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# Structural and electronic properties of the K/GaAs(110) surface

Nobuyuki Ishida and Kazuhisa Sueoka
*Graduate School of Information Science and Technology, Hokkaido University, kita-14, Nishi-9, Kita-ku, Sapporo 060-0814, Japan*

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Scanning tunneling microscopy and scanning tunneling spectroscopy were used to clarify the correlation between the geometric structure and the electronic properties of the K/GaAs(110) surface. The K asymmetric chains induce a surface state localized in the vicinity of the Ga atoms, which indicates the bonding between the K atoms and Ga atoms. The observed energy position of the surface state suggested that the surface potential was changed by the K adsorption. The obtained results are compared with theoretical work in order to explain the electronic properties.

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Alkali metals adsorbed on III-V(110) surfaces have been studied for decades due to the interest in the mechanisms of the Schottky barrier formation and the Fermi level pinning at metal-semiconductor interfaces.[1] These systems are thought to be the ideal playground for the investigation of metal-semiconductor interfaces due to the following reasons. (i) From a theoretical point of view, these systems provide a simplified model because only one valence electron at the outermost shell should be considered. (ii) Since the relaxation of the topmost atoms induces the movement of the surface states of the III-V(110) surfaces out of the fundamental band gap, the metal induced states within the band gap can be easily investigated. However, alkali metals adsorbed on III-V(110) surfaces exhibit complicated adsorption structures depending on their coverage.[2–8] As a consequence, it is difficult to investigate the correlation between the geometric structures and the electronic properties by using surface averaging techniques, such as photoemission spectroscopy (PES) and low energy electron diffraction. In PES experiments, the adsorption structure has to be indirectly deduced by, for example, monitoring the work function change.[9,10] On the other hand, scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) make it possible to correlate directly the structural and electronic properties.[11,13] However, most STM studies on these surfaces so far have focused on the geometric structures of the adsorbed alkali atoms.[2,5,7] Though a few papers have reported such STS data, only the width of the band gap obtained from the *I-V* curves was discussed to confirm whether the surface is semiconducting or not.[3,12] The lack of STS data may be attributed to the instability of the alkali atoms under a positive bias condition,[14,15] which makes the apex of the STM tip unstable.

Controversial issues include the adsorption structures of the alkali atoms as well as certain electronic properties, such as the insulating behavior of the alkali adlayer and the charge transfer from the alkali atoms to the substrate atoms.[1] Some reports have explained the insulating behavior in terms of the Mott-Hubbard mechanism by assuming a single adsorption site for the alkali atoms.[16,17] On the other hand, Calzolari *et al.* proposed an alternative explanation for the insulating behavior by assuming the existence of two inequivalent adsorption sites as follows.[18] In their proposed structure, the alkali atoms adsorb at two inequivalent sites and correlate with each other through lattice coupling, resulting in the formation of a dimerlike asymmetric chain structure. The two electrons of the alkali dimer (one for each alkali atom) are transferred to the one empty dangling bond state of the surface cation to form the bonding orbital. Consequently, one fully occupied surface band and one empty-surface band are formed. As a result of the charge transfer, one of the cation-derived bands is split from the bulk continuum and forms the surface state within the fundamental band gap localized on the cation participating in the bonding orbital. To clarify the above controversial issues, investigations of the geometric structures and the local electronic properties of the alkali atoms on the III-V(110) surfaces are essential. Although the model of Calzolari *et al.* has already had experimental support,[7,8] detailed comparisons with the local electronic properties have not been done yet.

In this work, STM and STS were used to investigate the correlation between the geometric structures and the local electronic properties of the K/GaAs(110) surface. We carefully chose the bias range for the STS measurements and successfully performed two-dimensional tunneling spectroscopy (2DTS).[19] From the 2DTS data, the differential tunneling conductance and the spatially resolved local density of states (LDOS) were derived. The obtained results were compared with theoretical work.

The ultrahigh vacuum system used in this experiment is composed of two chambers, that is, the main chamber equipped with an STM (JSTM-4500XT: JEOL Ltd.) and the treatment chamber equipped with a K deposition apparatus. The base pressure of both chambers was less than $1.0 \times 10^{-8}$ Pa. A *p*-GaAs(001) (Zn doped, $N_A = 1.0 \times 10^{19}$ cm$^{-3}$) wafer was cleaved *in situ* to obtain a clean GaAs(110) surface. After cleavage, K atoms were deposited on the surface at room temperature using a well-outgassed alkali dispenser (SAES Getters). The pressure during the deposition was less than $1.0 \times 10^{-7}$ Pa. After depositing K atoms, the sample was immediately transferred into the main chamber for STM measurements. An electrochemically etched polycrystalline W wire was used as an STM tip. The area density of the K atoms was determined by counting the adsorbed K atoms in the STM image. To investigate the electronic properties of the surface, we performed 2DTS measurements by obtaining *I-V* curves at each pixel of the image (128 × 128) with turning off the STM feedback loop during the scanning over the sample surface. The bias range for the

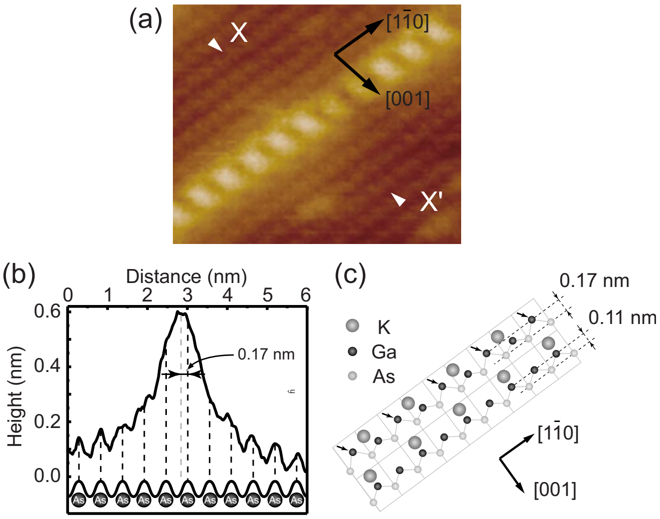

FIG. 1. (Color online) (a) Filled state STM image ($V_s$=−2.0 V, $I_t$=0.3 nA) of the K/GaAs(110) surface. The size of the image is $5.0\times7.0$ nm$^2$. K atoms form 1D asymmetric chains along the $[1\bar{1}0]$ direction. (b) The cross section taken along the [001] direction between $X$ and $X'$ in (a). The period of the As rows is fitted to the cross section. The distance between the peak and the nearest As row is about 0.17 nm. (c) Structural model of the asymmetric chain proposed in the theoretical work (Ref. 18). The Ga atoms participating in the bonding orbital with K atoms are indicated by the arrows.

*I-V* measurements was chosen from −2.0 to 0.2 V. In the case of the GaAs(110) surface with adsorbed alkali atoms, positive bias induces the surface diffusion of the alkali atoms,[14,15] which hamper the *I-V* measurements with a stable tip state. Therefore, high positive voltages must be avoided. To extract the information of the LDOS, the obtained *I-V* spectra were numerically differentiated and normalized to the total tunnel conductance using the method proposed by Feenstra.[20]

Our previous STM study of the K/GaAs(110) surfaces showed that the one-dimensional (1D) asymmetric chain was the dominant adsorption structure of the K atoms at low coverage range.[6] A typical filled state STM image ($V_s$=−2.0 V, $I_t$=0.3 nA) is shown in Fig. 1(a). The bright spots forming the 1D chains along the $[1\bar{1}0]$ direction arise from K atoms. The darker rows along the $[1\bar{1}0]$ direction correspond to surface As atoms.[21] The cross section along the [001] direction between $X$ and $X'$ is shown in Fig. 1(b). The starting and ending points of the cross section are located at the valley of the As peak along the $[1\bar{1}0]$ direction. The period of the As rows along the [001] direction is fitted to the cross section. The protrusion is broadened over the separation of three As rows. The peak is seen at the position slightly left of the nearest As row. The distance between the peak of the bright spot and the nearest As row is 0.17 ± 0.02 nm, which means that the peak is located near the Ga atom. The structural model of the asymmetric chain proposed by Calzolari *et al.* is shown in Fig. 1(c).[18] Their theoretical work predicted that the rotational relaxation of the substrate[21] is locally removed at every other Ga atoms along the $[1\bar{1}0]$ direction indicated by the arrows in the structural model [Fig. 1(c)]. The indicated Ga atoms participate in the bonding orbital with K atoms. This removal of the relaxation (unrelaxation) changes the horizontal distance between the Ga and the As atoms projected along the [001] direction from 0.11 to 0.17 nm [Fig. 1(c)].[18] The theoretical work also predicted that the bright spots in the filled state STM image were located in the vicinity of the unrelaxed Ga atoms. This means that the distance between the peak of the bright spot and the As row almost corresponds to the horizontal distance between the Ga and the As atoms projected along the [001] direction. Therefore, an obtained distance value of 0.17 ± 0.02 nm might reflect the unrelaxation of the Ga atom.

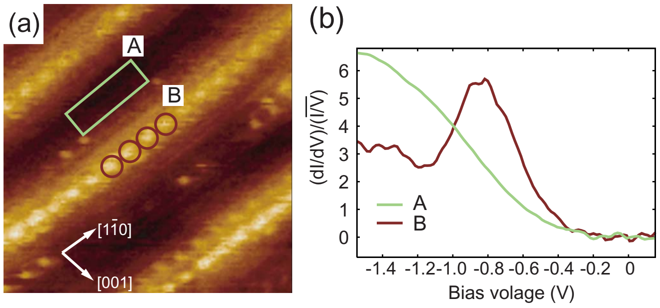

FIG. 2. (Color online) (a) Filled state STM image ($V_s$=−1.3 V, $I_t$=0.5 nA) of the K/GaAs(110) surface. The size of the image is $10\times10$ nm$^2$. K atoms form asymmetric chains. (b) Curve A and B are the $(dI/dV)/(\overline{I/V})$ spectra averaged over the region surrounded by a rectangle and circles, respectively. Curve B exhibits a clear peak at ∼−0.82 eV, suggesting the existence of a localized surface state.

Figure 2(a) shows a filled state STM image ($V_s$=−1.3 V, $I_t$=0.5 nA) of the K/GaAs(110) surface. Though the resolution of the image is not so good compared to the one in Fig. 1(a), the K atoms are thought to form the asymmetric chains, taking into account the K coverage and the width of the bright spot along the [001] direction.[6] On this surface, we performed a 2DTS measurement. The obtained $(dI/dV)/(\overline{I/V})$ spectrum averaged over the region indicated by the rectangle (labeled A) is shown in Fig. 2(b). This area corresponds to the bare GaAs site. No characteristic spectral features were observed. The $(dI/dV)/(\overline{I/V})$ spectrum averaged over the region surrounded by circles (labeled B) corresponding to the K adsorption site is also shown in Fig. 2(b). The spectrum shows nonmetallic behavior, that is, zero conductance at the Fermi level, and exhibits a clear peak at ∼−0.82 eV. The obtained peak suggests that there is a K induced surface state localized around the adsorbed K atoms.

To investigate the distribution of the surface state in detail, six $(dI/dV)/(\overline{I/V})$ spectra were extracted along the [001] direction indicated by the dotted line in Fig. 3(a). Each spectrum was averaged (about seven points) on the line labeled a–f along the $[1\bar{1}0]$ direction. Figure 3(a) shows the magnified STM image of Fig. 2(a). Figure 3(b) shows the obtained spectra at each point. The noisy character compared to the spectrum in Fig. 2(b) arises from the difference in the number of averaging points. The positions of As rows are indi-

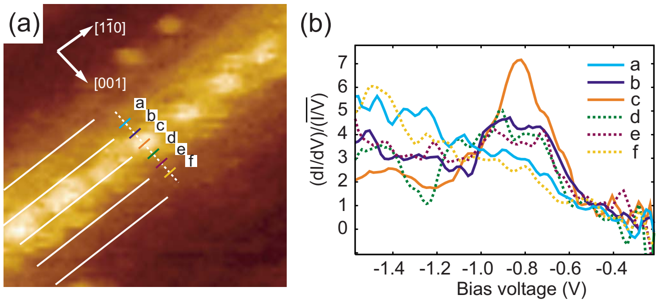

FIG. 3. (Color online) (a) Magnified STM image of Fig. 2(a) $(4.5\times4.5\ \mathrm{nm}^2)$. (b) Six $(dI/dV)/(\overline{I/V})$ spectra extracted along the [001] direction. Each spectrum was averaged (about seven points) on the line labeled a–f along the $[1\bar{1}0]$ direction.

cated by the lines along the $[1\bar{1}0]$ direction for guiding the eyes. The spectra obtained at b–e exhibit the peak, while the spectra at a and f have a similar character to the curve obtained at a GaAs site [Fig. 2(b)]. Careful inspection showed that the surface state was localized within ~0.7 nm along the [001] direction that is smaller than the separation of three As rows. Maximum peak was observed at the center of the bright spot (at c). The peaks diminish more rapidly along the $[00\bar{1}]$ direction than along the [001] direction with respect to c. Though the STM image at a and f is brighter than that of the GaAs site at the center between K chains, no characteristic modification of the spectra was observed. This fact suggests that the chemical nature and/or the geometric position of the Ga and As atoms at these sites are not affected by the adsorbed K atoms. Note that the electronic properties of the dangling bond states are very sensitive to the chemical nature and geometric position of the atoms. The perturbation of the STM image could arise from the change of electrostatic potential in the vicinity of the adsorbed K atoms.[22]

PES measurements on the K/GaAs(110) surface showed that a surface state was induced at 0.35 eV above the valence band edge of the GaAs at the beginning of the K adsorption process.[23] Theoretical work also predicted that the K atoms forming the asymmetric chain induced a surface state above the valence band edge.[18] The surface state is localized around the Ga atoms participating in the bonding orbital with the K atoms. Considering these experimental and theoretical works, we determined that the peak obtained in our spectrum arose from the surface state induced above the valence band edge by the adsorbed K atoms forming asymmetric chains. Indeed, the following facts are consistent with the results of the theoretical work. (i) The maximum peak in the spectrum was observed in the vicinity of the Ga atom. (ii) The distribution of the surface states was asymmetric about the Ga atom (at c) along the [001] direction and constrained within the separation of three As rows. However, one question remains, that is, the energy position of the peak was observed at an energy lower than the valence band edge of the GaAs, as shown in Fig. 2(b). There are two scenarios to explain the energy position of the peak. One is that the local downward band bending in the vicinity of the K atoms lowers the energy position of the surface state. The other is that the observed peak does not arise from the surface state above the valence band edge but from the surface resonance state located within the valence band of the GaAs. If the latter is correct, the clear peak could not be observed due to the additional contribution of the As related surface resonance state to the tunneling current. Hence, we determined that the local band bending lowered the energy position. The magnitude of the band bending is ~1.2 eV, taking into account the energy position of the peak with respect to the valence band edge observed in the PES experiment (0.35 eV).[23] In fact, the core-level PES measurement showed that the strong band bending (~1 eV) occurred on the $p$-type GaAs(110) surface at the beginning of the K adsorption process.[24] The observed slight difference could arise from the additional tip-induced band bending in the STM configuration. For the downward band bending, positive charges should exist at the surface. The surface state observed in the filled state cannot be positively charged because the state is filled by electrons. As mentioned above, the theoretical calculation predicted that the asymmetric alkali chain induces one fully occupied surface band and one empty-surface band as a result of the asymmetric charge transfer.[18] Therefore, we speculate that the origin of the positive charge could be the empty-surface state induced above the conduction band edge. Core-level PES experiments also attributed the strong band bending at the low coverage range to the donorlike empty state above the conduction band edge.[24–26] Assuming that the GaAs substrate feels one positive charge per adsorbed K dimer, a simple 1D electrostatic calculation shows that the area density of the K dimers ($\rho$), which is required to bend the band by $eV_s$, can be calculated as $\rho=(2\epsilon N_A|V_s|/e)^{1/2}$, where $\epsilon$ is the dielectric constant of GaAs, $V_s$ is the surface potential with respect to the bulk, $N_A$ is the concentration of the acceptor, and $e$ is the elementary electric charge. The calculated area density of the K dimers for a 1.2 eV band bending is $1.2\times10^{13}\ \mathrm{cm}^{-2}$. The area density of the K dimers in Fig. 2(a) is $\sim2.5\times10^{13}\ \mathrm{cm}^{-2}$, which is roughly comparable to the calculated value. Though a more realistic model is needed for the detailed analysis, the calculated density qualitatively accounts for the effect of the band bending.

In core-level PES experiments of alkali metals on the III-V(110) surface, two different components were observed in the alkali core-level spectrum,[27–30] which excludes a model assuming the single adsorption site for alkali atoms.[16,17] The K-derived protrusions observed in the STM image also support two inequivalent adsorption sites. There is controversy related to the bonding nature of the alkali atoms. Some reports have explained the two components of the core-level spectrum in terms of the alkali-cation and alkali-anion bondings,[27–29] while more recent data have been interpreted in terms of the alkali-cation bonding and the charge rehybridization on both the anion and cation.[30] Our STS data revealed that the surface state was strongly localized in the vicinity of the Ga (cation) atom, which supports the latter interpretation and is consistent with the theoretical prediction that the two electrons of the alkali dimer (one for each alkali atom) are transferred to the single Ga atom.[18] Also, the finding that the distribution of the surface state over the separation of three As rows indicates the charge rehybridization on both the anion and cation. The fact that the obtained results are consistent with the theoretical work suggests that the insulating behavior of the alkali adlayer on the III-V(110) surface can be explained by the asymmetric charge transfer without the electron-correlation effect (Mott-Hubbard mechanism).

In summary, we have experimentally shown the correlation between the geometric structure and the electronic properties of the K/GaAs(110) surface by means of STM and STS. 2DTS measurements revealed that the K asymmetric chains induce a surface state localized around the Ga atoms, suggesting bonding between the K atoms and Ga atoms. The observed energy position of the surface state indicates that the positively charged empty-surface states induced a strong downward band bending. The K-derived protrusion in the STM image and the characteristics of the electronic properties deduced from the STS data are consistent with theoretical calculations, which suggest that the insulating behavior of the alkali metal on the III-V(110) surface can be explained by asymmetric charge transfer between the K atoms and the substrate atoms.

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