

Filled-state scanning tunneling microscopy image of gold honeycomb structure on Si(111)7×7 at room temperature.

Self-Organized Gold Honeycomb Structure

STM Imaging of Growth Evolution of Au on Si(111)7×7

The early growth stage and growth evolution to a unique gold (Au) honeycomb nano-network on Si(111)7×7 at room temperature have been studied by direct filled-state and empty-state imaging by scanning tunneling microscopy (STM). The gold honeycomb structure is made up of six triangular gold clusters around the corner hole interconnected to one another in the dimer rows of the Si(111)7×7 substrate.

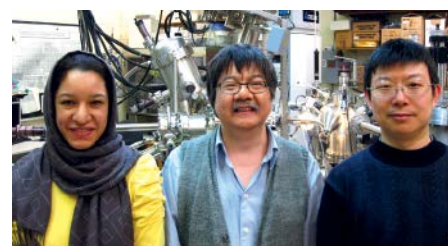
Introduction

Scanning tunneling microscopy is a powerful technique capable of atomic resolution to recognize the topmost adatoms and restatoms of the Si(111)7×7 surface [1], which provides a robust template for organization of two-dimensional nanodots or nanoclusters. One of the most interesting metal/Si interfaces is Au/Si because of its applications in nanoelectronics and nanocatalysis. Most of the previous studies have focused mainly on the initial stage of Au deposition [2,3,4] and the formation of disordered Au clusters [5,6,7]. Similar to that found for Ag-√3×√3 [8], honeycomb structures of (√3×√3)R30°-Au on unreconstructed Si(111), i.e., 1×1, surface [9] have been observed by STM. While self-organized honeycomb structures of Ga [10], Al, In [11], Mn [12] and Ge [13] on the

Si(111)7×7 reconstructed surface have been reported, no ordered honeycomb structure of Au has been observed on the 7×7 surface at room temperature. Here, we demonstrate that it is possible to convert a Si(111) semiconductor surface to a conductive Au honeycomb template by carefully controlling the epitaxial growth process. This new Au honeycomb nano-network offers new opportunity for not only nanocatalysis and nanoelectronics applications, but also biofunctionalization by organic molecules. This unique honeycomb structure, with well-ordered corner holes of the 7×7 surface exposed, in effect forms a template of nanopores (~1 nm in pore size), which are particularly interesting as they could function as molecular traps of small molecules including DNA-bases and organic molecules in a single-molecule detector.

Instrumentation

Our experiments were performed in an ultra-high vacuum multi-chamber system (Omicron), in which the analysis



f.i.t.r.: F. R. Rahsepar, K. T. Leung, L. Zhang
Department of Chemistry, University of Waterloo,
Ontario, Canada

chamber was equipped with an X-ray photoelectron spectrometer and a variable-temperature scanning probe microscope. After outgassing a n-type Si(111) chip (2×11 mm², 0.3 mm thick, and 0.005 Ωcm resistivity) at 400°C overnight, a 7×7 reconstructed surface was obtained by flash-annealing at 1200°C followed by rapid cooling to 800°C and slow cooling to room temperature. The cleanliness and crystallinity of the 7×7 surface so prepared were confirmed by its sharp STM images. The clean 7×7 substrate was then transferred into a molecular beam epitaxy growth chamber, in which Au (99.9999% purity) was deposited by thermal evaporation at 1040°C with the 7×7 substrate held at room temperature. STM images of the resulting Au/Si(111)7×7 were collected (in the analysis chamber) at room temperature using an electro-chemically etched W tip.

Keywords

Gold Honeycomb Nano-template, Self-organization, Growth Evolution, Si(111)7×7, Scanning Tunneling Microscopy

Experimental Results

We first present our STM observation of the evolution of the Au adsorption structures on Si(111)7×7 at room temperature in the early growth stage, from 0.004 ML to 0.186 ML (corresponding to exposure times of 10 sec to 30 min). One monolayer (1 ML = 7.8×10^{14} atoms/cm²) is defined as the coverage of one Au atom for each Si atom of the unreconstructed Si(111) surface. The filled-state STM image shown in figure 1a reveals several prominent features. First, there are “sextets” of bright protrusions at the adatom positions of the faulted half unit cell (FHUC) and “triads” of bright protrusions at the center-adatom positions of the unfaulted half unit cell (UHUC). The observed sextet and triad have been previously attributed to a highly mobile single Au atom moving rapidly among the respective adatom sites inside the HUC [14]. Closer examination of the sextets in the FHUC (fig. 1a, upright triangle) reveals that the corner-adatom protrusions appear brighter than the center-adatom protrusions, indicating that during movement the single Au atom stays at the corner-adatom sites longer than the center-adatom sites. Similarly, in the UHUC the center-adatom protrusions forming the triad (fig. 1a, circle) are brighter than the corner-adatom protrusions as a result of longer stay of the Au atom at the center-adatom sites [3]. Second, there are also notable “scribble” features over the HUC (fig. 1a, square). A scribble has been attributed to an Au dimer translocating (moving) rapidly in the center of the HUC [4]. Statistical analysis of several STM images obtained at this coverage (0.004 ML) shows that the Au occupancy at the FHUC sites is 1.4 times that at the UHUC sites. This FHUC to UHUC occupancy ratio is found to increase to 2.3 with increasing Au exposure to 3 min (or

0.026 ML), which confirms that the FHUC sites are more reactive and receptive to Au adsorption than the UHUC sites. Our statistical analysis also shows a similar trend for the scribble (dimer) features.

Increasing the Au exposure to 3 min (or 0.026 ML, fig. 1b) leads to formation of new clusters on the 7×7 sur-

face, including bright triangular shaped protrusions (“triangles”) located at the center of the HUCs (fig. 1b, upside-down triangle) and linear-edge protrusions (“edge-clusters”) located on the sides of the HUCs (fig. 1b, oval). It should be noted that the 7×7 reconstruction remains clearly visible, with the dimer

rows and corner holes defining the original registry of the 7×7 surface.

At a Au exposure of 12 min (or 0.133 ML, fig. 1c), larger protrusions (fig. 1c, rectangles) extending over an increasingly larger part of the HUCs are clearly visible. Continued exposure to 30 min (or 0.186 ML, fig. 1d) leads to enlargement of these larger protrusions and formation of horseshoe-like features that gradually cover the dimer rows. At 50 min exposure time (fig. 2a), the disordered horseshoe-like protrusions (fig. 1d) become more orderly and form a network of highly symmetric honeycomb structure. At 60 min exposure (fig. 2b), near-perfect honeycomb structures, extending over large terraces (of at least $0.5 \times 0.5 \mu\text{m}^2$ in size) of the 7×7 surface, become well established. A Fourier analysis of the honeycomb network (fig. 2b, inset) reveals a hexagonal pattern, confirming its remarkable highly ordered structure. It is important to note that the present honeycomb structure is different from the previously observed “chain-like” Au/Si(111)-(5×2) structures [15]. In the present honeycomb structure, the six triangular clusters in the HUCs connect with one another across the dimer rows and completely enclose the corner hole on the 7×7 surface. This arrangement is confirmed by their corresponding empty-state STM images (not shown). Further increase in the exposure time to 80 min (fig. 2c) causes filling of the corner holes by Au atoms and conversion of the ordered honeycomb structure to a nearly complete Au silicide overlayer, indicating total wetting of Au on Si. Finally, at 120 min exposure (fig. 2d), clear formation of Au nanocrystallites is observed only after completion of Au silicide layers, which suggests that Au follows the mixed layer-island (Stranski-Krastanov) growth mechanism on Si(111)7×7. This is also verified by our XPS results supporting that

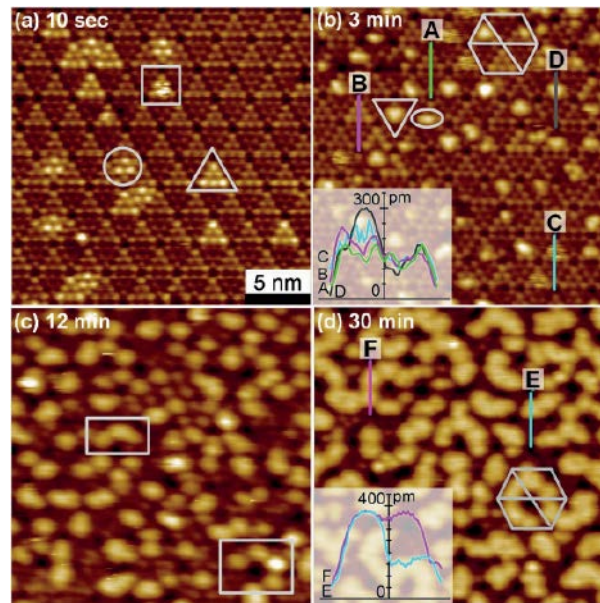


Fig. 1: (a)-(d) Filled-state STM images of growth evolution of single Au atoms to disordered horseshoe clusters on Si(111)7×7 at exposure times (each collected with a sample bias: -2.0 V; a tunneling current: 0.2 nA; and an image size: $25 \times 25 \text{ nm}^2$). The insets in (b) and (d) show the apparent height profiles along linescans (5 nm long) for different Au cluster features.

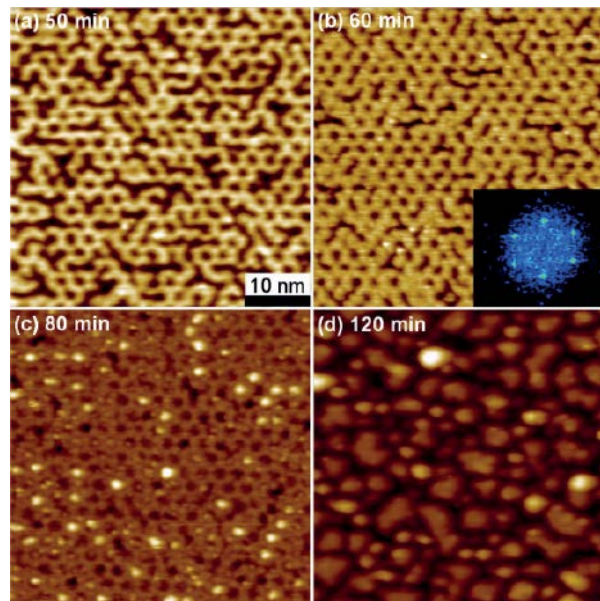


Fig. 2: (a)-(d) Filled-state STM images of growth evolution of well-ordered Au honeycomb structure to a disordered nanocrystallite phase on Si(111)7×7 at different coverage (each collected with a sample bias: -2.0 V; a tunneling current: 0.2 nA; and an image size: $50 \times 50 \text{ nm}^2$). The inset in (b) shows the Fourier analysis of the honeycomb structure, revealing the hexagonal symmetry.

the Au nanocrystallites are formed on a gold silicide layer (not shown).

Discussion and Outlook

To further characterize the nature of the clusters that give rise to the observed protrusions, we compare, in figure 1b and 1d, the apparent height profiles along selected linescans across the UC long-diagonal of a sextet (B), a scribble (C), a triangle (D), and edge-clusters of the honeycomb structures (E, F), along with that of an unoccupied HUC (A) used as a reference. These various clusters are found to follow the height ordering: edge-clusters of the honeycomb structure (330 pm) > triangle (300 pm) > scribble (260 pm) > sextet (240 pm) > unoccupied FHUC (180 pm). These height profiles enable us to locate the stacking/adsorption arrangement of gold atoms for the features of interest along a particular crystallographic direction of the 7×7 surface. For a single adsorbed Au atom (sextet), the height at the center-atom location appears smaller than the corner-atom location (linescan B), which confirms that the adsorbed Au atom is more probable to be located at the corner adatom sites at room temperature. Close examination of the triangle protrusion in figure 1b shows a dark depression at the center-atom sites in the adjoining UHUC, which appears as a minimum in the height profile along linescan D in the UHUC side. This depression is due to transfer charge from the Si center adatom to the Au cluster [13].

The difference in the apparent height maximum along linescan B (sextet) with respect to linescan A (unoccupied Si) is approximately 60 pm, which corresponds to one single Au atom based on STM observations. On the other hand, the apparent height difference between linescans C (scribble) and B (sextet) is ~ 20 pm. Since the difference in the apparent height between linescans D (triangle) and A (unoccupied Si) is about twice that between linescans B and A, we attribute a nonplanar Au cluster to the triangle protrusion. By considering the STM images (fig. 1b and 1d) and the corresponding linescans, we estimate the apparent height difference between linescans F (honeycomb) and D to be approximately 30 pm, which suggests that the honeycomb structure likely consists of more than two layers of Au atoms.

Early studies have proposed plausible molecular models for clusters of different metals on $\text{Si}(111)7\times 7$, including Cu [16], Al, Ga, In [11], Fe [17], and Zn [18], as well as Au [2]. By combining our present STM observation with XPS data and

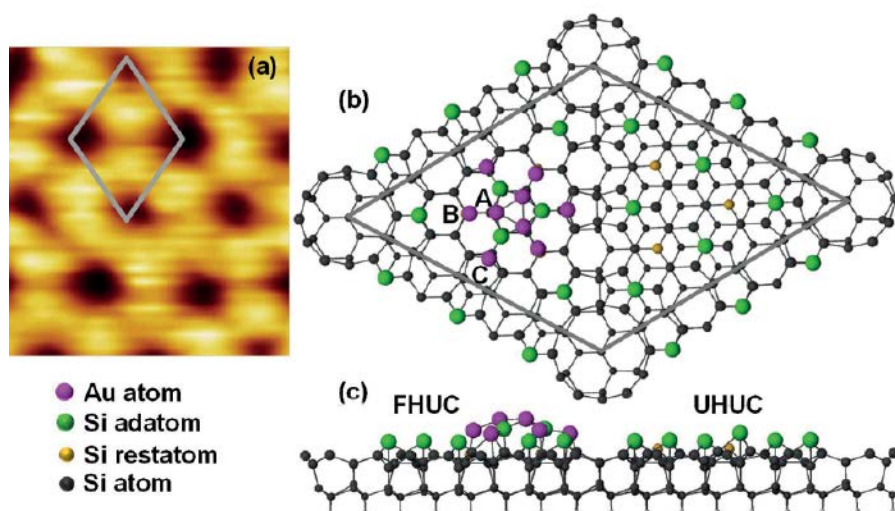


Fig. 3: (a) Filled-state STM image of Au honeycomb structure on $\text{Si}(111)7\times 7$, (b) top and (c) side views of a proposed Au_9Si_3 model for a possible nucleation center for one of the six segments of the honeycomb structure.

first-principle Density Functional Theory (DFT) calculations, we propose a Au_9Si_3 model for one of the six sectional building blocks of the Au honeycomb structure on $\text{Si}(111)7\times 7$, which is very similar to the Au(111) structure. Wu *et al.* have previously suggested a Au_6Si_3 structure as a possible model for the triangular Au cluster [2]. In the present preliminary modeling study, we propose a larger Au_9Si_3 structure for the triangle cluster, which is 0.03 eV/atom more stable than the Au_6Si_3 structure. The minimized structure in figure 3b illustrates three different types of adsorbed Au atoms: (A) three Au atoms placed on the top of pedestal atom sites of the restatoms, (B) three Au atoms located atop of the Si restatoms, and (C) three Au atoms located at the Si center adatom sites, displacing the three Si center adatoms to their pedestal atom sites. Our calculation shows that the nine Au atoms in the optimized structure are nonplanar and distributed at three different heights. This cluster represents a possible nucleation center for one of the six segments of the honeycomb structure. To connect one segment of the honeycomb structure in a HUC to the other segments, additional Au atoms covering across the dimer wall are clearly needed.

In summary, direct STM imaging is a powerful technique to probe the novel high-symmetry Au honeycomb nano-network, epitaxially grown on a $\text{Si}(111)7\times 7$ substrate for the first time. The intricate STM images reveal different stages of growth, from single Au atoms (sextets, triads), to Au dimers (scribbles) and disordered nanoclusters (triangles), to horseshoe-like structures, and finally to the Au honeycomb structures. The Au honeycomb structure on $\text{Si}(111)7\times 7$ represents

an unique nanoscale template of Au hexagonal grids (4 nm wide) and nanopores (~ 1 nm dia). Large-scale fabrication of this novel honeycomb structure promises new opportunities in using this highly ordered Au template for biofunctionalization for molecular traps and sensors, components for nanoelectronic devices, and arrays of active sites for nanocatalysis.

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Contact

F. R. Rahsepar
Dr. L. Zhang
Prof. Dr. K. T. Leung
Department of Chemistry
University of Waterloo
Ontario, Canada
tong@uwaterloo.ca
<http://leung.uwaterloo.ca>