Adatom Diffusion by Orchestrated Exchange on Semiconductor Surfaces

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Recent experiments show that low temperature diffusion on semiconductor surfaces such as Ge(111) can be many orders of magnitude slower than expected. We present a model which provides a detailed explanation for the observed rate of diffusion on this surface. The effect is shown to be the result of complicated motions that allow surface adatoms to exchange places by hopping in an orchestrated manner between low-energy positions.

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While a great deal is known about the motion of atoms on metal surfaces from field ion microscopy and related theoretical studies [1], the motion of atoms on semiconductor surfaces is still poorly understood. The complexity of atomic interactions on these surfaces makes the study of atom dynamics challenging both for experiment and for theory. Only recently, scanning tunneling microscopy (STM) experiments have begun to measure directly dynamical effects on semiconductor surfaces, such as atomic diffusion [2–4], growth [5], and phase transitions [6]. These STM studies have revealed a wealth of new and, in some cases, puzzling effects. One example is the observed rate of diffusion on Ge(111) surfaces, which at low temperatures is 5 to 6 orders of magnitude lower than expected from typical attempt frequencies and jump lengths [3]. Such large discrepancies between simple estimates and experimental observations call for a detailed theoretical analysis of possible diffusion mechanisms.

In this Letter we show how the slow diffusion rate can be explained by complicated collective motion which allows surface atoms to exchange positions without ever leaving the surface or breaking more than one covalent bond. This motion does not involve the presence of defects such as vacancies, which are usually needed to mediate diffusion. In this respect it is reminiscent of the concerted pair exchange, which has been considered as a possible mechanism for bulk [7] or surface [8] diffusion. However, our model differs from pair exchange in that many more surface atoms are involved in each diffusion event and their motion is not simultaneous, as in the concerted pair exchange, but sequential. This complex motion, to which we shall refer as "orchestrated exchange," ensures that a minimal number of covalent bonds are broken during diffusion. Since strong covalent bonding is prevalent on semiconductor surfaces, it is likely that this type of motion dominates the dynamics of atoms at low temperature. In order to account for the observed diffusion rates quantitatively, we use first-principles quantum mechanical calculations to obtain energy barriers and entropy factors for single-atom hops. We then introduce the concept of an exclusion zone, which takes into account the proper saturation of surface dangling bonds by adatoms and makes it feasible to study collective motion by classical Monte Carlo (MC) simulation [9].

We begin with a brief review of the salient experimental observations. The surface of Ge(111) exhibits a $c(2 \times 8)$ reconstruction, in which Ge adatoms saturate three surface dangling bonds each, while one quarter of the surface dangling bonds remain uncovered (rest atoms). The equilibrium $c(2 \times 8)$ periodicity is a long-range pattern assembled from subunits containing one adatom and one rest atom each [local domains of (2×2) periodicity are also quite common [4]]. The atomic motion is essentially determined by the structural features of the simple (2×2) unit cell, while the long-range $c(2 \times 8)$ periodicity produces anisotropic diffusion [3]. A Ge adatom in its equilibrium configuration resides at the T_4 position, directly above an atom belonging to the lower half of the surface bilayer (Fig. 1, left inset). The H_3 position, which is directly above the center of a hexagon composed of atoms of the surface bilayer (Fig. 1, right inset), is a metastable configuration. In the STM experiments a small amount (5%–10%) of the surface Ge adatoms were replaced by Pb atoms, which have similar chemical behavior, but can be easily identified in the images as brighter atoms [3]. The Pb adatoms serve both

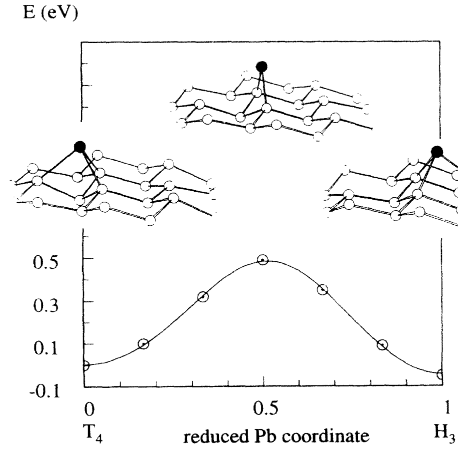

FIG. 1. The calculated energy (circles) vs position of the Pb adatom for a single T_4-to-H_3 hop (the line is a cosine expansion fit). The insets show the atomic structure of the T_4 (left), H_3 (right), and saddle point (middle) configurations, with the Pb atom shaded.

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as the tracers of a usual diffusion experiment and as diffusion enhancers due to the nature of their interaction with the surface (see below).

The natural elementary hop for an adatom is from the T_4 to the H_3 position. In both positions the Pb adatom is quite stable and does not interfere drastically with the presence of other adatoms (STM experiments occasionally find Pb adatoms in the H_3 position [4]). We have performed first-principles total energy calculations within local-density-functional theory [10] to determine the energy barrier for this elementary hop. The results are shown in Fig. 1. The activation energy for an entire layer of Pb adatoms hopping from the T_4 to the H_3 position is $\varepsilon_a = 0.56$ eV [11]. This hop breaks only one covalent bond (see Fig. 1, middle panel). An interesting feature is that Pb adatoms in T_4 and H_3 positions have equal energy (in the case of Ge adatoms the H_3 position has higher energy). This feature will enhance the rate at which Pb adatoms can move away from the T_4 position, since they can reside equally favorably in the H_3 position.

The calculated ε_a is in excellent agreement with the activation energy found by experiment [3], suggesting that the observed diffusion constant $D = D_0 e^{-\beta\varepsilon_a}$ ($\beta = 1/k_B T$) is related to a sequence of thermally activated single hops between T_4 and H_3 sites. What remains to be explained is why the measured value of the preexponential factor

$$D_0 = f \frac{1}{2d} \lambda^2 \nu_0 e^{S/k_B} \tag{1}$$

is lower than expected by many orders of magnitude [3]. In Eq. (1) f is a geometric factor ($f = 1$ for exchange events), d is the dimensionality of the system ($d = 2$ for surface diffusion), λ is the jump length for an elementary event, ν_0 is the bare attempt frequency, and S is the entropy.

There are two possible explanations for the unusually low value of D_0: (1) The effective attempt frequency of *individual single hops* ($\nu_{\text{eff}}^{(1)} = \nu_0^{(1)} \exp[S^{(1)}/k_B]$) is somehow orders of magnitude lower than expected. This can be the result of a very large negative entropy $S^{(1)}$ or a very low bare attempt frequency $\nu_0^{(1)}$ associated with individual single hops. (2) Alternatively, the actual interchange of adatom positions observed by experiment may involve the coordinated displacement and hopping of many adatoms, as hypothesized by Ganz *et al.* [3]. This could result in a much lower effective attempt frequency, which is a collective effect and cannot be accounted for by the dynamics of single hops.

The first possibility can be directly investigated within the framework of first-principles total energy calculations: using the energy surface that a moving adatom explores, it is possible to calculate both the entropy $S^{(1)}$, through Vineyard's transition state theory [12], and the bare attempt frequency $\nu_0^{(1)}$. Diffusion entropies can be calculated as the logarithm of the ratio of two Boltzmann integrals [13]: the numerator (saddle-point integral) is over a ($dQ - 1$)-dimensional surface that passes through the saddle-point configuration and the denominator (equilibrium integral) is over a (dQ)-dimensional volume around the equilibrium configuration (Q is the number of particles involved in the diffusion event and d the dimensionality). For practical reasons, the multidimensional integrals are approximated by the most important regions of integration, which leads to a lower bound estimate for the entropy (for details see [13]). In the case of Pb adatom diffusion on the Ge(111) surface, the variables that give the most significant contribution to the entropy of a single hop are the direction that links the T_4 and H_3 sites and the perpendicular direction. We have performed total energy calculations in the space of these two coordinates and evaluated numerically the phase space integrals. We obtain a lower bound for the entropy of a single hop $S^{(1)} = 1.55 k_B$ [14]. From these calculations we also obtain a bare attempt frequency (the average curvature of the energy surface around the equilibrium configuration) $\nu_0^{(1)} = 2 \times 10^{11}$ sec^{-1}. This is approximately 2 orders of magnitude lower than typical bulk values (10^{13} sec^{-1}), which justifies the assertion made earlier about weak coupling between the Pb adatom and the Ge surface. These results give an effective attempt frequency for single hops $\nu_{\text{eff}}^{(1)} = 9 \times 10^{11}$ sec^{-1}. Taking into account the fact that $S^{(1)}$ is a lower bound for the entropy of single hops [14], we arrive at a best estimate for $\nu_{\text{eff}}^{(1)} = 4 \times 10^{12}$ sec^{-1}. Thus, the first possibility of an unusually low effective attempt frequency associated with individual single hops is easily discarded from our calculations (see Table I).

The second possibility would involve a large number of atoms moving in a coordinated way. We assume, consistent with experimental observations [3,4], that no vacancies or other defects are responsible for mediating diffusion. Since in the present case the single-hop activation energy is already very close to experiment, one has to search for diffusion mechanisms that do not re-

TABLE I. Experimental and theoretical values for Pb adatom diffusion on Ge(111). The calculated attempt frequency $\nu_{\text{eff}}^{(1)}$ refers to single T_4-to-H_3 hops (best estimate). The theoretical value of λ corresponds to a single T_4-to-H_3 hop, while the one assumed in Ref. [3] corresponds to the distance between adatoms in a (2 × 2) ordered pattern. These results *do not include* collective effects (orchestrated exchange motion).

	Experiment [3]	Theory
ε_a (eV)	0.54 ± 0.03	0.56
$\nu_{\text{eff}}^{(1)}$ (sec^{-1})		4×10^{12}
ν_{eff} (sec^{-1})	7×10^5	
λ (Å)	8	2.3
D_0 (cm^2/sec)	1×10^{-9}	5×10^{-4}

sult in *higher* activation energy. For example, removing two adatoms out of the surface and interchanging their positions would give an activation energy much higher than the single T_4-to-H_3 hop, because it would involve the breaking of six covalent bonds simultaneously (three per adatom). Formation of vacancies or other defects would involve similarly large activation barriers. In the orchestrated exchange to be described below, we show that a large number of adatoms can perform single T_4-to-H_3 hops sequentially, thereby opening up a path for a pair of adatoms to exchange positions, without ever leaving the surface. Thus, the activation energy for the entire motion is that of single hops, whereas the preexponential rate is determined by the probability of occurrence of the complex moves that contribute to diffusion.

The requirement that adatoms always reside at T_4 or H_3 sites and can only hop from one site to the other is crucial in understanding the orchestrated exchange. Each adatom is accompanied by an *exclusion zone*, marked by +'s in Fig. 2: the local structure of the surface makes it impossible to put adatoms on any of the sites in the exclusion zone, because all the available substrate bonds have already been saturated. It is, however, possible to move an adatom from its regular T_4 position to one of the neighboring H_3 sites without violating any exclusion zones. When a T_4-to-H_3 move is made starting from the ideal pattern (e.g., adatom A in Fig. 2) the adatom carries its exclusion zone along (the new zone is marked by ×'s). As seen from the distribution of +'s and ×'s for the new position of A, no exclusion zones are violated by this move. When adatom A is placed at the new position some positions into which neighboring adatoms B and C were previously allowed to move are now part of the new exclusion zone of A (these positions are marked by a × but not a +). From its new position, adatom A can migrate further only when adatoms B or C have moved out of the way, whereas it can return unhindered to its original position. These observations already hint at the necessity of orchestrated motion, without which adatom A is trapped in the immediate neighborhood of its equilibrium position.

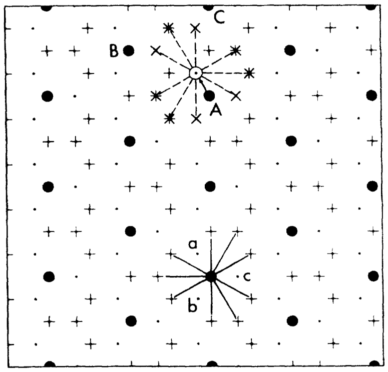

FIG. 2. Illustration of adatom motion with exclusion zones. Small dots represent possible T_4 and H_3 sites; large filled dots represent a (2×2) ordered pattern of adatoms at T_4 sites. The +'s indicate the exclusion zones of T_4 adatoms. One zone is identified by lines connecting a large solid dot to the neighboring +'s. The adjacent H_3 positions into which this particular adatom can move are labeled a, b, and c. A T_4-to-H_3 hop is also shown, with the adatom that moved labeled A and its new exclusion zone marked by ×'s (identified by dashed lines connecting the new position, open large circle, to the ×'s). Nearby adatoms whose subsequent motion is restricted because of A's motion are labeled B and C.

A complete interchange of positions between two adatoms may be achieved by a series of well chosen moves, involving sequential displacements in complicated pathways which never violate exclusion zones. In order to quantify the rate of such events we performed a MC simulation which included all the essential features of the problem: adatoms were allowed to move from T_4 to H_3 sites, while carrying along their exclusion zones. No violations of exclusion zones were permitted at any move. For realistic comparison to experiment, the $c(2\times8)$ pattern of adatoms was used in the simulation, in a 64 adatom cell with periodic boundary conditions. For the temperature range of interest, the MC simulation must leave the average occupation of the $c(2 \times 8)$ lattice unchanged over long times, as in experiment. This was accomplished by two different schemes: first, the adatoms were made to interact with a local harmonic potential that favors the proper ordered pattern; second, the hopping probabilities onto and out of the ordered pattern were skewed in favor of the ordered pattern. Both models were studied for a wide range of the parameters (effective temperature, the harmonic potential strength, and the relative hopping probabilities) in order to extract the physical behavior. The values of the parameters were then fixed so that they reproduce experimental observations [i.e., average ordered $c(2 \times 8)$ pattern at room temperature]. We find that the results from the two models are identical. The results can be summarized as follows:

(i) For a total number N of MC moves ($N = 10^8$ in our simulation), only a small fraction n lead to exchange of adatom positions. In both models we obtained $n = N \times 10^{-6\pm1}$. The effective retardation factor of $10^{-6\pm1}$ is very close to what is needed to bring theory in agreement with experiment (see Table I).

(ii) The moves that lead to exchange of adatom positions take place over a very small time interval and involve always more than two adatoms. The rest of the time adatoms move incessantly between T_4 and neighboring H_3 positions, without leaving the immediate neighborhood of their equilibrium position.

To illustrate the orchestrated exchange, we present in Fig. 3 a typical sequence of events observed in our simulation that leads to exchange of adatom positions. There are three types of adatoms in this figure: adatoms that do not participate in the exchange ("spectators," open circles), adatoms that must move in order for the exchange to take place but end up in the same position after the ex-

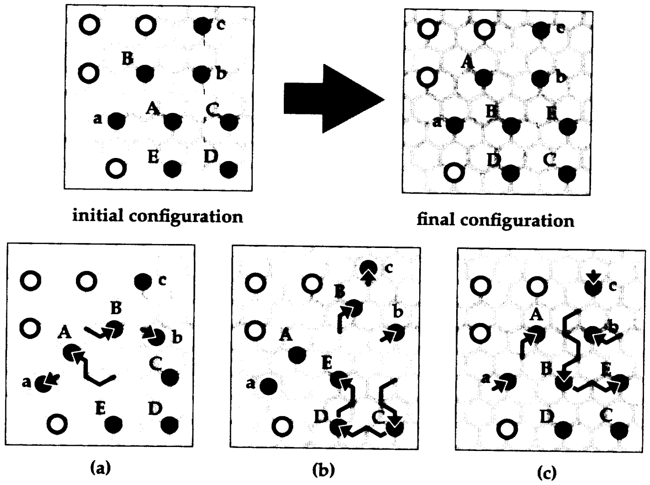

FIG. 3. Example of an orchestrated exchange. Three types of adatoms are involved: spectators (open circles), enablers (grey circles, a, b, c), and movers (black circles, A, B, C, D, E). The initial and final configurations of the event are shown on top. The event is broken into three parts, (a), (b), and (c), to explain the atomic motions (see text).

change ("enablers," grey circles), and adatoms that end up in different positions after the exchange ("movers," black circles). The exchange is analyzed in three steps. In part (a), two movers (A and B) move away from their equilibrium positions and two enablers (a and b) move slightly out of the way to facilitate the motion of A and B. In part (b), the enablers b and c move out of the way of mover B, which then wanders further from its initial position, allowing the movers C, D, and E to quickly change positions as indicated. In part (c), mover E goes to a new position, mover B takes the position of E, and mover A goes to a new position, while the enablers a, b, and c move back to their original positions. Comparing the initial and final configurations in Fig. 3, it is seen that movers A and B actually exchanged positions, while movers C, D, and E performed a complicated motion, with all three ending in different positions.

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[1] G. Ehrlich and F.G. Hudda, J. Chem. Phys. **44**, 1039 (1966); G. Ehrlich, *ibid.*, p. 1050; G.L. Kellog, T.T. Tsong, and P. Cowan, Surf. Sci. **70**, 485 (1978); T.T. Tsong, Rep. Prog. Phys. **51**, 759 (1988); G.L. Kellog and P.J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990); G.L. Kellog, *ibid.* **67**, 216 (1991); T.T. Tsong and C. Chen, Phys. Rev. B **43**, 2007 (1991); Nature (London) **355**, 328 (1992).

[2] Y.M. Mo, J. Kleiner, M.B. Webb, and M.G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).

[3] E. Ganz, S.K. Theiss, I.-S. Hwang, and J. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992).

[4] I.-S. Hwang and J. Golovchenko, Science **258**, 1119 (1992).

[5] R.M. Tromp, A.W. Denier van der Gon, and M.C. Reuter, Phys. Rev. Lett. **68**, 2313 (1992).

[6] I.-S. Hwang and J. Golovchenko, Phys. Rev. Lett. **71**, 255 (1993).

[7] K.C. Pandey, Phys. Rev. Lett. **57**, 2287 (1986).

[8] P.J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).

[9] For a recent example of MC simulation of diffusion on metal surfaces, see S. Liu, Z. Zhang, G. Comsa, and H. Metiu, Phys. Rev. Lett. **71**, 2967 (1993).

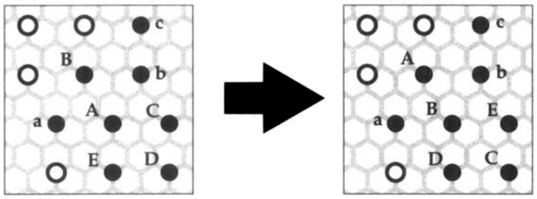
[10] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965). We use the exchange-correlation functional proposed by J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981), and norm-conserving pseudopotentials from G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982) to model the atomic cores. A plane wave basis with kinetic energy cutoff 8 Ry and a dense grid of sixteen surface Brillouin zone points for reciprocal space integrations were used. Full atomic relaxation is taken into account through minimization of the calculated Hellmann-Feynman forces. The accuracy of energy differences with these computational parameters is 0.05 eV.

[11] The activation energy for moving a single adatom while the rest of the surface is fixed may be slightly different. Our calculations of the energetics of Pb adatom motion indicate that the coupling of the Pb adatom to the Ge surface is sufficiently weak to make any changes in the activation energy very small.

[12] G.H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

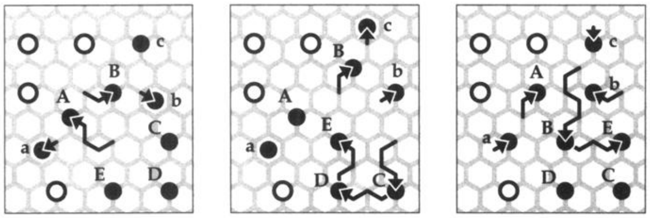
[13] K.C. Pandey and E. Kaxiras, Phys. Rev. Lett. **66**, 915 (1991); E. Kaxiras and K.C. Pandey, Phys. Rev. B **47**, 1659 (1993).

[14] Our experience with similar calculations for bulk diffusion in Si (see [13]) suggests that S can be enhanced by at most a factor of 2 by expanding the phase space of integrations.



initial configuration

final configuration



(a) (b) (c)

FIG. 3. Example of an orchestrated exchange. Three types of adatoms are involved: spectators (open circles), enablers (grey circles, a, b, c), and movers (black circles, A, B, C, D, E). The initial and final configurations of the event are shown on top. The event is broken into three parts, (a), (b), and (c), to explain the atomic motions (see text).