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Surface mass diffusion over an extended temperature range on Pt(111)

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Abstract

Surface mass diffusion is investigated on Pt(111) at temperatures in the range 710–1220 K. This greatly extends the range over which diffusion is known from step fluctuation spectroscopy (SFS). In the present research, a beam of Pt⁺ self-ions is employed to create a suitable structure on step edges. The surface mass diffusion coefficients then follow from the decay of Fourier components observed by low-energy electron microscopy (LEEM) at selected annealing temperatures. The results agree with SFS values where they overlap, and continue smoothly to low temperature. This makes it unlikely that diffusion along step edges plays a major role in step edge relaxation through the temperature range studied. The surface mass diffusion coefficient for the range 710–1520 K deduced from the present work, together with previous SFS data, is $D_s = 4 \times 10^{-3} \exp(-1.47 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$.

1. Introduction

The surface mass diffusion D_s determines the flux of surface atoms that flows, in accordance with the Nernst–Einstein equation, in response to a driving chemical potential gradient. It is a critical factor in a variety of contexts that have both scientific and technical importance. These include epitaxial crystal growth [1], irradiation effects [2], most particularly erosion and surface processing by ion beams [3], the synthesis of nanostructures [4], surface chemical reactivity [5], and a variety of other topics of current research. Processes such as grain boundary grooving were formerly employed to estimate D_s [6], but have been replaced in recent times by techniques such as step fluctuation spectroscopy (SFS), in which the Fourier modes of step edges are driven to relax by the step free energy [7]. The motion of surface steps was observed by early reflection electron microscopy [8], low-energy electron microscopy (LEEM) [9, 10] and scanning tunnelling microscopy (STM) [11] studies. Attempts

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to systemize the understanding of surface diffusion have occupied many decades of research effort [12–15]. The surface mass diffusion of interest here must be distinguished from hopping diffusion of surface species observed at atomic resolution, for example by field ion microscopy (FIM) [16, 17]. In particular, the surface self-mass diffusion coefficient determines the flow of an average surface host atom, and contains as a factor the concentration of those surface defects (adatoms, advacancies) by which the response to a gradient of chemical potential takes place. Recent studies of clean surfaces of close-packed metals have revealed an approximate universality that resembles that long established for bulk metals [18, 19].

There is a rich literature concerning surface diffusion on Pt. Step fluctuation spectroscopy observes the kinetics of step profiles in equilibrium. A study of fluctuations on Pt(111) showed the process dominated by terrace diffusion, with $D_s = 4.7 \times 10^{-4} \exp(-1.19 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$, and step edge stiffness $\beta(T) = (260 - 0.04 T) \text{ meV nm}^{-1}$ above 1190 K; an increasing contribution of bulk defects to diffusion was observed above $\sim 1400 \text{ K}$ [7]. FIM of single atoms and STM measurements of Pt dimer and island formation combined with kinetic Monte Carlo simulations yield a Pt adatom hopping energy of 0.26 eV [20, 21]. Several researchers have employed STM to observe step relaxation at atomic resolution. These indicate very different step energies at the lower temperatures (as suggested also by kink models of step behaviour) so the low- T and high- T results remain disparate. Thus, stiffnesses $\sim 3\text{--}4 \text{ eV nm}^{-1}$ are reported for T below 500 K by Jeong and Williams [22], based on data from [23]. Step motion on Pt(111) studied by STM in the range 530–800 K suggests diffusion along the steps (rather than over terraces) with activation energy $\sim 1 \text{ eV}$ [23]. Early work using decay of periodic structures (scratches) gave $E_d \sim 1.12 \text{ eV}$ averaged over grain orientations [6].

In addition to equilibrium processes, surface transport can be determined from the decay of non-equilibrium step profiles. Giesen and Icking-Konert [24] used the decay of Fourier modes for a deformed step edge on Cu(111) at 300 K to obtain results consistent with those from equilibrium methods. Earlier, Bartelt and Tromp [10] showed that step mobility and the equilibration of rough steps on Si(100) at $\sim 1070 \text{ K}$ are both driven by the Gibbs–Thompson effect.

In this paper we report an extension of SFS measurements of D_s by a factor $\sim 10^4$ to lower surface mass diffusion coefficients. A limitation of SFS as currently employed is that the microscopy is generally limited to video observation rates of $1/30 \text{ s}$ and that a convenient relaxation time t is thereby limited to a range $3 \text{ s} > \tau > 10^{-2} \text{ s}$. There the short-term limit is the video rate and the long-time limits are instrumental stability. Surface mass diffusion studies are thereby typically limited to $0.65 T_m > T > 0.5 T_m$, with T_m the melting temperature of the metal under investigation. In the present study we instead prepare steps in ‘frozen’ configurations that resemble Fourier modes, and then observe the decay of those modes under the influence of surface mass diffusion and step energetics. By LEEM it is possible to observe decay over extended time periods, without reference to long-term instrumental stability, and limited only by surface gases from the ambient vacuum (10^{-10} Torr). In this way, the increased sensitivity in D_s identified above becomes readily feasible.

As a means of synthesizing steps with suitable structure on Pt(111) we employ ion beam irradiation with a beam of Pt self-ions. The erosion from the beam is sufficiently rapid to nucleate advacancy islands that merge with pre-existing straight steps to create desired structure. The use of self-ions avoids contamination that could otherwise alter the surface energetics.

In what follows, details of the experimental arrangement, including the ion beam configuration, are first explained in section 2. Experimental results for surface mass diffusion on Pt(111) are then presented and discussed in section 3.

2. Experimental details

The Pt crystal, 9 mm in diameter and 0.9 mm thick (obtained from the Surface Preparation Laboratory, The Netherlands) was oriented to the (111) plane within $<0.2^\circ$. Initial surface cleaning was carried out in a separate UHV preparation chamber equipped with the LEED optics. Cycles of 1 keV Ar^+ ion beam bombardment at room temperature for 5–15 min, followed by annealing at 1300 K, were interspersed with occasional treatment in 1×10^{-6} Torr of O_2 . The pre-cleaned crystal was quickly transferred to the LEEM vacuum vessel, where cleaning cycles were continued. The eventual surface exhibited sharp 1×1 LEED spots with no trace of impurities detectable by LEEM or Auger spectroscopy (AES). LEEM was employed to observe the Pt surface at temperatures up to 1300 K with a base vacuum pressure in the low 10^{-11} Torr range (the pressure remained at $\sim 10^{-10}$ Torr for temperatures of 1250 K). Large areas of Pt surface exhibited well-spaced and relatively straight step edges similar to those reported in an earlier study [7]. In later studies using Pt^- self-ions, occasional larger flat areas of micrometre size developed upon sputtering.

Prior to this research, the LEEM was fitted with a negative ion accelerator, specifically a modified SNICS II source from National Electrostatic Corporation [25], that provided a beam of Pt^- ions at normal incidence on the sample surface. With impact energies tunable from 0 to 5 keV, and beam intensities up to $20 \mu\text{A cm}^{-2}$, the ion beam passing through the objective lens of the microscope was easily capable of nucleating new islands of either adatoms or advacancies, dependent on the selected beam energy. Details of the equipment are reported elsewhere [26].

Experiments proceeded by first processing selected areas of the surface using ion beams at elevated temperature. A beam density between 5 and $10 \mu\text{A cm}^{-2}$ of the Pt^- ions, impact energy 1 keV, was typically used to produced conveniently large advacancy islands. The surface was held at 950–1000 K during this erosion cycle. Steps were observed by LEEM during subsequent brief annealing, typically at 1150–1230 K. The sample temperature was changed to a selected test value immediately after the surface morphology simplified to leave few islands together with well-developed periodic step fluctuations, and maintained at that temperature as the step smoothed by surface mass diffusion. Video frames were processed, much as for SFS, to obtain a digital record of the step profile as a function of time lapse [7, 19]. To analyse these data, a convenient length of sinusoidal profile was chosen and the background line shape subtracted. Ideally the step becomes straight at long times, but in practice we used a polynomial fit through inflection points to remove residual large-radius curvature. A fast Fourier transformation then yielded Fourier amplitudes $A(q)$ as functions of time. Relaxation times τ fitted to the time decays then determined the surface mass diffusion coefficients, as in SFS [7].

The decay of the periodic line is purely a relaxation process that lacks mean rms (thermal equilibrium) amplitudes exploited in SFS. For this reason, values of the step edge stiffnesses $\tilde{\beta}$ needed to determine D_s from τ were not measured in the present work and instead were estimated from earlier SFS results. These revealed a small temperature dependence of stiffness on Pt(111) that extrapolates into the present temperature range as $\tilde{\beta}(T) = (260 - 0.04 T) \text{ meV nm}^{-1}$ (see [7]). The change is small relative to the very large changes of D_s determined here, into which $\tilde{\beta}$ enters as a multiplicative factor.

In all, 30 step edges were studied at ten different temperatures ranging from 710 to 1230 K. The upper temperature limit overlaps earlier SFS data [7].

3. Results and discussion

Figure 1(a) shows steps interacting with circular islands nucleated at 980 K by an applied beam of $5.3 \mu\text{A cm}^{-2}$ Pt^- self-ions of energy 1 keV. The islands nucleate and grow on wider terraces,

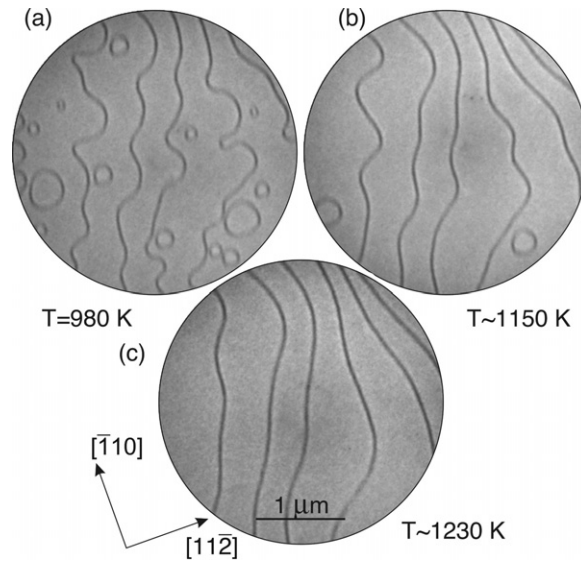


Figure 1. LEEM micrographs showing the creation of well-defined periodic structures on single steps. Vacancy islands were created by bombardment of $5.3 \mu\text{A cm}^{-2}$ of the Pt^- ions at impact energies of 1 kV at 980 K. After sputtering, the crystal was briefly annealed at ~ 1150 K (b), or higher (c) to produce tailored structure lacking islands. Well-spaced periodic steps, uncorrelated with neighbours, were chosen for decay study. The field of view is $4 \mu\text{m}$, impact energy $E = 17$ eV, with orientation from (1×1) LEED spots (not shown).

with surrounding steps flowing steadily uphill (left to right on all LEEM images). Frames (b) and (c) show the subsequent relaxation of steps as they anneal at selected temperatures of 1150 K and 1230 K respectively. Detailed step profiles, as modified by the ion beam, differ from point to point on the surface. The complex interaction among steps and nucleated islands yielded areas with useful step profiles and amplitudes of tenths of nanometres with acceptable frequency, so the procedure employed here to create suitable step structure is effective in practice.

Details of the decay process are reported in figure 2. Lines in the upper panel (a) smooth substantially over 15 min at 900 K. Profiles of the step on the far right (arrow), and the polynomial background fit, are shown in the lower figure.

Figure 3 shows the time decay of Fourier amplitudes obtained from an analysis of the step images in figure 2. The decays are exponential, with a small offset caused by the leak in the fast Fourier transform due to end effects. The dependence of $\tau(q)$ on q defines the surface mass diffusion coefficient D_s according to [22, 27, 28]

$$\tau_q^{-1} = 2A \tilde{\beta} D_s a q^3 / k_B T. \quad (1)$$

Here, A is the surface area per atom and a the interlayer spacing.

In connection with the values of D_s in figure 4, we note that surface diffusion causes relaxation rates to vary as q^3 with wavevector q of the Fourier mode. In the earlier SFS research [7], the dependence on q is verified directly from experimental observation involving many q values of $\tau_q^{-1} \sim q^3$ (as opposed, for example, to bulk diffusion with $\tau_q^{-1} \sim q^2$, or diffusion along the step edges with $\tau_q^{-1} \sim q^4$ [11, 22, 28]). No such ready confirmation is possible in the present research as the step profiles approximate single Fourier modes of a particular q . Notwithstanding this difficulty, the inset in figure 3 shows the measured dependence on q as q^α for three wavevectors. A reasonable fit gives $\alpha = 2.8$, consistent

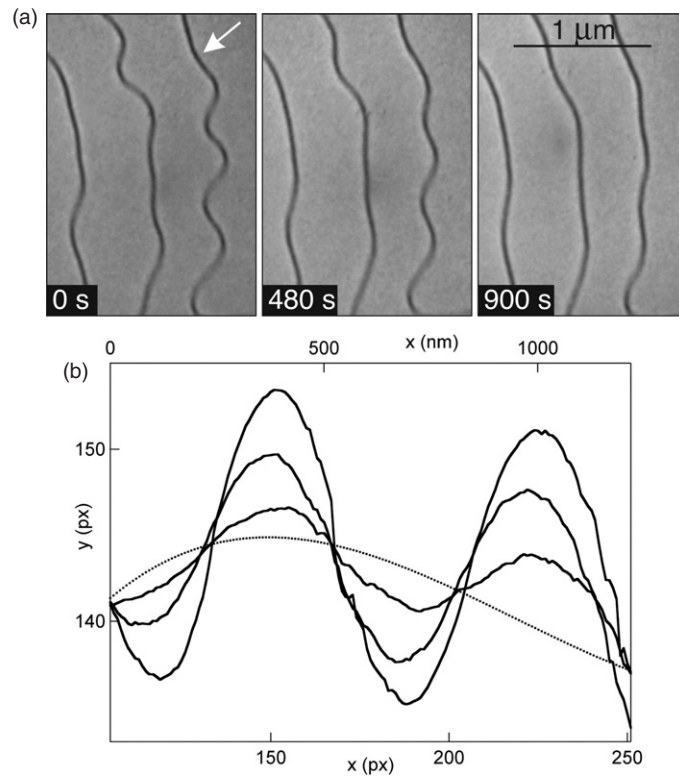


Figure 2. (a) Almost sinusoidal steps decaying with time at 900 K. The profile of the marked step (arrow) is shown in (b) with the dotted line a polynomial fit through the inflection points used to subtract the step shape at long times.

with the SFS results, although with considerable uncertainties. As mentioned above, SFS measurements for Pt(111) have been reported for temperatures close to those employed here. The continuity with the SFS results suggests that terrace diffusion prevails through the extended regime explored in the present research. It is generally believed that other mechanism such as diffusion along steps must intervene at low temperatures [22].

The surface diffusion coefficients determined from the decay curves for a range of annealing temperatures are presented as full circles in figure 4. Values determined earlier by SFS are included in figure 4 as open circles. Results for $T_m/T > 1.4$ (i.e. $T \gtrsim 1400$ K) include a significant increase from bulk vacancy diffusion [7] and are excluded from the present discussion. It is satisfactory that the remaining SFS data for $1.4 < T_m/T < 1.7$ fit with the data reported here where the data sets overlap. Figure 4 makes clear the large extension of results to lower temperature made possible by the present method.

A fit to the present data marked by the dotted Arrhenius plot in figure 4 gives $D_s = 7 \times 10^{-4} \exp(-1.34 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$ for the temperature range 710–1220 K. This is close to the value from an analysis of SFS data, specifically $D_s = 4.7 \times 10^{-4} \exp(-1.19 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$ for the temperature range 1190–1520 K. Given the scatter of the decay data and reasonable overlap near ~ 1200 K we have fitted the data over the entire range of observation 710–1520 K by

$$D_s = 4 \times 10^{-3} \exp(-1.47 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}. \quad (2)$$

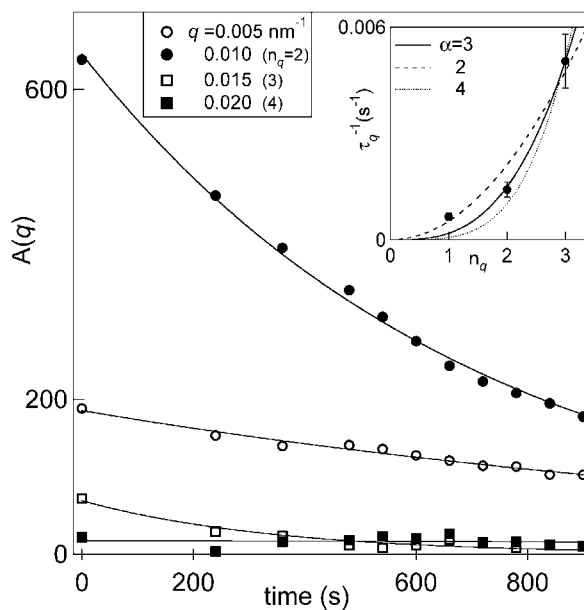


Figure 3. Fourier amplitudes $A(q)$ for a Pt step in figure 2; solid lines are exponential fits for wavevectors q indicated. Here, q (nm^{-1}) = $2\pi n_q/L$, $n_q = 1, 2, \dots$, integral, with $L \sim 1225$ nm. The inset shows a power-law dependence of mode relaxation times τ on n_q with data fitted by $\alpha = 2.8$ (not shown) consistent with adatom terrace diffusion. Shown are $\alpha = 3$ (solid line), $\alpha = 2$ (dashed), $\alpha = 4$ (dotted).

Upon subtracting the measured hopping energy for Pt adatoms of 0.26 eV [20, 21] from the activation energy in equation (2) we find an adatom formation energy (from kink sites) of 1.2 eV.

We note that reported research using STM evidence has identified step relaxation on Pt(111) in a temperature range that overlaps the present results as occurring by step edge diffusion [23]. In edge diffusion, the step profile relaxes by motion of atoms along the step itself, from one kink to the next, rather than over neighbouring terraces. The lack of activation onto terrace sites leads to an activation energy for edge diffusion smaller than that for terrace diffusion, probably by several tenths of an eV in magnitude for Pt(111). No sign of the break in slope this would entail on an Arrhenius plot can be discerned in the diffusion results presented in figure 4.

4. Summary

We have fitted a low-energy electron microscope with an accelerator that provides an intense beams of metal negative ions. Using Pt^- on Pt(111) at 1 keV we have demonstrated how to prepare experimental areas in which formerly straight step edges develop roughly sinusoidal profiles. The decay of these profiles at selected temperatures then yields the surface mass diffusion coefficient, given values of the step stiffness from step fluctuation spectroscopy. A merit of the technique is that probe characteristics such as long-term stability no longer limit the accessible range. As a result, diffusion can be examined over a greatly extended temperature range. With experimental periods up to days thus becoming feasible, the limiting factor is now

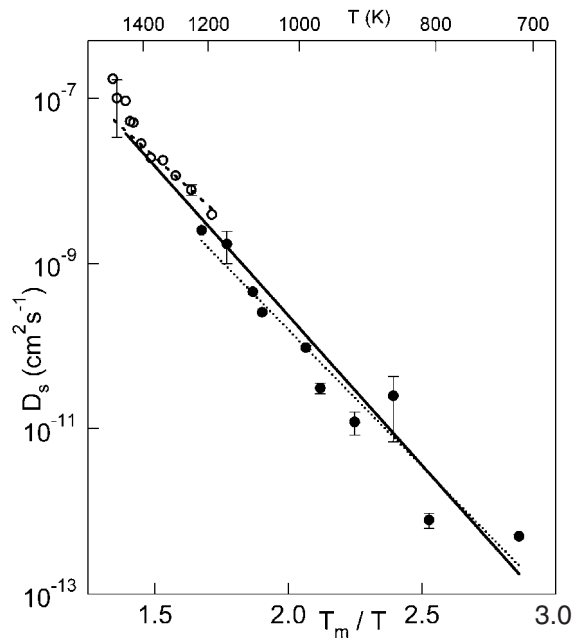


Figure 4. The solid circles are surface diffusion coefficients obtained from relaxation times (equation (1)) at different temperatures. The least-squares fit (dotted line) shows $D_s = 7 \times 10^{-4} \exp(-1.34 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$. The open circles and dashed fit are from previous work (SFS) [7]. A fit for a range $>10^5$ in D_s for 710–1520 K, gives $D_s = 4 \times 10^{-3} \exp(-1.47 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1}$ (solid line).

probably the sensitivity of diffusion to accumulated contaminants from the ambient vacuum at the particular operating temperature.

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