Germanene Epitaxial Growth by Segregation through Ag(111) Thin Films on Ge(111)

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Abstract: Large-scale two-dimensional sheets of graphenelike germanium, namely, germanene, have been epitaxially prepared on Ag(111) thin films grown on Ge(111), using a segregation method, differing from molecular beam epitaxy used in earlier reports. From the scanning tunneling microscopy (STM) images, the surface is completely covered with an atom-thin layer showing a highly ordered long-range superstructure in wide scale. Two types of protrusions, named hexagon and line, form a $(7\sqrt{7}\times7\sqrt{7})R19.1°$ supercell with respect to Ag(111) with a very large periodicity of 5.35 nm. Auger electron spectroscopy and high-resolution synchrotron radiation photoemission spectroscopy demonstrate that Ge atoms are segregated on the Ag(111) surface as an overlayer. Low-energy electron diffraction clearly shows incommensurate "(1.35×1.35)"R30° spots, corresponding to a lattice constant of 0.39 nm, in perfect accord with close-up STM images, which clearly reveal an internal honeycomb arrangement with corresponding parameter and low buckling within 0.01 nm. Since this 0.39 nm value is in good agreement with the theoretical lattice constant of freestanding germanene, conclusively, the segregated Ge atoms with trivalent bonding in honeycomb configuration, form a characteristic two-dimensional germanenelike structure.

KEYWORDS: germanene, two-dimensional sheet, segregation method, scanning tunneling microscopy (STM), core-level spectroscopy (CLS)

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After the isolation of graphene, the synthesis and characterization of two-dimensional (2D) elemental honeycomb lattices, such as silicene,[1,2] germanene,[3–5] stanene,[6–8] as well as phosphorene [9] and borophene [10] have been intensively reported for the purpose of utilization of characteristic 2D properties. Most studies adopted molecular beam epitaxy (MBE) as a synthesis method of 2D materials grown on crystalline surfaces, such as Au(111), Ag(111), Pt(111), Al(111), Cu(111) MoS_2, and graphite.[3,4,11–15] So far, to our knowledge, there is no publication on the utilization of surface segregation as a synthesis method of large scale 2D elemental post-graphene materials except one report on silicene on ZrB_2(0001) surface,[16] although the segregation method is a typical one for graphene formation, *e.g.*, graphene on Ni(111) [17] and Pt(111).[18] In a sense, the segregation method is convenient to realize 2D materials in comparison with the typical physical and chemical deposition, since it is possible to prepare them in a conventional UHV chamber without any evaporators. Therefore, it is highly expected to utilize a self-supply stamp of the 2D materials for industrial purposes if a segregated 2D material is easily transferred onto other substrates.[19]

Experimentally, the Ge/Ag(111) system initially exhibits at room temperature a Ag_2Ge surface alloy with ($\sqrt{3}\times\sqrt{3}$)R30° structure,[20–22] although first-principle calculations indicate that germanene can attach on Ag(111) *via* electrostatic interactions.[23] Few years ago, germanene growth on Ag(111) was proposed since low-energy electron diffraction (LEED) patterns showed a ($9\sqrt{3}\times9\sqrt{3}$)R30° moiré structure, which is analogous to the ($6\sqrt{3}\times6\sqrt{3}$)R30° pattern of graphene formation on SiC(0001).[11] Recently, two types of striped and quasi-freestanding phases associated with germanene on Ag(111) were reported.[24] A variety of phases come from sample preparation conditions, and, especially evaporation parameters, such as deposition rate, amount of deposition, and substrate temperature during or after deposition. Hence, it is highly desired to establish an easier way for the preparation of germanene.

In this work, we report the epitaxial growth of well-ordered, large area, germanene prepared onto Ag(111) thin films using a convenient segregation method. We examined the Ge thermal behavior and its chemical state by means of Auger electron spectroscopy (AES) and synchrotron radiation core-level spectroscopy (CLS), and identified the crystalline structure using LEED and scanning tunneling microscopy (STM).

RESULTS AND DISCUSSION

Figure 1 shows AES spectra of a silver thin film (50 nm thick) on a Ge(111) substrate after annealing at the substrate temperatures of 400 ˚C and 480 ˚C. On annealing at 400 ˚C, the Ag Auger peak is clearly seen, while the Ge, C, and O Auger signals are below detection limits. Then, a Ge Auger peak clearly appeared in addition to the Ag peak on annealing at the temperature of 480 ˚C. Therefore, germanium segregates onto the surface of Ag thin film.

The LEED patterns clearly exhibit a typical (1×1) pattern of Ag(111) on annealing at 400 ˚C (not shown). Since the (1×1) spots of the Ag(111) thin film are sharp and the positions are identical to the Ag(111) bulk crystal surface, the crystalline quality of Ag thin film is very high and the lattice constant is the same as a Ag(111) crystal surface. Therefore, it is established that a Ag(111) thin film is epitaxially grown on Ge(111) by solid-phase epitaxy (SPE). When the specimen is annealed at a higher temperature of 480 ˚C, the LEED patterns exhibit strong "(1.35×1.35)"R30° spots in addition to the primitive (1×1) spots of Ag(111), as shown in Figure 2 (a). Hence, it is determined that the segregated Ge atoms do not form the Ag_2Ge surface alloy,[25] but, instead, form an incommensurate "(1.35×1.35)"R30° superstructure with a lattice constant of 0.39 ± 0.01 nm at the rotation angle of 30°, possibly pointing to the fact that the Ge atoms form an overlayer film. Many other extra spots are recognized in the LEED patterns. Figure 2 (b)-(d) show patterns acquired at the electron primary energies of 30, 20, and 10 eV, respectively; clear spots at very low electron energies reveal a very large superstructure with

high crystalline quality. The hexagons rotated by ±R19°, drawn in Figure 2 (d), indicate that the very large superstructure has two domains. From the STM images, shown later, the surface has no secondary phase so that the "(1.35×1.35)"R30° structure and the very large superstructure have the same origin.

To study the chemical state of the germanium atoms segregated on the Ag(111) thin film in more details, we used synchrotron radiation CLS of Ge $3d$ CL's in highly surface sensitive conditions. The high-resolution Ge $3d$ spectra of germanium segregated on a Ag(111) thin film after annealing at the temperature of 480 ˚C is displayed in Fig. 3 (a). The $3d$ spectrum from the Ge(111) clean surface, measured as a reference, with full width at half maximum of about 0.8 eV and peak energy of 29.39 eV, consistent with earlier reports,[26] is shown in Fig. 3 (b). The segregated Ge atoms on Ag(111) exhibit also a rather narrow (spin-orbit splitted) line with similar FWHM but, instead, a maximum peak energy of 29.01 eV. The shift comes from the chemical environment that the segregated Ge atoms experience; it points to non tetravalent bonding, possibly to a trivalent one, indicating a 2D honeycomb structure, as will be confirmed below. The Ge $3d$ peak for the Ag_2Ge surface alloy prepared separately shows even lower binding energy of 28.6 eV (not shown), consistent with earlier report,[25] which distinguishes the Ge superstructure from such an alloy. The amount of Ge atoms segregated is calculated to correspond to an atomic layer, from the areal intensities of Ge $3d$ lines between the Ge(111) clean surface and the segregated Ge atoms on the Ag(111), not a multilayer.

Figure 4 shows the ratios (Ge $3d$)/(Ag $3d$) of the core-levels as a function of the photoelectron detection angles with consideration of the respective photo ionization cross sections.[27] If the Ge atoms were distributed in the Ag(111) thin film, the ratio should be independent of the detection angle. As the photon energy is 500 eV, the kinetic energy of the Ag $3d$ photoelectrons is about 115 eV, corresponding to an electron escape depth of roughly 0.5 nm. Therefore, if the Ge atoms are completely covering the Ag(111) surface as an overlayer,

the Ag signal contribution should be even less than 2 monolayers at normal emission, which is well consistent with the present result that the Ge/Ag ratio is 0.7. Further, at increasing detection angles from normal emission, the Ge/Ag ratio grows monotonically, thus demonstrating that the Ge atoms are located on the top surface of the Ag(111) thin film, clearly not in its bulk.

To summarize at this point, it is found that the Ag thin films are crystalline epitaxial Ag(111) thin films on low temperature annealing. Ge atoms segregate on top the Ag(111) thin film upon annealing at 480 °C, and form a 2D Ge overlayer, likely a honeycomb germanenelike structure. This structure with hexagonal lattice constant of 0.39 ± 0.01 nm and azimuthal rotation of 30° with respect to Ag(111), is shown as a ball model in Figure 5. The hexagonal lattice constant for the predicted free standing low buckled Ge honeycomb structure is calculated to be 0.397 nm.[28] Experimentally, it has been reported that the hexagonal lattice constants for the buckled Ge honeycomb structures on Au(111) and MoS_2 are both estimated to be 0.382 nm, in spite of, respectively, low and high bucklings of 0.04 nm and 0.086 nm.[4,13] With an hexagonal lattice constant of 0.39 ± 0.01 nm it can therefore be expected that some of the Ge atoms on the Ag(111) surface are likely to be buckled to refrain the local stress between them.

Figure 6a shows a wide-scaled STM image of the Ag(111) thin film on Ge(111) after annealing at the temperature of 480 ˚C, so that Ge atoms are segregated on top forming a "(1.35×1.35)"R30° structure. The terrace is very wide and flat and monoatomic steps are clearly observed. Remarkably, the local protrusions are regularly aligned over all terraces, revealing a carpet growth mode. The section profiles indicate that step heights are 0.23 ± 0.01 nm (Fig. 6b), in accordance with the monoatomic step height of Ag(111). The local protrusions are 0.05 nm higher than the rest of terrace. The step directions are mostly related to the <110> directions.

Close-up STM images clearly reveal a striking structure (Fig. 7a). Two types of protrusions, each respectively named hexagon and line, are aligned with a very large periodicity of 5.35 nm. The distance between hexagon and line is more than 1.5 nm so that there is no direct interaction

between them. However, there is perfect ordering in hexagonal arrangement of the hexagon protrusions, all with the same orientation, as well as the determined directions of the line protrusions. The length and width of a line protrusion are estimated to be 0.8 nm and 0.4 nm, respectively, while the diagonal size of the hexagon protrusion is 1.2 nm. The section profile indicates that the surface is basically very flat within 0.01 nm, but for two types of distant protrusions, namely, hexagons and lines, which are 0.05 nm higher than the rest (Fig. 7b).

Figure 8 shows a STM image at atomic-resolution of the very large superlattice. The superstructure, except for the two types of protrusions, is very flat, while honeycomb arrangements with a low buckling (0.01 nm) are clearly revealed, which points to a very low buckled germanene overlayer. The hexagon and line protrusions are now recognized as six and two individual spots, respectively, with heights 0.05 nm above the nearly flat areas forming a $(3\sqrt{21}\times3\sqrt{21})$ supercell wrt germanene, or $\begin{pmatrix} 3 & -12 \\ 15 & 3 \end{pmatrix}$ in matrix representation. The origin of the local protrusions is not obvious, but the positional relationship between the honeycomb structure and the bright spots is clearly recognized: the spots are basically located at the honeycomb centers.

The local structural model of germanene grown on Ag(111) displayed in Fig. 5 is further expanded at large scale to interpret the unique ordering of protrusions observed in the STM images. As shown in Figure 9, the local Ge honeycomb structure is developed into the $(3\sqrt{21}\times3\sqrt{21})$R10.9° germanene superstructure. This $(3\sqrt{21}\times3\sqrt{21})$R10.9° germanene superstructure matches with a Ag(111) $(7\sqrt{7}\times7\sqrt{7})$R19.1° superlattice, expressed as $\begin{pmatrix} 21 & 14 \\ 7 & 21 \end{pmatrix}$ in matrix form. The corresponding lattice constant is 5.35 nm. This is consistent with the unit cell of the very large superstructure observed in the STM images. According to this structural model, the six STM spots constituting an hexagon are related to six germanene

honeycomb structures in a circle, while the two spots making a line are related to two adjacent honeycomb structures in an oval, whose sizes are consistent with their STM images. Hence, 54 Ge atoms out of 378 are related to local protrusions in the $(3\sqrt{21}\times3\sqrt{21})$ germanene superstructure. In other words, 14 % Ge atoms in the germanene sheet are differently related to the Ag(111) substrate.

Finally, we want to emphasize the key role of the simple and repeatable synthesis of germanene by way of the segregation method using a Ag thin film on a Ge(111) substrate. Very recently, it was reported that Ge atoms deposited onto Au(111) templates form a "14×14" superstructure (with ~ 4.2 nm lattice constant) [29] upon annealing at 327 ˚C. The present results strongly suggest the possibility of germanene growth on Au(111) by the segregation method, and on other metal surfaces. This approach could be exploited for the transfer of the germanene sheet extracted from its substrate, as has been successfully realized for the fabrication of the first field effect transistors (FETs) with a single-layer silicene channel using the smartly devised process named silicene encapsulated delamination with native electrodes.[30,31]

CONCLUSIONS

We have successfully prepared germanene by a segregation method. We used a bare Ag thin film on a Ge substrate and achieved *in situ* its epitaxial growth. Auger electron spectroscopy and synchrotron radiation core-level spectroscopy further indicate that Ge atoms segregate on the Ag(111) surface at 480 °C. They are in an unsusual trivalent bonding configuration. LEED observations reveal a "1.35×1.35"R30° pattern originating from the Ge segregated structure. Wide-scale and atomic resolution STM images clearly demonstrate that a Ge honeycomb structure, namely, germanene, is grown epitaxially, forming a long-range and highly ordered superstructure in a $(7\sqrt{7}\times7\sqrt{7})$R19.1° coincidence cell wrt Ag(111). The growth of germanene,

akin to graphene and silicene, by a segregation method, is considered to be technically very important for the easy synthesis and transfer of this highly promising 2D electronic material.

METHODS

The experiments were performed using two ultrahigh-vacuum systems at Nagoya University (NU) and at the Aichi synchrotron radiation center. Each system consisted of a preparation chamber with a base pressure below 5×10^{-10} mbar, and an analysis chamber with a base pressure below 10^{-10} mbar.

Silver thin films for 50 nm in thickness were prepared on Ge(111) substrate by conventional thermal evaporation. The details of the sample preparation of Ag thin films on Ge(111) and segregation phenomena of the Ge atoms by subsequent annealing under N_2 ambient are described in earlier reports.[32–34] Clean Ag(111) crystalline surfaces were prepared by 2 keV Ar^+ ion sputtering and annealing at the temperature of 400 °C. Annealing was performed by electron bombardment of the sample holder at an emission current of 5 mA and a voltage of –650 V, and annealing is stopped after the Ar^+ ion sputtering is finished. The sample temperature was monitored with a radiation thermometer and a type K thermocouple mounted on the base plate of the sample holder. The cleanliness of the surface was measured by AES after sputtering and annealing; no contaminants, such as C and O, were observed within the detection limits, and a sharp (1×1) LEED pattern was observed. When the substrate temperatures were higher than 400 °C, AES spectra exhibited the Ge LMM peaks.

The system in NU was equipped with a rear-view LEED system operating with a LaB_6 filament and a UHV STM system (Omicron STM-1) at Nagoya University. All STM images presented were acquired at room temperature (RT) with W tips, electrochemically etched in a KOH solution, in constant current mode. All apparatuses were situated on an air damper with an active vibration isolation system (Kurashiki).

The CLS experiments were performed at the Aichi synchrotron radiation center (AichiSR). The system was equipped with a rear view MCP-LEED system and a 200 mm-radius hemispherical photoelectron analyzer (MB Scientific AB A-1) with a wide-angle electron lens. The CLS spectra were obtained at the sample temperature of 10 K. The overall resolution was better than 50 meV.

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Figure captions

Figure 1. AES spectra of an epitaxial Ag(111) thin film on Ge(111) after annealing at the substrate temperatures of (a) 400 ˚C and (b) 480 ˚C.

Figure 2. LEED patterns of an epitaxial Ag(111) thin film on Ge(111) after annealing. The incident electron energies are (a) 63 eV, (b) 30 eV, (c) 20 eV, and (d) 10 eV. The Ag(111) primitive spots (white circles) and "(1.35×1.35)"R30° spots (green circles) as well as other extra spots (blue circles) are marked in the image. Note that equivalent spots are marked identically in the series of images.

Figure 3. High-resolution synchrotron radiation Ge $3d$ core-level spectra measured at 10 K and taken at hν = 100 eV for (a) germanene prepared on a Ag(111) thin film by the segregation method and (b) a clean Ge(111) surface.

Figure 4. Core-levels intensity ratios (Ge $3d$)/(Ag $3d$) corrected for photoemission cross sections, as a function of the detection angles of the photoelectrons.

Figure 5. Structural model (top view) of a germanene overlayer on Ag(111) forming a "(1.35×1.35)"R30° unit cell. Green balls: Ge atoms ; grey balls Ag atoms.

Figure 6. (a) Large-scale STM image of a germanene overlayer grown as a carpet by segregation on an epitaxial Ag(111) thin film on a Ge(111) substrate. The image is recorded in a constant current mode with tunneling current of 200 pA and sample bias voltage of +0.3 V. A line profile in (b) gives a step height of 0.23 ± 0.01 nm, reflecting a Ag(111) monoatomic step.

Figure 7. (a) Close-up STM image of germanene epitaxially grown on a Ag(111) thin film by the segregation method. The image is recorded in a constant current mode with tunneling current of 200 pA and sample bias voltage of +0.3 V. The unit cell of the germanene overlayer forming a (7√7×7√7)R19.1° superstructure wrt Ag(111) is indicated by the lozenge. Line profiles along and next to the hexagon-line protrusions are displayed in (b) and (c), respectively.

Figure 8. Atomic scale STM image of germanene epitaxially grown on Ag(111) thin film by segregation method. The image is recorded in a constant current mode with tunneling current of 200 pA and sample bias voltage of +0.3 V. The unit cell of "(1.35×1.35)"R30° is indicated by the rectangle.

Figure 9. Structural model of germanene on Ag(111), locally keeping a germanene unit cell of (1.347×1.347)R30°. The germanene superstructure of $(3\sqrt{21}×3\sqrt{21})$ R10.9° is on Ag(111) $(7\sqrt{7}×7\sqrt{7})$R19.1°, indicated by the lozenge. The areal positions corresponding to the hexagon and line protrusions are marked in solid yellow line.

Fig. 1 J. Yuhara et al.

(a) Ag(111)(1 × 1)

"1.35 × 1.35"R30°

(b)

(c)

(d) ± 19°

Fig. 2 J. Yuhara et al.

Fig. 3 J. Yuhara et al.

$h\nu = 500$ eV

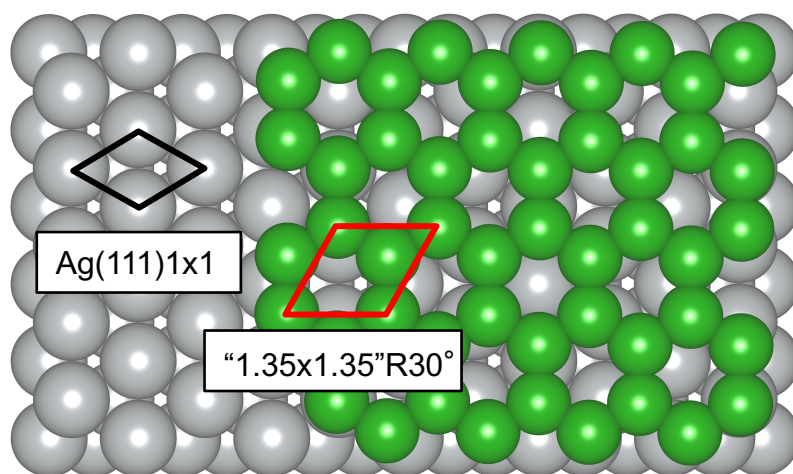Fig. 4 J. Yuhara et al.

Ag(111)1x1
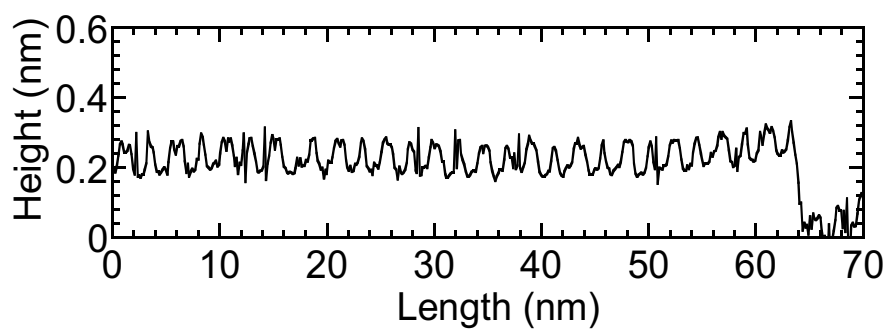
"1.35x1.35"R30˚

Fig. 5 J. Yuhara et al.

10 nm

Fig. 6 J. Yuhara et al.
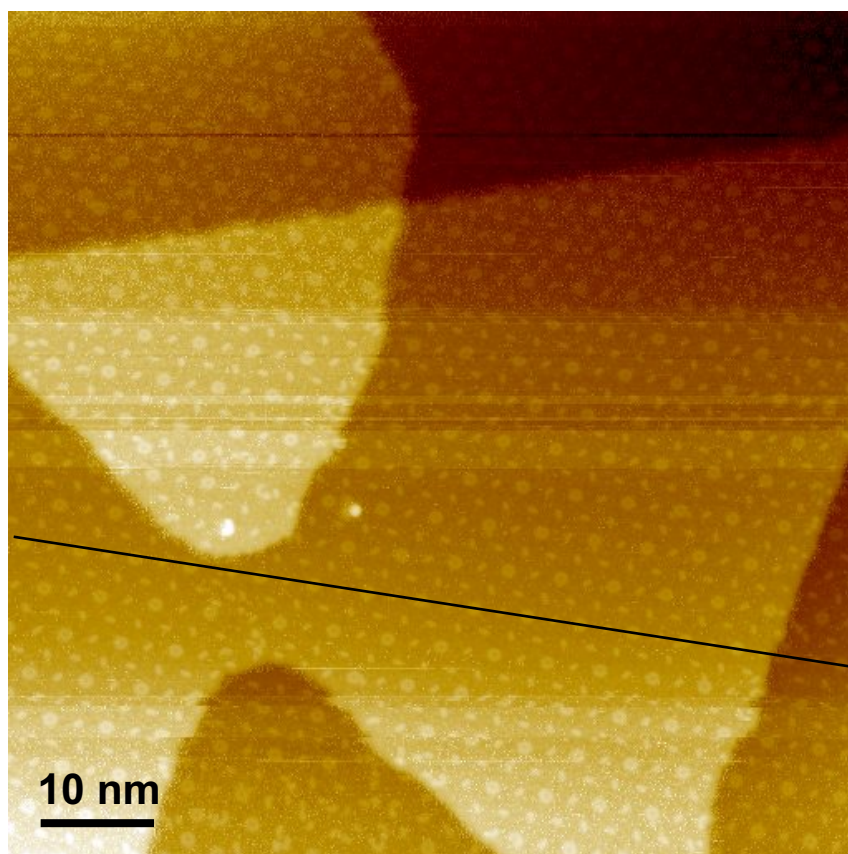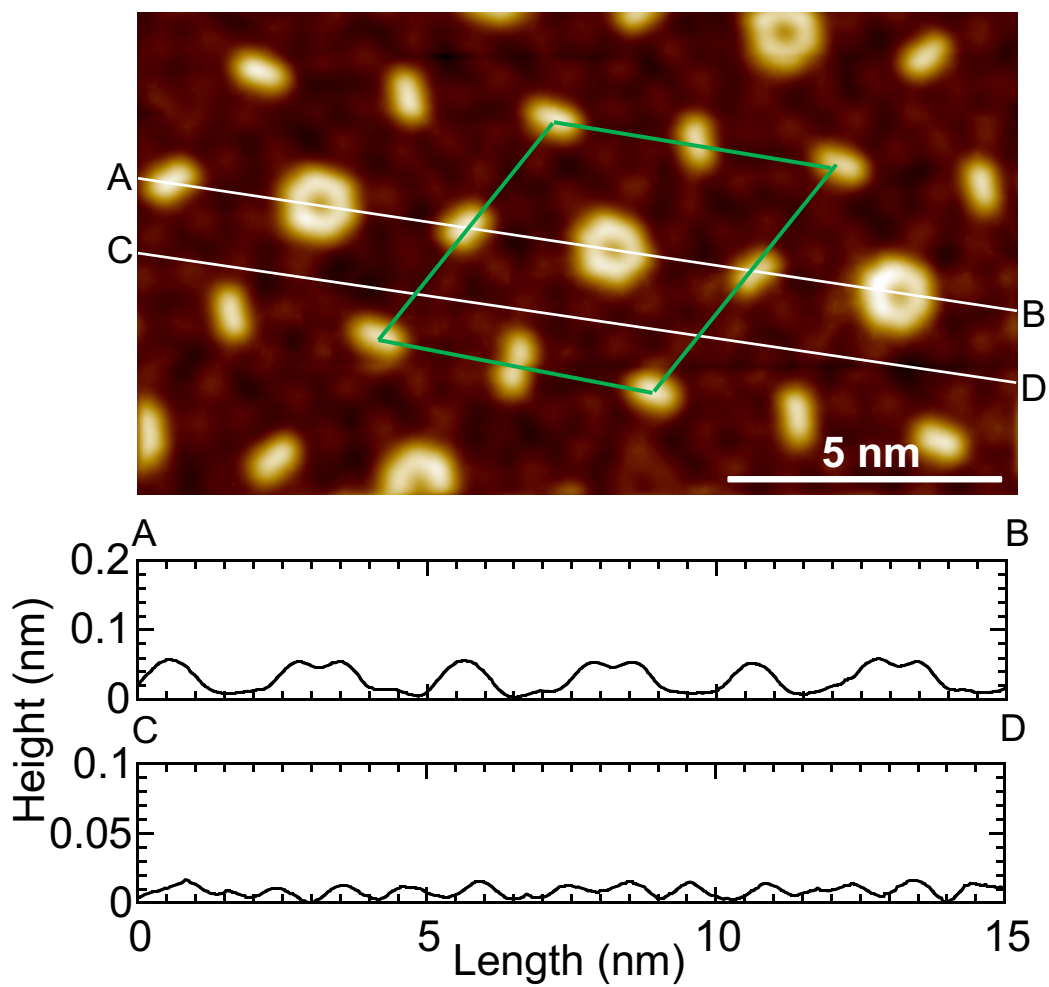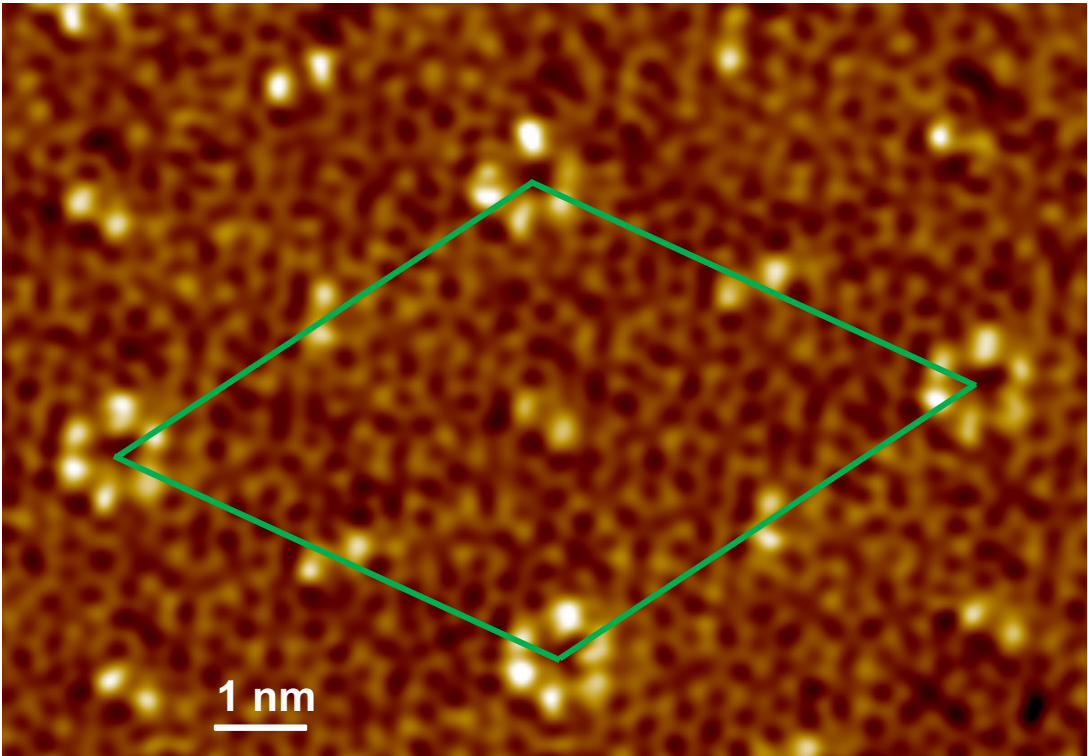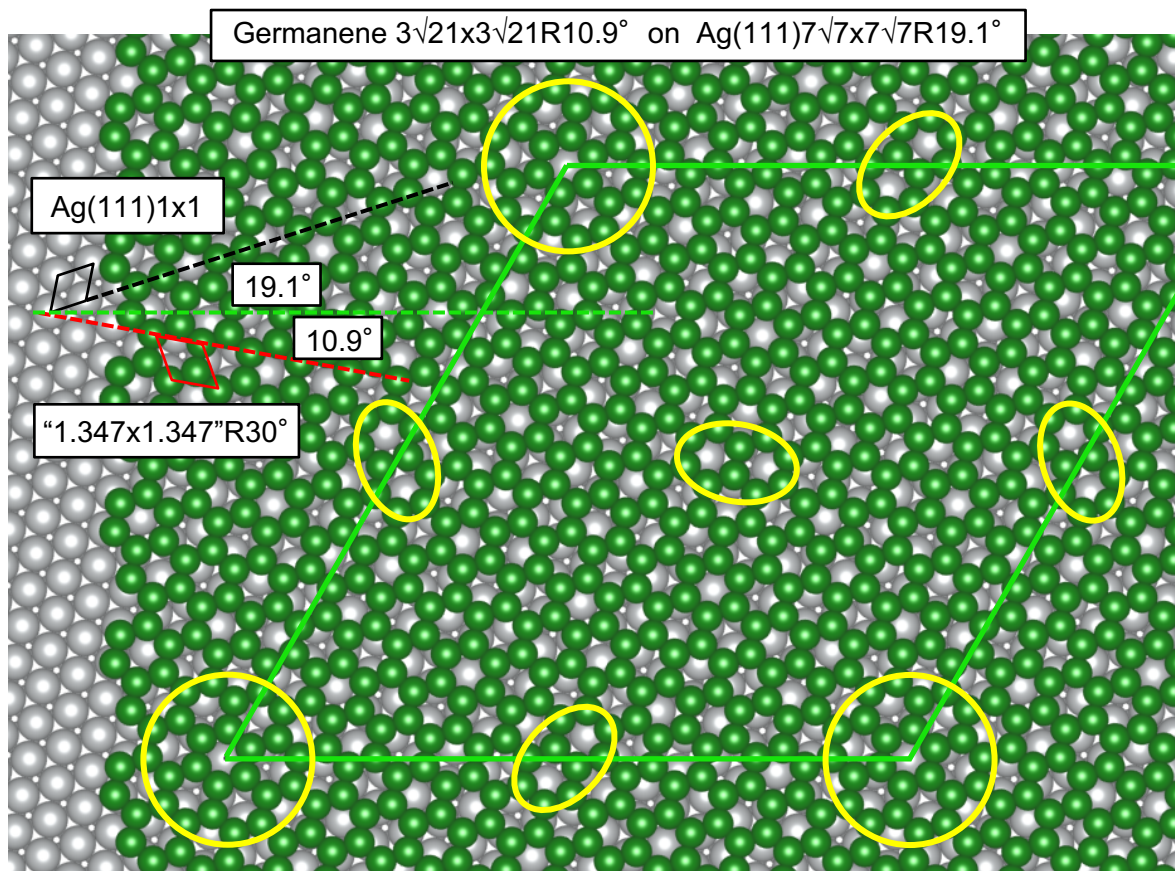
Fig. 7 J. Yuhara et al.

1 nm

Fig. 8 J. Yuhara et al.

Germanene 3√21x3√21R10.9° on Ag(111)7√7x7√7R19.1°

Ag(111)1x1

19.1°

10.9°

"1.347x1.347"R30°

Fig. 9 J. Yuhara et al.