



Coexistence of strongly buckled germanene phases on Al(111)

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Abstract

We report a study of structural and electronic properties of a germanium layer on Al(111) using scanning tunneling microscopy (STM), low energy electron diffraction and core-level photoelectron spectroscopy. Experimental results show that a germanium layer can be formed at a relatively high substrate temperature showing either (3×3) or $(\sqrt{7}\times\sqrt{7})R\pm 19.1^\circ$ reconstructions. First-principles calculations based on density functional theory suggest an atomic model consisting of a strongly buckled (2×2) germanene layer, which is stable in two different orientations on Al(111). Simulated STM of both orientations fit nicely with experimental STM images and the Ge 3d core-level data decomposed into four components is consistent with the suggested model.

Introduction

The properties of two-dimensional (2D) materials are currently subjected to intense experimental and theoretical studies. The research is focused on many important properties predicted by theory for various conceivable 2D materials. In similarity with graphene, some other materials are also predicted to show a linear electron dispersion near the Fermi level. Other important properties/phenomena that make 2D materials particularly interesting for incorporation in various devices are, magnetism, superconductivity, Rashba type spin-splitting, quantum spin Hall effect, amongst others. Based on the wealth of physical phenomena exhibited by various 2D materials, they are consid-

ered as important future materials of high potential for applications in nano-scale electronics and spintronics.

A sub-group of 2D materials is graphene-like structures formed by the group IV atoms Si, Ge and Sn, i.e., silicene, germanene and stanene. However, Si, Ge, and Sn atoms prefer sp^3 hybridization, resulting in a buckled honeycomb structure with a mixture of sp^2 - sp^3 character [1-3]. As a result, the spin-orbital coupling is enlarged and the quantum spin Hall effect is stronger than in graphene [3-6]. The formation of 2D sheets of group IV elements is a great experimental challenge. In this paper we

address the germanene case by characterizing a layer of Ge formed on Al(111).

Experimental efforts have been made to grow germanene on metallic substrates and band gap materials. Bampoulis et al. [7] proposed a germanene layer with very small buckling (0.2 Å) when they made Pt/Ge crystals by depositing and annealing of Pt on Ge(110). In an inverse case, Li et al. [8] chose Pt(111) as a substrate onto which Ge was evaporated at room temperature. This choice of substrate was motivated by a weaker interfacial interaction compared to other metals with adsorbed two-dimensional sheets such as graphene. They reported that Ge formed a ($\sqrt{19}\times\sqrt{19}$) superstructure on the Pt(111) surface. A model based on a distorted, buckled, germanene sheet was suggested and reported to be consistent with scanning tunneling microscopy (STM) data assuming that only 3 out of 18 Ge atoms inside the ($\sqrt{19}\times\sqrt{19}$) unit cell were observed. These three atoms were about 0.6 Å higher than the rest of the Ge atoms. Later, Švec et al. [9] studied a ($\sqrt{19}\times\sqrt{19}$) superstructure of “silicene” on Pt(111). Based on their theoretical calculation, they believed that a Si₃Pt surface alloy was formed that resembles a twisted kagome lattice. By an extension of their interpretation, they suggested that the ($\sqrt{19}\times\sqrt{19}$) superstructure of Ge on Pt(111) in [8] is also a surface alloy composed of Ge₃Pt tetramers. In another study, Au(111) was chosen as a possible substrate for the formation of germanene because alloy formation was believed to be avoided using this substrate. Deposition of one monolayer (ML) of Ge on Au(111) at ≈ 200 °C resulted in low energy electron diffraction (LEED) data showing some superstructure spots interpreted as diffraction from ($\sqrt{19}\times\sqrt{19}$), ($\sqrt{7}\times\sqrt{7}$) and (5×5) germanene phases [10]. Only the ($\sqrt{7}\times\sqrt{7}$) periodicity was observed by STM, but the resolution was not sufficient to identify an atomic structure directly from the image. Qin et al. [11] presented results of bilayer germanene on Cu(111) at room temperature. Scanning tunneling spectroscopy showed a “V” shaped density of states, which was also observed by Zhang et al. [12], who synthesized germanene on MoS₂ at room temperature. Al(111) was chosen as a substrate to deposit germanene by Derivaz et al. [13] with the motivation that it is a simple unreconstructed metal with surface density of states dominated by s-electrons. A monolayer of Ge formed at a “magic” temperature (in a range of 20 °C around 87 °C) was interpreted as a germanene layer. Well-resolved STM images showed a honeycomb arrangement of blobs corresponding to a (3×3) periodicity with respect to Al(111). An optimized model of (2×2) germanene on a (3×3) Al unit cell was presented. Two Ge atoms were located on top of Al atoms 1.21–1.23 Å higher than the other Ge atoms. Ge deposition at temperatures below the “magic” range was reported to show disorder with a blurred (1×1) LEED pattern, while higher temperatures were reported to result in a sharp (1×1) LEED pattern.

The structure of Ge on Al(111) and the model suggested in [13] were subjected to an investigation using total-reflection high-energy positron diffraction (TRHEPD) by Fukaya et al. [14]. In this study, 1 ML of Ge was deposited on Al(111) held at 350 K. The evaporation rate was ≈ 0.018 ML/min. These parameters are close to the ones in [13] and the formation of a (3×3) superstructure was confirmed by reflection high energy diffraction (RHEED). Interestingly, Fukaya et al. arrived at a different conclusion about the model for the (3×3) superstructure. From their TRHEPD data, they concluded that only one Ge atom per unit cell is higher than the other ones. They proposed an explanation to the discrepancy between the STM results in [13] and their results by suggesting that the second Ge atom might be displaced by the interaction with the STM tip (external electric field applied during scanning).

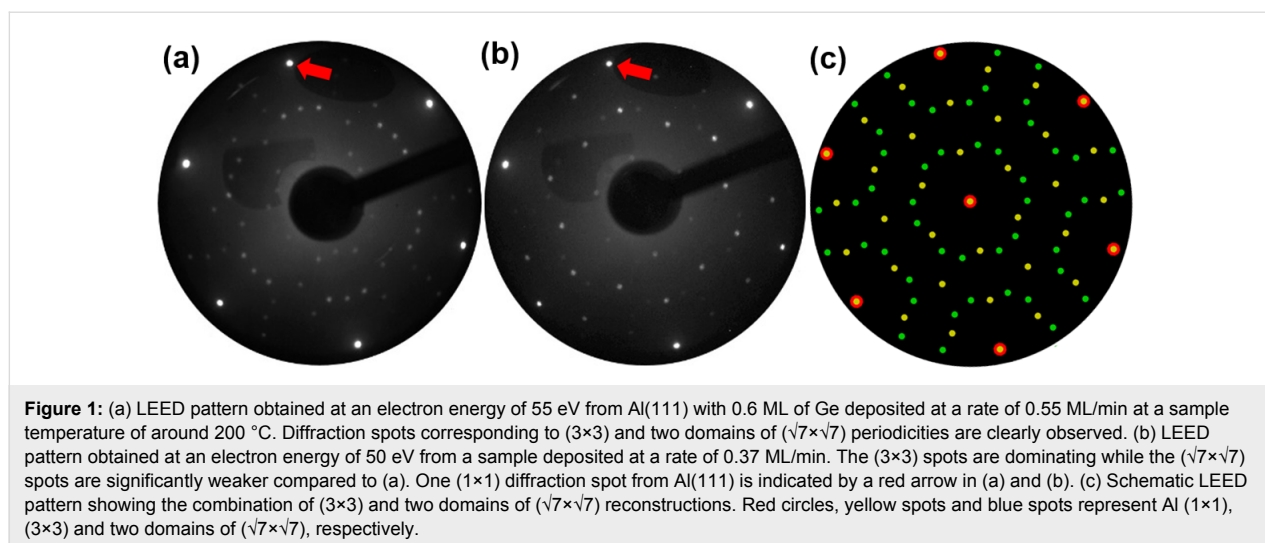
In this paper, we present new data on the Ge/Al(111) system which significantly broadens the view on germanene formation. We show that it is possible to grow well-ordered monolayer Ge at temperatures significantly higher than 87 °C. After deposition at a substrate temperature of ≈ 200 °C, sharp LEED patterns were observed for two phases, i.e., a 3×3 phase and a new $\sqrt{7}\times\sqrt{7}$ superstructure. These phases, formed at higher temperature, deviate from the low temperature phases in the sense that the STM images show hexagonal patterns in contrast to the honeycomb pattern reported in [13]. Our experimental data in combination with DFT calculations lead to a new model that can explain the experimental observations in terms of buckled germanene.

Results and Discussion

Figure 1a shows a LEED pattern, which clearly reveals the coexistence of (3×3) and ($\sqrt{7}\times\sqrt{7}$) periodicities. We find that these two reconstructions coexist with different relative intensities depending on the Ge deposition rate. At a higher rate, e.g., ≈ 0.55 ML/min the ($\sqrt{7}\times\sqrt{7}$) spots appear clearly in the LEED pattern. When Ge is deposited at a lower rate, e.g., ≈ 0.37 ML/min, (3×3) spots dominate, see Figure 1b.

Considering the theoretical value for the germanene lattice (3.92–4.06 Å) and the Al(111) surface lattice (2.864 Å) the (2×2) germanene on ($\sqrt{7}\times\sqrt{7}$) Al(111) has less mismatch than on (3×3) Al(111). Furthermore, these two reconstructions have different signs of the stress, so a coexistence could probably reduce the surface energy.

Figure 2a is an atomically resolved STM image showing two rotated domains of the ($\sqrt{7}\times\sqrt{7}$) reconstruction with a measured periodicity of ≈ 7.5 Å. The orientations of these two domains are indicated by two blue lines, which are labeled $\pm 19^\circ$, respectively. The 0° orientation is indicated by the line in Figure 2b,



which is an atomically resolved STM image of the (3×3) reconstruction with a measured periodicity of ≈ 8.5 Å. Both reconstructions show a hexagonal structure instead of the honeycomb structure of germanene prepared at low temperature (≈ 87 °C) [13].

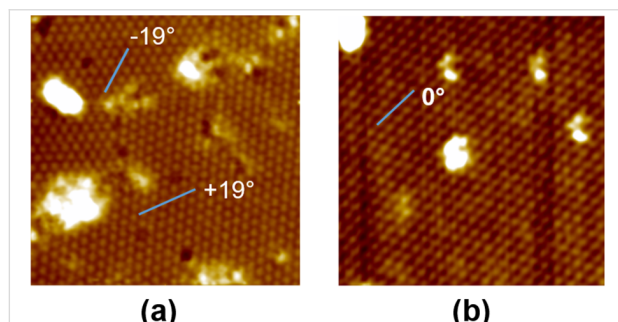
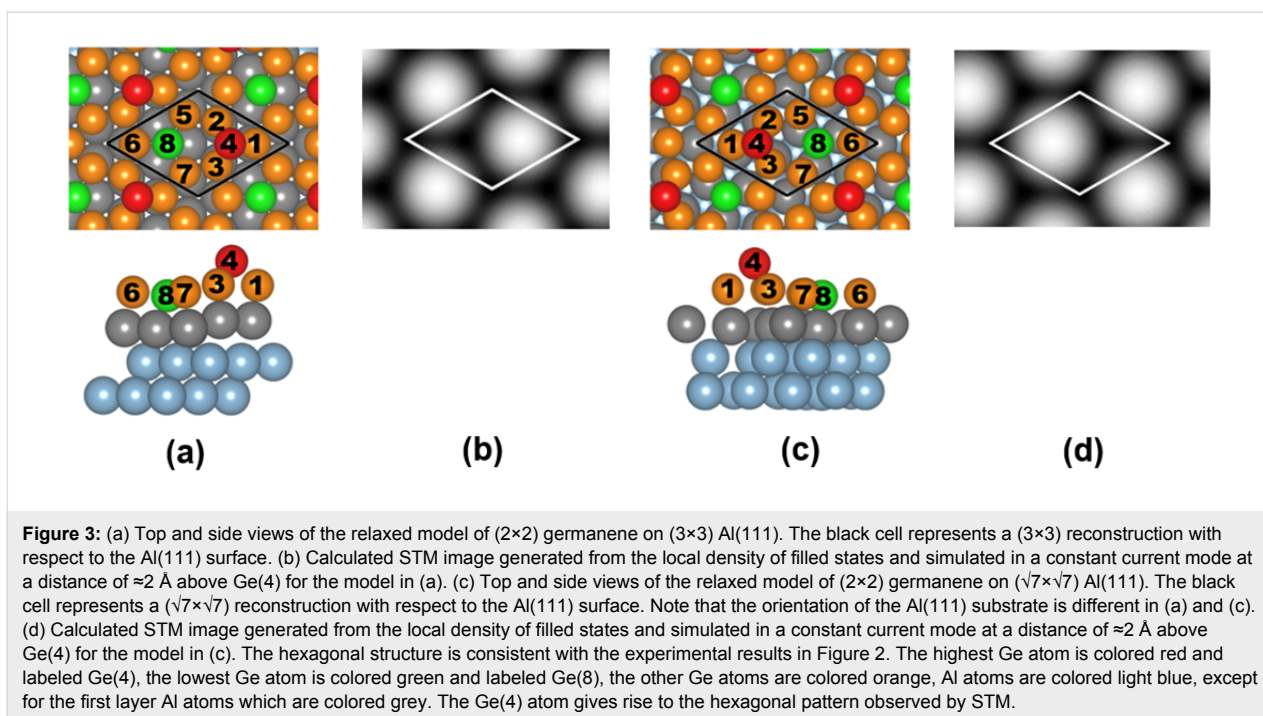


Figure 2: (a) Atomically resolved filled state STM image of a $\approx 19 \times 19$ nm² area showing two rotated hexagonal structures with $\sqrt{7}\times\sqrt{7}$ periodicity. The angle difference between the two blue lines is $\approx 38^\circ$ which corresponds to the $\pm 19.1^\circ$ orientations of the two $\sqrt{7}\times\sqrt{7}$ domains with respect to Al(111). (b) Atomically resolved filled state STM image of a $\approx 19 \times 19$ nm² area showing a single hexagonal structure with (3×3) periodicity. Both images were obtained at room temperature with a sample bias of -1.20 V and a tunneling current of 200 pA.

It is interesting to consider the structural results by Fukaya et al. [14] obtained from the (3×3) reconstruction prepared in a way similar to that in [13], i.e., at low sample temperature and a low evaporation rate. The results from the TRHEPD technique favored an interpretation of the structure as a germanene layer with one Ge atom per (3×3) cell being higher than the other ones and a corresponding model was presented. However, some restrictions during the relaxation prevented their model from being fully relaxed. Starting from their hexagonal model with one Ge atom higher, we find that it relaxes to the honeycomb structure of the model in [13].

We present a natural modification of the model proposed in [14] that can explain the hexagonal appearance of the Ge layer on Al(111). By making a lateral translation of the germanene layer, one can locate two Ge atoms (Ge(4) and Ge(8) in Figure 3) above threefold hollow sites of Al(111). Figure 3a and Figure 3c show fully relaxed atomic models for (2×2) germanene on (3×3)- and $(\sqrt{7}\times\sqrt{7})$ -Al(111). Atom 4 is high while atom 8 is close in height to the rest of the Ge atoms. The height difference (Δz) between Ge(4) and the average level of the other Ge atoms in the (3×3) and $(\sqrt{7}\times\sqrt{7})$ models in Figure 3 is 2.13 and 1.96 Å, respectively, which is much larger than the values (1.21–1.23 Å) in [13] and 0.94 Å in [14]. Figure 3b and Figure 3d show simulated STM images for the (3×3) and $(\sqrt{7}\times\sqrt{7})$ models, respectively, which reproduce the hexagonal structure of the STM images in Figure 2. The detailed information of these two models is available in Supporting Information File 1.

Stephan et al. [15] have presented electron spectroscopy data of the Al 2p and Ge 3d core levels for the (3×3) phase. The Ge layer was prepared at a temperature of about 87 °C and a low evaporation rate (0.005 ML/min) as in [13]. Although no structural information was obtained from the sample used for the core-level study, the authors assumed that the surface had the honeycomb type of (3×3) structure reported in [13]. A Ge 3d spectrum, obtained at a photon energy of 130 eV, was fitted by four components of which one only corresponded to 1 or 2% of the total intensity. The other three components were assigned to three groups of atoms that could be defined from the model. The assignment proposed in [15] implied that the 3d intensity from the two upper Ge atoms was significantly higher than the sum of the intensities from the six remaining Ge atoms. It was suggested that photoelectron diffraction effects could explain the obvious discrepancy between the number of atoms and the



core level intensities. An alternative assignment of the 3d components was suggested by Fukaya et al. [14]. It was proposed that the two smaller components, one on each side of the main component, should be assigned to the up and down Ge atoms and that the major component corresponds to the six remaining Ge atoms. Unfortunately, the intensities of the different components are not given in [15], so a quantitative evaluation is difficult.

In Figure 4, we present a Ge 3d core-level spectrum obtained from a surface on which the (3×3) reconstruction was dominating, as verified by LEED patterns at different electron energies. The spectrum was measured using a photon energy of 135 eV in normal emission. A first attempt to analyze the Ge 3d spectrum is based on grouping Ge atoms by their local environment. In this way one can identify four groups of atoms in the (3×3) model, i.e., Ge(1-3), Ge(4), Ge(5-7) and Ge(8). A calculation of the charges was made using the Bader scheme within VASP. The Ge(1-3) atoms gain 0.18–0.19 electron/atom, while Ge(4) loses 0.15 electron. Ge(5-7) atoms gain 0.33–0.34 electron/atom and Ge(8) gains 0.40 electron. Thus from the Bader charge, four distinct groups of Ge atoms can be verified. A fit using four spin-orbit split components is shown in Figure 4. The relative intensities of components SC1-4 deviate from the expectation that the relative intensities of the four components should be in rough agreement with 1:3:3:1. The intensity of SC2 is quite large while the intensity of SC3 is too small to match an expected intensity of the Ge(5-7) and Ge(1-3) atoms, respectively. Since the LEED pattern showed weak (√7×√7) spots, one has to

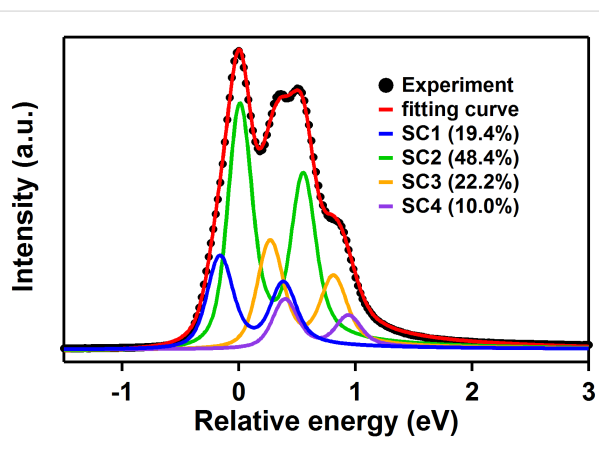


Figure 4: Ge 3d core-level spectrum obtained at a photon energy of 135 eV in normal emission. The dots are the experimental data and the fitting curve is the sum of the SC1 to SC4 components. The relative intensities of the four components are shown as a percentage of the total area in the figure. Fitting parameters: Spin-orbit split: 0.545 eV, Branching ratio: 0.67 for SC1 and SC2, 0.63 for SC3 and SC4. Gaussian widths: 177, 163, 183 and 174 meV, respectively, Lorentzian width: 110 meV. The asymmetry parameter of the Doniach–Šunjić line profile is 0.06. The energy shifts with respect to SC2 are –167, +269 and +389 meV.

consider contributions to the Ge 3d spectrum from (√7×√7) domains as well. Based on the Bader charges calculated for the (√7×√7) model, see Supporting Information File 1, one can expect contribution from (√7×√7) mainly to the intensity of SC2 while no intensity is expected at the position of SC3, which provides a plausible explanation to the difference in the SC2 and SC3 intensities. The above discussion of Ge 3d core level

spectrum is of course tentative and a rigorous analysis can only be done once truly single-phase samples can be achieved.

Conclusion

We have successfully grown monolayer Ge on Al(111) at a substrate temperature of about 200 °C, which is much higher than the “magic” temperature range mentioned in the literature. Our LEED and STM results confirm a coexistence of two well-ordered hexagonal structures with (3×3) and ($\sqrt{7}\times\sqrt{7}$) periodicities with respect to Al (1×1). Our DFT calculations show that the Ge layer relaxes to a hexagonal structure when two Ge atoms are positioned above threefold hollow sites on Al(111). The experimental and theoretical findings are consistent with a strongly buckled (2×2) germanene layer, which is stable in two different orientations on Al(111). The structural model of the germanene is further supported by simulated STM images. The Ge 3d core-level spectrum can be fitted by four components that are suggested by the calculation of charge.

Experimental and Theoretical Details

Samples were prepared in situ in two separate ultrahigh vacuum (UHV) systems. One was equipped with LEED and STM (at Linköping University) and the other with LEED and a 2D electron analyzer for photoelectron spectroscopy (at MAX-lab in Lund). A clean Al(111) surface was prepared by repeated cycles of sputtering by Ar⁺ ions (1 keV) and annealing at approximately 400 °C until a sharp (1×1) LEED pattern was obtained. About 0.6 ML of Ge was deposited at different rates between 0.37 ML/min and 0.55 ML/min while the Al(111) substrate was kept around 200 °C. The reason for depositing less than 1 ML of Ge is to avoid multi-layer formation and the confusion it may lead to. This type of preparation results in a sharp LEED pattern, which is a combination of diffraction from (3×3) and ($\sqrt{7}\times\sqrt{7}$)R=19.1° reconstructions with respect to Al. STM images were recorded at room temperature using an Omicron variable temperature STM in the UHV system at Linköping University. All STM images were measured in constant current mode with a tunneling current of 200 pA. First-principles density functional theory (DFT) calculations were used to investigate the atomic structure of the Ge layer on the Al(111) surface. The structure was modeled by a periodic slab which was built with nine Al layers, one layer of Ge and 15 Å of vacuum spacing. (2×2) germanene was put on top of Al(111)-(3×3) and -($\sqrt{7}\times\sqrt{7}$)R19.1° supercells, respectively. The positions of all atoms were fully relaxed using the functional of Perdew, Burke and Ernzerhof (PBE) and the projector augmented wave (PAW) method Vienna ab initio simulation package (VASP) code [16]. The energy cutoff of the plane-wave basis set was 465 eV, and the k-point mesh was (4×4×1) for both cases. All atoms were relaxed until the average force was within 0.01 eV/Å. Simulated STM images were generated from local density of states

according to the Tersoff–Hamann approach [17]. The charge transfer was calculated by the Bader scheme within VASP.

Supporting Information

Supporting Information File 1

Detailed information of the (3×3) and ($\sqrt{7}\times\sqrt{7}$) models.
[<http://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-8-195-S1.pdf>]

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