Adsorption of Al on Si(100) at high temperature

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A scanning tunneling microscopy investigation on the adsorption structure of Al on Si(100) deposited at substrate temperature of 500 °C is presented. The adsorption at high substrate temperature leads to a strong interaction of Al adatoms with surface atoms of Si(100) to form Al-Si subunits on the Si(100) surface. A structural model is proposed to describe the registration and composition of Al-Si subunits in terms of the charge transfer and the spatial distribution of the surface states. It is considered that each Al-Si subunit is composed of four Al atoms and one Si atom. [S0163-1829(99)16015-6]

The adsorption structures and coverage-dependent phases of aluminum on Si(100) surfaces have been the focus of many experimental and theoretical studies over the years because the importance of the Al/Si(100) interface in silicon metallization, and its believed simplicity in calculations of the electronic structure for metal-semiconductor interfaces. For the adsorption at low substrate temperature (below 350 °C) low-energy electron diffraction (LEED) studies[1–3] have indicated that the adsorption of Al on Si(100) surfaces creates several well-ordered phases which are coverage dependent. Scanning tunneling microscopy (STM) studies[4–6] further demonstrate that Al adatoms adsorb on Si(100) as dimers that are located between Si dimer rows and are parallel to Si dimers. In contrast to the low-temperature adsorption, no characteristic phase was observed for the adsorption of Al on the Si(100) surface at substrate temperatures above 350 °C, and the adsorption phases formed at high substrate temperature seem to be highly dependent on the conditions of sample preparation.[1,2] Recent STM studies[7,8] reveal that the deposition of Al onto the Si(100) surface at substrate temperatures above 500 °C leads to the formation of Al or Al–Si subunits (hereafter, we call these subuints as Al-related subunits), which likely run into local symmetries of $c(4\times 2n)$ depending on the coverage and deposition conditions. However, these studies were not able to give identical results and interpretations for the formation of $c(4\times 2n)$, and the atomic structure of Al-related subunits was also not sufficiently discussed. Estimations for the numbers of atoms involved in each Al-related subunit have been made to be 8 and 6 ± 1, respectively, based on the corresponding coverage.[7–9] Although these STM studies provide useful information, the growth mechanism and structure model for the high-temperature adsorption of Al on Si(100) have not yet been established and deserve further study.

In this communication, we report the STM investigation on the adsorption of Al on Si(100) at high substrate temperature. The purpose is to approach a better insight into the details of the atomic structure of Al/Si(100) surfaces formed at high substrate temperatures through carefully analyzing the spatial distribution of the local density of states observed in STM. An outline for the atom arrangement inside the Al-related subunit is depicted in terms of charge transfer.

The STM observations were performed in the ultrahigh vacuum (UHV) chamber with a base pressure below 5×10^{-9} Pa. The Si(100) samples were cut from a commercial *n*-type Sb-doped Si(100) wafer with a conductivity of 0.018 Ω cm. Before insertion into the UHV chamber Si(100) samples were ultrasonically cleaned in pure water. To prepare clean Si(100)-2×1 surfaces, the Si(100) samples were degassed at approximately 650 °C for more than 12 h and flash heated by direct current heating at 1200 °C followed by a slow cool from 900 °C down to room temperature, while the pressure of the chamber was maintained below 2×10^{-7} Pa. The temperature of the sample was monitored by infrared pyrometer. This procedure repeatably gives a well-ordered Si(100)-2×1 surface with the low density of defects.

The Al evaporation source was made by placing a piece of pure aluminum wire into an alumina tube wrapped with a tungsten coil. Before deposition, the evaporator was repeatedly heated up to 700 °C for degassing. After the clean Si(100)-2×1 reconstructed surface was confirmed by STM, the aluminum was deposited onto this surface with temperature of 500 °C at the deposition rate of 4.8×10^{11} cm^{-2} s^{-1}. The coverage was determined from the deposition rate and the exposure time of the sample to the evaporation source. The temperature of the substrate was determined from the power applied to the sample, calibrated with an alumel-chromel thermocouple. After deposition the samples were spontaneously cooled down to room temperature and then transferred to the STM holder for observations without any further treatment. All STM observations were made at room temperature using tungsten tips under the condition of constant tunneling current of 0.5 nA.

The adsorption of Al on the Si(100) surface at substrate temperatures above 350 °C is significantly different from

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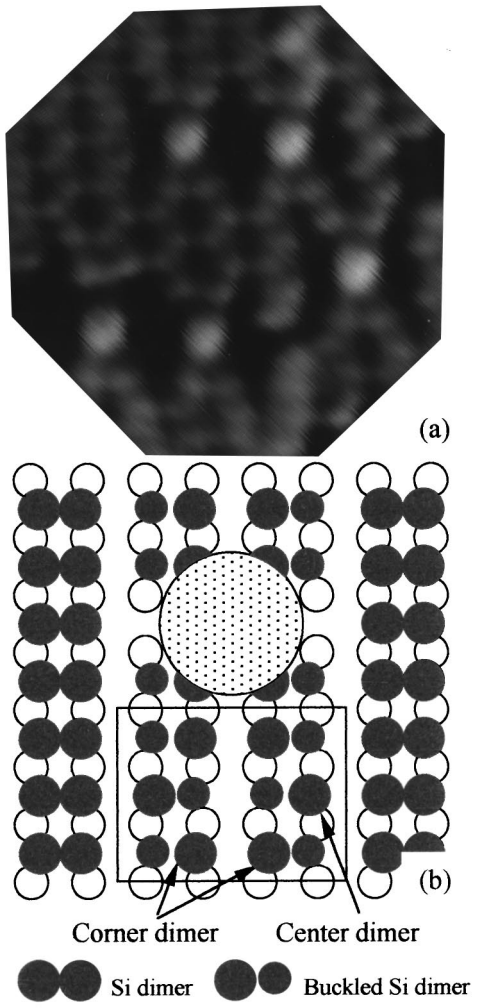

FIG. 1. (a) STM image of the Al/Si(100) surface after depositing 0.06 ML Al onto Si(100)-2×1 at substrate temperature of 500 °C, taken at sample bias of −2.2 V, showing the occupied surface states. Al-related subunits appear as ball-shaped protrusions. (b) A schematic drawing for a single Al-related subunit inferred from the STM image of occupied surface states to illustrate the registrations of Al-related subunits on Si(100). A Si dimer is shown as a pair of blacked circles and the largest dotted circle represents the Al-related subunit. Each Al-related subunit occupies a $3a\times4a$ Si unit cell which includes six Si dimers: four corner dimers and two center dimers as defined in the drawing for facilitating discussion.

that at temperatures below 350 °C. Figure 1(a) shows an STM topograph of the Al-adsorbed Si(100) surface after depositing 0.06 ML Al onto the Si(100)-2×1 surface at substrate temperature of 500 °C. The image was taken with negative sample bias of −2 V and constant tunneling current of 0.5 nA, where electrons tunnel out of the occupied surface states. Instead of forming Al dimers, the high-temperature adsorption of Al on Si(100) gives rise to the disruption of Si dimers and the formation of Al-related subunits appear as isolated ball-shaped protrusions located between Si dimer rows. The magnitude of the STM corrugations of isolated Al-related subunits is approximately $3a$ [where $a=3.84$ Å is the lattice constant of the ideal Si(100)-1×1 surface]. An illustration for the registration of Al-related subunits with the underlying Si lattice is schematically drawn in Fig. 1(b). Each Al-related subunit occupies a $3a\times4a$ Si unit cell that contains six Si dimers: four corner dimers and two center dimers as defined in Fig. 1(b). One more feature visible in the STM image is that ball-shaped protrusions between Si dimer rows act as knots in which two adjacent Si dimer rows are tied together. Moreover, the existence of ball-shaped protrusions apparently results in a pronounced buckling of adjacent Si dimer rows. These observations clearly indicate that the deposition of Al onto the Si(100) surface at high substrate temperature leads to the strong reaction and interdiffusion between Al adatoms and surface atoms of Si(100). A similar result was also observed in the study of the In/Si(100) system[9] when indium was deposited on Si(100) surfaces at substrate temperatures above 240 °C. Thus, this behavior might be a general mode for low-coverage growth of the group-III metals on the Si(100) surface at high substrate temperatures.

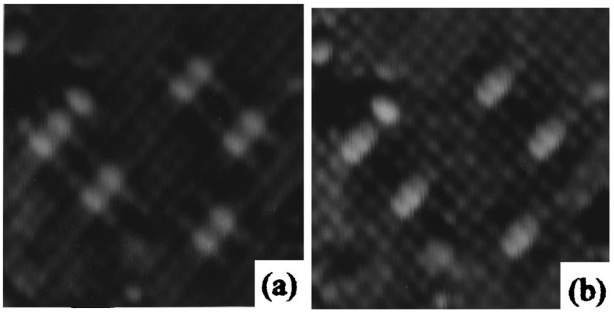

FIG. 2. STM images acquired at sample bias of (a) +2 V and (b) +1.5 V showing the spatial distribution of the unoccupied electronic states associated with Al-related subunits as shown in Fig. 1(a).

In order to approach the details of what these ball-shaped protrusions reflect in geometric and electronic structures, STM observations of Al-adsorbed Si(100) surfaces were performed with dual bias. Figure 2(a) shows the STM image of unoccupied surface states, acquired by scanning the same sample region of Fig. 1(a) at sample bias voltage of +2 V. The isolated Al-related subunits appear strikingly different in Fig. 1(a) and Fig. 2(a). Each ball-shaped protrusion observed in the image of occupied surface states splits into a pair of symmetric subprotrusions with a separation of $2a$ in the STM image of unoccupied surface states. The subprotrusions are elongated in the direction parallel to the Si dimers. The double maximums of each Si dimer in the unoccupied state reflect the symmetric property of the antibonding state of the clean Si(100) surface.[10] Because these two images show the same region of the sample, the pronounced differences between them result only from the differences in the spatial distribution of the occupied and unoccupied surface states, indicating that the protrusions observed in the STM images are primarily electronic.

When we further changed the values of bias voltage, it was found that the corrugation of protrusions seen in the STM images of occupied states are voltage independent in the accessible range between −0.8 V and −3.0 V, revealing a strong localized nature of occupied electronic states of Al-related subunits. Conversely, the brightness and shape of subprotrusions seen in the STM images of unoccupied states are apparently voltage dependent. The STM images of unoc-

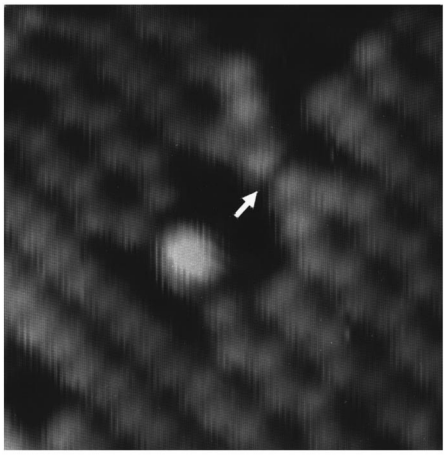

FIG. 3. STM image of the occupied surface state showing the disruption of an isolated Al-related subunit indicated by the arrow due to the absence of adatom(s).

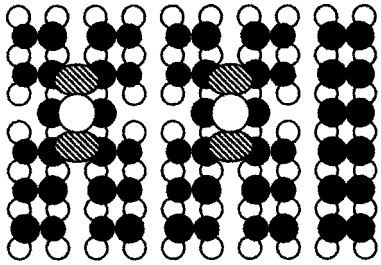

FIG. 4. A structural model showing the registration and atomic arrangement for Al-related subunits on Si(100). The largest circles outline the possible positions for Si adatoms (or together with Al adatoms) and shaded ovals outline the positions only for Al adatoms.

cupied surface states of Fig. 2 show the example of the voltage-dependent variation of subprotrusions, which reflects the spatial distribution of the surface density of unoccupied states associated with Al-related subunits. STM observations of unoccupied states reveal that, as the bias voltage decreases, the third maximum appears between two subprotrusions of each pair as shown in Fig. 2(b). That is, for low bias voltage, the corrugation profile of each Al-related subunit in unoccupied states consists of three peaks, two symmetric shoulder peaks on the corresponding subprotrusions and one center peak. The separations between the peaks is a. Three peaks involved in the STM corrugation of each Al-related subunit have the same heights at the sample bias of $+1.7$ V. The decrease in the sample bias voltage gives rise to an increase in the height of the center peak but a decrease in that of shoulder peaks. The same voltage-dependent variation of subprotrusions indicates that the subprotrusions arise from electronically, and hence structurally, equivalent structures. More details visible in the STM image of unoccupied states (Fig. 2) show that two center Si dimers in the 4×3 unit cell occupied by an Al-related subunit are removed due to the interaction with Al adatoms, and four dimer bonds of corner Si dimers keep intact although their π bond states are damaged, thereby remaining one dangling bond on each of corner Si dimers.

The strong voltage dependence of the STM images makes it impossible to definitively establish the atomic arrangement for the Al-related subunit from the STM images alone, without the aid of detailed electronic structure calculation. However, the outline of the atomic arrangement for the Al-related subunit is possibly derived from the STM images together with considering the effect of the charge transfer. It has been demonstrated that a charge transfer could occur between adsorbent atoms and surface atoms due to the electronegativity disparity of the interacted atoms.[11] In such cases one might observe a higher density of unoccupied states around one kind of atoms and a higher density of occupied states over the other kind of atoms. For the case of Al on the Si surface, previous studies[11,12] have indicated that the adsorption of Al on Si is accompanied by a small charge transfer from Al to Si as a result of the greater electronegativity of Si than Al, thereby leading to a shift of unoccupied state density toward Al adatoms. As our STM images clearly show an apparent shift between occupied and unoccupied states associated with the Al-related subunits, it is reasonable to consider that each Al-related subunit is composed of Al adatoms and Si adatom(s). The subprotrusions observed in the unoccupied surface states mainly result from Al adatoms, and the third maximum appeared between the two symmetric subprotrusions as well as ball-shaped protrusions observed in the occupied surface states mainly arise from Si adatoms. This attribution is further supported by the STM observation shown in Fig. 3. The STM image of the occupied surface states clearly shows a disruption of the Al-related subunit due to the absence of adatom(s) which makes a contribution to the occupied state density of Al-related subunits, indicating that the Al-related subunit should consist of Al adatoms and Si adatom(s).

Based on the above argument and STM observations, a possible structure model for the Al/Si(100) surface formed by depositing Al onto Si(100) at high substrate temperature is proposed in Fig. 4. In this schematic drawing, the arrangement of atoms inside Al-related subunits is outlined, where the largest circles outline the possible registrations for Si adatoms (or together with Al adatoms) and the shaded ovals represent the possible registrations only for Al adatoms. We estimate that each Al-related subunit is composed of four Al adatoms and one Si adatom. As a result, the atomic structure of the Al-related subunit cannot be determined from the STM results, and the structure model in Fig. 4 is intended only to provide a guide for the further structural determination.

In summary, instead of growing long one-dimensional Al dimer rows the adsorption of Al on Si(100) at high substrate temperatures leads to the formation of Al-related subunits due to a strong interaction between Al adatoms and underlying Si atoms. Al-related subunits are randomly distributed on the surface and each of them occupies a 4×3 Si unit cell in which two of the Si dimers are removed. The electronic structure of Al-related subunits observed in the STM images is strongly energy dependent. Although the exact geometrical structure of Al-related subunits cannot be extracted from the STM images alone, the electronic information has been linked to outline an structure model for the Al-related subunit. The argument of charge transfer indicates that each Al-related subunits should be composed of four Al atoms and one Si atom.

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