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Abstract

Germanene, a single-atom-thick germanium nanosheet in a honeycomb lattice, was proposed to be a Dirac fermion material beyond graphene. We performed scanning tunneling microscopy and in situ Raman spectroscopy studies combined with first-principles calculations on the atomic structures and the electronic and phonon properties of germanene on Au(111). The low-buckled 1×1 germanene honeycomb lattice was determined to exist in an unexpected rectangular $\sqrt{7} \times \sqrt{7}$ superstructure. Through in situ Raman measurements, distinctive vibrational phonon modes were discovered in $\sqrt{7} \times \sqrt{7}$ germanene, revealing the special coupling between the Dirac fermion and lattice vibrations, namely, electron-phonon coupling (EPC). The significant enhancement of EPC is correlated with the tensile strain, which is evoked by the singular buckled structure of $\sqrt{7} \times \sqrt{7}$ germanene on the Au(111) substrate. Our results present clear evidence for the existence of epitaxial germanene and elucidate the exotic properties of germanene on Au(111).

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Cooperative Electron-Phonon Coupling and Buckled Structure in Germanene on Au(111)

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Abstract

Germanene, single-atom-thick germanium nanosheet in a honeycomb lattice, was proposed to be a Dirac-fermion material beyond graphene. We performed scanning tunneling microscopy and *in-situ* Raman spectroscopy studies combined with first-principles calculations on the atomic structures, and the electronic and phonon properties of germanene on Au(111). The low-buckled 1×1 germanene honeycomb lattice was determined to exist in an unexpected rectangular $\sqrt{7} \times \sqrt{7}$ superstructure.

Through *in-situ* Raman measurements, distinctive

vibrational phonon modes were discovered in $\sqrt{7} \times \sqrt{7}$ germanene, revealing the special coupling between Dirac fermion and lattice vibrations, namely, electron-phonon coupling (EPC). The significant enhancement of EPC is correlated with the tensile strain which is evoked by the singular buckled structure of $\sqrt{7} \times \sqrt{7}$ germanene on Au(111) substrate. Our results present clear evidence for the existence of epitaxial germanene, and elucidate the exotic properties of germanene on Au(111).

Two-dimensional (2D) materials with Dirac fermion characteristics have attracted tremendous interest due to their exotic properties, which are relevant for both fundamental research and potential applications.¹⁻⁴ Among these, silicene and germanene, which are the silicon and germanium analogues of graphene, are intriguing because both of them have intrinsic energy gaps in addition to Dirac cones in their electronic band structures.⁵⁻¹³ Unlike the negligible gap of 1.55 meV in silicene, germanene is expected to possess a larger intrinsic gap of 24 meV at the Dirac point due to its greater spin-orbit coupling (SOC) effect.¹⁴⁻¹⁶ It is likely to be a highly promising approach to tune the Fermi level of germanene through electric gating, while keeping its ultra-high charge mobility. Therefore, germanene is regarded as a feasible candidate Dirac-fermion material for the development of high-speed and low-energy-consumption field-effect transistors.¹⁷

In fact, it is surprising that germanium atoms can crystallize into a 2D honeycomb lattice, because the Ge-Ge bond in the bulk germanium is too long to allow the lateral overlapping (shoulder-to-shoulder) of p_z orbitals, thus prohibiting sp^2 hybridization. Consequently, the energetically favorable hybridization state in bulk germanium is the sp^3 state. Theoretical simulations indicate that the adjacent Ge atoms in the germanene unit cell are slightly offset to each other in the out-of-plane directions.¹⁴ Although the elongated bond lengths weaken the π - π interaction in germanene, it may cause distinct coupling of σ and π bonds to form stable buckled structures.^{14,15} This hypothesis was soon verified in recent experiments, in which germanene layers have been successfully epitaxially grown on various metallic and semiconducting substrates.^{10-12,17-21} Abundant reconstructions of epitaxial germanene have been

observed subject to different substrates, for example, 3×3 and 2×2 germanene superstructures (with respect to 1×1 germanene) on Pt(111) and Al(111) surfaces, respectively.^{10,12} These reconstructions indicate that germanene may adopt complicated buckled structures, which are determined by the underlying substrates. Actually, the buckled height of germanene (Δz) seems to be predominantly due to the substrates. For example, Δz is 0.123 nm in germanene grown on Al(111) substrate, but is much smaller (0.064 nm) when the substrate is changed to Pt(111).^{10,12} Because the buckling will have a significant impact on the electronic structure of 2D materials through electron-phonon coupling (EPC),²² the substrate-modulated buckling may provide an additional way to tailor the electronic properties of germanene. Unfortunately, the details of the buckled structures in germanene are still unclear due to the great challenge in observing the 1×1 structure. Therefore, how these buckling structures influence the phonon and electronic properties in germanene remains a puzzle and deserves intensive study.

In this work, we have investigated the superstructures of germanium layers grown on Au(111) substrate by low-temperature scanning tunneling microscopy (STM) and *in-situ* Raman spectroscopy. The honeycomb arrangement of 1×1 germanene was revealed with atomic resolution in a rectangular superstructure, implying the 2D continuous nature of germanene. Combined with first-principles calculations, a structural mode of the $\sqrt{7} \times \sqrt{7}$ reconstruction in respect to buckled 1×1 germanene was identified for this rectangular superstructure. The distinctive phonon mode and EPC in the $\sqrt{7} \times \sqrt{7}$ germanene superstructure on Au(111) attributed to this buckled structure was revealed by *in-situ* Raman spectroscopy. An obvious shift

of the E_{2g} peak indicates large tensile strain residing in the germanene honeycomb lattice due to germanene-substrate interaction, giving rise to a significant enhancement of the EPC strength.

Results and Discussion

The close-packed Au(111) surface shows a $22 \times \sqrt{3}$ reconstruction with a long-range herringbone pattern on the scale of a few hundred nm, as shown in **Figure 1(a)** and **Figure S1** (Supporting Information).²³⁻²⁵ When the substrate temperature is lower than 350 K, Ge nanoclusters tend to form on the Au(111) substrate. With increasing substrate temperature to 400 K, the Ge atoms arrange themselves along the direction of herringbone patterns of Au(111) surface in the sub-monolayer film, establishing a spider-web-like network, as seen in **Figure S2(b)** of Supporting Information. Further deposition leads to Ge atoms growing along the edges of the networks and creates the broader Ge filaments, as shown in **Figure 1(b)**, **Figure S2(c)** and **S2(d)** of Supporting Information. The formation of such the self-assembled Ge network can be attributed to the local discrepancy in the surface electronic structure and molecular reactivity of the Au atoms across different surface sites.^{24,25} **Figure 1(c)** displays the large-scale STM image of Ge film with a coverage slightly more than 1 monolayer (ML) deposited at 400 K, on which the second layer Ge film starts to form in a striped appearance as marked by green arrows. With the increment of the coverage, the number of the stripes increases and their width becomes much broader, as shown in **Figure 1(d)** and **Figure S2(g)** to **S2(i)** of Supporting Information. The evolution of Ge films with different coverages is revealed by STM and is illustrated in **Figure S2** in Supporting Information. Typical high-resolution STM images of

first-layer and second-layer Ge films are shown in **Figure 1(e)** and **1(f)**, respectively. It is found that the first layer show a disordered rhombic-like atomic arrangement, while a long-ranged rectangular reconstruction appears in the second layer. Considering lattice mismatch between Au(111) and epitaxial Ge films, the first-layer Ge film is most likely a buffer layer the subsequent formation of second-layer Ge film. Based on the line profile taken on the second-layer Ge film [**Figure S3(d)** and **S3(e)**, Supporting Information], it reveals that the periodicity of the protrusions in the rectangular reconstruction is between 0.50 nm and 0.54 nm. When the substrate temperature was increased to 600 K in the deposition and found that Ge-Au alloy is formed instead of Ge films (see more details in **S4** part of Supporting Information).

In order to resolve detailed atomic structures in second-layer Ge film and eliminate the effect of the density of states (DOS) in the STM images, we acquired high-resolution STM images in the same area on the second-layer Ge film by applying different sample bias, as shown in **Figure 2(a)-2(c)**. The periodicity of the atomic structure exhibits obvious variation upon the bias. It was found that some protrusions observed in the rectangular reconstruction deviate from their previous sites upon different sample bias applied, as shown in **Figure 2**. The bias dependent surface topography indicates that some of the protrusions may be contributed by several surrounding Ge atoms or electronic effects rather than individual Ge atoms. This deduction is confirmed by STM image in higher resolution, as shown in **Figure 2(c)**, where only the protrusions at certain atomic sites in the superlattice unit cell (labelled by the green squares) are exactly allied to Ge atoms. Interestingly, a honeycomb arrangement with a low-buckled atomic structure was observed in the

second-layer Ge film when a low sample bias of 0.01 V was applied during scanning. The surface periodicity given by the distance between the dark depressions varies from 0.39 nm to 0.43 nm [see **Figure S4(f)-S4(h)**], which agree well with the value for low-buckled FS germanene (3.97–4.06 Å) predicted by theoretical calculations.^{14,26-30} This honeycomb unit cell in **Figure 2(c)** suggests that the second-layer Ge film is the 1×1 germanene layer. *The observation of 1×1 germanene with atomic resolution* provides solid evidence for the existence of germanene rather than the formation of Ge-Au alloy or bulk Ge(111) after deposition of Ge atoms on Au(111) substrate. The higher-resolution STM images are correlated to two factors. One is the small bias voltage, which corresponds to a short distance between tip and sample surface, and increases the atom tunneling current of the buckled-down atom. Another factor is the tip size effect. The high-resolution STM tips used in our work allow us to obtain STM image of 1×1 germanene unit cell.³¹⁻³⁵ In **Figure 2**, the superlattice labeled by the green square can be assigned as a $\sqrt{7} \times \sqrt{7}$ reconstruction in terms of 1×1 germanene. **Figure 2(d)** displays the fast Fourier transform (FFT) pattern of **Figure 2(c)**, where three groups of diffraction patterns are identified and labeled by circles with different colors. To reveal the origin of these patterns, the inverse FFT images of the green circles, yellow circles, and blue circles are displayed in **Figure 2(e)-2(g)**, respectively. Using the $\sqrt{7} \times \sqrt{7}$ unit cell as a reference, the green circles, yellow circles, and blue circles were identified as representing the 1×1 phase, $\sqrt{7}/2 \times \sqrt{7}/2$ phase, and $\sqrt{7} \times \sqrt{7}$ phase of germanene, respectively. The emergence of multiple atomic structures in one image indicates the distinctive but complicated buckling nature of germanene on Au(111).

Note that the lattice constants of the $\sqrt{7} \times \sqrt{7}$ superlattice of germanene are around 1.01 nm and 1.12 nm for the two lattice orientations, which are between $2\sqrt{3}$ times (1.00 nm) and 4 times (1.15 nm) the periodicity of Au(111) (0.288 nm). The $\sqrt{7} \times \sqrt{7}$ unit cell, however, could not be directly assigned to the 4×4 or $2\sqrt{3} \times 2\sqrt{3}$ superstructure [in respect to Au(111) surface], because both of the two superstructures should feature hexagonal symmetry rather than the rectangular unit cell observed in our STM images. Nevertheless, the $4 \times 2\sqrt{3}$ superstructure of Au(111) surface is in a rectangular arrangement, as shown in the schematic diagram of **Figure 3(a)**. Based on the experimental results, the structural model shown in **Figure 3(a)** and **3(b)** is thus proposed as follows: a bilayer germanium nanosheet with a honeycomb arrangement of Ge atoms is adsorbed on the Au(111) surface, where the lattice constant for the $4 \times 2\sqrt{3}$ unit cell of Au(111) matches that of the $\sqrt{7} \times \sqrt{7}$ superlattice in terms of 1×1 germanene. To build the co-periodic lattice of the germanene/Au hybrid system, germanene is stretched in the a direction by 7.3% and compressed in the b direction by 7.2%, respectively. Despite the contraction in the b direction, the Ge-Ge bond lengths in Au-supported germanene are longer than that in FS germanene. The average Ge-Ge bond length in buckled germanene is about 2.563 Å, compared with that in ideal FS germanene (2.443 Å). Detailed information on bond lengths is given in **Figure S8**. Meanwhile, the average height difference Δz between the red Ge atoms and the blue Ge atoms in **Figure 3(b)** is about 1.55 Å, which is two times the buckled height of FS germanene (0.68 Å). Such a large buckling height is the main reason for long Ge-Ge bond length in $\sqrt{7} \times \sqrt{7}$ reconstruction regardless of contraction in b direction. Evidently, the large buckled height in the supported

germanene can be attributed to the interaction with the Au substrate. It should be noted that both of the two Ge layers display the $\sqrt{7} \times \sqrt{7}$ arrangement rather than the direct stack of a $\sqrt{7} \times \sqrt{7}$ monolayer germanene on the top of Ge/Au alloy. Such bilayer germanene structure is stabilized by the interactions between adjacent Ge layers and between Ge nanosheets and Au(111) substrate. All these results manifest that the $\sqrt{7} \times \sqrt{7}$ reconstruction is not the FS germanene. The strong interaction between $\sqrt{7} \times \sqrt{7}$ germanene and Au(111) substrate leads to significant structural changes manifested by buckling height and Ge-Ge bond length. A simulated STM image of bilayer germanene on Au(111) surface is shown in **Figure 3(c)**. The evolution from the atomic structure model to the simulated STM image and then to the experimental STM image in **Figure 3(d)** indicates the agreement between the structural model and the experiment.

Raman spectroscopy is an insightful tool to probe the phonon dynamics in 2D Dirac fermion materials, which is distinct from that of their 3D bulk parent.³⁶ The phonon vibrational properties of all the germanene nanosheets were investigated by *in-situ* Raman measurements to prevent possible oxidization during *ex-situ* measurements. No Raman signal of Au(111) can be detected due to the Rayleigh scattering, as shown in **Figure S7(a)**. The Raman spectra of different Ge nanosheets are shown in **Figure 4(a)**. The buffer layer and Ge-Au alloy do not show any Raman signal, which may be ascribed to the absence of Ge-Ge covalent bonds after the formation of Ge-Au alloy. Interestingly, the Raman spectrum of $\sqrt{7} \times \sqrt{7}$ germanene phase shows two peaks at around 179 cm^{-1} (labeled as peak I) and 228 cm^{-1} (labeled as peak II), respectively. Both Raman peaks are far away from typical

E_{2g} peak of Ge(111). It verifies that the $\sqrt{7} \times \sqrt{7}$ germanene is not a reconstruction of Ge(111) surface.

In order to reveal the origin of these two vibrational modes of $\sqrt{7} \times \sqrt{7}$ germanene, we performed first-principles simulations of the vibration density of states for both FS germanene and bilayer $\sqrt{7} \times \sqrt{7}$ germanene on Au(111) by assuming a defect-free configuration, as shown in **Figure 4(b)**. The simulated spectrum of $\sqrt{7} \times \sqrt{7}$ germanene agree well with the experimental results, in which peak I and II correspond to the out-of-plane transverse optical (oTO) mode and E_{2g} mode, respectively. It should be noted that these two vibration modes could also be identified in simulated results of FS germanene. However, there are obvious frequency shifts for both vibration modes (especially for the E_{2g} mode) in FS germanene compared to these in $\sqrt{7} \times \sqrt{7}$ germanene. Considering the fact that the E_{2g} mode can be modulated by the strain effect in 2D materials,³⁷⁻⁴¹ the relationship between the frequency shift of the E_{2g} mode and stain can be described as:⁴⁰⁻⁴³

$$\Delta\omega = \omega_{Ge} - \omega_0 = -\frac{nv\omega_0(d_{Ge}-d_0)}{a_0} = \alpha\varepsilon \quad (1),$$

where ω_{Ge} and ω_0 are the frequencies of the E_{2g} mode in $\sqrt{7} \times \sqrt{7}$ germanene and FS germanene, respectively; n is the dimensionality of the material; v is the Grüneisen parameter; d_{Ge} and d_0 are the Ge-Ge bond lengths in $\sqrt{7} \times \sqrt{7}$ germanene and FS germanene, respectively. $d_{Ge} = 2.563 \text{ \AA}$ and $d_0 = 2.443 \text{ \AA}$ from our density functional theory (DFT) calculations, as displayed in **Figure S8** Supporting Information, gives 4.91% tensile strain (ε), leading to the frequency of the E_{2g} mode in $\sqrt{7} \times \sqrt{7}$ germanene being downshifted to 240 cm^{-1} by taking the coefficient $\alpha = -940 \text{ cm}^{-1}$, which is comparable to but still a bit larger than that of

peak II in Raman spectra (228 cm^{-1}). There should be another factor contributing to the shift of the phonon frequency if peak II corresponds to the E_{2g} mode of $\sqrt{7} \times \sqrt{7}$ germanene. In fact, the E_{2g} vibration at the zone center (Γ point) couples with Dirac fermions at the zone boundary (K points), which is allowed by germanene lattice symmetry. The carriers in the honeycomb lattice mutually interact with the E_{2g} mode through dynamical perturbations due to the creation and annihilation of virtual long-wavelength electron-hole pairs across the gapless Dirac point.⁴⁴ The energy range of the virtual electron-hole pairs allowed by the Pauli principle is determined by the position of the Fermi energy (E_F). The E_F of $\sqrt{7} \times \sqrt{7}$ germanene is expected to be lifted by the electron doping from the Au(111) substrate, leading to a shift of the mode frequency. The doping-induced shift of the E_{2g} frequency has been predicted by previous theoretical simulations.^{22,45} The Raman results for the $\sqrt{7} \times \sqrt{7}$ phase of germanene on Au(111) display distinctive phonon modes distinct from those of Ge(111), which can be used as the Raman fingerprint to identify germanene on the Au(111) surface.

The shift of the E_{2g} phonon frequencies in 2D materials reflects the variation of EPC strength by the following relationship: $\gamma = N_F V_{ep} \sim \omega^{-2}$, where γ is a dimensionless parameter representing the EPC strength, N_F is the electron density of states (EDOS) at the Fermi level, and V_{ep} is the mean electron-phonon coupling potential at the Fermi level.^{37,46,47} The N_F could be modulated by electron doping from substrate, while the tensile strain induced decrement of the energy of optical phonons in $\sqrt{7} \times \sqrt{7}$ germanene gives rise to higher electron-phonon potential. In order to make a quantitative analysis of the Raman frequency dependence of EPC

strength, the EPC matrix elements for the optical modes in germanene are introduced as:^{22,47}

$$g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\mathbf{qv}} = \langle \mathbf{k} + \mathbf{q} | V_{\mathbf{qv}} \delta\mu | \mathbf{k} \rangle \quad (2),$$

where $V_{\mathbf{qv}}$ is the deformation potential operator associated with the phonon mode ($\mathbf{q}$, v), and $\delta\mu$ is the zero-point oscillation amplitude of a quantum particle. In graphene, the optical branch dominating the EPC is the in-plane C-C stretching mode (E_{2g}) which is defined as a characteristic phonon mode (ω_0) in EPC matrix elements. Thus, the Equation (2) could be simplified as:

$$g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\mathbf{qv}} = \frac{\langle \mathbf{k}+\mathbf{q} | V_{\mathbf{qv}} | \mathbf{k} \rangle}{\sqrt{2M\omega_0}} \quad (3).$$

Considering that γ is correlated to the renormalization of electronic energy spectrum at Fermi surface, we calculated the value of γ by applying a simple second-order perturbation:

$$\gamma \approx \sum_{\mathbf{q},v} \frac{|g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\mathbf{qv}}|^2}{E_{\mathbf{k}+\mathbf{q}}^0 - E_{\mathbf{k}}^0} \delta(E_{\mathbf{k}+\mathbf{q}}^0 - E_{\mathbf{k}}^0 - \omega_0) \propto \omega^{-2} \quad (4).$$

This relation originates from the zero-point oscillation amplitude induced by large deformation and the energy reconstruction in the perturbation theory. According to the E_{2g} peak shift from 290 cm^{-1} (FS germanene) to 228 cm^{-1} ($\sqrt{7} \times \sqrt{7}$ germanene), the EPC in $\sqrt{7} \times \sqrt{7}$ germanene is enhanced by up to 60%. It should be noted that the intrinsic linewidth in a defect-free sample is contributed by two factors, namely, electron-phonon interaction and anharmonic phonon-phonon interaction.⁴⁸⁻⁵⁰ Therefore, the enhancement of EPC strength in $\sqrt{7} \times \sqrt{7}$ germanene on Au(111) substrate is expected to evoke a larger linewidth of E_{2g} peak similar to that in graphene.^{44,50,51} In fact, the E_{2g} peak linewidth of $\sqrt{7} \times \sqrt{7}$ germanene ($\sim 21.1 \text{ cm}^{-1}$)

is much larger than that of FS germanene ($\sim 1 \text{ cm}^{-1}$) from previous simulation,²² as shown in **Table I** of Supporting Information, confirming the indication of the enlarged EPC strength in $\sqrt{7} \times \sqrt{7}$ germanene. Both the simulated electronic density of state (EDOS) and experimentally measured scanning tunneling spectroscopy (STS) results reveal a metallic behavior of $\sqrt{7} \times \sqrt{7}$ germanene, as shown in **Figure S9(b)** and **S9(c)**. This distinguishes from the semimetal electronic structure of FS germanene. Such a tremendous change in $\sqrt{7} \times \sqrt{7}$ germanene could be partly ascribed to the enhanced EPC strength and the modulated phonon frequency by Au(111). The enhancement of the EPC is of particular interest because it gives rise to Kohn anomalies and superconductivity in the Bardeen-Cooper-Schrieffer (BCS) superconductors,^{44,47,52} paving the way to its further characterization and potential applications for this new 2D material.

Conclusion

In summary, germanium layers on Au(111) with different structures have been identified by STM and *in-situ* Raman spectroscopy. The honeycomb 1×1 germanene with buckled structure has been identified in a $\sqrt{7} \times \sqrt{7}$ superstructure, as demonstrated by both the atomic-resolution STM images and first-principles calculations. The *in-situ* Raman spectra reveal the distinct phonon modes in $\sqrt{7} \times \sqrt{7}$ germanene, which provides a clear evidence for the formation of germanene rather than the building blocks of bulk germanium crystal or Ge-Au alloy. Our results indicate a significant enhancement of the EPC strength in $\sqrt{7} \times \sqrt{7}$ germanene due to the lattice mismatch between the germanene layers and the Au(111) substrate, suggesting a possible means to modulate the physical properties of germanene and to

realize its possible integration with ubiquitous nanotechnology.

Methods

All samples used in this work were fabricated in a preparation chamber supplied with a low-temperature STM/scanning near-field optical microscopy system (LT-STM-SNOM, SNOM1400, Unisoku Co.). Clean Au(111) substrates were prepared by argon ion sputtering and annealed at 850 K for several cycles. The germanium nanosheets were then deposited on the Au(111) surfaces by evaporation of germanium from a heated germanium wafer. The deposition flux of Ge was 0.02 monolayers per minute (ML/min). *In-situ* Raman spectra were acquired on the samples for the same areas as in the STM measurements. The Raman laser irradiation ($\lambda = 532$ nm) was delivered through a single-mode optical fiber around 3 μm in diameter into the measurement chamber of the STM-SNOM system. All the measurements were carried on in ultrahigh vacuum (UHV) at 77 K.

In the case of the first-principles calculations, all geometry optimization and simulation of STM images of Au(111)-supported germanene were carried out using the Vienna *Ab Initio* Simulation Package (VASP) based on density functional theory and planewave basis.⁵³ The electron-ion interactions were represented by the projector augmented wave (PAW) potentials.⁵⁴ The STM images were simulated by using the Tersoff-Hamann approximation with a constant height of 2 Å above the buckled-up Ge atoms.⁵⁵ Meanwhile, the Raman spectrum and phonon vibrational modes of FS germanene were investigated using the CASTEP code based on DFT, the planewave basis, and norm conserving pseudopotentials.⁵⁶ In all DFT calculations, we chose the Perdew–Burke–Ernzerhof (PBE) functional within the generalized-gradient

approximation (GGA) to treat the exchange-correlation interaction of electrons.⁵⁷ A kinetic energy cut-off of 400 eV for the planewave basis and a convergence criterion of 10^{-5} eV for the total energies were carefully tested and adopted in all calculations.

Associated content

Supporting Information

STM images of Au(111) surface, Ge nanosheets with different coverages, STM images of striped structure with different orientations, and simulated Raman spectra and EDOS of FS germanene and $\sqrt{7} \times \sqrt{7}$ germanene as well as the experimental STS results of $\sqrt{7} \times \sqrt{7}$ germanene.

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References

1. Zhang, Y. B.; Tan, Y. W.; Stormer, H. L.; Kim, P. Experimental Observation of The Quantum Hall Effect and Berry's Phase in Graphene. *Nature* **2005**, *438*, 201-204.
2. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *438*, 197-200.
3. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109-162.
4. Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. Large-scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. *Nature* **2009**, *457*, 706-710.
5. Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M. C.; Resta, A.; Ealet, B.; Le Lay, G. Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. *Phys. Rev. Lett.* **2012**, *108*, 155501.
6. Feng, B. J.; Ding, Z. J.; Meng, S.; Yao, Y. G.; He, X. Y.; Cheng, P.; Chen, L.; Wu, K. H. Evidence of Silicene in Honeycomb Structures of Silicon on Ag(111). *Nano Lett.* **2012**, *12*, 3507-3511.
7. Fleurence, A.; Friedlein, R.; Ozaki, T.; Kawai, H.; Wang, Y.; Yamada-Takamura, Y. Experimental Evidence for Epitaxial Silicene on Diboride Thin Films. *Phys. Rev. Lett.* **2012**, *108*, 245501.
8. Meng, L.; Wang, Y. L.; Zhang, L. Z.; Du, S. X.; Wu, R. T.; Li, L. F.; Zhang, Y.; Li, G.; Zhou, H. T.; Hofer, W. A.; Gao, H. J. Buckled Silicene Formation on Ir(111). *Nano Lett.* **2013**, *13*, 685-690.

9. Du, Y.; Zhuang, J. C.; Liu, H. S.; Xu, X.; Eilers, S.; Wu, K. H.; Cheng, P.; Zhao, J. J.; Pi, X. D.; See, K. W.; Peleckis, G.; Wang, X. L.; Dou S. X. Tuning the Band Gap in Silicene by Oxidation. *ACS Nano* **2014**, *8*, 10019-10025.
10. Li, L. F.; Lu, S. Z.; Pan, J. B.; Qin, Z. H.; Wang, Y. Q.; Wang, Y. L.; Cao, G. Y.; Du, S. X.; Gao, H. J. Buckled Germanene Formation on Pt(111). *Adv. Mater.* **2014**, *26*, 4820-4824.
11. Dávila, M. E.; Xian, L.; Cahangirov, S.; Rubio, A.; Le Lay, G. Germanene: A Novel Two-Dimensional Germanium Allotrope Akin to Graphene and Silicene. *New J. Phys.* **2014**, *16*, 095002.
12. Derivaz, M.; Dentel, D.; Stephan, R.; Hanf, M. C.; Mehdaoui, A.; Sonnet, P.; Pirri, C. Continuous Germanene Layer on Al(111). *Nano Lett.* **2015**, *15*, 2510-2516.
13. Zhao, J.; Liu, H.; Yu, Z.; Quhe, R.; Zhou, S.; Wang, Y.; Liu, C. C.; Zhong, H.; Han, N. L. Rise of Silicene: A Competitive 2D Material. *Prog. Mater Sci.* **2016**, *83*, 24-151.
14. Liu, C. C.; Feng, W. X.; Yao, Y. G. Quantum Spin Hall Effect in Silicene and Two-Dimensional Germanium. *Phys. Rev. Lett.* **2011**, *107*, 076802.
15. Liu, C. C.; Jiang, H.; Yao, Y. G. Low-energy Effective Hamiltonian Involving Spin-Orbit Coupling in Silicene and Two-Dimensional Germanium and Tin. *Phys. Rev. B* **2011**, *84*, 195430.
16. Zhou, S.; Zhao, J. Electronic Structures of Germanene on MoS₂: Effect of Substrate and Molecular Adsorption. *J. Phys. Chem. C* **2016**, *120*, 21691-21698.
17. Dávila, M. E.; Le Lay, G. Few Layer Epitaxial Germanene: A Novel Two-Dimensional Dirac Material. *Sci. Rep.* **2016**, *6*, 20714.
18. Stephan, R.; Hanf, M. C.; Derivaz, M.; Dentel, D.; Asensio, M. C.; Avila, J.;

- Mehdaoui, A.; Sonnet, P.; Pirri, C. Germanene on Al(111): Interface Electronic States and Charge Transfer. *J. Phys. Chem. C* **2016**, *120*, 1580-1585.
19. Zhang, L.; Bampoulis, P.; van Houselt, A. Zandvliet, H. Two-Dimensional Dirac Signature of Germanene. *Appl. Phys. Lett.* **2015**, *107*, 111605.
20. d'Acapito, F.; Torrenco, S.; Xenogiannopoulou, E.; Tsipas, P.; Velasco, J. M.; Tsoutsou, D.; Dimoulas, A. Evidence for Germanene Growth on Epitaxial Hexagonal (h)-AlN on Ag(111). *J. Phys.: Condens. Matter* **2016**, *28*, 045002.
21. Zhang, L.; Bampoulis, P.; Rudenko, A.; Yao, Q.; van Houselt, A.; Poelsema, B.; Katsnelson, M.; Zandvliet, H. Structural and Electronic Properties of Germanene on MoS₂. *Phys. Rev. Lett.* **2016**, *116*, 256804.
22. Yan, J. A.; Stein, R.; Schaefer, D. M. Electron-Phonon Coupling in Two-Dimensional Silicene and Germanene. *Phys. Rev. B* **2013**, *88*, 121403.
23. Narasimhan, S.; Vanderbilt, D. Elastic Stress Domains and The Herringbone Reconstruction on Au(111). *Phys. Rev. Lett.* **1992**, *69*, 1564-1567.
24. Maksymovych, P.; Sorescu, D. C.; Yates, J. T. Gold-Adatom-Mediated Bonding in Self-Assembled Short-Chain Alkanethiolate Species on the Au(111) Surface. *Phys. Rev. Lett.* **2006**, *97*, 146103.
25. Hanke, F.; Björk, J. Structure and Local Reactivity of The Au(111) Surface Reconstruction. *Phys. Rev. B* **2013**, *87*, 235422.
26. Özçelik, V. O.; Durgun, E.; Ciraci, S. Physical Processes in Nanomaterials and Nanostructures. *J. Phys. Chem. Lett.* **2014**, *5*, 2694-2699.
27. O'Hare, A.; Kusmartsev, F. V.; Kugel, K. A Stable "Flat" Form of Two-Dimensional Crystals: Could Graphene, Silicene, Germanene Be Minigap

Semiconductors? *Nano Lett.* **2012**, *12*, 1045-1052.

28. Matthes, L.; Pulci, O.; Bechstedt, F. Optical Properties of Two-Dimensional Honeycomb Crystals Graphene, Silicene, Germanene, and Tinene From First Principles. *New J. Phys.* **2014**, *16*, 105007.

29. Scalise, E.; Houssa, M.; Pourtois, G.; van den Broek, B.; Afanas'ev, V.; Stesmans, A. Vibrational Properties of Silicene and Germanene. *Nano Res.* **2013**, *6*, 19-28.

30. Cahangirov, S.; Topsakal, M.; Aktürk, E.; Şahin, H.; Ciraci, S. Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium. *Phys. Rev. Lett.* **2009**, *102*, 236804.

31. Lee, H. J.; Ho, W. Single-Bond Formation and Characterization with a Scanning Tunneling Microscope. *Science* **1999**, *286*, 1719-1722.

32. Gross, L.; Moll, N.; Mohn, F.; Curioni, A.; Meyer, G.; Hanke, F.; Persson, M. High-Resolution Molecular Orbital Imaging Using a p-Wave STM Tip. *Phys. Rev. Lett.* **2011**, *107*, 086101.

33. Chaika, A. N.; Myagkov, A. N. Seeing the Atomic Orbitals in STM Images of A Si(111)-(7 × 7) Surface. *J. Phys. Conf. Ser.* **2008**, *100*, 012020.

34. Wang, Y. L.; Gao, H. J.; Guo, H. M.; Liu, H. W.; Batyrev, I. G.; McMahon, W. E.; Zhang, S. B. Tip size effect on the appearance of a STM image for complex surfaces: Theory *versus* experiment for Si(111)-(7×7). *Phys. Rev. B* **2004**, *70*, 073312.

35. Wang, Y. L.; Cheng, Z. H.; Deng, Z. T; Guo, H. M.; Du, S. X.; Gao, H. J. *CHIMIA* **2012**, *66*, 30-37.

36. Kopnin, N. B.; Sonin, E. B. BCS Superconductivity of Dirac Electrons in Graphene Layers. *Phys. Rev. Lett.* **2008**, *100*, 246808.

37. Zhuang, J. C.; Xu, X.; Du, Y.; Wu, K. H.; Chen, L.; Hao, W. C.; Wang, J. O.; Yeoh, W. K.; Wang, X. L.; Dou, S. X. Investigation of Electron-Phonon Coupling in Epitaxial Silicene by *In Situ* Raman Spectroscopy. *Phys. Rev. B* **2015**, *91*, 161409.
38. Speck, F.; Jobst, J.; Fromm, F.; Ostler, M.; Waldmann, D.; Hundhausen, M.; Weber, H. B.; Seyller, Th. The Quasi-Free-Standing Nature of Graphene on H-Saturated SiC(0001). *Appl. Phys. Lett.* **2011**, *99*, 122106.
39. Röhl, J.; Hundhausen, M.; Emtsev, K. V.; Seyller, Th.; Graupner, R.; Le Lay, G. Raman Spectra of Epitaxial Graphene on SiC(0001). *Appl. Phys. Lett.* **2008**, *92*, 201918.
40. Lockwood, D. J.; Baribeau, J. M. Strain-shift Coefficients for Phonons in $\text{Si}_{1-x}\text{Ge}_x$ Epilayers on Silicon. *Phys. Rev. B* **1992**, *45*, 8565-8571.
41. Wang, R. P.; Zhou, G. W.; Liu, Y. L.; Pan, S. H.; Zhang, H. Z.; Yu, D. P.; Zhang, Z. Raman Spectral Study of Silicon Nanowires: High-Order Scattering and Phonon Confinement Effects. *Phys. Rev. B* **2000**, *61*, 16827-16832.
42. Olego, D.; Cardona, M. Pressure Dependence of Raman phonons of Ge and 3C-SiC. *Phys. Rev. B* **1982**, *25*, 1151-1160.
43. Cerdeira, F.; Buchenauer, C. J.; Pollak, F. H.; Cardona, M. Stress-Induced Shifts of First-Order Raman Frequencies of Diamond- and Zinc-Blende-Type Semiconductors. *Phys. Rev. B* **1972**, *5*, 580-593.
44. Yan, J.; Zhang, Y. B.; Kim, P.; Pinczuk, A. Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene. *Phys. Rev. Lett.* **2007**, *98*, 166802.
45. Kopnin, N. B.; Sonin, E. B. BCS Superconductivity of Dirac Electrons in Graphene Layers. *Phys. Rev. Lett.* **2008**, *100*, 246808.

46. McMillan, W. Transition Temperature of Strong-Coupled Superconductors. *Phys. Rev.* **1968**, *167*, 331-344.
47. Si, C.; Liu, Z.; Duan, W. H.; Liu, F. First-Principles Calculations on the Effect of Doping and Biaxial Tensile Strain on Electron-Phonon Coupling in Graphene. *Phys. Rev. Lett.* **2013**, *111*, 196802.
48. Shukla, A.; Calandra, M.; d'Astuto, M.; Lazzeri, M.; Mauri, F.; Bellin, C.; Krisch, M.; Karpinski, J.; Kazakov, S. M.; Jun, J.; Daghero, D.; Parlinski, K. Phonon Dispersion and Lifetimes in MgB_2 . *Phys. Rev. Lett.* **2003**, *90*, 095506.
49. Debernardi, A.; Baroni, S.; Molinari, E. Anharmonic Phonon Lifetimes in Semiconductors from Density-Functional Perturbation Theory. *Phys. Rev. Lett.* **1995**, *75*, 1819-1822.
50. Bonini, N.; Lazzeri, M.; Marzari, N.; Mauri, F. Phonon Anharmonicities in Graphite and Graphene. *Phys. Rev. Lett.* **2007**, *99*, 176802.
51. Pisana, S.; Lazzeri, M.; Casiraghi, C.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Mauri F. Breakdown of the Adiabatic Born–Oppenheimer Approximation in Graphene. *Nat. Mater.* **2007**, *6*, 198-201.
52. Piscanec, S.; Lazzeri, M.; Mauri, F.; Ferrari, A. C.; Robertson, J. Kohn Anomalies and Electron-Phonon Interactions in Graphite. *Phys. Rev. Lett.* **2004**, *93*, 185503.
53. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *ab initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169-11186.
54. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758-1775.
55. Tersoff, J.; Hamann, D. R. Theory and Application for the Scanning Tunneling

Microscope. *Phys. Rev. Lett.* **1983**, 50, 1998-2001.

56. Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. First Principles Methods Using CASTEP. *J. Phys.: Condens. Matter* **2002**, 14, 2717-2744.

57. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

Figures and figure captions

Figure 1 Differential STM images of (a) clean Au(111) surface with herringbone pattern ($V_{\text{bias}} = -1.5$ V, $I = 50$ pA), (b) germanium sheet with 0.6 monolayer coverage ($V_{\text{bias}} = 4.0$ V, $I = 50$ pA), (c) germanium sheet with 1.0 monolayer coverage ($V_{\text{bias}} = 3.0$ V, $I = 50$ pA), and (d) germanium sheet with 1.3 monolayer coverage ($V_{\text{bias}} = 3.6$ V, $I = 50$ pA), respectively. The green arrows are labelled to point out the position of the second layer. High resolution STM images of (e) first layer germanium sheet ($V_{\text{bias}} = -3.0$ V, $I = 60$ pA) and (f) second layer germanium sheet ($V_{\text{bias}} = 0.02$ V, $I = 50$ pA), respectively.

Figure 2 STM images of $\sqrt{7} \times \sqrt{7}$ germanene phase scanned with different bias voltages: (a) $4 \text{ nm} \times 4 \text{ nm}$, $V_{\text{bias}} = 0.1 \text{ V}$, $I = 50 \text{ pA}$; (b) $4 \text{ nm} \times 4 \text{ nm}$, $V_{\text{bias}} = -0.04 \text{ V}$, $I = 50 \text{ pA}$; and (c) $4 \text{ nm} \times 4 \text{ nm}$, $V_{\text{bias}} = 0.01 \text{ V}$, $I = 50 \text{ pA}$. (d) FFT of panel (c) displays three groups of diffraction patterns, labelled by the green circles, yellow circles, and blue circles, respectively. (e)-(g) are the inverse FFT images of the green circles, yellow circles, and blue circles in panel (d), respectively. The green squares are plotted to illustrate the unit cell of $\sqrt{7} \times \sqrt{7}$ germanene. The red honeycomb in (e) stands for the unit cell of 1×1 germanene.

Figure 3 Top (a) and side (b) views of relaxed model of atomic structure of the $\sqrt{7} \times \sqrt{7}$ germanene/ $4 \times 2\sqrt{3}$ Au(111) configuration. Ge atoms in different layers with different heights are labelled by different colors. The red rectangle stands for the unit cell of $\sqrt{7} \times \sqrt{7}$ germanene. The a , b vectors stand for lattice directions. Δz stands for the buckling height of $\sqrt{7} \times \sqrt{7}$ germanene. The Ge atoms in the buffer layer are labeled by light blue, while the Ge atoms in the upper layer with different heights are labeled by red, green, and dark blue, respectively. (c) Simulated STM image of $\sqrt{7} \times \sqrt{7}$ germanene. (d) Schematic diagram of the evolution from the relaxed model of atomic structure to the simulated STM image and then to the experimental STM image (from left to right).

Figure 4 (a) Raman spectra of buffer layer, Ge-Au alloy, and $\sqrt{7} \times \sqrt{7}$ germanene phase. (b) DFT calculations of the vibration density of states of both FS monolayer germanene and $\sqrt{7} \times \sqrt{7}$ germanene on Au(111). (c) Simulated vibration modes of FS germanene and $\sqrt{7} \times \sqrt{7}$ germanene/ $4 \times 2\sqrt{3}$ Au(111) configuration, respectively. The green vectors in the insets show the eigendisplacements of the E_{2g} mode and oTO mode calculated from the dynamical matrix.

TOC