Brownian Motion of 2D Vacancy Islands by Adatom Terrace Diffusion

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We have studied the Brownian motion of two-dimensional (2D) vacancy islands on Ag(110) at temperatures between 175 and 215 K. While the detachment of adatoms from the island and their diffusion on the terrace are permitted in this temperature range, the periphery diffusion of single adatoms is prohibited. The present scanning tunneling microscopy results provide the first direct experimental proof that the Brownian motion of the islands follows a simple scaling law with terrace diffusion being the rate limiting process. The activation energy of the vacancy island motion is determined to 0.41 eV.

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The random or Brownian motion of two-dimensional islands has received much attention in recent years because of its relevance to crystal growth. An island migrates because fluctuations in its shape cause random shifts of its center of mass. The mechanisms for mass transport for islands between a few tens to about a thousand atoms on metal surfaces are considered to be (i) periphery diffusion, where adatoms hop along the step edge but do not detach from it, and (ii) correlated terrace diffusion, where adatoms detach from the step edges, diffuse on the terraces, and reattach to the step edge [1].

Substantial effort, both theoretical [2–5] and experimental [6–9], has been devoted to the investigation of whether the diffusion of smaller islands (10–1000 atoms) can be understood in terms of simple scaling laws [10]. It has been argued both from macroscopic theories [2] and from simple scaling relations [6,10] that the diffusion coefficient D of an island should depend on its diameter d and the temperature T via

$$D \propto e^{E/kT} d^{-\beta}. \tag{1}$$

Here E is the appropriate activation energy and k is the Boltzmann constant. The temperature independent exponent β is according to the simple scaling arguments found to depend on the rate limiting mass transport mechanism. Exponents of 3 and 2 have been predicted for periphery diffusion and correlated terrace diffusion, respectively [2,6,10]. If a simple universal scaling is valid as indicated in Eq. (1), it would have important consequences for the general applicability of data for island diffusion [4]. However, neither experiments nor kinetic Monte Carlo (kMC) simulations have so far unambiguously found simple scaling laws to be valid.

In this Letter, we present scanning tunneling microscopy (STM) results for the Brownian motion of 2D islands which give the first direct experimental proof that a simple universal scaling is indeed fulfilled in certain cases. The scaling of the experimental results is confirmed by kMC simulations. From the STM results, we have extracted the activation barrier for the atomic-scale mechanism controlling the island diffusion.

Experimentally, the Brownian motion of both vacancy and adatoms islands has so far been studied mainly on the *isotropic* surfaces of Ag and Cu [6–9]. On fcc(111) and fcc(100) surfaces, the energy barrier for adatom periphery diffusion is substantially lower than the detachment energy of atoms from the island edges. This is confirmed by detachment rates measured in ripening experiments [11]. The observed island displacements are thus due to periphery diffusion of the adatoms. However, it appears that the experimental results [7–9] do not fulfill the simple universal scaling relation in Eq. (1) with an integer value for β. The same applies for kMC simulations [3,4]. Rather noninteger β values between 1.5 and 2.5 were found for the dependence of the diffusivity on the island diameter. This exponent is not universal but rather depends on both temperature and material. In this case of periphery diffusion it seems by now well established that the reason for the deviation from the predicted universality scaling with integer β exponents is due to defects hindering the periphery diffusion, e.g., kinks, and the difficulty of core breakup, i.e., due to the difficulty associated with detaching an atom from a close-packed step edge [4,5,9,12]. In a model system where terrace diffusion is the rate limiting atomic-scale diffusion mechanism, we might anticipate Eq. (1) to hold, since in this case it is less obvious to see which obstacles may impede terrace diffusion.

For these reasons, we have studied the diffusion of vacancy islands on the anisotropic Ag(110) surface. As will be argued below, islands on Ag(110) move due to terrace diffusion, since detachment is energetically favorable over periphery diffusion. For the motion of vacancy islands in the $\langle 110 \rangle$ direction our STM results clearly reveal that a simple universal scaling is obeyed with an integer exponent $\beta = 2$ and an activation energy for the diffusivity of $E_D = (0.41 \pm 0.06)$ eV. We thus conclude that macroscopic scaling theories are indeed valid at least when terrace diffusion is the rate limiting step.

The following energetic reasoning further elaborates on our choice to investigate the motion of vacancy islands on Ag(110). In [13], we carried out molecular dynamics calculations using the approximate effective medium theory

(EMT) potentials [14] to calculate energy barriers for processes relevant for island decay (see Table 1 in [13]). We found that the barrier for detachment of adatoms from the open ⟨001⟩ step edge (0.45 eV) is substantially lower than the activation barrier for periphery diffusion of adatoms (0.56 eV) [13]. Island displacements in the ⟨110⟩ direction should thus be caused by terrace diffusion exclusively. On the anisotropic Ag(110) surface, whenever adatom detachment is possible, the adatom diffusion on the terrace is two dimensional, since the activation energy for diffusion perpendicular to the close-packed rows (0.39 eV) is lower than the detachment energy (0.45 eV) [13]. The parallel diffusion processes (0.28 eV) on this surface proceed via the hopping mechanism, while all perpendicular diffusion is due to exchange processes [13].

This energetic reasoning is relevant for both adatom and vacancy islands. We have chosen, however, to investigate the motion of vacancy islands, since the rate for the filling of vacancy islands is at 250 K a factor of 3 slower than the rate for adatom island decay. Thus the size of the vacancy islands is conserved for a longer period of time [15].

Previously, we have shown that for adatom islands on Ag(110) the detachment from the ⟨001⟩ open step edges is possible above ≈175 K, while periphery diffusion is inhibited up to a temperature of ≈220 K [13]. We have repeated these measurements for vacancy islands on Ag(110), and find similar conclusions. We have thus restricted our measurements to the temperature range 175–215 K to ensure that terrace diffusion is the underlying atomic-scale mechanism for the observed vacancy island motion.

The STM experiments have been performed in a UHV system equipped with a homebuilt, fast-scanning, variable-temperature STM as well as standard facilities for sample preparation and characterization [16]. The anisotropic Ag(110) surface is prepared by several sputtering (1 keV Ne^+) and annealing cycles (623 K) followed by a slow cooldown (10 K/min). This procedure results in a clean, well-ordered Ag(110) surface. Vacancy islands are created by 1 keV Ne^+ sputtering at 180 to 210 K for 1 to 5 s. At these temperatures the single vacancies are sufficiently mobile to agglomerate into vacancy islands of monatomic depth.

The Brownian motion of the vacancy islands is studied from so-called STM movies, i.e., series of time-lapsed STM images (256 × 256 pixels) [16] recorded at time intervals from ≈6 s to ≈20 s. Special care was taken to ensure that the island mobility data were not influenced by the STM imaging process [11].

Figures 1a and 1b show STM images recorded at 198 K and at 213 K. The displacement along the close-packed rows (⟨110⟩, x direction) is several nanometers on the time scale of minutes. To avoid any errors on the measured island diffusivities due to a possible thermal drift we always record the relative motion of two islands of approximately the same dimensions (Fig. 1c). The erratic motion of the center of mass of the vacancy islands extends over about eight atomic distances. The motion perpendicular to the close-packed rows is about 1 order of magnitude smaller.

How does the diffusivity D depend on the island size in the present anisotropic case? Using an approach similar to the one used for deriving Eq. (1) for the isotropic case [6] it can be shown that

$$D \propto e^{E/kT}\sqrt{A}^{-2} \tag{2}$$

for an island of area $A := l \cdot w$ with w its width and l its length.

In addition, we have performed kinetic Monte Carlo simulations. These kMC simulations have been extended from previously published ones [13] in the sense that we have incorporated also the possibility of a larger attempt frequency for exchange processes as suggested in [17].

The kMC simulation results for islands of different initial aspect ratios (from 11 to 0.4) with lengths of 2 nm $< l <$ 23 nm and widths of 1 nm $< w <$ 8 nm are shown in Fig. 2a where the diffusivity is plotted as a function of the square root of the island area $\sqrt{A}$. From these simulations it can directly be concluded that for this anisotropic case indeed a unique power law scaling of the diffusivity $D(\sqrt{A})$ exists consistent with Eq. (2). From the kMC results at 500 K (see Fig. 2a) the exponent β is found to be 1.95 ± 0.06 [18]. Also the kMC results at 300 K yield a scaling exponent close to 2 ($\beta = -1.96 \pm 0.06$, Fig. 2b) [19]. It has recently been suggested that exchange processes have an attempt frequency ν_{ex} more than 1 order

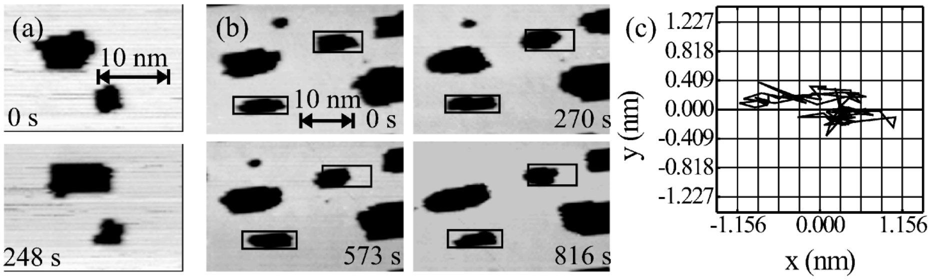

FIG. 1. STM images recording the Brownian motion of vacancy islands on Ag(110): shown are the first and the last images of a movie taken at (a) 198 K, $U = -0.5$ V, $I = 1.18$ nA, and (b) 213 K, $U = -0.5$ V, $I = 0.04$ nA. (c) is the relative displacement of the center of mass of two islands with $l_1 = 1.77$ nm, $l_2 = 1.89$ nm, $w_1 = 0.93$ nm, $w_2 = 0.75$ nm at 194 K, $\Delta t = 22$ s; number of images: 90.

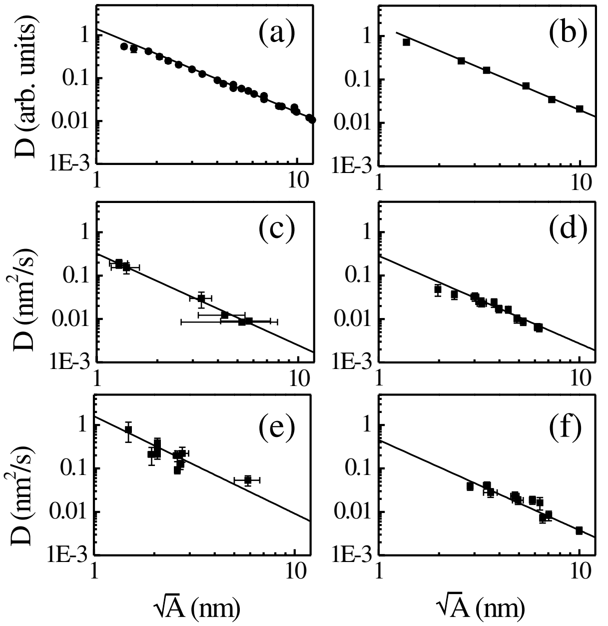

FIG. 2. Dependence of diffusivity D on $\sqrt{A} = \sqrt{l \cdot w}$ (a),(b) in kMC calculations and (c)–(f) in the experiments for different temperatures T. Solid lines represent power law fits to the data with slope β. The y-error bars represent statistical errors; x-error bars represent size fluctuations and size difference of the two islands considered: (a) $T =$ 500 K, $\beta = -1.94 \pm 0.06$, $\nu_{\mathrm{ex}}/\nu_D = 20$, (b) $T = 300$ K, $\beta = -1.96 \pm 0.06$, $\nu_{\mathrm{ex}}/\nu_D = 1$, (c) $T = 178$ K, $\beta = -2.11 \pm 0.32$, (d) $T = 194$ K, $\beta = -2.02 \pm 0.24$, (e) $T =$ 196 K, $\beta = -2.08 \pm 0.20$, and (f) $T = 204$ K, $\beta = -2.24 \pm 0.46$.

of magnitude larger than the ordinary attempt frequencies for surface diffusion ν_D [17]. However, the diffusivity of the islands in the x direction as determined via kMC simulations do not depend on the relative attempt frequency ν_{ex}/ν_D up to 70 [20]. Therefore the simple scaling law derived theoretically exists in kMC simulations for the motion of vacancy islands in the $\langle 110 \rangle$ direction on the Ag(110) surface independent of temperature (between 500 and 300 K) and of ν_{ex}/ν_D.

To analyze the experimentally measured Brownian motion of the 2D vacancy islands, we determine the relative mean square displacement $\langle (\Delta x)^2 \rangle$ from the time-lapsed STM movies recorded at different temperatures. The island diffusivity D is subsequently determined via $D = \langle (\Delta x)^2 \rangle / 4\Delta t$ [6] with Δt being the time elapsed between consecutive STM images. In Figs. 2(c)–2(f) we show double logarithmic plots of D versus $\sqrt{A}$ for selected temperatures as determined from the STM movies. The slope of the linear fits to the STM data is very close to the integer value of 2. Similar findings are obtained for three other temperatures. *We have thus experimentally shown that in the case of terrace diffusion a simple universal scaling for island diffusion indeed exists.* The parameter β is found to be 2, consistent with the kMC results and the scaling theory [cf. Eq. (1)].

From the determined diffusivities D we can also derive the activation barrier E for the island motion [see Eq. (2)] by dividing the islands into different area classes and subsequently plotting the diffusivity D versus $1/T$ (Fig. 3). As expected from Eq. (2) these Arrhenius plots (see Fig. 3) all depict straight lines, and from the derived slopes we have determined the activation barrier to be (0.41 ± 0.06) eV. From the EMT calculations two processes seem to be energetically relevant having energies close to 0.41 eV: The detachment energy of adatoms from the open $\langle 001 \rangle$ step edge is $E_e = 0.45$ eV, and the diffusion energy of atoms perpendicular to the close-packed rows is $E_a = 0.39$ eV [13]. Both of these energies are very relevant in connection with the Brownian motion of the vacancy islands. We can, however, not distinguish which of the two processes is the rate limiting one; in fact, it might be a combination of the two.

Finally, we will comment on the mobility of the islands in the y direction, i.e., perpendicular to the close-packed rows ($\langle 110 \rangle$ direction). As mentioned above, the center of mass motion of the islands in the y direction is very small and amounts to only approximately one atomic distance, basically reflecting a rearrangement of the $\langle 001 \rangle$ step [21]. At first sight, this may seem surprising in view of the 2D adatom motion on the terraces. However, the detachment from the close-packed step edge, i.e., core breakup, is with an energy of 0.85 eV very unlikely. Atoms that have detached from the open step edge may attach to the close-packed step edge, but this can cause only a very limited shape fluctuation. Furthermore, the island fluctuation perpendicular to the close-packed rows is reduced for the following reasons: (a) The number of adatoms reattaching to the $\langle 110 \rangle$ step is much lower than on the $\langle 001 \rangle$ step, because the adatom density is higher at the source. (b) After reaching the $\langle 110 \rangle$ step, the atoms can move very rapidly

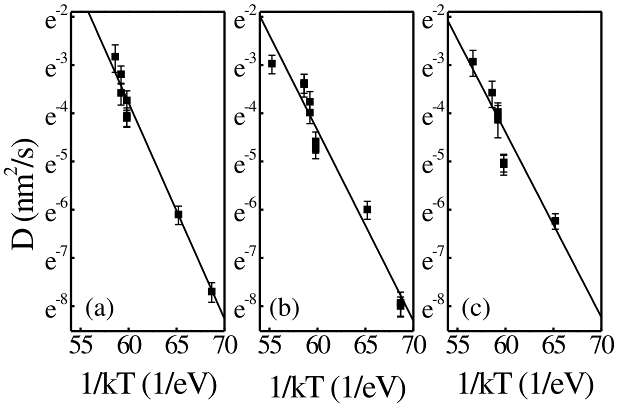

FIG. 3. Arrhenius plots of diffusivity D for different area classes. The solid lines are exponential fits to the data with exponent α: (a) 12 nm^2 $< A <$ 19 nm^2, $\alpha = -(0.448 \pm 0.028)$ eV, (b) 22 nm^2 $< A <$ 29 nm^2, $\alpha = -(0.395 \pm 0.028)$ eV, and (c) 32 nm^2 $< A <$ 40 nm^2, $\alpha = -(0.384 \pm 0.072)$ eV.

along this step (0.29 eV) and reattach to the ⟨001⟩ step before encountering another step adatom; i.e., they have a low chance of nucleation and thus of modifying the step position.

In conclusion, we have shown that the Brownian motion of vacancy islands on the Ag(110) surface in the ⟨001⟩ direction follows a simple universal scaling law. The scaling exponent of 2 is consistent with the fact that terrace diffusion is the rate limiting step in agreement with energetic reasoning. The present experimental findings will hopefully stimulate atomistic theoretical studies as were performed for isotropic surfaces [2–4] to gain further insight into the simple universal scaling law and into the rate limiting atomistic process that leads to an activation energy of 0.41 eV.

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[1] The third frequently discussed possibility [2,3] is uncorrelated terrace diffusion, also called the evaporation-recondensation mechanism. In the case of metal surface the prerequisite for this mechanism, i.e., an additional barrier for adatoms to attach to a step edge, does not exist.

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[18] Only for islands smaller than 20 atoms or 2.4 nm^2, we find that the kMC simulations deviate from this scaling behavior. For vacancy islands, terrace diffusion is hardly possible for these small island sizes and the much stronger fluctuations of the aspect ratio suggest a different process to be dominant in this case.

[19] Also simulations at 270 K are consistent with an exponent $\beta = 2$.

[20] In contrast, the diffusivity in the y direction shows a linear dependence on the relative attempt frequencies.

[21] For the motion in y the long-time limit is not yet reached (cf. [5]). In the kMC simulation the center of mass of the island only moves approximately one atomic distance, and different island sizes show very different exponents.