Selenium-treated GaAs(001)-2×3 surface studied by scanning tunneling microscopy

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An Se-passivated GaAs(001) surface was found to be stabilized by 2×3 reconstruction, previously reported as an intermediate structure, under the condition of a low Se chemical potential. Ordered elliptical protrusions with ~0.6-nm periodicity in the [110] direction were observed by scanning tunneling microscopy, the structure of which was in good agreement with a double-layered dimer model. A comprehensive model to explain the 2×3 structure together with the formation of a Ga_2Se_3-like structure with ordered 1/3 ML Ga vacancies was proposed.

With the progress in the atomic control of fine structures, modification of the surface and interface properties by adsorbates has attracted considerable attention in recent years. In particular, passivation of compound semiconductor surfaces by chalcogen atoms has been the focus of many experimental and theoretical studies because of its beneficial effects on the electronic properties of surfaces/interfaces.[1–10] In spite of all these efforts, the atomic structures of these technologically important surfaces remain to be clarified.

In most electron diffraction experiments on passivated surfaces (2×1) diffraction patterns are observed, indicating a doubling of the surface periodicity in one direction. Of the structural models proposed for these surfaces, the dimer model,[4] which appears to explain most of the experimental results, is the most widely supported. In this model, chalcogen atoms are adsorbed at bridge sites in the second layer forming chalcogen dimers with the 2×1 structure. First-principle study of the passivated surfaces also supported the possibility of such dimerization,[5] and, very recently, Se-passivated GaAs(001) surfaces with nearly perfect 2×1 dimer structure was observed by scanning tunneling microscopy (STM).[11] However, on the other hand, the Se-treated surface has been considered to have a more complicated structure; Ga_2Se_3-like structures with ordered Ga vacancies of 1/4–1/3 ML.[8] In order to understand the passivation mechanism, characterization of the passivated surface structure on an atomic scale is urgently needed. Recently, an intermediate 2×3 structure was found to exist on the Se-treated GaAs(001) surface, and reversible phase transition was observed between the 2×3 and the 2×1 structures during heat treatment.[6] Change in the photoemission spectra concerning the amount of Ga vacancies was observed upon the heat treatment. Therefore, from the standpoint that the Ga_2Se_3-like structure was grown from the original 2×1 dimer structure through phase transition between the 2×1 and the 2×3 structures, we studied the surface structures of the Se-passivated GaAs(001)-2×3 surface by STM.

Study of the chalcogen-passivated surface is also interesting from the standpoint of surface reconstruction based on dimer interaction. Recently, by state-of-the-art total energy calculation,[12] attractive interaction between the As dimers and relaxation of the As dimer block was shown to be essential to the stability of the As-rich GaAs(001) surface. On the other hand, adjacent chalcogen dimers of the passivated GaAs(001) surface are expected to interact repulsively due to the excess electrons, one electron per dimer, and dimer reconstruction differing from that on the surface of As/GaAs(001) is expected.[10] Stability of the 2×1 chalcogen dimer structures is a possible result of the repulsive interaction. Therefore, in addition to clarification of the passivation mechanism, understanding the surface stabilization mechanism of chalcogen-passivated compound semiconductor surfaces is very intriguing from both fundamental and practical points of view. Among the chalcogen-passivated GaAs(001) surfaces, the Se/GaAs(001) structure is the most interesting because the atomic radius of Se is closest to that of As.[13]

GaAs(001) surfaces, oriented to within 0.5° of the [001] direction and Si-doped at a dose of $\sim 1\times 10^{18}$ cm^{-3}, were prepared by thermal cleaning. After observation of 4×2 reflection high-energy electron diffraction (RHEED) pattern, selenium, to a thickness of 100–300 nm, was evaporated onto the GaAs(001) surface at room temperature. For the observation by STM, the samples were transferred from the preparation chamber to the STM chamber through air, and were heat treated under RHEED observation. The base pressure of the chamber was $\sim 4\times 10^{-11}$ Torr.

Generally, heat treatment is performed under Se flux of $\sim 10^{-6}$ Torr, and a 2×1 diffraction pattern is reported. However, recently an intermediate phase with a 2×3 diffraction pattern was observed at higher temperatures (⩾550 °C),[6] which suggests the importance of the Se-chemical potential in controlling this surface reconstruction similar to the change reported for As/GaAs(001) surfaces.[12] Therefore, samples were flash heated and the backpressure was kept lower than $\sim 1\times 10^{-10}$ Torr throughout the heat treatment in order to suppress the readsorption of desorbed Se atoms. Thereby, a 2×3 RHEED pattern (Fig. 1), previously reported as an intermediate phase appearing at high temperature (⩾550 °C) was obtained by lower temperature heat treatment around ~400 to ~500 °C and was stable even after the samples were cooled.[13]

Figure 2(a) shows an STM image of the Se-passivated

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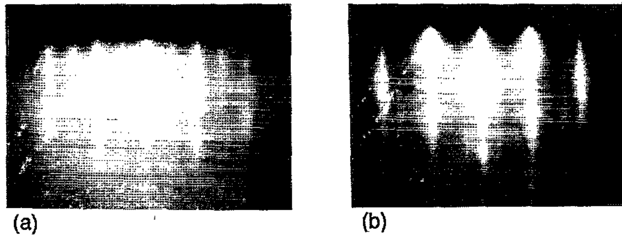

FIG. 1. The 2×3 RHEED patterns obtained for Se/GaAs(001): (a) [110] (b) [$\bar{1}$10].

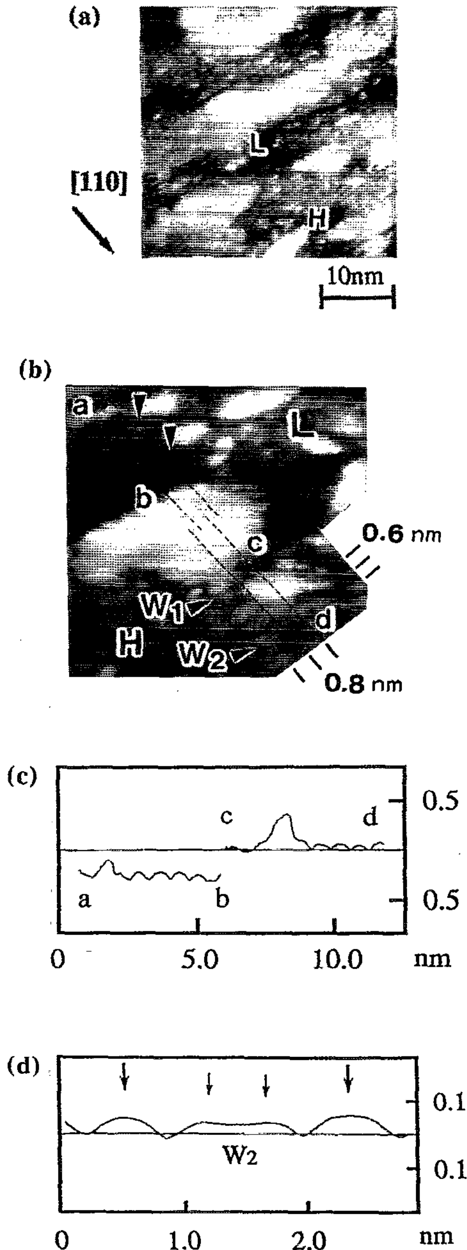

FIG. 2. (a) STM image of Se/GaAs(001) 2×3 structure: $V_s=-2.0$ V, $I_s=20$ pA. (b) Magnified image of (a). (c) Cross sections along a–b and c–d in (a). (d) Cross section along W_2 in (a).

surface taken after observation of the 2×3 RHEED pattern. The sample bias was −2.0 eV. STM imaging was performed in the constant current mode (setting current: $I_s=20$ pA). The obtained surface is rather rough, but ordered arrays consisting of elliptical protrusions can be observed in the flat area.

Figure 2(b) shows a magnified image, including a step, of Fig. 2(a), and the cross sections along a–b and c–d in Fig. 2(b) are shown in Fig. 2(c). The terrace labeled H in Fig. 2(a) is about ~0.28 nm higher than the neighboring terrace labeled L. The distance between the arrays is ~0.8 nm and the axes of the rows on both terraces are shifted by about ~0.2 (~0.6) nm as shown in Fig. 2(b), which agrees with the double-layered structure of the dimer model; the elliptical protrusions in the arrays are the Se dimers bonded to the Ga underlayer.

For the most part, the elliptical protrusions are aligned in the [110] direction with ~0.6-nm periodicity as shown in Figs. 2(b) and 2(c). In addition, some clusters with 0.4-nm periodicity exist in some parts as indicated by arrows in Fig. 2(b). Since reversible phase transition is observed between the 2×3 and the 2×1 structures during heat treatment,[6] we assign the former protrusions with ~0.6-nm periodicity to the 2×3 structure and the latter to the 2×1 structure remaining even after the heat treatment. The 2×1 dimer cluster W_1, which seems to have enough space on its side, should change into the 2×3 structure and the existence of this type of cluster may indicate an activation process for dimer reconstruction from the 2×1 to the 2×3 structure. Figure 2(d) shows the cross section along the 2×1 cluster W_2 in Fig. 2(b). As is shown in Fig. 2(d), the corrugation of the dimers in the 2×1 cluster is very small (~0.01 nm) compared to that of the 2×3 structure (~0.05 nm).

Since one chalcogen atom has six electrons, Se dimerization for the 2×1 structure will leave one excess electron for each Se dimer; the excess electrons occupy Se-Se or Ga-Se antibonding states. This configuration renders the interaction between the adjacent dimers at the bridge sites repulsive. The 2×3 structure observed is symmetric along the dimer rows in contrast to the clustered dimer structure formed by As dimers on the GaAs(001) surface,[12] which is thought to be caused by the repulsive interaction between the Se dimers; attractive interaction is essential in the case of As-dimer reconstruction.

Since the periodicity of the protrusions is ~0.6 nm along the row in the [110] direction, two adjacent dimers must be included to form the 2×3 structure (1.2 nm) in order to explain the observed 2×3 RHEED pattern; two alternative kinds of dimers or some other structures which produce the 1.2-nm period must exist to form the threefold periodicity. However, the reconstructed 2×3 structure is not very different from the 2×1 structure because of the finding that the 2×3 diffraction pattern transforms easily into the 2×1 pattern again when the substrate is cooled in Se atmosphere.[6] In consideration of the result that the difference in the corrugation is not very clear among the dimers as shown in Fig. 2(c), we adopt the latter model in this letter; we introduce another structure which produces the 1.2-nm period.

A possible structure exhibiting 2×3 periodicity is shown

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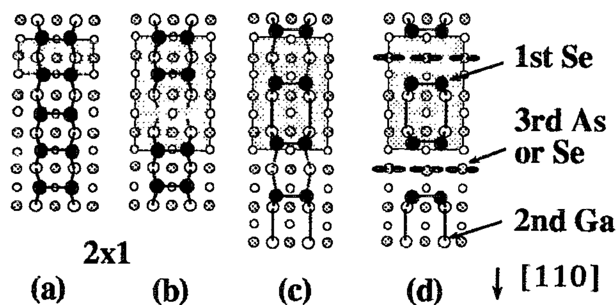

FIG. 3. A model for structural change from 2×1 (a) via Se-dimer desorption (b) to 2×3 (c), (d).

in Fig. 3. Here, Ga atoms form dimers in the second layer following the Se-dimer desorption. Such double-layered dimer structures with adsorbates often appear on semiconductor surfaces.[14] The number of excess electrons can thus be reduced; however, one electron still exists for every two dimers. Therefore, the excess electrons break the Ga-Se bonds on the other sides of Ga dimers, represented by dashed lines in Fig. 3(c), and the electrons transfer into the Ga dangling bond states created by the breaking of Ga-Se bonds. Actually, Se dimers are buckled as shown in Fig. 4, suggesting the existence of such charge transfer in the dimer layers.[12] According to the results obtained by photoelectron spectroscopy,[6] phase transition from the 2×1 to the 2×3 structure makes 0.2–0.4 eV shifts of the Se 3d core level toward higher binding energies, which agrees well with the charge transfer properties in our model. The ~0.6-nm periodicity in the STM images is formed by Se dimers pulled toward the Ga dimer as shown in Fig. 3(c). Se dimers in the 2×3 regions seem to be slightly higher than those in the 2×1 regions, as shown in Fig. 2(d). Since Ga atoms between the Ga dimers thus face outward, ordered Ga vacancies of 1/3 ML at maximum can be introduced easily, the value of which can be compared to the value obtained by the analyses of the photoemission spectra (1/4 ML) and the results of electron microscopy (1/3).[8]

Since the 2×1 clusters still remained after the samples were flash heated, the phase transition possibly remains at the initial step, as shown in Fig. 3(c). Actually, corrugations at the defects are ~0.15 nm, as shown in Fig. 5, which is close to the height of one GaAs(001) layer. When Ga vacancies are created, As atoms in the third layers can be replaced by Se atoms upon heat treatment as is shown in Fig. 3(d). In

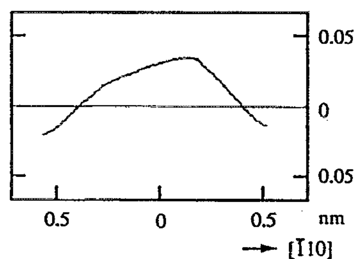

FIG. 4. Cross section of a Se dimer in the 2×3 region.

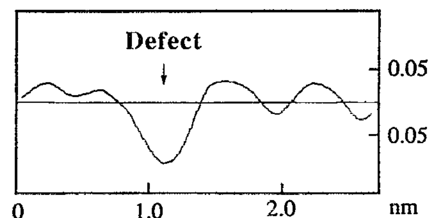

FIG. 5. Cross section of an Se defect in a dimer row.

such a case, the structure will remain intact even after the readsorption of Se dimers, and the structure becomes closer to the Ga vacancy zincblende structural model with ordered Ga vacancies.[8,12] In order to characterize the observed passivated structures, theoretical calculation is necessary.

In summary, a new 2×3 structure was obtained under the condition of a low chemical potential, the structure of which observed by means of STM, was in good agreement with the double-layered dimer model proposed in this letter. Formation of a Ga_2Se_3-like structure with ordered 1/3-ML Ga vacancies in the second layer could also be explained well by the model.

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