

## Electric Field-Dependent Diffusion Mechanisms of Ge-Si Dimers on Si(001)

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**Motivation**—The desire to develop ever smaller functional electronic and mechanical structures—in which just a few atoms out of place could destroy their utility—necessitates a complete understanding of atomic motion at solid surfaces and material interfaces. This is particularly important during heterogeneous growth where surface diffusion could lead to undesirable alloying or unintended segregation. The exploration of compound semiconductor structures, such as Si-Ge quantum dots, for future nanoelectronic devices motivates the present diffusion studies.

**Accomplishment**—When Ge atoms are deposited onto a Si(001) surface they pair with Si atoms to form dimers. These heterogeneous Ge-Si dimers are adsorbed on the surface and become mobile at elevated temperatures. Using an atom-tracking scanning tunneling microscope (STM), we measured the diffusion rate of adsorbed Ge-Si dimers on Si(001) as a function of electric field at 100 °C. Because the diffusion rate depends exponentially on the diffusion barrier, small changes in the barrier can be easily measured.

The measured field dependence for Ge-Si dimers is strikingly different than that for pure Si-Si dimers. The diffusion barrier of Si-Si dimers increases monotonically as the applied field is changed from negative to positive, i.e., a continuous positive slope. However, in the case of Ge-Si dimers, the slope changes from positive to negative as the applied field changes sign. These data are shown at the top of Fig. 1. At positive field we observe that the Ge atom in the adsorbed dimer is about 10 times more likely to exchange into the substrate than at negative field. Although the dimers sit at individual sites long enough to measure where they are, the transition from one

site to the next happens so fast that the pathway cannot be measured experimentally. Fortunately, state-of-the-art first-principles calculations can determine the relative likelihood of arbitrary paths. With theory, the problem lies in determining which paths are actually relevant. We used density functional theory, modified to include the effect of an externally applied electric field, to investigate the field dependence of various low-energy diffusion paths.

We found two distinct processes that have the same diffusion barrier within the uncertainty of the calculations. In so-called "walking" diffusion, the dimer bond remains intact throughout the transition and is oriented parallel to the substrate dimer bonds. In "piecewise" diffusion, the dimer bond is substantially stretched at the transition state and is oriented perpendicular to the substrate dimer bonds. The key feature of the calculations is that the electric field dependence for the two processes is opposite to each other. The results of the calculations are shown at the bottom of Fig. 1. Comparison of the theoretical calculations with the measurements enables us to conclude that the diffusion process in negative field is that of walking diffusion, whereas, in positive field the dimers diffuse via the piecewise mechanism.

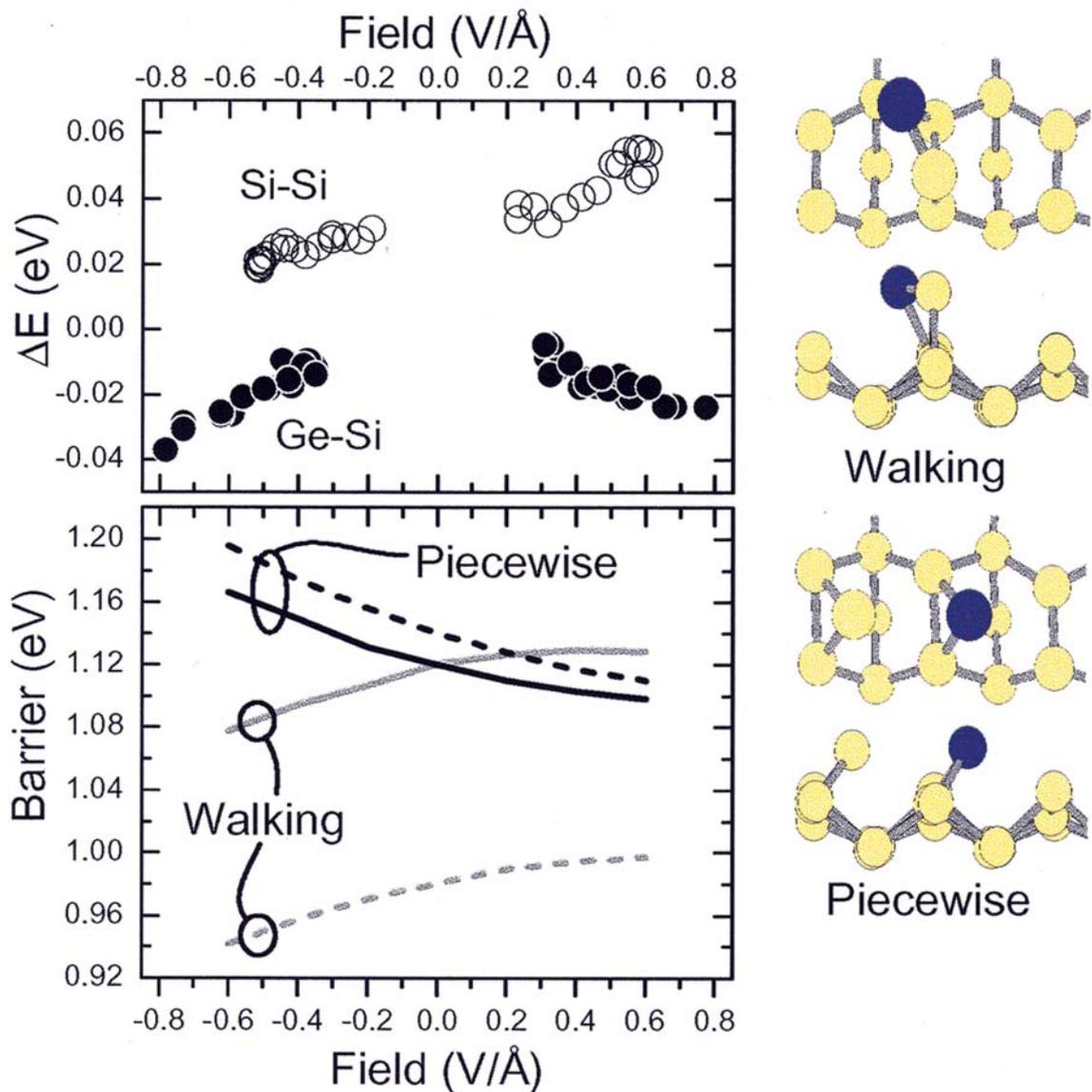
**Significance**—The electric field-dependence is a new way to control both the diffusion rate and material mixing during growth. As a research tool, field-dependent kinetic measurements combined with state-of-the-art first-principles total energy and barrier finding calculations provide a means to experimentally probe otherwise elusive transition state structures.

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**Figure 1.** Measured (top) and calculated (bottom) electric field dependence of adsorbed-dimer diffusion barrier on Si(001). Solid symbols are the measured change in Ge-Si barrier relative to the interpolated zero-field value. Open circles are measured Si-Si values offset from the Ge-Si data by their relative rates at at  $-0.4 \text{ V/\AA}$ . The bottom panel shows the calculated barrier values for the two Ge-Si diffusion mechanisms, "walking" and "piecewise". Solid (dashed) lines are the LDA (GGA) results. Models of the transition states of the two processes are shown at the right.