

Surface structure of selenium-treated GaAs (001) studied by field ion scanning tunneling microscopy

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For a selenium-treated GaAs (001) surface followed by heat treatment at $\sim 530^\circ\text{C}$, we have observed using field ion scanning tunneling microscopy ordered arrays with regular intervals of $4\times$ periodicity in the $[\bar{1}10]$ direction (1.6 nm) to line up in the $[110]$ direction. These ordered arrays are in good agreement with the 4×1 structure previously observed by other methods. In a closer view, the $4\times$ structure was found to be formed by closely placed double rows.

Formation of surface/interface states within the band gaps of compound semiconductors has been a persistent and important problem in developing an advanced technology in semiconductors. Thus, passivation of compound semiconductor surfaces has been studied extensively.^{1,2} Recently, sulfur and selenium treatments have been attracting considerable attention because of their beneficial effects on improving the electronic properties of compound semiconductor surfaces.³⁻⁹ Understanding the passivation mechanism employed by those materials is very important from both fundamental and practical points of view.

The surface/interface gap states have been considered to be caused by the formation of surface/interface defects.¹ However, recently, Feenstra *et al.* showed by scanning tunneling spectroscopy on metal/GaAs surfaces that, for certain metals such as Au, the metal-GaAs bonding states themselves are responsible for the gap states rather than defects.¹⁰⁻¹² Therefore, in such cases, the metal-GaAs bonds at the interfaces must be replaced by some other structures in addition to the formation of the ordered surface/interface without defects. Since the electronic properties of the Au-GaAs interface are improved by the S/Se treatments,^{4,7} the structures of the terminal layers formed by S or Se atoms are expected to satisfy the requirements given above.

According to the first-principle study of the GaAs (001)- 1×1 surfaces adsorbed with a monolayer of sulfur or selenium, the surface gap state density is markedly reduced by the formation of S/Se-Ga bondings.^{13,14} Recent experimental results support the S/Se-Ga bond formation at the interfaces; however, the structures observed experi-

mentally are rather complex compared to the structures used for the theoretical calculations; the interfaces are not abrupt, but involved a few layers at the interface boundary.^{5,15-17} In order to pinpoint the structural models and to understand the passivation mechanism, it is important and urgently needed to characterize the structure of the terminal layers on an atomic scale.

In this letter, we report the surface structure of Se-treated GaAs(001) observed by a field ion scanning tunneling microscope (FI-STM).¹⁸

GaAs (001) surfaces, oriented to within $1/2^\circ$ of the $[001]$ direction and Si doped at $\sim 1\times 10^{18}\text{ cm}^{-3}$, were prepared by thermal cleaning. Selenium was evaporated onto the GaAs (001) surface using a Knudsen cell with a Se backpressure of $\sim 1\times 10^{-6}$ Torr. The thicknesses of the Se films thus deposited were estimated to be 100-300 nm.

For the observation by the STM, the samples were transferred from the preparation chamber to the STM chamber through air. Heat treatments were given in the STM chamber, the base pressure of which was $\sim 4\times 10^{-11}$ Torr. Tungsten tips were prepared by electrochemical etching, and the surface condition of the tips was characterized and manipulated by means of a field ion microscope (FIM) mounted in the STM chamber.^{18,19}

According to the electron diffraction measurements on the Se-treated GaAs (001) surface, a stable 4×1 structure appears upon heat treatment at 500-600°C.^{5,8,20}

Figure 1 shows a STM image (40 nm \times 40 nm) of Se-treated GaAs (001) with heat treatment at $\sim 530^\circ\text{C}$. The sample bias was kept at -2.0 V throughout the measurement and STM imaging was performed in the constant

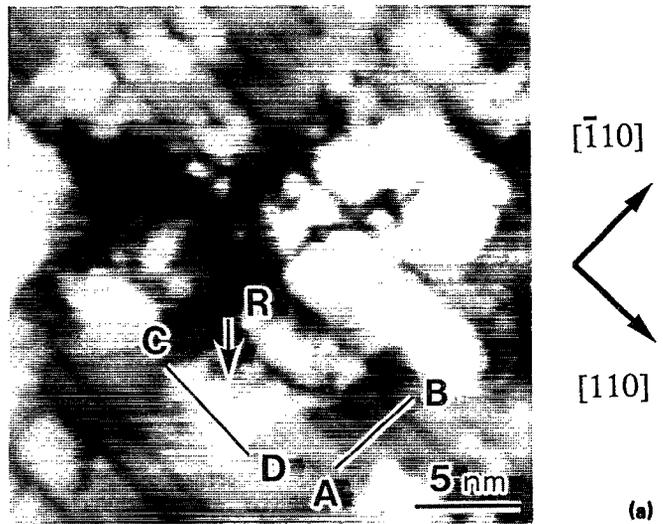
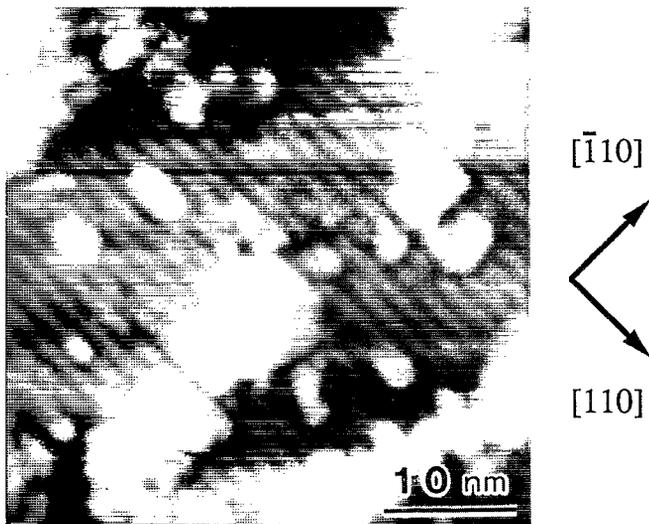


FIG. 1. STM image of the Se-treated GaAs (001) surface after heat treatment at $\sim 530^\circ\text{C}$ ($V_S = -2.0\text{ V}$, $I_S = 20\text{ pA}$, $40\text{ nm} \times 40\text{ nm}$).

current mode (setting current: $I_S = 20\text{ pA}$). As shown in Fig. 1, the surface is rather rough at an atomic level and there are many islands which are considered to be Se over-layers remaining on the surface. This roughness may be responsible for the diffuse low-energy electron diffraction patterns which have been reported concerning this surface. However, the ordered linear arrays are clearly seen lining up in the $[110]$ direction in the flat area of the surface. The distance between the rows is 1.6 nm and is very close to the $4\times$ periodicity of the GaAs (001) surface in the $[\bar{1}10]$ direction. This $4\times$ structure thus observed in the STM images is in good agreement with the 4×1 structure reported by Chambers *et al.*^{5,8}

Figure 2(a) shows another image of the treated surface ($25\text{ nm} \times 25\text{ nm}$), and a cross section is drawn along A–B in Fig. 2(b). The ordered arrays observed in Fig. 1 are resolved in this figure to have a double-row structure; each array which appears to be single in Fig. 1 consists of two closely placed rows as shown in Fig. 2. The $4\times$ periodicity of 1.6 nm is formed by two kinds of alternating distances between the rows, i.e., $D_1 = \sim 1.1\text{ nm}$ and $D_2 = \sim 0.5\text{ nm}$.

When a ~ 0.25 monolayer of aluminum is deposited on the GaAs (001)- 2×4 surface, a 4×1 symmetry appears.²¹ Donner *et al.* interpreted the $4\times$ structure in the $[110]$ direction as the pairing of the As-dimer rows, which they considered to occur through the Al adsorption between the dimer rows. A similar model is proposed for the GaAs (001)- 4×1 structure by Daweritz.²² In order to compare such models with our experimental results, the dimer structure is drawn schematically in the lower part of Fig. 2(b) in consideration of the symmetry of the cross section. Adsorption sites in the models are indicated by arrows.

Taking the recent experimental results into consideration, As atoms at the Se-treated surface may be partially replaced by Se atoms. If the gap states of the 4×1 surface are removed by the Ga–Se bond formation, as is calculated on the GaAs (001)- 1×1 surface,^{13,14} the passivation effect

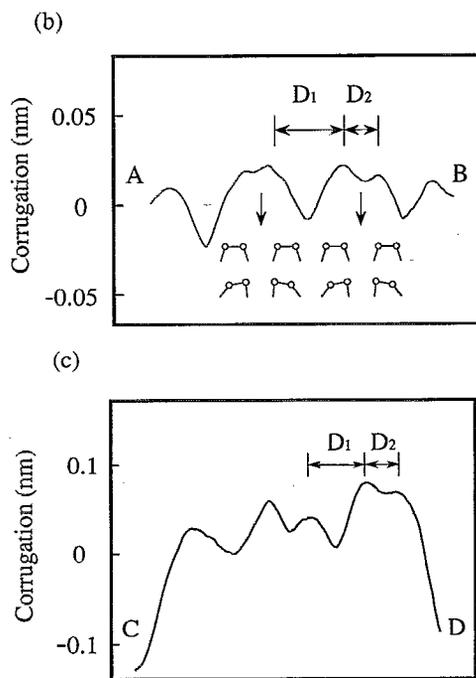


FIG. 2. (a) STM image of the Se-treated GaAs (001) surface after heat treatment at 530°C ($V_S = -2.0\text{ V}$, $I_S = 20\text{ pA}$, $25\text{ nm} \times 25\text{ nm}$). (b) Cross section along A–B in (a), normal dimer and buckled dimer structures are drawn together. (c) Cross section along C–D in (a). $D_1 = \sim 1.1\text{ nm}$, $D_2 = \sim 0.5\text{ nm}$.

will depend on the amount of Se atoms included in the surface dimer layer.

Since a dip structure around the adsorption sites between the dimers was observed experimentally, such charge transfer appearing in the GaAs (011) surface or modified adsorbate configuration must be introduced in order to interpret the Se–GaAs (001) surface structure with this model. For example, the double peaks, which are separated by the dip structure as shown in the cross section, may correspond to the two adsorbates on the dimers. Adsorption at the asymmetric positions on the bridge site is very likely because of the Jahn–Teller effect.²³ The coverage becomes equal to or higher than 0.5 monolayer in this case.

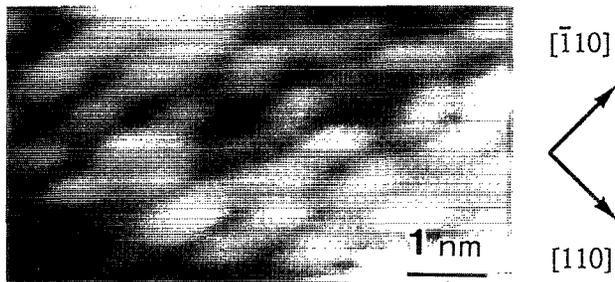


FIG. 3. STM image of the Se-treated GaAs (001) surface after complete removal of Se overlayers ($V_S = -2.0$ V, $I_S = 20$ pA, 6.0 nm \times 3.5 nm).

As is mentioned above, according to the recent experimental results, the Se/GaAs (001)- 4×1 surface has the GaAs $_{1-x}$ Se $_x$ structure over a few layers.^{5,8} Therefore the reconstruction such as dimer pairing may be caused by the partial replacement of As atoms by Se in the surface layers rather than by the adsorbate-induction mechanism. A buckling dimer may produce the $4\times$ periodicity in the $[\bar{1}10]$ direction in such a case, as shown schematically in Fig. 2(b) for comparison.²⁴

Overlayers with certain orderings can be seen in Fig. 2(a). Domain labeled *R* seems to have a structure similar to the $4\times$ layer below, but rotated by 90° . A cross section is drawn along C–D in Fig. 2(c). The corrugations of the double rows in both layers are ~ 0.05 nm. The thickness of the overlayer, determined by the heights of both edges of the cross section in Fig. 2(c), is ~ 0.15 nm, which corresponds to a single atomic layer of GaAs (001). Comparison of those cross sections show that, the $4\times$ layer consisting of double rows is probably a single atomic layer. Therefore, such a structure as a buckling dimer model without adsorbates is more probable.

Figure 3 shows a STM image of the treated surface after complete removal of the Se overlayers (6.0 nm \times 3.5 nm, $V_S = -2.0$ V, $I_S = 20$ pA). The 4×2 units consisting of three Ga dimers are resolved well. The STM image is similar to the As-rich GaAs (001)- 2×4 structure obtained by Pashley *et al.* except for a 90° rotation of the ordering.^{25–27} Since the GaAs (001) surfaces were prepared by thermal cleaning, the surfaces before the Se treatment are thought to have similar Ga-rich structures.

In order to complete the structural analysis and to understand the passivation mechanism, a well-controlled surface preparation technique is necessary, and a procedure for it is currently being under consideration. Precise measurements of the stoichiometry of the treated surface for the structures must be performed, together with detailed calculations.

In conclusion, for the Se-treated GaAs (001) surface with heat treatment at $\sim 530^\circ\text{C}$, the ordered arrays with regular intervals of $4\times$ periodicity in the $[\bar{1}10]$ direction (1.6 nm) were observed by FI-STM to line up in the $[110]$ direction, which is in good agreement with the 4×1 structure observed by the previous methods. In a close-up view, a $4\times$ structure was found to be formed by the closely adjacent double rows.

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