Direct Growth of Germanene at Interfaces between Van der Waals Materials and Ag(111)

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Germanene, a 2D honeycomb germanium crystal, is grown at graphene/Ag(111) and hexagonal boron nitride (h-BN)/Ag(111) interfaces by segregating germanium atoms. A simple annealing process in N\(_2\) or H\(_2\)/Ar at ambient pressure leads to the formation of germanene, indicating that an ultrahigh-vacuum condition is not necessary. The grown germanene is stable in air and uniform over the entire area covered with a van der Waals (vdW) material. As an important finding, it is necessary to use a vdW material as a cap layer for the present germanene growth method since the use of an Al\(_2\)O\(_3\) cap layer results in no germanene formation. The present study also proves that Raman spectroscopy in air is a powerful tool for characterizing germanene at the interfaces, which is concluded by multiple analyses including first-principles density functional theory calculations. The direct growth of h-BN-capped germanene on Ag(111), which is demonstrated in the present study, is considered to be a promising technique for the fabrication of future germanene-based electronic devices.

1. Introduction

Two-dimensional honeycomb lattices of group IV (group 14) elements, such as silicene,\(^1\) germanene,\(^{1c,2}\) stanene,\(^3\) and plumbene,\(^4\) are known as Xenes.\(^5\) On the basis of theoretical predictions, Xenes have electronic properties similar to those of graphene such as a Dirac cone with linear band dispersion, leading to an extremely high carrier mobility.\(^6\) In contrast to graphene, the crystal structure of Xenes has been suggested to be not flat but buckled. Xenes are particularly fascinating materials because of their intrinsically large spin-orbit coupling. The spin-orbit gaps of Xenes are substantially larger (≈0.7 meV for silicene,\(^7\) ≈24 meV for germanene,\(^7,8\) ≈0.3 eV for stanene,\(^7,9\) and ≈0.7 eV for plumbene\(^9\)), while that of graphene is much smaller (25–50 μeV).\(^7,8,10\) In addition, the bandgaps of Xenes can be controlled by applying an electric field owing to their buckled honeycomb lattice.\(^6a\) With increasing electric field, the spin-orbit gap closes to zero first corresponding to the transition from a topological insulator to a semimetal and opens again corresponding to the transition from a semimetal to a normal band insulator.\(^6d,8\) These transitions occur as the result of charge transfer from one sublattice to the other in buckled Xenes by the electric field. Such bandgap controllability would provide a way to overcome the problem of gapless graphene for future electronic device applications. Thus, the utilization of Xenes in electronics is highly desirable.

Xenes have been grown on various crystal surfaces. Germanene has been grown on Ag(111),\(^1\) Au(111),\(^1,2,12\) Cu(111),\(^1,13\) Al(111),\(^14\) Pt(111),\(^15\) graphite,\(^16\) and MoS\(_2\);\(^17\) and silicene has been grown on Ag(111),\(^1b,1b\) Ag(110),\(^18\) Al(111),\(^19\) Ir(111),\(^20\) ZrB\(_2\)(0001),\(^21\) and ZrC(111).\(^22\) A limited number of reports of stanene growth on Ag(111)\(^3\) and Cu(111),\(^3\) as well as one report of plumbene growth on a Pd\(_x\)Pb\(_{1-x}\)(111) alloy film on Pd(111),\(^4\) are available. Although the growth of Xenes has been widely reported, Xenes-based electronic devices have not been reported, except for silicene\(^21\) and hydrogenated germanane (germanene)\(^24\) based field-effect transistors (FETs). One of the reasons for this is the chemical instability of Xenes, in contrast to the stability of graphene.\(^25\) Although high-quality Xenes can be grown in ultrahigh vacuum (UHV), they are expected to be immediately oxidized when removed from the UHV chamber.\(^26\) Hence, for the realization of Xenes-based applications, we have to overcome this problem.

As one approach, we conceived the direct growth of Xenes at interfaces. The oxidation of an Xene should be prevented...
by placing it at an interface that provides a spatial separation between Xenes and oxidizing substances in air. A material with excellent gas barrier properties is required to form such an interface. In this paper, we report a novel method of growing germanene at interfaces between van der Waals (vdW) materials and Ag(111). Since vdW materials, such as graphene and hexagonal boron nitride (h-BN), have excellent gas barrier properties,[27] they were used as a cap layer to form an interface for germanene growth. The proposed method of growing germanene is schematically drawn in Figure 1. First, graphene or h-BN was transferred onto an Ag(111) thin film formed on Ge(111). To induce Ge segregation at the vdW material/Ag(111) interface, the sample was annealed in N2 or H2/Ar (H2 concentration ≈ 3%) ambient at atmospheric pressure. To characterize the germanene at the interface, Raman spectroscopy in air and first-principles density functional theory (DFT) and density functional perturbation theory (DFPT) calculations were performed, and the two Raman peaks observed at ≈155 and ≈255 cm–1 were assigned as out-of-plane and in-plane vibration modes of germanene, respectively. As a result, it was revealed that germanene was grown uniformly under the vdW material and was stable in air as expected. One of our key findings is that the germanene growth method requires a vdW material as a cap layer since the use of an Al2O3 cap layer resulted in the absence of germanene formation. To the best of our knowledge, this is the first report of the growth of an Xene at ambient pressure, which is beneficial from the viewpoint of reducing the cost of mass-producing future electronic devices based on germanene, as an alternative to conventional UHV growth.

2. Results and Discussion

Figure 2 shows Raman spectra of graphene/Ag(111)/Ge(111) after annealing at room temperature (RT), 550, and 700 °C, and the Raman spectrum of Ag(111)/Ge(111) without top graphene after annealing at 550 °C. The top graphene was placed on the Ag surface by the wet transfer of chemical vapor deposition (CVD) graphene. It was found that two new peaks appeared around 155 and 255 cm–1 after heating at 550 °C (Figure 2b) as well as after heating at 450, 500, and 600 °C (Figure S1, Supporting Information). The two peaks did not appear in the case without the top graphene (Figure 2c). On the other hand, a sharp peak at 300 cm–1, which corresponds to the Ge–Ge vibration mode of bulk Ge, was observed in the sample heated to 700 °C (Figure 2d). This was caused by the surface exposure of Ge(111) due to the disappearance of the Ag layer.[28] The disappearance of the Ag layer was due to its phase transition to a liquid and, as a result, most of the Ag diffused into the bulk Ge. This is reasonable because 700 °C is sufficiently higher than the eutectic melting point of the Ag-Ge system (~650 °C).[29] Note that the Raman peaks observed around 155 and 255 cm–1 are different from the Ge–Ge vibration mode observed in bulk Ge.

The graphene/Ag(111)/Ge(111) sample annealed at 550 °C with two new Raman peaks was characterized by angle-resolved X-ray photoelectron spectroscopy (XPS) to reveal the distribution of elements in the vicinity of its surface. Figure 3a shows the XPS spectrum obtained at a photoelectron detection angle of 45°. Carbon, sulfur, oxygen, germanium, and silver were detected. Figure 3b shows the atomic concentration of each element as a function of the photoelectron detection angle. The concentrations of carbon, sulfur, and oxygen increased and that of silver decreased with increasing detection angle.

Figure 1. Illustration of germanene growth at vdW material/Ag(111) interface and its characterization by Raman spectroscopy in air.

Figure 2. Raman spectra of graphene(G)/Ag(111)/Ge(111) after annealing at a) RT, b) 550, and d) 700 °C, and c) Raman spectrum of Ag(111)/Ge(111) without graphene after annealing at 550 °C. The top graphene was placed onto the Ag surface by the wet transfer of CVD graphene. The inset shows the areas where the spectra were obtained.
maximum concentration of Ge was observed at 45°. Since XPS with a larger detection angle is more sensitive to the surface, the mountain-like behavior of the Ge atomic concentration graph (Figure 3b) indicates that Ge atoms were located at the interface between graphene and Ag(111). The detected sulfur was thought to be mainly derived from impurities adsorbed on the Ag surface before the transfer of graphene. Figure 3c shows the Ge 3d peak obtained at 45° with high energy resolution. Elemental Ge is the main component (29.6 eV) and the minor peak originates from oxides of Ge (32.6 eV). This oxide formation may have been due to oxidation in the region uncovered with graphene (where bare Ge surface was exposed) and the diffusion of oxygen from graphene edges or defects. These results suggest that a crystal composed of elemental Ge that exhibits the newly observed Raman peaks can exist at the interface between graphene and Ag(111).

To assign the new Raman peaks at 155 and 255 cm⁻¹ (Figure 2d), first-principles DFPT calculations were performed. We only focused on monolayer germanene since cross-sectional scanning transmission electron microscopy (STEM) observation indicated that the segregated Ge at the interface is likely to be monolayer not multilayer (Figure S2, Supporting Information). Figure 4a,b shows the calculated phonon dispersions of bulk Ge and freestanding germanene, respectively, and Figure 4c shows an illustration of the Raman active vibration modes in germanene obtained by vibration analysis. Raman active phonons are basically located at the gamma point, except in special Raman processes such as double resonance Raman scattering in graphene.[30] Thus, bulk Ge and germanene have one and two Raman active phonons, respectively, which has also been reported elsewhere.[31] This feature explains the experimental Raman spectra in Figure 2. Bulk Ge has only one peak at 300 cm⁻¹ (Figure 2d), while germanene has two peaks at 155 and 255 cm⁻¹ for out-of-plane and in-plane vibration modes, respectively.

The experimentally observed phonon for the in-plane mode of germanene was ≈45 cm⁻¹ lower than that of bulk Ge. It seems that the experimentally observed germanene peaks are redshifted from the freestanding germanene peaks since the calculated phonon energies of bulk Ge and the in-plane mode in freestanding germanene are almost the same (Figure 4a,b). The energy shift of the phonon is caused by the change in bond length, which is generally induced by strain and charge transfer to the lattice. In the present case, rather than the top graphene, Ag(111) is considered to contribute to phonon energy shifts since the naked Ag(111) surface is chemically reactive.

To consider the redshift, we first examined the effect of strain on freestanding germanene. Figure 4d shows the phonon energies of the in-plane and out-of-plane modes and the Ge–Ge bond length in freestanding germanene as a function of in-plane biaxial strain. It is clear that tensile strain reduces the phonon energies for both modes and increases the Ge–Ge bond length. Subsequently, we calculated a possible lattice structure of germanene on an Ag(111) (7×7) surface. The DFT calculations yield buckled hexagonal germanene on an Ag(111) (7×7) surface as shown in the top and side views in Figure 4e,f, respectively. By extracting the coordinates of Ge atoms, the average Ge–Ge bond length was obtained as ≈2.49 Å, which corresponds to slightly tensile freestanding germanene (~3%). Since the corresponding phonon energies are ≈165 and ≈260 cm⁻¹ for the out-of-plane and in-plane modes, respectively, the strain induced by the Ag(111) surface is mainly responsible for the redshift. Although we cannot yet give a complete quantitative discussion, the above explanation may provide helpful ideas for explaining the observed Raman peaks of germanene at the graphene/Ag(111) interface.

To double-check that the observed Raman peaks were really derived from germanene, we grew germanene in a UHV chamber using the well-known surface segregation method reported by Yuhara et al.[32] The phonon energies of germanene were measured by in situ high-resolution electron energy-loss spectroscopy (HREELS) and ex situ Raman spectroscopy as illustrated in Figure 5a. First, Ge was cleaned by Kr⁺ sputtering and annealing at 700 °C, resulting in a c(2 × 8) reconstructed surface.[32] Ag was deposited at RT on the cleaned Ge by vacuum evaporation to form an Ag(111) epitaxial layer.
Germanene surface segregation was induced by heating at 450 °C for 10 min. The HREELS of germanene was performed in UHV to exclude the effects of impurities, such as oxygen, sulfur, and carbon. Subsequently, an amorphous boron (a-B) thin film was deposited at RT to protect the germanene from oxidation in air. Noted that the a-B deposition is our original idea, which has not been included in ref. [12]. The thickness of the a-B film was estimated to be about 2 nm from the signal decay of Ag and Ge observed by Auger electron spectroscopy (AES) upon a-B deposition. After that, the sample was removed...

Figure 5. In situ growth of germanene. a) Illustration of experimental procedure. b) AES spectrum of germanene on Ag(111). RHEED patterns of c) Ag(111) and d) germanene/Ag(111) surface. Streaks with arrows correspond to germanene. The azimuth of the incident e-beam is [112]. e) Raman spectrum of boron-coated germanene on Ag(111) recorded in air. f) Off specular HREEL spectrum of germanene on Ag(111). Black (B) and red (G) dotted lines show the phonon energies of germanene at the graphene/Ag(111) and boron/Ag(111) interfaces, respectively, which were obtained by Raman spectroscopy.
from the UHV chamber and examined by Raman spectroscopy in air. The Raman spectra were recorded within 3 h of removing the sample from the UHV chamber.

Figure 5b shows the AES spectrum after the segregation growth of germanene. Only Ag and Ge were detected on the surface, indicating an impurity-free surface. Figure 5c,d shows reflection high-energy electron diffraction (RHEED) patterns of Ag(111) and germanene/Ag(111), respectively, with the [112] azimuth. Two types of streaks (inner and outer) appeared in the RHEED pattern of germanene (Figure 5d), in addition to the fundamental streaks of Ag(111) (Figure 5c). The inner streak (indicated by the white arrows in Figure 5d) corresponds to germanene with a lattice constant of ≈3.89 Å at the rotation angle of 30°, which is in good agreement with that reported for germanene on Ag(111).[11a] The outer faint streak is caused by multiple diffractions by the Ag(111) lattice and germanene.

Figure 5e shows the Raman spectrum of the boron-coated germanene on Ag(111) recorded in air. Two peaks similar to those for germanene at the graphene/Ag(111) interface (Figure 2b) were observed, and these peaks were slightly blueshifted. These results provide further evidence that the Raman peaks in Figure 2b are derived from germanene. Note that we did not obtain any Raman peaks of germanene without the a-B layer in air.

To consider the aforementioned blueshift, we compared the Raman results with the off-specular HREEL spectrum of germanene on Ag(111) as shown in Figure 5f. Black (B) and red (G) dotted lines in Figure 5f show the phonon energies of germanene at the graphene/Ag(111) and boron/Ag(111) interfaces, respectively, which were obtained by Raman spectroscopy. The positions of the red dotted lines (G) match the peak at ≈32.5 meV (262 cm–1) and the shoulder peak at ≈19.5 meV (157 cm–1) in the HREELS spectrum, indicating that the phonon energies of surface germanene are almost the same as those of germanene at the graphene/Ag(111) interface rather than boron-coated germanene. This implies that the graphene layer does not disturb the structure of germanene on Ag(111). The a-B layer slightly interacted with germanene, resulting in the blueshift in Figure 5e. The limited interaction of graphene with germanene enabled the segregation growth by the simple heating of graphene/Ag(111)/Ge(111) samples at atmospheric pressure.

We analyzed the uniformity of germanene at the graphene/Ag(111) interface by Raman mapping. Figure 6a shows an optical microscopy image of the sample, and Figure 6b,c...
faces, such as graphene and h-BN, are significantly less reactive from Ag(111)/Ge(111). In contrast, the vdW inter-
face mobility comparable to that of graphene.\cite{25}

The stability of germanene at the h-BN/Ag(I1I) interface was also examined. Figure 8a shows Raman spectra of germanene at the interface after keeping the sample in air for 4, 39, and 55 days. The peak shape was preserved after 55 days in air. Figure 8b,c shows the extracted peak positions and FWHM of the out-of-plane and in-plane vibration modes, respectively. There are no significant changes in the features of the peaks, indicating that germanene at a vdW interface is stable in air.

We further investigated the spatial dependence of the stability of germanene at the interface by using 1D Raman line profile. Exfoliated graphite/germanene/Ag(I11) maintained in air for 210 days after the growth of germanene was used as a sample. Figure 9a shows optical microscope image and Raman spectra of the sample. The step size of the 1D Raman profile was 0.3 μm. Germanene peaks (≈155 and ≈255 cm\(^{-1}\)) were clearly observed in the center region of the graphite, indicating that the germanene was well protected after 210 days of long-term exposure to the air. On the other hand, the spectra at the outside of the graphite showed a broad peak around 235 cm\(^{-1}\) and no peak at ≈155 cm\(^{-1}\), indicating the absence of germanene. The broad peak around 235 cm\(^{-1}\) would be from the degraded germanene. We also found that the peak position and intensity of the in-plane vibration modes of germanene (≈255 cm\(^{-1}\)) were redshifted and decreased under the graphite near the edge, respectively. This indicates that germanene was slightly degraded from the edges. A possible mechanism of the degradation is the oxidation of germanene by intercalated oxidative gas molecules such as oxygen or water.

To estimate the effect of germanene degradation from the edge of cap layer, we plotted the peak positions of the in-plane vibration modes of the germanene along with the G peak intensity (graphite) as shown in Figure 9b. According to the evolution of the peak positions and intensities, the spatial locations of the graphite and non-degraded germanene can be estimated. From the spatial distribution of the G peak intensity, we assigned the graphite region to be in the range of ≈0.9 μm to +3.0 μm, as shown schematically in Figure 9b. On the other hand, the non-degraded germanene region was estimated to be in the range of ≈0.3 μm to +2.1 μm with reference to the peak position of germanene. Thus, the degradation of the germanene occurred up to =0.6 (+0.9) μm from the other edge to center of the graphite. Taking into account the long air exposure time of 210 days, the lateral degradation from the edges is very limited. These results further proved the stability of germanene at a vdW interface in air.

![Figure 7. Raman spectra of germanene with the different cap layers.](image)

show its Raman maps of the full width at half maximum (FWHM) of the G\(^{\prime}\) peak (graphene) and the peak intensity at 255 cm\(^{-1}\) (germanene), respectively. The germanene peaks were observed throughout the graphite-covered region, as schematically shown in Figure 6d, indicating that a large area of germanene with high uniformity can be grown by the present method.

To verify the possibility of using other types of cap layers, we tested multilayer exfoliated h-BN (≈30 nm thickness), exfoliated graphene (monolayer) stacked with h-BN, CVD graphene (monolayer), and sputtered Al\(_2\)O\(_3\) (≈20 nm thickness) were deposited on Ag(111)/Ge(111). The annealing conditions were 550 °C under N\(_2\) ambient with germanene, providing suitable conditions for growing germanene using the present method.

In addition, an h-BN cap layer is beneficial for the fabrication of germanene-based devices. As Tao et al. reported for the fabrication of silicene FETs,\cite{26} germanene can also be transferred onto an insulating substrate. In this case, the h-BN cap layer becomes the top protective layer of germanene FETs. Since h-BN is the most suitable substrate for graphene FETs in terms of its low carrier scattering by impurities,\cite{27} h-BN-capped germanene has great potential in terms of electronic properties, such as the tuning of its bandgap by an E-field and a high car-

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3. Conclusion

We have uniformly grown large-area germanene at a vdW material/Ag(111) interface by the segregation growth of germanane. A simple annealing process in N$_2$ or H$_2$/Ar at ambient pressure led to the formation of germanene, indicating that a UHV condition is not necessary. Owing to the chemical protection by the top vdW material, the grown germanene at the interface is stable in air. We found that it is necessary to use a vdW material as a cap layer for the present germanene growth method since the use of an Al$_2$O$_3$ cap layer resulted in the absence of germanene formation. We also proved that Raman spectroscopy in air is a powerful tool for characterizing germanene at an interface. The direct growth of h-BN-capped germanene is considered to be a promising technique for the fabrication of future germanene-based FETs.

4. Experimental Section

Ag Deposition: A Ge(111) surface was chemically cleaned by dipping in diluted HF for 1–3 min, then rinsed in deionized water, and dried by blowing N$_2$. Subsequently, an Ag thin film of 70 nm thickness was deposited at RT by an e-beam evaporator (RDEC Co., with the Ltd., RDEB-1206K). The deposition rate was 0.4 Å s$^{-1}$. The deposited Ag film was aligned with the (111) crystal direction by solid-phase epitaxy on Ge(111).[11a]

Transfer of CVD Graphene: CVD graphene was grown on a commercial Cu sheet (100 μm thickness, Nilaco) in a laboratory-made CVD system in the National Institute for Materials Science. The growth of polycrystalline monolayer graphene with high coverage was targeted. The typical growth process was as follows: i) increasing the temperature from RT to 1000 °C in Ar; ii) H$_2$ annealing at 1000 °C for 100 min; iii) graphene growth at 1000 °C by introducing methane with H$_2$ and Ar for 90 min; iv) cooling to RT in H$_2$/Ar. Details of the growth can be found elsewhere.[36] The grown graphene was transferred onto an Ag surface.
by a standard wet transfer using spin-coated poly(methyl methacrylate) (PMMA) as a mechanical support, (NH₄)₂S₂O₈ as the etchant for Cu, and acetone to remove the PMMA layer.[25,37] Transfer of Exfoliated Graphene/h-BN and h-BN: Graphene and h-BN flakes were placed on SiO₂/Si substrates by mechanical exfoliation using adhesive tapes. A dry transfer onto an Ag surface was conducted using laboratory-built transfer equipment and a viscoelastic polymer. Details are given elsewhere.[38] 

Al₂O₃ Cap Layer: An Al₂O₃ thin film was directly deposited on an Ag surface by radio frequency sputtering (Shibaura Mechatronics Corporation, CFS-4EP-LL) under Ar and O₂ flows (both at 10 standard cubic centimeters: sccm) at a pressure of 0.3 Pa. The deposition rate was 0.14 Å s⁻¹.

Table 1. Computational parameters for structural optimization.

| Material | Ecut [Ry] | Ecut* [Ry] | k point | Smearing | q point | Residual force each atom [mRy/bohr] | Convergence error [Ry/cell] |
|----------|-----------|------------|---------|-----------|---------|-----------------------------------|-----------------------------|
| Ge bulk  | 70        | 320        | 12 × 12 | 7.30      | 4 × 4    | <10⁻³                             |                             |
| Free-standing germannene | 70 | 320 | 36 × 36 × 1 | 2.50 | 8 × 8 | <10⁻³                             |                             |
| Germanene on Ag (111) | 30 | 320 | 1 × 1 × 1 | 7.50 | 0.01 | <10⁻³                             |                             |

Table 2. Computational parameters for phonon calculations.

| Material | Ecut [Ry] | Ecut* [Ry] | k point | Smearing | q point | Residual force each atom [mRy/bohr] | Convergence error [Ry/cell] |
|----------|-----------|------------|---------|-----------|---------|-----------------------------------|-----------------------------|
| Ge bulk  | 70        | 320        | 12 × 12 | 7.30      | 4 × 4    | <10⁻³                             |                             |
| Free-standing germanene | 70 | 320 | 36 × 36 × 1 | 2.50 | 8 × 8 | <10⁻³                             |                             |
| Germanene on Ag (111) | 30 | 320 | 1 × 1 × 1 | 7.50 | 0.01 | <10⁻³                             |                             |

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory, germanene, graphene, hexagonal boron nitride, Raman spectroscopy, van der Waals materials

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