Observation of the Si(100)"1×2"-Ba surface by scanning tunneling microscopy

Kaoru Ojima, Masamichi Yoshimura,* and Kazuyuki Ueda
Graduate school of Engineering, Toyota Technological Institute, Hisakata 2-12-1, Tempaku-ku, Nagoya 468-8511, Japan
(Received 7 August 2001; published 16 January 2002)

We have studied the ''1×2'' structure on $\frac{1}{2}$ ML Ba/Si(100) by scanning tunneling microscopy (STM). This phase has two mirror symmetric unit cells, $(4,0)\times(1,2)$ and $(4,0)\times(1,-2)$. Their combination leads a wavy structure in STM images. We discuss the structure in comparison with previous low-energy electron-diffraction studies, and propose a model of the ''1×2'' structure where buckled Ba dimers locate on the second Si layer reconstructed into a dimerized ''1×2'' phase.

DOI: 10.1103/PhysRevB.65.075408 PACS number(s): 68.35.Bs, 68.37.Ef

I. INTRODUCTION

Many studies of the adsorption structures of alkaline-earth metals [Ca,[1,2] Sr,[3–6] and Ba (Refs. 7–13)] on Si substrates have been reported for a decade. Those studies mainly aim to grow high-quality thin films of functional materials, such as ferroelectrics or high-temperature superconductors, for fabrication of electronic devices. Besides such technological applications, the system of alkaline-metal/Si has been examined in terms of the physical interest, especially in surface superstructures. It is known from by low-energy electron diffraction (LEED) and Auger electron spectroscopy studies that the system of Ba/Si(100) has a variety of surface superstructures, i.e., silicide structures, 2×4, ''1×2'', $2\times3+c(2\times6)$ and 2×3, depending on both Ba coverage and heating temperature.[7–13] The ''1×2'' and 2×3 structures have been observed in all of the LEED studies at Ba coverages of $\frac{1}{2}$ and $\frac{1}{3}$ ML, respectively. Compared to LEED studies, there have been a few scanning tunnel microscopy (STM) studies, where the 2×3 structure or the initial Ba adsorption structure was investigated.[14–17] To our knowledge, there has been no report about the ''1×2'' structure by STM.

In this paper, we report a high-resolution STM study on Si(100)''1×2''-Ba. The STM image shows a complex surface covered by a wavy structure consisting of two mirror symmetrical units. This structure is far from the model proposed in Ref. 7. Based on a detailed analysis of STM images, we propose a model where the Si substrate is reconstructed into a dimerized ''1×2'' phase, and buckled Ba dimers are located on the trough between dimers.

II. EXPERIMENT

All experiments were carried out in an ultrahigh vacuum system. A detailed experimental setup was described elsewhere.[17] A Si(100) specimen with a size of $1\times7\times0.5\,\mathrm{mm}^3$ was degassed by direct current heating at 850 K for more than 10 h. In order to obtain a clean surface, the specimen was flashed at ~1500 K.

Ba was evaporated using a commercial Ba dispenser (SAES getters). A crystal oscillator was used to monitor the Ba dosage and the deposition rate of Ba was estimated at ~0.07 ML/min. After Ba deposition on the clean Si(100) surface at room temperature, the sample was heated in the STM chamber at 1160 K to reconstruct the surface structure.

The sample was cooled to room temperature for 30 min before STM measurements in order to avoid the effect of thermal drift. An STM tip was cut from a tungsten rod with a diameter of 0.3 mm, and was electrochemically etched in a KOH solution. All STM images were obtained in a constant-current mode.

III. RESULTS

Figure 1 shows a filled-state image of the $\frac{1}{2}$ ML of a Ba-deposited Si(100) surface followed by annealing at 1160 K for 1 min [the sample bias voltage $(V_s)=-1.69$ V, and the tunneling current $(I_t)=0.21$ nA]. The whole sample surface is covered by a wavy structure. The step assignment of the original Si(100) surface, S_A or S_B, is decided based on the coexisting phases of wavy structure and 2×3 structure (shown below). The waves run parallel to the steps on the upper terraces of S_A steps and perpendicular on those of S_B steps, which is similar to the case of dimer rows on Si(100)2×1.

Figures 2(a) and 2(b) show (a) a filled-state image $(V_s=-2.2\,\mathrm{V},\ I_t=0.20\,\mathrm{nA})$ and (b) an empty-state image $(V_s=2.37\,\mathrm{V},\ I_t=0.20\,\mathrm{nA})$ obtained at the same area. The wavy structure consists of a range of protrusions with a combination of two kinds of unit cells (**U** and **U**′), as indicated by white rhombuses in Figs. 2(a) and 2(b). The two unit cells

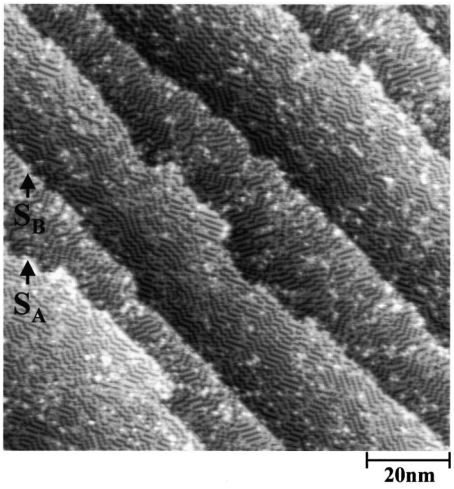

FIG. 1. A wide area STM image of the ''1×2'' structure obtained at the filled state ($V_s=-1.69$ V and $I_t=0.21$ nA).

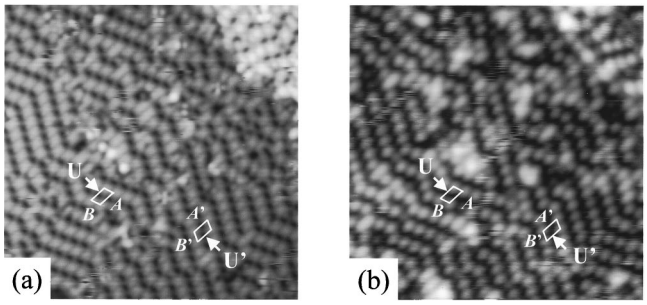

FIG. 2. (a) Filled-state ($V_s=-2.20$ V, and $I_t=0.20$ nA) and (b) empty-state ($V_s=2.37$ V and $I_t=0.20$ nA) STM images on the same area. **U** and **U**′ indicate mirror symmetric unit cells.

are mirror symmetric to one another. The long and short sides of the lattice translation vectors are indicated by **A** and **B**, respectively. STM images show that the length of vector **A** is $\sim 4a_0$ [a_0, the Si-Si distance of the bulk-terminated Si(100) surface is 0.384 nm], the distance between two long sides in a unit is $\sim 2a_0$ and the angle between **A** and **B**, θ, is about 60°–65°. In the filled-state image of Fig. 2(a), one protrusion is contained in a unit cell. However, in a higher-resolution STM image, the protrusion seems to split into four protrusions (shown below). In addition, in Fig. 2(a) we see faint lines running through the diagonal direction of the protrusion. A detailed discussion, together with a model of a Ba adsorption structure, is given in Sec. IV. In the empty-state image of Fig. 2(b), one elliptical protrusion is included in a unit cell. An additional feature is observed between two elliptical protrusions along vector **A** at a lower sample bias voltage than 1.5 V, though not shown here. Figure 3 shows a schematic of possible two mirror symmetrical unit cells [(4,0)×(1,2), **U**; and (4,0)×(1,−2), **U**′) superimposed on the lattice of bulk-terminated Si(100) surface. The experimental value of θ is in good accordance with the angle between **a** and **a**+**2b** (63.435°), where **a** and **b** are unit vectors of an ideal Si(100) surface ($|\mathbf{a}|=|\mathbf{b}|=0.384$ nm).

In order to make a model of a Ba adsorption structure, we analyze the surface where the wavy phase coexists with a 2×3 phase. Figure 4 shows a filled-state image of the coexisting surface on two different terraces. A unit cell

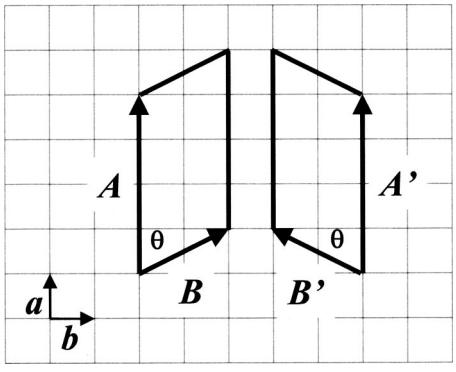

FIG. 3. Two building unit of the wavy structure superimposed on the bulk-terminated Si(100) ($|\mathbf{a}|=|\mathbf{b}|=a_0=0.384$ nm). The angle (θ) between *A* and *B* is 63.435°.

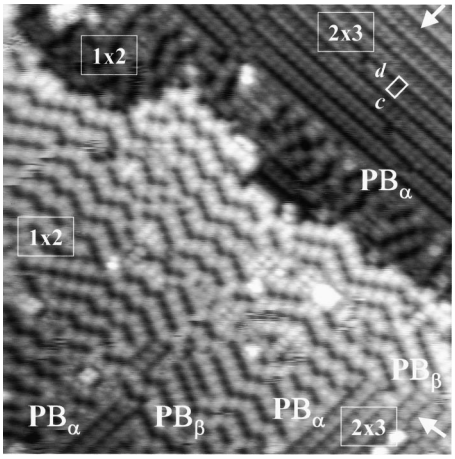

FIG. 4. A filled-state image of the coexisted area of the 2×3 and ''1×2'' phases ($V_s=-1.61$ V and $I_t=0.07$ nA). Arrows on the right of the figure indicate the direction of dimer rows on original Si(100) surface. PB_α and PB_β indicate two types of phase boundaries.

of the 2×3 structure with unit vectors $\boldsymbol{c}(|\mathbf{c}|=2a_0)$ and $\mathbf{d}$ ($|\mathbf{d}|=3a_0$) is also shown in the figure. The direction of **d** is in coincidence with that of dimer row of the Si(100)2×1 plane.[15,17] The phase boundaries are labeled PB_α and PB_β, where PB_α is parallel to **c** and PB_β is parallel to **d**. We note that the 2×3 phase and wavy phase connect abruptly at PB_α. Though not shown in this paper, coexisting surfaces of wavy structure and $c(2\times6)$ structure were also obtained. In a previous paper, we proposed a model of the 2×3 and the $c(2\times6)$ structures, where those structures were formed on the second Si layer after tearing off the first Si layer.[17] It seems from the STM image that the ''1×2'' structure is much higher than the 2×3 and $c(2\times6)$ structures. The line profile was measured, and it appeared that the difference of the height between the ''1×2'' structure and the others is about 0.05 nm. The value is much smaller than the diameter of the Si atom (0.235 nm) or Ba atom (0.43 nm). Thus it is hard to consider that adatoms on the 2×3 and the $c(2\times6)$ structures causes the ''1×2'' structure, and it seems to be reasonable to propose a model where a slight transition of atoms vertical to the surface causes the difference of the height.

IV. DISCUSSION

The wavy structure consists of a combination of two mirror symmetric unit cells, **U** and **U**′, as shown in Fig. 3. When different types of unit cells connect, a ''turn'' occurs. It is obvious that the same units do not continue at long range. The histogram in Fig. 5 shows how long the same units are continued along the lattice vectors **B** or **B**′. The unit of abscissa is $|\mathbf{B}|(=|\mathbf{B}'|)$, namely, the number of continued units. The ordinate is normalized so that $2|\mathbf{B}|$ ($n=2$) is 0.25. Since the two unit cells appear to be equivalent they are counted together in the histogram. The curve in the figure indicates the line of $(1/2)^n$ (n is an integer, $n\geqslant1$). This line implies that two unit cells appear randomly. Though the experimental ratio obeys the $(\frac{1}{2})^n$ line at $n\geqslant2$, the ratio of length $|\mathbf{B}|$ ($n=1$) is fairly smaller than the expected value of 0.5. This

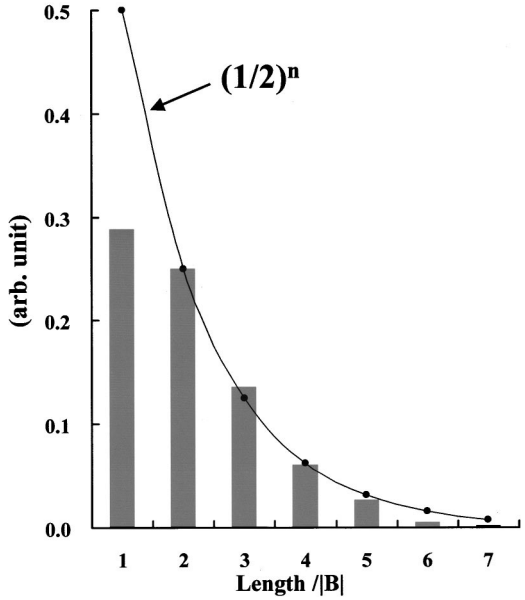

FIG. 5. Histogram of the continued length along the **B** direction in the ''1×2'' structure.

result implies that the single ''turn'' hardly occurs, and that the appearance of **U** and **U**′ is not entirely random. That is, there is a driving force such as first-neighbor interaction which prevents **U** and **U**′ from being arranged randomly. On the other hand, the periodicity perpendicular to vector **A** is kept at $2a_0$. In this sense, it can be said that the ''1×2'' structure comes from a wavy structure.

In some reports, a 4× streak or a $c(4\times4)$-like spot were observed with a ''1×2'' or 2×3 structure.[7,9,13] A pattern of double-domain reciprocal lattices of ''long-range ordered'' **U** and **U**′ is illustrated in Fig. 6 by open circles. In addition, the pattern of the 4×4 structure, which is realized by alternate arrangement of **U** and **U**′, is also shown in the figure by a cross. The 4×streak and $c(4\times4)$-like spot could be recognized in this figure. We note here that the pattern in Fig. 6 is

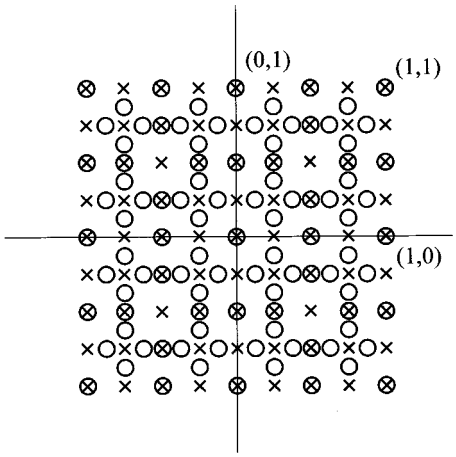

FIG. 6. Double-domain reciprocal lattices of ordered **U** and **U**′, and the 4×4 pattern expected from alternate appearances of two units. The former is illustrated with an open circle, and the latter with a cross.

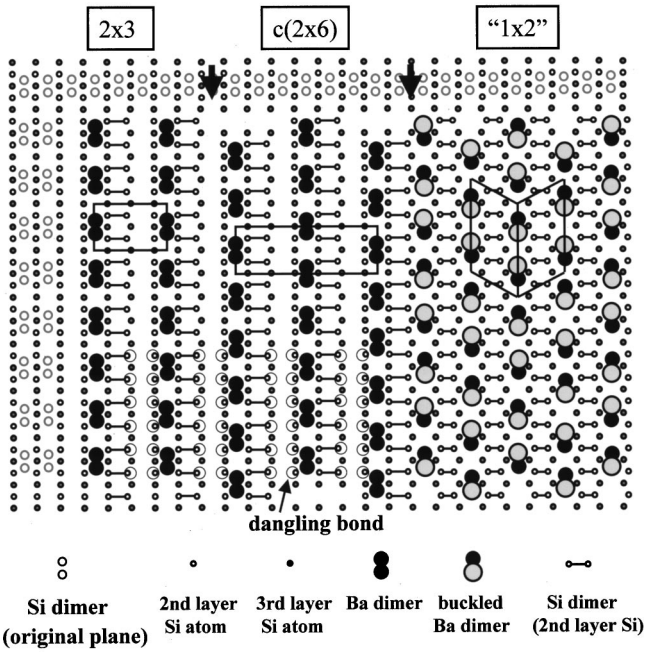

FIG. 7. Schematic model for the ''1×2'' structure. Proposed models for the 2×3 and $c(2\times6)$ structures (Ref. 17) are also illustrated on the left and center of the figure.

not realistic but is an ideal case. Practically, we have to consider the effect of randomness, a mixture of **U** and **U**′ as well as a substrate structure. Different sample preparations will give rise to different sample surfaces with a mixture of **U** and **U**′, resulting in dispersive LEED reports. Since the wavy structure was also formed on $\frac{1}{2}$ ML Ba-deposited Si(100) at room temperature (not shown here) without post-annealing, it is supposed that the dimerized Si(100)2×1 surface is preserved, and that Ba adatoms are responsible for the wavy structure. This substrate structure also contributes to the 1×2 periodicity.

Figure 7 illustrates a ''1×2'' model, based on the two following preconditions. (1) The ''1×2'' structure connects abruptly with the 2×3 or $c(2\times6)$ structure at PB_α. (2) The coverage of Ba on the ''1×2'' structure is $\frac{1}{2}$ ML. In previous LEED and AES studies,[7–13] the ''1×2'' structure was observed at a Ba coverage of $\frac{1}{2}$ ML, whereas the coverage of Ba on the 2×3 or $c(2\times6)$ structure was $\sim\frac{1}{3}$ ML. In the present work, as the ''1×2'' structure is formed at higher Ba coverages than that of the 2×3 and $c(2\times6)$ structures, it is assumed that prediction (2) is reasonable. We proposed a model for the 2×3 and $c(2\times6)$ structures in a previous paper.[17] The $c(2\times6)$ structure is always observed with the 2×3 structure, and has the same building unit as the 2×3 structure. Proposed 2×3 and $c(2\times6)$ structures are also indicated in Fig. 7. Two kinds of phase boundaries are indicated by arrows. Although the Si dimers of the original Si(100)2×1 structures can hardly be observed on the coexisting surface of the 2×3 and ''1×2'' phases, the registries of the 2×3 and $c(2\times6)$ structures on a Si(100) surface is already known.[17] Then Si dimers of the original Si(100)2×1 surface are illustrated in the top and on the left-hand side of Fig. 7, in order to clarify the positional relation between

Ba atoms and Si atoms of the substrate. In the 2×3 phase, a Ba dimer and two Si dimers consist of a unit cell, where a Ba dimer terminates four Si dangling bonds and there remain four unterminated Si dangling bonds. The $c(2\times6)$ phase is explained by the alternate shift of the unit cell of the 2×3 structure by a half-periodicity along the $2a_0$ direction. In a unit cell of the $c(2\times6)$ structures there are eight unterminated Si dangling bonds. The Si substrates of both the 2×3 and $c(2\times6)$ structures are reconstructed into a 1×3 structure. On the other hand, in the ''1×2'' phase, the Si substrate is reconstructed into a 1×2 structure, and Ba dimers terminate all Si dangling bonds; this is considered a stable configuration. In addition, adjacent Ba dimers along the direction of a reconstructed dimer row buckle in opposite directions because the interaction due to the narrowing in the distance between adjacent two Ba dimers. In Fig. 7, a buckled Ba dimer is indicated as a pair of a gray solid circle and a black solid circle, where a gray one shows an upper Ba atom and a black one a lower one. This model seems to be constructed on the original Si(100)2×1 surface. Considering that the ''1×2'' structure is observed at higher coverage than that of the 2×3 structure and that the direction of Si dimer in this model is orthogonalized with the direction of Si dimer of original plane, it is concluded that this structure is formed on the second Si layer. Since in this model, the building block of the ''1×2'' structure is similar to that of the 2×3 and $c(2\times6)$ structures except for buckling, the ''1×2'' phase can connect abruptly with the 2×3 or $c(2\times6)$ structures at the boundary PB_α. On the other hand, the connection at the boundary PB_β is not abrupt but random, presumably due to the discontinuity of periodicity between the 2×3 [or $c(2\times6)$] structures and the ''1×2'' structure along the direction perpendicular to Ba dimers at PB_β. It is distinct that the ''1×2'' structure comes from the dimerized 1×2 substrate.

It was described in Sec. III that a protrusion in a filled-state image is divided into four protrusions, and faint lines run through the diagonal direction. A higher-resolution STM image is shown in Fig. 8(a) and the corresponding atomic structure using our model is illustrated in Fig. 8(b), where the open circles (C_1 and C_2) and ellipse (E) indicate protrusions and a faint line in a filled-state image, respectively. C_1 and C_2 correspond to brighter and darker protrusions, respectively. In addition, protrusions observed in an empty-state image (not shown here) are also illustrated by gray open circles, where a small protrusion is also observed at low sample bias voltage. Considering the electronegativities of Ba(0.9) and Si(1.8), there is a charge transfer from Ba to Si. Therefore, it is assumed that protrusions observed in a filled-state image are due to Si atoms, and that the difference of brightness (C_1 and C_2) is presumably due to the differences of electronic states of Si atom. There are three kinds of Si dimers with different bonding conditions with Ba atoms [up-up, up-down, and down-down, shown in Fig. 8(b)]. In an empty-state image, a protrusion is observed at the center of four protrusions in a filled-state image, which corresponds to the position between two upper Ba atoms. Then an additional protrusion observed at a low sample bias voltage corresponds to the position between two lower Ba atoms. As described above, the model illustrated in Fig. 7 explains STM images coincidently. In order to decide the absolute atomic structure of the ''1×2'' phase, a further study by means of any other experimental methods, such as ion scattering spectroscopy, is needed.

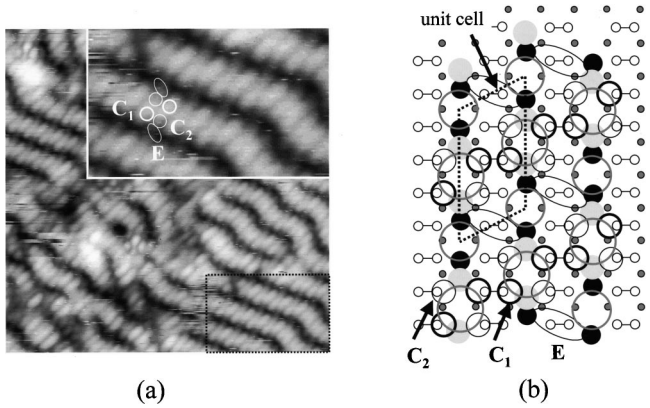

FIG. 8. (a) A high-resolution filled-state STM image ($V_s=-1.44$ V and $I_t=0.20$ nA) of the ''1×2'' structure, and (b) an illustration showing positions of protrusions on the corresponding model of the wavelike structure. C_1, C_2, and E indicate a brighter protrusion, a darker protrusion, and a faint line, respectively.

V. CONCLUSION

In this paper, Si(100)''1×2''-Ba is investigated by STM. It is found that the ''1×2'' structure is not simple but complicated with a wavy structure. The wavy structure consists of a combination of mirror-symmetric unit cells, $(4,0)\times(1,2)$ and $(4,0)\times(1,-2)$, where those units do not arrange in a long-range pattern. We propose a Ba adsorption model, where buckled Ba dimers are located on the second Si layer reconstructed into a dimerized 1×2 phase. It is concluded that the ''1×2'' structure comes from the random arrangement of $(4,0)\times(1,2)$ and $(4,0)\times(1,-2)$ as well as the ''1×2'' reconstructed substrate structure.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research (Encouragement of Young Scientists #12750029).

*Corresponding author: FAX: +81-52-809-1851. Email address: yoshi@toyota-ti.ac.jp

[1] A. A. Saranin, A. V. Zotov, V. G. Lifshits, M. Katayama, and K. Oura, Surf. Sci. **426**, 298 (1999).

[2] A. A. Saranin, V. G. Lifshits, K. V. Ignatovich, H. Bethge, R. Kayser, H. Goldbach, A. Kulst, J. Wollshläger, and M. Henzler, Surf. Sci. **448**, 87 (2000).

[3] W. C. Fan, N. J. Wu, and A. Ignatiev, Phys. Rev. B **42**, 1254 (1990).

[4] W. C. Fan, A. Mesarwi, and A. Ignatiev, J. Vac. Sci. Technol. A **8**,

4017 (1990).
[5] R. Z. Bakhtizin, J. Kishimoto, T. Hashizume, and T. Sakurai, J. Vac. Sci. Technol. B **14**, 1000 (1996).
[6] R. Z. Bakhtizin, J. Kishimoto, T. Hashizume, and T. Sakurai, Appl. Surf. Sci. **94/95**, 478 (1996).
[7] W. C. Fan and A. Ignatiev, Surf. Sci. **253**, 297 (1991).
[8] D. Vlachos, M. Kamaratos, and C. Papageorgopoulos, Solid State Commun. **90**, 175 (1994).
[9] T. Urano, K. Tamiya, K. Ojima, S. Hongo, and T. Kanaji, Surf. Sci. **357–358**, 459 (1996).
[10] Y. Takeda, T. Urano, T. Ohtani, K. Tamiya, and S. Hongo, Surf. Sci. **402–404**, 692 (1998).
[11] Y. Takeda, T. Ohtani, K. Ojima, T. Urano, and S. Hongo, J. Electron Spectrosc. Relat. Phenom. **88–91**, 619 (1998).
[12] J.-S. Kim, K.-W. Ihm, C.-C. Hwang, H.-S. Kim, Y.-K. Kim, C. Lee, and C.-Y. Park, Jpn. J. Appl. Phys. **38**, 6479 (1999).
[13] X. Hu, C. A. Peterson, D. Sarid, Z. Yu, J. Wang, D. S. Marshall, R. Droopad, J. A. Hallmark, and W. J. Ooms, Surf. Sci. **426**, 69 (1999).
[14] X. Yao, X. Hu, D. Sarid, Z. Yu, J. Wang, D. S. Marshall, R. Droopad, J. K. Abrokwah, J. A. Hallmark, and W. J. Ooms, Phys. Rev. B **59**, 5115 (1999).
[15] X. Hu, X. Yao, C. A. Peterson, D. Sarid, Z. Yu, J. Wang, D. S. Marshall, R. Droopad, J. A. Hallmark, and W. J. Ooms, Surf. Sci. **445**, 256 (2000).
[16] X. Hu, X. Yao, C. A. Peterson, D. Sarid, Z. Yu, J. Wang, D. S. Marshall, J. A. Curless, J. Ramdani, R. Droopad, J. A. Hallmark, and W. J. Ooms, Surf. Sci. **457**, L391 (2000).
[17] K. Ojima, M. Yoshimura, and K. Ueda, Surf. Sci. **491**, 169 (2001).