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Investigations into the Formation of Germanene using Electrochemical Atomic Layer Deposition (E-ALD)

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This paper will discuss possible formation of germanene electrochemically. Germanene should be a single layer allotrope of Ge. The techniques of in situ electrochemical STM (EC-STM), voltammetry, coulometry, and micro-Raman have been used to investigate the electrochemical formation of germanene. Studies on Au(111) show that the initial deposition of Ge is kinetically slow and somewhat unstable, whereas the self-limited layer of Ge is stable and shows atomic distances of about 0.44 nm ± 0.02 nm. Micro-Raman was performed on Ge nanofilms, but only displayed a shift near 290 cm^{-1} in one area. Given the STM results, it appears that the coherence of the germanene domains will need to be increased in order to more consistently produce the Raman signal. The data presented suggest that germanene has been formed electrochemically, although only as a minority species.

Introduction

The discovery of graphene[1] stimulated a great interest in 2D inorganic compounds.[2-4] Graphene's unique electronic and optical properties [5-7] have motivated researchers to look for similar or unique properties in other layered materials, which may eventually integrate into nanoelectronic technology.[5, 8] The idea that other group IV elements might have allotropes analogous to graphene is promising for device integration.[9-17] There are a number of recent publications concerning *ab initio* calculations of the structures of silicene and germanene, as well as the hydrogen terminated analog of germanene, referred to as Germanane.[12, 17-30] The general consensus of those studies is that the most stable germanene structure is a "chair" like configuration which has a Ge-Ge bond distance of ~2.4 Å and a buckle of ~0.65Å, as depicted in Figure 1. This is sometimes referred to as the "low buckle" structure. *Ab initio* calculations also predict a graphene like, or "G-like", Raman active mode occurring in the neighborhood of 290 cm^{-1}. [17, 31] As with graphene, the 2D structures of silicene and germanene should have unique electronic, optical, magnetic, thermal and mechanical properties. Theory has suggested that the buckled structure expected for germanene (Figure 1) should result in important differences relative to graphene, with "new possibilities for manipulating the dispersion of electrons."[32] It has been suggested that a monolayer of silicene or germanene might have a band gap tunable via an external electric field, possibly allowing FET formation,[29] and that they may be mini-gap semiconductors.[33]

They are also of interest for studies of the quantum spin Hall effect (QSHE),[25] Dirac Cones, and Valleytronics in general.[34]

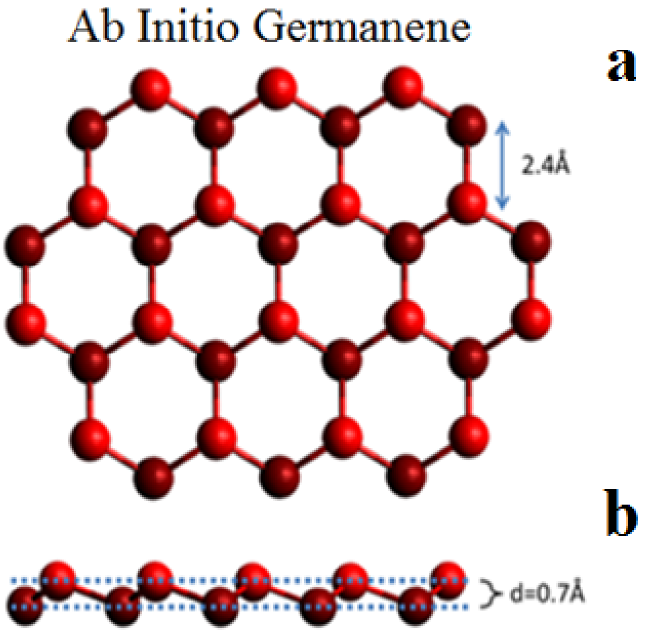

Figure 1. Low buckled structure proposed for germanene. One half of the Ge atoms are 0.07 nm higher than the other half.

There are reports that silicene has been formed on Ag(110) and Ag(111) surfaces in UHV.[17, 19, 29, 33, 35-37] The deposits were formed by sublimation of a Si wafer onto 250° C Ag single crystal surfaces in UHV, and the low energy electron diffraction (LEED) patterns and scanning tunneling microscopy (STM) images are striking.[38-41] Formation of silicene was also reported on Ir, annealed at 400^{o} C. [42] There are a few initial proposals that germanene may have been formed as well. [43-45]

Figure 1 is a structure proposed for germanene, consisting of an open hexagon of Ge atoms (honeycomb). The side view (Figure 1b) shows the low buckle structure, where half of the Ge atoms are higher than the other half. It is expected that the lower half of the atoms are harder to image with STM, so an image might only show the upper half of the Ge atoms, which would appear as a hexagonally close packed layer.

The work presented here was begun with a re-consideration of three previous studies by the PI concerning the electrodeposition of Ge.[46-48] The first study was an attempt to directly electrodeposit Ge from aqueous solutions on Au, characterized using in situ electrochemical scanning tunneling microscopy (EC-STM), voltammetry, coulometry, and combined electrochemical/UHV surface analysis (UHV-EC).[48] The second study involved development of electrochemical ALD (E-ALD) cycle chemistry for the growth of $Ge_xSb_yTe_z$, a phase change memory material.[47] The third study concerned the development of E-ALD cycle chemistry for deposition of elemental Ge, an outgrowth of the cycle developed for $Ge_xSb_yTe_z$. [46]

Initial coulometric studies of $HGeO_3^-$ reduction on Au indicated a limited amount of Ge could be formed, less than 3 monolayers (ML), where a ML was defined as one adsorbate per substrate surface atoms (Au(111)), or $1.35X10^{15}$ adsorbate atoms/cm^2.[48] Three ML was considerably more than expected for an electrochemical surface limited reaction, usually referred to as underpotential deposition (UPD). [49-53] UPD tends to result in a ML or less. UPD is the deposition of an atomic layer of one element on a second at a potential prior to that needed to deposit the first element on itself. The phenomenon results from the heat of formation of a surface compound or alloy. That deposition of Ge was limited to 3 ML suggested a mechanism different in nature to UPD, perhaps formation of a passivating layer, such as occurs during oxidation of a Au surface.[54] In retrospect, the limited deposition might also be explained by the formation of a passivating nanofilm of a van der Waals material, perhaps germanene. It is well known that electrodeposition on graphite does not proceed on the basal planes, but only at step edges or surface defects.[55, 56]

The report concerning $Ge_xSb_yTe_z$ formation by this group involved use of E-ALD.[47] Atomic layer deposition (ALD)[57], originally referred to as atomic layer epitaxy (ALE),[58, 59] is a group of techniques used to grow nanofilms of materials an atomic layer at a time. It is based on the use of surface limited reactions in a cycle to obtain atomic layer control over deposition. The vast majority of ALD is performed in vacuum. E-ALD involves the alternation of solutions of precursors and surface limited reactions to grow materials atomic layer by atomic layer.[60] Unlike vacuum ALD, E-ALD is the combination of ALD and UPD, and does not require volatile reactants, instead depositing atomic layers using aqueous solutions of electronic grade salts. A range of compounds (II-VI, some III-V, CdTe, CdSe, CdS, ZnTe, ZnS, CIS, CIGS, GeSbTe,…), metals (Pt, Ru, Cu, Ag, Pd,…) and Ge have been formed using E-ALD.[60-62]

During investigation of the formation of the phase change materials $Ge_xSb_yTe_z$ using E-ALD by this group, it was demonstrated that nearly any stoichiometry could be obtained using the E-ALD cycle developed, including stoichiometries with a very high mole fraction of Ge.[47] That work stimulated development of an E-ALD cycle for elemental Ge deposition, referred to here as the "bait and switch" cycle (B&S).[46] It was found that even though only 3 ML of Ge would be directly deposited on Au, if an atomic layer of Te was formed on top of the Ge, another atomic layer of Ge could then be deposited on top. The electrochemistry of Te is such that it can be reduced at around -1 V, to form soluble telluride species which diffuse away. By including this step in the EALD cycle, the atomic layer of Te could be reduced from the surface, leaving the new Ge atomic layer. That cycle was then repeated to grow films of elemental Ge an atomic layer per cycle. The B&S cycle for Ge was initially performed on Au substrates, though the films were not as homogenous as desired under visual inspection. It was assumed that hydrogen evolution, at the potentials used for Te reductive stripping (Figure 2), was interfering with film growth. A germanene deposit might be lifted from the surface by the formation of hydrogen bubbles, given the weak binding a van der Waals material would have. To help get around this problem, deposits were formed on Cu substrates, resulting in more homogeneous deposits, consistent with copper‘s higher hydrogen overpotential.

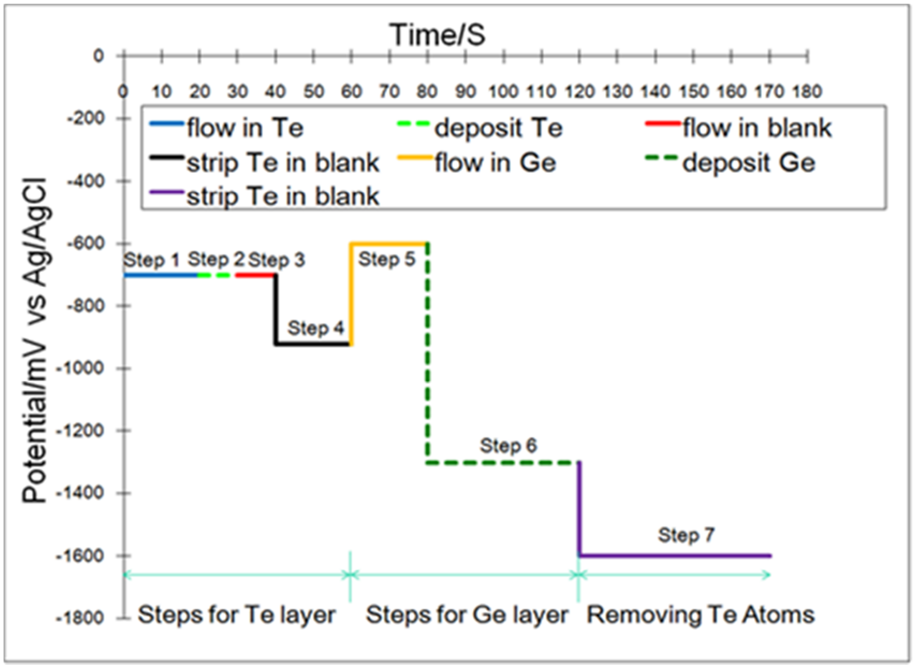

Figure 2. Diagram of the B&S E-ALD Ge deposition cycle.

Comparisons of nanofilms of Ge and compound semiconductors, grown using E-ALD, suggest that that the Ge films were significantly more fragile and susceptible to hydrogen formation. Deposits such as CdTe[63] and CIS[64], for instance, were covalently attached to the substrate and difficult to remove, while Ge deposits appear consistent with being held only by van der Waals interactions.

This report describes some subsequent results which the authors believe suggest that germanene can be grown electrochemically. Electrochemistry, micro-Raman and in-situ scanning tunneling microscopy (EC-STM) have been used to investigate the electrochemical growth of Ge from aqueous solutions, starting from fractions of a monolayer on Au(111).

Results and Discussion

Figure 3 is series of CVs of Ge deposition. Using CVs at 10 mV/s, Ge deposition appears to begin just negative of -500 mV. However, to better understand Ge growth initiation on Au, more detailed studies were performed at potentials of -500 mV and positive. Figure 4 displays oxidative stripping of Ge from Au on glass substrates, using an electrochemical flow cell, after sitting at -500 mV for increasing lengths of time. Those results indicate that Ge is deposited at potentials above -500 mV, but the process is very slow, and resulted in less than 0.1 ML.

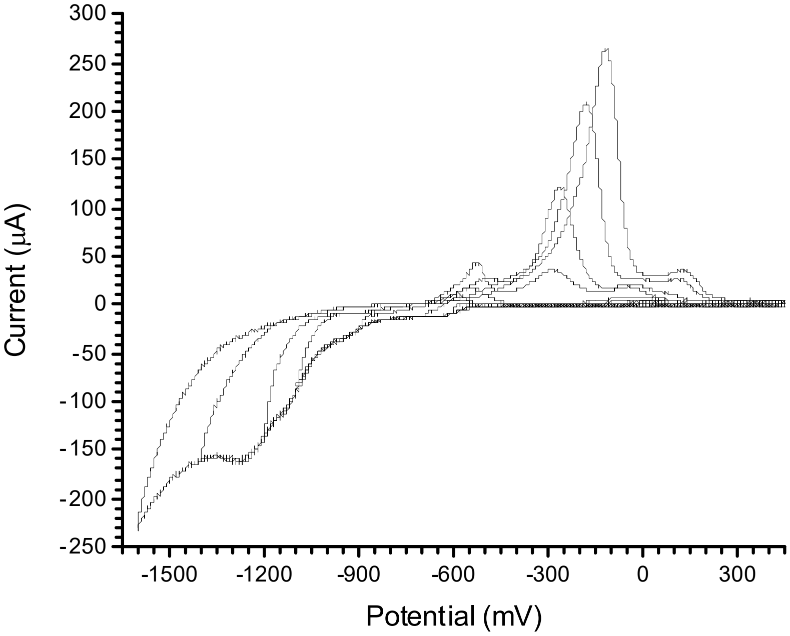

Figure 3. Window opening CVs of 0.5 mM GeO_2, 0.1 M $NaClO_4$ (pH 4.7) on a Au on glass substrate from cathodic limits of -400 mV to -1600 mV while the anodic limit was kept to 500 mV for each cycle. The scan rate used was 10 mV/s.

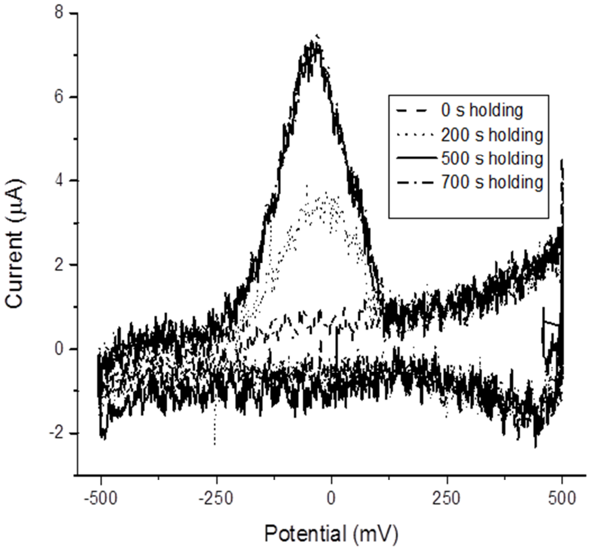

Figure 4. Oxidative stripping scans in 0.5 mM GeO_2, 0.1 M $NaClO_4$ (pH 4.7) on a Au on glass substrate, after holding the potential at -500 mV for 0, 200, 500, or 700 s. The stripping scan was performed at 10 mV/s, without solution flowing in the electrochemical flow cell. Assuming a 4 e^- process, the oxidation peak at -50 mV indicated the presences of 0.036 ML of Ge after 200 s, and 0.062 ML of Ge after 500 s & 700 s.

Figures 5, 6 and 7 are STM images taken at different potentials and after different lengths of time. Figure 5a was obtained at -300 mV, and shows the reconstructed (√3X22) "herringbone" structure expected, in the absence of Ge. The STM studies were performed on an Au(111) facet of a gold bead electrode.

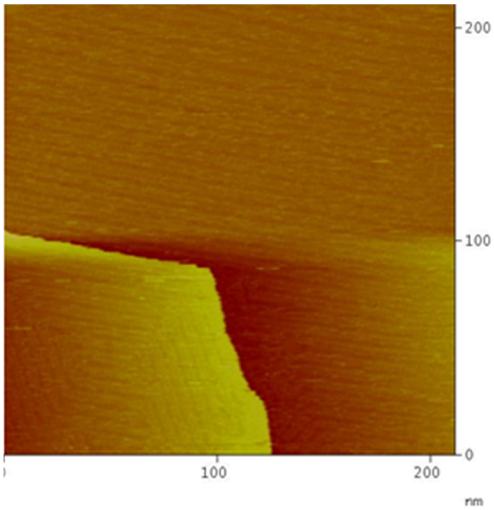

Figure 5a. STM image of Au(111) herringbone reconstruction in 1 mM GeO_2 and 0.1 M $KClO_4$ (pH 4.2) before Ge deposition, at -300 mV vs Ag/AgCl.

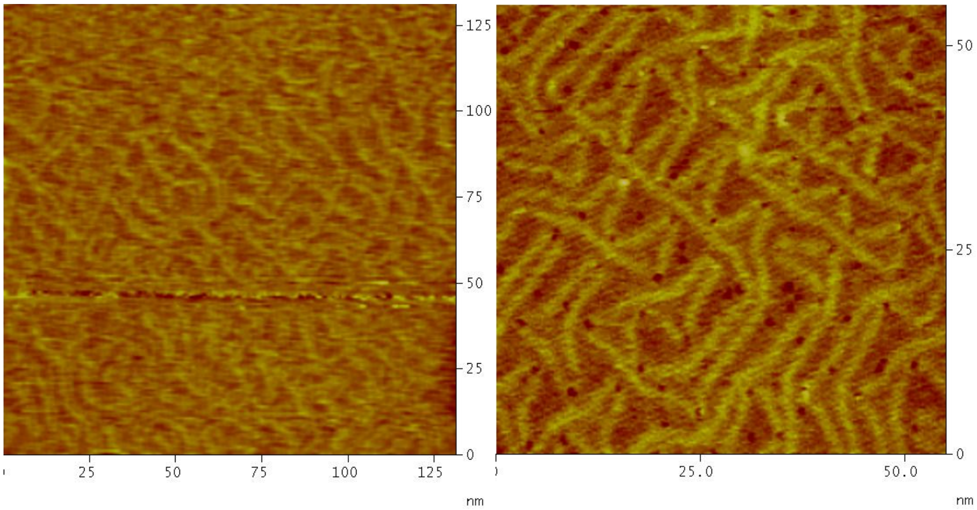

Figure 5b. STM images of Au(111) in 1 mM GeO_2 and 0.1 M $KClO_4$ (pH 4.2) at -600 mV vs Ag/AgCl.

As the potential was shifted to more negative potentials, several changes appeared, such as the breaking up of the herringbone pattern. At -600 mV (Figure 5b), a reconfiguration of the herringbone has become evident, as have small pits, mostly at the points where the reconstruction changes direction. This appears to result from the incorporation of Ge on the surface, as shown to occur in Figure 4, and the fact that such behavior does not occur without Ge present. That Ge incorporates into the Au surface has been shown by oxidative stripping of the Ge, above 0 mV, where an array of small pits were initially observed, suggesting the surface had been an Au-Ge alloy, such as that observed with Pb UPD. [65] Overall, it appears that Ge atoms begin to incorporate into the Au surface at potentials between about -400 and -600 mV, forming a surface alloy and changing the nature of the reconstructed surface, but not forming a separate Ge phase.

From Figure 6, the apparent beginning of a Ge phase starts between -600 and -700 mV, where Figure 6b displays a spray of small islands of Ge beginning to form. As the imaging continued at -700 mV, most of the small islands disappear, and the surface looks like there are some cuts in the first atomic layer (Figure 6c). By expanding the imaging range from 170 nm to 300 nm, piles of small Ge islands are evident billed on either side of the initially imaged area (Figure 6d). It is proposed here that these small Ge islands are only weekly attached to the surface, and are swept from the imaged area by the tunneling process. Again, such behavior is consistent with small islands of a van der Waals material such as germanene. The cuts suggest that a layer of germanene present on the Au-Ge alloy surface has been broken, and new islands are growing there where the layer edges are exposed (Figure 6d).

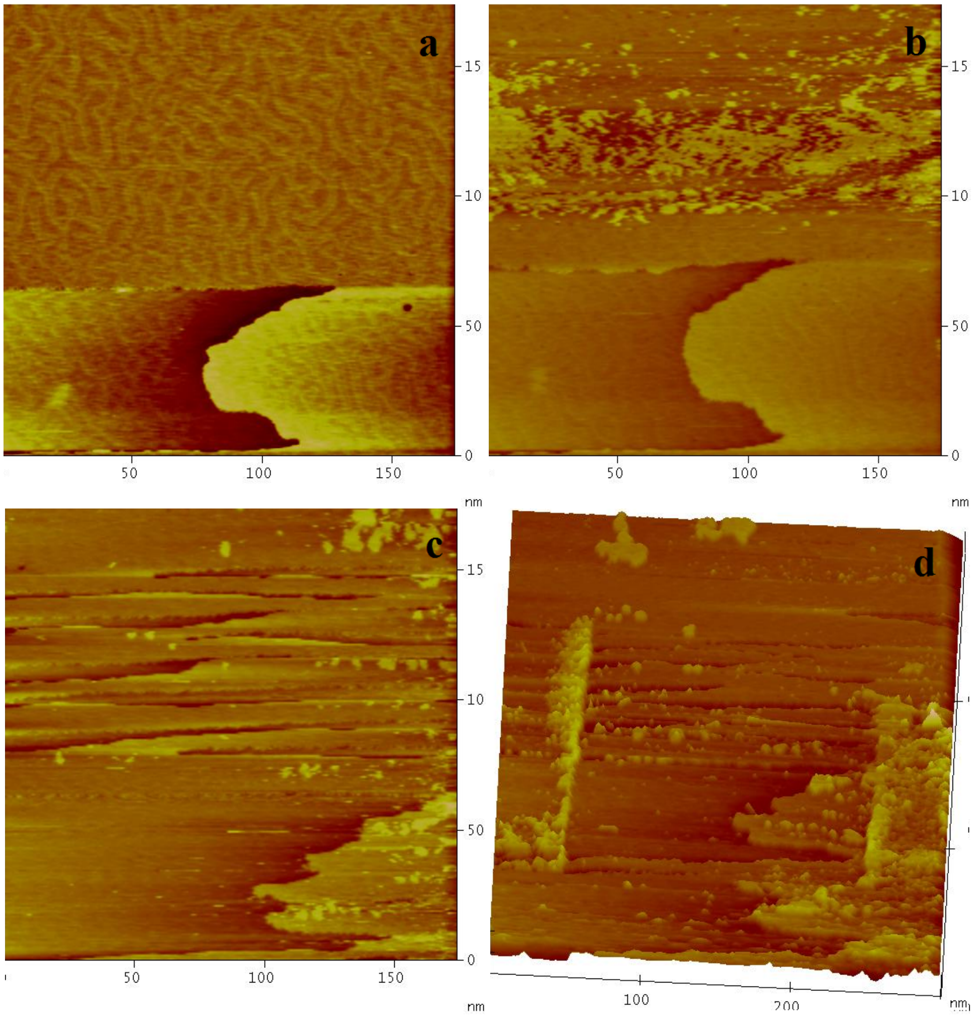

Figure 6. STM images of Au(111) in 1 mM GeO_2 and 0.1 M $KClO_4$ (pH 4.2) taken 30 s apart. a) at -600 mV vs Ag/AgCl; b) after the potential was stepped to -700 mV; c) no change in conditions; d) no conditions were changed, however the scan area was expanded to show the piles of Ge .

On the other hand, if instead of slowly moving the potential more negative to deposit Ge, the potential was scanned to -1400 mV and then back to -900 mV, images such as those shown in Figure 7 were obtained. Instead of the small islands, larger steps and islands are evident, apparently supporting some roughly hexagonal pattern on the surface. The structure is not a perfect hexagonal array, as might be expected considering the structure of graphene, but consists of small ordered domains, with small areas that are clearly hexagonal, but with random defects prevalent throughout the layer. Measurements of the distances between atoms (Figure 7b) were 0.44 nm ± 0.02 nm, consistent with the 0.4 nm from the low buckle structure in Figure 1.

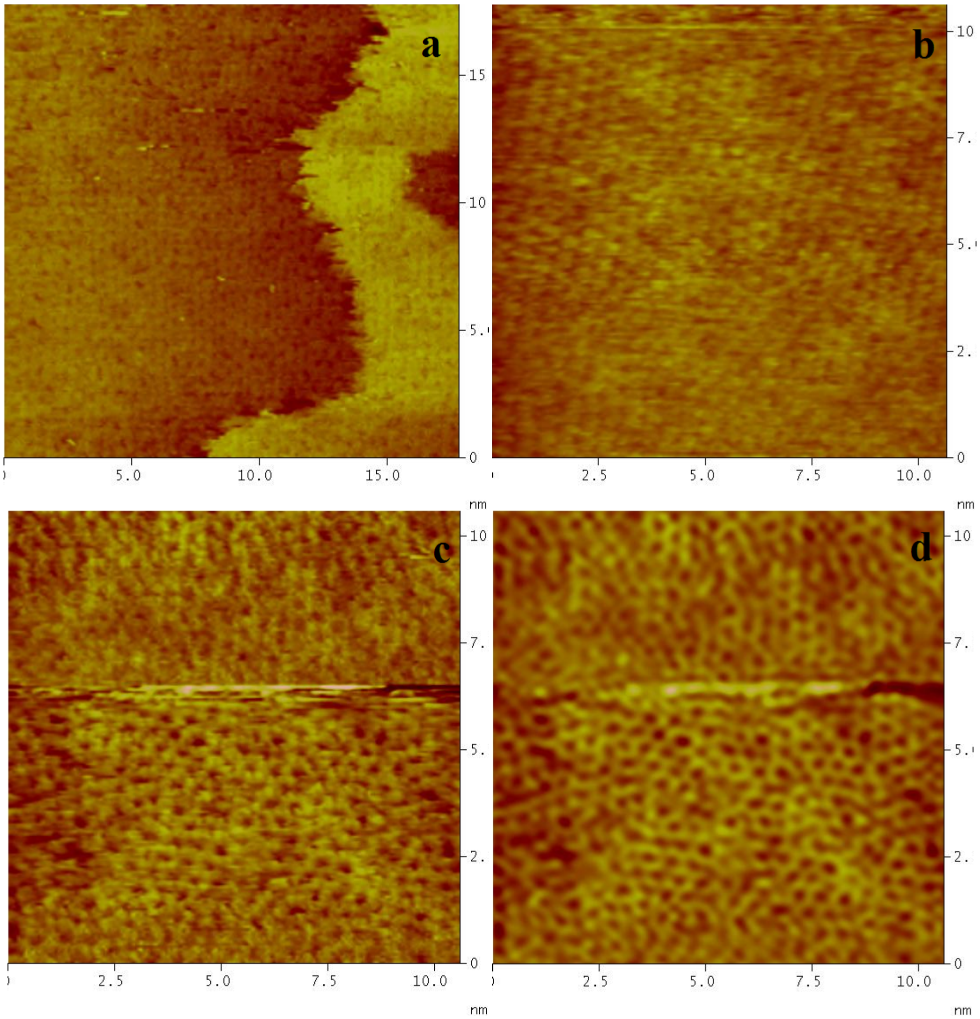

Figure 7. a-d are STM images of Au(111) in 1 mM GeO_2 and 0.1 M $KClO_4$ (pH 4.2) after the potential was scanned to -1.4 V and then to -900 mV vs Ag/AgCl. Distances between atoms on image b are 0.44 ± 0.02 nm. Image d is FFT processed image c to show honeycomb structure.

E-ALD was used by this group to grow Ge films thicker than the 3 ML that can be grown by direct electrodeposition.[46] Some of those deposits have been examined using micro-Raman to see if the predicted band at 290 cm^{-1} is present. Those deposits investigated had been grown several years ago, though they still showed predominantly the signature for amorphous Ge, as previously reported. [46] There were a very few spots where a peak near 290 cm^{-1}, expected for germanene, was present (Figure 8). Given the images in Figure 7, the absences of the 290 cm^{-1} band may be a lack of long range coherent domains of the germanene structure. Studies to identify the conditions needed to achieve a more perfect growth of the germanene are presently underway.

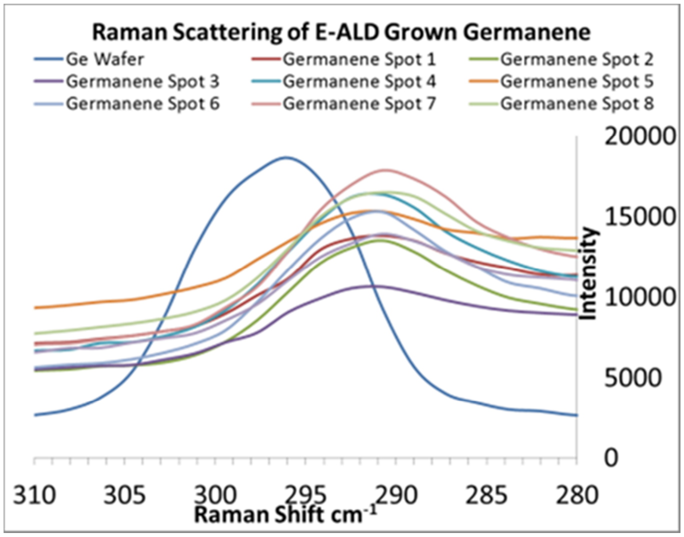

Figure 8: The blue line (on the left) is for a Ge wafer, as a standard. The other spectra are examples of where the 290 cm^{-1} band appeared. The 290 cm^{-1} band has only been observed in a very limited area of one sample.

Acknowledgements

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