Structure of the GaP(001)-4×2-In surface investigated with LEED, STM, photoelectron spectroscopy, and *ab initio* calculations

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Surface structures at the initial stage of indium adsorption on GaP(001) are studied by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), photoelectron spectroscopy (PES), and *ab initio* calculations. After indium deposition on the *P*-rich GaP(001)-2×1 surface followed by annealing at 400–450 °C, ×4 LEED spots were observed along the [110] direction. STM images obtained after 400 °C annealing show a 4×2-In reconstruction with row and hump structures. PES result for the 4×2-In surface shows existence of In atoms in two different chemical environments; one with In-In bonding and the other with In surrounded by phosphorus atoms at the surface. These LEED, STM, and PES results are consistent with the ζ structure, which was proposed for cation-rich clean surfaces of III-V semiconductors containing arsenic or antimony. Several plausible models derived from the original ζ model are examined by first-principles calculations for the GaP(001)-4×2-In surface.

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I. INTRODUCTION

The growth of nanostructures on III-V semiconductors is very important because of possible applications for electronic and optoelectronic devices. Depending on surface stoichiometry and substrate temperature, various stable and metastable reconstructions are formed on the III-V semiconductors. For cation-rich clean surfaces of a $A_{III}B_{V}(001)$ substrate, two reconstructions have been focused upon in a number of publications. (i) One is the $4\times2/c(8\times2)$ reconstruction (hereafter referred to as 4×2, since the structure of $c(8\times2)$ is essentially identical with that of 4×2 except for the array of the 4×2 unit cell). Until a decade ago, there was a consensus that the 4×2 reconstruction was made up of cation dimers.[1] However, Lee *et al.*[2] identified a new model called the ζ model by means of first-principles calculations and quantitative low-energy electron diffraction (LEED) analysis for the GaAs(001)-4×2 surface. Since then, from experimental and theoretical studies,[3–10] the ζ model [Fig. 1(a)] has been supported as a unified model for the 4×2 reconstruction of the GaAs(001), InAs(001), InSb(001), and In-adsorbed GaAs(001) surfaces. (ii) The other is the 2×4 reconstruction, which contains a heteroGa(In)-P dimer or called mixed dimer (MD) at the top layer of the unit cell [Fig. 1(b)] for the GaP(001), InP(001), and InGaP(001) surfaces.[11–15] Thus, group-V elements seem to have a great influence on the surface structure. However, so far it has not been discussed whether or not the ζ structure is applicable for group-III phosphides.

In this paper, the structures of the indium-adsorbed GaP(001) surface have been studied by LEED, scanning tunneling microscopy (STM), photoelectron spectroscopy (PES), and first-principles calculations. The 4×2 reconstruction was observed by LEED and STM and two possible structural models, based on the ζ structure, are proposed. This is a different report of the ζ structure formed on the III-V semiconductor with phosphorus.

II. EXPERIMENTAL AND THEORETICAL PROCEDURES

A GaP(001) sample was degreased by acetone and ethanol and subsequently rinsed by distilled water. After the sample was chemically etched by an acid solution ($HCl:HNO_3$ =1:1) at room temperature (RT), it was installed into an UHV chamber and was cleaned by ion bombardment and annealing (IBA): a few cycles of Ar^+ ion bombardment at 500 eV and annealing at 460–470 °C for 10 min. A clear 2×4 LEED pattern, corresponding to the Ga-rich 2×4 surface, was observed after the IBA treatment [Fig. 2(a)]. The sample was then exposed to *t*-butyl phosphine (TBP) at the substrate temperature of 350 °C and a 2×1/2×2 LEED pattern was observed [Fig. 2(b)] (Hereafter, 2×1/2×2 surface will be simply called 2×1). It is in agreement with our previous result.[16] A few monolayers of In were deposited onto the 2×1 surface using a Knudsen cell at RT. Then, postannealing was carried out up to 475 °C. LEED patterns were observed at the various annealing temperatures.

All STM (JEOL, JSTM-4500XT) images were taken at RT with a W tip. The surface periodic structures were examined by LEED. PES measurements were performed on the beamline 18A at the synchrotron facility KEK-PF (Tsukuba, Japan). PES spectra were measured using linear-polarized light and an angle-integrated analyzer.

The total-energy calculations were performed in the framework of the density-functional theory using the plane-wave pseudopotential method. The system was modeled within a periodic supercell geometry with the cell along the surface normal containing eight atomic layers of GaP, the In adlayer, and a vacuum region of 10 Å. Electron-ion interactions were considered by using norm-conserving and fully separable pseudopotentials,[17] electron-electron interaction was treated within the local-density approximation,[18] and the dangling bonds at the bottom of the atomic slab was saturated with fractionally charged pseudohydrogen atoms. A di-

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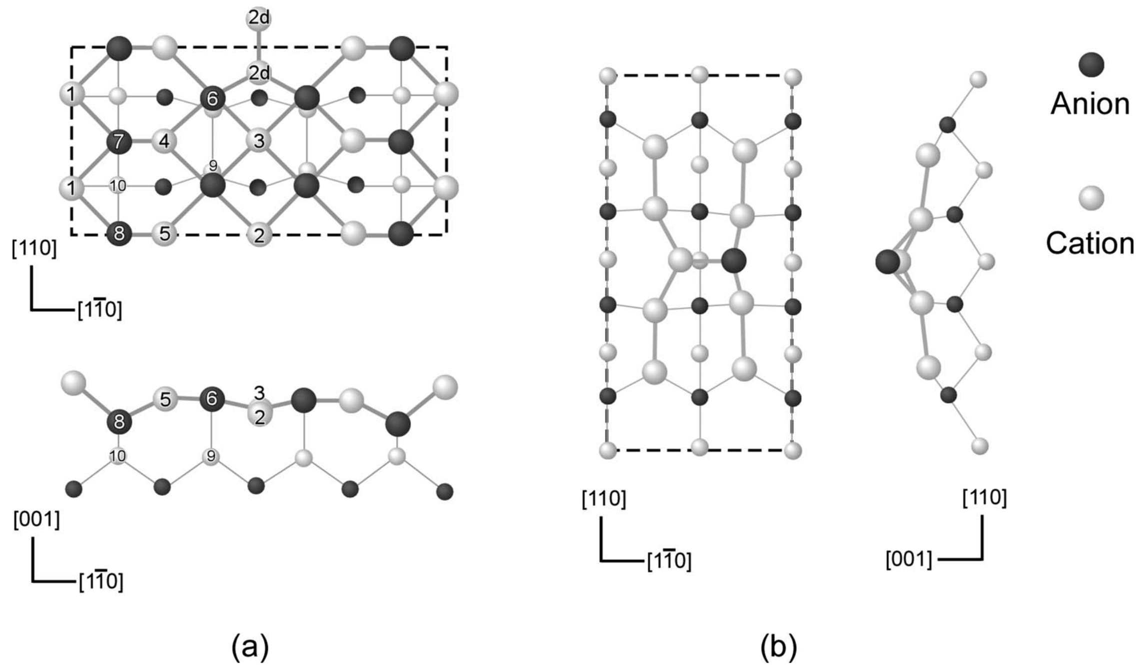

FIG. 1. Schematic top view of the (a) ζ model and (b) hetero(mixed)dimer model. For the ζ model, labeled atomic numbers are same with those in Ref. 4.

pole correction method was used to annul the effect of the spurious electrostatic field arising from the inequivalence of the two surfaces within a supercell. Kohn-Sham single particles were expanded in a basis of plane waves up to 12 Ry kinetic-energy cut off. Self-consistent electronic charge density was calculated by using a set of four special k points[19] in the irreducible part of the surface Brillouin zone. The six topmost atomic layers were fully relaxed toward the energy minimum configuration.

III. RESULTS AND DISCUSSION

Figures 2(c)–2(g) show LEED patterns of the In-deposited GaP(001) surface after annealing. In the LEED pattern after annealing at 375 °C [Fig. 2(c)], $2\times 1/2\times 2$ spots are observed. Although the periodicity is the same as the TBP-treated surface, the $\times 2$ streak derived from the zigzag row structure[16] does not exist and the background intensity is increased. These facts indicate that a local structure including In atoms starts to glow, although the periodicity of the reconstruction is not changed from 2×1. As in Fig. 2(d), $\times 4$ spots are observed along the $[1\bar{1}0]$ direction after annealing at 400 °C. Since the $\times 4$ spots cannot be seen in both the Ga-rich GaP(001)-2×4 and P-rich GaP(001)-2×1 surfaces, it is related to an ordered structure containing In atoms. There are no distinct spots of a super structure along the [110] direction. This point will be discussed later. After annealing at 450 °C [Fig. 2(f)], the $\times 4$ spots are also observed along the [110] direction, indicating the existence of the clean GaP(001)-2×4 surface. After annealing at 475 °C because of complete thermal desorption of In atoms, the LEED pattern [Fig. 2(g)] is the same as the clean 2×4 surface [Fig. 2(a)]. No significant amount of In was detected by PES at this annealing temperature.

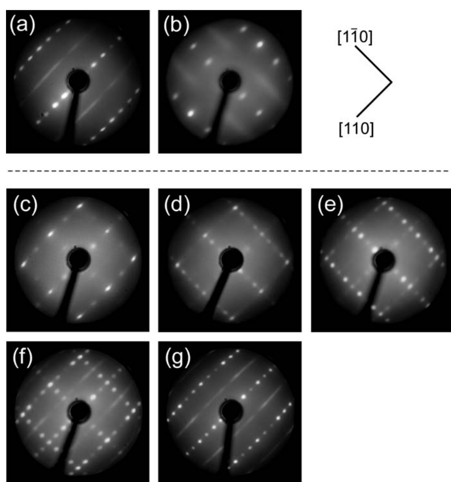

FIG. 2. LEED patterns of the clean [(a) Ga-rich 2×4, (b) P-rich 2×1] and In-adsorbed GaP(001) surfaces after annealing at (c) 375, (d) 400, (e) 425, (f) 450, and (g) 475 °C.

We measured STM images to clarify the structural change at an atomic scale. Figures 3(a) and 3(b) show STM images of the In-deposited GaP(001) surface after annealing at 400 and 450 °C, respectively. Row structures and humps between them are found in the expanded images in Fig. 3(a). The distance between the rows is 1.54 nm, which is in agreement with four times the 1×1 unit lattice periodicity ($=L_{1\times 1}=3.85$ Å). The distance between the nearest humps along the [110] direction is $2L_{1\times 1}$. The filled-state STM image in Fig. 3(a) closely resembles that of the GaAs(001)-4×2-In surface with the ladder-type pattern.[9] The row and hump structures are also observed in the STM image taken after annealing at 450 °C [Fig. 3(b)], although the number of the humps has decreased and the distance between the humps

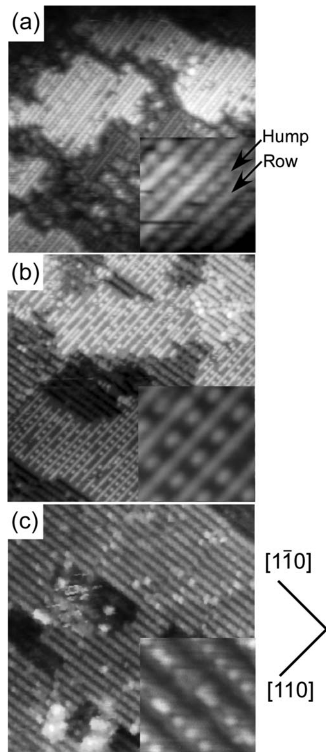

FIG. 3. Filled-state STM images of the In-adsorbed GaP(001) surfaces subsequently annealed at (a) 400, (b) 450, and (c) 475 °C taken at the sample bias of (a) −2.0 and (b) and (c) −3.0 V. The image sizes are 40×40 nm. The inset shows a high-resolution STM image.

is mostly $4L_{1\times1}$. Additional heating up to 475 °C causes almost complete desorption of In atoms and, consequently, the clean 2×4 surface based on the heterodimer structure is observed [Fig. 3(c)], which agrees with a filled-state STM image of the clean GaP(001)-2×4 surface.

Figure 4 shows a PES spectrum including In 4*d* and Ga 3*d* core lines of the GaP(001)-4×2-In surface after annealing at 410 °C when the 4×2 LEED spots were sharpest. The spectra can be fitted by three Ga and two In components. The separation between the two In components is 0.6 eV.

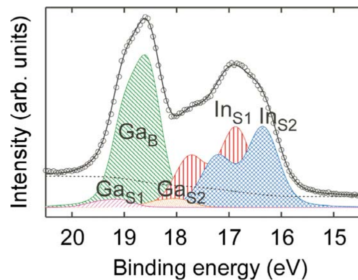

FIG. 4. (Color online) Core-level spectra of In 4*d* and Ga 3*d* taken after annealing at 410 °C. The photon energy was 40 eV. Open circles, solid line, and dotted line represent the experimental data, fitted curve, and Shirley background, respectively. Some fitting parameters are fixed as follows: spin-orbit splitting of Ga 3*d* (0.45 eV) and In 4*d* (0.88 eV), branching ratio of Ga 3*d* (1.5), Lorentzian width of Ga 3*d* (0.18 eV), and In 4*d* (0.20 eV).

The energy position of the high-energy component labeled In_{S1} is close in energy to that of bulk InP and, therefore, it is assigned as In bonded only to P atoms.[12] On the other hand, the energy position of the low-energy component (In_{S2}) is close to multilayered metallic In formed before the annealing process. Thus, the In-In bonding exists at the surface. The Ga 3*d* line consists of three components (one bulk and two surface components). Ga_{S1} and Ga_{S2} components are necessary to fit the experimental spectrum, although quantitative discussion is difficult because of their small intensities. One possible interpretation of these components is as follows: since the surface components are located at higher (Ga_{S1}) and lower (Ga_{S2}) binding-energy sides compared to the bulk component, positively charged Ga bonded to P in threefold coordination and Ga-Ga bonding may exist in the (4×2)-In structure. We also measured the P 2*p* line of the 4×2 surface (not shown here). The P 2*p* line can be fitted by only one component. It suggests that the chemical environment of surface phosphorus atoms is close to that of bulk atoms. When the sample was annealed at higher temperature, the In_{S2} component first decreased in intensity and after desorption over 50% of In_{S2}, the In_{S1} component started to decrease in intensity.

In addition to the LEED, STM, and PES results, we performed first-principles calculations to examine surface structural models for 4×2-In. It would be suitable to adopt the ζ model for the basic structure of the 4×2-In surface since the observed row and hump structure in STM [Fig. 3(a)] closely resembles that of the GaAs(001)-4×2-In surface.[9] First, we examined the same model as the GaAs(001)-4×2-In surface in which sites 2 and 3 in Fig. 1(a) are occupied by an In atom for GaP(001)-4×2-In. In the total-energy calculations, however, the surface indium atoms were aggregated during the optimization. Next, we built some models with an In-In dimer inserted at site 2*d* because the In-In bonding is expected for the 4×2 surface from our PES result and no atom are assumed to be at site 3. The result of calculations suggests that models with a depressed In-In dimer at site 2 and without an atom at site 3 always give the lower energy. Two possible slab models are shown in Fig. 5. The $\zeta-$I model in Fig. 5(a) does not include In atoms at site 1. This results in lone pairs of P at sites 7 and 8. The row structure in the STM images could be interpreted by linearly aligned lone pairs on the P atoms. The $\zeta-$II model in Fig. 5(b) contains fourfold coordinated In such as the GaAs(001)-4×2-In surface at site 1.[9] Both the models can be energetically optimized without aggregation of In. The calculations show that the $\zeta-$I and $\zeta-$II models have a semiconducting and metallic band structure, respectively. Thus, as the $\zeta-$I model does not include any partially filled dangling bonds, it would be more stable. Further experimental band-structure analysis could clarify this point.

During the STM measurements, we found that the hump structure is less stable than the row structure and can easily move or disappear even at RT. Figure 6 shows continuously measured STM images taken after annealing at 450 °C. To monitor the movement of the humps, we insert 4×4 unit cells in the figure. It is clear that the position of the humps changes even at RT. This could be due to electric-field effect of the STM tip. As seen in Fig. 3(b), the number of the

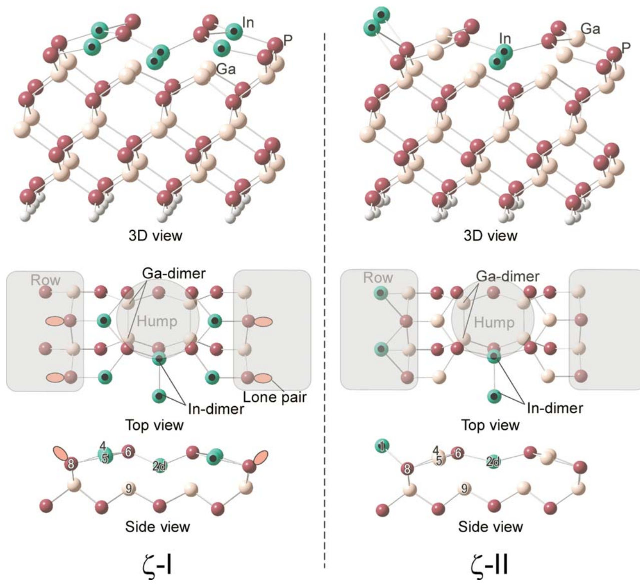

FIG. 5. (Color online) Periodic slab models (ζ−I and ζ−II) optimized by using the first-principles calculations. In the top view, the gray area represents the row and hump structures observed in STM.

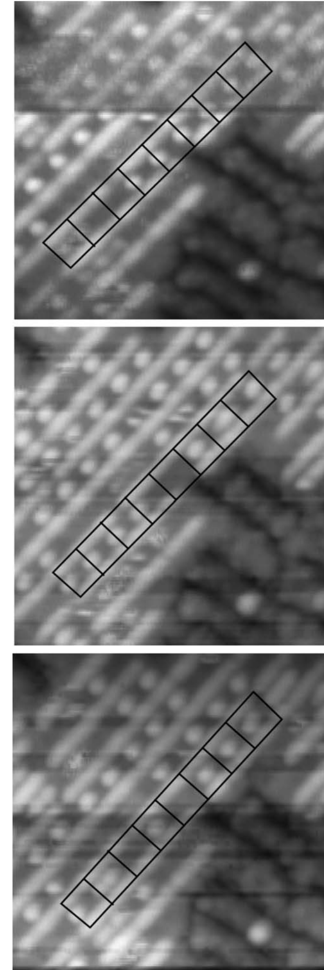

FIG. 6. Continuously measured STM images taken after annealing at 450 °C. 4×4 unit cells are inserted to guide the positions of the humps.

humps is also related to the substrate temperature. Thus, the potential barrier for reforming the hump structure is obviously lower than that of the row structure. Because of the variable distance between the humps, long-range ordering along the [110] direction is prevented. Thus, 4×1 LEED patterns are observed when the ζ structure is formed.

We have also tried to obtain the 4×2-In structure by following three other procedures: (1) In deposition on the Ga-rich GaP(001)-2×4 surface, (2) In deposition on the *P*-rich InP(001)-2×1 surface, and (3) triethyl indium deposition on the *P*-rich GaP(001)-2×1 surface at 300−400 °C. The procedures one and two failed and the clean 2×4 structure was formed after annealing. These facts indicate that compressive stress from the substrate and enough amounts of phosphorus are needed to construct the ζ structure for phosphides. On the other hand, the 4×2-In surface was successfully prepared through the procedure three. The substrate temperature at 350 °C when the $\times4$ LEED spots were clearly observed is lower than that using a *K* cell. This is because the energy for obtaining a free In atom from the metal organic source is less than that from an In cluster. Thus, the 4×2-In surface can be obtained by both solid and vapor phase epitaxies.

IV. CONCLUSIONS

The surface structure of the In-adsorbed GaP(001) surface has been studied by LEED, STM, PES, and first-principles calculations. After indium deposition on the *P*-rich GaP(001)-2×1 surface followed by annealing at 400−450 °C, the $\times4$ LEED spots are observed along the [110] direction. The STM observation shows that the GaP(001)-4×2-In structure consists of the row and hump structures. The filled-state image closely resembles that of the GaAs(001)-4×2-In surface of which the structure is explained by the ζ structure model. The PES result for the 4×2-In surface indicates the existence of In atoms in two different chemical environments; one with In-In bonding and the other with In surrounded by phosphorus atoms at the surface. We propose the two ζ models based on the first-principles calculations. Thus we clarified that the ζ structure is formed on a phosphide semiconductor.

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