

## Surface structure of phosphorus-terminated GaP(001)-(2×1)

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The surface structure of phosphorus-terminated GaP(001)-(2×1) has been studied by low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), scanning tunneling microscopy (STM), and synchrotron radiation photoemission spectroscopy. HREELS spectra indicate that hydrogen is adsorbed on the surface, leading to formation of a P—H bond. The intensity of the stretching vibration of the P—H remains constant for the (2×1) surface annealed at 300–600 K, where (2×1) LEED patterns also remain. The vibration mode and patterns disappeared simultaneously upon annealing at 700 K. STM filled state images show zigzag chain structures. On the other hand, straight rows along the [110] direction are seen in the empty state images. Surface core-level shifts are found: +0.60 eV for Ga 3*d* and –0.69 and +0.39 eV for P 2*p*. These results can well explain a theoretical model of buckled P-dimers with hydrogen adsorbed in an alternating sequence.

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### I. INTRODUCTION

III-V compound semiconductors containing phosphorus, for example, GaP and InP, are important materials for optoelectronic devices. Since they have been also used as substrates for quantum effect devices, surface structures of the substrates have been widely studied in an atomic level to fabricate good interfaces between the devices and substrates.

Recently, an interesting structure model of an InP(001)-(2×1)/(2×2) surface prepared by metalorganic chemical vapor deposition was proposed based on first-principles calculations<sup>1</sup> and supported by experiments:<sup>2</sup> a (2×1)/(2×2) reconstruction induced by hydrogen adsorbed in an alternating sequence on buckled P-dimers. It was reported that a GaP(001) surface terminated by phosphorus is also reconstructed into a (2×1)/(2×2) structure.<sup>3–9</sup> The first-principles calculations showed that the surface structure of GaP(001)-(2×1)/(2×2) is similar to the model for the InP(001)-(2×1)/(2×2) surface.<sup>10</sup> However, no detailed experimental results to support the model have been reported as yet. Especially, a direct evidence for existence of hydrogen on the surface has not found so far in spite that the hydrogen adsorption is crucially important for surface charge stability (electron counting rules) of the (2×1)/(2×2) reconstruction on the phosphorus-terminated GaP(001) surface.

In this paper, the GaP(001)-(2×1) surface prepared by *t*-butylphosphine (TBP) is studied by low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), scanning tunneling microscopy (STM), and synchrotron radiation photoemission spectroscopy (SRPES) to elucidate the surface structure. Comparison of the present work with the theoretical result is also made.

### II. EXPERIMENT

*n*-GaP(001) (carrier density:  $5.0 \times 10^{17}/\text{cm}^3$ ) and *p*-GaP(001) (carrier density:  $2.0 \times 10^{18}/\text{cm}^3$ ) samples are used for present experiments. The samples are degreased by acetone and ethanol, etched by acid solution

(HNO<sub>3</sub>:HCl=1:1) for 1 min, and then rinsed by deionized water. They were immersed in (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solution for 30 min to avoid surface oxidation in air, rinsed, and dried in a dry nitrogen stream, followed by being introduced into an ultra-high vacuum chamber. They were cleaned by cycles of sputtering with Ar ions (0.5 keV) and annealing at 733 K, leading to a (2×4) reconstruction without sulfur. The (2×4) surface was exposed to TBP [(CH<sub>3</sub>)<sub>3</sub>CPH<sub>2</sub>,  $2.6 \times 10^{-4}$  Pa] gas for 10 min at 633 K, resulting in a (2×1) reconstruction.

LEED observations were performed at RT to examine the surface structure after various treatments. Measurements of HREELS spectra were carried out at an incident energy of about 5 eV in the specular direction (60° off normal to the surface) with a total resolution of 15 meV. STM (JEOL: JSTM-4500XT) filled and empty states images were observed using a W tip on the *n*- and *p*-GaP(001)-(2×1) surfaces, respectively, because the latter images could not be obtained for the *n*-type surface. Core-level spectra of Ga 3*d* and P 2*p* were measured by SRPES (at the 13C beamline in KEK, Tsukuba, Japan) using photon energies of 100 and 170 eV, respectively. The spectra were fitted using a least-squares method. The background of the spectra was subtracted by using the Shirley method. Differences between the measured and fitted spectra were shown in the figures. A background pressure in the chambers was kept below  $3 \times 10^{-8}$  Pa.

### III. RESULTS AND DISCUSSION

The surface structure model presented by Hahn *et al.*<sup>10</sup> is shown in Fig. 1 where hydrogen is adsorbed on P-dimer in an alternating sequence. The surface unit cell in the model shows a (2×2) reconstruction, but it would lead to the (2×1) if the (×2) periodicity in the [–110] direction is lost in the longer length than the coherent one (5–10 nm) for the LEED observation. The latter reconstruction occurs in dominant domains on the surface studied here.

Figure 2 shows HREELS spectra of the GaP(001)-(2

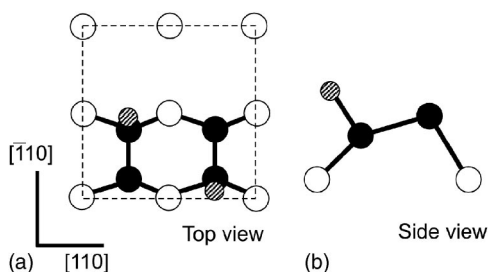


FIG. 1. A  $(2 \times 1)/(2 \times 2)$  structure model of the GaP(001)- $(2 \times 1)/(2 \times 2)$  surface. Top (a) and side (b) views are shown. Shaded, filled, and open circles correspond to hydrogen, phosphorus, and gallium atoms, respectively.

$\times 4)/c(2 \times 8)$  and  $-(2 \times 1)$  surfaces prepared *in situ* and annealed at various temperatures in the ultrahigh vacuum. Only the Fuchs-Kliwiler phonon peaks at 395, 782, and 1185  $\text{cm}^{-1}$  are seen on the  $(2 \times 4)/c(2 \times 8)$  surface. Two peaks at 2355 and 2984  $\text{cm}^{-1}$  are found, except for the Fuchs-Kliwiler phonon peak at 385  $\text{cm}^{-1}$  (not shown here) on the  $(2 \times 1)$  surface. This implies that the two peaks were caused by preparation of the  $(2 \times 1)$  surface. The peak at 2355  $\text{cm}^{-1}$  can be ascribed to a P—H stretching vibration mode<sup>11</sup> although a weak P—H<sub>2</sub> peak might not be separated from the P—H because the wave-number difference  $\Delta\nu$  is very small (about

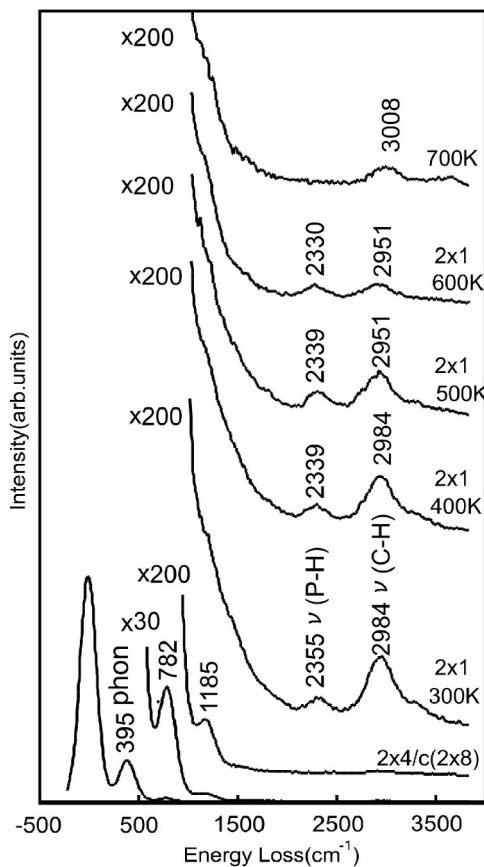


FIG. 2. HREELS spectra for the GaP(001)- $(2 \times 1)$  surface annealed at 300–700 K. The spectrum of the GaP(001)- $(2 \times 4)/c(2 \times 8)$  surface is also shown. The intensity ratio of the P—H vibration mode to the elastic peak remains almost constant up to 600 K.

20  $\text{cm}^{-1}$ ).<sup>12</sup> However, since a P—H bond is formed on the GaP(001)- $(2 \times 4)$  surface by adsorption of TBP,<sup>13</sup> the peak at 2355  $\text{cm}^{-1}$  would be due to the P—H bond. The 2984  $\text{cm}^{-1}$  peak can be assigned to the C—H stretching vibration mode,<sup>13</sup> implying that hydrocarbon species are also adsorbed on the surface. Since the  $(2 \times 1)$  surface was prepared using TBP gas at 633 K, the hydrocarbon decomposed from TBP would be adsorbed on the surface.

The  $(2 \times 1)$  surface was annealed at 300–700 K. The intensity ratio of the P—H vibration mode to the elastic peak remains almost constant and the  $(2 \times 1)$  LEED patterns were not changed upon annealing at 300–600 K. The P—H vibration disappeared at 700 K where the  $(2 \times 1)$  patterns were changed to the  $(2 \times 4)$ . The ratio for the hydrocarbon was gradually decreased upon annealing and it was decreased by 85% at 600 K. This concludes that the hydrocarbon is not responsible for the  $(2 \times 1)$  reconstruction.

If the amount of hydrogen bonded to phosphorus is small and it is contaminant on the surface, the hydrogen would not be responsible for the reconstruction. The intensity ratio for the P—H vibration mode was saturated at about  $1.2 \times 10^{-4}$  for the GaP(110) surface exposed to hydrogen atoms (600 L).<sup>11</sup> On the other hand, it is found to be about  $1.5 \times 10^{-4}$  for the present work, showing that both the values are close. The intensity ratio ( $I/I_{el}$ ) of a certain vibration mode ( $I$ ) for an adsorbate to the elastic peak ( $I_{el}$ ) is expressed in a dipole scattering at fixed measurement conditions as follows:<sup>14</sup>

$$I/I_{el} \propto A_v N_s / (1 + \sum A_e)^2,$$

where  $N_s$  is the number of the adsorbate,  $A_v$  an ionic polarizability, and  $A_e$  an electron polarizability. This implies that the ratio depends upon (1) the coverage, (2) the electron polarizability, and (3) the ionic polarizability. Since the hydrogen would be adsorbed at a considerable part of P sites on the GaP(110) surface at saturation of the ratio, and (2) and (3) would not be so different for both the GaP(110) and GaP(001)- $(2 \times 1)$  surfaces, the value for the latter would be large enough to cover the sufficient area of the surface.

An impact scattering might excite the P—H vibration because the P—H bond is tilted from the normal to the GaP(001)- $(2 \times 1)$  surface (see Fig. 1). On the other hand, the P—H bond on GaP(110) is perpendicular to the surface. The intensity of the dipole-scattered vibration is close to that of the impact scattered for a light element, such as hydrogen.<sup>14</sup> The above discussion would allow us the conclusion that the hydrogen is not the contaminant, but is responsible for the  $(2 \times 1)$  reconstruction.

STM filled and empty states images of the GaP(001)- $(2 \times 1)$  surface are displayed in Figs. 3(a) and 3(b), respectively. Zigzag chains arranged in the  $[110]$  direction are found in Fig. 3(a). The chains in and out of phase are also seen, resulting in formation of the  $(2 \times 2)$  and  $c(4 \times 2)$  structures, respectively. This filled state images are in good agreement with the calculation<sup>10</sup> and the previous result:<sup>9</sup> bright protrusions correspond to the phosphorus atom with a filled dangling bond of P-dimers. The empty state images could not be obtained for the  $n$ -GaP(001)- $(2 \times 1)$  surface. This

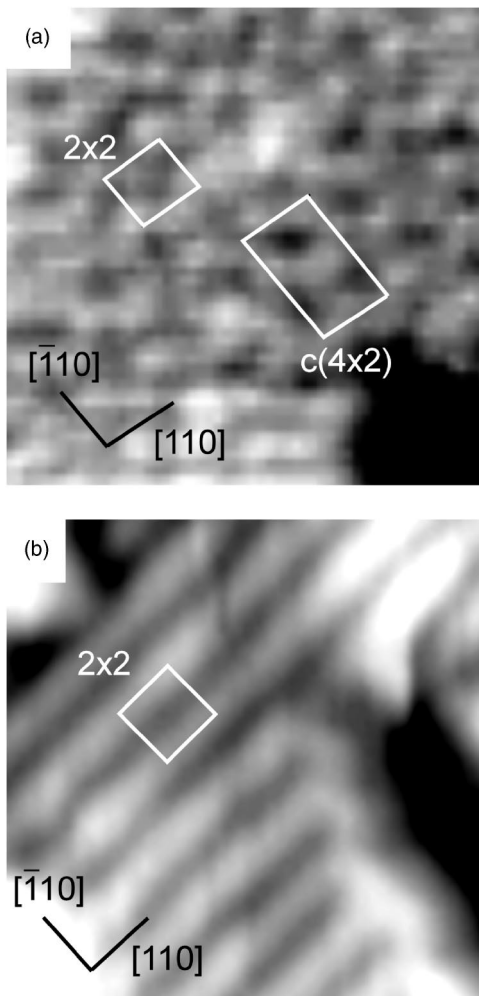


FIG. 3. STM filled (a) and empty (b) states images measured at bias voltages of  $-3.5$  and  $+3.0$  V (tunneling currents,  $0.20$  nA), respectively. The image sizes are  $4$  nm  $\times$   $4$  nm. The  $n$ - and  $p$ -GaP(001)- $(2 \times 1)$  surfaces are used for the measurements of the filled and empty states images, respectively. The  $(2 \times 2)$  and  $c(4 \times 2)$  unit cells are shown.

might be due to pinning of the Fermi level near the valence band maximum, analogous to the  $n$ -GaP(001)- $(2 \times 4)$  surface.<sup>15</sup> The empty state images are obtained on the  $p$ -type surface in Fig. 3(b). The images show straight rows arranged in the  $[110]$  direction. The calculation showed that density of empty states (C1, C2, and C3) spreads over the hydrogen-adsorbed P—P bond.<sup>10</sup> Therefore, the each protrusion could not be resolved within our resolution. This result is similar to the calculated images taking into account the resolution.

Core-level spectra of Ga  $3d$  are shown in Figs. 4(a) and 4(b). Fitting parameters of Ga  $3d$  are as follows: the Gaussian and Lorentzian widths,  $0.55$  and  $0.20$  eV, respectively; the spin-orbit separation (SOS),  $0.45$  eV; the spin-orbit branching ratio (SOBR),  $1.5$ . Bulk (B) and S1 components are separated. The fitted spectra, especially in Fig. 4(b), are in good agreement with the measured, which could rationalize the fitting. The component S1 is clearly enhanced in intensity at the detection angle  $80^\circ$  off normal to the surface, which implies that it can be ascribed to the surface compo-

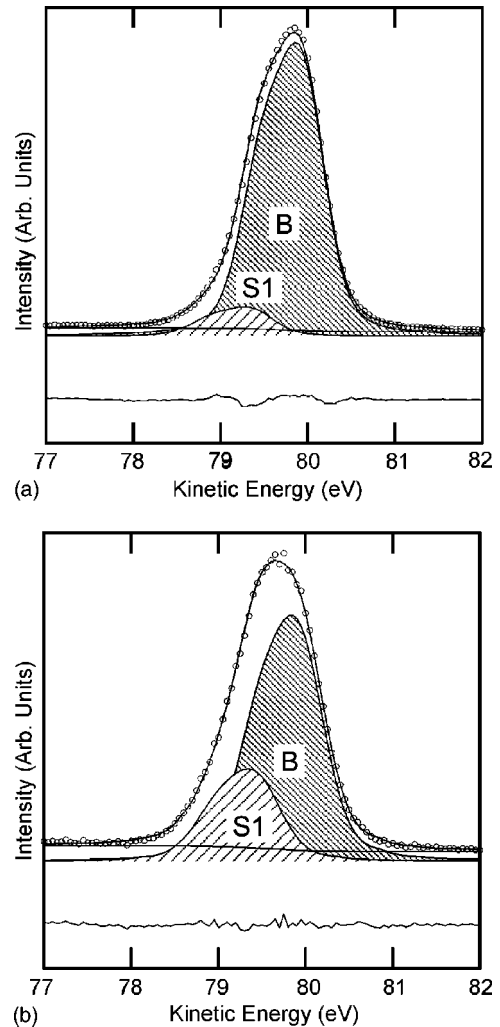


FIG. 4. Core-level spectra of Ga  $3d$  for the GaP(001)- $(2 \times 1)$  surface. The detection angle is  $0^\circ$  (a) and  $80^\circ$  (b) off normal to the surface. Photon energy of  $100$  eV was employed. The spectra are separated into two components: B (bulk) and S1 (surface). The measured and fitted spectra are shown by small open circles and solid lines, respectively. Differences between the measured and fitted spectra were shown below the spectra.

nent. The core-level shift is found to be  $+0.55$  eV that is higher than that ( $+0.31$  eV) of threefold Ga atoms with an empty dangling bond for the cleaved GaP(110)- $(1 \times 1)$  surface.<sup>16</sup> According to the presented model<sup>10</sup> (Fig. 1), the surface Ga atoms exist at the second layer and are bonded to two bulk-like P, P with a filled dangling bond, and fourfold P. Since the latter two P have excess and deficient electrons, respectively, the Ga atom might be predicted to have a similar binding energy to the bulk Ga. However, the Madelung energy has to be also taken into account for the surface core-level shift. Comparing the surface core-level shift of Ga  $3d$  for the GaAs(110)- $(1 \times 1)$  and  $-c(4 \times 4)$  surfaces, the latter ( $+0.41$  eV)<sup>17</sup> is larger than the former ( $+0.28$  eV).<sup>18</sup> The surface Ga atoms for the latter are located at the third layer and bonded to two bulk-like As atoms, As with a filled dangling bond, and fourfold As with deficient electrons. The chemical environment of this Ga atom is similar to that of the Ga at

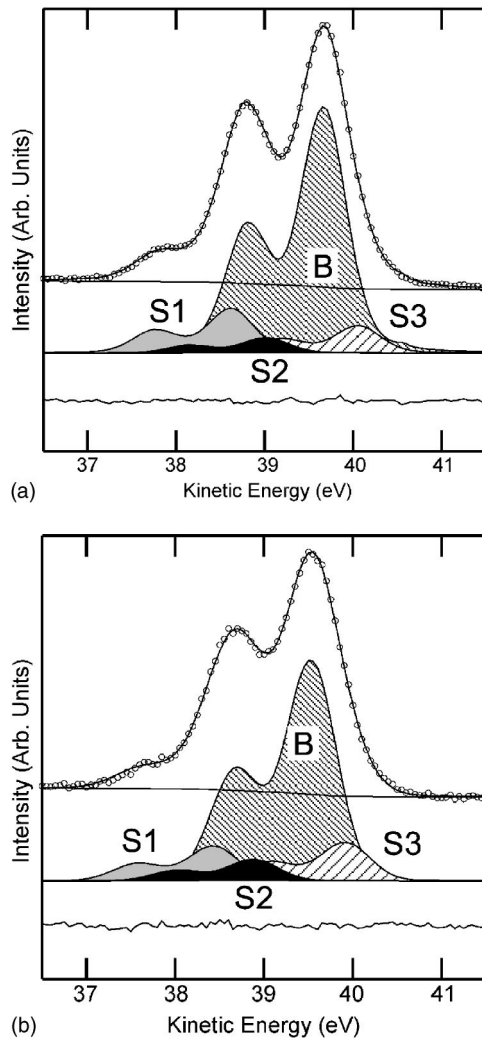


FIG. 5. Core-level spectra of P  $2p$  for the GaP(001)- $(2 \times 1)$  surface. The detection angle is  $0^\circ$  (a) and  $80^\circ$  (b) off normal to the surface. Photon energy of 170 eV was employed. The spectra are separated into one bulk (B) and three surface (S1, S2, and S3) components. The measured and fitted spectra are shown by small open circles and solid lines, respectively. Differences between the measured and fitted spectra are shown below the spectra.

the second layer of the model. The above discussion suggest us that the surface core-level shift of Ga  $3d$  in the present work can explain the model.

Core-level spectra of P  $2p$  measured at  $0^\circ$  and  $80^\circ$  off normal to the surface are displayed in Figs. 5(a) and 5(b), respectively. The spectra are separated into a bulk and three surface components (S1, S2, and S3) employing the following parameters: the Gaussian and Lorentzian widths, 0.63

and 0.03 eV, respectively; the SOS, 0.85 eV; the SOBR, 2. The sum of the four spectra is well fitted to the measured value, as seen in Fig. 5. The S2 and S3 components are relatively enhanced in intensity at  $80^\circ$  and shifted by  $-0.69$  and  $+0.39$  eV in the kinetic energy from the bulk energy, respectively. The S1 shifted by  $-1.10$  eV can be ascribed to P clusters at the surface, analogous to the result for the GaAs(001)- $c(4 \times 4)$  surface<sup>19</sup> and judging from the binding energy (BE) difference between GaP and elemental phosphorus.<sup>20</sup> Since the intensity of the S1 is not dependent upon the detection angle, it would not be the major surface component. The S3 can be assigned to phosphorus with the filled dangling bond because the component has the lower BE (higher kinetic energy) than that of the bulk. This is in good agreement with the shift ( $+0.40$  eV) of the P surface component with the filled dangling bond on GaP(110).<sup>16</sup> The S2 would be ascribed to phosphorus bonded to a more electronegative atom than gallium (electronegativity: 2.1) because the BE is higher than that of the bulk although the Madelung energy is not taken into account. The component corresponds to phosphorus bonded to hydrogen (electronegativity: 2.2). The trend of the present surface core-level shift for P  $2p$  is in agreement with the result for buckling dimers on the Si(001)- $(2 \times 1)$ <sup>21</sup> and InP(001)- $(2 \times 1)$ <sup>22</sup> surfaces.

#### IV. SUMMARY

The surface structure of phosphorus-terminated GaP(001)- $(2 \times 1)$  has been studied by LEED, HREELS, STM, and SRPES. The HREELS spectra indicate that hydrogen is adsorbed on the surface, leading to formation of the P—H bond. The intensity ratio of the P—H vibration mode to the elastic peak remains almost constant and the  $(2 \times 1)$  LEED patterns were not changed upon annealing at 300–600 K. On the other hand, the bond disappeared upon annealing at 700 K, where the LEED pattern was changed to the  $(2 \times 4)$  structure. Analysis of the HREELS data concludes that the P—H bonding is responsible for the  $(2 \times 1)$  reconstruction. The STM filled state images show the zigzag chain structures. The straight rows along the  $[110]$  direction are found in the empty state images. The surface core-level shifts are found:  $+0.60$  eV for Ga  $3d$  and  $-0.69$  and  $+0.39$  eV for P  $2p$ . These results can well explain the theoretical model of buckled P-dimers with hydrogen adsorbed in an alternating sequence.

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<sup>1</sup>W.G. Schmidt, P.H. Hahn, F. Bechstedt, N. Esser, P. Vogt, A. Wange, and W. Richter, Phys. Rev. Lett. **90**, 126101 (2003).

<sup>2</sup>G. Chen, S.F. Chen, D.J. Tobin, L. Li, R. Raghavachari, and R.F. Hicks, Phys. Rev. B **68**, 121303 (2003).

<sup>3</sup>A.J. Van Bommel and J.E. Crombeen, Surf. Sci. **76**, 499 (1973).

<sup>4</sup>I.M. Vitomirov, A. Raisanen, L.J. Brillson, C.L. Lin, D.T. McCl-

- tuff, P.D. Kirchner, and J.M. Woodall, *J. Vac. Sci. Technol. A* **11**, 841 (1993).
- <sup>5</sup>K. Knorr, M. Pristovsek, U.R. Esser, N. Esser, M. Zorn, and W. Richter, *J. Cryst. Growth* **170**, 230 (1970).
- <sup>6</sup>N. Sanada, S. Mochizuki, S. Ichikawa, N. Utsumi, M. Shimomura, G. Kaneda, A. Takeuchi, Y. Suzuki, Y. Fukuda, S. Tanaka, and M. Kamata, *Surf. Sci.* **419**, 120 (1999).
- <sup>7</sup>M. Zorn, B. Junno, T. Trepk, S. Bose, L. Samuelson, J.-T. Zettler, and W. Richter, *Phys. Rev. B* **60**, 11 557 (1999).
- <sup>8</sup>Y. Fukuda, N. Sekizawa, S. Mochizuki, and N. Sanada, *J. Cryst. Growth* **221**, 26 (2000).
- <sup>9</sup>L. Töben, T. Hannappel, K. Möller, H.-J. Crawack, C. Pettenkofer, and F. Willig, *Surf. Sci.* **494**, L755 (2001).
- <sup>10</sup>P.H. Hahn, W.G. Schmidt, F. Bechstedt, O. Pulci, and R. Del Sole, *Phys. Rev. B* **68**, 033311 (2003).
- <sup>11</sup>Y. Chen, D.J. Frankel, J.R. Anderson, and G.J. Lapeyre, *J. Vac. Sci. Technol. A* **6**, 752 (1988).
- <sup>12</sup>H. Nienhaus, S.P. Grabowski, and W. Mönch, *Surf. Sci.* **368**, 196 (1996).
- <sup>13</sup>G. Kaneda, N. Sanada, and Y. Fukuda, *Appl. Surf. Sci.* **142**, 1 (1999).
- <sup>14</sup>H. Ibach and D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1983).
- <sup>15</sup>Y. Fukuda, M. Shimomura, N. Sanada, and M. Nagoshi, *J. Appl. Phys.* **76**, 3632 (1994).
- <sup>16</sup>S. D'Addato, P. Bailey, J.M.C. Thornton, and D.A. Evans, *Surf. Sci.* **377–379**, 233 (1997).
- <sup>17</sup>M. Larive, G. Jezequel, J.P. Landesman, F. Solal, J. Nagle, B. Lepine, A. Taleb-Ibrahimi, G. Indlehofer, and X. Marcadet, *Surf. Sci.* **304**, 298 (1994).
- <sup>18</sup>A.B. McLean, *Surf. Sci.* **220**, L671 (1989).
- <sup>19</sup>P.K. Larsen, J.H. Neave, J.F. van der Veen, P.J. Dobson, and B.A. Joyce, *Phys. Rev. B* **27**, 4966 (1983).
- <sup>20</sup>J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, and J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy* (Phys. Electronics, Minnesota, 1992).
- <sup>21</sup>E. Landemark, C.J. Karlsson, Y.-C. Chao, and R.I.G. Uhrberg, *Phys. Rev. Lett.* **69**, 1588 (1992).
- <sup>22</sup>P. Vogt, A.M. Frisch, Th. Hannappel, S. Visbeck, F. Willig, C. Jung, R. Follath, W. Braun, W. Richter, and N. Esser, *Appl. Surf. Sci.* **166**, 190 (2000).