RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 8 15 FEBRUARY 1995-II

Cluster-ordered array on the Si(001) surface formed by Al deposition

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(Received 14 November 1994)

Local phases formed by Al deposition on Si(001) at an elevated temperature have been observed using ultrahigh-vacuum scanning tunneling microscopy. These phases, $c(4\times12)$, $c(4\times16)$, $c(4\times22)$, and $c(4\times24)$, and so on, are established above 0.5 ML of Al at 500 °C, and attributed to the formation of Al or an Al-Si cluster-ordered array. The sizes and heights of these clusters are very regular and they are remarkably ordered in the [110] or [1$\bar{1}$0] direction. On the other hand, the initial stages below 0.5 ML of Al show complicated changes of the surface structures, such as cluster formation, terrace etching, and trench formation. These phenomena are probably caused by an Al-Si reaction at an elevated temperature.

The investigation of group-III metals on Si surfaces has been one of the typical studies in surface science for many years. This system exhibits an abundance of surface structures depending on the coverage and the annealing process. Of the group-III metals, Al is a particularly important material for device applications. Thus far, initial stages of Al growth on Si(001) at room temperature (RT) have been studied using low-energy electron diffraction[1] (LEED) and scanning tunneling microscopy (STM).[2] The STM images clearly showed that Al dimers were formed up to the first 0.5 ML, where they ran perpendicular to the underlying Si dimer rows.[2] As for the structure of the Al dimers, *ab initio* calculations indicated that they were more likely to arrange parallel to the substrate Si dimer rows.[3] On the other hand, high-temperature phases of Al on Si(001) were also studied using LEED and Auger-electron spectroscopy.[4] At 500 °C, LEED patterns showed a 1×7 symmetry at coverages of 0.3–0.4 ML, and $c(4\times12)$ at coverages of 0.4–0.5 ML, respectively. Recently, Itoh *et al.* reported that Al on Si(001) at 500 °C formed molecular clusters, which resulted in the formation of $c(4\times2n)$ at very low coverage (0.16 ML) of Al.[5] However, structural changes related to Al-Si reaction during growth are not described in detail because their experiments focused on low coverage of Al. In this paper, we show interesting results of STM observations where various amounts of Al were deposited on the Si(001) surface at 500 °C. Above 400 °C, reaction and interdiffusion between Si and Al are widely known to occur at the surface and the interface.[6] The STM images showed such reaction-related phenomena up to 0.5 ML and a variety of cluster-ordered arrays above 0.5 ML.

An ultrahigh vacuum system and a specially designed STM unit described elsewhere[7] were used for this experiment. After introducing the tip or sample into the vacuum, cleaning or Al deposition was carried out in a heating stage that facilitates a variety of sample and tip treatments concurrently. The Si(001) substrate with a misorientation of 0.7° toward the [110] direction was atomically cleaned at 1200 °C by passing a dc current through it. The substrate temperature was monitored by an infrared pyrometer calibrated by another measurement using thermocouples. The vacuum level was maintained below 5×10^{-10} torr for all the experimental procedures. Al was deposited onto the substrate using a heating W filament. Al coverage was estimated from both the filament current and deposition time. The deposition rate was determined by counting the density of Al dimers deposited at RT, where the densest packing of the 2×2 structure was defined as the coverage of 0.5 ML (1 ML$=6.8\times10^{14}$ cm^{-2}).[2] The typical deposition rate was 0.2 ML/min for the initial stage and 0.8 nm/min for thicker Al films. All STM images were taken at RT in a constant-current mode, after transferring the sample from the deposition stage to the STM stage.

Figures 1(a)–1(d) show the evolution of the surface after Al deposition up to 0.5 ML at a substrate temperature of 500 °C. STM images were taken in different regions of the sample at a sample voltage of −2.5 V in Fig. 1(a) and −2.0 V in Figs. 1(b)–1(d), and a tunneling current of 0.4 nA. The [110] direction runs diagonally in the images. In contrast to RT deposition, not Al dimers but Al or Al-Si clusters (see white dots) are uniformly formed on the surface at 0.13 ML [Fig. 1(a)]. Such an Al-related cluster at the ini-

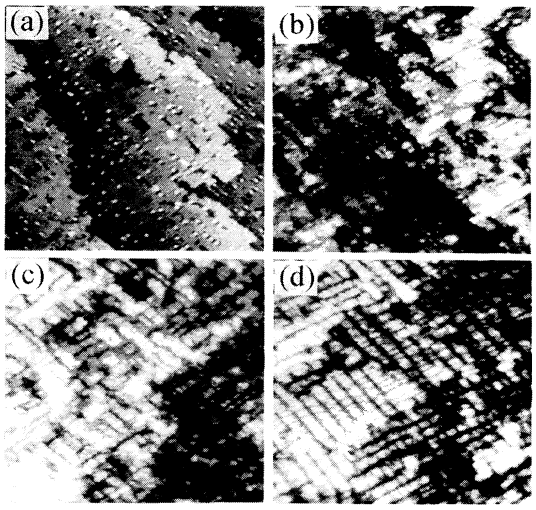

FIG. 1. STM images (55×55 nm^2) showing the coverage evolution with (a) 0.13-, (b) 0.24-, (c) 0.36-, and (d) 0.5-ML Al deposited at 500 °C. All images were taken at a sample voltage of −2.5 V in (a) and −2.0 V in (b)–(d) in different regions of the samples, but with the same substrate misoriented by 0.7°.

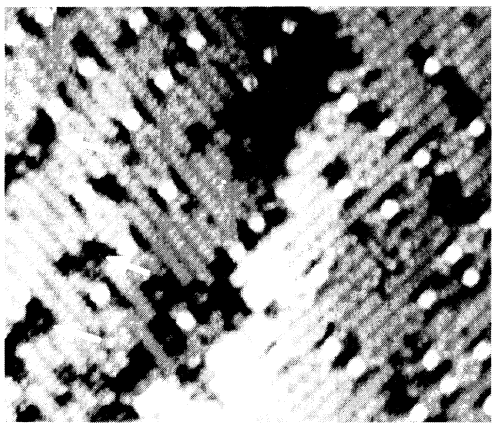

FIG. 2. STM image (22×20 nm^2) with a coverage of 0.13 ML, taken at a sample voltage of -2.0 V. A faint atomlike contrast is visible in the dark region on the terrace (denoted by arrows). Al-related clusters are randomly distributed between the Si dimer rows.

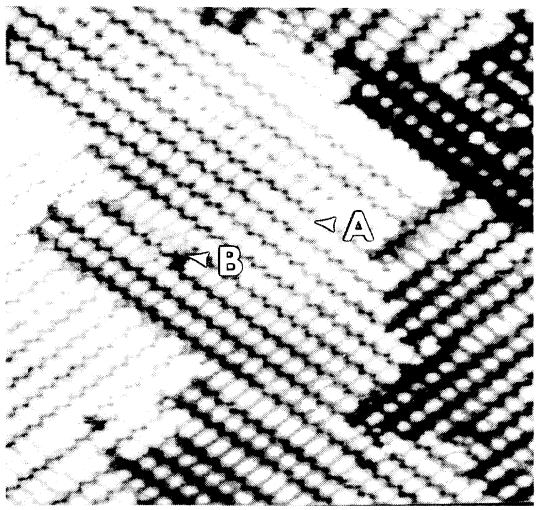

FIG. 3. STM image (45×45 nm^2) after Al deposition of 1 ML, taken at a sample voltge of -2.0 V. Cluster rows in the [110] or [1$\bar{1}$0] direction appear well ordered one dimensionally and rotate by 90° across the unit-height steps.

tial stage was also reported in Ref. 5. We estimated that one cluster consists of about eight atoms from the nominal deposition amount and the cluster density, if it is made of only Al atoms. Also, faint atomlike contrast was often visible in the dark regions on the terrace in high-magnification images, as indicated by arrows in Fig. 2. These are likely due to Al atoms that substituted into the Si terrace by a surface reaction. Si atoms removed from the terrace are considered to diffuse toward the neighboring steps and be trapped. So the step shape, thus, has changed from that usually observed on the vicinal Si(001) surface.

On an increase of the Al coverage up to 0.24 ML, the surface was covered with multiheight terraces that appeared as three levels of contrast and the original steps on the vicinal surface disappeared, as shown in Fig. 1(b). This may be caused by Al deposition and surface reaction that induces successive etching of the terrace and displacement of Si surface atoms. Some clusters are still visible in the image but do not form definite ordered structures. At 0.36 ML [Fig. 1(c)], trenches that appear as short dark lines in the [110] or [1$\bar{1}$0] direction, begin to form on the surface. At 0.5 ML [Fig. 1(d)], the width and direction of these trenches (denoted by arrows) became more clearly defined, while they elongated linearly. Also, each terrace became rather flat and different steps appeared. The trenches rotate by 90° across the unit-height steps, which have a very irregular shape. At this stage, domains with the same direction of the trenches are fairly small and involved with each other. We believe that this surface-flattening phenomenon is caused by enhancement of the diffusion length of Al on the Al-covered surface. It can be deduced that deposited Al atoms quickly react with Si atoms at an elevated temperature, thus resulting in the smaller diffusion length of Al on the bare Si suface than on the Al-covered surface. Though the previous STM study pointed out the formation of the $c(4\times12)$ structure at a coverage of 0.16 ML,[5] our results did not show distinct evidence for it below a coverage of 0.5 ML.

When we increased the Al coverage up to 1 ML, the surface became quite flat and different clusters appeared, i.e., one-dimensionally ordered arrays, as shown in Fig. 3. The image was taken at a sample voltage of -2.0 V and a tunneling current of 0.3 nA. The cluster rows are aligned in the [110] or [1$\bar{1}$0] direction on the underlying Si substrate, which runs diagonally in the image. Steps with heights almost equal to that of unit-height steps on the clean Si(001) surface, i.e., 1.36 Å, are also visible and the cluster rows rotate by 90° across these steps. Some defects are also observed; the defect denoted by *A* looks like a vacancy-type one, and that denoted by *B* is a dislocation-type defect. These clusters, thus, seem to behave like atoms that take part in the crystal growth. Individual clusters are located in between neighboring zigzag trenches. These clusters have 4 times the period of an ideal Si(001) unit cell (a_{110}, 3.84 Å) parallel to the cluster row, and 1 times the period perpendicular to it. The interval and phase shift of the neighboring trenches determine the local symmetry of the surface structure. Figure 4 schematically illustrates several examples of registrations appearing in Fig. 3. Figure 4(a) shows a $c(4\times12)$ structure that is the dominant domain in Fig. 3, where one cluster exists between neighboring trenches with a phase shift of π. The $c(4\times12)$ phase near the coverage of 0.5 ML was previously reported by LEED experiments.[4] The intevals of the neighboring trenches locally vary, 6, 8, and 11 times the period, which correspond to $c(4\times12)$, $c(4\times16)$, and $c(4\times22)$ symmetry, as shown in Figs. 4(a)–4(c), respectively. Here, note the following points. First, with the $c(4\times16)$ structure each cluster elongates perpendicular to the cluster row compared with the clusters in the $c(4\times12)$ structure. Second, with the $c(4\times22)$ structure two clusters exist between the neighboring trenches. Moreover, a phase shift of $\pi/2$ between the neighboring trenches is frequently observed, then the symmetry lowers by a factor of 2. Figure 4(d) shows a $c(4\times24)$ phase that comes from symmetry lowering of the $c(4\times12)$ structure.

Figures 5(a) and 5(b) show other phenomena of the cluster-ordered array, formed by Al deposition of more than 10 nm. Both samples were grown on the same substrate.

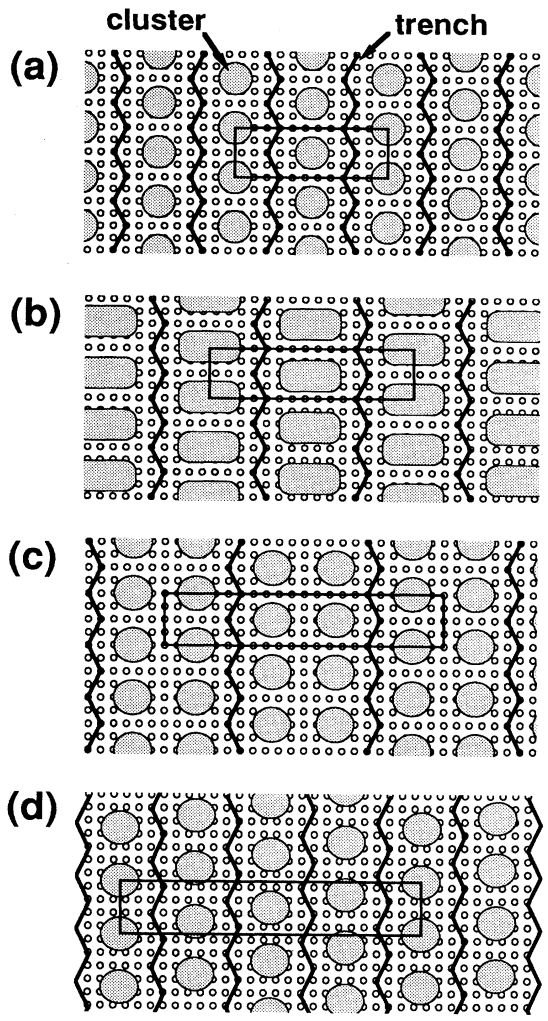

FIG. 4. Schematic diagrams of local symmetries in Fig. 3. Registrations of (a) $c(4\times12)$, (b) $c(4\times16)$, (c) $c(4\times22)$, and (d) $c(4\times24)$ phases are illustrated with respect to the underlying Si unit cell (open circles). Al-related clusters and zigzag trenches are described as shaded circles and heavy solid lines, respectively.

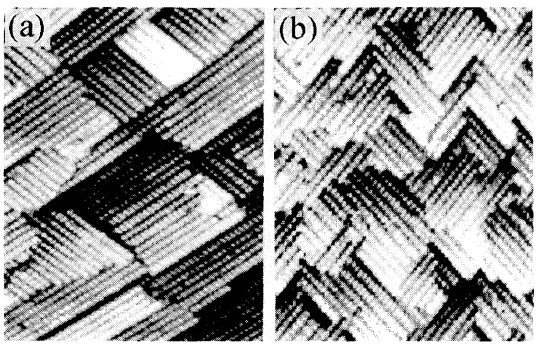

FIG. 5. Two STM images (65×90 nm^2) after Al deposition of more than 10 nm. Both samples were grown under simlar conditions including the substrates used. The step is oriented to the [110] direction in (a) and to the [100] direction in (b).

Scanning elecron microscopy images of these samples revealed a low density of large three-dimensional (3D) islands. This indicates that the growth mode at 500 °C also roughly conforms to the *S-K* mode, although the first type of cluster was formed at the initial stage of the growth.[8] At the upper middle of Fig. 5(a), two-dimensional islands of the clusters appear on the cluster-ordered terrace. In addition, the cluster row on the terrace often rotates slightly off the [110] or $[1\bar{1}0]$ direction, as seen in the bottom left of Fig. 5(a). While Fig. 5(a) exhibits the step front oriented to the [110] direction, Fig. 5(b) shows one oriented to the [100] direction. Moreover, the experiment using just a (001)-oriented substrate also showed similar step density. These results suggest that steps on the cluster-ordered array are formed during the process of Al-Si reaction irrespective of the substrate steps.

It should be noted that the cluster-ordered structure is considered to consist of not only Al atoms but also Si atoms, because this highly corrugated structure was formed during 0.5–1 ML coverage of Al. The nominal height of the clusters from the trenches was about 4 Å when the sample voltage was -2.0 V. The majority of Al atoms may diffuse on the surface during deposition, and then contribute to nucleation and growth of 3D islands. The residual Al atoms would be trapped at the terrace and diffuse to the interface between the cluster-ordered structure and the Si substrate through slow intermixing. Therefore, we can conclude that the cluster-ordered structure is stable and its thickness rarely increases, even if thicker Al is deposited. This was also verified by a reflection high-energy electron-diffraction pattern, in which fundamental reflection spots with the lattice constant of Si were visible after Al deposition of 10 nm. The coverage of $c(4\times22)$ or $c(4\times44)$ structures showed a tendency to increase with the amount of Al deposited. In some samples, these structures occupied more than 50% of the surface. The stability of the cluster-ordered structures seems to yield useful information about the Al-Si reaction at an elevated temperature. However, what causes the dramatic change in surface reactivity is not clear at present. Because the atomic configuration of the Al-related clusters and bond geometry with the underlying Si atoms have not been clarified, we are now trying transmission electron microscopy (TEM) experiments. TEM observations are expected to elucidate the thickness of the cluster-ordered regions, depth of the trenches, and the atomic structure of the clusters.

So far, many high-temperature phases of group-III metals on Si(001) have been studied, and some of them showed similar features to the case of Al. For example, the In (4×3) phase at 0.5 ML also showed a cluster-ordered array similar to that in Fig. 3.[9] However, there are distinct differences between the two as follows: First, the In-related cluster was reported to have two maxima in the empty states and a central maximum in the filled states in the STM image, while the Al-related one showed almost the same image in the empty and filled states. Second, the cluster-ordered array of In (4×3) was completed by a gradual increase of the number of clusters, as the coverage increased. This was not observed in the case of Al deposition. Third, In (4×3) was obtained by subsequent annealing of the substrate with predeposited In at RT. Annealing experiments of Al showed quite different features from those obtained after deposition at a high temperature. For example, when the substrate with

an Al coverage of 0.4 ML was annealed at 500 °C, the trenches and uniformly deposited features as shown in Fig. 1(c) were not obtained, but only clusters such as those shown in Fig. 1(a) were formed on the surface. Our annealing experiments, thus, have never produced cluster-ordered arrays as shown in Fig. 3. This suggests stronger condensation of Al than that of In.

Moreover, it has been reported that Ga deposition on Si(001) forms a $(n\times 8)$ phase above 450 °C, which also appeared as a cluster-ordered array.[10] However, STM images indicated that the $(n\times 8)$ phase coexisted with a (2×2) phase of Ga dimers. Such a situation has never been observed for the case of Al. Besides the group-III metals, Sn on a Si(001) surface revealed similar features, i.e., trench formation and Sn substitution into the surface layer and so on.[11] These same features were also obtained by subsequent annealing of the substrate. To date, it is ambiguous whether other group-III metals or Sn lead to cluster ordering at an elevated temperature during deposition.

In summary, Al deposition on Si(001) at 500 °C has been examined using STM. Isolated clusters associated with Al are uniformly distributed on the surface at a very low coverage, then complicated changes such as terrace etching, Al substitution into the surface layer, and trench formation take place up to 0.5 ML. When the Al coverage exceeds 0.5 ML, another type of cluster is formed, accompanied by well-defined arrangements of zigzag trenches. These clusters are located between neighboring trenches and have a variety of local symmetries, $c(4\times 12)$, $c(4\times 16)$, $c(4\times 22)$, and $c(4\times 24)$, and so on, depending on the interval and phase shift of the neighboring trenches.

The authors would like to thank Professor K. Yagi of the Tokyo Institute of Technology for useful discussions and Dr. T. Nakamura for cooperation in the development of the STM. We also acknowledge Dr. K. Nakajima for his encouragement.

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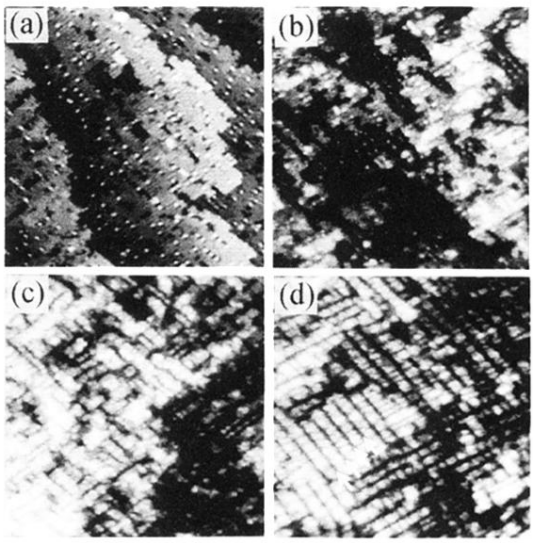

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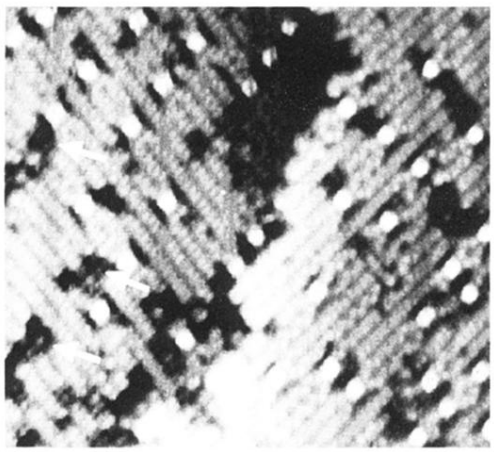

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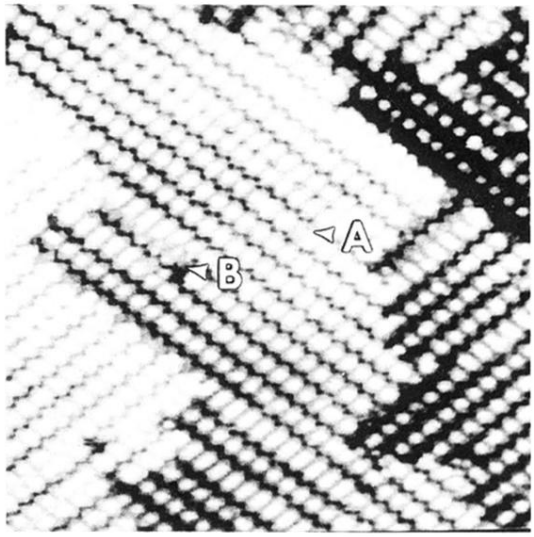

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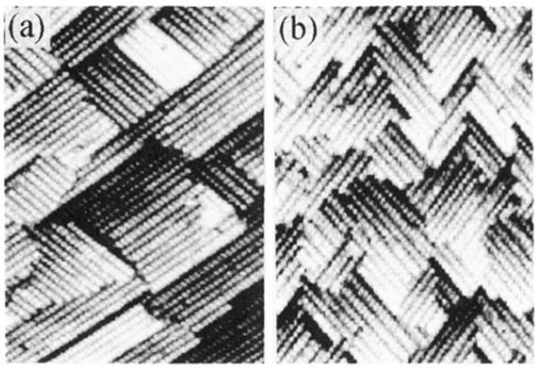

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