Determination of Step Free Energies from Island Shape Fluctuations on Metal Surfaces

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The absolute measurement of free energies associated with crystal steps on a metal surface has been a long-standing problem. We report a reliable estimate of the step free energy on a Cu(111) crystal surface, based on an analysis of island shape fluctuations directly imaged by scanning tunneling microscopy. The result of 0.22 eV per atomic distance for steps running into close-packed directions is in good agreement with theoretical predictions. [S0031-9007(99)09095-X]

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The step free energy is one of the fundamental quantities used to describe real crystal surfaces. It is defined as the free energy required to create a crystal step and it can be regarded as the low-dimensional analog of the surface free energy. Just as the angular variation of the surface free energy determines the equilibrium shape of three-dimensional crystals via the famous Wulff construction [1], the variation of the step free energy with angle determines the equilibrium shape of monolayer islands on a crystal surface. Moreover, as stated by the well-known Gibbs-Thomson relation [1], this quantity is proportional to the chemical potential of monolayer islands and curved steps, and hence its magnitude is directly linked to mass transport rates close to equilibrium.

Given the fundamental importance of this material parameter, it is amazing how little experimental information is available on this quantity, at least for metal surfaces. While several estimates based on various computational schemes exist, experiments have mostly been limited to the determination of the *relative* magnitude of the free energies of differently oriented steps from equilibrium island shapes. A prominent example of studies of this type is the work of Michely *et al.* who determined a ratio of 0.87 ± 0.02 for the step energies of so-called type B and type A steps on Pt(111), i.e., the (111)- and (100)-microfaceted close-packed steps [2]. This experimental result has been a challenge for advanced *ab initio* energy calculations [3], and could be reproduced only recently by calculations of Boisvert *et al.* [4]. Experiments suited to reliably determine the *absolute* value of the step free energy on metal surfaces, however, are hardly available [5]. Bonzel has estimated absolute step energies on metals by extrapolating old results on surface free energies at temperatures close to the melting point to low temperatures using the terrace-ledge-kink model and available estimates of step entropies [6]. For the Ag(111) surface, Morgenstern *et al.* have estimated the step free energy at about room temperature to 0.22 eV per atomic distance a by studying the decay of Ag adatom islands and fitting the shape of island decay curves with a theoretical model based on the Gibbs-Thomson equation [7]. This result is not unreasonable but still significantly larger than the corresponding theory result for the step formation energy of 0.156 eV$/a$ at 0 K as calculated by Stoltze using effective medium theory (EMT) [8]. The same experimental procedure applied to the Cu(111) surface by Schulze Icking-Konert *et al.* [9] resulted in an even larger discrepancy: 0.45 eV$/a$ compared to an EMT result of 0.208 eV$/a$ [8], questioning whether or not this approach measures indeed the true step free energy [10].

In this paper we describe a method to determine the step free energy on metal surfaces which appears to be more reliable. We measure the amplitude of island shape fluctuations around the equilibrium shape which can be directly related to the step free energy. The advantage of this approach is that the experiments are performed under conditions of equilibrium and constant island size, and hence the method does not require the knowledge of any mass transport rates and is immune against peculiar size effects as, for instance, size-dependent electronic contributions to the free energy of an island [11]. In this paper, we study the shape fluctuations of monatomically deep vacancy islands on a Cu(111) surface at temperatures between 263 and 343 K using scanning tunneling microscopy (STM). From the amplitude of the fluctuations we obtain an estimate for the step free energy of $\gamma = 0.22 \pm 0.02$ eV$/a$. This value is in good agreement with the EMT result of 0.208 eV$/a$ [8].

The experiments were performed in a ultrahigh vacuum chamber with a base pressure of 8×10^{-11} mbar. The

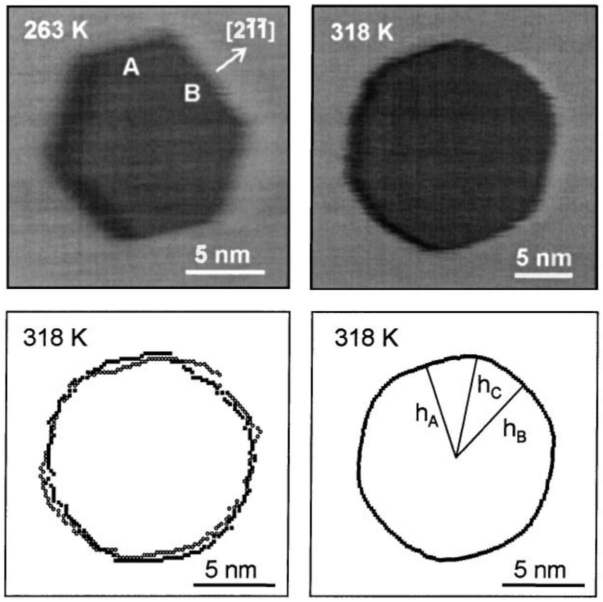

FIG. 1. Shapes of vacancy clusters on Cu(111). Top: STM images of vacancy clusters at 263 K (left) and 318 K (right). The two different types of close-packed steps (i.e., steps running in $\langle 110 \rangle$ directions) are indicated (labeled A and B for the $\{100\}$- and $\{111\}$-microfaceted steps, respectively). Bottom: Cluster contours at 318 K derived from two single STM images (left) and averaged over 17 images (right).

STM itself is a modified "beetle" similar to the ones described in [12]. The sample was prepared by cycles of sputtering with Ar^+ ions (600 eV) and annealing to 850 K. The mean terrace width of the sample was more than 200 nm. Monatomically deep vacancy islands were induced by bombardment with Ar ions at 270–290 K. The sample was then heated to 350 K to let the adatom islands decay which were also produced by the ion pulse. Finally, the sample was cooled to the temperature of the experiments.

In each measurement, a sequence of STM images was recorded at time intervals of 20 s and a spatial resolution (pixel size) of $0.36 \times 0.36\ \mathrm{nm}^2$. The time interval appeared to be long enough to avoid correlations between consecutively measured cluster shapes. Moreover, we did not find an influence of the finite scanning time of one island (typically 1 s) on the shape fluctuations. Tunneling voltage and current were in the range of $|U| = 0.7{-}1.0$ V and $I = 0.3{-}0.5$ nA, respectively. For the high gap resistances corresponding to these values, no tip effect on island dynamics was observed [13]. During a measurement (lasting up to 1200 s), the vacancy cluster size did not change significantly (at the highest temperature of 343 K, the size decreases only by $\approx 10\%$ in one hour due to adatoms filling the vacancy islands). Details about the apparatus and the experimental procedure are described elsewhere [13].

The fluctuation of the vacancy cluster shape is derived from STM measurements by comparing the shape found in a single image to the mean cluster shape obtained by averaging a large number of STM images of the same cluster. Figure 1 (top) shows representative STM images of vacancy clusters at two temperatures. Also shown [Fig. 1 (bottom)] are contours found in two single measurements and the mean shape of a cluster at 318 K derived from 17 consecutively measured STM images. The mean shape represents the equilibrium shape, and hence we can derive the ratio of the free energies of A and B steps from the ratio of the normal distances h_A and h_B (cf. Fig. 1). The result of $\gamma_B/\gamma_A = h_B/h_A = 1.02 \pm 0.02$ is in agreement with previous work [14]. Because of the almost perfect hexagonal symmetry, we can further estimate the anisotropy of the step free energy (i.e., the maximum variation of γ with polar angle) from the ratio of h_C to h_A, where h_C denotes the normal distance of the corners (cf. Fig. 1). We obtain an anisotropy of about 7% at temperatures between 318 and 343 K, and about 10% at 263 K.

To quantify the shape fluctuations, we follow the work of Khare and Einstein [15] and define the instantaneous position of the cluster edge in cylindrical coordinates by a function $r(\theta, t)$, where r and θ are the radius and polar angle, respectively, and t is the time. Since the origin of the coordinate system can be chosen freely, we define it at any time in such a way that it coincides with the center of mass of the cluster. If we define the function $R(\theta)$ as the time-averaged position of the cluster's edge relative to its center of mass, we may describe the deviation from the average shape in terms of a dimensionless variable $g(\theta, t)$ [15]:

$$g(\theta, t) = \frac{r(\theta, t) - R(\theta)}{R(\theta)}\,. \tag{1}$$

We further define a fluctuation function G by

$$G = \frac{R^2}{2\pi} \int_0^{2\pi} g^2(\theta, t)\, d\theta\,, \tag{2}$$

where R denotes the average value of $R(\theta)$. By writing $g(\theta, t)$ in Fourier representation $\sum_n g_n(t) \exp(in\theta)$, one can express G in terms of the Fourier components g_n (for which the condition $g_n = g_{-n}^*$ guarantees that g is real):

$$G = R^2 \sum_{|n|>1} |g_n(t)|^2. \tag{3}$$

Note that the sum extends only over values $|n| > 1$ because, if the deviation from the equilibrium shape is small and the origin has been chosen at the cluster's center of mass, g_1 and g_{-1} vanish and the contribution of $n = 0$ can be neglected.

To relate the measurable quantity G to the step free energy we use the theory of shape fluctuations of nearly circular clusters (cf. [15]). The free energy of the cluster contour is given by $F = \int_r \gamma\, ds$, where $ds = \sqrt{r^2 + (\partial r/\partial\theta)^2}$. Substitution of Eq. (1) results in an expression for the increase in free energy due to a deviation from the equilibrium shape:

$$\Delta F = F - F_0 = \pi \overline{\gamma} R \sum_{|n|>1} (n^2 - \alpha)\, |g_n(t)|^2, \tag{4}$$

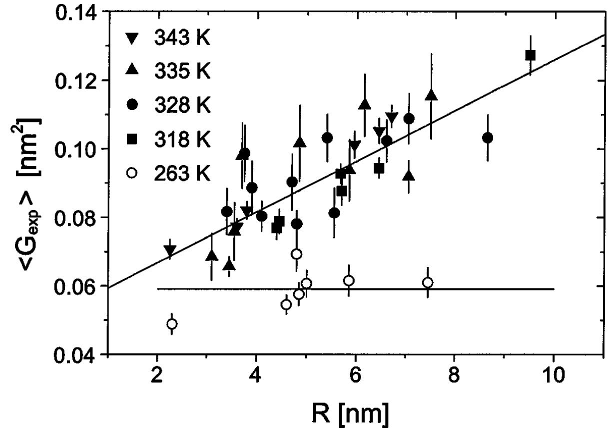

FIG. 2. Shape fluctuation function $G_{\rm exp}$ (for a definition, see text) as a function of mean cluster radius R for different temperatures as indicated.

where $F_0 = \int_R \gamma\, ds$ (i.e., the line integral of γ along the averaged contour of the island, i.e., the equilibrium-shaped island). In the limit in which $\gamma(\theta)$, and thus also $R(\theta)$, can be assumed to be constant, $\alpha = 1$ and $\overline{\gamma}$ is equal to the line tension γ. If $\gamma(\theta)$ and $R(\theta)$ are not constant, α may deviate slightly from unity, and $\overline{\gamma}$ is an effective line tension given by some average over the function $\Gamma(\theta) = [\gamma(\theta)/R][R(\theta)^2/\rho(\theta)]$ with $\rho(\theta) = \sqrt{R(\theta)^2 + [\partial R(\theta)/\partial\theta]^2}$ [16]. The function Γ has a broad minimum at angles corresponding to the side faces A and B of the islands, where it has a value of $\gamma_{A,B} h_{A,B}/R$, i.e., a few percent lower than the step free energy of close-packed steps. The sharper maximum is assumed in the direction of the island corners (C) and it has a value of $\gamma_C h_C/R$, i.e., about 14% higher than the minimum, as can be estimated directly from the measured equilibrium shape. The average value $\overline{\gamma}$ will be in between the maximum and the minimum and will thus differ from the step free energy of close-packed steps by only a factor 1.05 ± 0.07, the error being certainly overestimated.

Equipartition of energy demands that on the time average an amount of $kT/2$ is stored in each of the independent modes n, i.e., $\langle \Delta F_n(t)\rangle = kT/2$ [17]. Hence, one obtains for the Fourier components g_n ($n \neq 0$):

$$\langle |g_n(t)|^2\rangle = \frac{kT}{2\pi\overline{\gamma}R(n^2-\alpha)}\,. \tag{5}$$

Combining Eqs. (3) and (5), and noting that $\sum_{|n|>1} 1/(n^2-1) = 3/2$, one gets the following for $\alpha = 1$:

$$\overline{\gamma} = \frac{0.75kTR}{\pi\langle G\rangle}\,. \tag{6}$$

This equation is also a good approximation for the island shapes observed in our experiments for which the possible systematic deviation of α from unity is estimated to be 20% [16]. Changing α by 20% results in a change of $\sum_{|n|>1} 1/(n^2-\alpha)$ by only 3.5%. Thus, Eq. (6) allows one to determine $\overline{\gamma}$ by substituting the time-averaged fluctuation function determined from experiment.

In Fig. 2 the shape fluctuation function $\langle G_{\rm exp}\rangle$ measured at five temperatures is shown as a function of the cluster radius R. At the higher temperatures (318–343 K) a clear dependence on R is found. Within the experimental resolution, this dependence is the same for the four temperatures (as expected because $\langle G\rangle$ is directly proportional to the temperature which varies only by ±4%) and can be well described by a linear function $\langle G_{\rm exp}\rangle = G_0 + G_1 R$. Error-weighted linear regression yields parameters $G_0 = (5.2 \pm 0.4) \times 10^{-2}$ nm^2 and $G_1 = (7.4 \pm 0.8) \times 10^{-3}$ nm.

The constant contribution, G_0, to the measured fluctuation function is interpreted as a systematic experimental error caused by the limited spatial resolution. While $R(\theta)$ is derived by averaging and the uncertainty of this quantity can therefore be reduced as much as wanted, the value of $r(\theta,t)$ obtained from one measurement does have an error $\Delta r(\theta,t)$ (which, on average, is expected to be of the order of half the pixel size). This error can be regarded as statistically independent and thus leads to an additive contribution to the fluctuation function:

$$\langle G_{\rm exp}\rangle = \frac{R^2}{2\pi}\left\langle \int_0^{2\pi}\left(\frac{r(\theta,t)+\Delta r - R(\theta)}{R(\theta)}\right)^2 d\theta\right\rangle = \langle G\rangle + \langle \Delta r^2\rangle\,. \tag{7}$$

We thus identify $G_0 = 5.2 \times 10^{-2}$ nm^2 with the mean square experimental error $\langle \Delta r^2\rangle$, i.e., $r(\theta,t)$ is measured with an average error $\sqrt{\langle \Delta r^2\rangle} = 0.23$ nm which corresponds rather well to the expected accuracy of about 0.18 nm, i.e., half the pixel diameter of 0.36 nm. This interpretation is also backed up by the observation that, at the lower temperature of 263 K, $\langle G_{\rm exp}\rangle$ is essentially constant and equal to $(5.9 \pm 0.3) \times 10^{-2}$ nm^2 (although a slight decrease at small R cannot be excluded). At this lower temperature, the island edges are relatively straight (cf. Fig. 1) and any diffusion process requiring the breakup of close-packed island ledges is frozen out [13]. The observed $\langle G_{\rm exp}\rangle$ at 263 K can therefore be interpreted as being due to the mean experimental error, with possibly an additional small contribution of 0.01 nm^2 caused by a few mobile step adatoms which are not part of the closed island edges.

Thus, one finally gets for the shape fluctuation function $\langle G\rangle = G_1 R = (7.4 \times 10^{-3}\ \text{nm})R$. By substituting into Eq. (6) the mean temperature (330 K) and the value of $\langle G\rangle$, we obtain a value for the line tension of $\overline{\gamma} = 0.92 \pm 0.09$ eV/nm $= 0.23 \pm 0.02$ eV/a. A slightly lower value of $\overline{\gamma} = 0.22 \pm 0.02$ eV/a, and a slightly better fit is obtained if we fit $\langle G_{\rm exp}\rangle$ for each temperature separately and calculate the average value of the $\overline{\gamma}$ values obtained in this way. As $\overline{\gamma}$ is most likely to be about 5% higher than the step free energy of close-packed steps (see above), we give this lower value as our best estimate for the step free energy of close-packed steps on Cu(111).

Note, however, that this estimate might still be slightly too large because, in deriving Eq. (6) equipartition is assumed to apply for values of $|n|$ sufficiently large to approximate the summation of $1/(n^2 - 1)$ by $3/2$ (i.e., the infinite sum). It is clear, however, that because of the discrete nature of the island edge the sum has a cutoff at some value $n_{\max}$ which is determined by both the island size and the temperature. Using as an estimate for $n_{\max}$ half the number of edge atoms in the smallest islands (i.e., $n_{\max} = 25$), we find that our estimate is too high by 5% at most [18].

To compare our estimate to the step formation energy at 0 K of 0.208 eV/a as calculated by Stoltze using effective medium theory [8], we further need to discuss the effect of finite temperature, i.e., the contribution of step entropy to the step free energy. As an upper bound for this contribution we can use the literature value for the step entropy of close-packed steps on Cu(111) at temperatures between 1100 and 1300 K of 1.2×10^{-4} eV/a K [6,19], yielding an entropic contribution to the step free energy at 330 K of -0.04 eV/a. A more realistic estimate can be obtained on the basis of the configurational step entropy $2k \exp \times (-\epsilon/kT)$ [20] with a kink creation energy $\epsilon = 0.13$ eV [21] resulting in an entropic contribution of less than -10^{-3} eV/a. Hence, one can conclude that the entropic contribution to the step free energy at the temperatures used here is most likely to be smaller than the error bar of the measurement. Taking further into account that the effective medium theory typically slightly underestimates energy values, we can safely conclude that our experimental result is in good agreement with the theory result.

In conclusion, we have studied the fluctuations of two-dimensional vacancy islands around their equilibrium shape on Cu(111) at temperatures between 318 and 343 K. From the amplitude of these fluctuations we have estimated an absolute value of the free energy of close-packed steps of 0.22 ± 0.02 eV per atomic distance. This result is in good agreement with effective medium theory calculations and can serve as a basis for further studies of energetics and dynamics on similar metal surfaces.

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