRHEPD technique [Fig. 3(a)] [13].

Figure 3(b) shows the rocking curves of specular (0 0) spots for graphene (Gr) on substrates of Co(0001) (upper) and Cu(111) (lower). The circles denote the measured curves. The solid lines are the curves calculated using the optimum parameters. The incident azimuths correspond to the one-beam condition.

FIG. 3. (a) Structure of graphene on a Co(0001) substrate (upper: top view, lower: side view). Gray and blue circles denote C and Co atoms, respectively. The unit cell is indicated by a rhombus. (b) Rocking curves of specular (0 0) spots for graphene (Gr) on substrates of Co(0001) (upper) and Cu(111) (lower). The circles denote the measured curves. The solid lines are the curves calculated using the optimum parameters. The incident azimuths correspond to the one-beam condition.

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condition, the intensities of specular spots can be approximated by a function of the surface-normal (z) components of atomic positions. The rocking curves observed for graphene on Co(0001) and Cu(111) substrates exhibit the distinct difference in the peak positions. The intensity analysis based on dynamical diffraction theory shows that the spacing between the graphene and the Co(0001) substrate is determined as 2.06 Å, which is much smaller than the layer distance (3.35 Å) in a graphite. The spacing for the Cu(111) case was found to be 3.34 Å, which is nearly the same as the graphite. No buckling was observed for graphene on both substrates. The result indicates that the interaction between the graphene and the Co(0001) substrate is much greater than that for the Cu(111) case. As pointed out in the previous theoretical study [25], the spacing between the graphene and the substrate was determined as 0.94 Å and 2.51 Å, respectively. The latter is close to the interatomic distance (3.35 Å) in a graphite. The spacing for the Cu(111) case was found to be 3.34 Å, which is nearly the same as the graphite. No buckling was observed for graphene on both substrates. The result indicates that the interaction between the graphene and the Co(0001) substrate is much greater than that for the Cu(111) case. As pointed out in the previous theoretical study [25], the spacing between the graphene and the substrate was determined as 0.94 Å and 2.51 Å, respectively. The latter is close to the interatomic distance (3.35 Å) in a graphite. The spacing for the Cu(111) case was found to be 3.34 Å, which is nearly the same as the graphite. No buckling was observed for graphene on both substrates. The result indicates that the interaction between the graphene and the Co(0001) substrate is much greater than that for the Cu(111) case.

B. Silicene/Ag(111) and germanene/Al(111)

Unlike a graphene, silicene and germanene are expected to have a buckled structure due to the strong sp³-bonding character [5, 26]. The theoretical calculations demonstrated that the electronic structure for a flat silicene has the Dirac cone at the K points, similar to a graphene. When the structure is slightly buckled, the Dirac cone still keeps its shape. However, the Dirac cone disappears for the highly buckled structure. Therefore, the electronic structure strongly depends on the magnitude of the buckling. Although the theoretical calculations demonstrated the buckled structure for silicene on a Ag(111) substrate [Fig. 4(a)] [6, 7], there was no experimental verification. We then determined the atomic configuration of the silicene on a Ag(111) single crystal thin film grown on a Si(111)-7 × 7 surface [14].

Figure 4(b) shows the rocking curves measured from a 1 × 1 structure of Ag(111) thin film surface and a 4 × 4 structure of silicene on its surface. The shape of the rocking curve is dramatically changed after the silicene formation. The rocking curves measured for silicene/Ag(111) cannot be explained by considering a flat structure of silicene (denoted as gray line). From the intensity analysis on the basis of dynamical diffraction theory, the magnitude of the buckling and the distance between the silicene and the substrate were determined as 0.83 Å and 2.14 Å, respectively. The latter is close to the interatomic distance (0.78 Å) of the bilayer in the Si bulk. The rocking curve analysis on the in-plane components of the atomic positions also shows the agreement with the theoretical calculations within the experimental error [6, 7]. Therefore, it was verified experimentally that the silicene on the Ag(111) substrate has a buckled structure.

The 2D atomic sheets with heavier elements are expected to have stronger spin-orbit interaction. In 2015, a uniform large-area germanene has been successfully fabricated on an Al(111) substrate [11], where eight Ge atoms are included in the unit cell [Fig. 5(a)]. In the previous studies [11, 27], it was suggested that two Ge atoms in the unit cell are shifted upwards, leading to a symmetric structure with respect to the ⟨110⟩ direction. However, the detailed atomic positions related to the buckling of the germanene and the spacing between the germanene and the Al(111) substrate remained unresolved. We then experimentally determined these structural parameters by using the TRHEPD technique [15].

The rocking curves observed for the germanene on the Al(111) substrate show the lack of mirror symmetry with respect to the ⟨110⟩ direction, as shown in Fig. 5(b). The result is in sharp contrast to the symmetric one of the previous reports [11, 27]. From the intensity analysis based on the dynamical diffraction theory, we found that only one Ge atom in the unit cell is shifted upwards, giving rise to an asymmetric structure with respect to the ⟨110⟩ direction [Fig. 5(a)]. The magnitude of the buckling and the spacing between the germanene and the Al(111) substrate were determined as 0.94 Å and 2.51 Å, respectively. The both values are greater than those for the silicene on the Ag(111) substrate [14]. This infer that the larger magnitude of the buckling for germanene is responsible
for the larger atomic radius and the wider spacing is the weaker interaction with the substrate as compared with silicene/Ag(111).

Our result contradicts earlier scanning tunneling microscopy (STM) observations, which showed the symmetric images having two bright protrusions in the unit cell [11]. Here, we suggest that the energy difference between the asymmetric and its mirror-image structures or between the asymmetric and the symmetric structures is very small. Thus, the STM image observed looks like a symmetric one due to the superimposition of two different configurations, which may be induced by the external electric field from a tip during the scanning. Further experimental and theoretical investigations are needed to understand the properties of germanene on the Al(111) substrate.

V. SUMMARY

We investigated the structures of graphene, silicene, and germanene on a metal substrate by using TRHEPD technique. We verified experimentally that silicene/Ag(111) and germanene/Al(111) have a buckling structure, unlike a flat structure of graphene. We also found the symmetric structure for silicene/Ag(111), whilst asymmetric for germanene/Al(111). Due to a variety of possible buckled configurations, the structure of 2D atomic sheets becomes complex, regardless of the less number of atoms. The structure analysis by surface-sensitive diffraction methods will help to solve the complicated structure of 2D atomic sheets on the substrates and promote the deeper understanding in the properties.

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