

Functionalization of silicon step arrays I: Au passivation of stepped Si(111) templates

A. Kirakosian, J.-L. Lin, D. Y. Petrovykh, J. N. Crain, and F. J. Himpsel^{a)}
Department of Physics, University of Wisconsin Madison, Madison, Wisconsin 53706

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The growth mode of Au on stepped Si(111)7×7 surfaces is determined by scanning tunneling microscopy, with the goal of providing a continuous gold layer that replicates the step morphology. Functionalization with gold allows attaching organic and biomolecules via thiol groups (e.g., alkanes and DNA). On clean Si(111), gold grows in the Stranski–Krastanov mode and produces islands with a size comparable to the step spacing. A Ti wetting layer produces smooth Au films that preserve the step topography down to a scale of a few nanometers. © 2001 American Institute of Physics. [DOI: 10.1063/1.1397288]

I. INTRODUCTION

Connecting biochemistry with Si electronics enables the design of electronic biosensors for proteins, antibodies, and viruses.^{1–3} It also offers opportunities for making electrical connections to cardiac muscle cells⁴ and neurons⁵ in order to read out their activity and to incorporate them into logical circuits. With the synthesis of organic molecules that exhibit switching behavior a whole new field of molecular electronics has opened up, where molecules act as memory cells or switches.^{6–8} For contacting these molecules to standard silicon microelectronics it will be necessary to generate nanowire arrays and to cross-link them with the molecules. One of the possibilities for generating wire arrays by self-assembly is the use of a stepped silicon surface as a template. We have been able to fabricate step arrays on Si(111)7×7 surfaces that are atomically straight for up to 20 000 atoms and periodic with atomic perfection for up to 600 atom rows.^{9–13} Periodicities range from 6 to 80 nm. Furthermore, these steps have been replicated with calcium fluoride stripes to form an inert mask,¹⁴ and 3 nm wide iron wires have been grown selectively between a stripe mask.¹⁵

The goal of this work and of a companion article¹⁶ is the attachment of organic and biomolecules to step and stripe patterns on silicon. Here we report a method for attaching molecules without destroying the step structure of the substrate or denaturing the molecules. Clean silicon exposed to a molecular solution oxidizes into a rough surface that loses most of its step topography.¹⁷ Molecules deposited onto clean silicon from the vapor phase degenerate by reacting with the broken silicon bonds at the surface. Therefore the surface needs to be passivated such that the nanometer-sized step features are preserved and adsorbed molecules do not break apart. We use a thin gold layer for passivating the surface and, at the same time, functionalizing it for the adsorption of thiol-derivatives of organic molecules and biomolecules. Particular attention is paid to the morphology of the surface. In a companion article¹⁶ we study the uptake and orientation of alkanes and DNA on such surfaces, using

polarization-dependent core level absorption spectroscopy.

We find that gold by itself is not adequate to replicate and functionalize the step structure at the surface. It forms islands that roughen the surface and obliterate the step structure, particularly after annealing. A wetting layer of titanium solves that problem.¹⁸ In the companion article we find that that a minimum gold thickness of 3 nm (12 monolayers) on top of the titanium is required for reaching the full coverage of organic molecules.

II. EXPERIMENTAL METHOD

Si(111) wafers (*p*-type, resistivity 5–10 Ω cm) with 3.5° miscut towards $[11\bar{2}]$ were used in the experiment. A special heating sequence facilitated the formation of wide, atomically flat terraces (60 ± 10 nm) separated by facets consisting of 13–15 bunched steps.^{9,10} For heating we used dc current parallel to the steps, brought in through tantalum electrodes. First, the samples were flashed to 1250 °C for 10 s in order to diffuse carbon impurities from the surface into the bulk. The subsequent cooling sequence consisted of fast ramping to 1060 °C in 1 min, followed by slow cooling down to 650 °C at a rate of 0.5 °C per min. The samples then remained at 650 °C for at least 30 min. Cooling slowly through the phase transition from 1×1 to 7×7 at 870 °C allows the development of regular arrays of bunched steps with a self-limited terrace size.¹⁰ During the final stages of the heating procedure the pressure in the UHV chamber was below 1×10^{-10} Torr. After cooling to room temperature, Au was evaporated from a Mo wire basket. The coverage was calibrated by low energy electron diffraction (LEED) of surface structures with a well-defined Au coverage, such as 5×2 at 0.4 monolayers.¹³ One monolayer is defined by the density of Si(111) surface atoms (7.84×10^{14} cm⁻²). To produce smooth Au films a Ti wetting layer was evaporated on the Si surface using Ta–Ti alloy wire with 25% Ti content. In order to optimize the smoothness of the metal films we tested post-anneals at various temperatures for 10 min each.

The topography of the silicon surfaces was examined by scanning tunneling microscopy (STM). Images were obtained at a tunneling current of 0.3–1.0 nA and a sample bias

^{a)}Electronic mail: fhimpsel@facstaff.wisc.edu

of -0.5 – 2.0 V. Instead of the topography we display the x derivative of the topography in all figures, which gives the appearance of a surface illuminated from the left with the steps casting shadows to the right. Typical results are given in Fig. 1 for various surface preparation stages. A variety of morphologies is observed, ranging from islands for Au deposited directly onto Si to smooth when deposited on top of a Ti wetting layer.

A. Au adsorption on clean Si(111)7×7

Figures 2 and 3 show the topography of Au deposited directly onto Si(111)7×7 for various postannealing temperatures. Lighter areas represent atomically flat 7×7 terraces and dark areas contain bunched steps. All images exhibit a periodicity of 80 ± 10 nm for the combined width of the light and dark areas, which is consistent with the periodicity of 75 ± 10 nm reported for samples with similar miscut.¹⁰

With 2 monolayers of Au deposited at room temperature the whole surface is covered by a disordered Au film, which gives it a rough appearance in Fig. 2(a). Upon annealing to 225 °C small Au islands appear on a textured surface, as shown in Fig. 2(b). The underlying texture on the terraces is identified as the Si(111)6×6-Au surface reconstruction, which has been reported previously for a Au coverage of >1 monolayer.¹⁹ The inset in Fig. 2(b) shows the two-dimensional Fourier transform. The diffuse horizontal streak is due to the steps running in the vertical direction. The bright spots above and below it are the corners of a hexagon that originates from the 6×6 reconstruction. In stepped areas there is a coagulation of Au into large, three-dimensional islands 10–15 nm across and 1.2–1.9 nm high (5–8 monolayers). On terraces, on the other hand, the gold islands are only 3–6 nm across and 0.24 nm high (one monolayer). Their separation is 10–25 nm, whereas the distance between the large islands in the stepped regions ranges from 25 to 50 nm. The larger size and separation of the islands in the stepped regions indicates a higher diffusion length of Au atoms. After further annealing to 275 °C the small Au islands have been swept off the terraces almost completely by diffusion [Fig. 2(c)]. Now, most of the gold on the surface is in the stepped areas where it agglomerates into islands 15–20 nm across and 1.7–3.3 nm high (7–14 monolayers). Such a preferential formation of Au clusters at elevated temperature suggests nucleation sites with high binding energy in the stepped regions.

Increasing the Au coverage produces a similar growth mode, but with larger islands. (see Fig. 3 for 1.4 nm \approx 6 monolayers). The initial 6×6 layer is followed by three-dimensional Au islands on top [Fig. 3(a)]. That is characteristic of Stranski–Krastanov growth. There is enough diffusion at room temperature to generate a rough surface with typical island sizes of 10–20 nm and heights up to 1.4 nm. The underlying step structure starts to become obscured already. Annealing to 225 °C produces large, flat-topped Au islands on the terraces and hemispherical islands near the steps [Fig. 3(b)]. An increase in the annealing temperature shifts the equilibrium towards the hemispherical islands in the stepped regions [Fig. 3(c)]. They form linear arrays along

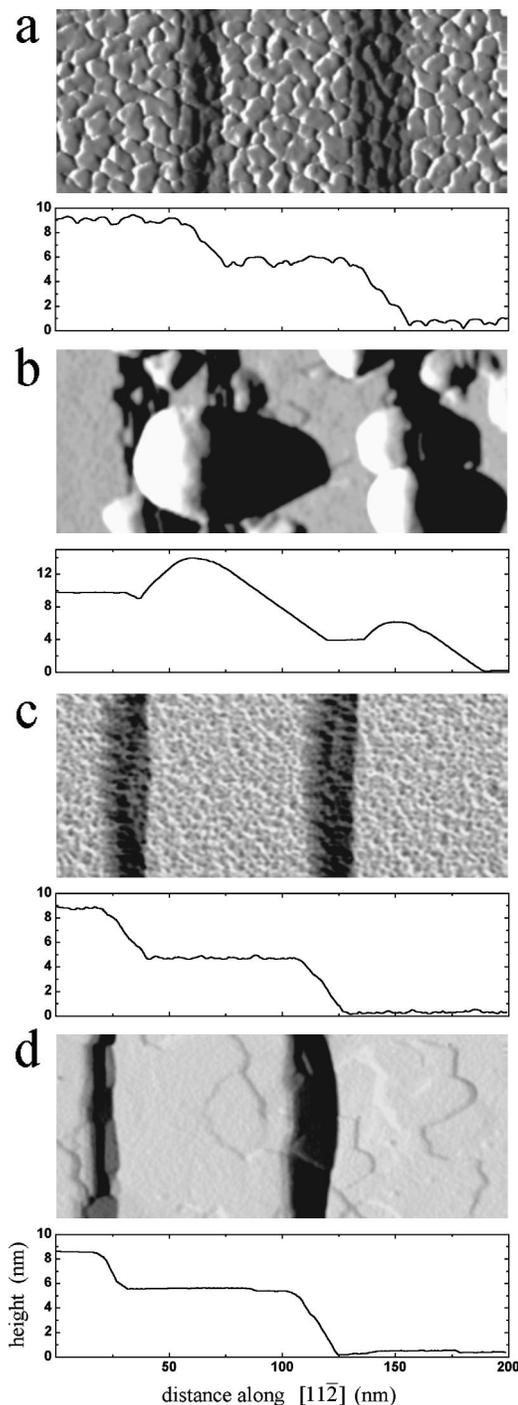


FIG. 1. Overview of various stages in the passivation of stepped Si(111) templates by Au. Topographic line scans show that gold distorts the step topography (a, b), whereas a titanium wetting layer preserves it (c, d). The derivative of the STM topography is shown, giving the impression of a surface illuminated from the left with the $[11\bar{2}]$ downhill direction to the right. The dark bands are step bunches, 80 ± 10 nm apart and 5 nm high. 200×75 nm²: (a) 1.4 nm (\approx 6 monolayers) of Au deposited on Si(111)7×7 at room temperature produces islands with a size of 10–20 nm. (b) After annealing (a) to 275 °C Au coagulates into larger hemispherical islands next to the steps. Island size increases to 20–50 nm. (c) 0.7 nm (\approx 4 monolayers) of Ti deposited onto Si(111)7×7 at room temperature. The surface roughness increases compared to clean Si(111)7×7 but the step morphology is well preserved. (d) 1.4 nm (\approx 6 monolayers) of Au deposited onto (c) and annealed to 275 °C. The overall roughness is reduced to a single atomic layer as Au spreads evenly over the Ti wetting layer.

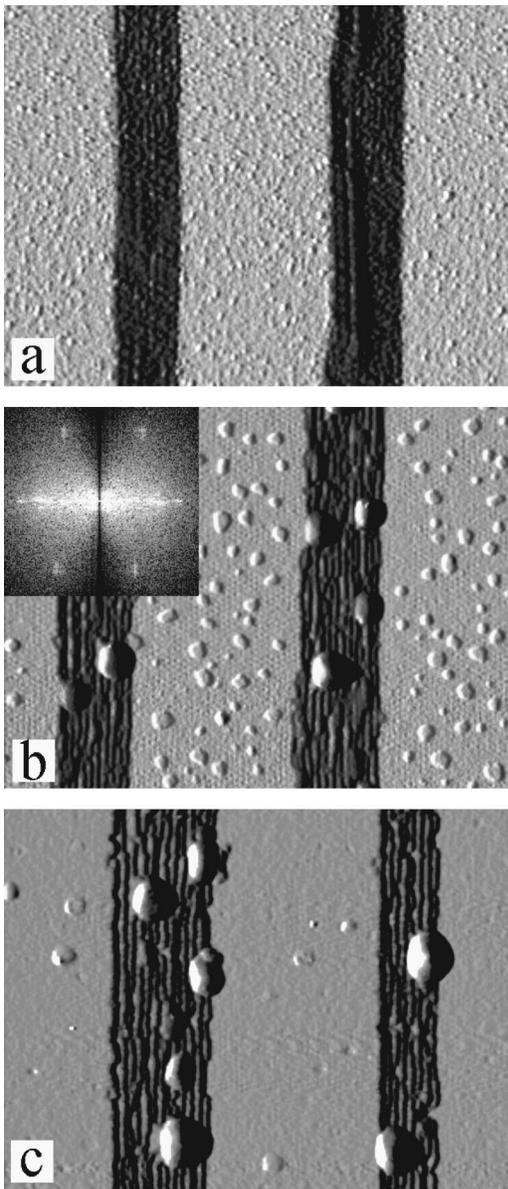


FIG. 2. Au adsorption on Si(111)7×7 versus annealing. 200×150 nm²: (a) 0.5 nm of Au on Si (≈2 monolayers) deposited at room temperature. (b) After a 225 °C anneal, Au coagulates into islands, which are smaller on the terraces and larger in the stepped regions. The inset shows a Fourier transform with the 6×6 diffraction pattern of the first Au layer. (c) After a 275 °C anneal, smaller Au islands are almost completely swept off the terraces by diffusion, whereas islands in the stepped regions grow in size.

the steps (cf. Ref. 20) that are similar to the chains of noble metal islands²¹ found on lithographically patterned Si(111). It would be interesting to test whether this growth mode can be optimized for forming linear arrays of quantum dots with uniform size and spacing.

B. Use of a Ti wetting layer

In order to avoid three-dimensional island structures that obscure the step pattern we coat Si with a wetting layer of titanium before depositing the gold. Cr and Ti wetting layers have been used on glass and silicon for this purpose.¹⁸ These are highly reactive materials which increase the surface energy such that Au will spread out.

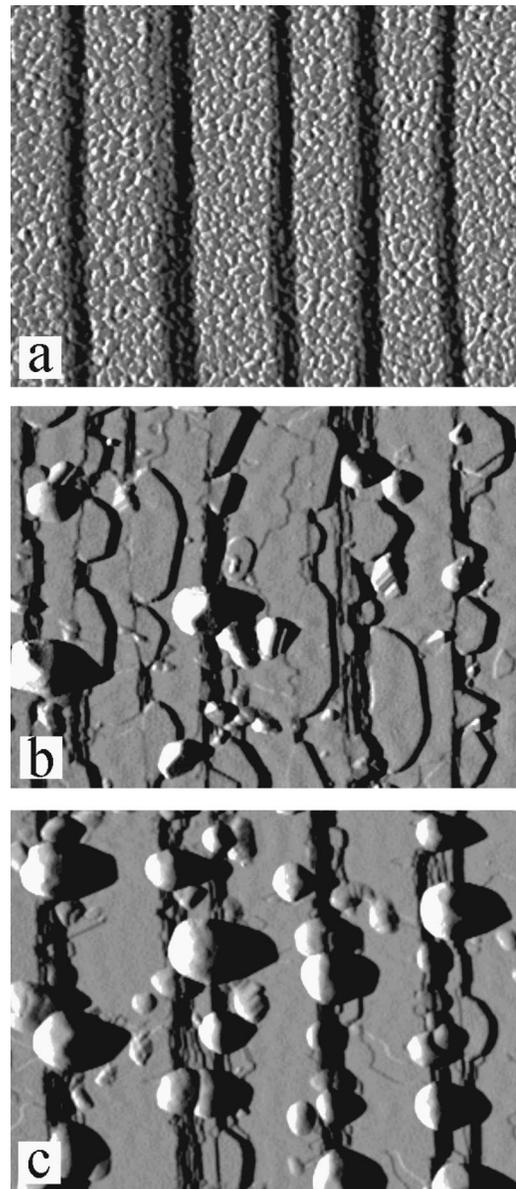


FIG. 3. Similar to Fig. 2, except for a thicker Au film (1.4 nm≈6 monolayers) and with a larger scan area of 400×300 nm². (a) Au deposited on Si(111)7×7 at room temperature produces a rough surface with typical island sizes of 10–20 nm. (b) After annealing (a) to 225 °C the Au coagulates into large, flat-topped islands on the terraces, and into hemispherical islands next to the steps. (c) After a 275 °C anneal the hemispherical islands along the steps dominate.

Figure 4(a) shows 0.7 nm of Ti (4 monolayers) deposited onto stepped Si(111)7×7 at room temperature. Due to their high reactivity Ti atoms stick wherever they arrive and do not diffuse across the surface. Thereby they coat the surface uniformly and preserve the step structure. There is no distinction between terraces and stepped regions as far as the surface roughness is concerned. That holds for a ten times finer step pattern, too, as shown in Figs. 5(a) and 5(b).

When Au is added to the Ti wetting layer at room temperature the steps are preserved, but the surface becomes rougher [see Fig. 4(b) for 6 monolayers of Au]. This situation, in fact, is comparable to that without a wetting layer [compare Fig. 3(a)]. However, annealing to 225 °C reduces

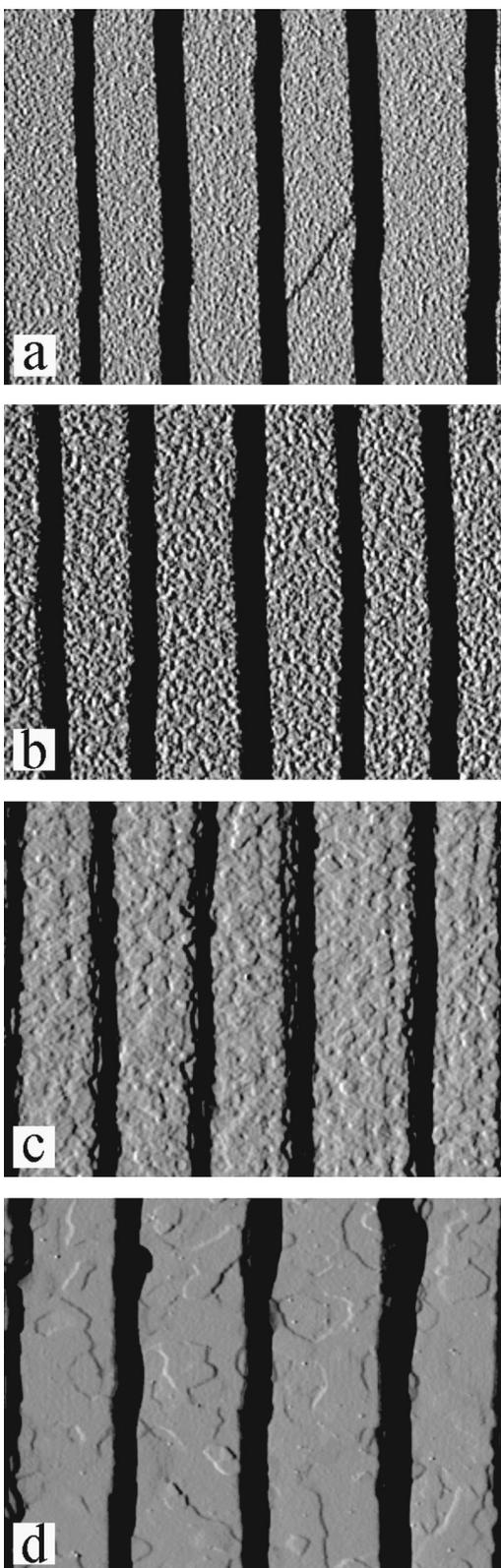


FIG. 4. Au adsorption on Ti-covered Si(111)7 \times 7 versus annealing. The Ti wetting layer smoothens the Au film after annealing. 400 \times 300 nm²: (a) 0.7 nm (\approx 4 monolayers) of Ti deposited onto Si(111)7 \times 7 at room temperature. (b) 1.4 nm (\approx 6 monolayers) of Au added to (a) at room temperature. (c) After annealing (b) to 225 $^{\circ}$ C the overall roughness decreases as Au spreads evenly over the stepped surface. (d) After adding another 1.4 nm (\approx 6 monolayers) of Au to (c), which brings the total coverage to 2.8 nm (\approx 12 monolayers) and annealing to 275 $^{\circ}$ C. The roughness is reduced to a single atomic layer.

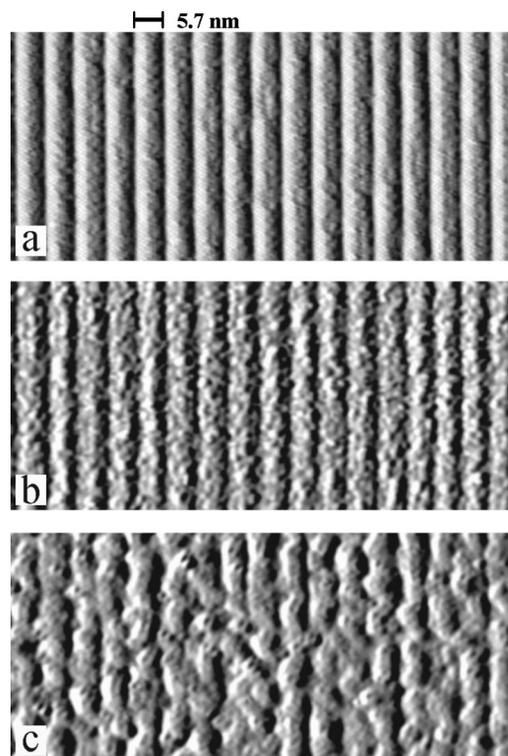


FIG. 5. Au adsorption on Ti-covered Si(557) preserving structures down to 5 nm. 95 \times 45 nm²: (a) Clean Si(557) showing an array of triple steps with 5.7 nm period. (b) The step topography is preserved after depositing a wetting layer of 0.35 nm Ti (\approx 2 monolayers). (c) A layer of 0.7 nm Au (\approx 3 monolayers) is deposited on top of (b) and annealed to 275 $^{\circ}$ C.

the overall roughness by removing the components with high spatial frequency, as shown in Fig. 4(c). This tendency continues after adding another 6 monolayers of Au to the same surface and annealing it to 275 $^{\circ}$ C, as shown in Fig. 4(d). The corrugation on the terraces is reduced to a single atomic step height of Au, and the bunched steps are preserved. The Ti wetting layer has prevented the growth of Au islands at elevated temperatures.²² Comparing Figs. 3(a)–3(c) and 4(d) clearly demonstrates the influence of the Ti layer.

In order to test the limits of this method we have tried it for step structures with smaller periods, such as the gratings with 5.7 nm period that we obtained recently for Si(557).¹² The period is more than an order of magnitude smaller than for the bunched steps discussed so far. Figure 5 shows that such fine structures push our technique to its limit. The Ti wetting layer preserves the step structure fairly well, but the subsequent Au layer nearly obliterates it. A judicious choice of the thickness for the Ti and Au layers is critical for optimally replicating the substrate (0.34 nm Ti and 0.7 nm Au, i.e., 2 monolayers Ti and 3 monolayers Au). If the Ti layer is too thin, it becomes prone to the formation of pinholes that allow Au islands to nucleate on the Si substrate. If it is too thick, the step structure becomes washed out. Likewise, there is a minimum thickness for the Au layer to get the organic thiol derivatives to stick¹⁶ and a maximum thickness to prevent blurring of the step features.

III. SUMMARY AND OUTLOOK

In summary we have explored methods to passivate and functionalize stepped silicon templates with gold while preserving their topography. Gold grows in the Stranski–Krastanov mode on clean Si(111), forming small islands at room temperature that coalesce into large islands upon annealing. These are preferentially located at the steps and form linear arrays of dots. A 0.7 nm titanium wetting layer yields a continuous and smooth Au coating after annealing to 275 °C. The underlying step morphology can be preserved down to dimensions of <5 nm. That is an order of magnitude finer than the templates functionalized with Au previously. Self-assembled step and dot patterns with single digit nanometer dimensions^{14,15} become accessible for use as wires and dots in molecular electronics.²³ Thiol derivatives of biomolecules, such as DNA¹⁶ and proteins, could find use in patterned biosensors.

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