Ordered 2D Structure Formed upon the Molecular Beam Epitaxy Growth of Ge on the Silicene/Ag(111) Surface

Han-De Chen and Deng-Sung Lin*

Department of Physics, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu 30013, Taiwan

ABSTRACT: Growth of Ge by molecular beam epitaxy (MBE) on top of the silicene monolayer on the Ag(111) surface results in either a dispersed adlayer or a two-dimensional (2D) ordered structure depending on the silicene phase. Scanning tunneling microscopy (STM) images show that the ordered adsorbed Ge atoms on (3 × 3)\textsubscript{silicene} domains occupy a position directly on top of down atoms in the buckled silicene layer, similar to the adatom positions on the Ge(111)-c(2 × 8) surface. By contrast, no long-range ordering of Ge adatoms is observed on the (√7 × √7)\textsubscript{Si}R19.1° domain, possibly partly because of the interference effects of the Ag substrate. Results herein suggest that the deposited Ge atoms tend to build an additional three-dimensional bulk layer on the silicene monolayer and that the growth of the 2D germanene/silicene heterostructure may not be achieved in a straightforward manner.

I. INTRODUCTION

The rich electronic features of graphene and its possible novel applications have led to the extensive search for an equivalent of graphene for silicon and germanium, that is, silicene and germanene.\textsuperscript{1-8} Germanene, silicene, and graphene share several peculiar and interesting electronic properties. The electrons near the K and K' points of the Brillouin zone behave as relativistic massless particles known as Dirac fermions. Certainly, some differences exist between these 2D allotropes of the group IV elements. For example, the honeycomb lattice of graphene is fully planar, whereas the honeycomb lattices of freestanding germanene and silicene are buckled.\textsuperscript{2,9} Additionally, because of the larger atomic number of germanium and silicon as compared with that of carbon and the buckling structure, germanene and silicene have a much stronger spin–orbit coupling and consequently lead to the opening of a small band gap of 1.55 and 23.9 meV at the Dirac points, respectively.\textsuperscript{10} As a result, only silicene and germanene can practically exhibit the quantum spin Hall state.

Experimentally, silicene has been synthesized and observed on various substrates including Ag(111),\textsuperscript{7,11-16} ZrB\textsubscript{2}(0001),\textsuperscript{17} Al(111),\textsuperscript{18} and Ir(111).\textsuperscript{19} Because of a strong interaction with the substrate, the silicene monolayer is strongly modulated into a structure that is more complex than that of the simple flat honeycomb organization. Examples of experimentally observed structures on the most widely studied substrate Ag(111) include (3 × 3)\textsubscript{silicene}, (√7 × √7)\textsubscript{Si}R19.1°, (4 × 4)\textsubscript{Ag}, (√13 × √13)\textsubscript{Ag}R13.9°, (3.5 × 3.5)\textsubscript{Ag}, and (2√3 × 2√3)\textsubscript{Ag}R30°.\textsuperscript{12,16,20-22} The subscript “Ag” refers to the Ag(111) surface lattice vectors; the subscript “Si” indicates a possibly incommensurate silicene structure with respect to that of Ag(111); and the Wood’s notation refers to the silicene lattice vectors. Similarly, germanene has been synthesized on several metallic substrates and MoS\textsubscript{2}.\textsuperscript{23} Li et al. reported the growth of germanene on Pt(111) by germanium MBE at room temperature (RT) followed by a 30 min annealing at 600–750 K.\textsuperscript{24} Using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM), they found a (√19 × √19)\textsubscript{Pt}R23.4° (√19\textsubscript{Pt} for short) periodicity with respect to the Pt(111) lattice. A density functional theory (DFT) calculation revealed that a (√19\textsubscript{Pt}) unit cell of a buckled germanene 2D layer is commensurate with a (3 × 3)\textsubscript{Ge} cell with respect to germanene unit vectors,\textsuperscript{25} whereas Sumiya et al. suggested that the (√19\textsubscript{Pt}) reconstruction on Pt(111) is actually a surface alloy composed of Ge3Pt tetramers.\textsuperscript{25} Davila et al. have grown 1.0 ML germanene on Au(111) at 200 °C and identified three different phases using LEED: a (√19 × √19)\textsubscript{Au}R23.4° phase, a (3 × 3)\textsubscript{Au} phase, and a (√7 × √7)\textsubscript{Au}R19.1° (√7\textsubscript{Au} for short) phase.\textsuperscript{26} On the basis of STM observations and DFT calculations, the authors attributed the (√7\textsubscript{Au}) phase as a (3√3 × 3√3)\textsubscript{Au}R30° germanene layer commensurate with a (√7\textsubscript{Au}) super cell. Bampoulis et al. studied the growth of Pt on a Ge(110) substrate.\textsuperscript{27} The deposition of a few monolayers of Pt on Ge(110) followed by annealing at temperatures around 1100 K led to the formation of three-dimensional (3D) nanocrystals on the Ge(110) substrate. The surface of the 3D crystals had a buckled honeycomb structure, which was suggested to be germanene. On the Al(111) surface, Deviraz et al. found a (3 × 3) phase with respect to the Al(111) lattice vector ((3 × 3)\textsubscript{Al}).\textsuperscript{21} Using DFT calculations, a buckled (2 × 2) germanene unit cell ((2 × 2)\textsubscript{Ge}) is shown to overlay on a (3 × 3)\textsubscript{Al} unit cell.

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Formation of multilayer silicene, the silicon analogue of graphene, upon increasing the Si coverage beyond a full layer has been explored for Si growth on the Ag(111) surface. The structure observed is a honeycomb-like ($\sqrt{3} \times \sqrt{3}$)$_{\text{Ag}}$R30° ($\sqrt{3}_\text{Si}$ for short) structure. 28–31 However, several studies have revealed that the so-called multilayer silicene on Ag(111) is actually a thin film of bulklike silicon and that the $\sqrt{3}_\text{Si}$ surface is chemically the same as that on Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°. 32–37 Similar efforts have been made for the synthesis of few-layer germanene. For example, Dávila et al. performed the MBE growth of Ge on Au(111) at ~200°C and found that a ($3\sqrt{3} \times 3\sqrt{3}$) reconstructed germanene cell coincides with an ($8 \times 8$) supercell of Au(111). 26

Recently, the rapid advance of the research on 2D materials has led to the fabrication and device applications of various vertical and horizontal heterostructures based on these atomically thin crystals. Tunneling diodes with negative differential resistance, tunneling transistors, photovoltaic devices, and so on have been demonstrated to be operational. 38–40 Also, the strain and the breaking of sublattice symmetry between the heterostructures of silicene, germanene, and graphene often enlarge the energy band gap by tens of meV, 4 which can help the realization of quantum spin Hall effects at RT. This study initiates an attempt to grow vertical heterostructures of silicene and germanene. We have performed Ge growth by MBE on top of the silicene monolayer on the Ag(111) surface and found that, on the ($3 \times 3$)$_{\text{Si}}$ silicene domains, Ge adatoms coalesce into a 2D ordered overlayer with the same ($3 \times 3$)$_{\text{Si}}$ superstructure. In contrast, no long-range ordering of Ge adatoms is observed on the ($\sqrt{7} \times \sqrt{7}$)$_{\text{Ag}}$R19.1° domains. The atomic model of the observed features suggests that the bonding sites of Ge adatoms are similar to those observed on the Si(111)-($7 \times 7$) surface. No germanene is formed under the explored growth conditions.

II. EXPERIMENTAL DETAILS

The STM experiments were conducted in an ultrahigh vacuum (UHV) chamber, with a base pressure of $2 \times 10^{-10}$ Torr. The Ag(111) substrate, with a surface area of $16 \times 3$ mm$^2$, was cleaned by several cycles of Ar$^+$ sputtering (1.0 keV and 1×10$^{-5}$ Torr) and subsequent annealing by electron beam bombardment at 500 °C for 20 min. Temperature calibration of the sample above RT was performed by bringing a tiny type-K thermocouple into contact with the sample. Below RT, a type-T thermocouple was used. The error in temperature measurements was estimated to be within ±10 °C. Silicon was deposited in situ at a rate of ~0.05 ML per min by passing a direct current through a piece of Si wafer located about 10 cm away from the Ag(111) substrate maintained at 250 °C, which is much lower than the typical homoepitaxial growth temperature for Si. The coverage of Si is specified in terms of the site density of the Ag(111)-($1 \times 1$) surface: 1 ML = $1.38 \times 10^{15}$ cm$^{-2}$. Ge atomic vapor is generated from an e-beam-heated crucible. The sample LT-STM measurement was carried out at 77 K in a constant-current mode.

III. RESULTS AND DISCUSSION

The STM images taken after the deposition of nominal 0.8 ML Si at a substrate temperature of ~190 °C show that the surface is largely covered by a silicene monolayer with the ($\sqrt{7} \times \sqrt{7}$)$_{\text{Ag}}$R19.1° ($\sqrt{7}_\text{Si}$ for short) structure (~80% of surface area), the ($3 \times 3$)$_{\text{Si}}$ structure (~15%), and other minor structures (a few percentage). Both ($3 \times 3$)$_{\text{Si}}$ and $\sqrt{7}_\text{Si}$ phases consist of a complete silicene lattice with different ordering in the buckling of Si atoms. 30,41 Figure 1a depicts a surface area of the Ag(111) surface after 0.8 ML Si MBE. The STM images taken after the deposition of nominal 0.8 ML Si MBE $V_\text{s} = -1.50$ V; $I_\text{t} = 1.0$ nA; regions labeled ($3 \times 3$)$_{\text{Si}}$ and $\sqrt{7}_\text{Si}$ are surface areas with the ($3 \times 3$)$_{\text{Si}}$ and ($\sqrt{7} \times \sqrt{7}$)$_{\text{Ag}}$R19.1° structures, respectively. Size: 30×30 nm$^2$ (left and right insets) 4.5×4.5 nm$^2$ zoomed-in images for the corresponding surface areas with the ($3 \times 3$)$_{\text{Si}}$ and $\sqrt{7}_\text{Si}$ structures as labeled. (b) Fourier transform of the image on (a). The white solid arrows and yellow dashed ones point to first-order diffraction spots corresponding to the unit cell vectors in the insets of (a).

Figure 1. (a) STM image of the Ag(111) surface after 0.8 ML Si MBE $V_\text{s} = -1.50$ V; $I_\text{t} = 1.0$ nA; regions labeled ($3 \times 3$)$_{\text{Si}}$ and $\sqrt{7}_\text{Si}$ are surface areas with the ($3 \times 3$)$_{\text{Si}}$ and ($\sqrt{7} \times \sqrt{7}$)$_{\text{Ag}}$R19.1° structures, respectively. Size: 30×30 nm$^2$ (left and right insets) 4.5×4.5 nm$^2$ zoomed-in images for the corresponding surface areas with the ($3 \times 3$)$_{\text{Si}}$ and $\sqrt{7}_\text{Si}$ structures as labeled. (b) Fourier transform of the image on (a). The white solid arrows and yellow dashed ones point to first-order diffraction spots corresponding to the unit cell vectors in the insets of (a).
calibration shows that the sample temperature increases after the sample transport changes from about $-100$ to $-7$, $-1$, and $5 \, ^\circ \text{C}$, respectively, for a deposition time of 20, 30, and 40 min. STM images taken after 30 min of Ge deposition (Figure 2a)

Figure 2. STM images of the surface shown in Figure 1 after a (a) 30 min, (b) 60 min, (c) 120 min deposition of Ge. $V_s = -1.50 \, \text{V}; I_t = 1.0 \, \text{nA}$; size: (a) $60 \times 60 \, \text{nm}^2$ and (b,c) $60 \times 30 \, \text{nm}^2$. Regions labeled $\sqrt{3} \, \text{Si}$ are surface areas with the $(\sqrt{3} \times \sqrt{3})_\text{R30}^\circ$ structure. Typical heights for the 3D Ge clusters (i.e. bright protrusions in (b) and (c)) are between $\sim 0.25$ and $\sim 0.45 \, \text{nm}$ and roughly proportional to their lateral size.

show that Ge atoms form patches of ordered 2D islands on the $(3 \times 3)\text{Si}$ areas, but not on the $\sqrt{7} \, \text{Si}$ areas. On the $\sqrt{3} \, \text{Si}$ areas, Ge atoms cluster into 3D islands around the edges. The formation of 2D Ge overlayer on the Si film suggests that the Ge adatoms upon adsorption are mobile well below RT. As shown in Figure 2b, the areas of the ordered 2D islands on the $(3 \times 3)\text{Si}$ areas increase initially with the coverage. However, as shown in Figure 2c, further additions of Ge do not cover the entire surface but cluster into 3D islands and even patches of the $(3 \times 3)\text{Si}$ areas are still available for adsorption. Because the sample temperature increases to near RT at a later part of the 120 min deposition process, the 3D island formation can also be due in part to the enhanced mobility of Ge adatoms at around RT.

Figure 3a,b shows the zoomed-in images on the $(3 \times 3)\text{Si}$ and $\sqrt{7} \, \text{Si}$ areas, respectively. In Figure 3a, patches of ordered adsorbates are clearly seen on the upper right corner. The white rhombus mesh outlines the $(3 \times 3)\text{Si}$ lattice net. In each unit cell, a protrusion labeled $V_s$ can be located on one side of the half-unit cell (HUC), indicating that the overlayer has the same $(3 \times 3)\text{Si}$ structure as that of the silicene monolayer underneath.

Figure 3. $14.0 \times 10.0 \, \text{nm}^2$ zoomed-in images on the (a) $(3 \times 3)\text{Si}$ and (b) $\sqrt{7} \, \text{Si}$ areas, areas of same surface shown in Figure 2a. The protrusions labeled $V_s$, $V_C$, and $H'$ are Ge adsorption sites. The white rhombus mesh is a guide for eyes for the unit cells. $V_s = -1.50 \, \text{V}; I_t = 1.0 \, \text{nA}$ (c) Z-height profile along the solid line in (a).

Some protrusions (labeled $V_C$, $H'$, showing reddish rings in Figure 3a) occupy different positions in a $(3 \times 3)\text{Si}$ cell and have larger apparent heights by about $0.6 \, \text{Å}$ than that of most protrusions $V_s$ in the periodic lattice as shown in Figure 3c. All filled-state and empty-state images taken at bias voltages between $0.50$ and $1.50 \, \text{V}$ exhibit similar features and the apparent height of adsorbates. The $V_C$ and $H'$ protrusions are typically more isolated from other adsorbates. These observations indicate that the $V_C$ and $H'$ adsorbates have configurations different from that of $V_s$ and that adsorbate–adsorbate interactions play a role in the formation of the ordered structure and in the bonding configurations of adsorbates. By contrast, each of Ge adsorbates in the $\sqrt{7} \, \text{Si}$ domain, as shown in Figure 3b, occupies a slightly different position in each HUC. It is likely that the interference effects between the substrate and the silicene lattice lead not only to the moiré-pattern-like superstructure but also to the adsorption configurations of Ge adatoms.

To elucidate the atomic configuration of Ge adsorbates, a comparison of the atomic model and atomic-resolved images is needed. Figure 4a shows that the $(3 \times 3)\text{Si}$ phase has a characteristic hexagonal arrangement of triangular structures around dark centers. Each unit cell consists of two equilateral triangular HUCs, and each HUC consists of three protrusions.
coordination site G, which is near the midway between H and a hexagonal ring atom, has the lowest energy for Ge adsorption on Si(111)-(7×7) and that the T₄ site has the second lowest one.⁴⁶ By comparing the relative positions of the protrusions in Figure 3a, it can be established that the adsorption sites in the ordered (3×3)₆ areas are regular arrays of the V₅ site and many dispersed (reddish) adsorbates occupy the sites H’, which is also a high-coordination site like a G site in Si(111). In other words, the bonding configurations of adsorbed Ge atoms on the (3×3)₆ areas of the silicene monolayer near RT is similar to that found for Si(111)-(7×7). Apparently, the Ge adatom density on the (3×3)₆ areas is quite low, with only one atom per (3×3)₆ unit cell. The difference in Ge adsorption configurations (a H’ site for an isolated Ge adatom and V₅ sites for ordered arrays of Ge adatoms) and the low adatom density indicate that substantial adsorbate—adsorbate interactions exist, likely with the modifications of silicene monolayer upon adsorption.

IV. CONCLUSIONS

In summary, we have studied the MBE growth of Ge on the silicene monolayer on the Ag(111) surface below RT. High-resolution LT-STM images reveal the detailed adsorption configurations and very different degrees of ordering on the two complete monolayer silicene phases: (3×3)₆ and (√7×√7)₁₄R19.1°. On the (3×3)₆ silicene domains, 2D ordered overlayer with the same superstructure is formed below a surface coverage of ∼40%. STM images show that each of the ordered adsorbed Ge atoms occupies a valley site, which is directly above the down-atoms in the buckled silicene layer, similar to the adatom positions on the Ge(111)-c(2×8) surface. The atomic ratio of Ge and Si on this ordering phase is very low, only 1/18, suggesting a strong adsorbate—adsorbate interaction. On the (√7×√7)₁₄R19.1° phase, no apparent ordering of Ge adsorbates is observed, possibly partly because of the interference effects between the silicene layer and the Ag substrate. These observations suggest that the adsorbed Ge adatoms tend to build a 3D bulk layer on silicene. These results indicate that novel approaches are needed to realize 2D germanene/silicene heterostructures.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dslin@phys.nthu.edu.tw.

Notes

The authors declare no competing financial interest.

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