High-density ultrasmall epitaxial Ge islands on Si(111) surfaces with a SiO_2 coverage

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Epitaxial Ge islands less than 7 nm in base diameter and 2.5 nm in height, and with a number density of about $2\times10^{12}\,cm^{-2}$ were created on Si(111) surfaces covered with 0.3-nm-thick SiO_2 films. The low- and high-temperature limits for the epitaxy were found to be dependent on the Ge deposition flux. The experimental results suggest that the island nuclei and the conditions for epitaxial growth appear through a reaction between individual Ge adatoms and SiO_2, and the mechanism of island formation corresponds to a growth model with the critical island size $i^*=0$. The relationship between the rate of the nucleation reaction and the diffusion coefficient of Ge adatoms was used to estimate the island density.

The study of atomic processes pertinent to nanostructure technology is very important for reproducible fabrication of islands whose number density is high and whose size is sufficiently small for applications of quantum confinement phenomena. To use the effects of quantum carrier confinement at near room temperature, the quantum dots in nanostructures have to be smaller than 10 nm for Si-based electronics.[1–3] However, the process of self-organization of strained Ge layers on Si substrates creates three-dimensional (3D) Ge islands larger than 30 nm, because the equilibrium surface morphology is formed through unstable intermediate phases.[4,5] In the intermediate phase of epitaxial growth of Ge on Si(100), ''hut'' clusters appear, which transform into ''macroscopic'' clusters under annealing conditions.[4] A surface component of Ge wetting layers on Si(111) surfaces disintegrates after 3D island nucleation. The disintegration supports spontaneous growth of the islands even in the absence of a deposition flux.[5] Therefore, the formation of equilibrium 3D Ge islands less than 10 nm in size on Si surfaces is hindered by the kinetics of island formation. In order to create smaller islands, modification of the initial conditions on Si surfaces has been performed by deposition of certain materials in amounts up to 1 monolayer (ML), which stimulated island nucleation.[6,7] In this work, we used ultrathin SiO_2 films on Si(111) substrates as an intermediate coverage for Ge deposition. We found a temperature range between 430 and 670 °C in which the deposited Ge appears as epitaxial islands with a base diameter of less than 7 nm and with a number density of about $2\times10^{12}\,cm^{-2}$. It is thought that areas of bare Si, which allowed epitaxial island growth, were created when SiO and GeO molecules evaporated during Ge deposition at elevated temperatures. Epitaxial Ge islands with minimum size and high density can be fabricated by decreasing the Ge coverage. The observed dependencies of the island density on the Ge coverage, deposition temperature, and Ge flux were considered in determining the mechanism of island formation.

The experiments were carried out in an ultrahigh-vacuum (UHV) chamber with a base pressure of about 1×10^{-8} Pa. The chamber was equipped with a scanning tunneling microscope (STM) and a UHV field-emission scanning-electron-microscope (SEM) gun, a microprobe reflection high-energy electron diffraction (μ-RHEED) detector, and a secondary-electron detector. The scanning reflection electron microscopy (SREM) images were formed using the (444) specular spot intensity in the RHEED pattern. For the 30-kV accelerating voltage of the electron beam, this specular spot corresponds to a glancing angle of the beams on the sample surface of about 2.3°. This glancing angle was also used to obtain RHEED patterns for Ge deposited on oxidized Si(111) surfaces. The STM apparatus was specially developed to be combined with the SEM gun. The condition of the W tip and manipulations with the tip on the Si surface were monitored with the SREM. The STM images were usually obtained with a tip bias voltage of either -1.5 or -2.0 V and a constant current between 0.15 and 0.3 nA. Details of the apparatus have been described elsewhere.[8]

A $12\times1.5\times0.4\text{-}mm^3$ sample was cut from an *n*-type Si(111) wafer with a miscut angle of $<1'$ and a resistivity of 5–10 Ω cm. Clean Si surfaces were prepared by flash direct-current heating at 1200 °C. To oxidize the surface, we raised the sample temperature from room temperature to 620 °C for 10 min after oxygen had been introduced into the chamber at a pressure of 2×10^{-6} Torr. The thickness and chemical composition of the oxide films were characterized by producing oxide films under the same conditions in a separate x-ray photoelectron spectroscopy system.[9] The film thickness was estimated to be 0.3 nm and the oxide films were mainly composed of silicon dioxide (SiO_2). A Knudsen cell with a PBN crucible was used to deposit Ge at a deposition rate between 0.05 and 2.0 BL/min [1 bilayer (BL) $\approx1.6\times10^{15}$ atoms/cm^2] which was calibrated with the STM for Ge wetting layer growth on Si(111) surfaces. The deposition temperature was set for 0.5 min before starting the Ge deposition and was maintained for 0.5 min after finishing the deposition.

Figure 1 shows the STM images of Ge islands appearing on Si(111) surfaces covered with 0.3-nm-thick SiO_2 films after 2.6-BL Ge deposition. At a deposition temperature of 430 °C [Figs. 1(a), 1(c), and 1(e)], the Ge islands had a rounded shape with a base diameter of predominantly 7.5 ± 1.5 nm and a height of about 2.3 nm. The number density of islands was approximately $1.8\times10^{12}\,cm^{-2}$. At such a diameter and density, some of the islands were touching each

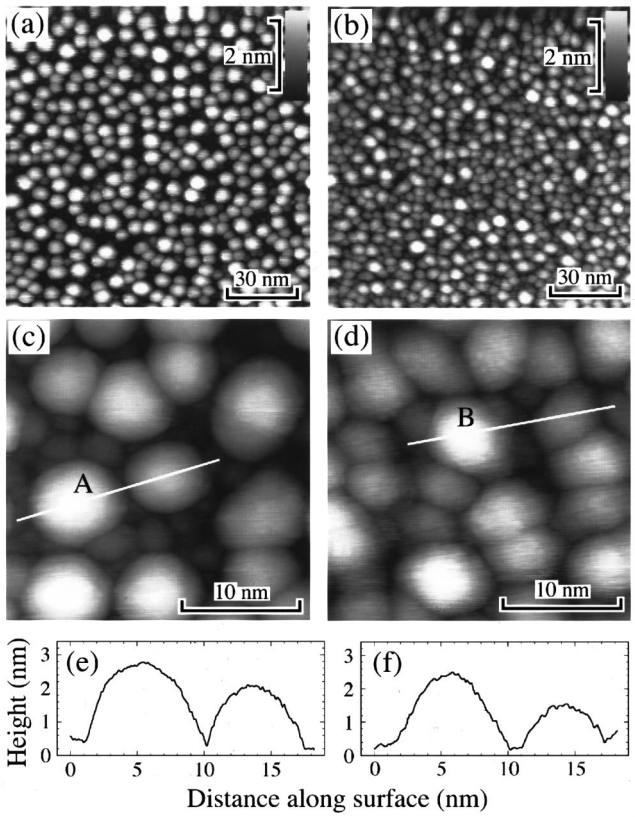

FIG. 1. STM data for Ge islands appearing after 2.6-BL Ge deposition on Si(111) surfaces covered with 0.3-nm-thick SiO_2 films. The deposition temperature was 430 °C in (a) and (c), and 670 °C in (b) and (d). The Ge deposition rate was 0.5 BL/min. (e) and (f) Height profiles along the white lines marked, respectively, by A in (c), and by B in (d). The island height was estimated assuming that 0.5 BL of Ge was evaporated through volatile GeO formation at the beginning of Ge deposition.

other. At a higher temperature of 670 °C [Figs. 1(b), 1(d), and 1(f)], the number density of islands was about 1.4 times larger than that at 430 °C, and the base diameter of islands was predominantly 5.5 ± 2.0 nm. It is to be noted that the base diameter of islands might actually be somewhat smaller than that shown in the STM images, because of the possible effect of the diameter of the STM tip apex on the image of the foot of islands, particularly when the islands have a hemispherical shape.

In spite of the fact that the Ge was deposited on the amorphous SiO_2 films, the RHEED patterns (Fig. 2) show that Ge islands were epitaxially grown on the Si(111) substrate under certain temperatures and Ge deposition rates. The Ge deposition can create areas of bare Si through the reaction

$$SiO_2(s) + Ge(ad) \rightarrow SiO(g) + GeO(g), \quad (1)$$

in which the evaporation of SiO and GeO molecules can be significant at temperatures higher than 500 °C for SiO and 360 °C for GeO, as has been obtained for reactions of O_2 with Si (Refs. 10 and 11) and Ge (Ref. 12) surfaces. These areas of bare Si provided conditions for the epitaxial growth of 3D islands. The RHEED patterns show that for a Ge deposition rate of 0.5 BL/min, the lowest temperature for the epitaxial growth was slightly above 430 °C. At temperatures

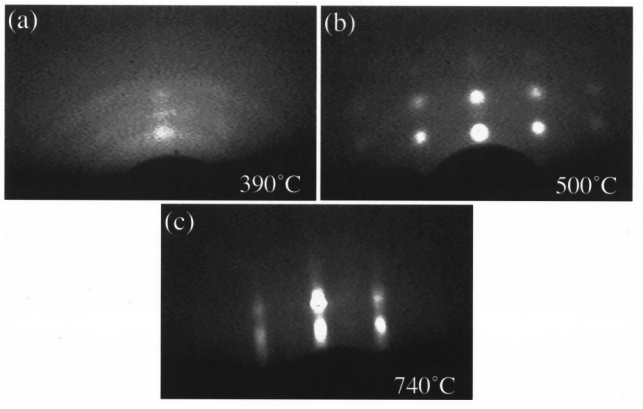

FIG. 2. RHEED patterns of Ge islands grown during 2.6-BL Ge deposition on Si(111) surfaces covered with 0.3-nm-thick SiO_2 films. The deposition temperatures are shown in the patterns. The Ge deposition rate was 0.5 BL/min.

lower than 430 °C, the RHEED pattern contains Debye rings from the diffraction on the 3D Ge islands arbitrarily oriented to the Si substrate, as shown in Fig. 2(a). The bright points in the RHEED pattern [Fig. 2(b)] appear from the diffraction on the epitaxial 3D islands grown at temperatures higher than 430 °C.

There is also an upper temperature limit for the island formation. The STM images (Fig. 3) showed that, at temperatures higher than 670 °C, the Ge islands appear to coalesce and flatten. The flattening of the surface morphology can also be discerned from the RHEED pattern in Fig. 2(c). Such high temperatures are expected to lead to complete decomposition of SiO_2 films, approaching the experimental conditions under which Ge growth occurs on bare Si surfaces.

The temperature range for the epitaxial formation of Ge islands was found to depend on the Ge deposition rate. The RHEED patterns indicate that at 430 °C, the Ge islands grown at a deposition rate of 0.05 BL/min were epitaxial [Fig. 4(a)], whereas the Ge islands grown at a higher deposition rate of 2.0 BL/min were randomly oriented to the substrate [Fig. 4(b)]. Because a lower deposition rate corresponds to a longer growth time (that is the period during which the substrate is held at an elevated temperature) it is important to determine whether the epitaxial Ge islands form owing to the creation of areas of bare Si through reaction (1) between SiO_2 and individual Ge adatoms coming to the sur-

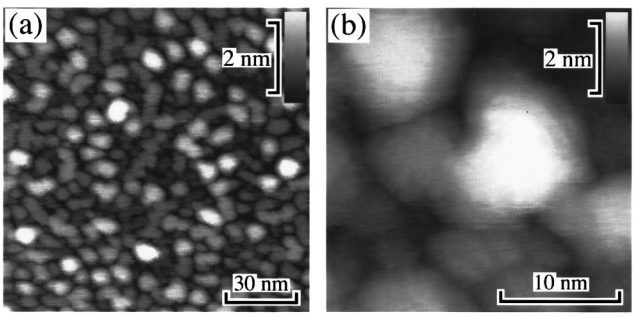

FIG. 3. STM images of surfaces obtained after 2.6-BL Ge deposition at 740 °C on Si(111) substrates covered with 0.3-nm-thick SiO_2 films. The rate of Ge deposition was 0.5 BL/min.

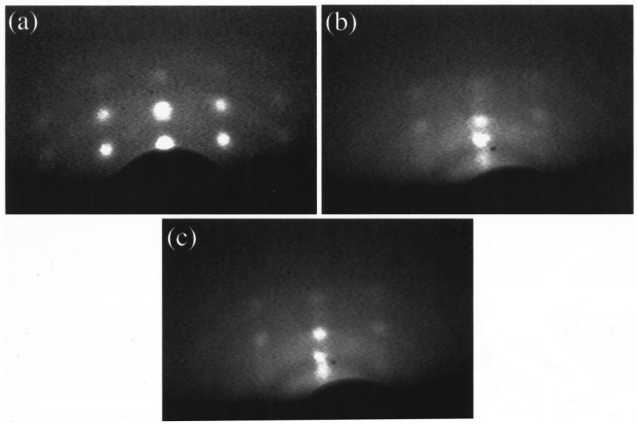

FIG. 4. (a) and (b) RHEED patterns of surfaces obtained after 2.6-BL Ge deposition at 430 °C on Si(111) substrates covered with 0.3-nm-thick SiO_2 films. The deposition rates were 0.05 BL/min in (a) and 2.0 BL/min in (b). Pattern (c) was obtained after annealing the sample in (b) for 30 min at 430 °C.

face from the deposited flux, or whether epitaxial island formation occurs during the whole deposition process through reactions between SiO_2 and Ge incorporated into islands. To distinguish the roles of these reactions, we annealed the surface containing the nonepitaxial Ge islands [the RHEED pattern of this surface is shown in Fig. 4(b)] for 30 min at the deposition temperature. The resulting RHEED pattern, shown in Fig. 4(c), shows that the nonepitaxial Ge islands did not transform into epitaxial ones after the postdeposition annealing. Therefore, the conditions for epitaxial growth were created because of reaction (1) between SiO_2 and Ge adatoms, that is, before the deposited Ge is incorporated into islands. The STM images also showed that the epitaxial and nonepitaxial islands were thermally stable. The islands did not change significantly after postdeposition annealing for 30 min at deposition temperatures.

Thermal decomposition of SiO_2 films occurs through formation of voids appearing at sites of structural defects in the SiO_2.[13] The number density[14] of the voids in ultrathin SiO_2 films is about $10^{10}\,cm^{-2}$, which is two orders of magnitude lower than the number density of the Ge islands. The STM images of surfaces before and after Ge deposition, shown in Fig. 5, did not show any evidence indicating that the nucleation of Ge islands occurred at sites of structural defects in the SiO_2. The Ge islands have a number density in the same range as that in the case of metallic particles on SiO_2, where the density depends on the sort of deposited metals.[15] These observations indicate that Ge island growth is not simply the next stage after void formation, similar to the homoepitaxy in the case of Si windows in ultrathin SiO_2 films.[14] The STM images of the surface obtained after deposition of Ge with various coverages (Fig. 5) showed that the number of Ge islands either remains fixed or decreases as the Ge coverage increases. This feature is one of the key aspects that characterize the mechanism of island formation, and it implies that the probability of Ge adatoms being captured by the existing islands is much higher than that of the occurrence of island nucleation reactions. This feature can be used to reduce the size of islands by decreasing the amount of Ge deposited. Figure 5 shows that the base diameter of islands decreased from 7.0 ± 1.5 to 3.3 ± 1.0 nm when the amount of Ge was

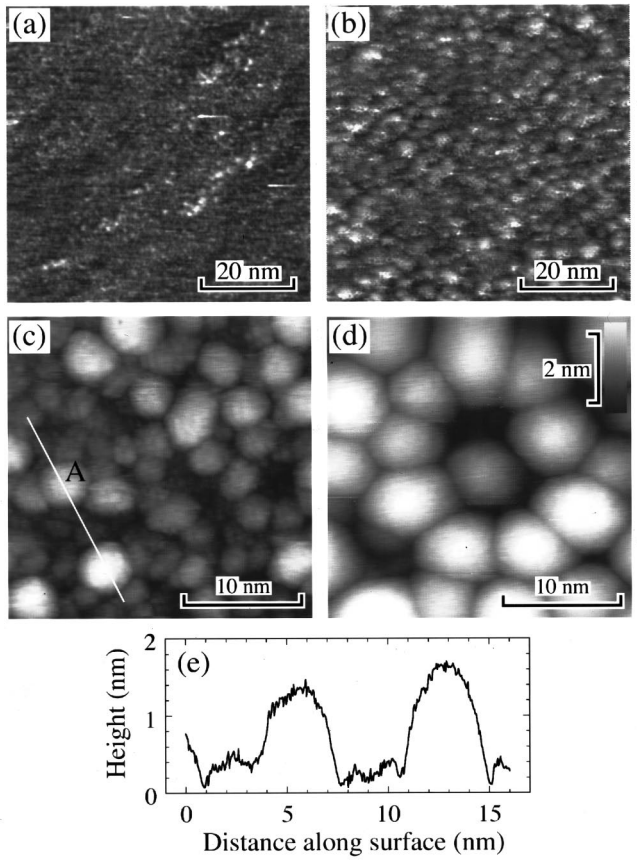

FIG. 5. STM images of surfaces obtained (a) before and (b)–(d) after Ge deposition at 600 °C on Si(111) substrates covered with 0.3-nm-thick SiO_2 films. The amount of Ge deposited was 0.5 BL in (b), 1.0 BL in (c), and 2.6 BL in (d). The rate of Ge deposition was 0.5 BL/min. (e) Height profile along the white line marked by A in (c). The STM images in (a) and (b) were obtained at an elevated tip bias voltage of -3.0 V and a tunneling current of 0.2 nA.

decreased from 2.6 to 1.0 BL's. The average height of the reduced Ge islands was estimated to be about 1.2 nm, which corresponds to approximately four atomic (111) biplanes in the Ge lattice. Such a small island size is about the practical limit for nanostructure technology and has been demanded in order to obtain well pronounced quantum confinement effects according to recent estimations.[1–3] Note that the rest of the SiO_2 films served to conserve the 3D Ge islands against decay during island formation and postdeposition annealing. This role of SiO_2 is similar to that observed in the case of 3D Si islands on Si(100) windows in SiO_2 films, when the islands decayed during annealing only in local areas where the SiO_2 was removed with the STM.[16] This property of SiO_2 allows the epitaxial Ge islands to be fabricated over a wide temperature range up to the temperature of thermal decomposition of SiO_2.

Other aspects that must be taken into account in determining the mechanism of island formation are the temperature and flux dependencies of the island density. The temperature dependence was found to be very weak; for example, the island density was almost equal at 430 and 600 °C, as can be seen from Figs. 1 and 5, and it was about 1.4 times larger at 670 °C. The island density n was measured and found to be independent of the Ge deposition flux F in the range between

0.05 and 2 BL/min, that is, $n \sim F^p$ with the exponent $p \approx 0$. This behavior is essentially different from Ge island formation on the Si(111) surface, where the exponent p is about 0.78, indicating a large critical island size.[17] It is to be noted that the case in theory where monomers on the surface can spontaneously freeze, thereby forming stable nuclei, corresponds to the critical island size $i^* = 0$ and $p = 0$.[18,19] Such a value of $p \approx 0$ directly indicates that nucleation is insensitive to the density of Ge adatoms on the surface, the nuclei appear in the reaction of individual Ge adatoms with SiO_2, probably by breaking Si-O bonds. The lifetime τ_r of Ge adatoms on the surface, determined by the rate of the nucleation reaction, is given by

$$\tau_r^{-1} = k_r^{(0)} \exp(-E_r/kT), \tag{2}$$

where $k_r^{(0)}$ is the prefactor of the reaction rate constant and E_r is the activation energy of the reaction. The island density is defined as $n = (\tau_r D)^{-1}$, where $D = \nu a^2 \exp(-E_d/kT)$ is the diffusion coefficient of Ge adatoms on SiO_2, here ν is the frequency factor ($\nu \approx 10^{13}\,s^{-1}$), a is the jump distance, of the order of the surface repeat distance ($a \approx 0.3$ nm on SiO_2), and E_d is the diffusion activation energy. For n, we obtain

$$n = [k_r^{(0)}/(\nu a^2)] \exp[(E_d - E_r)/kT]. \tag{3}$$

The temperature dependence of n suggests that $E_d \approx E_r$. For reactions on the surface, $k_r^{(0)}$ is not simply equal to ν (not each atomic vibration causes the reaction), but $k_r^{(0)}/\nu$ is usually in the range[20] between 10^{-2} and 10^{-3}. Then, the island density is estimated to be $n \sim 10^{12}\,cm^{-2}$, which is of the same order of magnitude as the Ge island density measured in this work. It is to be noted that the same order of magnitude was also observed for densities of metal particles on such substrates as SiO_2, amorphous carbon, and CaF_2.[15,21] Expressions for n similar to Eq. (3) have been derived in various studies of nucleation occurring at saturated adatom densities maintained by the balance between deposition and fast adatom desorption.[22,23] The specific aspects of the present study are that stable nuclei appear in the reaction between individual adatoms (mobile monomers) and the substrate, and the lifetime of adatoms is determined by the nucleation reaction that can be followed by formation of volatile GeO and SiO molecules.

It has been found that certain materials, such as Sb (Ref. 6) and C (Ref. 7), deposited on Si surfaces prior to the Ge epitaxy can initiate nucleation of 3D Ge islands and thereby increase their density. Using a 1-ML Sb adlayer, Peng *et al.* created Ge islands predominately 8 nm in diameter and 1–2 nm in height, with a number density of $5 \times 10^{11}\,cm^{-2}$ in Si/Ge superlattices on Si(100) substrates.[24] Using a 0.3-ML precoverage of C on Si(100) surfaces, Butz and Lüth reduced the average size of Ge islands to 4 nm when the density of the islands was $3.6 \times 10^{11}\,cm^{-2}$ for 4-ML Ge coverage.[25] The different mechanism of Ge island nucleation in our study provides a density of islands several times higher. Moreover, the Ge islands created in this work were more uniform in shape on Si(111) surfaces than those created with C on Si(100).[25]

In conclusion, Ge deposition on Si(111) surfaces covered with ultrathin SiO_2 films results in epitaxial island growth in the temperature range between 430 and 670 °C depending, on the deposition flux. The effect of postdeposition annealing and the dependencies of the island number density on the Ge coverage, deposition temperature, and Ge flux suggest that the island nuclei and the conditions for epitaxial island growth form through a reaction between individual Ge adatoms and SiO_2. The island number density was estimated from the relationship between the adatom lifetime determined by the nucleation reaction and the diffusion coefficient of Ge adatoms on the surface. The epitaxial islands appeared to have a high number density of about $2 \times 10^{12}\,cm^{-2}$ and the size, which was controllable by varying the amount of deposited Ge. These properties of islands are favorable for nanostructure fabrications.

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[1] D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids*, edited by B. Altshuler *et al.* (Elsevier, Amsterdam, 1991), p. 173.

[2] E. Leobandung *et al.*, Appl. Phys. Lett. **67**, 938 (1995).

[3] A. I. Yakimov *et al.*, J. Phys.: Condens. Matter **6**, 2573 (1994).

[4] Y.-W. Mo *et al.*, Phys. Rev. Lett. **65**, 1020 (1990).

[5] A. A. Shklyaev *et al.*, Phys. Rev. B **58**, 15 647 (1998).

[6] M. Horn-von Hoegen *et al.*, Phys. Rev. B **49**, 2637 (1994).

[7] O. G. Schmidt *et al.*, Appl. Phys. Lett. **71**, 2340 (1997).

[8] S. Maruno *et al.*, Rev. Sci. Instrum. **68**, 116 (1997).

[9] H. Watanabe and M. Ichikawa, Rev. Sci. Instrum. **67**, 4185 (1996).

[10] N. Shimizu *et al.*, Ultramicroscopy **18**, 453 (1985).

[11] A. A. Shklyaev *et al.*, Surf. Sci. **423**, 61 (1999).

[12] A. A. Frantsuzov and N. I. Makrushin, Surf. Sci. **40**, 320 (1973).

[13] R. Tromp *et al.*, Phys. Rev. Lett. **55**, 2332 (1985).

[14] K. Fujita *et al.*, J. Cryst. Growth **188**, 197 (1998).

[15] A. A. Schmidt *et al.*, Surf. Sci. **349**, 301 (1996).

[16] M. Shibata *et al.*, Phys. Rev. B **61**, 7499 (2000).

[17] A. A. Shklyaev *et al.*, Surf. Sci. **416**, 192 (1998).

[18] D. D. Chambliss and K. E. Johnson, Phys. Rev. B **50**, 5012 (1994).

[19] M. Zinke-Allmang, Thin Solid Films **346**, 1 (1999).

[20] W. H. Weinberg, in *Kinetics of Interface Reactions*, edited by N. Grunze and H. J. Kreuzer (Springer-Verlag, New York, 1987), p. 94.

[21] K. R. Heim *et al.*, J. Appl. Phys. **80**, 1161 (1996).

[22] D. R. Frankl and J. A. Venables, Adv. Phys. **19**, 409 (1970).

[23] C. T. Campbell, Surf. Sci. Rep. **27**, 1 (1997).

[24] C. S. Peng *et al.*, Phys. Rev. B **57**, 8805 (1998).

[25] R. Butz and H. Lüth, Thin Solid Films **336**, 69 (1998).