Contents lists available at ScienceDirect

Surface Science



An STM study on the diffusion of O atoms on a CO-covered Ru(0001) surface—The role of domain boundaries



^a Department of Chemistry, Ludwig-Maximilians-Universität München, 81377, Munich, Germany
^b Center for NanoScience, Schellingstr. 4, 80799, Munich, Germany

A	R	Т	I	С	L	Е	I	N	F	0

Keywords: High-speed STM Ru(0001) Oxygen Carbon monoxide Surface diffusion Domain boundaries Grain boundary diffusion

ABSTRACT

We investigate tracer diffusion at the domain boundaries in an adsorption layer, an effect that corresponds to grain boundary diffusion in 3D polycrystalline solids. Experiments were performed on adsorbed O atoms on a Ru (0001) surface in a layer of CO molecules. The CO molecules form a $(\sqrt{3} \times \sqrt{3})$ R30° structure which displays translational domains. High-speed scanning tunneling microscopy (STM) was used to image the motion of the O atoms. The data show that single O atoms preferentially move along the domain walls which in the STM movies appear as disordered, fluctuating stripes between the ordered domains. The diffusion coefficient of the O atoms is one order of magnitude higher than the diffusion coefficient in the ordered domains. By comparison with previous experiments on completely disordered CO layers, it is concluded that the diffusion is similarly promoted by the enhanced fluctuations in the disordered domain walls.

1. Introduction

Grain boundary diffusion, the transport of atoms along the interfaces between the single crystalline domains of a three-dimensional polycrystalline solid, is much faster than diffusion through the bulk of the crystals [1]. For example, for self-diffusion in polycrystalline Cu, the grain boundary diffusion coefficient at temperatures between 800 and 1000 K is 5 - 6 orders of magnitude higher than the diffusion coefficient in the Cu lattice [2]. Properties of materials that are based on mass transport like, e.g., sintering or some forms of plastic deformation, are therefore strongly determined by grain boundary diffusion. The underlying atomic mechanisms are complex, but there is evidence that they are not just variations of the standard 3D lattice diffusion mechanisms such as the vacancy or the interstitial mechanisms [3,4].

Adsorption layers on single crystal surfaces can be expected to display corresponding effects in 2D for the diffusion of adsorbed atoms or molecules in the layers. In most cases, the unit cell of an adsorption superstructure is larger than the unit cell of the underlying surface and/ or has a lower symmetry, giving rise to translational, rotational, and mirror domains. An ordered adsorption layer that forms a 2D solid is therefore usually polycrystalline, and one can ask whether the domain walls in such a layer might play a similar role for mass transport on a surface as the grain boundaries in a 3D solid. Scanning tunneling

microscopy (STM) is, in principle, suitable for investigating such effects, but one finds that domain boundary diffusion has only rarely been observed. It has been seen in electrochemical work on a Cu(100) electrode which was covered with a c(2x2) structure of Cl atoms. It was shown that co-adsorbed S atoms moved faster along the domain boundaries of the Cl structure than in the c(2x2) lattice [5]. By contrast, on an Au(100) electrode, the mobility of Cl atoms in the domain boundaries of the c(2x2)Cl structure was low [6]. For catalytic reactions, the role of domain boundary diffusion has been investigated by theory for the CO oxidation on (100) surfaces of fcc platinum metals [7]. The spatio-temporal patterns displayed by this reaction under certain conditions require surface diffusion of adsorbed CO molecules on a partially O-covered surface. It was shown that the diffusion takes place at the domain boundaries of the c(2x2) structure formed by the O atoms.

In our own previous studies on surface diffusion by high-speed STM we have investigated tracer diffusion of O atoms through layers of adsorbed CO molecules on a Ru(0001) surface. Experiments were performed with 0.33 monolayers of CO (ML, in units of CO molecules per Ru atom) [8,9], a coverage at which the molecules form an ordered $(\sqrt{3} \times \sqrt{3})$ R30° structure, and also at a higher CO coverage of $\Theta = 0.47$ ML, where the CO layer is disordered [10]. At a coverage of $\Theta = 0.33$ ML, it was shown that the O atoms move by what we called a "door-opening mechanism". It consists of local density fluctuations of the CO

* Corresponding author at: Department of Chemistry, Ludwig-Maximilians-Universität München, 81377, Munich, Germany. *E-mail address:* wintterlin@cup.uni-muenchen.de (J. Wintterlin).

https://doi.org/10.1016/j.susc.2024.122597

Received 28 June 2024; Received in revised form 20 August 2024; Accepted 5 September 2024 Available online 5 September 2024

0039-6028/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).





layer which open low-energy paths along which the O atoms can move through the CO layer. The mechanism is different from the vacancy and interstitial mechanisms known from 3D lattice diffusion. In the disordered layer at a CO coverage of $\Theta = 0.47$ ML, local density fluctuations are stronger, so that low-energy paths for the jumps of the O atoms open more frequently and, correspondingly, the mobility of the O atoms is higher [10].

From its symmetry, the $(\sqrt{3} x \sqrt{3})$ R30°-CO structure can form three translational domains, so that the adsorption layer at $\Theta = 0.33$ ML can display domain boundaries. The STM data show such boundaries and, moreover, they show that the boundaries affect the tracer diffusion of the O atoms. Here we analyze the effect quantitatively and extract a mechanism. Like for grain boundary diffusion in 3D solids, we find an increased diffusion coefficient with respect to lattice diffusion. However, the enhancement is considerably lower than typically observed for 3D solids.

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) chamber at a base pressure of 1×10^{-10} mbar. The UHV system is equipped with an Auger electron spectrometer (AES), an ion gun for sputtering, a quadrupole mass spectrometer (QMS) for residual gas analysis, a sample manipulator, and a variable-temperature, high-speed STM. In the STM experiments, sample temperatures can be varied between approximately 50 and 500 K. At temperatures below 300 K this is achieved by liquid He cooling and simultaneous heating by a hot filament at the back of the sample. A type S thermocouple spot-welded to the sample is used for temperature measurements, and a clamp provides contact between the thermocouple at the sample and corresponding wires at the mounting stage when the sample is transferred from the manipulator to the STM. Details of the STM setup have been described previously [11].

The Ru(0001) sample was prepared by Ar⁺ ion sputtering (1 keV, 10 min), dosing of 2 – 10 Langmuirs (L, with 1 L = 1.33×10^{-6} mbar s) of oxygen at 500 - 600 °C to oxidize residual surface carbon, and flash annealing to 1450 °C to anneal sputter defects and desorb excess oxygen. To prepare the adsorption layers, first 0.05 L of O₂ were dosed with the sample at room temperature, which leads to a low coverage of adsorbed O atoms. Then 1.0 L of CO were dosed to prepare the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -CO structure. Finally, the temperature was set, and the STM experiments were started.

The STM images presented here are single frames from movies acquired at a rate of 12 frames s⁻¹. The movies were recorded in the constant height mode at negative bias voltages. Under these conditions, the oxygen atoms appear bright and the CO molecules appear dark, corresponding to an inverted image contrast with respect to the contrast in the standard constant height mode. Because of the sinusoidal scanning voltage applied in the high-speed mode the raw data display a distortion that is removed by the image processing software. Filtering or other image processing routines are not applied. The distributions of directions of the (exchange) jumps in the ordered $(\sqrt{3} x \sqrt{3})R30^\circ$ structure and in the fully disordered structure were uniform, verifying that the scanning of the tip had no measurable effect on the diffusion. The trajectories of the O atoms are determined by a software based on a wavelet transformation that identifies and tracks the atoms at the enhanced noise of the movie data (compared to standard, slow constant height data) [12]. During a movie, it occasionally happens that two O atoms come close together up to a distance where they start to interact with each other, an effect that slows down the motion; to prevent an impact on the diffusion parameters, these sections of the trajectories are automatically removed by the tracking software.

3. Results

Fig. 1(a) shows one frame from an STM movie (3731 frames, 1450 of which on the same position), recorded at 272 K. The hexagonally ordered pattern of dark dots is the $(\sqrt{3} x \sqrt{3})R30^\circ$ structure of CO molecules, and the blurred stripe running from the top edge of the image to the right edge is a boundary between two translational domains of the structure. The fuzziness of the domain wall is a dynamic effect caused by rapid fluctuations of the positions of the CO molecules in the boundary. On the time scale of one frame (1/12 s) the width of these fluctuations is of the order of 10 Å, and on the time scale of the 1450 frames (121 s) the average position of the boundary changes by approximately the same distance (SI, movie S1). Upon closer inspection, one can identify four bright atomic features located at or in the domain wall (red arrows). These features, from their positions with respect to the CO molecules in the $(\sqrt{3} x \sqrt{3})R30^\circ$ structure and from their appearance in the STM, can safely be interpreted as O atoms. The experiments occasionally showed that domain boundaries originated at small (2 \times 2) islands of O atoms, indicating that these islands pin the boundaries or induce their formation when the CO layer forms during CO dosing. We rule out that the boundaries are thermally excited because, at $\Theta = 0.33$ ML, the orderdisorder transition of the $(\sqrt{3} \times \sqrt{3})$ R30°-CO structure is theoretically predicted to happen at a temperature significantly higher than 400 K (CO desorbs before) [13,14].

A model of the marked area in Fig. 1(a) is shown in Fig. 1(b) with the two translational domains color-coded. The information about the adsorption sites, i.e., that the CO molecules (blue balls) occupy on-top sites and the O atoms (red balls) occupy threefold hcp sites, is based on the extensive vibrational spectroscopy and structure analysis literature, and also on theory [15–19]. The model shown in Fig. 1(b) suggests a heavy domain wall, i.e., a boundary with a locally higher CO coverage than $\Theta = 0.33$ ML in the neighboring ordered domains. However, because of the high jump rates of the CO molecules - with the calculated barrier of 0.3 eV [8] one estimates a jump rate of 3 \times 10 7 s $^{-1}$ at 272 K the exact locations of some of the CO molecules in the domain boundary are uncertain; e.g., the apparent pairs of CO molecules on neighboring sites in the model could also be interpreted as single molecules that rapidly change positions. A light domain wall with a local coverage lower than 0.33 ML is therefore also possible [Fig. 1(c)]. In both cases, the atomic configurations vary depending on the local direction along which the boundary runs. However, no systematic effect of the directions was observed on the diffusion rate of the O atoms. Note that the models are only snapshots of rapidly changing configurations.

Fig. 2 shows two frames from a second movie (2327 frames, 2169 on the same area, SI movie S2) taken at 272 K on the same area as Fig. 1. In Fig. 2(a), the arrows mark the four O atoms which are still found in the imaged area but have moved to other positions. In Fig. 2(b) we have overlaid (on another frame of the movie) the trajectories of these atoms (from 2169 frames). Obviously, the trajectories preferentially run along the domain boundary and extend only little beyond the width of the short-time boundary fluctuations of ~10 Å. That the trajectories in the upper part of Fig. 2(b) seem to extend more deeply into the ordered $(\sqrt{3} x \sqrt{3})R30^{\circ}$ domain is mainly caused by the fact that on the time scale of the 2169 frames (181 s) the average position of the boundary varies more strongly than the positions of the O atoms perpendicularly to the boundary. Overall, the O atoms are only rarely found outside the domain wall. The data thus show 2D domain boundary diffusion.

The shapes of the trajectories contain information about what happens atomically in the domain wall during this diffusion process. Fig. 3 (a) shows another frame of the same STM movie as Fig. 2 overlaid with only two of the trajectories, and Fig. 3(b) and (c) show expanded versions of the two trajectories with color-coded frame numbers. In the upper trajectory [Fig. 3(b)] one can identify at least two different types of motions of the O atom. For certain time periods (e.g., during the yellow vertical zig-zag line, frames 843–962) it travels along the



(caption on next column)

Fig. 1. (a) Single frame from an STM movie of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO structure with coadsorbed O atoms (indicated by red arrows) in a domain boundary. STM parameters: Tunneling voltage: $V_t = -0.7$ V, tunneling current: $I_t = 3$ nA, image size: 89 Å x 89 Å, imaging rate: 12 frames s⁻¹. (b) Model of the area marked in (a) assuming a heavy domain wall. Translational domains are indicated by yellow and green shading, CO molecules by blue balls, O atoms by red balls, and Ru atoms by grey balls. Black arrows are possible CO displacements that create diffusional paths for the O atoms by forming single additional nearest-neighbor CO pairs. (c) Model of the same area assuming a light domain wall. Arrows are CO displacements that create diffusional paths for the O atoms cons along some still blocked directions by forming single (or no) nearest-neighbor CO pairs.

direction of the domain wall, jumping along a row of neighboring hcp sites (in the $\sqrt{3}$ direction of the Ru(0001) surface the hcp sites form zigzag lines). For other time periods (at the outer parts to the left and right of the yellow line) the atom travels between and partially also through the rims of the ordered domains. The small triangles visible in these periods (arrow marks) are characteristic features caused by jumps of the O atoms between the three hcp sites in the vacancies of the ordered $(\sqrt{3} x \sqrt{3})R30^\circ$ structure [8]. These periods are not so much caused by the O atoms moving into the ordered domain but more by the rapidly fluctuating position of the domain boundary (see movies S1 and S2). Not all trajectories are affected by these fluctuations which are a random effect possibly related to the curvature in the geometric directions of the domain wall. For example, the lower trajectory doesn't show the triangles, and the O atom mainly jumps along the direction of the domain wall.

We find that diffusion of the O atoms along the boundaries is significantly faster than diffusion in the ordered $(\sqrt{3} x \sqrt{3})R30^\circ$ phase at the same temperature. For a quantitative comparison we cannot use the O hopping rates, the quantities evaluated in our previous work on the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure [8], because the coordination of the O atoms by CO molecules in the domain walls permanently changes between two (or even more) qualitatively different situations (in particular between ordered and disordered areas). This complexity precludes constructing an atomic hopping model which would be needed to extract jump rates from the displacement distributions of the O atoms [8, 10]. What we did instead was to evaluate a diffusion coefficient in the domain boundaries, D_{db}, which contains the various processes in an averaged way, by using the mean square displacements $\langle r^2 \rangle$ per frame extracted from the trajectories. From the dataset of Fig. 2, from altogether 4870 measurement points, a value of $\langle r^2 \rangle = (4.63 \pm 0.64) \text{ Å}^2$ is obtained. With the time period of t = 1/12 s given by the frame rate, one obtains, for the 2D case of an isotropic surface, a diffusion coefficient of $D_{\rm db} = \langle r^2 \rangle / 4t = (13.9 \pm 1.9) \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$. For purely 1D diffusion, the diffusion coefficient is $D_{\rm db} = \langle r^2 \rangle / 2t = (27.8 \pm 3.8) \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$. Because of the finite width of the domain walls, the actual situation is somewhere in between 1D and 2D, so that the diffusion coefficient is between these limits. These values represent averages over the relatively fast processes within the domain walls and the slower processes when the O atom is intermediately in the ordered domains.

For the diffusion in the reference system, the ordered $(\sqrt{3} x \sqrt{3})R30^\circ$ lattice, precise hopping rates are available [8]. A minor complication with these data is the fact that the motion of an O atom in this lattice consists of two processes, a fast wiggling of the O atom between the three hcp sites inside a vacancy in the CO layer, and a slower exchange with neighboring CO molecules. However, only the latter leads to diffusional transport, so that we can just use the corresponding hopping rate, Γ_2 , of this latter process [8]. At 272 K, we obtain, by applying the experimental Arrhenius parameters, a Γ_2 value of 0.27 s⁻¹ [8]. The jump length of the O atom is one lattice constant of the Ru (0001) surface, a = 2.706 Å. However, after the O atom has jumped and exchanged sites with a CO molecule, the wiggling in the vacancy quickly randomizes the position within the vacancy. The site inside the original



Fig. 2. Two frames from another STM movie of the same area as in Fig. 1, recorded at two different time instants. $V_t = -0.7$ V, $I_t = 3$ nA, 129 Å x 129 Å, 12 frames s⁻¹. (a) The arrows mark four O atoms. (b) Red lines are the trajectories of the four O atoms.

vacancy, before the exchange with CO, is also randomized by the wiggling. The diffusion length that appears in the lattice diffusion equation is, therefore, the distance between two vacancies in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, i.e., $d = \sqrt{3}a$. With $D_{\sqrt{3}} = (d^2/4) \Gamma_2$, we thus obtain a diffusion coefficient of $D_{\sqrt{3}} = 1.48 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for the motion in the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.

As a result, we find that the domain boundary diffusion coefficient is one order of magnitude higher than the lattice diffusion coefficient at the same temperature.



Fig. 3. (a) Another frame from the movie of Fig. 2 (movie S2) with only two overlaid trajectories. (b) shows the upper one of the two trajectories in (a) with color-coded frame numbers, and (c) shows the lower one of the two trajectories in (a), also with color-coded frame numbers. $V_t = -0.7$ V, $I_t = 3$ nA, 129 Å x 129 Å, 12 frames s⁻¹.

4. Discussion

Diffusion of O atoms along the domain boundaries of the $(\sqrt{3} x \sqrt{3})R30^{\circ}$ -CO structure on Ru(0001) is thus distinctly faster than

diffusion through the ordered lattice. On the other hand, the enhancement by one order of magnitude is much lower than the enhancement factors of 5 - 6 orders of magnitude typically found for grain boundary diffusion with respect to lattice diffusion in 3D solids (at temperatures below roughly 0.6 T_m , where T_m is the melting temperature of the solid) [1].

This discrepancy points to distinct mechanistic differences. For 3D solids, the newer literature assumes that grain boundary diffusion follows mechanisms that are qualitatively different from the usual lattice diffusion mechanisms [3,4]. For example, lattice self-diffusion in metals usually follows a vacancy mechanism, whereas in the grain boundaries, according to kinetic Monte-Carlo and molecular dynamics simulations, interstitial atoms and collective motions of several atoms play an equally important role [4].

We propose that the discrepancy between the $(\sqrt{3} x \sqrt{3})R30^{\circ}$ -CO/ O case on the one hand and the 3D solids on the other can be explained by the fact that in the adsorption layer no such qualitative differences between domain boundary and lattice diffusion exist and that the mechanisms are, in principle, equivalent. Within this hypothesis, the enhanced diffusion along the domain boundaries is explained by easier excitations of the same atomic processes as in the lattice.

We thus claim that the mechanism in the domain boundaries is equivalent to the previously derived "door-opening mechanism" of surface diffusion of O atoms in the ordered $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -CO lattice [8]. In this mechanism, a hopping event of an O atom that leads to an exchange with a CO molecule, has two steps that affect the rate. In the first step, one of the CO molecules at the rim of the vacancy, in which the O atom is located, is displaced to an interstitial site of the $(\sqrt{3} x \sqrt{3})R30^{\circ}$ -CO lattice. This step costs an activation energy of 0.3 eV. It also lifts the ground state energy by 0.16 eV compared to the original configuration because the displaced CO molecule has two CO molecules on nearest-neighbor sites. Nearest-neighbor configurations are repulsive by 75 - 85 meV per CO-CO pair [9]. (The energies are from DFT calculations.) Because of the low barrier, the CO displacement is a fast pre-equilibrium that affects the rate by the lifted ground state energy (not by its own barrier). In the second step, the O atom can jump through the door opened by the displaced CO molecule to a site outside the original vacancy. The atom takes a path from its original hcp site over a bridge site to an intermediate fcc site and from there over a second bridge site to a neighboring hcp site, connected with an activation energy of 0.62 eV. In a third step, several CO molecules rearrange to give a configuration equivalent to the original configuration; this process is fast and does not appear in the overall rate. The overall activation energy of 0.16 eV + 0.62 eV = 0.78 eV was in reasonable agreement with the experimental value of 0.63 eV [8].

In a heavy domain wall of the $(\sqrt{3} \times \sqrt{3})$ R30°-CO structure, one can devise a similar sequence of steps consisting of displacements of CO molecules and subsequent jumps of O atoms. Also in this case, an O atom can only jump to a site outside its CO vacancy, when a neighboring hcp site is empty, i.e., when all three Ru atoms forming the hcp site do not have an adsorbed CO molecule. This is achieved by displacements of CO molecules.

What is different in the heavy domain boundary is the coordination of the CO molecules around the O atom. As shown in the model of Fig. 1 (b), all four O atoms in this particular situation are coordinated by CO molecules of which at least one molecule already has a second CO molecule on a nearest-neighbor site. When these molecules are displaced to neighboring on-top sites, e.g., along the directions indicated by black arrows, creating an empty hcp site for the jump of an O atom, the number of nearest-neighbor CO pairs increases by one rather than by two as in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO lattice. The ground state energy therefore increases by ~80 meV rather than by 0.16 eV. Accordingly, the overall activation energy is ~80 meV lower than in the ordered lattice. A second effect working in the same direction is the shorter average distances between the O atoms and the surrounding CO molecules at the higher coverage in the heavy domain wall. The repulsion between O and CO corresponds to a lower adsorption energy of the O atoms, resulting in a lower jump barrier. This effect is weaker, \sim 40 meV or less [10]. Overall, the barrier is lowered by a value of the order of 100 meV. Similar arguments have previously been used to explain the faster diffusion of O atoms through the disordered CO layer at a coverage of 0.47 ML [10].

For the alternative light domain walls, one can construct a model by removing all CO molecules from nearest-neighbor pair configurations. As shown in Fig. 1(c), most O trajectories through such a configuration do not require CO displacements at all, and only for jumps in certain directions displacements are required that create single CO-CO pairs on nearest-neighbor sites. Accordingly, the barrier with respect to the ordered lattice would be reduced by 0.16 eV or less. There are no configurations with closer O/CO distances than in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO lattice, so that the barrier would not further be lowered by this effect. Hence, in light domain walls, the barrier would also be lowered by a value of the order of 100 meV.

There are two observations that support these considerations. Firstly, when we interpret the ratio of domain boundary and lattice diffusion coefficients entirely in terms of activation energies, neglecting possible differences between the preexponential factors, then application of Arrhenius equations for both types of diffusions gives

$$\Delta E^* = -k_BT \, \mathrm{ln} rac{D_{\mathrm{db}}}{D_{\sqrt{3}}}.$$

 $\Delta E^* = E_{db}^* - E_{\sqrt{3}}^*$ is the difference between the activation energies of the domain boundary and $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO lattice diffusion. With T = 272 K and using the D_{db} values from the present study and the above evaluated $D_{\sqrt{3}}$ value from the previous work, we obtain $\Delta E^* = -(52 - 69)$ meV (the range is given by the two D_{db} values for the purely 2D and 1D cases). The domain boundary diffusion barrier is thus lower than the lattice diffusion barrier by a value of the order of 100 meV. This reduction is in quite good agreement with the values estimated above by using DFT data for the processes in the disordered CO layer. Note that the activation energies for a 3D case like Cu selfdiffusion by grain boundary and lattice diffusion, 1.24 eV and 2.04–2.19 eV [20–22], respectively, differ by a value that is one order of magnitude higher than the difference obtained in the present case, consistent with the much higher ratio of the grain boundary and lattice diffusion coefficients.

Secondly, D_{db} can also be compared with an experimental value. It has been observed that in a disordered CO layer at a CO coverage of Θ = 0.47 ML the oxygen hopping rate is higher than in the ordered structure [10]. Using the Arrhenius parameters determined in these experiments, the hopping rate of the O atoms in the disordered layer at 272 K is Γ = 6.66 s⁻¹. With $D_{dis} = (a^2/4)\Gamma$, this value translates into a diffusion coefficient of $D_{dis} = 12.19 \times 10^{-16}$ cm² s⁻¹. (For D_{dis} we here use the fact that at the higher CO coverage the O atoms do not wiggle in the smaller vacancies, so that the effective jump length is just a = 2.706 Å.) The value thus obtained almost quantitatively agrees with the present D_{db} values for the domain walls, indicating that the same effects operate in the disordered layer and in the domain walls. In both cases, diffusion follows an enhanced door-opening mechanism.

5. Conclusions

High-speed STM has been used to study the diffusion of O atoms on a Ru(0001) surface covered by 0.33 ML of CO. In contrast to our previous studies on the diffusion of adsorbed O atoms on the ordered lattice of the $(\sqrt{3} \times \sqrt{3})$ R30°-CO structure [8,9], we here investigated diffusion at domain boundaries. In the STM, the boundaries appear as disordered, fluctuating stripes. We find that the O atoms preferentially move along the domain boundaries and that the diffusion coefficient in the domain

walls is one order of magnitude higher than the diffusion coefficient in the ordered $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ domains. It is almost identical to the diffusion coefficient in the disordered CO layer at $\Theta = 0.47$ ML at the same temperature [10], indicating that it follows the same mechanism. We propose that the domain boundary diffusion is based on the same CO displacement and O hopping processes as in the door-opening mechanism in the ordered $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -CO structure. However, these processes happen at an increased rate in the disordered configurations in the domain walls.

CRediT authorship contribution statement

Ann-Kathrin Kügler: Writing – review & editing, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Hannah Illner:** Writing – review & editing, Visualization, Software, Formal analysis, Data curation. **Joost Wintterlin:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available in the Open Data LMU repository at https://doi.org/10.5282/ubm/data.502 or can be obtained from the authors upon reasonable request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2024.122597.

References

 Y.M.I. Kaur, W. Gust, Fundamentals of Grain and Interface Boundary Diffusion, Wiley, Chichester, 1995.

- [2] I. Kaur, W. Gust, L. Kozma, Handbook of Grain and Interphase Boundary Diffusion Data, Ziegler, Stuttgart, 1989.
- [3] H. Mehrer, Diffusion in Solids, 1st. ed., Springer, Berlin, Heidelberg, 2007.
- [4] A. Suzuki, Y. Mishin, Atomic mechanisms of grain boundary diffusion: low versus high temperatures, J. Mat. Sci. 40 (2005) 3155–3161.
- [5] T. Tansel, A. Taranovskyy, O.M. Magnussen, In situ video-STM studies of adsorbate dynamics at electrochemical interfaces, ChemPhysChem 11 (2010) 1438–1445.
- [6] Y.-C. Yang, K. Hecker, O.M. Magnussen, In situ video-scanning tunneling microscopy studies of the structure and dynamics of Cl adlayers on Au(100) electrodes, Electrochim. Acta 112 (2013) 881–886.
- [7] D.-J. Liu, J.W. Evans, Surface diffusion in mixed overlayers with superlattice ordering: percolative transport around obstacles and along domain boundaries, J. Chem. Phys. 113 (2000) 10252–10264.
- [8] A.-K. Henß, S. Sakong, P.K. Messer, J. Wiechers, R. Schuster, D.C. Lamb, A. Groß, J. Wintterlin, Density fluctuations as door-opener for diffusion on crowded surfaces, Science 363 (2019) 715–718.
- [9] S. Sakong, A.-K. Henß, J. Wintterlin, A. Groß, Diffusion on a crowded surface: KMC simulations, J. Phys. Chem. C 124 (2020) 15216–15224.
- [10] H. Illner, S. Sakong, A.-K. Henß, A. Groß, J. Wintterlin, Diffusion of O atoms on a CO-covered Ru(0001) surface-a combined high-speed scanning tunneling microscopy and density functional theory study at an enhanced CO coverage, J. Phys. Chem. C 127 (2023) 7197–7210.
- [11] A.K. Henß, J. Wiechers, R. Schuster, V. Platschkowski, J. Wintterlin, A beetle-type, variable-temperature scanning tunneling microscope for video-rate imaging, Jpn. J. Appl. Phys. 59 (2020) SN1007.
- [12] P.K. Messer, A.K. Henß, D.C. Lamb, J. Wintterlin, A multiscale wavelet algorithm for atom tracking in STM movies, New J. Phys. 24 (2022) 033016.
- [13] H. Pfnür, D. Menzel, Lateral interactions for CO/Ru(001): order-disorder transitions of the $\sqrt{3}$ structure, Surf. Sci. 148 (1984) 411–438.
- [14] H. Pfnür, H.J. Heier, Order-disorder phenomena in the system CO/Ru(001), Ber. Bunsenges. Phys. Chem. 90 (1986) 272–277.
- [15] G.E. Thomas, W.H. Weinberg, The vibrational spectrum and adsorption site of CO on the Ru(001) surface, J. Chem. Phys. 70 (1979) 1437–1439.
- [16] H. Pfnür, D. Menzel, F.M. Hoffmann, A. Ortega, A.M. Bradshaw, High resolution vibrational spectroscopy of CO on Ru(001): the importance of lateral interactions, Surf. Sci. 93 (1980) 431–452.
- [17] G. Michalk, W. Moritz, H. Pfnür, D. Menzel, A LEED determination of the structures of Ru(001) and of CO/Ru(001)– $\sqrt{3} \times \sqrt{3}$ R30°, Surf. Sci. 129 (1983) 92–106.
- [18] M. Lindroos, H. Pfnür, G. Held, D. Menzel, Adsorbate induced reconstruction by strong chemisorption: Ru(001)p(2×2)-O, Surf. Sci. 222 (1989) 451–463.
- [19] C. Stampfl, M. Scheffler, Theoretical study of O adlayers on Ru(0001), Phys. Rev. B 54 (1996) 2868–2872.
- [20] B. Burton, G.W. Greenwood, The contribution of grain-boundary diffusion to creep at low stresses, Met. Sci. J. 4 (1970) 215–218.
- [21] A. Kuper, H. Letaw, L. Slifkin, E. Sonder, C.T. Tomizuka, Self-diffusion in copper, Phys. Rev. 98 (1955) 1870.
- [22] D.B. Butrymowicz, J.R. Manning, M.E. Read, Diffusion in copper and copper alloys. Part I. volume and surface self-diffusion in copper, J. Phys. Chem. Ref. Data 2 (1973) 643–656.