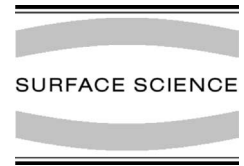




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Surface Science 492 (2001) L671–L676



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Surface Science Letters

# Step wandering on Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) surface at high temperatures

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Received 19 June 2001; accepted for publication 19 July 2001

## Abstract

Step fluctuations on a multi-component surface of Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) were studied using variable-temperature STM at temperatures 770–1020 K. The reduced step diffusivity,  $b^2/a$ , has been found to vary from 0.45 Å at 770 K up to 1.00 Å at 1020 K. Its temperature dependence follows the expected exponential law, from which the effective energy of kink formation has been determined to be 0.214 eV. Above 870 K, temporal effects complicate the analysis of the spatial pair correlation function. It is demonstrated that consistent results can be obtained in this case by employing surfaces quenched to room temperature. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Equilibrium thermodynamics and statistical mechanics; Scanning tunneling microscopy; Aluminum; Silicon; Stepped single crystal surfaces; Metal–semiconductor interfaces

Steps play a fundamental role in determining the morphology of crystal surfaces and in many important surface processes, both at low and high temperatures. 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 [1,2]). Direct imaging techniques, such as low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) allow *quantitative* examination of individual step configurations and their fluctuations. Surprisingly, there

are few experimental studies of step behavior on surfaces modified by adsorption-induced reconstruction [3–5], including metal–semiconductor systems, despite their technological and scientific significance. In addition, most STM studies have been carried out with STM at or within a few hundred degrees of room temperature. This temperature range is sufficient for equilibrating many metal surface structures [6,7], but semiconductor surface mobilities are generally too low for equilibration near room temperature. Room temperature STM has often been used previously to obtain information on step wandering at high temperatures by measuring the quenched surfaces [3,5, 8–11]. Evaluating the equilibrium temperature, required to extract accurate values of step parameters from experimental data, poses a particularly severe problem in interpreting the measurements. In addition, it is unclear how accurately these

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measurements reproduce the actual step-fluctuation parameters at elevated temperatures. In this letter we report on a temperature-dependent STM study of the step fluctuations on the chemically heterogeneous surface of Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) at high temperatures. We have compared the step correlation functions measured at high temperature and on quenched surface, and used the temperature dependence of the step diffusivity to determine the effective kink formation energy, which controls the individual step fluctuations on an atomic scale.

The experiments were conducted in a UHV chamber (base pressure  $\sim 6 \times 10^{-11}$  Torr) equipped with a variable-temperature STM (Omicron), a rear-view LEED (Physical Electronics Industries), and a mass spectrometer (Pfeiffer Vacuum). The vicinal Si(1 1 1) samples (as-doped, 10 m $\Omega$ cm) were misoriented by 0.5° towards the  $[\bar{1}\bar{1}2]$ -direction. The Si surface was cleaned by several 5 s flashes at 1250 °C with subsequent slow cooling ( $\sim 20^\circ/\text{min}$ ) through the (1  $\times$  1) to (7  $\times$  7) phase transition. The Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ )R30° reconstructed surface (Al coverage of 0.25–0.33 ML [12]) was prepared by Al evaporation at a deposition rate of 0.5 ML/min on a Si substrate held at 750 °C [12,13] and was monitored by LEED. The pressure rise during evaporation was below  $3 \times 10^{-10}$  Torr, and the Al flux was controlled by a water-cooled quartz microbalance (Leybold Inficon). The sample was resistively heated by direct current and temperature was controlled with an infrared pyrometer, which was calibrated to the (1  $\times$  1)-(7  $\times$  7) phase transition temperature of 850 °C. We found no difference in surface morphology for different heating current directions after Al deposition. The sample heating power was also calibrated to control sample temperature during STM measurements. Before STM measurements at elevated temperatures, we have waited  $\sim 0.5$  h to allow thermal stabilization of the instrument. Quantitative information on step wandering has been obtained from a statistical analysis of STM images. Studies in this work have focused on step fluctuations and one of the fundamental step parameters—diffusivity. Investigation of the terrace width distribution was not included because of non-uniformities in surface morphology

over large length scales, due to the phase separation of the forced kinks [14] (which are present because of the small azimuthal misorientation from the  $[\bar{1}\bar{1}2]$  direction), and also due to the mixture of single- and double-layer steps on the Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) surface. For measurements of the step correlation functions, only segments of the monatomic steps that are free of forced kinks have been analyzed. Thus, the results presented correspond to the step diffusivity of a step with no azimuthal misorientation. Single step segments used for analyzing the correlation function ranged in length from 200 to 500 nm, with typically 10–20 such segments were used in the analysis of the correlation function. Scan rates used in the measurements ranged from 3 to 15  $\mu\text{m/s}$ . To check that tip interactions do not perturb the measurement, the invariance of the correlation function to forward vs. reverse scanning and to the scanning rate was confirmed.

To acquire information about thermal fluctuations of steps at elevated temperatures, we have collected STM images in the temperature range 770–1020 K. The upper temperature limit is set by decomposition of the ( $\sqrt{3} \times \sqrt{3}$ )-phase due to both Al diffusion into the bulk and evaporation at temperatures above 1020 K. The low temperature limit is required to ensure enough step mobility for equilibration. A typical STM image of the Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) surface at 970 K, containing several single-height steps, is shown in Fig. 1a. The surface height decreases from right to left in the  $[\bar{1}\bar{1}2]$  direction. The terrace widths are 400–500 Å. The overall step structure appears to be close to equilibrium, at least up to the length scale of an image, since we have not observed significant changes in surface morphology even after several hours at high temperature. 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 [15,16]. Such frizziness has been observed earlier on a number of metal surfaces [16–18], and, essentially, is caused by step motion between sequential scans of the STM image. For this reason, at higher temperatures an image represents not only spatial but also temporal step fluctuations [16,17]. At lower tem-

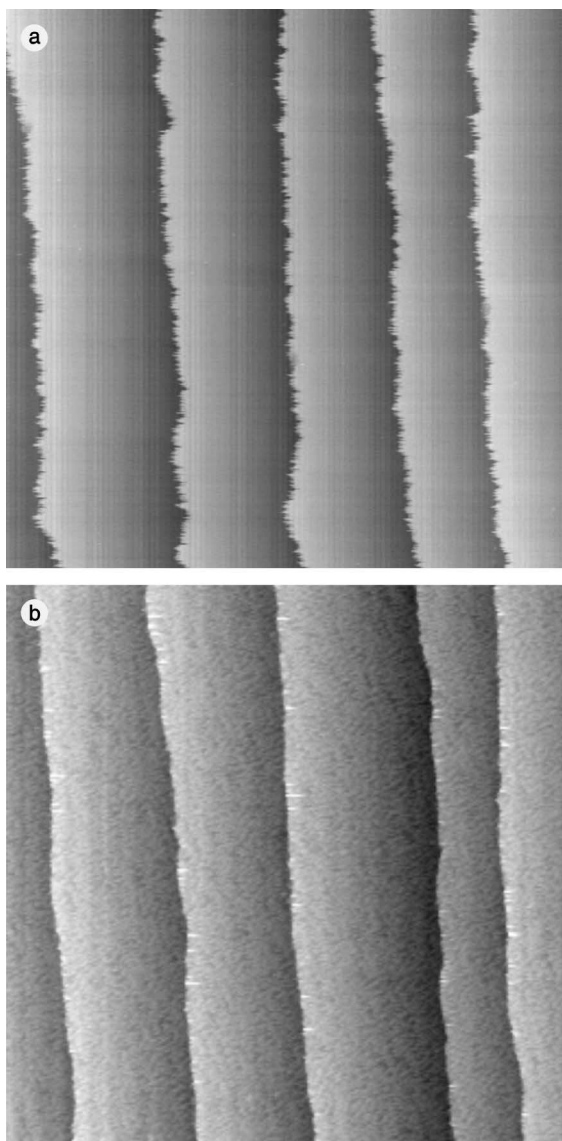


Fig. 1.  $2500 \times 2500 \text{ \AA}^2$  STM images ( $I = 0.05 \text{ nA}$ ,  $V = -3.5 \text{ V}$ ,  $S = 9000 \text{ nm/s}$ ) of an Al/Si(1 1 1)- $(\sqrt{3} \times \sqrt{3})$  surface (a) taken at 970 K and (b) quenched from 970 K and taken at room temperature.

peratures the step mobility is decreased, and for the Al/Si(1 1 1)- $(\sqrt{3} \times \sqrt{3})$  structure at  $\leq 870 \text{ K}$  the frizzled appearance of the step edges is significantly reduced. The spatial step fluctuations have been analyzed in terms of the mean-square step displacements by finding the step correlation function,  $G(y)$ :

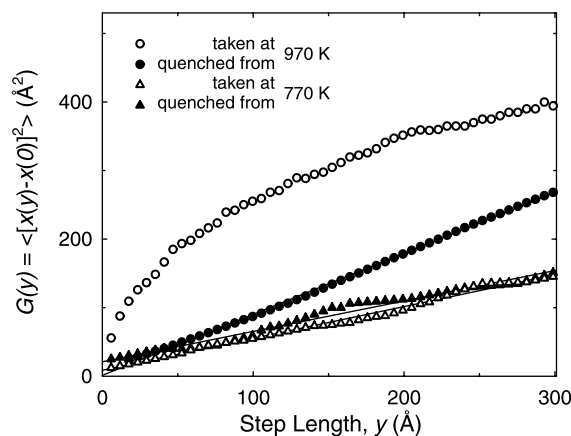


Fig. 2. Initial parts of the step correlation functions  $G(y)$  (cf. Eq. (1)) for 970 and 770 K acquired from STM images of surfaces both at elevated temperatures and quenched to the room temperature. The straight lines (cf. Eq. (2)) are the linear regressions.

$$G(y) = \langle [x(y + y_0) - x(y_0)]^2 \rangle, \quad (1)$$

where  $x$  and  $y$  are coordinates perpendicular and parallel to the step edge. Fig. 2 shows the initial parts of  $G(y)$  as a function of the step-edge distance  $y$  for two temperatures: 770 and 970 K. The correlation function behavior is quite different at these temperatures: it is linear at 770 K but deviates significantly from linearity at 970 K. From the well-known small- $y$  result of the continuum step model [19]:

$$G(y) = yb^2/a_p \quad (2)$$

(where  $b^2$  is the step diffusivity and  $a_p$  is the unit cell constant parallel to the step edge), the low temperature reduced step diffusivity,  $b^2/a_p$ , can be extracted from the initial linear region of the correlation function. With increasing temperature, the correlation function has the form of a fractional power law. This is due to the non-negligible time structure of step fluctuations [16,17]. Hence, the initial slope of the correlation functions obtained from STM images taken at temperatures above 870 K cannot be used for evaluation of the step diffusivity in the same simple way.

To obtain the dependence of the step diffusivity on temperature in the range above 870 K, we used samples which were prepared at such elevated

temperatures, then quenched to room temperature at an initial cooling rate of more than 200 K/s. Fig. 1b displays an STM image of the surface quenched from the temperature of 970 K and taken at room temperature. In comparison with the image taken at 970 K, Fig. 1a, the steps appear straighter here due to the absence of the frizzy kink-like features caused by the time fluctuations, and a number of ‘real’ kinks are clearly visible.<sup>2</sup> The initial parts of the step correlation functions for the surfaces quenched from 770 and 970 K are also shown in Fig. 2. The correlation functions measured at 770 K and on the surface quenched from 770 K are practically the same; in particular, they have the same initial slope. This is direct evidence that step configurations on a quenched surface correspond to an ‘effective’ temperature which is very close to the temperature prior to quenching. For the structure quenched from 970 K, the correlation function is also linear; thus, its slope should lead to a reasonable estimate of the diffusivity at 970 K.

In Fig. 3, we present the step correlation functions in the studied temperature range, using images taken at elevated temperatures for 770–870 K and images of quenched surfaces for higher temperatures 920–1020 K. All functions are linear up to spacings  $y$  along the step edge of 800 Å, and their slopes increase with increasing of temperature from  $b^2/a_p$  equaling 0.45 Å at 770 K up to 1.00 Å at 1020 K.<sup>3</sup> At larger  $y$ , the slopes decrease due to the step–step repulsions [22]. For the somewhat similar Ga/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) system, the step diffusivity was found to be larger (3.4 Å at 820 K) [4]. The values of step diffusivities deter-

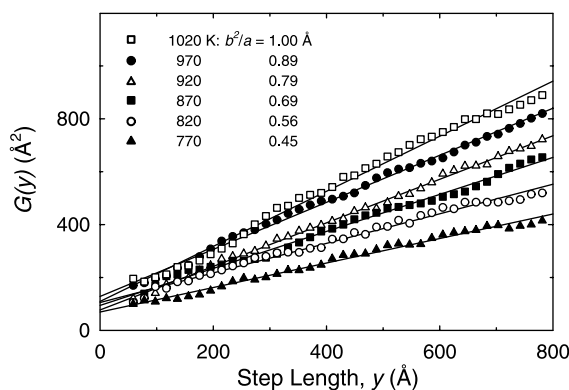


Fig. 3. Step correlation functions in the studied temperature range 770–1020 K. The images taken at elevated temperatures and the images of quenched surfaces were used for temperatures  $\leq 870$  and  $\geq 920$  K, respectively. Straight lines are the linear regressions for each temperature.

mined in the present work are also smaller than obtained in an earlier investigation of the Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) surface in our group (2.2 Å at 1040 K) [5]. The difference, most likely, is due to the probable coexistence of another Al–Si surface phase, the  $\gamma$ -phase, in that study. This phase starts to nucleate at step edges resulting in the formation of a corrugated structure along the steps [12,20], that resembles steps with increased wandering.

Within the TSK model the diffusivity depends exponentially on the ratio of the kink and thermal energies [19,22], and for a hexagonal (1 1 1) lattice (in low temperature limit) [23,24]:

$$b^2/a_p = (3/2)a_p \exp(-\varepsilon/kT). \quad (3)$$

This or similar expressions were employed previously to estimate the kink energy,  $\varepsilon$ , based on data collected at a single temperature. In this case, the specific value extracted for the kink energy depends explicitly on the prefactor, and thus the details of the lattice model used to describe the system. From an Arrhenius plot of the measured diffusivities (Fig. 4), we can extract an effective kink energy, independent of any assumptions about the atomic nature of the elemental excitation. The data points for different temperatures fall fairly well along a common line, giving a value of the activation energy of 0.214 eV for kink creation. This linear dependence is quantitative confirmation that evi-

<sup>2</sup> There is another difference between these two images: the terraces at 970 K look featureless while there are small bright and dark spots on terraces in the image of the quenched surface. These different spots correspond to the Al atoms and Si substitutions of Al atoms in the ( $\sqrt{3} \times \sqrt{3}$ )-overlayer [21]. Therefore, this observation may indicate that the frequency of exchange of Al and Si atoms is so high at 970 K that a uniform (average) background in the STM image results.

<sup>3</sup> The non-zero offset, larger than in Fig. 2, originates mostly from increase of the uncertainties in the measurement of the step position with increasing pixel size in STM image. The data in Fig. 3 have been extracted from images larger by order of magnitude—( $1 \times 1 \mu\text{m}^2$ ) to increase statistics by registering more steps per image.

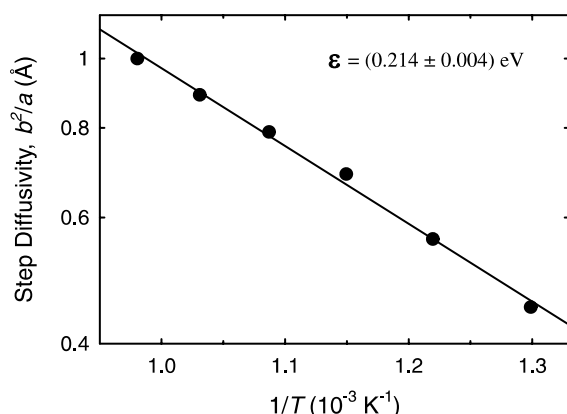


Fig. 4. Arrhenius plot of the reduced step diffusivity (the straight line is a linear regression).

dently the quenched surfaces maintain the correlation functions of the temperatures from which they were quenched. As noted above, this approach to analysis of the diffusivity by averaging data over all temperature range is not sensitive to the exact form of the exponential prefactor in Eq. (3) and increases the accuracy of the kink energy determination, which has been  $\pm 0.004$  eV. The relatively low kink energy for Al-induced surface reconstruction is responsible for the rather high amount of step wandering observed in the studied temperature range. Since to the best of our knowledge the kink energy for the steps on Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) surface has never been calculated, the value for the similar <sup>4</sup> Si(1 1 1)-(1  $\times$  1) surface may serve for comparison. Both the value of 0.466 eV, calculated using empirical potential [26], and the value of 0.23 eV, derived from experiment [9,27], indicate that the magnitude of kink energy obtained in this study is reasonable.

In summary, the temperature dependent study of step wandering on a chemically heterogeneous metal–semiconductor surface of Al/Si(1 1 1)-( $\sqrt{3} \times \sqrt{3}$ ) has been carried out using variable-temperature STM at temperatures 770–1020 K. At temperatures above 870 K, strong temporal fluctuations affect the step edge appearance in the STM images,

<sup>4</sup> The ( $\sqrt{3} \times \sqrt{3}$ ) surface phase is formed by the bonding of Al adatoms to the Si(1  $\times$  1)-layer at T<sub>4</sub> sites [21,25].

and cause temporal information to be coupled into the measured spatial correlation function. This effect can be removed, while preserving the spatial variations of high temperature, by employing surfaces quenched to room temperature. The resulting dependence of reduced step diffusivity on temperature follows the expected exponential dependence on  $1/kT$ , with magnitude that varies from 0.45 Å at 770 K to 1.00 Å at 1020 K. The effective energy of kink formation has been determined to be 0.214 eV, consistent with typical values of kink formation energies on Si(1 1 1)-(1  $\times$  1) surfaces.

### Acknowledgements

This work has been supported by the NSF-MRSEC under grant DMR-00-80008.

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