

## Na Adsorption on the Si(111)-(7 × 7) Surface: From Two-Dimensional Gas to Nanocluster Array

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We have systematically investigated Na adsorption on the Si(111)-(7 × 7) surface at room temperature using scanning tunneling microscopy (STM). Below the critical coverage of 0.08 monolayer, we find intriguing contrast modulation instead of localized Na adsorbates, coupled with streaky noise in the STM images, which is accompanied by monotonic work function drop. Above the critical coverage, Na clusters emerge and form a self-assembled array. Combined with first-principles theoretical simulations, we conclude that the Na atoms on the (7 × 7) surface are, while strongly bound (~ 2.2 eV) to the surface, highly mobile in “basins” around the Si rest atoms, forming a two-dimensional gas phase at the initial coverage, and that the cluster at the higher coverage consists of six Na atoms together with three Si adatoms.

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Self-assembled nanoclusters have received much attention because they offer the possibility to fabricate and pattern micro/nanoelectronics, ultrahigh-density memories, and nanocatalysts [1–3]. Recently, fabrication of nanocluster superstructures of metals using a periodic template with a large unit cell, such as the Si(111)-(7 × 7) superlattice, has also been demonstrated [4]. However, to date, little attention has been paid to the fundamental mechanisms of the self-assembly. As a prototype system, alkali metal (AM) growth on semiconductor surfaces has long been studied by various spectroscopic techniques [5–7] and by scanning tunneling microscopy (STM) more recently [8,9]. However, the important aspects of the adsorption of AMs on the Si(111)-(7 × 7) surface are still elusive. For example, because of the hydrogenlike electronic structure, there has been a general tendency to assume that AM atoms would react with the dangling bonds on Si(111)-(7 × 7) at the initial coverage [10–16], similar to the behavior of atomic hydrogen [17–19]. However, this assumption has been questioned [20]. Moreover, the clustering of AMs has not been addressed much so far.

In this Letter, we report that Na atoms do not adsorb on the Si dangling bonds below the critical coverage,  $\theta_c$  of 0.08 monolayer (ML) at room temperature (RT), and that they, instead, form a two-dimensional (2D) gas system, which is characterized by contrast modulations and streaky noise in the STM images with the 7 × 7 periodicity. We also show that above the critical coverage the Na gas condenses to form a self-assembled cluster array consisting of six Na atoms per cluster. With the help of first-principles calculations we propose a new scheme for the Na adsorption on the Si(111)-(7 × 7) surface.

Our experiments were performed in an extremely high vacuum ( $< 1 \times 10^{-11}$  Torr) STM in a specially processed stainless steel chamber (NKK “clean-Z”) [21] to minimize contamination (AMs are very reactive). The system was equipped with a high-resolution electron energy loss spectroscopy, which we used to measure the surface work function change ( $\Delta\phi$ ) with an energy resolution of 20 meV [22]. The Si(111)-(7 × 7) surface was prepared by standard flashing to 1100 °C. Sodium was evaporated from a well-outgassed commercial SAES dispenser on the Si substrate held at RT, with the pressure rise during evaporation  $< 2 \times 10^{-11}$  Torr. For each Na coverage, the surface was examined by STM, and the corresponding  $\Delta\phi$  was measured to independently determine the Na coverage. The Na flux was calibrated by using the Si(100)-(4 × 1)-Na system, which is known to have the well-defined Na coverage of 1/4 ML at  $\Delta\phi = -1.5$  eV [23–25].

In Figs. 1(a)–1(f) we show the filled state STM images of the Si(111)-(7 × 7) surface with increasing Na coverage up to 0.10 ML [where 1 ML refers to the in-plane atomic density of Si(111), i.e.,  $7.8 \times 10^{14}$  cm<sup>-2</sup>]. The corresponding work function decreases rapidly by as much as 0.75 eV at  $\theta = 0.08$  ML [four atoms per unit cell (UC)] as shown in Fig. 2. According to the conventional Si dangling bond adsorption model, one would expect to observe a monotonic increase of darkly imaged spots at the Si adatom sites [16], due to the removal of the adatom dangling bond states by Na adsorption [11,13]. However, there are no such sites observed in the STM images. Instead, we notice intriguing contrast modulation in Figs. 1(b)–1(f), which are demonstrated more clearly [Figs. 1(h)–1(l)] by subtracting the background

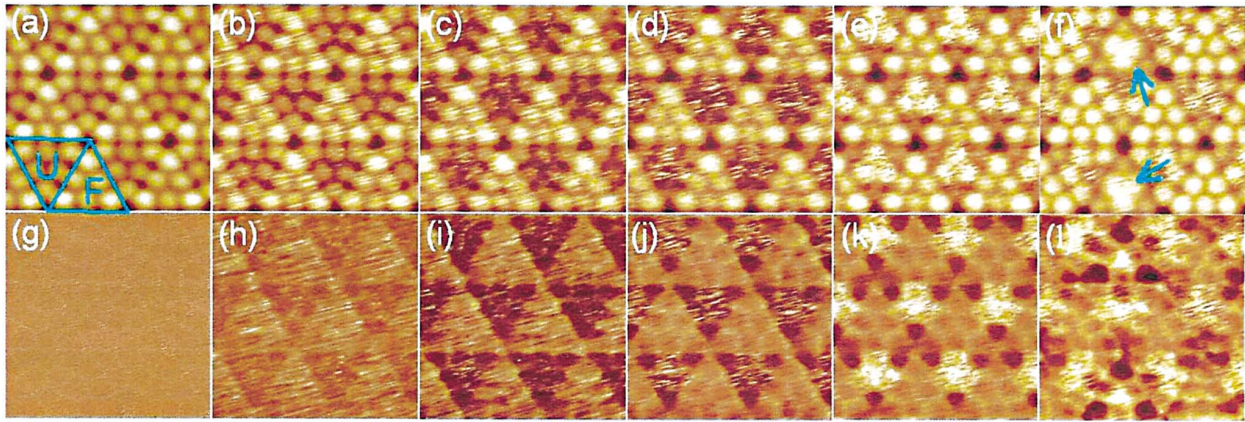


FIG. 1 (color). Filled state STM images (at  $-1.3$  V sample bias,  $20$  pA) of the Si(111)- $(7 \times 7)$  surface with Na coverage at (a) 0; (b) 0.02; (c) 0.04; (d) 0.06; (e) 0.08; and (f) 0.10 ML. A  $(7 \times 7)$  unit cell is marked by two green triangles in (a), where F is the FHUC and U is the UHUC. At coverage (f) of 0.10 ML, Na clusters start to form (two blue arrows). (g)–(l) show the contrast modulation upon Na adsorption for images (a)–(f) by subtracting the image of the clean  $(7 \times 7)$  surface.

contribution of a clean  $(7 \times 7)$  image [Fig. 1(a)]. In the coverage range of  $0 < \theta < 0.04$  ML [Figs. 1(b) and 1(c)], the faulted-half unit cell (FHUC) appears increasingly brighter than the unfaulted half (UHUC). In the range of  $0.04 < \theta < 0.08$  ML [Figs. 1(d) and 1(e)], the UHUC also becomes bright and finally as bright as the FHUC. Note the contrast modulation keeps the periodicity of the  $(7 \times 7)$  substrate.

Above the critical coverage of 0.08 ML, Na clusters form with a well-defined triangular shape as shown in Fig. 1(f) (blue arrows). Figures 3(a) and 3(b) show full details of the cluster array formed at coverage of  $\theta = 0.22$  ML. In both filled and empty state images, bright triangular clusters appear at the center of FHUCs and UHUCs. The clusters have the identical threefold sym-

metry and are compact in the filled states while they are split and enlarged in the empty states. Little bias dependence is observed for the clusters in the bias range of 2.5 to 0.6 V (empty states) and  $-0.5$  to  $-2.5$  V (filled

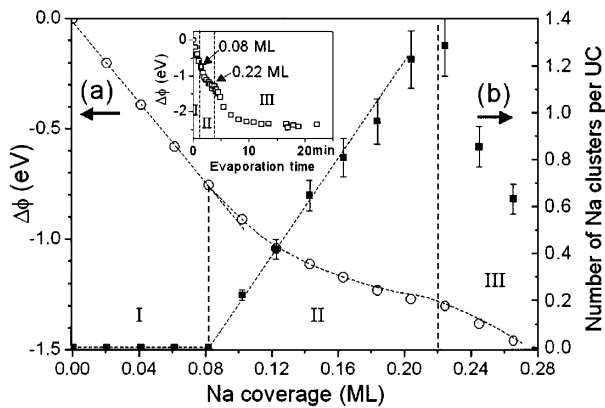


FIG. 2. (a) The surface work function change ( $\Delta\phi$ ) as a function of the Na coverage ( $\theta$ ). (b) The corresponding number of Na clusters per unit cell. The inset shows the entire work function change up to the Na saturation coverage ( $\Delta\phi = -2.5$  eV). Two inflection points are clearly evident at 0.08 and 0.22 ML, dividing into the three distinctly different adsorption stages.

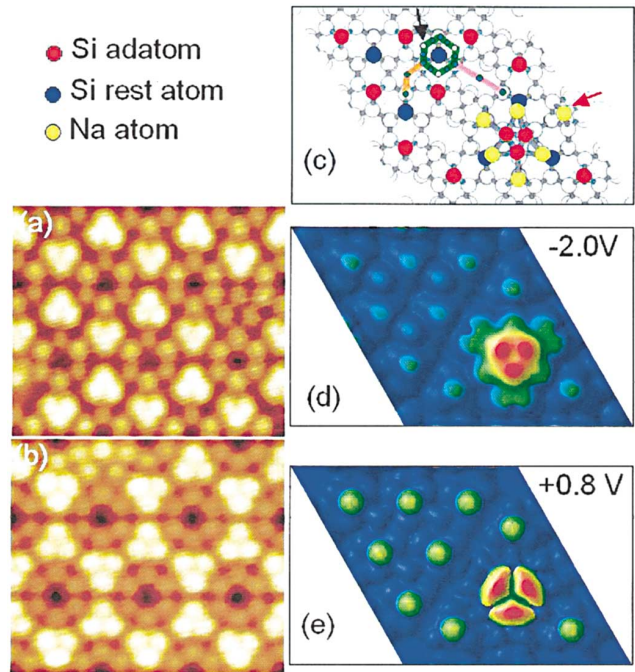


FIG. 3 (color). Filled and empty state images of the Na clusters with bias voltage of  $-2.0$  V for (a) and  $+0.8$  V for (b). (c) The structural model of the Na cluster with the highest  $E_b$  ( $2.13$  eV/atom). One of the Na adatoms near the Si dimer is pushed outwards (red arrow), the structure being triply degenerated. (d),(e) Simulated filled and empty state STM images, at  $-2.0$  V and  $+0.8$  V, respectively. The top part of (c) shows the adsorption scheme for a single Na atom. The green hexagon indicates an “attraction basin.” The three open circles (black arrow marked) correspond to the lowest energy sites ( $E_b = 2.26$  eV for the FHUC and  $2.20$  eV for the UHUC).

states). The cluster array appears to be semiconducting since it is difficult to obtain a tunneling current at bias within  $\pm 0.5$  V.

While STM images do not register the individual Na atom on the surface at  $\theta < 0.08$  ML, the marked work function drop and the STM contrast modulation have clear implication that Na atoms are present on the surface. Possible configurations of Na atoms are (i) incorporated near surface selvedge or (ii) moving faster than STM tip scan speed. We can exclude the first possibility since random and localized adsorbates in the selvedge will not yield a periodic contrast modulation or the streaky noise in Figs. 1(b)–1(f), which are independent of the STM tip conditions. Similar noise has been attributed to the movement of adsorbates in many cases, including Si on the Si(111)-(7  $\times$  7) surface [26,27].

Furthermore, we have performed low temperature STM experiments by quenching the Na/Si(111)-(7  $\times$  7) surface to 35 K, and successfully observed individual bright spots, whose number density is in proportion to the Na exposure [28]. Thus we can safely conclude that the Na atoms are present on the Si(111)-(7  $\times$  7) surface and are moving rapidly below the critical coverage of 0.08 ML at RT. The contrast modulation in STM images can be explained by a time-averaged charge transfer from the moving Na atoms to the Si surface, since the observation of the work function drop clearly suggests a significant charge transfer from the Na atoms to the surface, thus lifting the surface Fermi level.

Figure 2 also plots the number density of the Na clusters as a function of the Na coverage together with the corresponding value of  $\Delta\phi$ . The Na cluster begins to form at  $\theta_c = 0.08$  ML (4 atom/UC) and its number density increases monotonically with Na coverage. The slope of the curve yields that each cluster should contain six Na atoms. Above 0.22 ML, we notice that the density of the Na clusters decreases and disordered features appear, indicating that the clusters undergo a drastic structural change (becoming irregular) by taking on additional Na atoms. We found that the maximum density of the Na clusters is around 1.3 clusters/UC, instead of 2 expected for a perfect array of Na clusters.

Present STM investigation suggests that there are three adsorption stages: (I) a gaslike phase ( $\theta < 0.08$  ML); (II) formation of Na clusters ( $0.08 < \theta < 0.22$  ML); (III) decay of clusters ( $\theta > 0.22$  ML). Correspondingly,  $\Delta\phi$  also shows three regions, with two inflection points at 0.08 and 0.22 ML (Fig. 2). Our results nicely illustrate a correlation between the work function change (charge transfer) and structure changes.

To understand these observations in detail, first-principles calculations were performed. For example, Cho and Kaxiras calculated K adsorption on the Si(111)-(2  $\times$  2) and suggested that the most stable adsorption site is not the on-top site of Si adatoms, but is rather several high coordination sites, which form “attraction

basins” [20]. They predicted that K atoms move freely within the basins at RT since the potential energy surface in the basin is almost flat, although the binding energy ( $E_b$ ) is high ( $\sim 2.0$  eV). In their study, however, only the small (2  $\times$  2) unit cell is employed [which is representative of the local periodicity of the (7  $\times$  7) unit cell], and the interaction among K adsorbates is not included. Since our experiment indicates that the adsorption behavior of Na differs between the FHUC and UHUC, and shows significant coverage dependence, extensive *ab initio* calculations with the real (7  $\times$  7) unit cell are warranted.

Our model consists of a 6-layer (7  $\times$  7) unit cell having 298 Si atoms, 49 terminating H atoms, and a vacuum layer of 9 Å. A plane-wave method [29] with ultrasoft pseudopotentials was used within the generalized gradient approximation for the exchange-correlation energy [30]. The plane-wave cutoff energy was 11 Ry, and the Brillouin zone was sampled at the  $\Gamma$  point. All atoms were fully relaxed until the forces were  $< 5$  meV/Å.

For the single Na atom adsorption, we find that neither the Si adatom site ( $E_b = 1.80$  eV in FHUC) nor the Si rest atom site ( $E_b = 2.04$  eV in FHUC) is a favorable site. The lowest energy site is located around the Si rest atoms [three equivalent sites noted by open circles in Fig. 3(c)]. The binding energy is 2.26 eV for FHUC and 2.20 eV for UHUC. Several other sites around the Si rest atom have only slightly ( $< 0.14$  eV) smaller binding energies than the lowest energy site. Thus these sites form a “basin” [as marked by a green hexagon in Fig. 3(c)], agreeing with Cho and Kaxiras. A Na atom can diffuse rapidly within the basin due to the small energy barrier of 0.14 eV ( $10^{10}$  hopping/s at RT) in good agreement with our experiments. The diffusion barrier is 0.36 eV (i.e.,  $10^7$  hopping/s at RT) for hopping among the three neighboring basins within the half unit cell [denoted by the orange path in Fig. 3(c)] and 0.42 eV (i.e.,  $10^6$  hopping/s at RT) for crossing the (7  $\times$  7) half unit cell boundary (denoted by the pink path). In addition, we find that the Na atom transfers charge to the nearest Si adatom, making it brighter in the filled state STM images. As the FHUC is more favorable than the UHUC ( $\Delta E_b = 0.06$  eV), the Na atom stays longer in the FHUC, making it even brighter in the filled state STM images [Figs. 1(b) and 1(c)].

For the higher coverages, various configurations have been calculated with  $n$  ( $n = 2$  to 12) Na atoms adsorbed on various sites in the (7  $\times$  7) unit cell. When two Na atoms are distributed among the neighboring basins in the FHUC, the resulting binding energy is  $2.26 \pm 0.01$  eV/atom for all possible configurations, which is virtually identical to that of the single Na atom in the FHUC, indicating that the interaction among the Na atoms in the neighboring basins is negligible.

Interestingly,  $E_b$  reduces to 2.12 eV/atom in the FHUC when two Na atoms are placed in the same basin, indicating that a significant repulsive or “mutually exclusive”

interaction is exerted between the two Na atoms in the same basin. As a result, the incoming Na atoms avoid the basins that are already occupied in the initial coverage.

In each  $(7 \times 7)$  unit cell, there are six basins (states): three in the FHUC ( $E_b = 2.26$  eV/atom for single Na and  $E_b = 2.12$  eV/atom for double Na occupation), and three in the UHUC ( $E_b = 2.20$  eV/atom for single Na and  $E_b = 2.06$  eV/atom for double Na occupation). We can calculate the distribution of Na atoms in the FHUC ( $N$ ) starting with the grand canonical ensemble.  $N$  can be reduced to  $N = 3/(e^{(\varepsilon_1 - \mu)/kT} + 1)$ , identical to the Fermi-Dirac distribution if  $(\varepsilon_2 - \varepsilon_1) + (\varepsilon_1 - \mu) \gg kT$ , where  $\varepsilon_1$  and  $\varepsilon_2$  are the energy per Na atom when a basin is occupied by one or two Na atoms, respectively ( $\varepsilon_2 - \varepsilon_1 = 0.14$  eV),  $\mu$  is the chemical potential of Na. The factor 3 indicates that there are three basins (states) in each half unit cell. We find that the incoming Na atoms initially go to the FHUCs [Figs. 1(b) and 1(c)], and then to the UHUCs [Figs. 1(d) and 1(e)]. This explains the observation of the image brightness increase dominated in the FHUCs initially, and then in the UHUCs.

To understand the formation mechanism of the Na clusters above  $\theta_c = 0.08$  ML, we carried out an extensive search for the cluster model, covering over 20 plausible configurations. Our calculation shows that the most stable cluster structure ( $E_b = 2.13$  eV/atom) is the one presented in Fig. 3(c). This structure involves significant displacement of the Si adatoms. Three central Si adatoms move inward to form a trimer with a bond length of 2.44 Å, and the six Na atoms form a triangle centered around this trimer. One of the corner Na atoms is pushed outwards, resulting in a triply degenerate mirror symmetric structure (the other two states can be obtained by 120° rotations). Figures 3(d) and 3(e) show the simulated STM images for the filled and empty states, respectively, averaged over the degenerate states. Both images feature three protrusions near the Si center adatoms. The filled state image is compact, and the empty state image is slightly extended outward, in excellent agreement with our experiments [Figs. 3(a) and 3(b)].

With the increasing Na coverage, the Na chemical potential increases, and more Na atoms are forced into same basins. As this happens, the system will try to lower its energy by forming Na clusters, which increases  $E_b$  from 2.12 to 2.13 eV/atom. Meanwhile, the energy gained by clustering is not large (0.01 eV/atom), hence Na clusters are destroyed by further Na deposition, resulting in surface disordering (decay of Na clusters), as observed in our experiment (stage III).

In conclusion, we show a new scheme, from 2D gas to self-assembled nanocluster array, for the Na adsorption on Si(111)-(7 × 7) at RT. Our results shed a new insight to some ongoing puzzles, such as the work function change for this well-studied system in atomistic details. The picture established also helps the understanding of a

self-assembly mechanism of metals on a periodic template such as the Si(111)-(7 × 7).

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