PHYSICAL REVIEW B VOLUME 54, NUMBER 4 15 JULY 1996-II

Self-diffusion on Si(111) surfaces

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(Received 16 October 1995; revised manuscript received 28 March 1996)

Using *in situ* ultrahigh vacuum reflection electron microscopy we have investigated the transition between step-flow and nucleation regimes of homoepitaxy on a Si(111) surface. The minimal interstep distance for two-dimensional nucleation was measured at temperatures 500–850 °C and at the rates of atom deposition 0.01–0.7 ML /s. Dependence of the activation energy on atoms flux, evaluated from the Arrhenius plots of the critical distance, are more complicated than predicted for the simple Einstein relation. Obtained results are discussed in the frames of modest atomistic theories of nucleation. [S0163-1829(96)05727-X]

I. INTRODUCTION

Understanding basic mechanisms in diffusion of adatoms on crystal surfaces during epitaxial growth has been a long-term problem that has attracted much interest, not only to obtain new fundamental knowledge, but also because it has great technological importance for fabrication of electronic devices. Since surface diffusion plays an essential role in most surface transport processes, this topic is currently under intensive consideration. Various macroscopic and microscopic experimental techniques of structural analysis have been successfully applied for studies of diffusion parameters (see, for an example, Ref. 1). However, in spite of the importance of diffusion, adatom migration parameters have not been satisfactorily measured. The development of *in situ* techniques of direct observations of real surfaces allows one to study the mechanism of epitaxial growth and to understand the role of surface steps during island formation at dynamical conditions.[2–6]

We considered a typical process of homoepitaxial growth on crystal surfaces. Deposition of adatoms is one reason for step motion in the step-down direction, consistent with the BCF theory.[7] This mechanism of growth is well known as a step-flow regime of growth. On increasing supersaturation, two-dimensional nucleation occurs on terraces between the steps. Problems of the transition from step flow to nucleation have been widely treated theoretically[8–12] and experimentally.[2–4,6] One of the crucial parameters of these treatments is the diffusion length of adatoms, which determined the transition between different modes of growth. According to the classical Einstein relation, the diffusion length of atoms adsorbed on the surface λ_s at the temperature T is defined[7] as

$$\lambda_s^2 = 2D_s\tau_s, \tag{1}$$

where $D_s = D_0\exp(-E_s/kT)$ is the diffusion constant for single adatoms, E_s is the activation energy for single adatom diffusion, $D_0 = \nu a^2\exp(S/k)$ is the preexponential factor described by the adatom vibration frequency (ν) and by the nearest-neighbor hopping distance (a), S is an entropy of activation, $\tau_s = \nu^{-1}\exp(E_{\rm des}/kT)$ is the surface lifetime of a single adatom, $E_{\rm des}$ is the desorption energy, and k is Boltzmann's constant. For the step-flow mode of epitaxial growth, the diffusion length is larger than half of the interstep distance d and adatoms deposited on the terrace have the possibility to migrate from the central part of the terrace into steps. The critical distance $d_{\rm crit} = 2\lambda_s$ exists, where two-dimensional nucleation occurs on an increase of the interstep distance and/or on a decrease of the diffusion length because λ_s is insufficient for all atoms to reach steps. Therefore, diffusion parameters of adatoms can be found from analyses of these critical distances $d_{\rm crit}$ for the formation of a two-dimensional nucleus.

In this paper, our attention was focused on the more simplified case of self-diffusion on the Si(111) surface and the main goal was to measure the energy activation of surface diffusion during homoepitaxial growth. Also, there are no detailed data about the influence of the supersaturation on adatom migration properties.

II. EXPERIMENT

Experimental results presented in this paper were performed in an UHV reflection electron microscopy (REM) technique on the basis of a home-modified commercial transmission electron microscope as described previously.[13] A residual pressure inside of the UHV chamber was not measured directly because a chamber with unusually small sizes was used in the microscope. According to our estimations, the pressure around the sample was better than 10^{-9} Torr. The number of parameters and results, obtained during previous investigations, allows one to conclude about enough satisfactory vacuum conditions near the specimen.[6,13] Specimens ($7\times1\times0.3$ mm^3 in sizes) with a nominally flat surface were cut from a silicon wafer (111) with electrical resistance a few Ω cm such that the longer side of the specimen was parallel to ⟨110⟩. The incident electron beam was directed along the ⟨112⟩ direction and was almost parallel to the monoatomic steps. The specimen was heated by direct electric current (dc) passing through the longer side of the sample. As is well known, a local step orientation depends dramatically on the cleanness of the surface,[14] so more careful treatments of chemical etching and cleaning were applied to produce a clean silicon surface with a nominally small level of impurity in the manner described previously.[13] The silicon evaporator was mounted in front of the specimen at a distance of about 1 cm and represents a silicon plate heated

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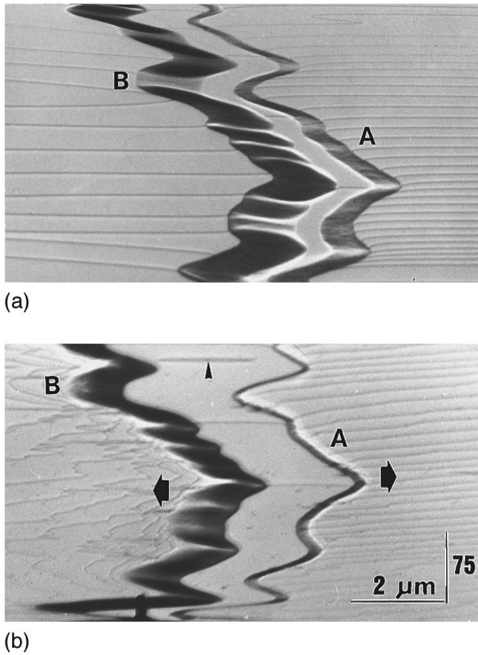

FIG. 1. REM images of the same Si(111) surface containing the step band and antiband (marked by B and A, respectively) before (a) and during initial stage of homoepitaxy (b). Directions of the step band and antiband movement during step-flow growth are shown by horizontal arrows. The two-dimensional nucleus is marked by the vertical arrow in (b).

by dc. The deposition rate (0.1–0.7 ML/s, where 1 ML= 1.6×10^{15} cm^{-2}) was determined from the time period of intensity oscillations of the specular electron beam.

III. RESULTS AND DISCUSSION

For measurements of the distance $d_{\rm crit}$, a surface containing step bands[15] and antibands was used.[16] Figure 1(a) reproduces the REM image of a vicinal Si(111) surface after high-temperature cleaning in the column of the electron microscope. Dark lines are monoatomic steps ($\approx$3.1 Å in height), which move in the step-up direction during sublimation and in the step-down direction during growth. The step band (marked by B) and antiband (marked by A) represent the surface regions with the high density of steps with the opposite sense for the band and antiband. There is a singular (111) surface region between step band and antiband with the width denoted by d_{B-A}. Note that the small grazing angle of observation is a reason to foreshorten the REM images parallel to the electron beam incidence. So the REM images have two scales of magnification. The schematic representation of the surface morphology shown in Fig. 1(a) is presented in Fig. 2(a) where, for simplicity, only three steps are shown at the band and antiband.

During atom deposition on the surface, the movement of the band and antiband in opposite directions (marked by horizontal arrows) was observed due to migration and attachment of the adatoms into steps in the step-flow growth mode [Fig. 1(b) and Fig. 2(b)]. As a result the width between the step band and antiband was increased up to $d_{\rm crit}$ [Fig. 2(c)]. According to the BCF theory, the rate of step-band motion depends on the number of atomic steps in a band or antiband.

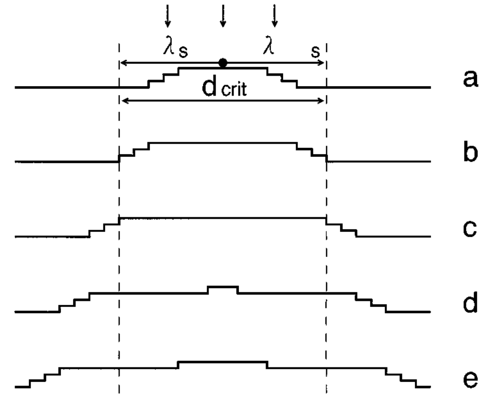

FIG. 2. Schematic representation of surface morphology during epitaxial growth given in Fig. 1. See text for details.

So the motion of the antiband was measured mainly experimentally because the quantity of steps in the band (B) was drastically larger than in the antiband (A). When the distance d_{B-A} increases more than $d_{\rm crit}$, the formation of two-dimensional islands should be expected [Fig. 2(d)]. In fact, simultaneously with step displacement there was nucleation on surface areas with the largest distance between the band and antiband [Fig. 1(b)]. The growth island (marked by vertical arrow) was imaged on the REM micrography as a dark strip caused by the foreshortening effect. Then, growth in step-flow mode continued [Fig. 2(e)]. The appearance of two-dimensional islands on the terrace between the steps gives evidence that the two times larger migration length of adatoms is lower than the terrace width. We assumed that step motion was very slow compared with diffusion and the so-called ''Schwoebel'' phenomenon was neglected.[17] Therefore, the silicon deposition on the vicinal silicon surface with step band and antiband morphology allows one to determine the critical interstep distance $d_{\rm crit}$ for island growth, which related to the adatom diffusion length λ_s.

The temperature dependence of $d^2_{\rm crit}(T^{-1})$ in Arrhenius plots gives the effective activation energy $E_{\rm eff}$ for various flux J (Fig. 3). Inspection of these data reveals that there are two regions, which have different dependence on the atom flux determined by the value $J_* \approx 3\times10^{14}$ cm^{-2} s^{-1}. For an interpretation of the obtained dependence of $E_{\rm eff}(J)$, let us

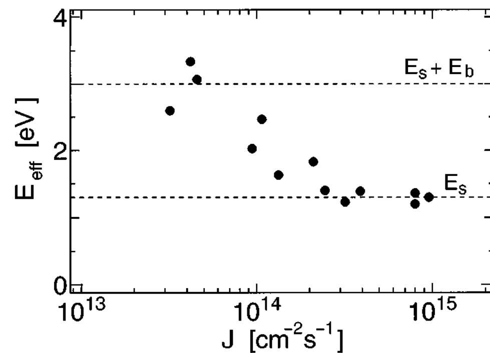

FIG. 3. Dependence of the effective activation energy on atom beam fluxes during homoepitaxy on Si(111) surface, which was evaluated from the temperature dependence of $d^2_{\rm crit}$ drawn in the Arrhenius plots.

reconsider Eq. (1). In practical cases, the evaporation of adatoms can be neglected because enough small growth temperatures are used. This means τ_s is essentially larger than another characteristic time of growth. At high supersaturation the lifetime of adatoms is restricted by the interarrival time of atoms per site from the evaporator $\tau_i = N_s/J$, where $N_s = 1.6\times10^{15}$ cm^{-2} is the surface atom density of the (111) plate. Then, under the assumption that the size of the critical nucleus is only one atom, Eq. (1) can be rewritten as

$$d_{\text{crit}}^2 = N_s J^{-1} \nu a^2 \exp(-E_s/kT). \tag{2}$$

For simplicity, here and later we removed the numeral coefficient, which did not influence the values of the obtained parameters. The relation $d_{\text{crit}}^2 \propto \exp(-E_s/kT)$ has been used for characterization of growth on GaAs substrates.[18,19] According to Eq. (2), the effective activation energy found from the slope of d_{crit}^2 should be independent of the atom flux. It shows excellent agreement with the experimental results presented in Fig. 3. One can see that at $J \geqslant J_*$, the effective activation energy has a tendency to hold approximately the same value on an increase of the rate of atom deposition. This plateau ($E_{\text{eff}} = 1.3$ eV) is equivalent to the energy barrier of adatom diffusion on the substrate, i.e., $E_{\text{eff}} = E_s$. The sample holder used allows one to measure correctly the relative temperatures of the specimen but these data depended on the accuracy of measurements of absolute temperatures also. In any case, the precision of our measurements was estimated to be less than ± 0.2 eV. It must be noted that, in our consideration, the adatom attachment into steps was simplified to be the same for all temperatures. We believed that this assumption was plausible for Si(111), at least for the temperatures treated here.

On a decrease of supersaturation by increasing the temperature and/or decreasing the atom flux from the evaporator, the lifetime of adatoms on the surface was expected to be restricted by the capture time τ_c of adatoms to be absorbed by steps or two-dimensional nuclei.[11] Actually decreasing the flux to less than J_* leads to an increase the value of E_{eff} (Fig. 3). Hence, Einstein's relation is not applicable in the general form of Eq. (1) for the adatom lifetime less than $\tau_i^* = N_s/J_*$ and the lifetime of adatoms should be computed on the basis of the atomistic theory of nucleation.

The modest conceptions of the critical nucleus were reviewed in the papers of Venables *et al.*[8,20] and Stoyanov.[9] Analyzing atomistic processes responsible for epitaxial growth on a crystal surface, the relation between d_{crit} and size i^* of the critical nucleus was derived in the form

$$2\ln d_{\text{crit}} \propto \Gamma_{i*}[\ln J^{-1} - (E_{i*}/i^* + E_s)/kT], \tag{3}$$

where E_{i*} is the binding energy of a critical nucleus of size i^* and Γ_{i*} is the island-size ratio given as $i^*(i^*+1)^{-1}$ in Ref. 9 or $i^*(i^*+2)^{-1}$ in Ref. 8. Note that, again, E_s can be found clearly only for $E_{i*}=0$, which is valid at $i^*=1$. Theoretical approaches for analysis of depleted areas around steps free from nuclei, known as denuded zones, were made with the assumption that two adatoms form a stable nucleus.[2,11,18] Mo *et al.*[2] have shown that the denuded zone size is related to the surface diffusion coefficient as $D_s^{1/6}$. Irisawa, Arima, and Kuroda[11] have found the relation $\lambda_c \propto D_s^{1/4}$, where λ_c is a migration length of adatoms before capture by steps or nucleus. Villain, Pimpinelli, and Wolf[21] have considered that the characteristic length on the growing surface in certain cases was dependent in a complex form on the atom beam flux and diffusion coefficient. One can see that, according to the definition of Γ_{i*}, Eq. (4) transforms to the relations, proposed by Irisawa, Arima, and Kuroda[11] or by Mo *et al.*,[2] respectively, at $i^*=1$. The increase of i^* leads to the increase of E_{eff} because an additional member $E_{i*}/i^* = E_b(i^*-1)/i^*$ is involved in the description of effective energy, where the Si-Si binding energy $E_b = 1.7$ eV (Ref. 22) or $E_b = 2.2$.[23,6] Following the discussion above, we expected that with the decrease of the flux less than J^*, the effective activation energy was displayed by

$$E_{\text{eff}} = (E_{i*}/i^* + E_s)i^*/(i^*+1). \tag{4}$$

For a large enough size of critical nuclei ($i^* \geqslant 5$ in Ref. 24) Eq. (4) can be simplified to $E_{\text{eff}} = E_b + E_s$. This is in good agreement with the experimental results presented in Fig. 3.

Thus the experimental results obtained are qualitatively consistent with theoretical atomistic considerations for two-dimensional nucleation on isotropic surfaces. In the frames of these considerations, conclusions can be made that the activation energy of single-atom diffusion can be correctly found from Einstein's relation only for high rates of atom deposition.

Finally, we now discuss the plausibility of the obtained value of the activation energy for adatom migration. Previously $E_s \approx 1.3$ eV was reported in a number of papers.[4,6,24] Also the activation energy for surface diffusion during sublimation was estimated between 1.1 and 1.6 eV, which was close to our experimental data.[15,31–35] Nevertheless, we should point out that there is a significant dispersion in magnitudes of this activation energy from 0.7 eV (Refs. 25–28) up to 3.6 eV.[30] Presented results indicate that the value of the effective activation energy between 1.3 and 3 eV should be explained by the dependence of the measured activation energy on the atom flux on the substrate.

In addition, recently Nakahara, Ichikawa, and Stoyanov[29] have reported from Monte Carlo simulations that the relationship between denuded zone size and D_s is expected to be different for low and high temperatures and that, also, the number of deposited atoms influences diffusion processes. They have clearly demonstrated that, for small rates of deposition, E_{eff} was larger for small temperature than for high ones. At the limiting case, the denuded zone width is equal obviously to the critical interstep distance for two-dimensional nucleation.[24] Note, also, that Nakahara and Ichimiya[30] have deduced the activation energy from sizes of superstructural domains about 0.9 eV and, then, have estimated E_s to be equal to 3.6 eV related to the distance between domains $\propto D_s^{1/4}$.[11] However, application to this case of the simple Einstein relation leads to $E_s = 1.8$ eV and that is the activation energy from the range deduced in this paper.

It is remarkable that the activation energy about 0.7 eV is deduced at the condition characterized by substantially smaller deposition rates of atoms and by smaller tempera-

tures of substrate compared with experiments given the large E_s.

IV. CONCLUSION

In conclusion, we have carried out *in situ* observations of homoepitaxial growth on the Si(111) surface by UHV REM. A method of measurement of the critical interstep distance for transition from two-dimensional nucleation to the step-flow mode was preposed on the basis of band and antiband morphology. Measurements of the critical distance at various temperatures and rates of atom deposition show strong dependence of the effective activation energy of the adatom migration on the rate of atom deposition. The activation energy of single adatom diffusion was evaluated to be equal to 1.3 ± 0.2 eV from Einstein's relation for high rates of atom deposition.

ACKNOWLEDGMENTS

This work was partly supported by International Sciences Foundation of Soros under Grant No. U86000 and Russian Foundation of Fundamental Researches under Grants No. 95-02-04597 and No. 94-02-06138. A.V.L would like to thank Professor T. Nishinaga and Professor A. Ichimiya for helpful discussions on the topic of this paper. Also A.V.L. thanks the group of Professor K. Yagi (Tokyo Institute of Technology) for hospitality during preparation of this manuscript.

[1] T. Nishinaga, in *Handbook of Crystal Growth, Thin Films and Epitaxy*, edited by D.T.J. Hurle (North-Holland, Amsterdam, 1994), Vol. 3b.
[2] Y.-W. Mo, J. Kleiner, M.B. Webb, and M.G. Lagally, Surf. Sci. **268**, 275 (1992).
[3] B. Voigtlander and A. Zinner, Surf. Sci. Lett. **292**, L775 (1993).
[4] M. Ichikawa and T. Doi, Appl. Phys. Lett. **50**, 1141 (1987).
[5] K. Yagi, Surf. Sci. Rep. **17**, 305 (1993).
[6] A.V. Latyshev, A.B. Krasilnikov, A.L. Aseev, and S.I. Stenin, Phys. Status Solidi A **113**, 421 (1989).
[7] W.K. Burton, N. Cabrera, and F.C. Frank, Philos. Trans. R. Soc. London A **243**, 299 (1951).
[8] J.A. Venables, Surf. Sci. **299/300**, 798 (1994).
[9] S. Stoyanov, J. Cryst. Growth **94**, 751 (1989).
[10] M.C. Bartelt and J.W. Evans, Surf. Sci. **314**, L835 (1994).
[11] T. Irisawa, Y. Arima, and T. Kuroda, J. Cryst. Growth **99**, 491 (1990).
[12] C. Ratsch, A. Zangwill, P. Smilauer, and D.D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994).
[13] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, and S.I. Stenin, Surf. Sci. **227**, 24 (1990).
[14] Y.-N. Yang and Ellen D. Williams, J. Vac. Sci. Technol. A **8**, 2481 (1990).
[15] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, and S.I. Stenin, Surf. Sci. **213**, 157 (1989).
[16] A.V. Latyshev, A.B. Krasilnikov, and A.L. Aseev, Surf. Sci. **227**, 24 (1994).
[17] R.L. Schwoebel and E.J. Shipsey, J. Appl. Phys. **37**, 3682 (1969).
[18] B.A. Joyce, J. Zhang, T. Shitara, J.H. Neave, A. Taylor, S. Armstrong, M.E. Pemble, and C.T. Foxon, J. Cryst. Growth **115**, 338 (1991).
[19] J.M. Van Hove and P.I. Cohen, J. Cryst. Growth **81**, 13 (1987).
[20] J.A. Venables, G.D.T. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984).
[21] J. Villain, A. Pimpinelli, and D. Wolf, Comm. Condens. Matter Phys. **16**, 1 (1992).
[22] V.N. Kondratiev, in *Bond Dislocation Energies, Ionization Potentials and Electron Assinities* (Nauka, Moscow, 1974).
[23] R.E. Honig and D.A. Kramer, RCA Rev. **285**, 1610 (1969).
[24] H. Nakahara, M. Ichikawa, and S. Stoyanov, Ultramicrosc. **48**, 417 (1993).
[25] B. Voigtlander, A. Zinner, T. Weber, and H.P. Bonzel, Phys. Rev. B **51**, 7583 (1995).
[26] H. Minoda, Y. Tanishiro, and K. Yagi (unpublished).
[27] S. Iwanari and K. Takayanagi, J. Cryst. Growth **119**, 229 (1992).
[28] J. Chevrire, A. Cruz, N. Pinto, I. Berbezier, and J. Derrien, J. Phys. I (France) **4**, 1309 (1994).
[29] H. Nakahara, M. Ichikawa, and S. Stoyanov, Surf. Sci. **329**, 115 (1995).
[30] H. Nakahara and Ayahiko Ichimiya, Surf. Sci. **241**, 124 (1991).
[31] R.F.C. Farrow, J. Electrochem. Soc. **121**, 899 (1974).
[32] C. Alfonso, J.C. Heyraud, and J.J. Metois, Surf. Sci. Lett. **291**, L745 (1993).
[33] S.M. Bedair, Surf. Sci. **42**, 595 (1974).
[34] E. Kasper, Appl. Phys. A **28**, 129 (1982).
[35] A. Pimpinelli, J. Villain, D.E. Wolf, J.J. Metois, J.C. Heyraud, I. Elkinani, and G. Uimin, Surf. Sci. **295**, 143 (1993).