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Initial stages of Au adsorption on the Si(111)-(7×7) surface studied by scanning tunneling microscopy

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Initial stages of Au adsorption up to coverage of $\Theta \sim 3$ monolayers (ML) on the Si(111)-(7×7) surface at room temperature (RT) have been studied by scanning tunneling microscopy (STM). At very low Au coverages ($\Theta \sim 0.01-0.05$ ML) STM images show that some of the triangular subunit cells have slightly larger apparent height which is interpreted to be due to the adsorption of Au atoms on the Si rest atom sites. At higher coverages ($\Theta > 0.1$ ML) small Au clusters form preferentially on top of the Si center adatoms and, to a less extent, on top of the Si corner adatoms. Stacking fault does not have an appreciable effect on Au adsorption in this coverage regime. The results for Au are compared to the data on the adsorption of other metals on the Si(111)-(7×7) surface and mechanisms governing preference of the adsorbates for a particular bonding site are discussed. [S0163-1829(97)03843-5]

I. INTRODUCTION

The growth of thin Au films on the Si(111)-(7×7) surface at room temperature (RT) has been extensively studied in the past years.[1–15] These studies aimed at the understanding of the formation of the Au/Si interface as a model metal-semiconductor system. Many techniques includinguger electron spectroscopy,[1,3,6,11,12] photoemission spectroscopy,[2,6,7,9–11,13,15] low-energy electron diffraction,[3,6,13] electron-energy-loss spectroscopy,[3,4] ion scattering technique,[5] x-ray standing-wave spectroscopy,[8] and ballistic electron emission microscopy[14] have been applied to study the behavior of Au RT growth on the Si(111) surface. Scanning tunneling microscopy (STM) studies mainly concentrated on the investigation of structures of the annealed interfaces.[16]

The general picture established by these studies implies that the Au/Si interface has a sandwich structure, namely, the top few layers of a Au film grown on the Si substrate contain a silicidelike compound with approximate stoichiometry of Au_3Si. In other words, even for thick films, Si is present in the top layer of the Au film. Beneath this silicidelike layer there is a layer of metallic Au bonded to the Si substrate. Recent photoemission studies[13] show that the growth starts with the formation of a silicidelike layer up to coverage of $\Theta \sim 4$ monolayers (ML) and then metallic Au starts to nucleate beneath it. At $\Theta \sim 4-5$ ML the silicidelike layer is detached from the Si substrate and then the growth proceeds by the accumulation of a buried layer of metallic Au. The interface between metallic Au and the Si substrate is abrupt.

However, the initial stages of Au RT growth on the Si(111)-(7×7) surface are not well understood. In particular, it is not clear whether Au atoms react with the Si substrate from the very beginning of deposition (''interstitial'' model) (Ref. 17) or the formation of a silicidelike compound starts at some critical coverage (''screening'' model).[3,10,18] Also the adsorption sites of Au atoms within the 7×7 unit cell are not known. X-ray standing-wave spectroscopy studies[8] show that Au atoms occupy positions beneath the top layer of Si atoms indicating some amount of intermixing. Photoemission studies[7] reveal that thin Au films grown at RT and annealed Au films with the $\sqrt{3}\times\sqrt{3}$ reconstruction exhibit very similar electronic structure. This fact was taken as a possible indication that the bonding arrangement of Au atoms in thin RT grown films is very similar to the trimer bonding arrangement in the $\sqrt{3}\times\sqrt{3}$ reconstruction.

The other incentive for studying the RT growth of metals on the Si(111)-(7×7) surface at submonolayer coverages comes from the need to understand the basic trends of the adsorption of metals on this surface. Due to its large unit cell and a variety of dangling bond sites the Si(111)-(7×7) surface is a very good model surface for studying local surface chemistry of adsorption. Figure 1 shows the dimer-adatom-stacking-fault (DAS) model proposed by Takayanagi *et al.*[19] According to this model the 7×7 unit cell consists of two triangular halves (subunit cells) one of which has a stacking fault. Due to the formation of the 7×7 reconstruction the

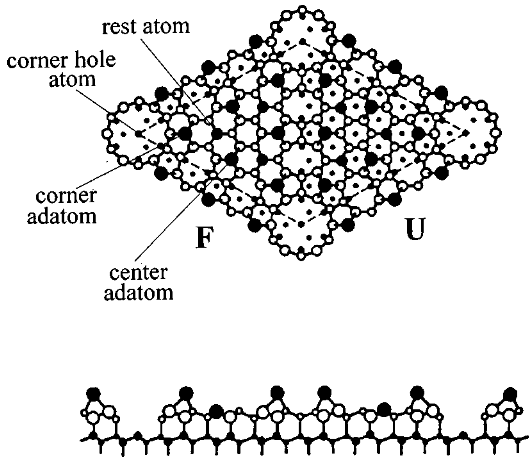

FIG. 1. Dimer-adatom-stacking-fault (DAS) model of the Si(111)-(7×7) unit cell proposed by Takayanagi *et al.* (Ref. 19). Corner and center adatoms, rest atoms, and corner holes are shown on the drawing. Faulted (*F*) and unfaulted (*U*) halves of the 7×7 unit cell are also marked.

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number of dangling bonds is drastically reduced as compared to the unreconstructed Si(111) surface. Each half of the 7×7 unit cell has only 9 dangling bonds located on 6 adatoms and 3 rest atoms (large filled circles in Fig. 1). Besides there is a dangling bond at each corner of the triangular subunit cell at the corner hole site. Thus, there are 19 dangling bonds per 7×7 unit cell (12 adatoms, 6 rest atoms and 1 corner hole). These dangling bonds provide natural adsorption sites for adsorbed species. STM has proved to be an indispensable tool for determination of specific bonding sites of metal atoms on semiconductor surfaces including the Si(111)-(7×7) surface. Adsorption of many different metals on the Si(111)-(7×7) surface at submonolayer coverages has been studied by STM to date.[20–29] Despite differences in the properties of these metals, some general trends can be noticed in their adsorption behavior on the Si(111)-(7×7) surface. In particular, almost all the metals studied exhibit preference for the adsorption on the faulted half of the unit cell and many of them prefer to occupy positions on top of the Si adatoms and especially the center Si adatoms.

The issue of preferential adsorption has been addressed theoretically by Brommer *et al.*,[30] who explained the observed trends in the adsorption by employing the concept of ''local softness'' and ''hardness'' which determine the most energetically favorable reaction site. According to the authors, adsorption behavior should be very different for elements that are electrophilic reactants or acceptors (i.e., their electronegativity is greater than the electronegativity of the Si(111)-(7×7) surface which is taken to be equal to its work function of 4.8 eV) and nucleophilic reactants or donors [i.e., their electronegativity is less than that of the Si(111)-(7×7) surface]. So far only adsorption of metals that are donors with respect to the Si(111)-(7×7) surface has been studied. Au with an electronegativity of 5.77 eV (Ref. 31) is an *acceptor* with respect to the Si(111)-(7×7) surface and thus it might be expected to show quite different site-selective adsorption behavior.

In this paper the STM results for initial stages of Au adsorption on the Si(111)-(7×7) surface up to $\Theta \sim 3$ ML will be presented. The implications of these results for better understanding of the formation of the Au/Si interface as well as the trends of RT adsorption of metals on the Si(111)-(7×7) surface will be discussed.

II. EXPERIMENT

The experiments were performed in the UHV chamber with the pressure of $\sim 3 \times 10^{-10}$ Torr. Commercial n-type Si(111) samples were used. The 7×7 reconstruction was prepared by resistive heating at $\sim 800\,^\circ$C for several hours followed by annealing at $\sim 1200\,^\circ$C for 1–2 min. This procedure routinely yields a well-ordered clean surface as confirmed by low-energy electron diffraction (LEED) and STM.

Au was evaporated from a heated tungsten filament. The typical evaporation rate was 0.05–0.2 monolayers per minute (ML/min) as measured by quartz-crystal thickness monitor. One monolayer is defined as coverage at which one Au atom corresponds to one atom of the unreconstructed Si(111) surface ($1\ \mathrm{ML} = 7.8 \times 10^{14}$ atoms/cm^2). The cleanliness of the Au source was assured by careful degassing and the observation of the 5×2 LEED pattern when the surface was annealed at $\sim 400\,^\circ$C. All STM images presented here were taken at RT.

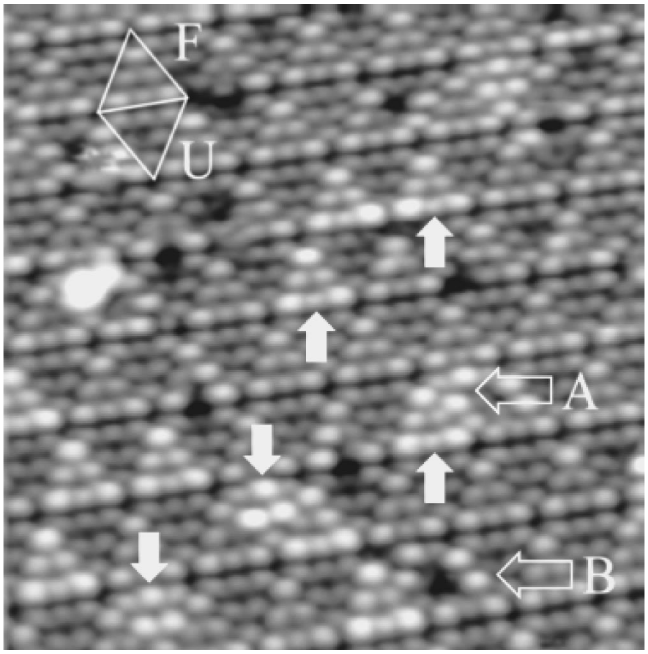

FIG. 2. Filled-state ($195\ \text{Å} \times 195\ \text{Å}$, sample bias $V_S = -0.7$ V, tunneling current $I = 0.06$ nA) STM image showing the Si(111)-(7×7) surface with ~ 0.01 ML of Au. The faulted (F) and unfaulted (U) halves of the 7×7 unit cell are shown. Some of the triangular subunit cells appear highlighted as marked by the filled arrows. An unfaulted subunit cell with two brighter center adatoms and a faulted subunit cell with three brighter adatoms (one center and two corner) are marked A and B, respectively.

III. RESULTS

Figure 2 presents a STM image of the Si(111)-(7×7) surface covered with ~ 0.01 ML of Au. This image has been taken at negative sample bias (-0.7 V) applied to the sample and, therefore, it reflects the spacial distribution of occupied surface electronic states (filled-state image). The surface is composed of diamond-shaped 7×7 unit cells. In the STM images a 7×7 unit cell has 12 distinct protrusions, each corresponding to a Si adatom. Faulted halves of the 7×7 unit cells can be distinguished from the unfaulted halves by its brighter appearance in the filled-state images. The image shown in Fig. 2 is identical to the STM images of the clean Si(111)-(7×7) surface with the exception of some triangular subunit cells which exhibit larger (by ~ 0.3–0.6 Å) corrugations and appear brighter than the others. These subunit cells are marked by filled arrows in Fig. 2. It should be noted that in the marked *faulted* subunit cells *corner adatoms* exhibit stronger corrugations while in the marked *unfaulted* subunit cells *center adatoms* exhibit stronger corrugations. In some subunit cells (marked by open arrows in Fig. 2) not all the adatoms have larger apparent height. For example, the unfaulted subunit cell marked A has only two brighter center adatoms, while the faulted subunit cell marked B has three brighter adatoms (one-center and two-corner adatoms).

To our knowledge no such peculiar features have been observed before during the adsorption of metals on the

Si(111)-(7×7) surface. These features appear only in the filled-state STM images while the empty-state images are completely identical to those of the clean Si(111)-(7×7) surface. Therefore, it can be concluded that the observed change in the apparent height is caused by the redistribution of charge near the Si adatom sites rather than Au adsorption on top of the Si adatoms or the substitution of the Si adatoms by the Au atoms.

We speculate that the observed features may arise from the charge transfer from the rest atoms to the adatoms caused by the adsorption of Au atoms on the rest atom sites. Since the rest atom dangling bonds are completely filled,[30,32] the adsorption of the Au atoms on these sites would lead to the transfer of extra charge to adatom dangling bonds. Si rest atoms are not imaged by the STM and, therefore, it is difficult to determine the presence of an adsorbate on a rest atom site directly. However, the adsorption event affects the distribution of charge on the rest atom site and neighboring adatom sites. These subtle changes manifest themselves in scanning tunneling spectroscopy (STS) current-voltage characteristics, as has been convincingly shown by Avouris and Wolkow[33] for the NH_3/Si(111)-(7×7) system. However, the authors did not observe any changes in adatom apparent height, possibly, because of a large number of already reacted adatoms.

In the framework of our interpretation, the triangular subunit cells with larger apparent height should contain three Au atoms adsorbed on top of three Si rest atoms. However, the redistribution of charge caused by the adsorption is apparently different for faulted and unfaulted halves of the 7×7 unit cell. Since the corner adatoms appear brighter in the highlighted faulted subunit cells, it is reasonable to conclude that Au adsorption on the rest atom sites leads to the charge transfer mainly to the corner adatoms, while for the unfaulted subunit cells the extra charge goes primarily to the center adatoms.

Occasionally, partially highlighted subunit cells such as *A* and *B* in Fig. 2 have been observed. In the framework of our interpretation, configuration *A* would correspond to one adsorbed Au atom (charge transfer mainly to two neighboring center adatoms) and configuration *B* would correspond to two adsorbed Au atoms (charge transfer to one-center and two-corner adatoms). However, the Au atoms do not adsorb randomly on the Si rest atom sites, but rather tend to group in the same subunit cell. This may suggest that the adsorption of one Au atom changes the local potential in such a way that the adsorption of another Au atom on the rest atom site in the same subunit cell becomes favorable. The Au atoms also tend to favor the adsorption on the faulted half of the 7×7 unit cell with ~70% of all Au atoms going to the faulted subunit cells.

Upon further deposition of Au, new features appear on the surface. Figure 3(a) presents a typical filled-state STM image of the Si(111)-(7×7) surface covered with ~0.1 ML of Au. A number of Au related features is seen in this image. Examination shows that the most abundant features are trimers located on top of center adatoms (marked *T*) and round clusters (marked *C*). Even at this low coverage Au already shows tendency for clustering. The distribution of these clusters on the surface appears to be quite random. In particular, unlike in the very low coverage regime, they do not exhibit any preference for the faulted half of the 7×7 unit cell.

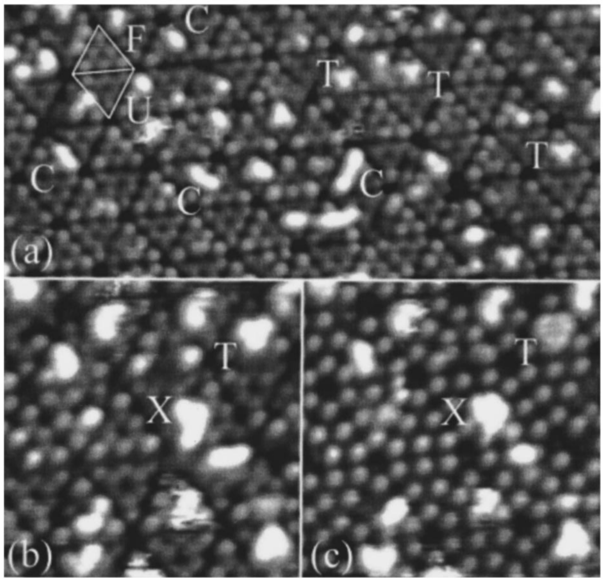

FIG. 3. (a) Filled-state (240 Å×110 Å, $V_S = -1.7$ V, $I = 0.2$ nA) STM image showing a Si(111)-(7×7) surface covered with ~0.1 ML of Au. Some of the adsorbate-related features are marked on the image: trimers (*T*), clusters of round shape (*C*). (b) and (c) A pair of STM images of the same area (90 Å×90 Å) showing Si(111)-(7×7) surface covered with ~0.1 ML of Au. Image (b) has been taken at $V_S = -1.6$ V, $I = 0.2$ nA and image (c) at $V_S = +1.6$ V, $I = 0.2$ nA. A cluster marked *X* appears bigger and of different shape in the filled-state image as compared to the empty-state image. Trimer (marked *T*) appears to be fuzzy in the empty-state image.

Figures 3(b) and 3(c) present higher-resolution filled- and empty-state STM images of the surface at this coverage ($\Theta \sim 0.1$ ML), respectively. These images show a closeup view of some of the Au structures adsorbed on the surface. Trimers [one of them marked *T* in Figs. 3(b) and 3(c)] appear in the filled-state STM images as three connected bright protrusions with the height of ~1 Å located above the positions of the center Si adatoms. This indicates that they consist of at least three Au atoms adsorbed on top of the center Si adatoms. Since at lower coverage Au atoms may adsorb on the rest atom sites, as discussed above, these trimers may in fact consist of six Au atoms—three on top of the Si adatoms and three on top of the Si rest atoms. In the empty-state images trimers have lower apparent height (~0.2–0.3 Å). STM images also indicate that clusters appear to have different shape and even size in the filled- and empty-state images. A cluster marked *X* in Figs. 3(b) and 3(c) clearly shows this behavior. In general, clusters appear bigger in filled-state images. Some Si adatoms that appear to be covered by Au cluster in the filled-state images are clearly seen in the empty-state images. Such an enhancement of the Au features (especially trimers) in the filled-state images is probably due to a charge transfer from the Si substrate to the adsorbed Au (Au is more electronegative than Si and therefore the charge in the Au-Si bonds should be shifted towards Au atoms).

The counting of specific dangling bond sites of the Si(111)-(7×7) surface that are covered with Au provides the information about preferential sites of adsorption. The

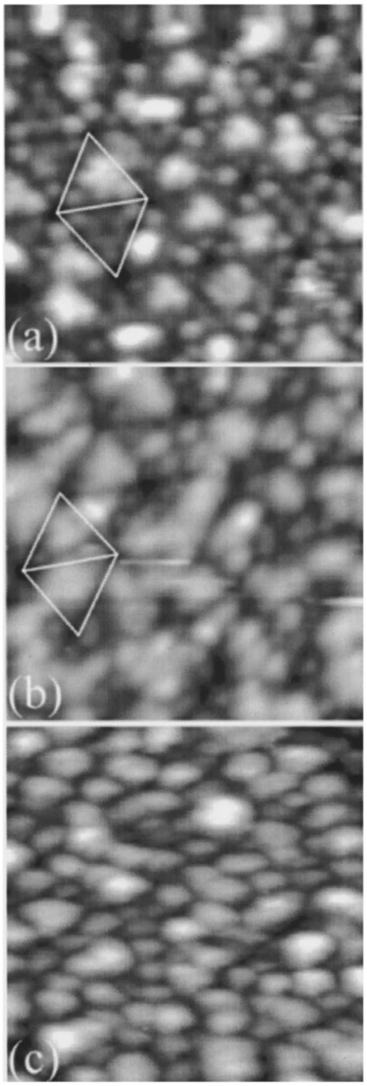

FIG. 4. Filled-state STM images of the Si(111)-(7×7) surface with different Au coverage: (a) $\Theta \sim 0.3$ ML (100 Å×100 Å, $V_S = -1.9$ V, $I = 0.5$ nA); (b) $\Theta \sim 0.6$ ML (100 Å×100 Å, $V_S = -2.0$ V, $I = 0.8$ nA); (c) $\Theta \sim 3$ ML (500 Å×500 Å, $V_S = 0.8$ V, $I = 0.5$ nA).

first observation is that the center adatoms are more reactive than the corner adatoms with the ratio of reacted center and corner adatoms ~2.5:1. Another important observation is the fact that the Au atoms do not show any appreciable preference for a particular half of the 7×7 unit cell. This behavior is quite different from the behavior of other metals which usually exhibit preference (sometimes, very strong as in the case of alkali metals[22]) for the faulted half of the 7×7 unit cell.

Figure 4 shows filled-state STM images of the Si(111)-(7×7) surface at higher Au coverages [$\Theta \sim 0.3$ ML (a), $\Theta \sim 0.6$ ML (b), and $\Theta \sim 3$ ML (c)]. At $\Theta \sim 0.3$ ML [Fig. 4(a)] Au forms clusters preferentially in the center of the 7×7 triangular subunit cells and the overwhelming majority of the corner hole sites as well as many corner adatoms remain uncovered. At $\Theta \sim 0.6$ ML [Fig. 4(b)] clusters grow bigger and begin to cover the dimer walls separating triangular subunit cells even though many corner adatoms still remain uncovered. This behavior is unusual because other metals like Pb,[25] Li,[26] tend to decorate the 7×7 triangular subunit cells completely forming a quasiordered net of triangular islands before these islands start to coalesce covering the dimer walls. At higher coverages islands coalesce and form a continuous film [Fig. 4(c)] with the granular structure independent of the underlying 7×7 reconstruction.

IV. DISCUSSION

As has been pointed out in the Introduction, Brommer *et al.*[30] analyzed the reactivity patterns of the Si(111)-(7×7) surface based on principles of local softness and electronegativity. The authors predicted that the Si dangling bonds should react with the *nucleophilic* elemental species in the order *adatoms>corner holes>rest atoms*, while for the *electrophilic* species the order should be *corner holes>rest atoms>adatoms*. For electrophilic reactants the adsorption on the faulted half of the 7×7 unit cell should be preferred but there is no difference between center and corner adatoms in the same half of the unit cell. Au is classified as an electrophilic reactant since its electronegativity 5.77 eV is greater than that of the Si substrate (4.8 eV).

The STM images taken at very low coverages ($\Theta \sim 0.01$ ML, Fig. 2) show that some of the triangular subunit cells of the 7×7 reconstruction have slightly larger apparent height. These features have been interpreted to be due to the charge transfer from the Si rest atoms to the Si adatoms caused by the adsorption of the Au atoms on the Si rest atom sites. Thus, the STM data suggest that the Au atoms react with the Si rest atoms before they react with the Si adatoms which is in line with the theoretical predictions. It should be noted that for other metals features similar to those seen in Fig. 2 have never been observed. This fact can also be readily explained in the frame work of our interpretation since to date only the room-temperature adsorption of metals which are classified as nucleophilic reactants has been studied on the Si(111)-(7×7) surface. These metals should react first with the Si adatom rather than Si rest atom dangling bonds.

At higher coverages ($\Theta > 0.1$ ML) Au forms clusters preferentially on top of the center adatoms and, to a less extent, on top of the corner adatoms while theoretical predictions are that the center and corner adatoms should be equally reactive. We believe that the observed discrepancy arises as an effect of the adsorbate-adsorbate interaction. The results of Brommer *et al.*[30] pertain to a single adsorbate atom occupying a dangling bond site within the 7×7 unit cell and rely on the assumption that the most favorable adsorption site is determined solely by the interaction between the adsorbate and the substrate. However, Au clustering has been observed even at low coverage which suggests that there exists a significant attractive Au-Au interaction. Thus, at this coverage the theoretical conclusions may not be directly applicable to the experimental situation.

According to the STM data, the most favorable site for the formation of a small Au cluster is the center of a triangular subunit cell of the 7×7 structure, which includes three Si center adatoms and three rest atoms. Intuitively, one can expect that since by clustering at this site the Au atoms may satisfy six dangling bonds and form a compact hexagonal structure. The corner adatoms do not offer such an advantage since they are adjacent to the dimer rows which are devoid of the dangling bond sites. Corner hole dangling bonds are located ~ 4.5 Å below the adatoms and are encircled by the wall of the Si dimers, which makes them an unattractive site for the cluster formation.

The STM images show that deposited Au appears as bright features on the Si(111)-(7×7) surface. The presence of such highly symmetric features as trimers (see Fig. 3) suggests that Au adsorbs on top of the surface rather than diffuses into the subsurface layer with the formation of amorphous Au-Si alloy. The absence of intermixing has been also claimed for the RT growth of Au on the Si(100) surface.[34] Though some amount of intermixing cannot be completely ruled out since the STM cannot provide information about chemical composition of the observed clusters as well as their spacial extent into the surface, possible intermixing is restricted to local areas and does not involve the whole surface. We believe that these results favor the ''screening'' model of the growth of this interface which implies the existence of some critical coverage at which the formation of the silicidelike compound starts.

V. CONCLUSIONS

The STM experiments on the room-temperature Au adsorption on the Si(111)-(7×7) surface suggest that at $\Theta < 0.05$ ML the Au atoms most probably adsorb on the Si rest atom sites preferentially in the faulted half of the 7×7 unit cell which is in agreement with the theoretical predictions.[30] At $\Theta \sim 0.1$ ML small Au clusters are formed mainly on the Si center and, to a lesser extent, Si corner adatoms. There is no appreciable preference for the adsorption of Au on a particular half of the unit cell in this coverage regime. The STM data also suggest that the Au adsorbates stay on top of the Si(111)-(7×7) surface and do not intermix or diffuse into the surface. Thus, the results favor the ''screening'' model which suggests some critical Au coverage for the intermixing to start.

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