Diffusion and Atomic Hopping of N Atoms on Ru(0001) Studied by Scanning Tunneling Microscopy

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The dynamic behavior of N atoms adsorbed on a Ru(0001) surface was studied by scanning tunneling microscopy. N atoms formed by dissociation of NO molecules show an initial sharp concentration profile at atomic steps. Its decay was followed as a function of time, providing a quasicontinuum diffusion constant; the activation energy is 0.94 eV and the prefactor is 2×10^{-2} cm^2 s^{-1}. The diffusion constant was determined also at equilibrium, from statistical jumps of individual N atoms in a uniform overlayer, and is found to be identical to the Fickian value.

Diffusion is a macroscopic nonequilibrium phenomenon, described by a continuum theory and quantified by the Fickian diffusion constant D_x (x stands for a certain direction). It is connected to the equilibrium hopping of individual particles, described by statistical mechanics, by the Einstein-Smoluchowski relation $D_x = \langle x^2 \rangle / 2t$, where $\langle x^2 \rangle$ is the mean square displacement of a random walker after time t, projected onto this direction. Experimental verification of this equation proves, however, extremely difficult. The reason is that experiments that determine the Fickian diffusion constant, e.g., by following the decay of a concentration profile of adsorbed particles on a surface, naturally require finite coverages of the particles. This gives rise to a thermodynamic factor that relates the Fickian, or chemical, diffusion constant D to the diffusion constant D^*, connected with the random motion of individual particles, by $D = D^* [\partial(\mu/kT)/\partial \ln \Theta]_T$ (μ is the chemical potential and Θ the coverage) [1]. In general, the thermodynamic factor is unity only for $\Theta \to 0$. A serious difficulty in macroscopic experiments on adsorbate diffusion is that even well prepared single crystal surfaces exhibit defects, mostly atomic steps and impurities, at which the binding of the adparticles is different, so that the macroscopic diffusion constant averages over various hopping rates. This problem is not encountered in measurements by field ion microscopy (FIM) (e.g., [2]) or by scanning tunneling microscopy (STM) [3,4], where hopping rates of individual particles can be measured on defect-free parts. As expected, large differences in the diffusion parameters were found in the few cases where the same systems (metal self-diffusion) have been studied with FIM and some macroscopic technique [5].

In this Letter we show for the first time the decay of a concentration profile of adsorbed atoms with atomic resolution, using STM observation of N atoms adsorbed on a Ru(0001) surface. In contrast to the usual situation, the Fickian diffusion constant thus obtained is found to be identical to that obtained from measurements of the equilibrium hopping rate of single N atoms, as predicted by the Einstein-Smoluchowski relation.

The experiments were performed with an ultrahigh vacuum apparatus described in an earlier publication [6]. The Ru(0001) sample was prepared by a sputter-annealing-oxidation procedure as reported by other authors [7]. Nitrogen was adsorbed either by exposure to NO, at temperatures between 300 and 350 K, which leads to complete dissociation of the NO molecules into N and O atoms in the coverage regime studied here [8], or by exposure to N$_2$ in the presence of a hot filament [9,10]. Because exposures around 10^4 L (1 L $= 10^{-6}$ mbar s) were needed for the latter procedure a special gas inlet and nitrogen of purity >99.9999% were used, and the adsorption was performed at 500 K to avoid CO coadsorption. In both cases STM images were recorded at 300 K; tunneling voltages (with respect to the sample) and currents are given in the figure captions.

The two small scale STM images, displayed in Fig. 1, were recorded after adsorption of 0.1 L NO at 300 K. The dark spots represent the nitrogen atoms, the streaky, diffuse objects are caused by the O atoms, whereby identification of the two surface species is based on experiments with pure N and O layers [11]. Both kinds of atoms are imaged as depressions, the imaging depth of oxygen being somewhat larger than that of nitrogen. That oxygen atoms appear only as streaks results from fast hopping which is of the same order as the line frequency of the scans [11]; successive lines show the O atoms therefore at different positions. Comparison of Figs. 1(a) and 1(b), which were recorded within 12.5 s on the same area, shows that from the 12 N atoms visible in 1(a) the four marked ones in 1(b) have moved to new positions. Hence, the hopping of N occurs at a rate similar to the frequency of full images and can, in contrast to oxygen, be conveniently studied with the STM. The jump distance is about 3 Å, which corresponds to the Ru lattice constant of 2.7 Å.

In extensive investigations on the adsorption of NO on Ru(0001) we found that, for the small exposures used here, dissociation into N and O atoms occurs exclusively at atomic steps. Figure 2(a) shows a larger topograph
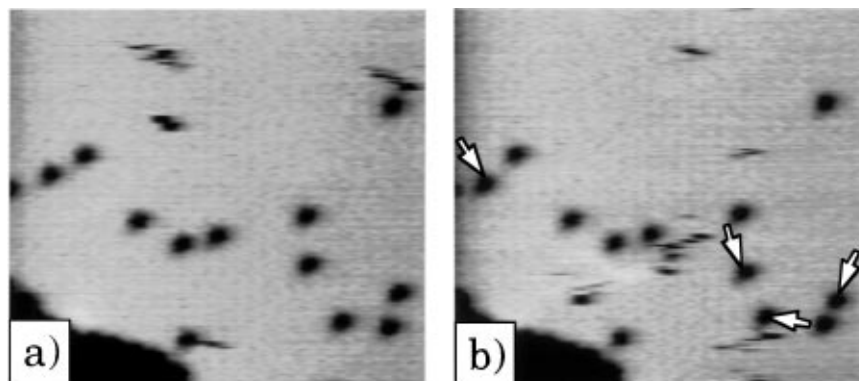
FIG. 1. STM topographs of Ru(0001) recorded after adsorption of 0.1 L NO at 300 K. (a) and (b) were recorded successively on the same area; arrows mark N atoms that have moved between (a) and (b). 70 Å $\times$ 70 Å, -0.6 V, 1 nA.

recorded 6 min after exposure of 0.1 L of NO at 300 K. The N atoms, again represented by the dark spots, are exclusively located near the monatomic step which appears as the dark stripe at the upper half of the image. Figure 2(b) shows the same area 2 h later: The N atoms have then diffused away from the step and are more evenly distributed. The black streaks of the O atoms are at random positions on the terraces already in Fig. 2(a), indicating that oxygen diffuses away from the step much more rapidly than the N atoms. The local concentration of O atoms is therefore small for the NO exposures used here (Θ_{Ox} around 0.01), and possible, short-range interactions with N atoms can be neglected. The dissociation of NO thus enables us to prepare an almost atomically sharp initial concentration profile of N atoms and to follow its broadening as a function of time.

The quantitative analysis was performed with a time series of larger images containing about 100 N atoms, for which the distances x of the atoms from the step were measured at time instances between 360 and 7080 s after the adsorption; Fig. 2(c) shows the mean square distances $\langle x^2 \rangle$ as a function of time. It is seen that the data fall on a straight line, indicating that the diffusion constant is—within experimental limits—independent of time and hence of coverage; from the slope a diffusion constant of $D = (3.4 \pm 0.4) \times 10^{-18}$ cm^2 s^{-1} is obtained. The line does not exactly go through the origin which points to a finite spread of atoms already at $t = 0$. Note that the offset corresponds to a distance of only $x = 8$ Å. We suggest that it is a consequence of the dissociation process, during which the atoms are propelled some distance away from the step while the binding energy is released to the heat bath of the crystal (for an extreme such case see [6]). If the diffusion constant is independent of concentration, the solution to Fick's second law is a Gaussian. With the initial condition that at $t = 0$ all particles are located at $x = 0$ and, because N atoms do not cross the step at 300 K, the boundary condition of semi-infinite space, it assumes the form

$$n(x,t) = \frac{N\Delta x}{\sqrt{\pi D t}} e^{-x^2/4Dt}.$$

$n(x, t)$ is the number of atoms contained in narrow stripes (width Δx) parallel to the step, N the total number of atoms, and D is isotropic because of the hexagonal symmetry of Ru(0001). The Gaussian describes the data very well, as is shown by the inset in Fig. 2(c) for the data set at 7080 s. We mention that there is no fit parameter or axis scaling involved; the value for D was kept at the number derived above; the results for times between 3000 and 7080 s are equally good. At shorter times deviations occur which are, for the main part, caused by the fact that the Gaussian is a reasonable description only when $\sqrt{2Dt}$ is sufficiently large compared to the initial width of the profile.

Temperature dependent measurements were performed by keeping the sample, after exposure to NO, for given intervals at T between 300 and 350 K, while holding it in the manipulator for a better temperature control. After cooldown and transfer to the STM coverage profiles were recorded. The diffusion coefficients thus obtained contain a small correction for motion during the time between cooldown and start of the STM experiment. An Arrhenius plot of the diffusion coefficient is shown in Fig. 3; using $D = D_0 \exp(-E_a/kT)$ we find an activation energy of $E_a = 0.94 \pm 0.15$ eV and a prefactor $D_0 = 10^{-1.7\pm1.5}$ cm^2 s^{-1}. Both values are in the range of expectations: The diffusion barrier is close to a fraction of $\frac{1}{5}$ of the adsorption energy (5.7 eV [9,10]), which is considered to be typical for adsorbates; D_0 is close to the value of 10^{-3} cm^2 s^{-1} expected for an attempt frequency of 10^{13} s^{-1}.

Analysis of individual hopping steps was performed via dissociation of N_2 that allows the creation of larger coverages without producing oxygen atoms at that same time. Because of the adsorption temperature of 500 K the N layer is close to thermodynamic equilibrium, and the equilibrium hopping rate of N atoms can be determined from time series of STM images. In contrast to NO adsorption at lower temperatures concentration gradients are absent. Figure 4 shows two STM topographs, recorded after exposure of 6000 L of N_2. Figure 4(a) was recorded by scanning from top to bottom, Fig. 4(b) from bottom to top on the same area. Many atoms at the bottom of
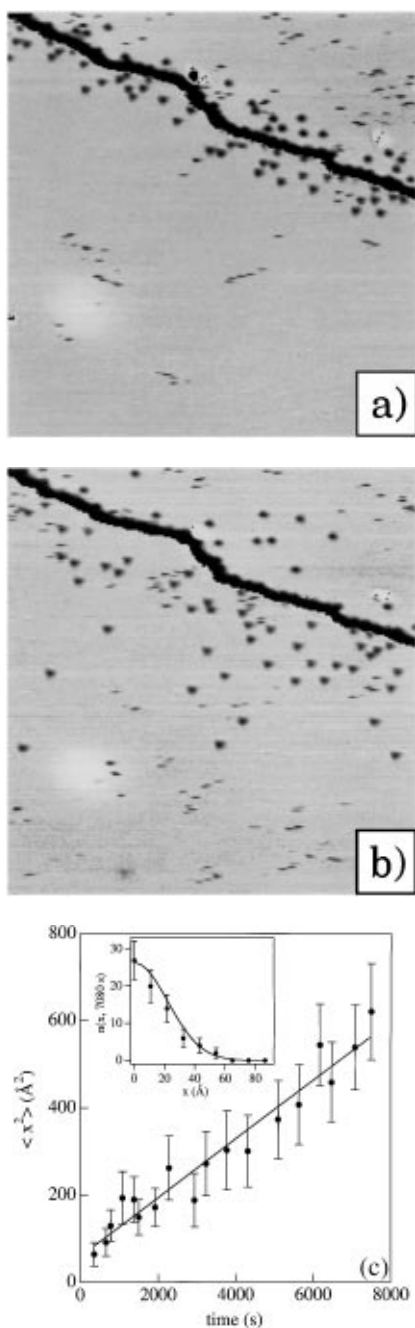
FIG. 2. (a) STM topograph recorded 6 min after adsorption of 0.1 L NO at 300 K. 180 Å × 200 Å, −0.6 V, 1 nA. (b) Same area after 2 h. (c) Mean square distances of N atoms from the step as a function of time after adsorption; the inset shows the measured distribution of distances at 7080 s (points) and a Gaussian with fixed parameters (full line).

Fig. 4(b) are therefore seen on the same positions as in Fig. 4(a), whereas towards the upper border of Fig. 4(b) an increasing number of atoms has moved. The vertical axis thus provides also the time scale. Counting of the atoms that have not moved yields the probability P that atoms are still found on their original sites at time t. If the jumps are statistically independent, $P(t) = \exp(-t/\tau)$, with τ the mean time an N atom spends on its adsorption site. For a data set of 174 atoms we actually find an

exponential decay of $P(t)$, from which we get $\tau = 45 \pm 17$ s (for 300 K). The length (λ) of these jumps is one lattice constant of Ru(0001) (2.7 Å), as follows from our observations that all N atoms sit on identical threefold sites [11] and that only about 3 Å wide jumps were detected (Fig. 1). Longer jumps as reported by FIM for Pd atoms on W [12] and by STM for Pb on Ge(111) [4] were not observed here. Making use of the fact that on a two-dimensional hexagonal lattice $\langle x^2 \rangle / 2t = \lambda^2 / 4\tau$ we obtain a diffusion constant of $(4.0 \pm 1.5) \times 10^{-18} \, \text{cm}^2 \, \text{s}^{-1}$, which is identical to the Fickian value of $(3.4 \pm 0.4) \times 10^{-18} \, \text{cm}^2 \, \text{s}^{-1}$ derived above.

This good agreement is explained by the following reasons.

(1) The thermodynamic factor [1] by which the Fickian diffusion constant differs from that connected with the random walk of single particles must be close to unity which implies that interactions between the particles in the applied coverage regime are small. For the present system the N-N interaction potential was determined in an independent experiment, by analysis of equilibrium distributions in larger images, similar to that of Fig. 4 [11]. It turns out that the interaction is very well described by a hard sphere potential, which blocks nearest and next nearest sites without affecting all other sites. A change of the diffusion barrier [13] by neighboring N atoms can therefore be only small. A second point is that site blocking caused by the hard sphere potentials has only small effects because of the small coverages employed: It can be shown that the Fickian diffusion coefficient is by about 20% larger than the zero coverage value and that the hopping frequency of the random walkers in equilibrium is by about 30% smaller than at the zero coverage limit [14]. It is therefore a result of the small coverages and the small interaction energy between the N atoms that no measurable differences were found.

(2) Interactions of adsorbates with defects, e.g., trapping at steps, often affect macroscopic diffusion experiments. This could be ruled out here simply by limiting the diffusion measurements to single terraces.
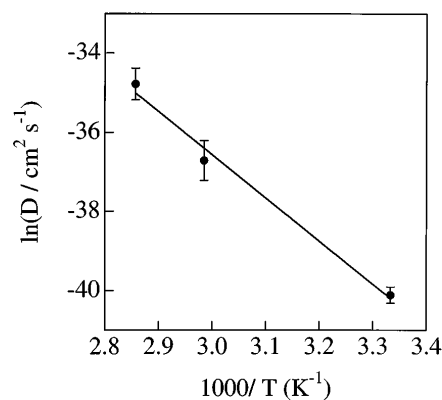

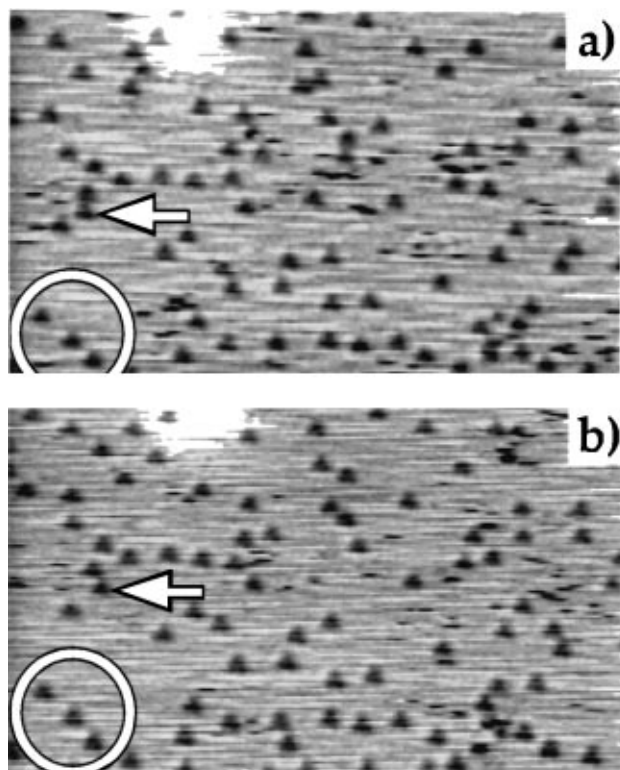FIG. 3. Arrhenius plot of diffusion constants measured at three different temperatures.

FIG. 4.   STM topographs of Ru(0001) recorded after exposure to 6000 L N_2. (a) Scanned from top to bottom. (b) Same area, scanned from bottom to top. The circle marks three atoms that remained on their positions; the arrow points to an atom that has moved. 133 Å × 68 Å, −0.6 V, 30 nA.

(3) In principle, one has to consider effects of the STM on the diffusion, e.g., by inelastic tunneling, by local heating, or by the electric field. In fact, an increase of the hopping rate caused by the tunneling has been observed for Pt atoms on a Pt(111) surface [3]. However, if for the N atoms the main part of the hopping were in fact induced by any local excitation, $P(t)$ should be a constant, since the interaction time of the tip with each atom is constant. In contrast we see an exponential behavior as predicted for a process of statistically independent jumps. A larger scale heating can be ruled out because of the large thermal conductivity of the metal substrate.

In conclusion, we find identical values for the diffusion constants from measurements of the decay of a concentration profile (i.e., by a continuum description), and from the statistical hopping of individual atoms, as predicted by the Einstein-Smoluchowski relation.

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