An interesting ordered phase of germanene on Ag(111) with several repeating motifs and a sharp Fourier transform spectrum, and yet no translational symmetry.

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ABSTRACT

While the family of 2D materials under active study has exploded over the last decade or two (Xenes, TMDs and others) They are usually studied experimentally in their simplest and most pristine (ordered, crystalline) state, which is what theoretical models based on unit cells model (e.g. DFT). But unusual and interesting behaviors can arise in materials which deviate from their perfectly ordered "ideal" forms (e.g. high entropy alloys and quasicrystals).

Here we examine in detail a particularly interesting ordered honeycomb phase of germanene formed on Ag(111) made of a mixture of 5, 6, and 7 sided rings with several repeating local motifs, and surprisingly sharp Fourier transforms which differ for different height cuts, and yet no obvious translational symmetry! We leverage pattern recognition techniques to search a large area, atomic resolution scan to find all instances of each motif and map their distribution.

A final comparison of these results to published, mathematically proven 2D quasicrystals is included.

INTRODUCTION

The growth mechanisms of two-dimensional or "2D" materials are varied. Even for the simplest honeycomb Xenes growth via segregation (diffusion of atoms up through the substrate) CVD nucleation and growth, and dealloying of an initial stoichiometric alloy are all observed and exploited. For germanene formation on Ag(111), evolution from Ag_2Ge through $AgGe_2$ to stripe phase (SP) germanene relaxing to quasi-freestanding (QP) germaene retaining its 30˚ rotation wrt the underlying Ag(111) surface from the initial (√3, √3)R30 alloy origin is well documented. Once the QP phase relaxes to its natural lattice constant of about 3.9Å, the resulting, predictable moiré pattern is seen in both low energy electron diffraction (LEED) and in scanning tunneling microscopy imaging and it's Fourier transform (STM/FT-STM) as shown below.

We discovered that by growing adjacent domains of Pb(111) next to 30˚ QP germanene, we were able to improve the QP quality (as inferred from sharper LEED diffraction and FT-STM spots) an simultaneously induce a +/- 3˚ from it's initial 30˚ orientation.

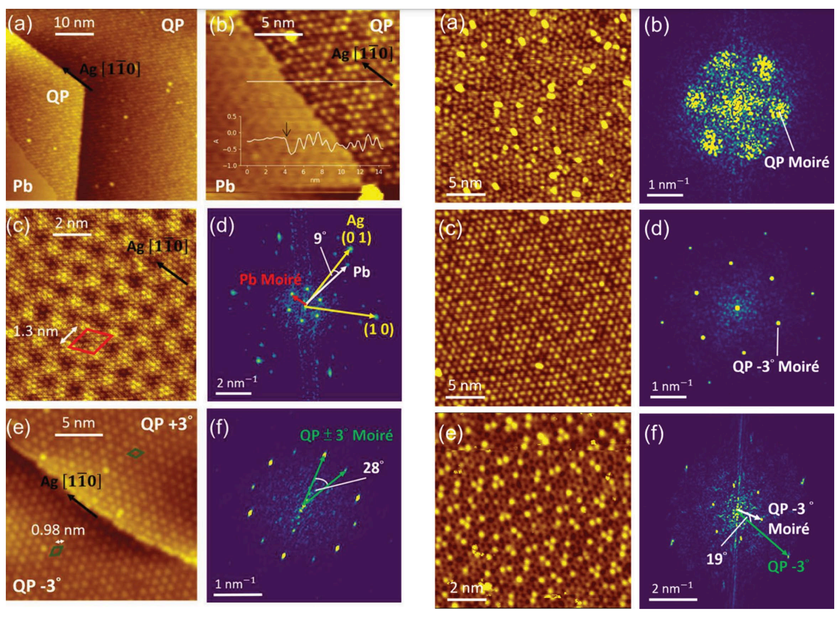
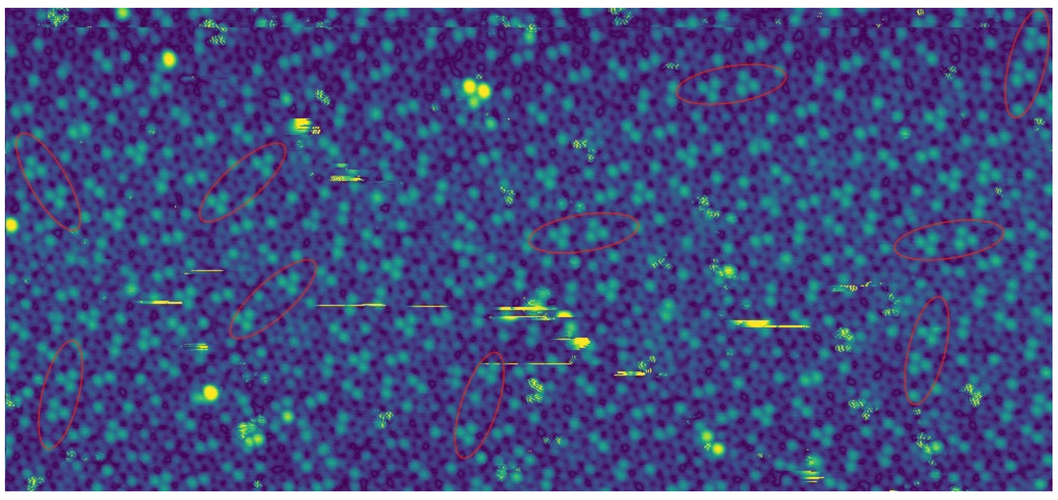


FIG. 6. Scanning tunneling microscopy (STM) images for coexisting quasifreestanding-phase (QP) germanene and monatomic Pb layer. (a) The topographic view of coexisting QP germanene domains separated by Ag step edges and a monatomic Pb layer. (b) The topographic view near the boundary between monatomic Pb layer and QP germanene, cropped from the bottom left of (a). The line profile of height is superimposed with an arrow indicating the position of boundary [50 × 50 nm, 1.05 V, and 0.47 nA for (a) and 20 × 20 nm, 1.05 V, and 0.47 nA for (b)]. (c) The magnified view of monatomic Pb layer (10 × 10 nm, 0.002 V, and 1.0 nA). (d) The Fourier transform of (c). (e) The topographic view of the two domains of QP germanene (√13/√7 × √13/√7)R30 ± 3◦, with a Ag(111) step edge as the domain boundary (20 × 20 nm, 1.0 V, and 0.41 nA). (f) The Fourier transform of (e).

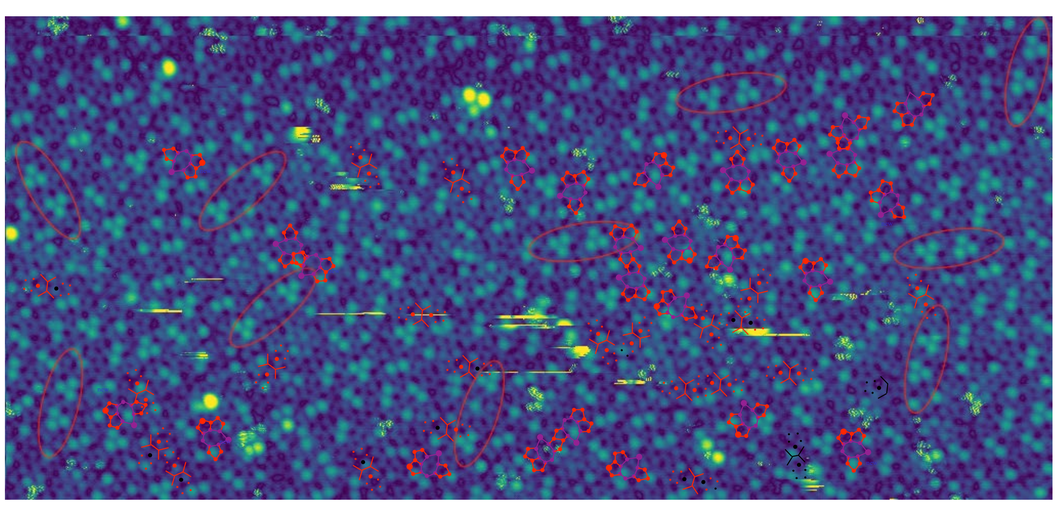
FIG. 7. Comparison between the quasifreestanding-phase (QP) germanene coexisting with monatomic Pb layer and the standalone QP germanene on Ag(111) on lattice. (a) Scanning tunneling microscopy (STM) topographic view of moiré lattice of standalone QP germanene on Ag(111), ~ (7√3/9 × 7√3/9)R30◦ (25 × 25 nm, 1.0 V, and 1.0 nA). (b) The Fourier transform of (a). (c) STM topographic view of moiré lattice of QP germanene (√13/√7 × √13/√7) R30−3◦, coexisting with monatomic Pb layer (25 × 25 nm, 1.0 V, and 0.45 nA). (d) The Fourier transform of (c). (e) The magnified view of QP germanene (√13/√7 × √13/√7) R30−3◦, coexisting with monatomic Pb layer to reveal honeycomb lattice (10 × 10 nm, 0.002 V, and 1.36 nA). (f) The Fourier transform of (e).

ATOMIC RESOLUTION

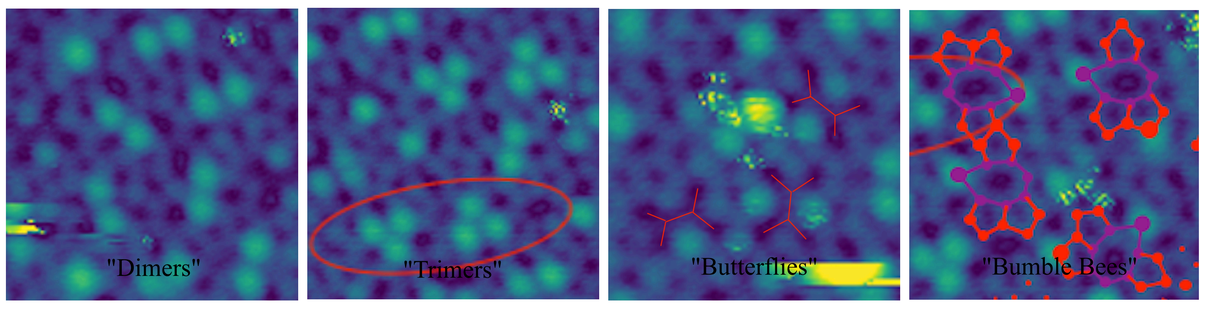
ATOMIC RESOLUTION STM IMAGE OF GERMANENE
topography mode; sample bias: +1.75 mV, current: 1.36 nA, temperature: 0.76 K



ATOMIC RESOLUTION STM IMAGE OF GERMANENE – with annotations



ATOMIC RESOLUTION STM IMAGE OF GERMANENE – various "motifs" noticed



While the resolution of the STM image is not quite good enough to unambiguously identify the germanium atoms that comprise the net, it is clear that it is made of primarily 5, 6 and 7-sided polygons with vertices almost always produced by the intersection of three edges, as would be expected for glass-like amorphous germanene. ***However***, further on we will see that there is substantial mid- and long-range order within this large scan.

EXAMPLES OF TEMPLATES FORMED BY AVERAGING MANY INSTANCES

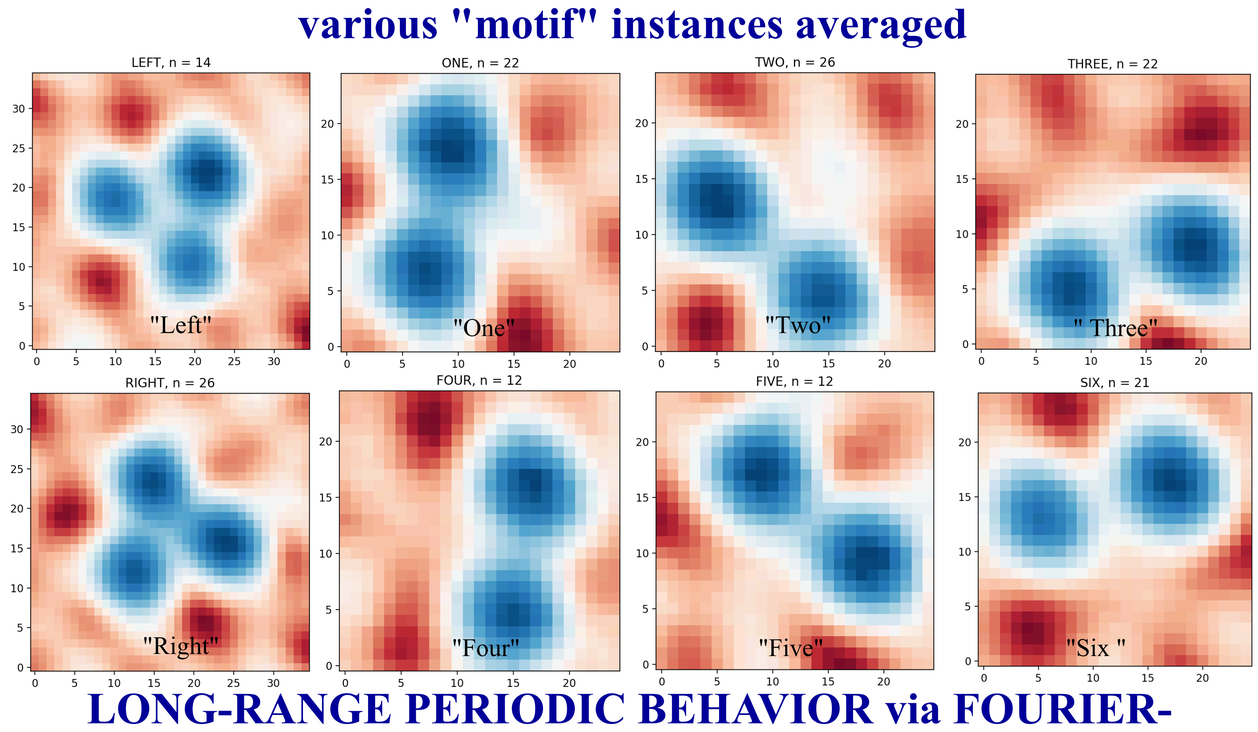
The search is on!

There is much work yet to be done to find all recurring motifs and all of the long-range order present in the data. This is a work-in-progress.

For the Dimers and Trimers – the easiest-to-spot patterns, we identified about 150 and 50 instances for each (respectively, removed a few of the nosiest instances and then aligned and averaged the remainders to form "templates" with which we can go back and scan the data for all possible matches.

We found two orientations for the trimers, called "left" and "right"-pointing. We recognized that the dimers are most likely imperfectly formed trimers – with one of the three bright spots not achieving full brightness. The broken symmetry of the inner trimer results in six possible orientations, simply named "one" through "six".

ATOMIC RESOLUTION STM IMAGE OF GERMANENE – various "motif" instances averaged

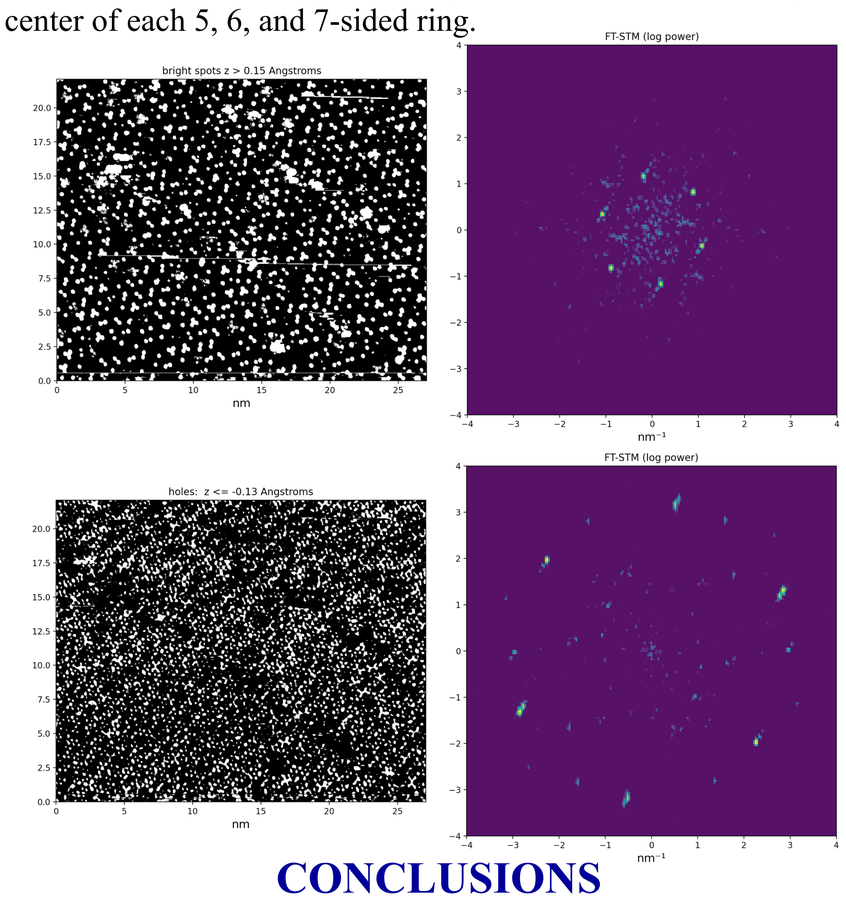


LONG-RANGE PERIODIC BEHAVIOR via FOURIER-TRANSFORM STM

The 'big picture"

In addition to the study of short-range order via the repeating motifs in the atomic-resolution STM image, we simultaneously look for any long-range periodic information from this data by taking the Fourier transform of the topography information.

Using height cuts in the topography data, we can separate out the bright features (monomers, dimers and trimers) and the honeycomb-like net by isolating the "holes" or dark spots at the center of each 5, 6, and 7-sided ring.



CONCLUSIONS

There is much more work to be done!

The germanene shown here was originally produced by dealloying from the Ag(111) surface, then rotated by +/- 3˚ by the side-by-side growth of additional domains of Pb(111). While this seems to have improved the long range periodicity as shown in sharp FT-STM spots, it also has produced a very interesting array of local "motifs" and repeating patterns.

We have begun to systematically find and characterize all instances of all motifs to better understand the configuration and check carefully to see if we can identify a recognizable tiling of the surface which might be indicative of quasicrystalline or QC behavior.

The hallmark of QC structure is the lack of simple translational symmetry and yet sharp spots in diffraction/FT processing, something clearly seen here.

To be continued...