Scanning-tunneling-microscopy observation of aluminum on GaAs(110) surfaces

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The surface structure of aluminum overlayers on cleaved *p*-type GaAs (110) is studied by scanning tunneling microscopy (STM) in ultrahigh vacuum. About three monolayers of aluminum were deposited on the surfaces at room temperature. We observed that aluminum atoms form clusters, and found that one cluster, consisting of about 200 atoms, has nonmetallic characteristics with a band gap of 1 eV. We also observed adsorbed atoms located over Ga sites in STM images of both occupied and unoccupied states. Their corrugation amplitudes are about 1 Å above the GaAs surface.

Additional surface structures of semiconductors or metals have been revealed by scanning tunneling microscopy (STM).[1] Among the compound semiconductors, GaAs surfaces have been vigorously studied with STM. Although artificial GaAs surfaces are of interest because of their practical aspects,[2,3] for several decades cleaved (110) surfaces have also been studied to reveal the basis of Schottky-barrier formation and surface reactions. Many areas proposed by experimental and theoretical studies before the appearance of STM should be investigated by STM.

Since the time when Feenstra *et al.* demonstrated that Ga and As atoms are selectively imaged by STM because of the difference of electronic states,[4] the initial stages of the Schottky-barrier formation have been studied for Fe,[5] Au,[6] Sn,[7] and Sm (Ref. 8) on GaAs(110). Group-V and -III elements on GaAs surfaces are interesting because they might clarify the initial stage of crystal growth in ternary compound semiconductors as well as Schottky-barrier formation. Group-V elements Sb (Ref. 9) and Bi (Ref. 10) on the GaAs (110) were investigated, but no group-III element has been studied by STM. Al on GaAs(100) is perhaps one of the most extensively studied systems.

Medium-energy ion scattering[11] and photoemission spectroscopy[12] (PES) studies have shown that aluminum makes clusters when it is deposited at room temperature on GaAs(110), and PES (Ref. 13) and low-energy electron diffraction (LEED) characterization[14] have revealed that a replacement takes place between the deposited Al and the Ga in the surface of several monolayers. Also, tight-binding calculation has shown that an exchange reaction between chemisorbed Al and the surface Ga will occur.[15] Ihm and Joannopoulos extended the calculation using a first-principles method and found that at low coverage Al atoms replace the second-layer Ga atoms and that Al atoms tend to cluster at higher coverage.[16] The relationship between the experimental data and the theoretical calculations has been discussed in detail.[17] Kelpeis and Harrison used self-consistent tight-binding calculations with Coulomb effects to show that the Ga site is favored over the As site for many kinds of isolated neutral metallic adatoms.[18] In this paper, we present STM experiments on aluminum cluster formation and the adsorption sites of aluminum on a GaAs(110) system.

The STM experiments used a commercial scanning tunneling microscope[19] in an ultrahigh vacuum chamber equipped with facilities for cleaving, annealing, and evaporations, LEED optics, and a cylindrical mirror analyzer for Auger electron spectroscopy (AES). A chamber pressure of less than 7×10^{-11} Torr was maintained with ion pumps. GaAs(110) surfaces were prepared by cleaving a *p*-type GaAs rod (Zn doped, 6.0×10^{18} cm^{-3}) on the manipulator. Mechanical movements such as cleaving and sample transfer degraded the base pressure, but it did not exceed 3×10^{-10} Torr. STM observations were made at lower pressures, in the range of 10^{-11} Torr. Tungsten tips prepared by electrochemical etching were used as STM probes. STM images were obtained in constant current mode, where the tunneling current was controlled to between 0.4 and 0.9 nA and the bias voltage applied to the tip was 2.0–2.5 V in both polarities. Scanning areas were calibrated according to the GaAs(110) 1×1 structure so that the Ga or As atoms form 4.0-Å ($[1\bar{1}0]$ direction) $\times$5.7-Å ([001] direction) rectangular unit cells. The vertical scaling was calibrated by a single step on the GaAs(110) surface. After the confirmation of the tip performance and surface cleanliness by atomic images of the cleaved GaAs(110) surfaces, aluminum was evaporated using a tungsten basket at room temperature and at a pressure below 7×10^{-10} Torr. Metal coverage, about 2.8 monolayers (ML's) (1 ML$=8.84\times10^{14}$ atoms/cm$^2=1.47$ Å), was estimated by *in situ* AES measurements and *ex situ* x-ray photoelectron spectroscopy following the STM experiments.

A typical STM image of the aluminum deposited GaAs(110) surface is shown in Fig. 1(a). The image was acquired with a sample bias of -2.4 V and a tunneling current of 0.4 nA so that tunneling occurred from occupied GaAs states to the tip, therefore, surface As atoms are imaged.[4] The As atoms are observed as modulated atomic rows along the $[1\bar{1}0]$ direction. The corrugation

amplitudes of these As rows are 0.4–0.6 Å across the [001] direction. Some Al clusters 10–20 Å in diameter and 3–5 Å high are shown in Fig. 1(a). The number of the aluminum atoms in the cluster including point b is estimated to be 200, assuming a part of a spherical shape. The clustering of the deposited Al atoms at room temperature is consistent with previous experimental[11,12] and theoretical[16] results. Furthermore, a cluster does not seem to correlate to the crystallographic direction of the substrate. Figure 1(b) shows the *I-V* characteristics on the Al cluster and the GaAs surface. Curve *a* corresponds to point a on the GaAs substrate, and curve *b* was taken at the central point b of the aluminum cluster. We should note that although the surface band gap narrows in the center of the aluminum cluster, it is still 1.0 eV [Figure 1(b), curve *b*]. Therefore an Al cluster of 200 atoms is not metallic, and has a semiconductor character.

We could occasionally identify some very bright atomic-size spots near Al clusters. Figure 2 shows a STM image of unoccupied states, which were obtained with a positive sample bias, emphasizing Ga atoms. Beside the atomically resolved Ga atoms, there are bright spots in the middle of the right side. These bright spots correspond to five Ga sites; the upper two atoms and the lower three atoms observed are continuous electronic states. The upper two atoms align exactly in the [1$\bar{1}$0] direction, and the positions of two atoms coincide with the Ga sites. On the other hand, the position of the lower three atoms slightly shift toward the center of this triangle. Two unit cells of the GaAs(110) 1×1 are shown in the upper left region of Fig. 2(a), where the crystallographic positions of As atoms related to Ga atoms have been confirmed by

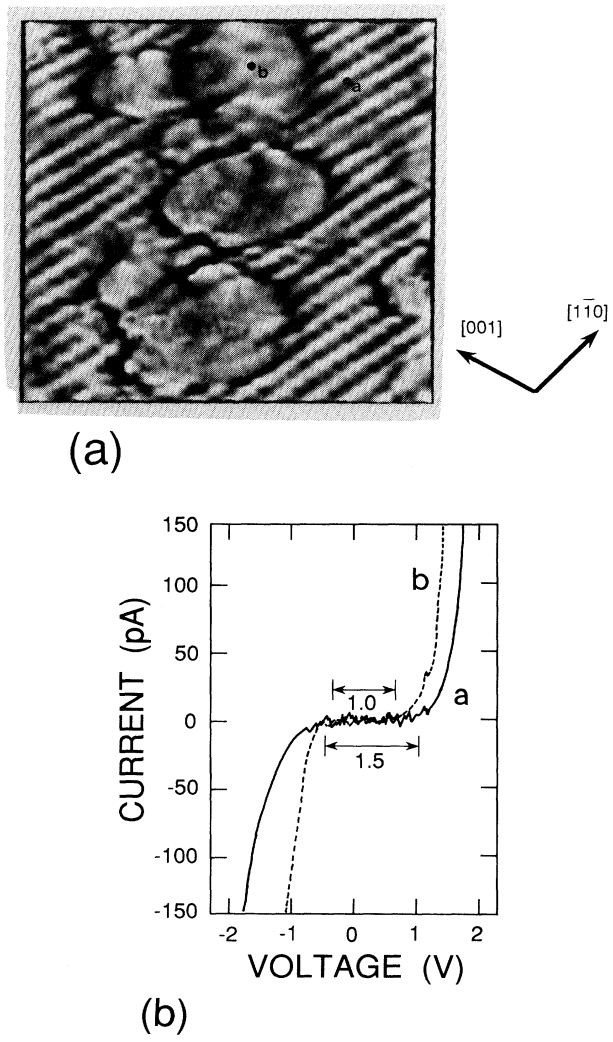

FIG. 1. (a) Perspective view, 100×100 Å^2, processed to mimic artificial illumination of STM image of a cleaved GaAs(110) surface covered with three ML's of Al. The image is taken at a sample bias of −2.4 V; tunneling current is held constant at 0.4 nA. (b) Tunneling current vs voltage characteristics at the points of the GaAs(110) bare surface a and the Al cluster b as indicated in (a). The curves *a* (solid line) and *b* (dashed line) exhibit the band gaps of 1.5 and 1.0 eV, respectively.

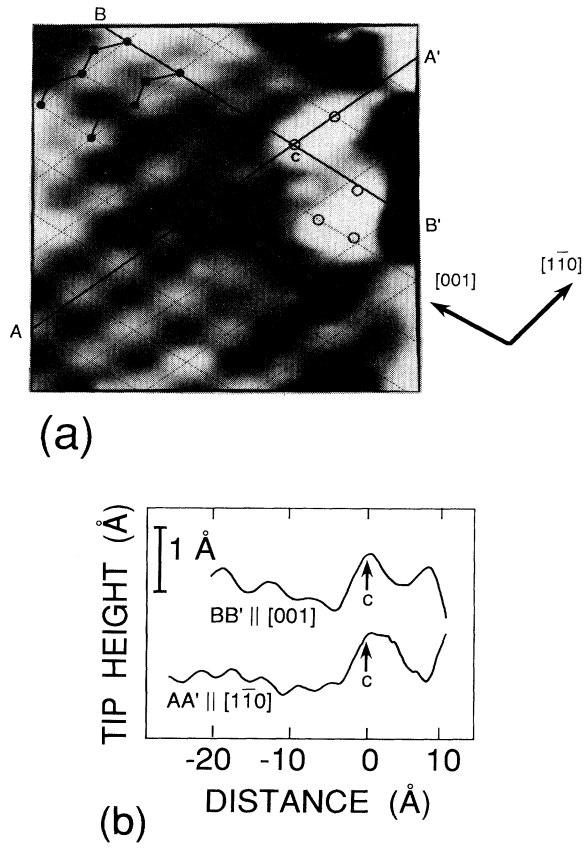

FIG. 2. (a) Unoccupied state STM image of a GaAs(110) surface with atomic adsorbed atoms denoted by open circles. Gray scale top view, 28×28 Å^2, taken at a sample bias of +2.1 V and a tunneling current of 0.9 nA. The dotted lines correspond to the Ga [1$\bar{1}$0] rows and [001] rows. Therefore the cross points coincide with Ga sites. Two unit cells are shown in the left upper corner; circles and squares correspond to Ga and As atoms. (b) Cross-sectional profiles along *AA'* and *BB'* in (a), parallel to [1$\bar{1}$0] and [001]. They cross at point c.

simultaneous STM observation of both the occupied and unoccupied electronic states before Al deposition. The corrugation for the upper atoms is about 0.8 Å in the cross-sectional profile AA', along the $[1\bar{1}0]$ direction. It is difficult to recognize a cluster along $[1\bar{1}0]$ as separated atoms because the density of states (DOS) of the GaAs(110) substrate is easily changed in regions adjacent to or beneath the adsorbed atoms. Another cross-sectional profile BB', along the [001] direction shows about 1 Å above the GaAs level.

Figure 3 shows STM images of occupied states with a negative sample bias. The imaged area was not the same region shown in Fig. 2, but the distance between the regions was less than several hundred angstroms. Although we observed modulated As atomic rows, we could not clearly identify each As atom as was possible for the unoccupied states (Fig. 2). We can see a smaller protrusion of four atomic corrugations along the line CC'. The adsorbed atoms appear to lie along the $[1\bar{1}0]$ direction, and are spaced halfway between the As [001] rows. The linear cluster of these four adsorbed atoms in the $[1\bar{1}0]$ direction is shifted from the As $[1\bar{1}0]$ row. The cross-sectional profile of line CC' confirms the existence of the four adsorbed atoms, whose electronic state is considered to be localized compared with the unoccupied state because the neighboring atoms can be separately observed. Cross-sectional profiles DD' and EE' along the [001] direction are also shown. The lines DD' and EE' cross line CC' at points d and e. This shows that point d corresponds to a peak of the corrugation amplitude, and point e corresponds to a bottom. This result is consistent with the configuration in which the adsorbed atoms are at the on-top site of the Ga atoms as shown in Fig. 2. There is a bright area in the left side in Fig. 3 and we can apply six to seven As atoms in this area. We believe that several Al atoms form a small cluster here, resulting in a continuous electronic state.

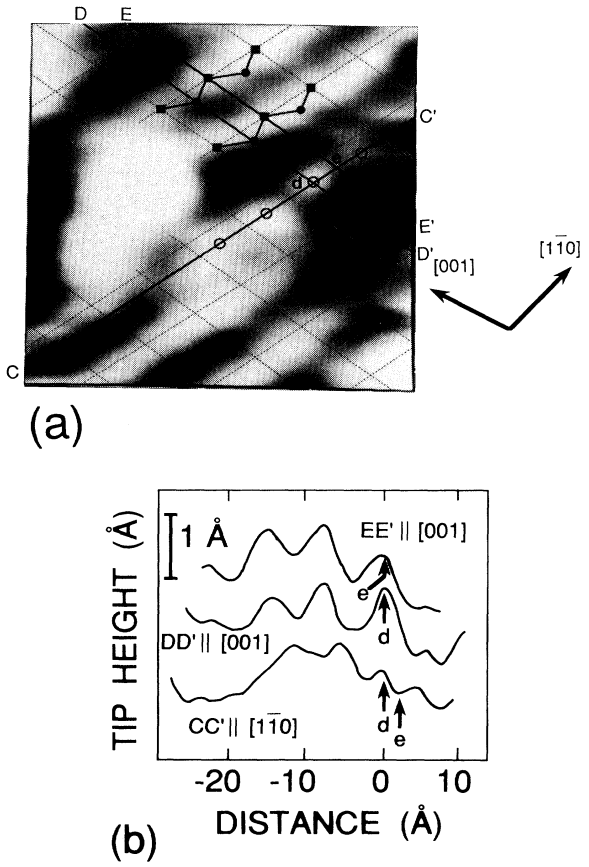

FIG. 3. (a) Occupied state STM image of a GaAs(110) surface with atomic adsorbed atoms denoted open circles. Gray scale top view, 30×30 Å^2, taken at a sample bias of -2.4 V and a tunneling current of 0.4 nA. The dotted lines correspond to the As $[1\bar{1}0]$ rows. Therefore the cross points coincide with As sites. Two unit cells are shown in the middle upper area; circles and squares correspond to Ga and As atoms. The bright area in the left middle area is considered to correspond to a several-atom cluster. (b) Cross-sectional profiles along CC', DD', and EE' in (a), parallel to $[1\bar{1}0]$ and [001]. The lines DD' and EE' cross with AA' at points d and e.

Ihm and Joannopoulos[16] found that deposited Al atoms tend to adsorb on the twofold site and pointed out that the configuration of the twofold chemisorption site is not stable enough and Al atoms hop around very frequently to meet other Al atoms and form clusters. According our STM images, we must conclude the Al atoms prefer to adsorb just over Ga sites in the initial stage after deposition. It seems to contradict with their conclusion regarding the twofold site adsorption. However, since we could not find an isolated single Al atom, we should conclude that it is very easy for Al atoms to form clusters. This result is in agreement with Ihm and Joannopoulos finding that Al atoms prefer to cluster very quickly.

Our results about clustering and the I-V characterization are also qualitatively consistent with Zunger's discussion[17] in which Al atoms are likely to form small Al clusters, and most clusters have band gaps overlapping the semiconductor gap region.[20] Zunger also proposed that the Ga site is more stable than the As site for a monovalent Al atom.[17] Klepeis and Harrison showed that neutral Al atoms have lower energy when bonded to Ga atoms than when bonded to As atoms.[18] We consider that Al atoms in a very small cluster are stabilized to the neutral or monovalent form, resulting in Al—Ga bonding, because if an Al atom is positively charged, it is considered to bond to an As atom easy.[18]

Lindau *et al.*[13] reported that a replacement occurs between deposited Al atoms and Ga atoms in the topmost GaAs surface layer. Mele and Joannapoulos[15] presented the theoretical valence-band DOS for models where an Al atom exchanges with a Ga atom and an exchanged Ga atom bonds to an As atom. They showed a drastic change of DOS due to the exchange effect as well as a buckling effect of an Al atom. However, they did not perform the calculation for the DOS in the geometry in which an adsorbed Al atom or an exchange Ga atom was on the top of the Ga site. We also could not measure the I-V characteristics on the atomic Ga site for a bare GaAs surface region and on the adsorbed position because for fear of an atomic scale thermal drift. The kinetics of the replacement interaction might be revealed by the obser-

vation of temperature dependence and/or coverage dependence in a very-low-coverage region using a sophisticated spectroscopic measurement, if they could be compared with theoretical results for a greater variety of geometries.

In summary, we have observed aluminum on a cleaved GaAs(110) system by STM. Deposited Al atoms form clusters at the coverge of about three ML's and at room temperature. We observed the tunneling characteristics on one of the clusters, which was 4.5 Å high and 10 Å in diameter, and it was nonmetallic with a gap of about 1 eV. We also observed very small clusters consisting of several atoms. They are located over Ga sites with an atomic corrugation of about 1 Å above the GaAs surface.

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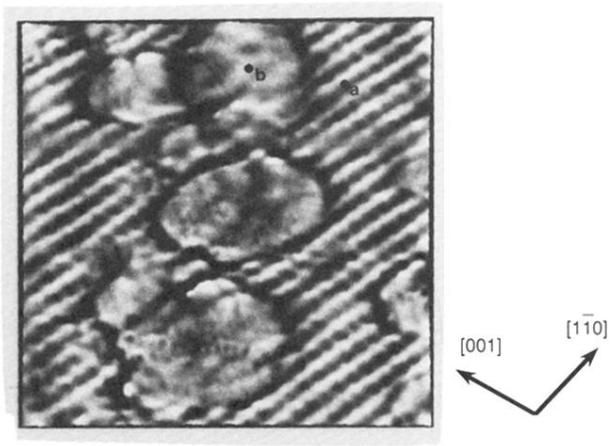
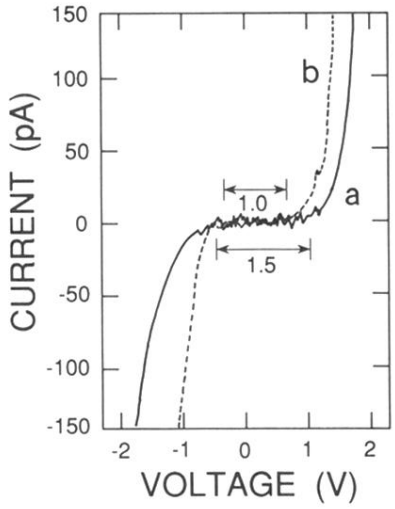
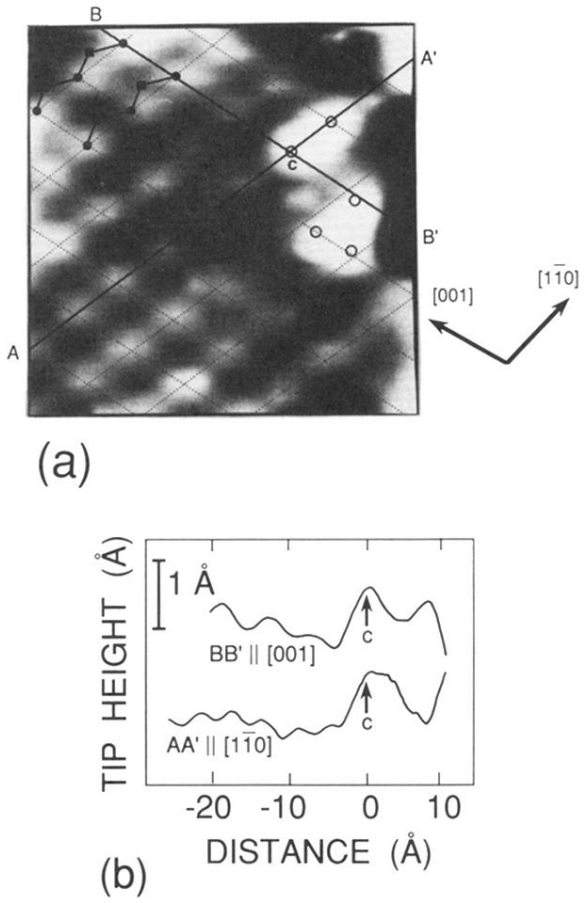


(a)



(b)

FIG. 1. (a) Perspective view, 100×100 Å^2, processed to mimic artificial illumination of STM image of a cleaved GaAs(110) surface covered with three ML's of Al. The image is taken at a sample bias of -2.4 V; tunneling current is held constant at 0.4 nA. (b) Tunneling current vs voltage characteristics at the points of the GaAs(110) bare surface a and the Al cluster b as indicated in (a). The curves *a* (solid line) and *b* (dashed line) exhibit the band gaps of 1.5 and 1.0 eV, respectively.



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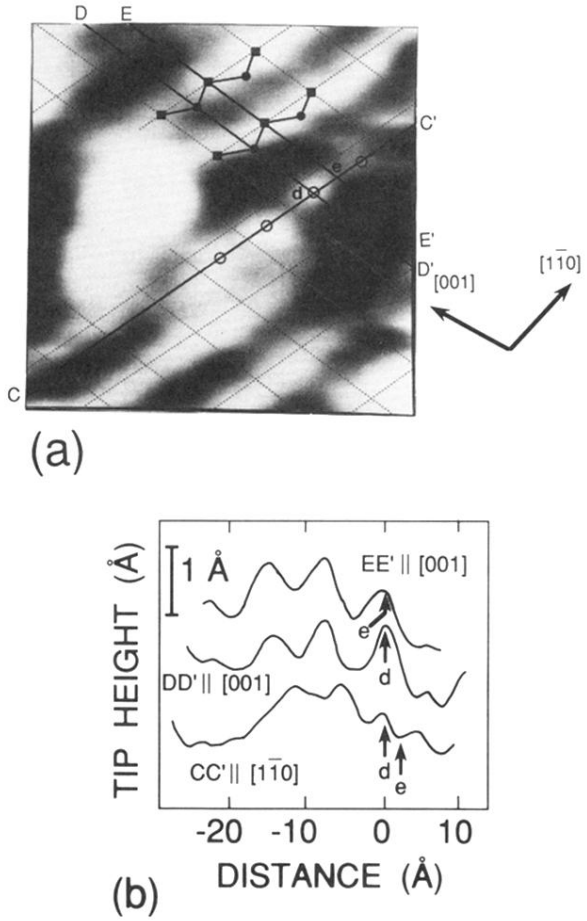

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