Evidence for Germanene growth on epitaxial hexagonal (h)-AlN on Ag(1 1 1)

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Abstract

In this work, a structural analysis of Ge layers deposited by molecular beam epitaxy (MBE) on Ag(1 1 1) surfaces with and without an AlN buffer layer have been investigated by x-ray Absorption Spectroscopy (XAS) at the Ge-K edge. For the Ge layers deposited on h-AlN buffer layer on Ag(1 1 1) an interatomic Ge–Ge distance $R_{Ge-Ge} = 2.38 \text{ Å}$ is found, typical of 2-Dimensional Ge layers and in agreement with the theoretical predictions for free standing low-buckled Germanene presented in literature. First principles calculations, performed in the density functional theory (DFT) framework, supported the experimental RHEED and XAS findings, providing evidence for the epitaxial 2-D Ge layer formation on h-AlN/Ag(1 1 1) template.

Keywords: Germanene, x-ray absorption spectroscopy, RHEED, Ab initio structural modeling, angular resolved photoemission spectroscopy

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(Some figures may appear in colour only in the online journal)

1. Introduction

The isolation of a free standing graphene [1] layer with exceptional electronic properties has opened the path for synthesizing other two-dimensional (2D) graphite-like layered materials with exploitable properties and applications. Early theoretical studies [2] predicted that free standing silicene and Germanene, the silicon and germanium sp²-hybridized analogues to graphene, can be stable in the low-buckled (LB) configuration, preserving the Dirac cone at $K$-points of a Brillouin zone (BZ). The first experimental works reported the silicene growth on Ag(1 1 1) [3] crystal and other metallic substrates such as ZrB$_2$(0001) [4] and Ir(1 1 1) [5] with numerous studies following [6]. On the other hand, experimental studies specifically on Germanene growth appeared only recently, reporting on the Germanene formation on Pt(1 1 1) [7], Au(1 1 1) [8], Al(1 1 1) [9] substrates, and on the topmost layer of the Ge$_2$Pt alloy [10, 11]. The free-standing LB Germanene [2] has been predicted to have a symmetric buckling of 0.64 Å, with hexagonal lattice constant of 2D LB honeycomb structure of 3.97 Å and nearest neighbor distance of 2.38 Å. There are a number of reports on the formation of Germanene, mainly on metallic substrates. STM reveals [7–9] a variety of superstructures and buckling configurations depending on the substrate used. These are all explained by assuming a Germanene honeycomb lattice superimposed on the particular substrate lattice arrangement. More specifically, Li et al [7] observed the formation of $(\sqrt{7} \times \sqrt{7})$ a superstructure of Germanium on Pt(1 1 1) with periodicity of 1.2 nm, attributing it to a $(3 \times 3)$ Germanene with non-symmetric buckling of 0.6 Å. Davila et al [8] provided evidence of $(\sqrt{3} \times \sqrt{3})$ Germanene layer on $(\sqrt{7} \times \sqrt{7})$ Au(1 1 1) a surface with low symmetric buckling of 0.47 Å and Ge–Ge distance of 2.58 Å. Derivaz et al [9] reported the formation of a $(3 \times 3)$ Ge superstructure on
Al(1 1 1) corresponding to a (2 × 2) Germanene with high symmetric buckling of 1.23 Å and Ge–Ge distance of 2.60–2.65 Å. Remarkably, a Germanene honeycomb lattice with a low symmetric buckling of 0.2 Å and Ge–Ge distance of 2.5 Å is directly observed in [10, 11] at the termination of 3D Ge2Pt islands on Ge(1 1 0). At this point, there is no information in the literature about the electronic band structure by ARPES and the possible existence of a Dirac cone similar to graphene is elusive. However, in a recent work by Zhang et al [11] on Germanene-coated Ge2Pt clusters, a V-shaped differential conductivity is measured with the minimum of conductivity close to the Fermi level with a non-zero value, which could be attributed to a 2D Dirac system with metallic character.

Nevertheless, the growth of metal-supported silicene and Germanene has drawbacks because of the strong interactions between the substrate and the 2D layers. It has been shown experimentally [12, 13] that the surface states of a silicene/Ag(1 1 1) system originate from hybridization with Ag d-bands, while for the Germanene/Ag(1 1 1) system it has been theoretically predicted [14] that the Dirac cone is absent because of structural distortion due to the strong interaction with the Ag(1 1 1) surface. Experimentally, Ge on Ag(1 1 1) at 1/3 coverage shows highly dispersive cone-like features in the valence band structure which are associated with the formation of Ag2Ge ordered surface alloy [15]. A way to mitigate the influence of the substrate is to grow silicene and Germanene on another 2D graphite-like material, preferably insulating material that could couple with weak Van der Waals (VDW) forces [16, 17]. It has been theoretically shown that silicene can preserve the graphene-like electronic structure when embedded between two ultra-thin hexagonal (h)-aluminum nitride (AIN) layers [18] and also that Germanene can be stably attached to a hexagonal (h)-boron nitride (BN) [14] template through weak VDW interactions. Since the synthesis of Germanene has been achieved only on metallic substrates, which is unsuitable for electronic devices, the use of a graphite-like 2D insulator as a template for Germanene is highly desirable for the realization of functional field-effect electronic devices. Based on the aforementioned predictions [14, 18] both h-BN and h-AIN dielectrics could be good candidates for Germanene overgrowth. The choice between the two depends on the methodology used for the dielectric and Germanene growth. Good quality h-BN on Cu(1 1 1) by chemical vapor deposition (CVD) has been demonstrated [19]. On the other hand, epitaxial growth of h-AIN has been achieved on Ag(1 1 1) by our team [20] using plasma-enhanced MBE. This offers the possibility to obtain h-AIN and Germanene in one MBE growth step, thus preserving the integrity of the Germanene/AIN interface.

In this work we provide evidence that Germanene can be obtained on 2D hexagonal (h)-AIN nanosheets which are epitaxially grown on Ag(1 1 1). Ge layers were deposited by molecular beam epitaxy (MBE) on Ag(1 1 1) with and without h-AIN buffer layer and were structurally characterized by reflection high-energy diffraction (RHEED) and extended X-Ray absorption fine structure (EXAFS) measurements. EXAFS provides evidence for Ge layer growth with an interatomic distance of \( R_{\text{Ge–Ge}} \approx 2.38 \) Å, which is the value of bond length in free-standing Germanene as predicted by the density functional theory (DFT) calculations. This implies the formation of Germanene which is also compatible with the RHEED observation of (4 × 4) reconstruction with respect to (1 × 1) h-AIN. The valence band structure of Ge layer on h-AIN/Ag(1 1 1) was investigated by in situ angle resolved Ultraviolet Photoelectron Spectroscopy (AR-UPS) showing the existence of a Ge-related band near Γ-point of BZ.

### 2. Experimental

#### 2.1. Samples growth

The growth experiments have been performed in a UHV/MBE system with base pressure in the high 10⁻¹⁰ mbar range, equipped with Reflection High Energy Electron Diffraction (RHEED). Ag(1 1 1) single crystals were commercially available with pre-marked in-plane orientation. Ag substrate was cleaned in vacuum by repeated cycles of Ar ion sputtering (1.5 keV for 30 min at 5 × 10⁻⁵ mbar) with subsequent annealing in vacuum (500 °C for 30 min). In situ XPS (X-ray photoelectron spectroscopy) verified that clean surfaces free of C and O contaminants were obtained. Additionally, the flat and well-ordered Ag surfaces presented streaky (1 × 1) reconstructed RHEED patterns.

AIN buffer layers were grown epitaxially by plasma-assisted MBE on Ag(1 1 1) substrates. Al metal was evaporated from a cold-lip pyrolytic boron nitride (PBN) effusion cell in the presence of a reactive atomic nitrogen beam generated by a remote radio frequency (rf) plasma source. AlN was deposited on Ag(1 1 1) substrate at 650 °C with a deposition rate of 0.22 Å s⁻¹, under partial \( N_2 \) pressure of 4 × 10⁻⁸ mbar using an rf power of 210 W [20].

Ge is evaporated from a W effusion cell with an evaporation rate of 1.4 Å min⁻¹. Ge films are prepared either directly on bare Ag(1 1 1) substrate or using the AlN nanosheets on Ag(1 1 1) (AIN/Ag) as a buffer layer. The deposition of Ge directly on bare Ag(1 1 1) is performed at room temperature, following a post-deposition annealing at 140 °C for improved crystallinity, while the deposition on AIN/Ag(1 1 1) template is achieved at a temperature of 450 °C. Table 1 resumes the samples used in the present investigation. Based on evaporation rates [20] the AlN layer thickness is estimated to be 1 ML. 1 and 2 ML Ge on AlN/Ag (see table 1) correspond nominally to one and two layers of Germanene (see sections 2.2 and 2.3) respectively. XPS measurements performed after the deposition of Ge on AlN/Ag(1 1 1), showed that there is no detectable reaction between Ge and AlN within the sensitivity limits of our measurements (see supplemental information (stacks.iop.org/JPhysCM/28/045002/mmedia), SI).

### Table 1. Preparation parameters of the samples.

| Sample | Substrate | Buffer | Layer, thick.(ML) | Cap, thick. (nm) |
|--------|-----------|--------|------------------|-----------------|
| 1 ML Ge/Ag | Ag(1 1 1) | Ge | 1 | Al₂O₃, 9 |
| 1 ML Ge/AI/Ag | Ag(1 1 1) | AIN | Ge, 1 | Al₂O₃, 9 |
| 2 ML Ge/AI/Ag | Ag(1 1 1) | AIN | Ge, 2 | Al₂O₃, 9 |
In order to protect the Ge films from the exposure to ambient conditions during the transport to the synchrotron and the XPS measurements, all samples were capped with an Al$_2$O$_3$ layer of $\approx 9$ nm.

### 2.2. RHEED measurements

All growth procedures are monitored by RHEED technique using a 15 keV electron gun. The RHEED patterns of bare Ag(1 1 1) along [1 1 0] and [1 1 −2] azimuths are given in figure 1(a) showing a flat Ag(1 1 1) surface with a streaky (1×1) reconstruction. After the AlN deposition (figure 1(b)) extra streaks are observed, as indicated by white arrows, due to the epitaxial AlN layer. The AlN streaks are sharp and correspond to a flat hexagonal h-AlN [20] layer. Upon deposition of 1 monolayer (ML) Ge on the flat epitaxial AlN buffer layer on Ag(1 1 1) the RHEED patterns (figure 1(c)) present new faint diffraction streaks due to Ge growth, as indicated by red arrows. The latter indicate a (4×4) Germanene phase with respect to (1×1) h-AlN, or a (3×3) hexagonal reconstruction with respect to (1×1) Germanene, complying with the lattice-matching condition of: $3a_{\text{Germanene}} \approx 4a_{\text{h-AlN}}$. Given the $a_{\text{Germanene}} \approx 3.928$ Å and $a_{\text{h-AlN}} \approx 3.04$ Å. Although the existence of other phases cannot be excluded, these cannot be confirmed within the detection limits of our RHEED which indicates that, at the particular growth conditions, the 4×4 phase is dominant. The RHEED pattern observed in figure 1(c) is due to diffraction from the AlN surface.

The faint (4×4) superstructure is due to a multiplication of periodicity of the “Ge-decorated” AlN surface in real space by a factor of four due to the coincidence lattice described above ($3a_{\text{Germanene}} \approx 4a_{\text{h-AlN}}$). Despite the fact that Germanene is symmetrically buckled (see section 2.3) it is possible to generate a 4×4 reconstruction. This is because electronic density around the Al and N surface atoms changes periodically every 4 AlN lattice spacing due to the proximity of the overlying Ge atoms, thus modifying the electron diffraction. The large separation of Germanene from the AlN (see section 2.3) could explain the faint appearance of the 4×4 streaks. The interpretation of the diffraction results is partly supported by a simulation of RHEED diffraction (see SI) from symmetrically buckled Germanene on AlN/Ag which shows a (4×4) pattern similar to that obtained from 1 ML Ge sample (figure 1(c)) except from the 3/4th order streak which is more intense in the simulated pattern. This can be explained considering that the (1×1) Germanene diffraction is dominant in that case. As the growth increases above 1 ML (figures 1(d)–(e)) the signal from the (4×4) reconstruction faints out and the streaks at distance of 3/4 of h-AlN streaks are observed.

**Figure 1.** RHEED patterns of: (a) bare Ag(1 1 1), (b) epitaxial AlN buffer layer on Ag(1 1 1) and ((c)–(e)) 1 ML, 5/3 ML and 2 ML Ge deposited on epitaxial AlN/Ag(1 1 1) template, along [1 1 0] (left) and [1 1 −2] (right) azimuths of silver respectively. The white and red arrows indicate the AlN and Ge diffraction streaks, respectively. In (b) the (1×1) hexagonal AlN reconstruction is shown while in (c) the (4×4) Ge reconstruction with respect to (1×1) hexagonal-AlN is observed. In ((d)–(e)) the (4×4) reconstruction faints out and the streaks at distance of 3/4 of h-AlN streaks are observed.
2.3. First principles calculations

First principle calculations are performed within the DFT framework using the VASP [21] code. A general gradient approximation [22] (GGA) exchange-correlation functional in the Perdew–Burke–Ernzerhof (PBE) [23] form is used. For Van der Waals corrections we used DFT-D2 method of Grimme [24].

Firstly, the h-AlN on Ag(1 1 1) system was optimized, in order to obtain the template structure that will be subsequently used in the simulation of Germanene on h-AlN/Ag(1 1 1) system. For this purpose, a single layer AlN is placed on a six layer slab of Ag(1 1 1). All the atoms, with the exception of the two bottom Ag layers, were allowed to relax until the force and the energy were converged to $10^{-3}$ eV Å$^{-1}$ and $5.0 \times 10^{-4}$ eV, respectively. A plane wave basis is used up to the cutoff energy of 350 eV and a single $\Gamma$-point centered $k$-grid [25] was employed for sampling the reciprocal space.

To simulate the Germanene on h-AlN/Ag(1 1 1) a slab super-cell approach with periodic boundary conditions was employed. The slab consisted of a $(3 \times 3)$ Germanene on the $(4 \times 4)$ h-AlN on the $(4 \times 4)$ four layers of Ag(1 1 1) with only the bottom layer kept fixed (figure 2). Although a larger number of Ag(1 1 1) layers is preferable, the present calculations capture the trend. More than 16 Å of vacuum was included to ensure the isolation of the two sides of the system to avoid the interaction due to the periodic conditions. As before, a PBE potential is used. A plane wave basis was used up to the cutoff energy of 350 eV and a single k-point centered at $\Gamma$ was employed for sampling the reciprocal space. All the system was allowed to relax until the force and the energy converged to $10^{-3}$ eV Å$^{-1}$ and $5.0 \times 10^{-4}$ eV, respectively. The DFT optimized atomic configuration of Germanene on h-AlN is given in figure 2. Germanene on h-AlN is found to be low-buckled with $\Delta_{Ge} \approx 0.705$ Å and a Ge–Ge atoms distance of $R_{Ge-Ge} \approx 2.372$ Å on average, which are in very good agreement with the buckling of 0.64 Å and the $R_{Ge-Ge}$ distance of 2.38 Å, predicted free-standing low buckled Germanene [2].

Additionally, the same Ge–Ge interatomic distance is verified by the XAS measurements described in the next section. The Germanene lattice constant found is $a_{Ge} \approx 3.93$ Å while the respective value for free standing LB Germanene is 3.97 Å. It is remarkable that, unlike the case of (4 × 4) silicone/Ag(1 1 1) [3] and the $(3 \times 3)$ Germanene/Pt(1 1 1) [7] where a highly asymmetric buckling occurs, here the Germanene buckling is essentially symmetric, as in the case of free standing Germanene. The symmetric buckling is interpreted as being a result of the weak interaction of Germanene with the 2D h-AlN template. Therefore, the atomic configuration of Ge on h-AlN/Ag(1 1 1) appears to be similar to free standing Germanene as there is evidence of a honeycomb lattice (supported by XAS) and low buckling (supported by DFT), which are both compatible with RHEED observations.

The main difference between the $(3 \times 3)$ Germanene/AlN and the free-standing (FS) low-buckled (LB) $(1 \times 1)$ Germanene is that the $\pi$-band crossing in the former appears at the $\Gamma$-point because of zone folding. There may be minor changes in the states near the $\Gamma$-point caused by the slightly different buckling but we cannot make a quantitative comparison with the data in [2] since we do not have the raw data from that paper.

From figure 2 in [2], however, we see that there is a qualitative agreement between our $(3 \times 3)$ and [2] $(1 \times 1)$ free-standing LB Germanene. This agreement is also observed in our calculated band structure of $(1 \times 1)$ FS-LB-Germanene, compared with the $(3 \times 3)$ FS-LB-Germanene given in figure S5 (SI). At $\Gamma$-point, no difference is observed in the energy position of s-band minimum (above Fermi level) and the $\sigma(p_x, p_y)$-band maximum (below Fermi level). The small increase in buckling in $(3 \times 3)$ Germanene in our experiment, compared to free-standing Germanene is attributed to the minor influence of the AlN substrate. In figure S6 (SI) we compared the calculated band structures of $(1 \times 1)$ FS-LB Germanene with slightly different buckling of $\Delta \approx 0.65$ Å and $\Delta \approx 0.7$ Å. In the case of $\Delta \approx 0.7$ Å, a small shift upwards in the energy diagram is observed in the s-band (at $\Gamma$-point above Fermi level) and the $\sigma(p_x, p_y)$-band (at $\Gamma$-point below the Fermi level).
The EXAFS measurements at the Ge-K edge (11,103 eV) have been carried out at the GILDA beamline (BM08) at the European Synchrotron Radiation Facility in Grenoble [26]. The monochromator was equipped with a pair of Si(3 1 1) crystals and run in dynamical focusing mode. Harmonics rejection was achieved by using a pair of Pd-coated mirrors with an estimated cut-off of 18 keV. Data were collected in grazing incidence mode (incidence angle 0.2 deg) in the dedicated experimental apparatus available on the beamline [27] in order to enhance the signal from the surface and minimize the spurious signal from the substrate. Data collection was carried out in fluorescence mode using a 12 element hyperpure Ge detector.

The EXAFS signal $\chi(k)$ was extracted from the absorption raw data $\mu(E)$ with the ATHENA program [28] and the quantitative analysis was carried out with the ARTEMIS programs [28, 29]. Theoretical EXAFS signals were computed with the FEFF8.4 code [30] using muffin tin potentials and the Hedin-Lundqvist approximation for their energy-dependent part. Spectra were reproduced with a 2 shell model Ge–Ag and Ge–Ge using as free parameters for the each coordination shell the coordination number $N_i$, the shell radius $R_i$ and the Debye-Waller factor $\sigma^2_i$ ($i =$ Ge–Ag or Ge–Ge). A common $\Delta E_0$ value was used whereas the $S_0^2$ was fixed to 0.9 as found in the crystalline Ge model compound. Fit were attempted also with a second shell made up of Si/Al ions but the results tended to yield negative $\sigma^2$ values so this route was abandoned. The attribution of the two peaks to two different phases of Ge comes from the consideration that Ge and Ag are poorly mixable. The phase diagram [31] reports negligible solubility of Ag in Ge and a max solubility of Ge in Ag of 9.6%. The appearance of Ge–Ge bonds in a AgGe alloy, then, is unlikely as also confirmed by crystallographic analysis of hexagonal and FCC solid solutions [32] where no same-atom bonds are reported in the first coordination shell of Ge. As a consequence, the origin of Ge–Ge bonds is a distinct pure Ge phase that will be determined via the quantitative analysis.

The EXAFS spectra are shown in figure 3 whereas the corresponding Fourier Transforms (FT) are shown in figure 4. The oscillations in the EXAFS spectra are coincident in 1 ML and 2 ML Ge/AlN/Ag samples and are at different positions and Ge–Ge using as free parameters for the each coordination shell the coordination number $N_i$, the shell radius $R_i$ and the Debye-Waller factor $\sigma^2_i$ ($i =$ Ge–Ag or Ge–Ge). A common $\Delta E_0$ value was used whereas the $S_0^2$ was fixed to 0.9 as found in the crystalline Ge model compound. Fit were attempted also with a second shell made up of Si/Al ions but the results tended to yield negative $\sigma^2$ values so this route was abandoned. The attribution of the two peaks to two different phases of Ge comes from the consideration that Ge and Ag are poorly mixable. The phase diagram [31] reports negligible solubility of Ag in Ge and a max solubility of Ge in Ag of 9.6%. The appearance of Ge–Ge bonds in a AgGe alloy, then, is unlikely as also confirmed by crystallographic analysis of hexagonal and FCC solid solutions [32] where no same-atom bonds are reported in the first coordination shell of Ge. As a consequence, the origin of Ge–Ge bonds is a distinct pure Ge phase that will be determined via the quantitative analysis.

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with respect to sample 1 ML Ge/Ag. This means that a different structure is realized in these samples. Minor differences between the 1 ML and 2 ML spectra can be attributed to spurious effects due to coherent scattering from the substrate. The FT exhibit a double peak due to two correlations that were revealed to be Ge–Ge and Ge–Ag respectively for the first and second peak. This means that Ge is present in two distinct phases: one Ge-coordinated that will be either diamond Ge or Germanene and the other an Ag–Ge alloy. Other possibilities have been tested for the attribution of these peaks (namely Ge–Al correlation) but the fit gave unphysical results (negative $\sigma^2$ or exceedingly high $\Delta E_0$) and were ruled out. The Ge–Ge peak (marked by a $\#$ in figure 4) moves at lower distances from 1 ML Ge/Ag to to 1 ML and 2 ML Ge/AlN/Ag samples whereas the Ge–Ag peak (marked by a $\&$ in figure 4) remains substantially at the same position. This means that the Ge–Ge bond length value changes from the sample grown on Ag to those grown on AlN. The results of the quantitative data analysis are shown in table 2 and they confirm this qualitative finding. Here it can be noticed that the main difference between the samples comes from the Ge–Ge separation that is 2.44 Å in 1 ML Ge/AlN sample and 2.39 Å in 1 ML and 2 ML Ge/AlN/Ag samples. This has considerable consequences for the structure as discussed below. The Ge–Ag separation is about 2.65 Å and it is the same in all samples.

It was not possible to reproduce the peaks at low R with a Ge–O contribution meaning that this phase is not detectable by XAS and the peaks are due to low-frequency noise.

2.5. Angle resolved ultraviolet photoelectron spectroscopy

The valence band structure of prepared samples was investigated in situ by angle resolved Ultraviolet Photoelectron Spectroscopy (AR-UPS) at room temperature, without breaking vacuum in a $\mu$-metal analytical chamber (10$^{-9}$ mbar base pressure). The lab-based system is equipped with a 100 mm hemispherical electron analyzer (SPECS PHOIBOS100) and the excitation is achieved using the He I (21.22 eV) radiation from a He discharge lamp (SPECS UVS35/10). Photoelectrons emitted by the samples are measured in the energy distribution curve (EDC) mode. Figure 5(a) shows the valence band spectra of the AlN/Ag(1 1 1) and 1 ML Ge-deposited AlN/Ag(1 1 1) recorded at polar angle $0^\circ$, around the $\Gamma$ point of Brillouin zone. The feature observed at binding energy $\approx$1 eV is related to Ge. (b) EDCs of 1 ML Ge on h-AlN/Ag(1 1 1) sample, recorded along the $\Gamma$K direction of Ag(1 1 1). The Ge related feature has a dispersion around $\Gamma$ point. (c) DFT band structure calculation of 1 ML Germanene on h-AlN on Ag(1 1 1). The $\pi$ and $\pi^*$ bands are located at $\Gamma$-point due to band folding of the $(3 \times 3)$ Germanene reconstruction. The Fermi level corresponds to the zero energy. Ge, Al and N bands contribution are marked by different symbols as shown in the figure.

with a step angle of $\Gamma$. The Ge-related feature has a dispersion around $\Gamma$-point at 1 eV binding energy.

The DFT calculated band structure of 1 ML Germanene on h-AlN/Ag(1 1 1) superlattice is given in figure 5(c). The low resolution and the non-ideal epitaxial quality of Germanene on AlN do not permit the observation of the $\pi$ and $\pi^*$ bands in the AR-UPS experiments. Nevertheless, a Ge-related feature observed in AR-UPS could be associated with the $\sigma$ bands of Germanene predicted to be about 0.5 eV below the Fermi level in the DFT calculations in figure 5(c). The difference of about 0.5 eV between the experimental and the theoretical energy position of the $\sigma$ bands may be attributed to small positive

| Sample          | N   | R (Å) | $\sigma^2$ | N   | R (Å) | $\sigma^2$ |
|-----------------|-----|-------|------------|-----|-------|------------|
| 1 ML Ge/Ag      | 2.6(9) | 2.44(2) | 0.012(4) | 1.8(4) | 2.65(2) | 0.011(4) |
| 1 ML Ge/AlN/Ag  | 1.6(2) | 2.38(2) | 0.007  | 2.6(7) | 2.62(2) | 0.015(4) |
| 2 ML Ge/AlN/Ag  | 1.3(2) | 2.39(2) | 0.007  | 3.0(6) | 2.63(2) | 0.016(3) |
| Ge bulk         | 4.0  | 2.45  |          |       |       |            |

Figure 5. (a) Valence band spectra of the h-AlN/Ag(1 1 1) and 1 ML Ge-deposited AlN/Ag(1 1 1) recorded at polar angle $0^\circ$, around the $\Gamma$ point of Brillouin zone. The feature observed at binding energy $\approx$1 eV is related to Ge. (b) EDCs of 1 ML Ge on h-AlN/Ag(1 1 1) sample, recorded along the $\Gamma$K direction of Ag(1 1 1). The Ge related feature has a dispersion around $\Gamma$ point. (c) DFT band structure calculation of 1 ML Germanene on h-AlN on Ag(1 1 1). The $\pi$ and $\pi^*$ bands are located at $\Gamma$-point due to band folding of the $(3 \times 3)$ Germanene reconstruction. The Fermi level corresponds to the zero energy. Ge, Al and N bands contribution are marked by different symbols as shown in the figure.
charging of the Ge/AlN layer, typically observed in UPS experiments, which increases the electron binding energy. Other effects could also change the energy position of the $\sigma$ band. Indeed, our DFT calculations show that charge transfer between the substrate and the Germanene layer can shift the $\sigma$ band to higher binding energy, but only by a small amount ($\approx$55 meV) which cannot fully account for the UPS observations.

In the reduced zone scheme, due to zone folding, the $\pi^*$ and $\pi$ bands of Germanene are predicted to be at the $\Gamma$-point instead of the $K$-point, remaining intact with the Dirac point clearly seen at the Fermi level. The unperturbed Germanene $\pi$ and $\pi^*$ bands shown in the DFT calculations are a result of the symmetric buckling due to the weak interaction of Germanene with the h-AlN/Ag(1 1 1) template. The latter has a small influence on band structure at $\Gamma$-point compared to the free-standing (FS) low-buckled (LB) Germanene as discussed in the SI.

UPS data of the 2 ML Ge sample are not presented because no signal was observed associated with Ge. We anticipate that the addition of the second Ge layer drastically modifies the band structure. This is supported by a DFT calculation of 2 ML Ge in a honeycomb arrangement (See SI). The $\sigma$-band (consisting in $p_z$ and $p_x$ orbitals) present in 1 ML Germanene (figure 5(c)) is strongly modified after the deposition of an additional layer of Germanene.

3. Discussion

The data presented here show that it is possible to grow 2-Dimensional Germanene layers on hexagonal AlN. This is evidenced by the different Ge–Ge bond length values in the samples studied here as determined by x-ray absorption spectroscopy. The 1 ML Ge/Ag sample, grown directly on Ag, exhibits a distance typical of bulk Ge so it can be suggested that in this case Ge formed islands on the Ag surface with a bulk-like structure. On the other hand, 1 ML and 2 ML Ge/AlN/Ag samples present a considerably smaller separation (2.38–2.39 Å) and this is a strong argument for the formation of Germanene. Indeed, structural ab-initio calculations for free-standing Germanene layers [2] predict a structure consisting in an hexagonal network with lattice parameter $a_{hex} = 3.97$ Å with a slight buckling ($b = 0.66$ Å) and a Ge–Ge separation $R_{Ge–Ge} = 2.39$ Å. The reduction of the Ge–Ge distance is a direct consequence of the valence orbitals hybridization and, thus, of the formation of Germanene. Taking theoretical predictions for Ge hydrides [34] with different computational schemes a Ge–Ge separation of 2.20–2.26 Å is reported for Ge$_2$H$_5$ ($sp$ hybridization), 2.27–3.45 Å for Ge$_2$H$_6$ ($sp^2$), and 2.42–2.46 Å for Ge$_2$H$_8$ ($sp^3$). Our data and crystallographic data for diamond Ge perfectly match these predictions respectively for the $sp^2$ and $sp^3$ cases. In principle, a contraction of the bond length could also be found by application of strain; indeed values around 2.38 Å are reported in literature for the Ge–Ge separation, but at considerably high pressure values: 7 GPa (diamond Ge, [35]) or 60 GPa (shorter bond in the $\beta$-Sn form of Ge, [36]). These phases can be safely ruled out in our samples at ambient pressure; even considering nanoclusters in a matrix the values reported for these systems are of the order of a fraction of a GPa [37], largely below the needed value. It is worth noticing that a precise determination of the second shell distance would be crucial in the determination of the buckling of the layer. In the experimental data this shell appears to be within the noise level and the question is whether this comes from a highly disordered sample or it is an intrinsic feature. For this purpose a simulation of the XAS spectrum of a low-buckled Germanene at room temperature has been carried out via Molecular Dynamics [38] (see SI). It was found (figure S4) that the atomic vibrations severely dampen this peak. The spectrum in figure S4 is in good qualitative agreement with the experimental data (namely the curve of sample 1 ML Ge/AlN/Ag) showing that the present experimental data are compatible with a model of low-buckled Germanene.

Ab-initio structural modeling has been carried out on Germanene layers on AlN in order to see the structural effect of the interaction with this substrate. The result is that the predicted Germanene lattice parameter is $a_{Ge} \approx 3.928$ Å and the buckling is $\Delta_{Ge} \approx 0.705$ Å leading to a Ge–Ge atoms distance of $R_{Ge–Ge} \approx 2.372$ Å. The buckling is found to be symmetric as expected for a low-interacting substrate. These data are in close agreement with free-standing Germanene and, compared with the XAS results, evidence that in the case of growth on AlN, Ge forms layers of Germanene. The formation of the 2-Dimensional layer is also supported by RHEED data that evidence an epitaxial growth of the layer with a reconstruction such that three times the lattice parameter of Germanene is equal to four times the lattice parameter of the AlN substrate. AR-UPS of 1 ML Germanene on h-AlN/Ag(1 1 1) show a feature at a binding energy value of 1 eV related to the Ge deposition and this feature has a dispersion around the $\Gamma$ point.

XAS has also evidenced a Ge–Ag bond, presumably due to Ge atoms that came in contact with the metallic substrate due to an incomplete coverage by AlN. In all cases we found Ge–Ag bonds at a distance of 2.65 Å and attempts to attribute this distance to other components (Ge–Si or Ge–Al) lead to unphysical results. This value is considerably smaller than that reported for Ge impurities in Ag ([39] $R_{Ge–Ag} = 2.87$ Å) but it is exactly the sum of the covalent radii ([40], $R_{Ge} = 1.45$ Å, $R_{Ag} = 1.20$ Å) of the two elements. From the values of the coordination numbers it is possible to derive the amount of Ge in each phase by applying a linear scaling with the constraint that the values of Ge fraction in the two phases must sum to 1. It will be considered that Ge is 3-coordinated to Ge in Germanene and 4-coordinated in diamond Ge, whereas a coordination number of 6 can be inferred for Ge–Ag in the surface alloy, being half of the value found in [39]. From the results of table 2 it can be derived that 30–50% of Ge goes in the alloy, presumably in corresponding zones of the substrate not covered by AlN.

4. Conclusions and outlook

The analysis of the structural data from layers deposited on a thin hexagonal AlN layer epitaxially grown on Ag(1 1 1) suggests an unusual Ge–Ge bond distance $R_{Ge–Ge} = 2.38$ Å
that is predicted for 2D layers with the honeycomb structure in free-standing form which is known as Germanene. Germanene produces a $4 \times 4$ super-structure with respect to underlying AlN, detectable in the high-energy electron diffraction pattern, as a result of a coincidence lattice in which three times the lattice constant of Germanene matches four times the lattice constant of AlN. The deposition on the pure Ag surface on the other hand, leads to a Ge–Ge distance compatible with the formation of bulk Ge islands. Future experiments should focus on the study of Germanene formation as a function of the AlN layer thickness. While ultrathin AlN adopts the planar, graphite-like hexagonal metastable structure which may favor the formation of 2D Ge lattices like Germanene, at larger thickness, AlN transforms to the more stable bulk wurtzite structure. In such a case we need to know whether Germanene can be stabilized on thicker w-AlN layers which provide a better isolation, allowing the measurement of Germanene electrical properties.

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