Changing the Diffusion Mechanism of Ge-Si Dimers on Si(001) using an Electric Field

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We change the diffusion mechanism of adsorbed Ge-Si dimers on Si(001) using the electric field of a scanning tunneling microscope tip. By comparing the measured field dependence with first-principles calculations we conclude that, in negative field, i.e., when electrons are attracted towards the vacuum, the dimer diffuses as a unit, rotating as it translates, whereas, in positive field the dimer bond is substantially stretched at the transition state as it slides along the substrate. Furthermore, the active mechanism in positive fields facilitates intermixing of Ge in the Si lattice, whereas intermixing is suppressed in negative fields.

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It is a long-standing course of study to investigate the dynamic behavior of atoms and molecules at surfaces and interfaces in order to understand diffusion, reaction rates, growth, and alloying. This has become even more important with the recent push to develop ever smaller functional electronic and mechanical structures, in which, at the lowest limit, a few atoms out of place can destroy their utility. Understanding the details of the transition states is necessary to uncover the principles that govern surface chemistry. In addition, knowledge of the nature of available reaction paths allows us to systematically modify the kinetics of an atomic system and thus to modify its time evolution and structure. This measure of atomic level control may be especially useful for manufacturing novel electronics devices based on Si-Ge nanostructures [1].

In this Letter, we report measurements and first-principles calculations of the field dependence of adsorbed Ge-Si dimer diffusion on the Si(001) surface. We find that in negative field, i.e., when electrons are attracted towards the vacuum, the dimer diffuses as a unit, rotating as it translates. However, in positive field a different diffusion mechanism occurs in which the dimer bond is highly stretched at the transition state as it slides along the surface. We also observe that the mechanism in positive field enhances the probability of exchange between the Ge atom and the substrate. Not only does the electric field provide a "knob" to alter the diffusion rate, but also changes the mechanism itself and, in so doing, the rate of intermixing.

Determining the kinetic path is not a simple task, for it is the nature of kinetic processes that atomic configurations are arranged in low energy states most of the time. The move from one low energy state to another occurs on time scales usually not accessible to experimental observation. However, it *is* possible to accurately measure the barrier energy, due to the exponential dependence of the rate at which kinetic processes occur on this value. On the other hand, modern total-energy techniques based on density functional theory (DFT) can determine the energy and forces of arbitrary atomic configurations with some accuracy. Here, the challenge is in finding all configurations that are physically relevant. Techniques that attempt to explore the relevant portions of phase space, like the nudged-elastic-band [2] method, are applied to the problem of determining the low barrier transitions. However, there is no guarantee that an important process is not overlooked. This is especially true for situations with many degrees of freedom typical for low-coordination, low-symmetry systems such as covalent semiconductors and surfaces. Additional uncertainty arises from the inherent inaccuracy of current DFT approximations. The two most common choices for the exchange-correlation functional, local density approximation (LDA) and generalized gradient approximation (GGA), typically lead to barrier values differing on the order of $1/10$ eV. For diffusion on Si(001) a different ordering of the energy of various paths (and even the stable configurations) has been observed [3,4]. Because of this energy uncertainty and the impossibility of performing an exhaustive search for all potential processes, it is suspect to rely solely on theory to determine the active process based on the lowest-barrier-to-date criterion.

One method to acquire additional information about the transition state is to measure the change in activation barrier as a function of an externally applied electric field. Kellogg showed that the rate of exchange diffusion of Pt on Pt(001) is strongly affected by an external field [5], and, furthermore, at high enough field a possible crossover to hopping diffusion was observed. Feibelman subsequently modified the VASP DFT code to include the effect of an external electric field to theoretically corroborate these measurements [6]. The calculations were in excellent agreement with the measured field dependence but could not explain a crossover to hopping diffusion.

Recently, Mattsson *et al.* calculated the electric field dependence of diffusion of adsorbed Si dimers on the Si(001) surface [4] to compare with the detailed measurements of Carpinelli [7]. The calculations revealed that the generally accepted (lowest-barrier) diffusion

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mechanism, so-called "piecewise diffusion" [8], had the opposite field dependence to what is observed and therefore could not be active. Furthermore, they discovered a different diffusion path, "walking" diffusion, with a similarly low barrier that has the correct field dependence. In walking diffusion the atoms of the adsorbed dimer remain bonded during the entire path, rotating as they pass through the transition state [9], as opposed to piecewise diffusion in which the atoms are separated at the transition state. These results give us confidence that measurements of the electric field dependence of kinetic processes in concert with calculations of transition state electronic structure can yield valuable insight into the elusive transition state.

Our experiments were performed in ultrahigh vacuum (1×10^{-10} torr) using a variable-temperature STM. The silicon samples were cleaned by resistive heating to ~1250 °C for 45 s and then radiation cooled before Ge deposition. Ge atoms were deposited from a resistively heated tungsten wire basket containing bulk Ge, and the samples then placed on the STM stage for imaging.

When Ge atoms are deposited onto the Si(001) surface, dimers form that sit on top of the substrate dimer rows. The vast majority of dimers are heterogeneous or "mixed," composed of one silicon and one germanium atom [10]. Mixed dimers are highly buckled with the Ge atom always in the up position [10], and are easily distinguished from homogeneous, "pure," Si-Si dimers by this buckling as well as by their rotation behavior [11]. Si-Si dimers appear symmetric and can rotate between configurations in which the adsorbed dimer bond is parallel or perpendicular to the substrate dimer rows [3]. Mixed dimers are never observed with their dimer bond perpendicular to the substrate rows. The signature of a mixed-dimer rotation event is that the buckling switches from one side of the adsorbed dimer to the other as the Ge atom trades places with the Si atom [11]. At room temperature both mixed and pure dimers rotate on the time scale of seconds.

We measured the adsorbed dimer kinetics in detail using atom-tracking STM [12]. In atom-tracking mode, the STM probe tip is locked onto the highest point of the dimer using lateral feedback that moves the tip "uphill." The X, Y, and Z positions of the tip are continuously recorded (typically at 1 kHz), which increases the time resolution with which dynamic events can be measured by about a factor of 1000 over conventional STM imaging. Additionally, because the spatial resolution of atom tracking is much better than a lattice constant, it is easy to distinguish and measure the rotation events of a dimer at a single lattice site, and, by the rotation behavior, to determine whether the adsorbed dimer is a pure Si-Si dimer or a mixed Ge-Si dimer [11].

At elevated temperatures the adsorbed dimers diffuse along the substrate dimer rows. In Fig. 1 we plot the atom-tracking data for an adsorbed dimer acquired at 100 °C. The dimer starts off as a mixed Ge-Si dimer, the signature of which is two rotation maxima at each lattice site. After 100 s an atomic exchange event occurs in which the Ge atom in the adsorbed dimer exchanges with a substrate Si atom, leaving the Ge atom in the substrate and a pure Si-Si dimer to diffuse [11]. Because of the symmetry of a Si-Si dimer there is only one maximum in the tracking data at each lattice site.

From the temperature dependence of the diffusion rates, the barriers for both pure and mixed dimers were determined to be the same (~1 eV)—within the error of the measurements. In two separate measurements, the Si-Si diffusion barrier is reported to be 0.94 ± 0.09 eV [12] and 1.09 ± 0.05 eV [13], while the Ge-Si diffusion barrier is reported to be 1.01 ± 0.09 eV [11]. Although the difference of diffusion barriers cannot be determined from comparison of these separate experiments, assuming identical prefactors, measuring relative rates at a constant temperature enables very accurate determination of energy differences [14]. We measure the relative diffusion rates of mixed and pure dimers under identical experimental conditions by taking advantage of the fact that occasionally the Ge atom in a mixed dimer exchanges with a substrate Si atom. Measuring the diffusion rates before and after an exchange event ensures identical temperature and neighborhood conditions for both the mixed and the pure dimers. At 100 °C we find that the diffusion rate of a Si-Si dimer is 3.5 times slower than a Ge-Si dimer, implying a higher diffusion barrier of ~40 meV (assuming identical prefactors). These data were acquired at an electric field of -0.4 V/Å. Here, it is important to specify the value of the electric field because the diffusion barriers can be altered by as much as 50 meV by fields between ± 1 V/Å.

Because the tip is continually maintained over the position of the adsorbed dimer during atom tracking, the dimer is constantly exposed to the electric field between the tip and the sample. This advantageously enables a comprehensive measurement of how the electric field alters the motion of the dimer [3,7]. The electric field depends on both the bias and the distance between the tip and the sample. For our measurements, we approximate this field using the value of the applied bias divided by the difference between the distance of the tip at the applied bias and at zero bias [7]. Negative field is defined as the sample at negative bias with respect to the tip.

We plot the measured change in diffusion barrier for adsorbed Ge-Si dimers as a function of electric field at 100 °C in Fig. 2 as solid symbols. The individual data points represent 30–80 min continuous tracking of an individual dimer. The scatter in the data is attributed to several factors: changes in the unknown and, more importantly, uncontrollable tip geometry, which affect both the field and field gradient; the fact that many different dimers, diffusing on different one-dimensional segments of substrate bounded by different defects (vacancies,

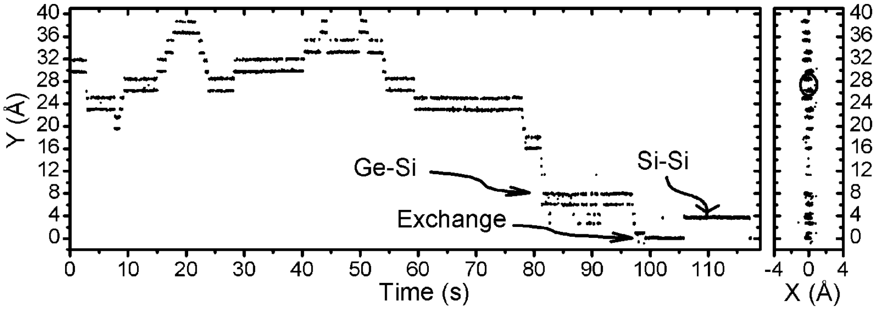

FIG. 1. Atom-tracking data for adsorbed dimer diffusion acquired at positive bias. Position versus time on the left and 2D scatter plot on the right. Ge-Si dimer is characterized by two clear rotation maxima at each lattice site. Data at a single lattice site are circled in the scatter plot. After an exchange event, Si-Si dimer has only one maximum at each site.

clusters) were measured; and small changes in temperature between experiments. The statistical, $\sqrt{N}$, error is much smaller than these. The data were acquired with bias voltages between ±3 V and tunnel currents between 0.05 and 0.15 nA.

For comparison we plot the electric field dependence for pure Si-Si dimers from Ref. [7] as open symbols. The offset of 0.04 eV between the Ge-Si and the Si-Si data is determined from their relative diffusion rates at 100 °C as described above. The field behavior of Si-Si dimers was analyzed in detail in Ref. [4]. Here, we find a significant difference between the field behavior of mixed Ge-Si dimers and pure Si-Si dimers. Specifically, for mixed dimers the slope of the barrier with field changes sign between negative and positive fields.

To determine the origin of this behavior, we performed DFT calculations of the field dependence for diffusion of adsorbed Ge-Si dimers. We used the VASP [15] electronic total-energy code, its ultrasoft pseudopotentials [16], with both the LDA and the Perdew-Wang 1991 version of the GGA [17] for the exchange-correlation functional. The Si(001) surface is modeled by a six layer slab with a 4×4 surface unit cell. The bottom two layers are fixed and terminated with hydrogen. Periodic images of the slab are separated by 10 Å of vacuum. One special k point is used to sample the irreducible quarter of the surface Brillouin zone. We used a plane-wave cutoff of 150 eV. To compute transition barrier energies we used the nudged elastic band method of Jónsson *et al.* [2]. The external electric field is implemented via a dipole layer in the vacuum [6].

The calculated field dependence of the barriers for the two processes using both GGA and LDA are shown with the measured data in Fig. 2. Consistent with previous calculations for Si-Si dimers [4], we find that the slope at zero field is about 90% determined by the difference in (zero-field) electric dipole between the transition states and the stable, lowest-energy, dimer configuration. This means that for any given process, the activation barrier is mostly linear in the field. Polarization effects that introduce quadratic or higher terms are small (see Fig. 2). The experimentally measured change in the sign of the slope therefore arises from two distinct processes in which the *difference* in dipole moment between the transition and stable states changes sign. In this case, the positive slope is due to so-called walking diffusion, and the negative slope is due to "piecewise" diffusion. That is, we induce a crossover between two distinct diffusion mechanisms with the electric field.

The dipole moments of the stable state and both transition states have the same sign (negative end toward the vacuum), which is not reversed by the field. We emphasize that whether the slope of the field dependence is positive or negative depends only on whether the dipole moment of the transition state is larger or smaller than the stable state. In our exploration of various mechanisms, only transition states with a broken dimer bond have dipole moments smaller than the stable state, which leads to a

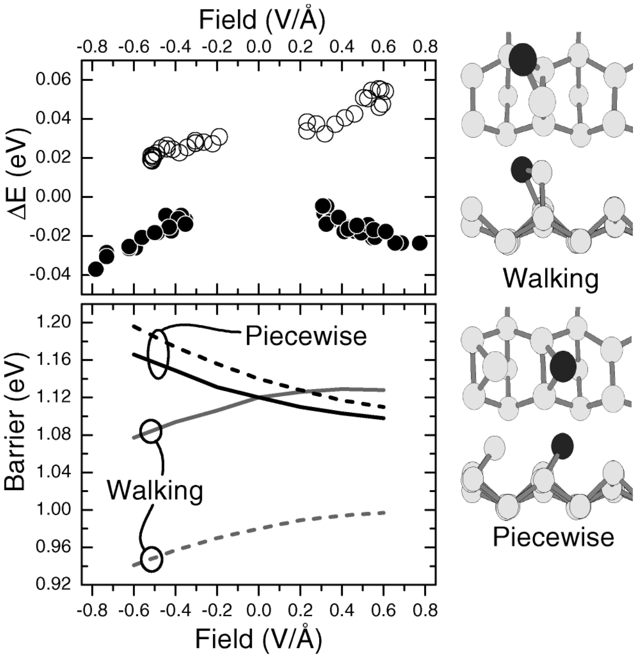

FIG. 2. Measured (top) and calculated (bottom) electric field dependence of adsorbed-dimer diffusion barrier. Solid symbols are the measured change in Ge-Si barrier relative to the interpolated zero-field value. Open circles are previously measured Si-Si data from Ref. [7] offset by their measured relative rate at −0.4 V/Å. The bottom panel shows the calculated barrier values for the two Ge-Si diffusion mechanisms, "walking" and "piecewise." Solid (dashed) lines are our LDA (GGA) results. Models of the transition states of the two processes are shown on the right.

TABLE I. Calculated and measured barriers for diffusion of Ge-Si and Si-Si ad-dimers. The diffusion mechanism cannot be determined in the experiments.

	Barrier (eV)		Barrier (eV)
	GGA	LDA	Experiment
Ge-Si walking	0.98	1.12	1.01 ± 0.09
Ge-Si piecewise	1.14	1.12	
Si-Si walking	1.06	1.22	0.94 ± 0.09 [12]; 1.09 ± 0.05 [13]
Si-Si piecewise	1.18	1.16	

negative slope of the energy barrier as a function of field. The smaller dipole moment is caused by a reduced filling of the dangling bond states that point toward the vacuum.

Further evidence that piecewise diffusion occurs at positive field is given by the fact that intermixing the Ge atom into the Si substrate is about an order of magnitude more likely at positive field than at negative field. In zero-field calculations, Lu *et al.* theoretically predicted the facilitation of Ge exchange by piecewise diffusion [18].

A more quantitative comparison between DFT and experiment is hindered by both uncertainties in the calculation and the experiment. The biggest source of theoretical uncertainty is the exchange-correlation (XC) approximation. Table I shows that LDA and GGA lead to barriers that differ by up to 0.16 eV and even the energetic ordering of barriers is XC-functional dependent [4]. However, the change in energy due to small changes in configuration or applied field is much more reliable.

The experimental uncertainty lies in approximating the magnitude of the applied electric field because of the difficulty in measuring the tip-sample separation and the falloff of the field within the semiconducting sample. Although the exact value of the field is difficult to ascertain, the sign of the field and the sign of the slope are measured with certainty.

In this work we have shown that measurements of the electric field dependence of kinetic processes combined with first-principles total-energy calculations can yield valuable information about the transition states. This increases our confidence when asserting the relevance of a particular calculated process based on necessarily incomplete transition state explorations. In addition, we can turn on and off the exchange mechanism by alternating the field with an STM. It may also be possible to alter intermixing in an electrolytic cell or by adsorption of weakly bound charged atoms like Cs. This technique would be an alternative to using adsorbed hydrogen to control the intermixing in Si-Ge multilayers [19].

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