Growth of high-density small Ag islands on the Si(111)7×7 surface with adatom defects

H. Hirayama, H. Okamoto, and K. Takayanagi
Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuda, Yokohama 226-8502, Japan
(Received 9 July 1999)

We studied the growth of Ag islands on the Si(111)7×7 surfaces with missing adatoms created by 0.5-keV Ar-ion bombardment. Ag atoms were deposited at room temperature, and the growths were observed by using scanning tunneling microscope. In the initial stage, bright spots including several Ag atoms appeared on triangular half unit cells of the 7×7 reconstruction. The spots appeared as to avoid missing adatom sites. As the coverage increased, the number of the spots increased, and occasionally spots in neighboring cells kissed to form clusters. At ~0.8 monolayer, the surface was mostly covered by the clusters of kissing spots, but the avoiding growth of the spots at the missing adatom sites caused gaps between the clusters here and there. In further deposition, three-dimensional (3D) Ag islands started to nucleate on the clusters. The size and density of the 3D islands strongly depended on the number of missing adatoms at the initial surface. With an increase of missing adatoms, the island size decreased while the island density increased drastically. The change in the island size and density were attributed to the substantial increase of the density and the reduction of the surface migration of the Ag atoms due to the gaps. [S0163-1829(99)12143-X]

I. INTRODUCTION

In the Ag deposition on the Si(111)7×7 surface at room temperature, it has been confirmed that no alloying happened[1] and the 7×7 periodicity of the Si surface was preserved at the Ag/Si interface.[2,3] On the other hand, Shottky barrier height (SBH) has been pointed out to be influenced by the structure of the metal/semiconductor interface.[4] In this respect, the Ag/Si(111) interface with the 7×7 periodicity is expected to show a reproducible SBH. However, the SBH reported for the Ag/*n*-type Si(111)7×7 system scattered in a wide range from 0.56 to 0.80 eV.[5] The scattering has been attributed to the inhomogeneities of the SBH at the interface.[6] Among factors causing the inhomogeneities, defects at the Si(111)7×7 surface is one of the most probable one. The defects could cause a peculiar growth of Ag film, and would result in the inhomogeneities of the interface structure and SBH. However, an effect of the surface defects on the growth of Ag films has not been elucidated, though the growth of the Ag films at Si(111)7×7 surfaces has been studied at room temperature[8,7] and at temperatures 80-100 K.[9] In this study, we introduced adatom defects at the Si(111) surface intentionally by low energy Ar ion bombardment,[10–12] and studied their effect on the growth of Ag films at room temperature.

II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum (UHV) apparatus consisting of a loading chamber, a preparation chamber with the Ar-ion gun, and a main chamber with the scanning tunneling microscope (STM) unit (JEOL JSTM 4000XV). The base pressure of the preparation and the main chamber was less than 1×10^{-8} Pa. The sample, cut out from *n*-type Si(111) wafer, was degassed at 500 °C for 10 h. Then, the sample was flashed at 1200 °C, and was slowly cooled down to room temperature. The surface cleanliness was confirmed by observing the 7×7 dimer-adatom-stacking fault (DAS) reconstruction using STM.[13,14] Missing adatom defects were introduced by bombarding the Si(111)7×7 surfaces with 500 eV Ar ions.[10] The density of missing adatoms was controlled by the bombarding time. On the surfaces with various missing adatom densities, Ag atoms were deposited at room temperature. The growths of Ag films on the surfaces with missing adatoms were observed by using STM.

Ag atoms were deposited by a resistivity heated W basket. The deposition rate was calibrated as follows. Ag atoms were deposited for various deposition times at the Si(111)7×7 surfaces without missing adatoms. The subsequent annealing at 500 °C converted the 7×7 surface reconstruction to the $\sqrt{3}\times\sqrt{3}$ (Ref. 15) locally. The area of the $\sqrt{3}\times\sqrt{3}$ local domains were measured by using STM. With an assumption that the $\sqrt{3}\times\sqrt{3}$ surface include Ag atoms of 1 ML,[16] the Ag coverage (θ) was estimated. From the linear dependence of the coverage on the deposition time, the deposition rate was estimated to be 0.017 monolayer (ML)/min (1 ML = 7.6×10^{14} atoms/cm^2).

III. RESULTS

In Fig. 1, we show STM images taken in the growth of Ag films on the Si(111)7×7 surfaces without missing adatoms. At very low coverages, several half unit cells of the 7×7 reconstruction became brighter[7] [Fig. 1(b)]. Then, at the coverage above 0.03 ML, some bright cells started to change to a bright spot [Fig. 1(b)] as has been reported previously.[7,8] With the coverage, the number of the bright spots increased and their size became larger. Although each spot did not stick out the underlying frame of triangular half unit cell, spots in neighboring cells occasionally kissed to form clusters [Fig. 1(c)]. At ~0.8 ML, the surface was mostly covered by the clusters of kissing spots. In further deposition, three-dimensional (3D) Ag islands started to nucleate on the

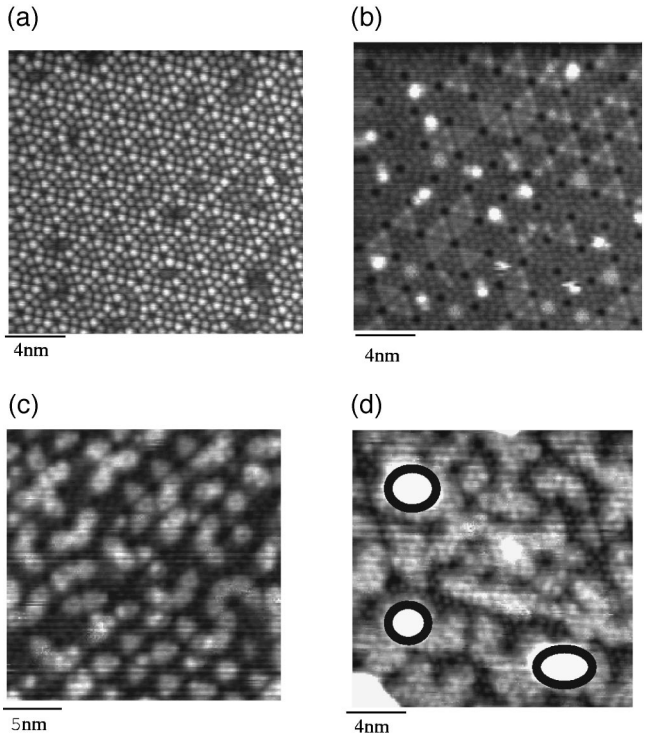

FIG. 1. STM images showing the growth of Ag films at the Si(111)7×7 surface which was not bombarded by Ar ions (V_s = 2.0 V). (a) θ=0 ML. (b) θ=0.034 ML. Some triangular half unit cells became brighter. Bright spots were also observed on some of half unit cells. (c) θ=0.34 ML. The number of bright spots increased. Neighboring spots kissed to form clusters. (d) θ =0.77 ML. On the clusters of kissing spots, 3D Ag islands started to grow. The 3D islands are highlighted by open circles.

clusters [Fig. 1(d)]. During the deposition of Ag atoms, the density of the bright triangles (N_t) increased in proportion to θ at $\theta \leqslant 0.025$ ML. From $dN_t/d\theta$. each bright triangle was estimated to contain one Ag atom. However, N_t leveled off at θ=0.03 ML, and then decreased. Meanwhile, the density of the bright spot (N_s) started to increase at $\theta \geqslant 0.03$ ML. From $dN_s/d\theta$, each bright spot was estimated to contain five Ag atoms on an average at $\theta \sim 0.03$ ML. However, $dN_s/d\theta$ decreased with the coverage; indicating that the bright spot contained more than five Ag atoms in the late stage. At $\theta \sim 0.25$ ML, one spot was roughly estimated to include 15 Ag atoms.

In Fig. 2, we show typical STM images of the growth of Ag films on the Si(111)7×7 surface with missing adatoms created by Ar bombardments. The surface bombarded for 16 s is shown in Fig. 2(a). The bombardment with 500 eV Ar ions caused missing of adatoms, but the second layer (i.e., rest atom layer) was kept to be not damaged[10]. In the bombardment for 16 s, 30% of adatoms were missed at the surface. When Ag atoms were deposited on the surface with missing adatoms, the bright triangles were rarely observed. The bright spots appeared directly even at very low coverages. The bright spots appeared on perfect half unit cells and the half unit cells including one or two missing adatom sites. On the half unit cells with one or two missing adatom sites, the spots were characteristic to appear as to avoid the missing adatom sites [Fig. 2(b)]. However, on the half unit cells including several missing adatom sites, the bright spot never

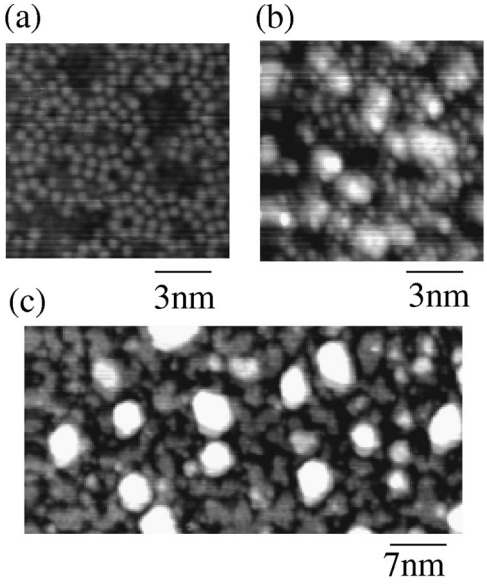

FIG. 2. STM images showing the growth of Ag films at the Si(111)7×7 surfaces with missing adatoms (V_s=2.0 V). (a) The surface bombarded for 16 s. θ_s=0 ML. Some of adatoms were missed from the surface. (b) θ=0.26 ML, on the surface bombarded for 64 s. The bright spots appeared on the surface. They are characteristic to avoid the missing adatom sites. (c) θ=0.77 ML, on the surface bombarded for 32 s. Since the spots appeared as to avoid missing adatom sites, gaps existed between clusters of kissing spots. The 3D islands started to grow on the clusters of kissing spots, while the island growth never happened in the gaps.

appeared. During the deposition, the contrast of the missing adatom sites was always dark and did not change. This indicates that Ag atoms adsorbed only on the adatom sites remaining after the bombardment. In the deposition, the number of the spots increased, and the clusters of kissing spots appeared, as well as on the surface without missing adatoms. However, because of the avoiding growth of the spots at the missing adatom sites, gaps appeared here and there between the clusters [Figs. 2(b) and (c)]. Leaving the gaps unfilled, most of the surface became covered by the clusters of kissing spots. Then, the nucleation of 3D Ag islands started on the clusters [Fig. 2(c)]. But the nucleation never happened in the gaps. Although the 3D islands became larger with the coverage and stuck out from the clusters into the gaps in the late stage of the 3D island growth, no nucleation of the 3D islands started in the gaps on the surface with missing adatoms.

The density of the 3D Ag islands strongly depended on the number of missing adatom sites at the starting surfaces. Figure 3 is the STM images of the 3D Ag islands grown on the surface without missing adatoms, and on the surfaces bombarded for 16, 32, and 64 s. The coverage was 1.6 ML for all the cases. By the bombardment for 16, 32, and 64, 30%, 40%, and 60% of adatoms were missed at the starting surfaces, respectively. The density of the 3D islands increased while their size became smaller with the number of missing adatoms at the starting surfaces. The 3D island density on the surface bombarded for 64 s was ~10 times larger than that on the surface without missing adatoms. The size of the 3D islands became larger with increasing the coverage, but their density did not change at θ=0.8–1.8 ML.

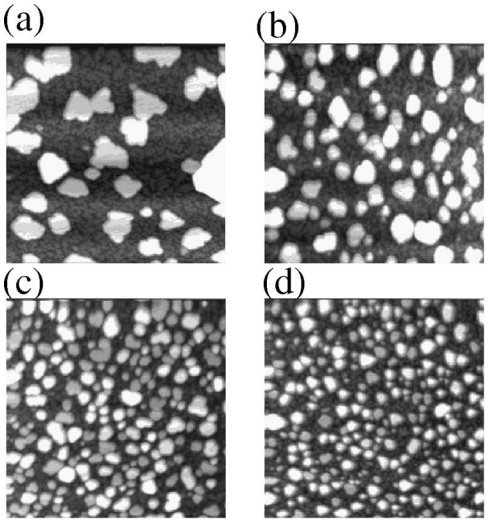

FIG. 3. STM images (100×100 nm^2) of the 3D islands grown on the surface ($V_s=2.0$ V) (a) without bombarded, (b) bombarded for 16 s, (c) bombarded for 32 s, (d) bombarded for 64 s. The coverage was 1.6 ML for all the cases. With increasing the missing adatom sites at the starting surfaces, the density of the 3D islands became larger.

IV. DISCUSSIONS

At the very low coverages, the triangular half unit cell became brighter by containing one Ag atom. Ag atom has one valence electron at the $5s$ orbital, and works as an electron donor in the adsorption at the surface. A theoretical calculation of the site-specific nucleophilic reactant power has shown that the adatom sites are preferable, but the rest of the atom sites are useless for the Ag adsorption at the Si(111)7×7 surface.[17] With this respect, we attribute the triangular contrast to a single Ag atom, which was trapped in a half unit cell, but hopped all the adatom sites in the cell freely. Similar bright triangles have been observed in the very initial stage of the Pb adsorption at the Si(111)7×7 surface. In the Pb/Si(111), the triangle has also been attributed to the highly mobile single Pb atoms trapped in a half unit cell.[18,19]

By containing more Ag atoms, the bright triangle changed to the bright spot. This suggests that the addition of Ag atoms stopped the hopping of the single Ag atom in the triangular half unit cell by forming a stable cluster of Ag atoms at an adatom site. In a real-time STM observation, we observed that one of two bright triangles in neighboring cells disappeared occasionally, and one bright spot newly appeared. This means that two Ag atoms are enough to construct the spot, though the $dN_s/d\theta$ showed that one spot included five Ag atoms in one spot on an average at $\theta\sim0.03$ ML. To the newborn spot, Ag atoms attached furthermore. It caused the increase of the number of Ag atoms contained in a spot with the coverage. As we observed, the spot contained 15 Ag atoms at $\theta\sim0.25$ ML. Here, the number of Ag atoms contained in the spot (15) is larger than the number of adatom sites in the half unit cell (6). This is due to that the Ag atoms condensated with an interatomic distance close to that of the Ag crystal to the smallest nucleus of the spot with two Ag atoms. Actually, 36 Ag atoms can be contained at most in a two-dimensional close packed arrangement with the lattice constant of the Ag crystal in a half unit cell of the 7×7 reconstruction.[8] From this viewpoint, it is reasonable that the spot contained 15 Ag atoms at $\theta\sim0.25$ ML.

The Ar ion bombardment caused missing of adatoms at the surface. At the 7×7 reconstructed surface, the missing of one adatom results in the appearance of three rest atom sites. However, as described above, the rest atom site is unfavorable for the Ag adsorption. Thus, the number of adsorption sites reduced substantially at the bombarded surfaces. Especially, the missing of adatoms was serious for the bright triangle formation. Since the triangular half unit cell of the 7×7 reconstruction contains six adatoms, a uniform distribution of 16% missing adatoms makes all the cell defective. Meanwhile, several tenth % of adatoms were missed at our bombarded surfaces. Therefore, most of all the half unit cells are regarded to include missing adatoms, though the distribution of missing adatoms was not necessarily uniform. Because the Ag adatom did not hop to the missing adatom site, the visiting of all over the adatom sites was restricted in the cell with adatom defect. This resulted in the localization of the Ag atom in the cell, and the suppression of forming the bright triangle.

Due to the suppression of the bright triangle formation, the bright spot seemed to appear directly at the bombarded surfaces. Since the missing adatom sites were unfavorable for the Ag adsorption, the critical nucleus of the spot appeared only on the adatom sites remaining after the bombardment. This is the reason why the bright spots appeared as to avoid the missing adatom sites on the half unit cells including $1-2$ missing adatoms. Probably for the same reason, the bright spots did not appear on the half unit cell including several missing adatoms. Although the spot became larger during the deposition, the spot still avoided the missing adatom sites because the missing adatom sites are unfavorable even in the nucleation of the Ag atoms to the critical spots. As a result, the gaps appeared here and there between the clusters of kissing spots on the bombarded surfaces.

In further deposition on the clusters separated by the gaps, the 3D islands nucleated only on the clusters. This means that Ag atoms preferred to nucleate into 3D islands on the cluster, while the gaps were still unpreferable for the nucleation of the 3D Ag islands. However, the 3D islands did not appear on all the clusters separated by the gaps, though Ag atoms fell on all the clusters and gaps in the deposition. Furthermore, the number of the 3D islands did not change with the coverage. These suggest that the Ag atoms could migrate from cluster to cluster by crossing the gaps. In their traveling over gaps, the Ag atoms nucleated to the 3D island occasionally on some of the clusters. In these respects, the gaps could effect on the growth of the 3D islands through a substantial increase of the density and a suppression of the migration of Ag atoms. Since the Ag atoms fallen on the surface avoided the gaps, the gaps caused a substantial increase in the density of the Ag atoms on the clusters contributing to the 3D island growth. By crossing the gaps, the migration of the Ag atoms would be also reduced.

From the above viewpoints, the difference between the growth on the surfaces with and without missing adatoms should be caused by the gap induced increase of the density and the suppression of the migration of Ag atoms. In this

respect, we consider an analytical equation for the density of the 3D islands grown on a flat surface by parametrizing the density and migration of Ag atoms during the growth. In our experimental condition, Ag atoms did not re-evaporate from the surface. The direct impingement of Ag atoms onto the islands could also be negligible as a driving force for the island growth. In this limit, a rate equation analysis of the nucleation processes on a flat surface has shown that the density of the 3D islands over the critical size (n_x) is given by the following equation:[20]

$$\frac{n_x(\Theta)}{N_0} \sim \eta(\Theta)(R/N_0\nu)^{1/i+2.5} \exp\left(\frac{(E_i+iE_d)/(i+2.5)}{kT}\right). \tag{1}$$

Here, Θ is the coverage of Ag atoms on the surface. Since the 3D Ag islands grew on the clusters of kissing spots, Θ is taken as $\theta-0.7$ ML with an assumption that the 3D island growth started at 0.7 ML on the bombarded surfaces. R, N_0, ν, E_i, E_d are the arrival rate of Ag atoms at the surface, the density of the adsorption sites, the surface vibration frequency, the binding energy of the critical island including i atoms, and the diffusion barrier for migrating Ag atoms, respectively. The coverage dependence of n_x is given by the function $\eta(\Theta)$. A numerical simulation has shown that η depends weakly on Θ for the 3D island growth.[20] This is consistent with our observation that the density of the 3D islands on the clusters hardly varied in $\theta=0.8-1.6$ ML.

The critical size of the 3D islands is determined by the supersaturation (α), which is proportional to the local density of the migrating Ag atoms. Meanwhile, the density of Ag atoms contributing to the grwoth of 3D Ag islands was inversely proportional to area of the clusters of kissing spots, because the Ag atoms existed only on the clusters. Thus, the supersaturation is expressed by $\alpha_0/(1-\delta)$, where α_0 is the supersaturation on the clusters at the surface without missing adatoms, and δ is the area ratio of the avoiding gaps. Roughly, δ is regarded to be equal to the ratio of the missing adatoms sites at the starting surfaces. For a given α, the critical radius (r_c) of the semispherical 3D island is presented as $r_c=2\gamma a^3/kTln\alpha$.[21] Substituting the surface energy $\gamma=0.62J/m^2$ for Ag/Ag(111),[22] the inter Ag atom distance $a\sim0.29$ nm. and $T=300$ K, r_c of the 3D island on the surfaces bombarded for 16, 32, and 64 s ($\delta=0.3$, 0.4, and 0.6, respectively) were estimated to be $0.67r_0$, $0.22r_0$. and $0.14r_0$ (r_0 is the critical radius of the 3D island at the surface without missing adatoms). Thus, the number of Ag atoms included in the 3D critical islands ''i'' becomes smaller with the missing adatoms. Judging from the size of the 3D islands shown Fig. 1(d), i was roughly estimated to be ~1000 on the surface without missing adatoms with assumptions of a semispherical shape of the island and the Ag atom density equal to that of the bulk Ag crystal. On the bombarded surfaces, the critical size was difficult to be determined. However, using that i is proportional to $(r_c)^3$, the i is regarded to be ~3 for the islands on the surface bombarded for 64 s of $0.14r_0$.

Assuming the surface vibration frequency $\nu\sim10^{13}$ s^{-1}, $E_i\sim3iE_b$ (E_b is 0.3 eV) and $E_d\sim0.4$ eV of Ag/W(110),[23] n_x was numerically evaluated for the surface bombarded for 64 s. Since the surface bombarded for 64 s missed 60% of adatoms, N_0 was regarded to be reduced by a factor 0.4. The reduced N_0 corresponds to the substantial increase of the Ag atom density migrating on the surface, and resulted in the increase of n_x due to the term $R/(N_0\nu)$ in Eq. (1). However, without changing E_d, this increase was overcome by the decrease of i, and n_x was calculated to decrease for the bombarded surface. To make the calculation consistent with the experimental result (n_x increased by a factor ten for the bombarded surface), E_d was necessary to be increased to 1.7 eV. Although this calculation was crude, it indicated, at least qualitatively, that both the increase of the Ag atom density and the increase of the diffusion energy E_d (i.e., the reduction of the migration) are the reasons for the increase of the 3D island density. In the 3D islands formation on the bombarded surfaces, the migration of the Ag atoms was reduced due to the gaps between clusters of kissing spots. At the same time, the gaps made the Ag atoms condense on the clusters and their effective density for the 3D island nucleation larger. These resulted in the nucleation of high-density, small 3D islands.

V. SUMMARY

In summary, we studied the growth of Ag films at the Si(111)7×7 surfaces with missing adatoms. In the initial stage of the growth, the spots with Ag atoms appeared on the half unit cells of the 7×7 reconstruction. The spots appeared as to avoid the missing adatom sites. With the coverage, the size of each spot became larger and the number of spots increased. The neighboring spots kissed each other, and the surface was covered by the clusters of kissing spots at $\theta\sim0.7$ ML. However, due to the avoiding growth of the spots on the missing adatom sites, the gaps existed here and there between the clusters. Without filling the gaps, 3D islands started to grow on the clusters. With the number of missing adatom sites at the initial surfaces, the density of the 3D islands increased. This was attributed to the substantial increase in the density and the reduction of the surface migration of the Ag atoms on the surfaces of the clusters separated by the gaps.

[1] E.J. van Leonen, M. Iwami, R.M. Tromp, and J.F. van der Veen, Surf. Sci. **137**, 1 (1984).

[2] H. Hong, R.D. Aburano, D.-S. Lin, H. Chen, T.-C. Chiang, P. Zschack, and E.D. Specht, Phys. Rev. Lett. **68**, 507 (1992).

[3] R.D. Aburano, H. Hong, J.M. Roesler, K. Chang, D.-S. Lin, P. Zschack, H. Chen, and T.-C. Chiang, Phys. Rev. B **52**, 1839 (1995).

[4] D.R. Heslinga, H.H. Weitering, D.P. van der Werf, T.M. Klapwijk, and T. Hibma, Phys. Rev. Lett. **64**, 1589 (1990).

[5] H.H. Weitering, J.P. Sullivan, R.J. Carolissen, P. Perez-Sandoz, W.R. Graham, and R.T. Tung, J. Appl. Phys. **79**, 7820 (1996), and references therein.

[6] R.T. Tung, Phys. Rev. B **45**, 13 509 (1992).
[7] A. Shibata, Y. Kimura, and K. Takayanagi, Surf. Sci. **303**, 161 (1994).
[8] St. Tosch and H. Neddermeyer, Phys. Rev. Lett. **61**, 349 (1988).
[9] G. Meyer and K.H. Rieder, Appl. Phys. Lett. **64**, 3560 (1994).
[10] A. Takashima, H. Hirayama, and K. Takayanagi, Phys. Rev. B **57**, 7292 (1998).
[11] D.J. Bedrossian, M.-J. Caturla, and T. Diaz de la Rubia, Appl. Phys. Lett. **70**, 176 (1997).
[12] H.J. Zandvliet, H.B. Elswijk, E.J. van Leonen, I.S.T. Tsong, Phys. Rev. B **46**, 7581 (1992).
[13] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).
[14] R.J. Hamers, Annu. Rev. Phys. Chem. **40**, 531 (1989).
[15] Y. Gotoh and S. Ino, Jpn. J. Appl. Phys. **17**, 2097 (1978).
[16] T. Takahashi and S. Nakatani, Surf. Sci. **282**, 17 (1993).
[17] K.D. Brommer, M. Galvan, A. Dal Pino, Jr., and J.D. Joannopoulos, Surf. Sci. **314**, 57 (1994).
[18] J.M. Gomez-Rodriguez, J.J. Saenz, A.M. Baro, J.-Y. Veuillen, and R.C. Cinti, Phys. Rev. Lett. **76**, 799 (1996).
[19] J.-Y. Veuillen, J.M. Gomez-Rodriguez, A.M. Baro, and R.C. Cinti, Surf. Sci. **377**, 847 (1997).
[20] J.A. Venable, G.D.T. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984).
[21] A. Ohkawa, *Crystal Growth* (Shokabo, Tokyo, 1977) (in Japanese).
[22] L. Huang, S.J. Chey, and J.H. Weaver, Phys. Rev. Lett. **80**, 4095 (1998).
[23] J.A. Venables, Phys. Rev. B **36**, 4153 (1987).