Dynamics of step fluctuations on a chemically heterogeneous surface of Al/Si(111)-(\sqrt{3}\times\sqrt{3})

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Received 14 December 2001; revised manuscript received 19 June 2002; published 29 August 2002

The analysis of the dynamics of equilibrium step fluctuations has been extended to a chemically heterogeneous surface. The multicomponent reconstructed Al/Si(111)-(\sqrt{3}\times\sqrt{3}) surface has been studied using variable-temperature scanning tunneling microscopy at elevated temperatures. The temporal correlation functions for both single steps and step arrays follow a $t^{1/2}$ dependence over the entire temperature range (770–1020 K), consistent with a rate limiting mechanism of random attachment and detachment of atoms at step edges. The alternative mechanism, diffusion from step-to-step, is shown to be inconsistent with more detailed analytic approximations to the correlation function for the measured step-step separation. An activation energy of 1.9 eV and the major kinetic parameters that govern surface mass transport and step equilibration processes have been determined.

DOI: 10.1103/PhysRevB.66.085327 PACS number: 68.37.Ef, 68.35.Md

INTRODUCTION

Steps play a significant role in determining the morphology of crystal surfaces and in such important processes as catalysis and thin film growth. Hence, step dynamics and their manifestation in the equilibrium thermal fluctuations of the step positions have attracted much attention, both experimental and theoretical (for recent reviews see Refs. 1, 2). Direct imaging techniques, such as low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) allow quantitative examination of step fluctuation dynamics based on analysis of the time-dependent correlation function $G(t)$:

$$G(t) = \langle [x(t + t_0) - x(t_0)]^2 \rangle,$$

where $x$ is the coordinate perpendicular to the step edge, $t$ is time, and the average is taken over all possible initial times. According to the basic Langevin approach, the temporal correlation function often obeys a power law

$$G(t) = C(T)t^\alpha.$$

The time exponent $\alpha$ depends only on the atomic mass transport processes involved in the step fluctuations, while the temperature dependent prefactor $C(T)$, is determined by the detailed energetics of the surface.\textsuperscript{3,4} Typical values of $\frac{1}{2}$ and $\frac{1}{4}$, observed for $\alpha$, correspond to cases $A$ and $B$ of dynamic critical phenomena,\textsuperscript{5} where random attachment/detachment of atoms at step edges and diffusion along step edges are examples of surface mass transport mechanisms belonging to these cases, respectively.

Surprisingly, experimental studies of step-fluctuation dynamics have so far been focused exclusively on clean surfaces of metals or semiconductors, despite the technological and scientific significance of chemically heterogeneous surfaces, in particular, metal-semiconductor systems. For a majority of the metal surfaces studied, only the $t^{1/4}$ dependence of the time correlation functions was observed, though a transition to $t^{1/2}$ behavior was found on Cu(111) with increasing temperature.\textsuperscript{7} In contrast, for semiconductors, silicon in particular, only $t^{1/2}$ dependence has been observed.\textsuperscript{1,2} For multicomponent systems, important questions to address are how adsorbate-induced reconstruction affects the time dependence of the temporal correlation function for a metal-semiconductor system in comparison with a clean semiconductor surface, and whether there is a single rate-limiting mass transport mechanism over a broad temperature range. In this report we present results of the study of the step fluctuation dynamics on a chemically heterogeneous surface, using the model metal-semiconductor Al/Si(111)-(\sqrt{3}\times\sqrt{3}) system. Step fluctuations have been studied as a function of time as well as temperature using variable temperature (VT) STM. We have determined a dominant (rate-limiting) microscopic mechanism, its effective activation energy, and the major kinetic parameters governing equilibrium step fluctuations and surface mass transport at elevated temperatures.

EXPERIMENT

The experiments were conducted in a UHV chamber (base pressure $\sim 6 \times 10^{-11}$ Torr) equipped with a VT STM (Omicron), a rear-view LEED (Physical Electronics Industries), and a mass spectrometer (Pfeiffer Vacuum). The vicinal Si(111) samples (As-doped, 10 mOcm) were misoriented by 0.5° towards the [112] direction. The Si surface was cleaned by several 5-s flashes at 1250 °C with subsequent slow cooling (~20°/min.) through the (1×1)-(7×7) phase transition. The Al/Si(111)-(\sqrt{3}\times\sqrt{3})R30° reconstructed surface was prepared by evaporation of 0.25–0.33 ML of Al at a deposition rate of 0.5 ML/min on a Si substrate held at 750 °C,\textsuperscript{8,9} and was monitored by LEED. The pressure rise during evaporation was below $3 \times 10^{-10}$ Torr, and the Al flux was monitored by a water-cooled quartz microbalance (Leybold Infinicon). The sample was resistively heated by direct current; temperature was controlled with an infrared pyrometer, which was calibrated to the (1×1)-(7×7) phase transition temperature of 850 °C. The sample heating power was also calibrated to control sample temperature during STM measurements. Before STM measurements at elevated temperatures, we waited $\sim 0.5$ h to allow thermal stabilization of the instrument. Quantitative information on the time dependence of the step fluctuations has been obtained from a...
measurements ranged from 3 to 9 nm/s. The invariance of the correlation function to the scanning shows that tip interactions do not perturb the measurement.

EXPERIMENTAL RESULTS

To acquire information about temporal fluctuations of steps at elevated temperatures, we collected STM time images in the temperature range 770–1020 K. The upper temperature limit is due to the decomposition of the (\(\sqrt{3} \times \sqrt{3}\)) phase via both Al diffusion into the bulk and evaporation at temperatures above 1020 K. At temperatures less than 770 K, step fluctuations are practically absent in the studied time intervals up to several minutes. In Fig. 1 is a typical STM time image of the scan line across two single-height steps on the Al/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) surface at 970 K. Notice that during a few seconds the step can fluctuate on the order of 100 Å. Because of fast atomic hopping processes at high temperatures and finite STM scanning speed, the apparent step edge position is different in each scan line, resulting in a frizzy appearance of the step edge, as has been observed earlier on several metal surfaces.11–14

Figure 2 shows the initial parts (\(t<3\) s) of the time correlation functions in a log-log plot for different temperatures between 770 and 1020 K. It is clear that the plots at each temperature are linear, and hence follow a power law.15 The time exponents vary between 0.41 and 0.52 with an average of 0.47, as shown in Table I. The corresponding prefactors, \(C(T)\) are shown in the last column of the table. They show a strong temperature dependence (\(\approx30\) increase) over the range of the measurements.

The measured exponents are consistent with \(t^{1/2}\) scaling of the temporal correlation function. Unfortunately, the observed scaling does not unambiguously determine the rate-limiting mechanism governing the fluctuations. An exponent of \(\frac{1}{2}\) is predicted theoretically5–7 for three distinct mass transport mechanisms. The first, exchange of atoms with the vapor phase, can be ruled out since the experiments were performed below the onset of decomposition that would indicate a loss of aluminum from the surface. The second, random attachment and detachment (AD) of atoms to/from an isolated step edge, is a likely possibility in the temperature regime studied. Steps on a vicinal surface are not strictly isolated, however, and this fact requires the careful consideration of a third mass transport mechanism: slow diffusion of atoms between neighboring steps with fast attachment and detachment at the steps themselves. This case, referred to as diffusion from step to step (DSS) in Ref. 5,
requires that the steps be close enough together (as discussed in the following section) to permit exchange.

Independent information about the kinetic mechanisms can be obtained by evaluating the multistep correlations. Khare and Einstein have shown theoretically\textsuperscript{5} that, for an infinite array of steps, the DSS mechanism has a distinguishing behavior of the correlation function of the sum of all step positions at time \( t \)

\[
x_S(t) = \sum_{k=-\infty}^{\infty} x_k(t),
\]

where \( k \) indexes the steps. The “in-phase” correlation function

\[
G_S(t) = \langle [x_S(t + t_0) - x_S(t_0)]^2 \rangle,
\]

is predicted to scale as \( t^{1/4} \) for DSS limited kinetics and \( t^{1/2} \) for AD limited kinetics. Figure 3 displays typical time correlation functions for the sum of real step positions in an array of 4 steps at 870 and 970 K. (Due to the presence of double steps on the surface, four was the largest array of adjacent monatomic steps available for consideration in the present study.) The average of the exponents, which are 0.37 and 0.45, is significantly closer to 0.5 than 0.25, supporting the likelihood that attachment and detachment from the step edges is rate limiting. However, the above scaling arguments are only strictly valid for an infinite step array. Thus, further theoretical analysis of the scaling for finite step arrays would be needed to conclusively interpret the results for \( G_S \) as eliminating the possibility that DSS may be the rate-limiting mechanism.

**ANALYSIS AND DISCUSSION**

Analysis of the equilibrium step fluctuations can provide both information about the rate-limiting kinetic mechanism and the quantitative values of the corresponding rate parameters. As noted in the presentation of the data above, the observed exponent of the time correlation function does not uniquely specify the mechanism. In the following, we will first provide an analysis based on the attachment/detachment mechanism, for which analytical expressions already exist in the literature.\textsuperscript{1-5} This will be followed by a discussion of the appropriate analysis for the diffusion step-to-step (DSS) case, and an evaluation of the relative applicability of the two cases.

The analytical expression relating the real-space time-correlation function to the underlying rate parameters for the attachment/detachment limited case is

\[
G(t) = [4 \Gamma b^2 / \pi a_p]^1/2 t^{1/2},
\]

where \( \Gamma \) is the step “mobility,” \( b^2 \) is the step diffusivity (see Table I), and \( a_p \) is the unit cell constant parallel to the step edge (5.76 Å).\textsuperscript{17} By equating the measured prefactors to the prefactor of Eq. (5), the values of step mobilities have been extracted and are listed in Table II. Over the temperature range from 770 to 1020 K, the step mobility increases from \( 2.4 \times 10^5 \) to \( 2.3 \times 10^6 \) Å\(^2\)/s. The step mobility describes how a step relaxes towards equilibrium and is related to the microscopic time scale for the underlying attachment and detachment mechanism as \( \Gamma = a_p^2 a_p / \tau \), where \( \tau \) is the mean microscopic time between successive random attachment or detachment events on an arbitrary step site, and \( a_p \) is the unit cell constant normal to the step edge.\textsuperscript{17} Since each local movement of a [112] step proceeds in half units of the (v3xv3) reconstruction,\textsuperscript{18} the value of 3.33 Å has been used for \( a_n \). Consequently, we deduce that the time constant decreases from 260 to 0.28 ms when temperature increases from 770 to 1020 K, as shown in Table II. The attachment and detachment times extracted here correspond to the quite substantial exchange rates 1/\( \tau \) between steps and terraces of \( \sim 4 - 4500 \) atoms/s per site. Such rates are sufficient for the steps to maintain an equilibrium concentration of adatoms on terraces, for the case that the exchange rates are not limited by terrace diffusion.\textsuperscript{19,20}

The evaluation of the kinetic parameters from real-space fluctuation data is less straightforward for the DSS case. This is because the DSS mechanism is valid over a limited range of fluctuation wavelengths. Specifically, DSS only occurs for wavelength wavelengths \( \lambda > 4 \) - 4500 atoms/s per site. Such rates are sufficient for the steps to maintain an equilibrium concentration of adatoms on terraces, for the case that the exchange rates are not limited by terrace diffusion.\textsuperscript{19,20}

![Graph](image-url)
crossover to terrace diffusion (TD) limited kinetics (for which the time correlation function is proportional to $t^{1/3}$) should be observed. This crossover occurs in a narrow range and recent detailed analysis shows that it can be approximated as occurring abruptly at a wavelength $q \sim 1.0/L$. A resulting expression for the real-space time correlation function is obtained by integrating the wavelength-dependent DSS behavior’ from $q = 0$ to $q = 1/L$, yielding

$$G(t) = \frac{2b^2L}{\pi a_p} \left[ \sqrt{\frac{tA_3}{L^3}} \text{Erf} \left( \sqrt{\frac{A_3}{L^3}} \right) + \left( \frac{tA_3}{L^3} \right)^{1/3} \Gamma \left( \frac{2}{3}, \frac{tA_3}{L^3} \right) \right],$$

where $c_t$ and $D_t$ are the concentration and diffusion constant for atoms on terraces, respectively. Using this formula with $L$ fixed at 450 Å and only $c_t D_t$, as a variable parameter results in a poor fit to the experimentally determined correlation functions. The values of $c_t D_t$ found in this way are abnormally low, varying within $10^2$ s$^{-1}$ at 1020 K to 0.01 s$^{-1}$ at 770 K. The only way to force a reasonable fit was to reduce the mean terrace width in Eq. (6) by at least a factor of 10. The fact that Eq. (6) cannot be used to fit the correlation function with the true step separation demonstrates that the steps are too far apart for DSS to contribute to the fluctuation kinetics.

The weight of the evidence leads us to interpret the observations in terms of a physical mechanism that is rate limited by atomic attachment/detachment events at the step edge. Given no prior measurements on chemically heterogeneous surfaces, attachment/detachment times may best be compared with the time constant determined for the similar Si(111)-(1×1) surface at 1170 K. The (v3×v3) surface phase is indeed formed by the bonding of Al adatoms to the Si (1×1) layer at $T_A$ sites. If the step fluctuations on the Si(111)-(1×1) surface are evaluated in terms of the attachment and detachment mechanism, the time constant is found to be $\tau \sim 10^{-3}$ ms, about $10^{-2}$ times the value obtained here for Al/Si(111)-(v3×v3) at 1020 K. The difference is consistent with an activation process with an energy in the 1–2 eV range, confirming that the magnitudes of time constants obtained in this study are reasonable.

Since the atom exchange between step and terrace is a thermally activated process, its rate can be related to the activation energy $E$ through

$$1/\tau = v_0 \exp(-E/kT),$$

where the pre-exponential factor $v_0$ is an attempt frequency. Figure 4 shows an Arrhenius plot for the attachment rate. The data points for different temperatures fall along a straight line, yielding an activation energy of $1.9 \pm 0.1$ eV. This activation energy is much greater than the kink formation energy of $\sim 0.2$ eV. This fact is reflected in the great difference in the temperature variation of the step mobility and step diffusivity evident in Tables I and II. From the intercept of the linear fit, a pre-exponential factor of $6 \times 10^{12} \pm 2$ s$^{-1}$ has been found, in reasonable agreement with the canonical vibration frequency $kT/h$. The interpretation of the measured activation energy is not straightforward, because the Al-Si(111)-(v3×v3) surface is reconstructed and also has more than one component. Although details of the atomic transport process leading to the step fluctuations are unknown, the rate-limiting detachment event probably involves the motion of one aluminum atom along with concerted motion of several silicon atoms, since each Al atom interacts with three Si atoms of the underlying Si (1×1) layer. The attachment will require similarly complex structural changes to simultaneously incorporate additional Al and Si atoms into the step edge. It is plausible that, despite the multiple bond breakings and formations involved, the rate-limiting activation energy would be close to a single Si-Si or Si-Al bond strength of $\sim 2$ eV. Just for comparison, we note that an attachment activation energy for the Si(111)-(1×1) surface was estimated to be $\sim 1.5$ eV.

**CONCLUSIONS**

In summary, analysis of the dynamics of equilibrium step fluctuations has been extended to a chemically heterogeneous surface for the first time. The temperature-dependent study on a model metal-semiconductor surface of Al/Si(111)-(v3×v3) has been carried out using variable-temperature STM. Quantitative examination of step fluctuation dynamics was based on analysis of the time-dependent correlation function for both single steps and step arrays. In the entire temperature range 770–1020 K, where step mobilities are high enough to ensure equilibration, the correlation function displays power-law time dependence with an average exponent of 0.47±0.04. The possibility that the observed behavior is due to slow terrace diffusion from step to step (DSS) was not consistent with either an analysis of the in-phase multistep correlation function or fits to a recent analytic approximation that properly includes the contribution of terrace-diffusion limited behavior at wavelengths much smaller than the step separation. Thus the surface mass transport mechanism is most likely the random attachment and detachment of atoms at the step edge. The kinetic parameters governing mass transport and step equilibration have been extracted in the studied temperature range, with a micro-
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scoposcopic time constant and step mobility varying between 0.28–260 ms and 2 \times 10^5 – 2 \times 10^7 \text{ Å}^3/s, correspondingly. From the temperature dependence of the kinetic parameters, the activation energy for the rate-limiting step in attachment from the terrace onto the step edge has been found to be 1.9 eV. A case such as this, where the underlying atomic mechanisms must involve correlated bond making and breaking among several different species, poses a serious challenge for an analysis based on identifying a small number of rate-limiting parameters which dominate the overall behavior. The strength of the continuum step model is that it does focus attention on the macroscopic kinetic parameters rather than microscopic energies, the physical interpretation of which must be viewed with some skepticism. The success of this approach for the Al/Si multicomponent system, especially over a broad temperature range, provides increased confidence in the applicability of the kinetic parameters extracted from analysis of step fluctuation data.

ACKNOWLEDGMENT

This work has been supported by the NSF-MRSEC under Grant No. DMR-00-80008.

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At larger times, the experimental points deviate from linear behavior when the fluctuations become limited as the amplitude increases to be comparable to the terrace width [N. C. Bartelt, T. L. Einstein, and E. D. Williams, Surf. Sci. 276, 308 (1992); M. Giesen-Seibert, F. Schmitz, R. Jentjens, and H. Ibach, ibid. 329, 47 (1995)].


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Even if the usual pure power law behavior for DSS is assumed as in Ref. 2, the temperature range of the present study requires that a crossover from TD to DSS be observed. From Ref. 21, \( q_{\text{cross}}^2 = 2 \pi / \lambda_{\text{cross}} \sim 1.0 / L \), or \( \lambda_{\text{cross}} \sim 2800 \text{ Å} \) for \( L = 450 \text{ Å} \). For diffusion limited step fluctuations (as in DSS) the time constant of a given wavelength fluctuation is (Refs. 3 and 5) \( \tau(\lambda) = b^2 L \lambda^2 / (2 \pi)^2 a_p \Omega^2 c D \). Thus, using a conservative estimate of 5 s for the times sampled in our measured correlation functions shows that the 870 and 920 K measurements only sample wavelengths less than the crossover. Using the better approximation in Eq. (6) allows the more transparent interpretation in terms of mean terrace width.


