Al Nucleation on Monohydride and Bare Si(001) Surfaces: Atomic Scale Patterning

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Submonolayer coverages of Al were evaporated onto hydrogen-terminated Si(001)-(2 × 1) surfaces and studied by scanning tunneling microscopy (STM). Nanoscale patterns of bare Si were created by STM desorption of hydrogen, and the size and number density of Al islands on bare and monohydride areas of the surface were compared. Dramatic differences in island nucleation are observed which suggest that the diffusion length of Al adatoms on the monohydride region is much longer than on bare Si. With lowered deposition rates or faster diffusing species, the effects studied here may provide a basis for selective metal patterning at atomic dimensions. [S0031-9007(97)02371-5]

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In this Letter we report a study comparing the differences in diffusion and sticking behavior of Al adatoms on bare Si(001)-(2 × 1) with the dangling-bond-free monohydride surface obtained by *in situ* hydrogen passivation. Using scanning tunneling microscope (STM) to selectively desorb individual H atoms, nanoscale patterns of bare Si were created on an otherwise H-terminated surface. The coexistence of these two different surfaces separated by nanometer distances presents a unique opportunity to compare the nucleation processes which form stable Al islands. In addition to kinetic properties of Al adatoms on Si surfaces at room temperature (RT), we also investigated how small Al clusters behave at elevated temperatures. Our central conclusion is that individual Al atoms can diffuse relatively large distances over H-terminated portions of the surface before colliding to form immobilized Al clusters. The diffusion length of Al adatoms is much smaller on bare Si, due to rapid Al-Si bonding and formation of stable Al ad-dimers. This raises the intriguing possibility of nanoscale metal patterning, utilizing the demonstrated atomic resolution of STM-induced hydrogen desorption to create templates of bare silicon as selective nucleation sites.

Samples were cut from B-doped Si(001) wafers with 0.1 Ω cm resistivity. After verifying a uniform monohydride 2 × 1 surface by STM [1], Al was evaporated from a coated W filament using a quartz-crystal thickness monitor to measure coverage. The chamber pressure was $<5 \times 10^{-10}$ Torr during evaporation. The deposition rate in these experiments is 0.01 Å/s unless otherwise noted, and one monolayer (ML) is defined as 6.78×10^{14} atoms/cm^2. Coverage estimates were verified to 10% by direct counting of Al ad-dimers on STM images of bare Si(001)-(2 × 1) surfaces at low coverage. Details of desorbing H by STM to create patterns have been described previously [2,3].

Figure 1(a) shows a typical STM image after depositing 0.1 ML Al onto a monohydride Si(001) surface. The apparent diameter of the clusters (which varies slightly with STM tip radius) has a Gaussian-like distribution as shown in Fig. 2(a), with a maximum height of 3–4 Å. The density of these Al clusters is $\sim 3.1 \times 10^{12}$ cm^{-2} at 0.1 ML nominal coverage, so the number of Al atoms within an average cluster is ~20. Since the smallest cluster is only one atomic layer high and about one dimer wide, we can infer that a two-atom nucleus is a stable configuration. Clusters of this small size do not move even after annealing at ~40 °C for 10 min. It is interesting to compare these isotropic Al clusters on the monohydride surface with Fig. 1(b), where the same amount of Al was deposited onto bare Si(001)-(2 × 1) under the same conditions. The number density of 1D Al chains seen here is $\sim 2.1 \times 10^{13}$ cm^{-2}. The chain-length distribution is found to decrease near exponentially from the stable one-dimer nucleus in Fig. 2(b). The general characteristics of Figs. 2(a) and 2(b) are very similar to the calculated island-size distribution based on the dynamic scaling theory [4], which predicts that the density of smaller islands approaches zero or nonzero depending on the size of the smallest stable island being greater or less than a dimer. Although a single Al atom on bare Si(001) has never been observed, the cause of the fundamental difference of these two systems seems to be on the interaction of the Al adatoms with the substrate.

Al deposition on the bare Si(001)-(2 × 1) surface has been extensively studied both theoretically [5,6] and experimentally [7–11]. At low coverage, one-dimensional (1D) Al chains are formed perpendicular to the underlying Si dimer rows as in Fig. 1(b). These chains have been identified by STM [10] as consisting of Al ad-dimers oriented parallel to the underlying Si dimers. The formation of ad-dimer chains on the bare Si(001)-(2 × 1) surface is quite common. Like Al, other group III elements Ga, In and group IV elements Si, Ge, Sn, Pb all form similar chains of parallel or perpendicular ad-dimers for low coverages at RT. One naturally expects that adatom diffusion will be anisotropic on the reconstructed Si(001)-(2 × 1) surface, but it is not obvious in which direction the

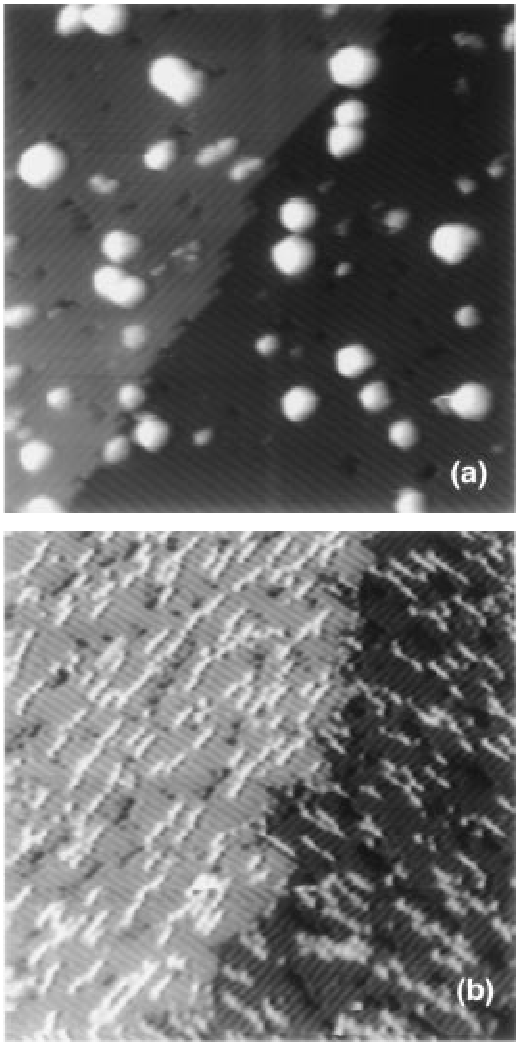

FIG. 1. 400 × 400 Å STM image of (a) a monohydride Si(001) surface and (b) bare Si(001)-(2 × 1) surface following deposition of 0.1 ML Al. Both images were taken at sample bias −2 V and current 0.1 nA.

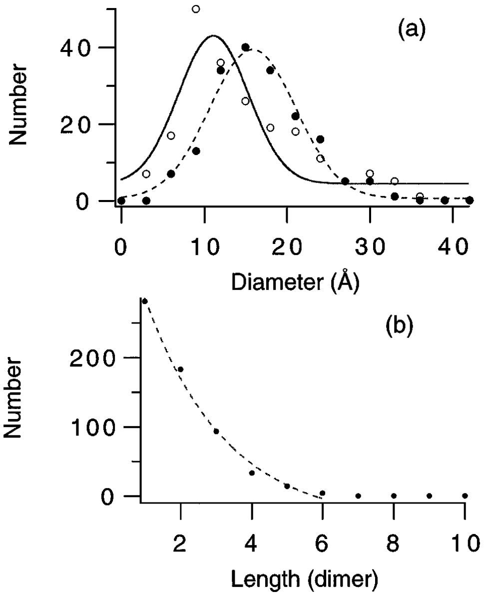

FIG. 2. (a) Lateral size distribution of Al clusters on monohydride Si(001). Open circles are data for 0.1 ML and filled circles are for 0.25 ML deposition. (b) Length distribution of Al chains on Si(001) for 0.1 ML deposition. The solid or broken lines are Gaussian or exponential fittings.

mobility of the adatoms will be higher. Calculations by Brocks and co-workers [6,12] indicate that the direction of easy diffusion for Si adatoms is along the underlying Si dimer rows, whereas the easy diffusion for Al adatoms is perpendicular. Since the long axes of the 1D chains formed by all of the aforementioned elements lie perpendicular to the Si dimer rows, this implies that the diffusion anisotropy alone is not responsible for the resulting island shape. This conclusion has been reached earlier by Mo and co-workers [13] from results of Monte Carlo calculations of Si on the Si(001) surface. An anisotropic sticking model was proposed [13] to account for the island shape anisotropy in the case of Si on Si(001), and confirmed by recent high-temperature-STM measurements of the anisotropic sticking ratio [14]. It is found that the sticking probability for Si adatoms at the end sites of a chain is ~50 times greater than the sticking probability at side sites. In the case of Al adatoms on Si(001), the preferential sticking at end sites of a chain can be understood from a calculation of the Al ad-dimer plus Si substrate minimum energy configuration [6]. After forming local bonds with the Al ad-dimer, the original Si dimer π bonds are broken leaving two dangling bond states on the Si atoms bonded to the Al ad-dimer at each end. These surface dangling bonds provide the reactive sites for binding of a third Al adatom, which in turn attracts a fourth to form the second Al ad-dimer. This "surface polymerization" mechanism [6] can be repeated to form chains of arbitrary length under appropriate conditions. The role of surface dangling bonds in the process is obviously crucial. When the Si surface is terminated by H atoms, there will be no available Si dangling bonds to initiate the polymerization reaction. Although the atomic structure on the surface still has the same 2 × 1 symmetry, formation of Al chains is not expected. Indeed, we find that Al adatoms form isotropic clusters randomly distributed over the monohydride surface as in Fig. 1(a).

The fact that the number density of Al clusters on the H-terminated surface is lower by a factor of ~7 compared to the chain density on bare Si(001) implies a lower nucleation rate on the monohydride surface. From the spherical shape of the clusters, one can conclude that without bare dangling bonds, Al-Al sticking is fairly isotropic. Also, no significant diffusional anisotropy is expected in this system based on a first-principles calculation [15]. Since both the diffusion and sticking are isotropic and the deposition time (10 s) is much longer than the lifetime of a monomer, we can test the relation, $N^3 \propto R\theta/D$, given in Ref. [16] between N the island density, R the deposition rate, θ the coverage, and D the diffusion coefficient. Indeed, we find that increasing the evaporation rate by a factor of 2.5 increases the observed cluster density by 2, close to the value 1.8 given by this relation for the same duration and sample temperature. Higher coverage causes the diameter and height of the clusters to increase as expected in Fig. 2(a). The above relation cannot be applied in a straightforward manner to compare with results on bare Si(001), however, due to anisotropic diffusion and different sticking coefficients on that surface.

In order to directly compare binding of Al adatoms between bare and H-terminated Si(001) surfaces, we have used STM to pattern the monohydride. Electrons emitted from a STM tip can locally desorb H atoms from areas as small as a single dimer row [3] on H-terminated Si(001)-(2 × 1). Once the Si dangling bonds are exposed, patterned regions appear brighter as in Fig. 3(a). After depositing 0.1 ML of Al at RT, the Al decorated pattern and monohydride background have even greater contrast in Fig. 3(b). In the close-up image of Fig. 3(c), it is apparent that Al islands nucleate much more readily on the bare Si patterns than on the surrounding monohydride. Because of this, monohydride regions "confined" between bare Si lines are observed to contain fewer and smaller Al clusters than "open" monohydride areas far from the pattern. By varying the width of the confined region, we find that the Al cluster density is constant from open regions down to a width of 70 Å. In the pattern of Fig. 3(c), the smallest confined monohydride areas are ~35 Å wide and the density of Al clusters is only half that in the open regions. These results imply that the diffusion length of an Al adatom on the monohydride surface at RT at a deposition rate of 0.01 Å/s lies between 35 and 70 Å. Closer examination of the border with a patterned area in Fig. 3(d) shows that the density of Al clusters at the boundary between bare and monohydride Si regions is much higher than in the interior of either. This indicates that Al-Si binding on bare Si(001) is much easier than Al-H/Si binding on the monohydride surface, due to the exposed dangling bonds of the Si dimers. Since clusters on the boundary have the same general appearance as those on the monohydride surface, most of the growth of these clusters comes from diffusion of Al adatoms from the monohydride side. Thus, we conclude that the diffusion length of an Al adatom is much greater on the monohydride side than on the bare Si side. The difference in binding probability between the two surfaces leads to a significantly lower final density of the Al adatoms in the confined monohydride regions and also to smaller cluster sizes.

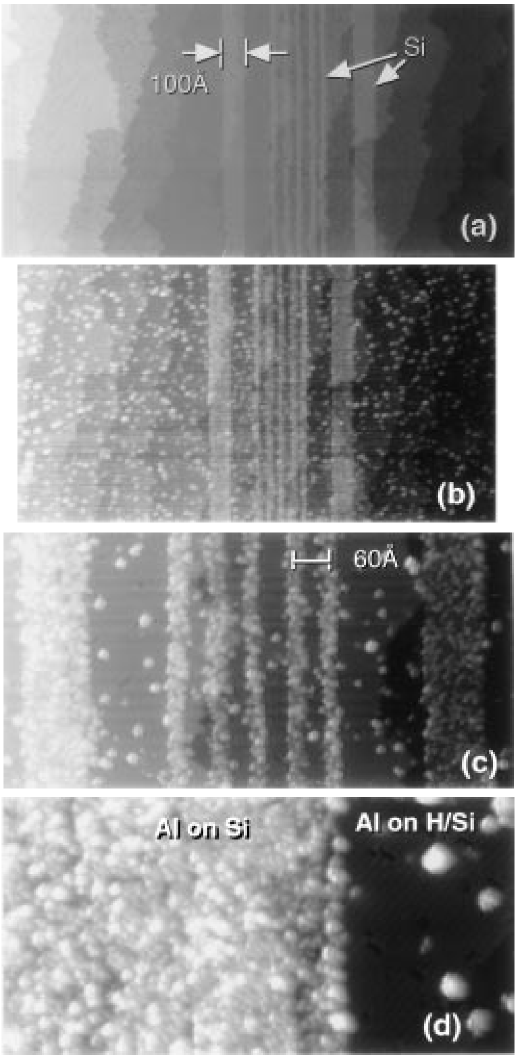

FIG. 3. (a) 2400 × 1200 Å image of a pattern created by STM with a sample bias of 4 V current 4 nA, and line dose 2×10^{-3} C/cm. The two 100 Å-wide lines were made by writing 9 passes with 10 Å pitch, while the tin lines were made by writing a single pass each with 60 Å pitch. This image was taken at sample bias −2 V, current 0.1 nA. (b) Same pattern after deposit of 0.1 ML Al. (c) 800 × 400 Å close-up image of (b). (d) 400 × 200 Å image of a pattern boundary.

The partial selectivity of Al deposition seen in Figs. 3(c) and 3(d) suggests a new method for the patterning of metals on Si(001) at or near atomic dimensions. By greatly reducing the deposition rate and adjusting sample temperature and/or metal species to maximize surface adatom diffusion over the hydrogen termination, it may be possible to approach total selectivity in patterns ~50 Å or less in feature size. Single-dimer resolution has previously been demonstrated in STM-induced desorption of hydrogen from the monohydride surface, so that quasiatomic patterning of metal lines might be achieved. Unlike single-atom manipulation by STM, this method offers a practical means for the linking of metal nanostructures to external electrodes. Eventually, the two might be employed in combination to fabricate atom-scale electronic devices.

Processing at elevated temperatures is unavoidable in device fabrication, and it is therefore interesting to know how metal atoms behave upon annealing. In the case

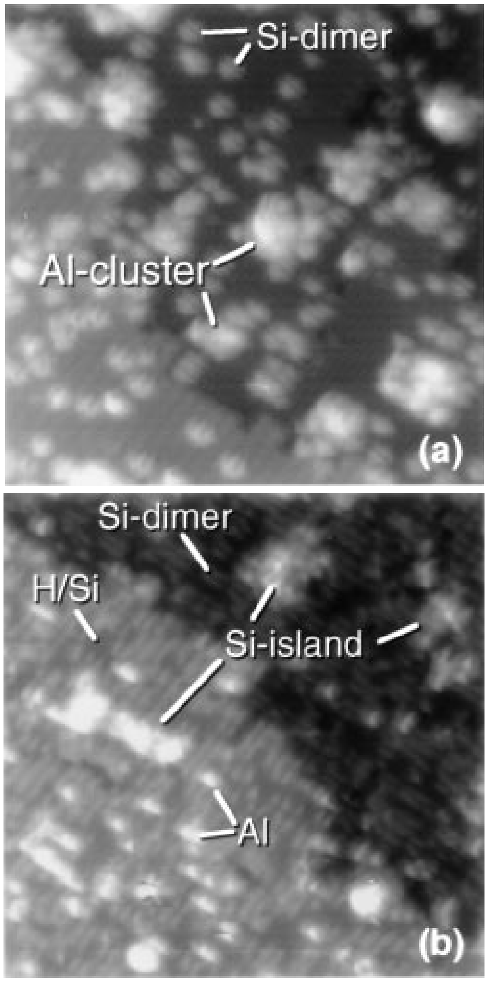

FIG. 4. (a) 240 × 240 Å STM image of a monohydride Si(001) surface deposited with 0.1 ML Al following 5 s annealing at 470 °C, and (b) after a subsequent annealing of 5 s at 490 °C.

of the bare Si(001)-(2 × 1) surface, we find that the 1D chains disappear as Al diffuses into the Si bulk around 500 °C [17]. On the monohydride surface, the structure of Al clusters shows little change until the temperature approaches 500 °C. It is known, however, that H_2 desorption from the monohydride Si(001) surface peaks at 522 °C [18], so that the behavior of Al clusters could be complicated by the H desorption in this case. Instead of moving as a whole, the Al clusters start to dissociate at about 470 °C as indicated in Fig. 4(a). At this temperature, hydrogen has started to desorb from the surface. The small bright sites with nodal lines across the center in Fig. 4(a) are bare Si dimers due to thermal desorption of H-atom pairs [19]. At 490 °C, more H_2 is desorbed and the Al clusters in Fig. 4(b) have mostly broken up into individual Al atoms which diffuse either across the remaining monohydride regions to find bare Si dimers and form short chains or into the bulk. As a result of Al in-diffusion, Si atoms are ejected outward and form islands on the surface. There are three levels of brightness on the same terrace in Fig. 4(b). The very bright sites are Si or Al islands which can be distinguished by comparing the occupied-states image with an unoccupied-states image of the same areas [17]. The brighter rows are the dangling bonds of the newly formed Si dimers, while grey areas are the original monohydride regions. Upon further annealing the Si islands diffuse towards step edges and Al diffuses further into the bulk [17] until the bare 2 × 1 reconstruction is recovered.

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