Activation Energy for Surface Diffusion of Si on Si(001): A Scanning-Tunneling-Microscopy Study

Y. W. Mo,[a] J. Kleiner, M. B. Webb, and M. G. Lagally
University of Wisconsin–Madison, Madison, Wisconsin 53706
(Received 4 February 1991)

The migration of Si on Si(001) has been investigated by analyzing the number density of islands formed during deposition using scanning tunneling microscopy. The activation energy and prefactor for diffusion in the fast direction, which is along the surface dimer rows, are found to be 0.67 ± 0.08 eV and $\sim 10^{-3}$ cm^2/sec, respectively.

PACS numbers: 61.16.Di

The diffusion of adatoms on a solid is a fundamental problem in surface science, one that has attracted attention over many years. Despite their importance, however, reliable measurements of surface diffusion coefficients are rare, especially for semiconductor surfaces. In particular, the diffusion coefficient at zero coverage, i.e., the pure migration of individual adatoms on the surface, is difficult to determine. Macroscopic methods based on the observation of the spreading of an initially well-defined distribution of adatoms[1] or the decay of intensity oscillations in reflection high-energy electron diffraction with increasing temperature[2] may be ambiguous because of the influence of surface defects such as steps and interactions between adatoms themselves. Field-ion microscopy[3] can measure the pure migration of single adatoms in an elegant manner. However, it is limited in the materials that can be studied because of the high field necessary for imaging, and has seen little application to semiconductors. In this Letter, we present an investigation of the surface self-diffusion of Si adatoms on Si(001), using a method based on the scanning-tunneling-microscopy (STM) analysis of the number density of stable islands formed during submonolayer deposition. We show that it is possible in this way to study the pure migration of adatoms, independent of the complicating influence of interactions inherent in techniques with less spatial resolution. In earlier work[4] we have shown that diffusion of Si on Si(001) is highly anisotropic; it is of the order of 1000 times faster along the surface dimer rows than across them. Here we report the activation energy and preexponential factor for the migration of the Si adatoms.

The deposition of adatoms onto a surface drives the system into supersaturation, from which it will try to relax back to equilibrium by forming a condensed phase of 2D or 3D islands. The formation of islands from a supersaturated 2D lattice gas involves nucleation and subsequent growth. Arriving adatoms make random walks on the terraces and, when meeting each other, form islands. All islands larger than the critical nucleus [which we have shown[5] to be a single atom for Si on Si(001)] will grow by further addition of adatoms from the 2D lattice gas. Nucleation and growth are competing processes, because an arriving adatom can either form a new island with another free adatom (nucleation) or walk into an existing island (growth). The diffusion coefficient of the adatoms determines how large an area, i.e., how many distinct sites, an adatom interrogates in unit time. Therefore, the diffusion coefficient determines the outcome of the competition between nucleation and growth, and hence determines the number density of stable islands after deposition to a certain dose at a given deposition rate.[6] A large diffusion coefficient, for instance, means a high probability for an arriving adatom to find an existing island before another adatom is deposited in its vicinity to provide a chance for nucleation, yielding a lower number density of stable islands after deposition.

To give an understanding of the relationship between the diffusion and the island number density, we provide the following simple dimensional argument. In an isotropic 2D random walk the number of distinct sites visited after H hops[7] (for large H's) is $\pi H/\ln H$. For a large range of H, $\ln H$ can be regarded as nearly constant compared to H, and hence the number of distinct sites visited after H hops is $\sim H$. Now consider an array of islands on the surface, with a number density of N (cm^{-2}). On the average, an area of $1/N$ is associated with each island and the number of lattice sites in this area is equal to $1/Na^2$, where a is the lattice spacing. When the total coverage is low, each island covers a very small portion of its associated area and can be considered as a point target. In order to find one of the existing islands, an arriving adatom needs to visit roughly $1/Na^2$ distinct sites, i.e., the adatom needs to make $\sim 1/Na^2$ hops. Therefore the lifetime for an adatom landing on the surface to find an existing island is given by

$$\tau = 1/\sigma_s J N a^2 = 1/\sigma_s D N , \qquad (1)$$

where σ_s is the capture number of stable islands of size s.[6] The same argument applies to the nucleation process, except that an adatom needs to find another single adatom instead of an existing island. If the concentration of monomers on the surface is n (cm^{-2}), the lifetime τ_n for the nucleation process has the same form as Eq. (1), except for the substitution of σ_1 for σ_s where σ_1 is the capture number for single adatoms. Therefore the nucleation rate is

$$dN/dt = n/\tau_n = \sigma_1 D n^2 . \qquad (2)$$

Single adatoms deposited at a rate R onto the surface

 © 1991 The American Physical Society

produce a concentration $n=R\tau$,[8] where τ is the lifetime of single adatoms given by Eq. (1). Thus,

$$N^2 dN = (\sigma_1 R^2/\sigma_s^2 D)\,dt\,. \tag{3}$$

Theoretical studies[6] have shown that σ_s is a very slow function of the island size s and lies between 5 and 10, while σ_1 lies between 2 and 4. We can eliminate these constants without affecting the functional form of the relation. By integration, we have

$$N^3 = 3R\theta/D\,, \tag{4}$$

where $\theta = RT$ is the total dose deposited up to time t. With both R and θ being externally controllable parameters, Eq. (4) establishes a simple relation between the surface diffusion coefficient of the monomers and the number density of stable islands formed after a submonolayer deposition.

When the diffusion is anisotropic, the number of distinct sites visited by a random walker is less than that visited by an isotropic random walker for the same total number of hops. In the extreme case when the diffusion of adatoms becomes 1D, the number of distinct sites visited after making H hops is $\sim H^{1/2}$. Using the same procedure as above, it is easy to show that

$$N^7 = 7R^2\theta/D^2 a^4\,; \tag{5}$$

i.e., the island number density is proportional to $D^{-2/7}$, a weaker dependence on the diffusion coefficient than that for isotropic diffusion. These simple analytical formulations are directly supported by computer simulations as will be shown below. The conditions on deposition rate (slow enough) and total dose (low) for which Eqs. (1)-(4) are valid are discussed elsewhere.[5] Our experimental conditions are adjusted so that the functional forms of these equations are applicable.

The experiment was carried out in a chamber containing an STM and Si deposition source. Sample cleaning has been discussed previously.[9] The number density of islands formed during deposition can be directly measured in the STM by simple counting. The procedure is as follows: A submonolayer (ML) dose (e.g., 0.07 ML) of Si adatoms is deposited onto Si(001) substrates held at different temperatures; when the deposition is shut off,

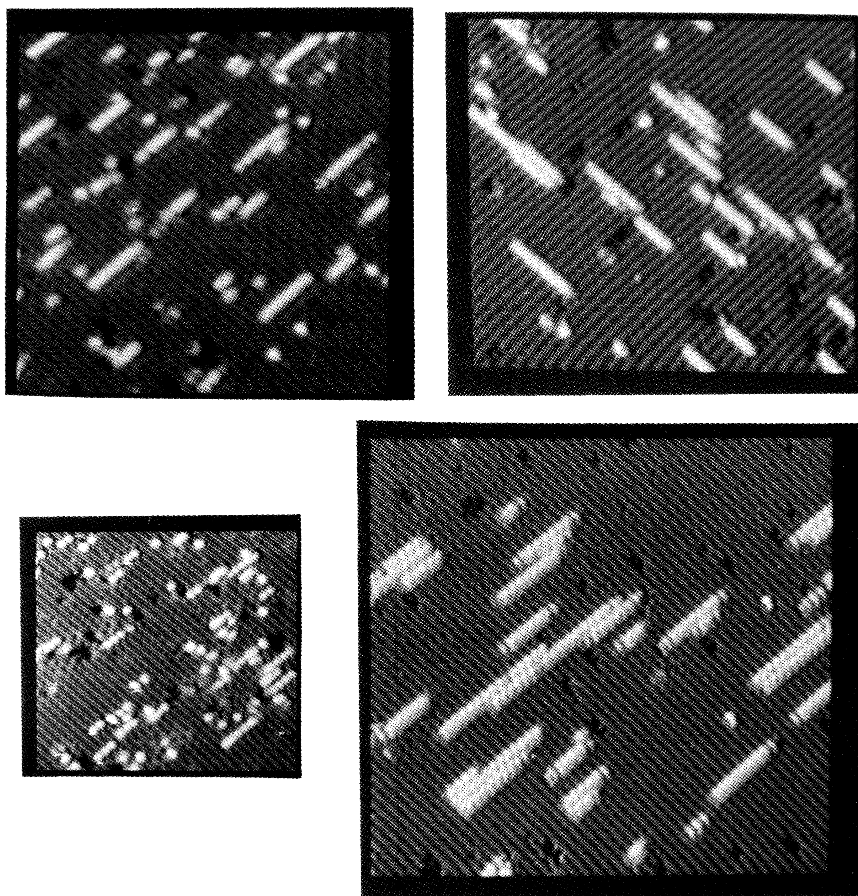

FIG. 1. STM images of islands formed after deposition at different substrate temperatures with a deposition rate of $\frac{1}{600}$ ML/sec and to a dose of 0.07 ML. Lower left panel: $T=348$ K, 250×250 Å; top left: $T=400$ K, 300×300 Å; top right: $T=443$ K, 300×300 Å; lower right: $T=500$ K, 400×400 Å. The islands formed at higher deposition temperatures are larger than those at lower temperatures, with lower number densities, because of the larger diffusion coefficients.

the sample temperature is simultaneously quenched to near RT by turning off the heating power; the sample is then transferred to the STM for scanning; scans are made near the centers of large terraces to avoid the interference of steps; many scans are obtained to achieve good statistics; and the number of islands in each scan is counted to obtain an average number density.

Figure 1 shows examples of islands formed after depositions at four different temperatures. The smallest islands that have been observed are single dimers; they are stable at room temperature. Figure 2(a) shows the island number densities at temperatures ranging from 348 to 653 K. For temperatures higher than 573 K, the island number density drops drastically. This effect is caused by island coarsening, an additional ordering mechanism that becomes important at higher temperatures. It is driven by the desire of the system to reduce the boundary free energy by eliminating small islands while increasing the size of large ones.[10] The process involves both migration of adatoms across terraces and the lateral evaporation of atoms from islands. It is therefore not surprising that the island number density should become a much steeper function of temperature.

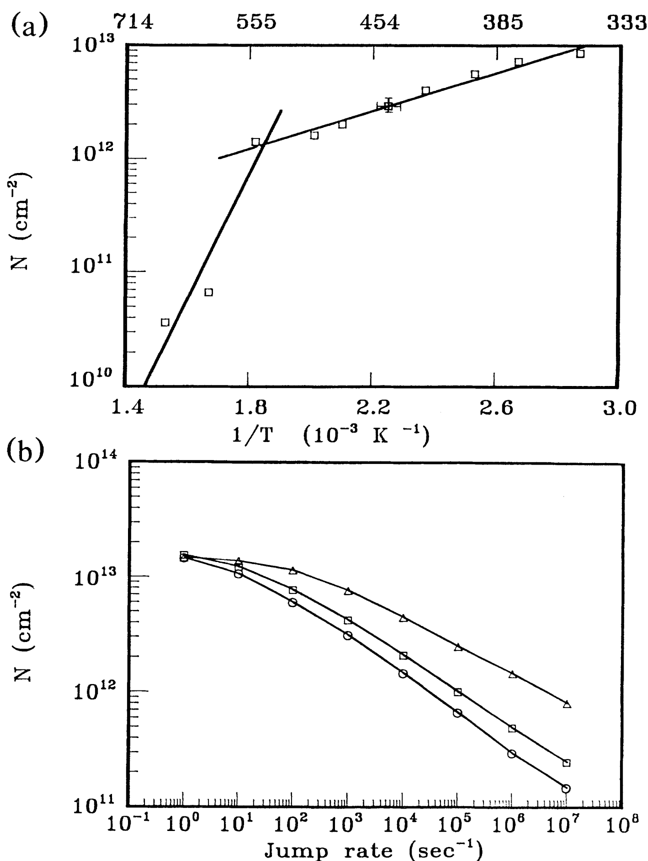

FIG. 2. (a) Measured island number density as a function of the deposition temperature between 348 and 653 K. For temperatures higher than 573 K, coarsening becomes important and the island number density rapidly decreases. (b) Simulation of the dependence of the island number density on jump rates of the adatoms using different anisotropy assumptions. Circles, isotropic bonding and diffusion; squares, anisotropic bonding and isotropic diffusion; triangles, anisotropic bonding and diffusion. Anisotropic diffusion assumes a jump rate along the dimer rows 1000 times that across the rows. Anisotropic bonding assumes perfect sticking on ends and zero sticking on sides of islands. It is evident that the degree of anisotropy in bonding does not affect the curves significantly.

Although Eqs. (1)-(4) provide a physical rationalization of the relationship between island number density and diffusion, they do not allow a quantitative calculation. To do so, we have made computer simulations using a solid-on-solid model. Adatoms are randomly dropped onto an area of 200×200 lattice sites, with periodic boundary conditions. The adatoms make random walks on the sample with an assigned jump rate $J=D/a^2$ and, when meeting each other, form islands. The islands can be grown by further addition of adatoms. The deposition is stopped after a total dose corresponding to the experimental value is reached. The number density averaged over ~10 runs is plotted for a range of jump rates. To include anisotropic diffusion, the ratio of J_x to J_y can be varied. The effect of a difference in the sticking coefficient at the sides and ends of islands[11] can be included. Figure 2(b) is a plot of calculated number density of islands versus the jump rate incorporating different diffusional and sticking anisotropies. It can be seen that the simulation curves are consistent with the previous dimensional argument. For a sufficiently high jump rate, the island number density is proportional to $J^{-1/3}$. The curve incorporating anisotropic diffusion has a smaller slope as discussed earlier. For smaller J's, N changes very slowly with J and becomes almost independent of J at one hop per second at this deposition rate. This is easily seen using Eq. (2): At these small J's the lifetime of adatoms to find an existing island is longer than the total deposition time and most islands are not formed during the period of deposi-

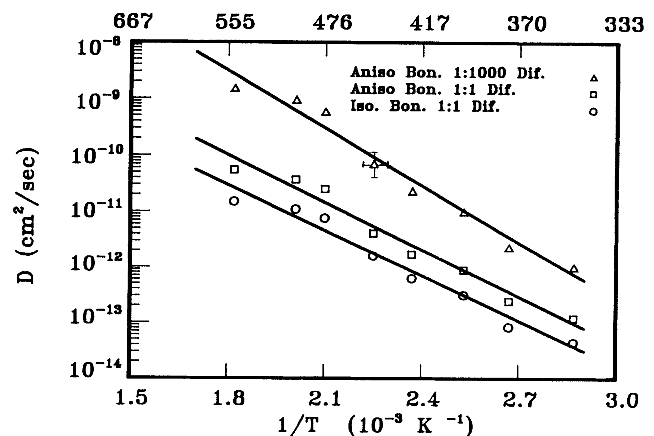

FIG. 3. Diffusion coefficients obtained by comparing the measured island number densities with those from simulations using the models of Fig. 2(b). The symbols correspond to those in Fig. 2(b). Triangles, $E_a=0.67\pm0.08$ eV.

tion but after it. For such conditions, the island number density becomes a constant.[5]

One can use the data in Fig. 2(a) with the calculations in Fig. 2(b) to determine the diffusion coefficient as a function of temperature. Figure 3 shows diffusion coefficients obtained from the three models in Fig. 2(b). The slope of the curve corresponding to 1000:1 anisotropic diffusion yields an activation energy for surface diffusion of adatoms of 0.67 ± 0.08 eV, and a preexponential factor of $\sim 10^{-3}$ cm^2/sec. The error analysis takes into account the uncertainties in the island number density, the deposition rate, and the substrate temperatures. The activation energies and prefactors for anisotropic bonding and isotropic diffusion are 0.56 ± 0.07 eV and $\sim 10^{-5}$ cm^2/sec, and for both isotropic bonding and diffusion 0.56 ± 0.07 eV and $\sim 10^{-6}$ cm^2/sec, respectively. The slightly higher activation energy obtained with the anisotropic-diffusion model is consistent with the previous dimensional argument. Quantitatively for pure 1D diffusion the relationship between island number density and the diffusion coefficient is a $-\frac{2}{7}$ power law, while that for isotropic diffusion is a $-\frac{1}{3}$ power law. The ratio of these two exponents is the same, within 3%, as the ratio of the two activation energies (0.56 and 0.67 eV, respectively), using isotropic- and anisotropic-diffusion models. We believe that the model with anisotropic bonding and 1:1000 diffusion anisotropy best represents the actual situation for Si diffusion on Si(001).[4] Hence we conclude that the activation energy and the prefactor are 0.67 eV and $\sim 10^{-3}$ cm^2/sec, respectively, and that these numbers reflect the diffusion along the easy direction, i.e., along the dimer rows. If the diffusional anisotropy is all ascribed to a difference in activation energy (i.e., the prefactors are assumed the same for jumps along or across rows), the activation energy for diffusion across rows becomes ~ 1 eV. There is no basis, however, for assuming that the prefactors should be the same.

Because the random walk of the adatoms is terminated when they meet each other, if there is no long-range interaction between Si adatoms, the diffusion coefficient and hence the activation energy measured here correspond to the pure random-walk motion of individual Si adatoms on flat Si(001), without the influence of adatomadatom interactions. As can be seen in Fig. 1, however, there are always some divacancy defects in the substrate. The lowest concentration of surface divacancies obtainable so far is 0.5%. The present measurements were made on such surfaces. The interaction of adatoms with the vacancies is unknown. The nucleation sites of islands are not correlated with the vacancies. Furthermore, the adatoms do not preferentially fill vacancies. The fact that we have obtained a number density of islands much lower than the number density of defect sites at higher deposition temperatures indicates that the divacancy defects are not perfect traps. It would not be surprising, however, if the defects slow down the surface migration of adatoms somewhat or decrease the anisotropy in the migration by providing some easier channels for crossing the dimer rows.[12]

Recent theoretical studies of Si/Si(001) diffusion give values similar to our measurements. In first-principles calculations of the energies of a Si adatom adsorbed on Si(001) at various symmetry sites, a value of 0.6 eV for the migration along the dimer rows is obtained[13,14] and a value of 1.0 eV across the rows.[14] Molecular-dynamics (MD) simulations give an activation energy of 0.75 eV along the dimer rows.[15] Combined Monte Carlo and MD simulations indicate that qualitatively the diffusion barrier is lower along the dimer rows than across them.[16]

In summary, the surface migration corresponding to the random walk of Si adatoms on Si(001) was investigated by STM analysis of the islands formed after submonolayer depositions. The theoretical dependence of the number density of islands formed during deposition on the surface diffusion coefficient has been obtained. Comparison between simulations and STM measurements gives the surface diffusion coefficients at temperatures between 348 and 573 K. An activation energy for the diffusion of 0.67 ± 0.08 eV and a prefactor $\sim 10^{-3}$ cm^2/sec are found. Both of these correspond to the migration of single adatoms along the surface dimer rows.

This work was supported by ONR, Chemistry Program. We thank F. Wu, D. Raitt, B. S. Swartzentruber, and R. Kariotis for help and useful discussions. Dr. P. Wagner, Wacker Chemitronic, Germany, has provided well-oriented Si(001) wafers for this study.

[a]Present address: IBM Research Center, Yorktown Heights, NY 10598.

[1]H. P. Bonzel, in *Surface Physics of Materials*, edited by J. M. Blakely (Academic, New York, 1975); C. H. Mak, J. L. Brand, G. B. Koehler, and S. M. George, Surf. Sci. **191**, 108 (1987).

[2]J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A **31**, 1 (1983).

[3]G. Ehrlich and F. G. Hudda, J. Chem. Phys. **44**, 1039 (1966).

[4]Y. W. Mo and M. G. Lagally, Surf. Sci. (to be published).

[5]Y. W. Mo, Ph.D. thesis, University of Wisconsin–Madison (unpublished); Y. W. Mo and M. G. Lagally (to be published).

[6]J. A. Venables, Philos. Mag. **27**, 697 (1973).

[7]E. W. Montroll, Proc. Symp. Appl. Math. **16**, 193 (1964).

[8]B. Lewis and D. S. Campbell, J. Vac. Sci. Technol. **4**, 209 (1967).

[9]B. S. Swartzentruber, Y. W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

[10]I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961).

[11]Y. W. Mo, B. S. Swartzentruber, R. Kariotis, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **63**, 2393 (1989).

[12]A. Rockett, Surf. Sci. **227**, 208 (1990).

[13]T. Miyazaki, H. Hiramoto, and M. Okazaki, Jpn. J. Appl. Phys. **29**, L1165 (1990).

[14]G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[15]D. Srivastava and B. J. Garrison (to be published).

[16]Z. Zhang, Y. T. Lu, and H. Metiu (to be published).

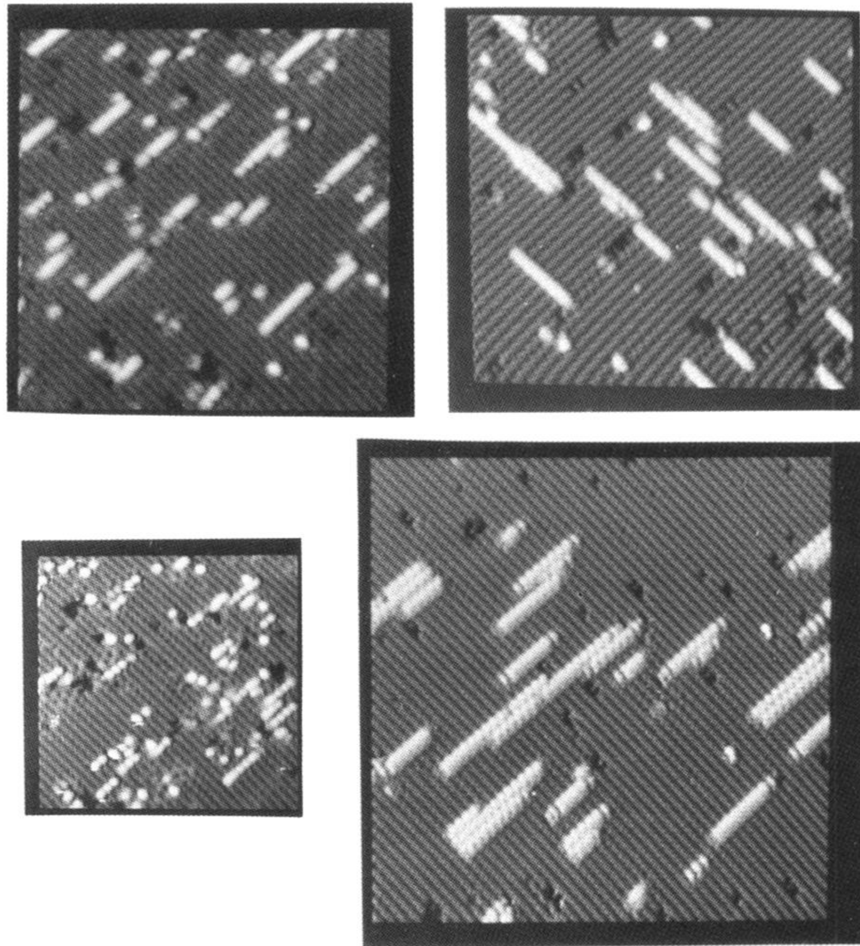

FIG. 1. STM images of islands formed after deposition at different substrate temperatures with a deposition rate of $\frac{1}{600}$ ML/sec and to a dose of 0.07 ML. Lower left panel: $T = 348$ K, 250×250 Å; top left: $T = 400$ K, 300×300 Å; top right: $T = 443$ K, 300×300 Å; lower right: $T = 500$ K, 400×400 Å. The islands formed at higher deposition temperatures are larger than those at lower temperatures, with lower number densities, because of the larger diffusion coefficients.