Grazing incidence ion erosion in the presence of adsorbates

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Abstract. The effect of a background pressure of adsorbable species on sputtering and surface damage in grazing incidence ion erosion of Pt(111) is investigated by scanning tunneling microscopy and molecular dynamics simulations. The background pressure implies a partial surface coverage with adsorbates, which in turn causes an enhancement of the erosion rate by a factor of up to 40 compared to the clean case. Partial pressures of molecular oxygen and carbon monoxide were maintained during ion erosion with 5 keV Ar$^+$ for various grazing angles between 81° and 87° and temperatures ranging from 400 to 550 K.

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1. Introduction

Whether adsorption influences the sputtering yield is a question rarely posed and usually considered to be irrelevant. Indeed, in normal incidence ion bombardment the energy of the primary ion is efficiently transferred to the substrate atoms, irrespective of whether adsorbates are present or not. In consequence, a collision cascade and a subsequent thermal spike develop resulting in substrate atom sputtering and adparticle desorption. Therefore a background pressure of adsorbable species will usually have only a small effect on the sputtering yield.

The situation differs for grazing incidence ion bombardment. In this geometry, the energy of motion in the direction normal to the surface is small. Surface channeling of the ions takes place, which can be considered as a series of small angle binary collisions with the atoms of the topmost layer [1]. In consequence the ions are reflected at the planar surface potential. The series of small angle binary collisions implies only little transfer of energy and consequently marginal sputtering and surface damage. For keV ions with an angle of incidence which deviates only by a few degrees from the surface, sputtering and surface damage will even be absent. Adsorbates disturb the planarity of the surface potential and large angle scattering events take place. Ions hitting the adsorbate become scattered and will energize the adsorbate, thereby causing not only a vastly increased energy transfer to the surface with the consequence of sputtering, but also adsorbate desorption. This property is used in low-energy ion scattering measurements (LEIS) to determine the structure, coverage and sticking coefficient of adsorbates [2]–[4]. The ion-induced desorption has been studied in detail, however, morphology changes due to large scattering events have not been studied extensively.

The situation of grazing incidence ion bombardment is not uncommon. It has become an efficient method to create ripple patterns on surfaces through self-organization [5]–[9]. Grazing incidence geometry is also used in ion scattering experiments investigating the charge transfer and electronic excitations of atoms near surfaces [10, 11].

We therefore carried out a scanning tunneling microscopy (STM) and molecular dynamics (MD) simulation study investigating adsorbate desorption, adsorbate-induced sputtering and adsorbate induced surface damage through grazing incidence ions. We use 5 keV Ar⁺ ions impinging at angles between 81° and 87° with respect to the surface normal on Pt(111).
Molecular oxygen (O$_2$) and carbon monoxide (CO) are used to study the ion–adsorbate interaction. The changes due to adsorbates are investigated for low ion fluences and flat initial surfaces as then adsorbates disturb surface channeling most significantly. We find that adsorbates increase sputtering in grazing incidence geometry by orders of magnitude compared to the clean case. As a result of our investigations it appears likely that erosion observed experimentally at grazing angles under nominally clean conditions is significantly influenced by unavoidable adsorption from the background gas in vacuum systems.

Before proceeding to the results, we summarize a few facts on the interaction of ions with crystal surfaces at off-normal incidence. Increasing the angle of incidence $\theta$ with respect to the surface normal results in a decrease of the ion penetration depth. More energy is deposited near the surface causing an increase of the sputtering yield. Usually $Y_s$ reaches its maximum at $\theta = 50^\circ$ to $\theta = 60^\circ$. At about $75^\circ$, the erosion rate splits into two components, which result from sputtering on the flat terrace and sputtering at ascending step edges [12]. On the terrace the impinging ions are no longer able to overcome the collective repulsive potential of the surface atoms and surface channeling sets in. Sputtering and surface damage cease. The terrace sputtering yield on Pt(111) is 0.08 for 5 keV Ar$^+$ ions impinging at $\theta = 83^\circ$ [13]. At ascending steps illuminated by the ion beam, however, the impinging ions are able to transfer a large amount of their total kinetic energy to the crystal. A thermal spike occurs and the sputtering yield is two orders of magnitude larger than on the flat terrace. Under grazing incidence conditions the sputtering yield $Y_s$ is thus a morphology-dependent weighted average of the terrace and the step edge yield [12, 13].

2. Experimental

The experiments were performed in an ultrahigh vacuum variable temperature STM apparatus with a base pressure in the 10$^{-11}$ mbar range. Cleaning of the Pt(111) single crystal was accomplished by cycles of ion beam erosion at room temperature and flash annealing to 1270 K. Prior to each experiment, the sample is heated to 770 K in an oxygen partial pressure of 1 $\times$ 10$^{-6}$ mbar for 5 min followed by flash annealing to 1270 K.

A mass separated 5 keV Ar$^+$ ion beam is used in the experiments, incident under a large angle $\vartheta$ measured with respect to the surface normal. The projection of the ion beam direction onto the surface is along the [110] direction. The ion flux $f$ is measured with a Faraday cup prior to and after each experiment and is set to 1.8 $\times$ 10$^{16}$ ions m$^{-2}$ s$^{-1}$. For simplicity the ion fluence $F = f \cdot t$ is denoted in monolayer equivalents (MLE), where 1 MLE equals the areal density of the surface layer atoms on Pt(111) (1.504 $\times$ 10$^{19}$ atoms m$^{-2}$). $F$ ranged between 0.25 and 1.5 MLE. Through the use of a differentially pumped ion source the total pressure in the sample chamber could be kept typically at 2 $\times$ 10$^{-8}$ mbar during ion exposure.

The effect of a CO background pressure on surface damage and sputtering is described in section 4. A CO partial pressure of $P_{CO} = 1 \times 10^{-8}$ mbar starting 300 s prior to ion exposure was found to be sufficient to establish an initial adsorption–desorption equilibrium at 400 K with a molecular coverage $\Theta_{CO} = 0.12$ ML, as estimated on the basis of the data of Poelsema et al [14]. An ion exposure $F = 1$ MLE and $\vartheta = 87^\circ$ were used. Due to repulsive CO–CO interaction [15] and at $\Theta_{CO} = 0.12$ ML the CO overlayer must be assumed to be disordered, however, with a preferential adsorption to step edges. At the temperature of 400 K used in the adsorption experiments the initial sticking coefficient $S_{CO}$ of CO differs only little from 0.8, the value measured at room temperature [15].
For the experiments investigating the effect of an oxygen background pressure on surface damage and sputtering described in section 5, a clean adsorbate-free surface is prepared. The sample temperature is set to 550 K and then the sample is exposed to a preset oxygen partial pressure \( P_0 \) up to \( 1 \times 10^{-5} \) mbar through backfilling of the vacuum chamber. Immediately after establishing \( P_0 \) the ion bombardment with \( \vartheta = 85.5^\circ \) started and terminated after \( F = 0.5 \) MLE was reached. Oxygen adsorbs dissociatively on the Pt(111) surface at temperatures above 150 K forming an adlayer with a saturation coverage of oxygen amounting to \( \Theta_1 \). At 550 K the oxygen adlayer forms a disordered adsorbate layer, as the p(2×2) LEED adlayer spots diminish in intensity with temperature and are at 400 K already only faintly visible [16]. At 550 K the initial sticking coefficient \( S_0 \) of oxygen molecules is 0.03 [17]. Desorption of oxygen becomes significant at 600 K [18, 19].

For the experiments investigating the effect of the incidence angle on surface damage and sputtering at 550 K described in section 7 an adsorbate free situation is compared to one with the sample exposed to \( P_0 = 5 \times 10^{-6} \) mbar and \( \vartheta \) is varied from \( \vartheta = 81^\circ–87^\circ \). In order to achieve comparable results, \( F \) has been selected such that the removed amounts of material \( \Theta_S \) were comparable and well below 1 ML.

STM imaging has been performed at room temperature, where the surface morphology is frozen.

3. Simulation setup

Our Pt simulation crystallite contains 15 layers; each layer extends 87 Å in the direction of the ion beam, and is 100 Å broad. Thus the total number of Pt atoms in the crystallite amounts to 20 170. We employ a many-body interaction potential [20] for the Pt–Pt interaction. The simulation is performed at 0 K by relaxing the target structure to minimum potential energy and quenching the kinetic energy. An oxygen adsorbate atom is put at a stable fcc adatom site on top of the crystallite. Its position, as well as that of all surface atoms, is relaxed. The adsorbate atom interacts with Pt atoms via a Morse potential

\[
V(r) = D\{\exp\left[-2\alpha(r - r_0)\right] - 2\exp[-\alpha(r - r_0)]\}. \tag{1}
\]

It is characterized by three parameters: the bond strength \( D \), the equilibrium bond distance \( r_0 \), and the potential fall-off \( \alpha \). These have been fitted to available experimental and \textit{ab initio} data of O adsorbed on Pt(111) [21]–[24]. Using the values \( D = 1.73 \) eV, \( r_0 = 1.96 \) Å and \( \alpha = 2.02 \) Å\(^{-1} \), this potential predicts a binding energy of O on Pt as 5.182 eV, a vibration frequency of 14.7 THz and a binding distance of 1.96 Å between the O atom and a surface Pt atom; these data are in close agreement with available data (5.28 eV, 14.7 THz and 2.00 Å).

The height of the adsorbate atom above the surface then results as \( h = 1.13 \) Å.

The Morse potential is cut off at \( r_c = 3.05 \) Å, which makes it a nearest-neighbor potential, and splined smoothly to zero in this distance. Towards small \( r \) we spline the Morse potential to the repulsive potential of [22],

\[
V(r) = Ae^{-br-cr^2}, \tag{2}
\]

where \( A = 6.84 \) keV, \( b = 3.49 \) Å\(^{-1} \) and \( c = 1.40 \) Å\(^{-2} \). We consider the impact of 5 keV Ar atoms on Pt(111) incident at \( \vartheta = 85.5^\circ \). The incidence azimuth is chosen such that its projection onto the surface is aligned in the [110] direction. The Ar projectile interacts via the purely repulsive ZBL potential [25] with the Pt and O atoms. In total, a number of 900 impact events
Figure 1. STM topographs after 1.0 MLE of 5 keV Ar$^+$ ions incident at 87° on Pt(111) at 400 K. (a) Ion exposure in the absence of a CO partial pressure, (b) $P_{\text{CO}} = 1 \times 10^{-8}$ mbar. The direction of the impinging ions is indicated with a black arrow. The image size is 1750 Å × 1750 Å. The dotted line is the projection of the preexisting step edge to the position where the number of vacancy islands starts to increase (see text).

are simulated. These ions impact on a stratified grid around the adsorbate; the length in ion beam direction amounts to 45 Å and the width is 2.5 Å. This area is subdivided in 225 cells with a size of 0.5 Å$^2$; 4 ions impinge randomly into each cell. Each trajectory is followed for 25 ps. This time is sufficient to decide on the fate of the projectile and the adsorbate atom, and also to determine the sputter yield reliably. The damage production on the surface, however, may still change somewhat after this time due to relaxation and diffusion processes. We are confident, though, that the qualitative features of the damage production may be analyzed already at this time. We consider all those atoms as sputtered that have zero-potential interaction energy with the target; due to our cutoff radius of 5.1 Å this means that they are a distance of at least 5.1 Å away from all substrate atoms and the adsorbate atom. The damage production may be quantified by counting all those atoms as adatoms, which are above the initial substrate surface.

Neglecting the many-body nature of the Pt–O interaction by implementing it as a Morse potential appears to be a potential source of systematic error. During the ion–surface interaction, the O atom is dynamically exposed to different bonding environments, ranging from implantation (12 Pt neighbors) to desorption (0 Pt neighbors), which are not all properly accounted for by the Morse potential. We checked the influence of the bonding part of the Pt–O potential by performing a reference simulation (for a restricted number of events), in which bonding was entirely switched off; i.e. only the repulsive potential, equation (1), is used to describe the interaction: no statistically significant deviations from our result with the full (repulsive and attractive) potential were found. We conclude that it is mainly the repulsive part of the Pt–O interaction that is relevant for the fate of the adsorbate and the induced sputtering.

4. The effect of a CO background pressure

Figure 1 compares the surface morphology after 1.0 MLE 5 keV Ar$^+$ ions incident at 87° on Pt(111) at 400 K in the absence (figure 1(a)) and in the presence (figure 1(b)) of a CO partial
pressure of $P_{\text{CO}} = 1 \times 10^{-8}$ mbar. From the comparison of the topographs it is obvious that the removed amount of surface layer Pt is substantially increased through the presence of the $P_{\text{CO}}$. While in figure 1(a) only small vacancy islands of monolayer depth are visible, in figure 1(b) both number and size of the vacancy islands are largely increased. The vacancy islands are frequently elongated along the ion beam direction. Also a few adatom islands are visible, which result from the nucleation of atoms pushed onto the surface in consequence of large angle scattering events. The removed amount $\Theta_S$ is increased from $\Theta_{S,\text{clean}} = 0.04$ ML to $\Theta_S = 0.28$ ML due to the adsorbed CO, i.e. the adsorbate induced increase is $\Delta \Theta_S = 0.24$ ML.

Due to the admittance of the CO 300 s prior to the beginning of ion exposure a coverage $\Theta_{\text{CO}} \approx 0.12$ ML is established. Although this coverage diminishes under the action of the ion beam, it must be concluded that the adsorbed molecules are the origin of the enhanced $\Theta_S$.

How does the adsorbed CO increase $\Theta_S$? To this end we first consider the interaction of the ion beam with the clean, adsorbate free substrate. At $\vartheta = 87^\circ$ the ions perform surface channeling. The kinetic energy for the motion in the direction normal to the surface $E_{\perp} = E_0 \times \cos^2 \vartheta$ amounts to only 14 eV and is not sufficient to induce sputtering on a perfect terrace. At most adatom–surface vacancy pairs are created. Although these pairs most frequently recombine due to diffusion eventually a few vacancy and adatom clusters form. Adatoms and adatom clusters are elevations exposed to the ion beam. Thus, they are efficiently sputtered through the large-angle scattering processes of impinging ions. Also larger vacancy clusters expose an illuminated step to the ion beam allowing impinging ions to transfer kinetic energy to the substrate through large-angle scattering processes, which cause sputtering. Let us now consider the interaction of the ion beam with a surface of randomly positioned adsorbates. The adsorbates are illuminated by the ion beam and large-angle scattering processes take place right from the beginning and in large numbers at the adsorbate locations. These scattering processes have two consequences: (i) the adsorbed molecules are partially desorbed from the surface and (ii) the scattered primary ion or the energized molecule transfers a significant amount of energy to substrate atoms causing sputtering and adatom formation. Note that the desorbed CO molecules are partly replenished from the CO background pressure. An indirect consequence of the adsorbate-induced sputtering is the rapid formation of vacancy islands (and to a lesser extent of adatom islands), which themselves display steps to the ion beam and are sputtered. In this sense, the direct adsorbate-induced sputtering is amplified by the ensuing formation of steps illuminated by the ion beam.

An interesting detail is visible in figure 1(b). The descending step edge displays in the shadow of the ion beam on the lower terrace a depletion zone where the number of vacancy islands is reduced in comparison to the flat terrace. The dotted line indicates the boundary of the vacancy depleted shadow zone. Through the step shadow ions do not or only with lower probability hit the terrace and the adsorbed particles. The distance between the step edge and the dotted line is $137 \pm 15$ Å.

As CO is one of the major components in the background gas of ultra high-vacuum systems and as CO has typically a large initial sticking coefficient on metal surfaces (e.g. $S_{\text{CO},0} = 0.8$ for Pt(111) [15]), CO adsorption cannot be avoided at room temperature [27]. Therefore ion scattering experiments on metal surfaces using the grazing incidence geometry are always subject to enhanced surface sputtering and roughening due to adsorbate scattering. The removed material under nominally clean conditions as visible in figure 1(a) is likely to be to a significant extent caused by a minute and unavoidable amount of adsorbed particles from the background gas.
Figure 2. STM topographs after a fluence of 0.5 MLE 5 keV Ar\textsuperscript{+} ions at 550 K and 85.5\degree with respect to the surface normal. (a) No oxygen partial pressure $P_O$, (b) $P_O = 1 \times 10^{-7}$ mbar, (c) $P_O = 1 \times 10^{-6}$ mbar, (d) $P_O = 1 \times 10^{-5}$ mbar. In (a), the direction of the ion beam is indicated by an arrow. The insets display the corresponding topographs after annealing to 720 K for 120 s. The image sizes are 1750 Å $\times$ 1750 Å, the inset sizes are 1000 Å $\times$ 1000 Å.

5. Oxygen-covered surface

Figures 2(a)–(d) compare the surface morphology after exposure to 0.5 MLE 5 keV Ar\textsuperscript{+} at 550 K in the absence (figure 2(a)) and in the presence of oxygen partial pressures $P_O = 1 \times 10^{-7}$ mbar (figure 2(b)), $P_O = 1 \times 10^{-6}$ mbar (figure 2(c)) and $P_O = 1 \times 10^{-5}$ mbar (figure 2(d)). It is obvious that the amount of removed material visible as vacancy islands of monolayer depth depends dramatically on the oxygen partial pressure. Already for $P_O = 1 \times 10^{-7}$ mbar in figure 2(b) the number density of vacancy islands increased by a factor of six compared to the clean experiment represented by figure 2(a). The higher oxygen partial pressures of figures 2(c, d) increase the size of the vacancy clusters, whereas their number density stays roughly constant. For $P_O = 1 \times 10^{-5}$ mbar in figure 2(d) also a significant number of adatom clusters is visible (small bright dots in figure 2(d)). To establish $\Theta_S$ quantitatively, after imaging the samples were annealed for 120 s to 720 K and subsequently reimaged (insets in figure 2). The bulk vacancies created by ion impacts migrate during the annealing step to the surface such that afterwards the area of the monolayer islands represents $\Theta_S$ to a very good...
Figure 3. Amount of removed material $\Theta_S$ as a function of oxygen partial pressure $P_O$. The solid curve is a fit to the experimental data using equation (5). The inset shows the evolution of the oxygen coverage versus ion fluence $F$ for the values of $P_O$ used, calculated on the basis of (A.4) and the measured desorption cross section $\sigma$ (see text).

approximation [28]. $\Theta_S$ plotted in figure 3 increases from 0.015 ML to roughly 0.20 ML with increasing $P_O$, corresponding to an increase by a factor of 13. Qualitatively the increase of $\Theta_S$ with $P_O$ may be understood similar to the case of adsorbed CO molecules: (i) it is due to direct sputtering caused by the energized adsorbate or the scattered primary ion. (ii) The direct sputtering associated with the adsorbate fosters formation of vacancy islands and adatom clusters, which are sputtered by ions illuminating them.

In order to study the effect of adsorbates in more detail the time-dependent oxygen coverage $\Theta_O(t)$ is calculated. It is determined by the balance of adsorption from the background pressure and desorption due to the impinging ions. Desorption due to impinging ions is quantified through the desorption cross section $\sigma_O$ being the average number of oxygen atoms desorbed per incident ion $Y_O$ normalized with the adsorbate concentration $\rho_O$:

$$\sigma_O = \frac{Y_O(t)}{\rho_O(t)} = \frac{Y_O(t)}{\Theta_O(t)} \cdot \Omega.$$  (3)

Here $\Omega = 6.67 \text{ Å}^2$ is the area of a Pt surface site. $\sigma_O$ can be interpreted as the average surface area depleted from adsorbates by a single incident ion. In the following analysis, we assume $\sigma_O$ to be independent of $\rho_O$. This is certainly valid for small $\rho_O$, but a serious approximation for large $\rho_O$. $\Theta_O$ is calculated explicitly in the appendix and may be considered for the present purpose as a function of time $t$ and of $\sigma_O$. The simplest reasonable assumption on the dependence of the additional sputtering yield on $\Theta_O(t, \sigma_O)$ is a linear dependence, i.e.

$$Y_S(t) - Y_{S,\text{clean}} = \Delta Y_S(t) = \gamma \cdot \Theta_O(t, \sigma_O),$$  (4)

where $Y_S(t)$ is the number of surface atoms sputtered per incident ion for a given $\Theta_O$ (the sputtering yield for $\Theta_O \neq 0$), $Y_{S,\text{clean}}$ is the number of surface atoms sputtered per incident ion for $\Theta_O = 0$ (the sputtering yield of the clean surface), $\Delta Y_S$ is the number of additionally sputtered.
atoms per incident ion due to the presence of oxygen adsorbates (the additional sputtering yield) and $\gamma$ a proportionality factor. $\Theta_S$ measured in the experiment is the result of ion exposure to a fluence $F$ for a certain period of time $\tau$. Thus

$$\Theta_S = f \cdot \Omega \cdot \int_0^\tau Y_S(t) \, dt = f \cdot \Omega \cdot \int_0^\tau (\gamma \cdot \Theta_O(t, \sigma_O) + Y_{S,\text{clean}}) \, dt. \quad (5)$$

Here $f \cdot \Omega$ is the flux of incident ions in units of MLE s$^{-1}$. The sputtering yield of the clean surface is measured experimentally to be $Y_{S,\text{clean}} = 0.03$. Equation (5) is fitted to the experimental data by adjusting the parameters $\gamma$ and $\sigma_O$. The best fit is plotted in figure 3 (solid curve) for $\gamma = 1.61 \pm 0.1$ and $\sigma_O = 20 \pm 14 \text{ Å}^2$. In view of the simplicity of our approach the experimental data are well reproduced by the fit.

The proportionality constant $\gamma$ fitted above has also a substantial interpretation. To characterize the ability of an adsorbed oxygen to induce additional sputtering we may define in analogy to the desorption cross section the sputtering cross section

$$\sigma_S = \frac{\Delta Y_S(t)}{\rho_O(t)} = \frac{\Delta Y_S(t)}{\Theta_O(t)} \cdot \Omega. \quad (6)$$

The sputtering cross section $\sigma_S$ can be interpreted as the additional average surface area, which is sputtered by a single ion due to adsorbed oxygen. Comparison of our definition (6) with (4) makes plain that

$$\gamma = \frac{\sigma_S}{\Omega}. \quad (7)$$

Thus by fitting (5) to obtain $\gamma$ we also determined $\sigma_S = 10.7 \pm 0.6 \text{ Å}^2$. Some scatter of the data around the fit for larger $P_O$ is not surprising since the model used is crude. To derive an explicit expression for $\Theta_O(t)$ in the appendix we assumed a coverage independent sticking coefficient, which is especially for larger $\Theta_O$ a poor approximation. Moreover, we attributed the entire increase of $Y_S$ implicitly to the large-angle scattering processes of ions at adsorbates. However, the increased $Y_S$ in the presence of oxygen adsorbates leads to an increased number of steps illuminated by the ion beam. Due to the large-angle scattering processes enabled by steps in grazing incidence ion bombardment (not necessary involving O-atoms) $Y_S$ is further enhanced. We also note that the increased number of illuminated steps is not only due to vacancy islands. For the largest $P_O$ also tiny adatom islands are visible (compare figure 2(d)). Apparently the presence of oxygen hinders recombination of impact-induced atoms with surface vacancies by a reduced adatom diffusion. This effect further enhances surface roughening and thus the average sputtering yield. The inset in figure 3 shows the calculated oxygen coverage $\Theta_O$ deduced from (A.4) derived in the appendix for the different $P_O$. The comparison of this graph with the evolution of $\Theta_S$ as a function of $P_O$ makes obvious why there is now further increase of $\Theta_S$ for large $P_O$. The surface is nearly saturated with adsorbates for most of the experimental time.

6. Simulation results

MD simulations were performed for 5 keV Ar$^+$ ions incident at $\theta = 85.5^\circ$ on a Pt(111) simulation cell with a single-adsorbed oxygen atom to gain a deeper insight into the interaction of the primary ion with the oxygen adsorbate and its effect on substrate sputtering. Let us denote as the $x$-axis a line parallel to the [110] azimuth and within a plane parallel to the surface passing through the adsorbate atom at $x = 0$ (compare figure 4). We first consider two ion

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Figure 4. Schematics of ion–adsorbate scattering dynamics above the Pt surface. Ion (full) and adsorbate (dashed) trajectories are taken from realistic MD simulations in the direct-hit (a) and the indirect-hit (b) regimes. Open circles: Pt surface atoms. Full circle: adsorbate atom. Thin black lines denote the incoming asymptotes of the trajectories. Their intersection with the x-axis (at the height of the adsorbate atom) defines the impact points. These are at (a) \( x = -12 \ \text{Å} \) and (b) \( x = 0 \). Note the different scalings in the horizontal and vertical directions.

trajectories labeled (a) and (b) in figure 4. The impact point of such a trajectory is defined as the intersection of the incoming asymptote of the trajectory with the x-axis (compare figure 4). The two trajectories of figure 4 represent two categories of trajectories: (a) represents an ion hitting the adsorbate directly (‘direct hit’) and (b) represents an ion hitting the adsorbate after being reflected off the surface in front of the adsorbate (‘indirect hit’). An analysis of the MD trajectories reveals that ions with impact points \( x > -5 \ \text{Å} \) belong to the first class, whereas those with impact points \( x < -5 \ \text{Å} \) belong to the second class.

Figure 5(a) shows how sputtering of the Pt target and desorption of the O adsorbate depend on the impact position of the ion. Here, the ordinates show the laterally averaged (i.e. averaged along the coordinate normal to the x-axis in a plane parallel to the surface) local sputter and desorption yields \( Y_S(x) \) and \( Y_O(x) \). Our simulations show that the projectile never induces sputtering directly, i.e. by being deflected towards the Pt substrate; rather it accelerates the adsorbate towards the surface, which in turn induces Pt sputtering. Consistent with the discussion above, the peaks of \( Y_S(x) \) between \(-25 \ \text{Å} < x < -5 \ \text{Å} \), correspond to sputtering induced by adsorbates, which have been energized via indirect hits, while peaks between \(-5 \ \text{Å} < x < 5 \ \text{Å} \) are due to sputtering caused by direct hits. The O desorption yield displayed in figure 5(b) is rather structureless; here, all projectile impacts between \(-25 \ \text{Å} < x < 7 \ \text{Å} \) contribute to desorption, and no clear distinction between direct and indirect hits is discernible. The reason for this insensitivity is given by the weak bonding of the adsorbate and its exposed position above the surface, which allows for even weak energy transfers to desorb it.
We quantify our results by calculating the sputter and desorption cross sections, equations (3) and (6). In analogy to these, we can also define the cross sections for damage creation (by measuring the number of adatoms produced) and for adsorbate implantation into the substrate. All these cross sections can be extrapolated to a coverage of $\Theta_{O,\text{sat}} = 0.25$ by assuming a linear dependence as in section 5. For the sputter yield, we thus obtain

$$Y_{sp}(\Theta_{O,\text{sat}}) = \Theta_{O,\text{sat}} \frac{\sigma_{sp}}{\Omega},$$

and analogous for the other quantities. Note that in these formulae, we make use of the fact that a flat clean terrace neither sputters nor produces damage at our impact conditions. Our simulations give cross sections of $\sigma_S = 11.3 \text{ Å}^2$, $\sigma_O = 32.6 \text{ Å}^2$; the cross section for damage creation amounts to $\sigma_{ad} = 48.8 \text{ Å}^2$, and the cross section for adsorbate implantation is $\sigma_{impl} = 43.8 \text{ Å}^2$ (see table 1). Extrapolation to the saturation oxygen coverage of $\Theta_{O,\text{sat}} = 0.25$ gives the yields as $Y_S = 0.42$, $Y_O = 1.22$, $Y_{ad} = 1.83$ and $Y_{impl} = 1.64$.

The experimental value $\sigma_O = 20 \pm 14 \text{ Å}^2$ agrees reasonably with the simulated desorption cross section of $\sigma_O = 32.6 \text{ Å}^2$. The experimental value $\sigma_S = 10.7 \pm 0.6 \text{ Å}^2$ agrees favorably with the simulated sputtering cross section of $\sigma_S = 11.3 \text{ Å}^2$ (see also section 8). At an oxygen background pressure of $1 \times 10^{-5} \text{ mbar}$ $\Theta_O$ is close to saturation for most of the erosion time as evidenced by the inset of figure 3. Experimentally under these conditions after an ion fluence 0.5 MLE, $\Theta_S$ is equal to 0.2 ML corresponding to an experimental yield of $Y_S \approx 0.4$ in good agreement with our simulations.

To link experimental and simulation results we made use of the linear relations (3) and (6) connecting the single adsorbate properties $\sigma_O$ and $\sigma_S$ with properties resulting from an ensemble of adsorbates ($\Theta_O$, $Y_O$ and $\Delta Y_S$). From our previous work with isolated Pt adatoms on a Pt(111) surface [26], we could derive a criterion for the maximum coverage $\Theta_{\text{lin}}$ for which the single adatom results could be extrapolated linearly to finite coverages,

$$\Theta_{\text{lin}} \approx \frac{\Omega}{A_{\text{infl}}},$$

(9)

Figure 5. Local sputter yield $Y_S(x)$ (a) and local oxygen atom desorption yield $Y_O(x)$ (b) in dependence on the ion impact point along the ion beam direction (see text). The data have been averaged in the direction perpendicular to the ion incidence plane.
Table 1. Cross sections for sputtering, adatom formation, oxygen desorption and oxygen implantation on a Pt(111) surface covered with a single adsorbate atom (5 keV Ar impact at 85.5° incidence). Experimental and simulational data for an oxygen-covered Pt surface obtained in the present work. Simulation data obtained for Pt surface covered with a single Pt adatom (5 keV Ar impact at 83° incidence) taken from [26]; the adatom formation cross section has been determined at 10 ps after impact and may still somewhat change at later times.

|               | \(\sigma_S (\text{Å}^2)\) | \(\sigma_{ad} (\text{Å}^2)\) | \(\sigma_O (\text{Å}^2)\) | \(\sigma_{impl} (\text{Å}^2)\) |
|---------------|------------------|------------------|------------------|------------------|
| Experiment    | 10.7             | n.a.             | 20               | n.a.             |
| Simulation    | 11.3             | 48.8             | 32.6             | 43.8             |
| Simulation for Pt adatom | 110             | 323              | 22.9             | 3.9              |

Here \(A_{\text{infl}}\) denotes the zone of influence around the adatom, into which the projectile must hit in order to collide with the adsorbate atom; depending on the process of interest (e.g. sputtering or adsorbate desorption), this zone of influence may assume slightly different values. The idea behind equation (9) is that linearity holds as long as the zones of influence of the individual adsorbate atoms do not overlap. In our case, we measure a value of \(A_{\text{infl}} = 19 \text{ Å}^2\) for sputtering and \(A_{\text{infl}} = 48.5 \text{ Å}^2\) for desorption. Thus we may trust our results up to coverages of \(\Theta_{\text{lin}} \approx 0.35\) for sputtering; this includes the O saturation coverage of 0.25. For oxygen desorption, it is \(\Theta_{\text{lin}} \approx 0.14\) and our linear extrapolation, equation (8), to the saturation coverage is subject to a larger error.

In the present context, it is also of interest to compare the effect of a single adsorbate with that of a single Pt adatom [26]. As table 1 shows, the desorption cross sections for the adsorbate and the Pt adatom are of similar magnitude. However, the Pt adatom gives rise to an order of magnitude larger sputter and adatom-creation effect, while the O adsorbate is implanted with an order of magnitude larger efficiency. The first feature can be understood by the small O/Pt mass ratio: even though the O adsorbate can receive quite large energies from the Ar projectile, its sputter efficiency is small. The larger implantation cross section of O can be traced back to the small atomic radius of O which lets it fit easier into the Pt crystal than a Pt atom.

7. Surface damage and sputtering as a function of the angle of incidence \(\theta\)

Figures 6(a) and (b) compare STM topographs after 0.25 MLE 5 keV Ar\(^+\) incident at \(\theta = 81^\circ\) at 550 K in the absence and in the presence of \(P_O = 5 \times 10^{-6}\) mbar, respectively. Figures 6(c) and (d) compare STM topographs after 1.5 MLE 5 keV Ar\(^+\) incident at \(\theta = 87^\circ\) at 550 K in the absence and in the presence of \(P_O = 5 \times 10^{-6}\) mbar, respectively. As expected, in both cases the presence of the background pressure increases \(\Theta_S\). To quantify the effect of the oxygen background pressure the ratio \(\Delta \Theta\) of the amount of material removed \(\Theta_S (P_O = 5 \times 10^{-6}\) mbar) from the oxygen covered surface to the amount of material removed from the clean surface \(\Theta_S (P_O = 0)\) is plotted against \(\theta\) in figure 7.

It increases from a factor of 2 at 81° and 83° to about a factor of 40 at \(\theta = 87^\circ\). The enhancement of surface damage by adsorbates increases so strongly with \(\theta\), as sputtering on a clean surface ceases with increasing \(\theta\) (compare figures 6(a) and (c)), thus bringing the denominator in the ratio of \(\Delta \Theta\) to zero and \(\Delta \Theta\) to infinity. As pointed out already in section 4,
the kinetic energy in the direction normal to the surface $E_\perp$ becomes smaller and smaller with increasing $\vartheta$. The variation of $\vartheta$ from $81^\circ$ to $87^\circ$ changes $E_\perp$ from 122 to 14 eV in the case of 5 keV ions. With increasing $\vartheta$ the transferred $E_\perp$ thus first drops below the sputtering threshold (around 50 eV for Pt) and then below the threshold for adatom production. In our MD simulations, we find that sputtering ceases for $\vartheta > 82^\circ$ and adatom production for $\vartheta > 83^\circ$ if 5 keV Ar$^+$ is used on Pt(111). Although experimentally we find indeed a drastic decrease of sputtering from $81^\circ$ and $87^\circ$ (compare figures 6(a) and (c)) it is not absent entirely at $\vartheta = 87^\circ$ (most likely due to unintended traces of adsorption) thus keeping $\Delta \Theta$ finite.

8. Discussion

A number of issues not yet discussed in the previous sections will be addressed here. Ion-induced adsorbate desorption may be simply calculated using the classical-trajectory description developed by Winters and Sigmund [29]. According to our MD simulations desorption is due to direct or indirect hits of the adsorbate atom, hence in the Winters/Sigmund description only knock off desorption has to be considered. The desorption cross section $\sigma_1$ due to knock off is calculated by using a power potential for the interaction between the collision partners.
Figure 7. Ratio $\Delta \Theta$ of the removed material from the oxygen-covered surface $\Theta_S (P_O = 5 \times 10^{-6} \text{ mbar})$ to the clean surface $\Theta_S (P_O = 0 \text{ mbar})$ as a function of $\vartheta$.

([ion $\equiv$ (1), surface atom $\equiv$ (2) and adsorbate $\equiv$ (3)] through

$$\sigma_1 = \frac{C_{13}}{\cos \vartheta \cdot m} (E_{U_3})^{-m} (1 - X^{-m}).$$

(10)

The coefficient $C_{13}$ depends on the mass ratio between the colliding particles and the nuclear charge and is specified in [30]. For a universal potential of the Lenz–Jensen type, a value $m = 0.25$ results [31]. The kinetic energy of the impinging particles is denoted with $E$, $U_3$ is the binding energy of the oxygen adsorbate ($U_3 = 5.18 \text{ eV}$, see section 3) and the factor $X$ is defined as $X = \gamma_{13} (E / U_3)$ with $\gamma_{13} = 4M_1M_3/(M_1 + M_3)^2$. With (10), Winters et al were able to reproduce their experimental findings for nitrogen desorption on tungsten through keV ions with an accuracy better than a factor of two. Using (10) for our situation results in $\sigma_O = 36 \text{ Å}^2$. This value is in reasonable agreement with our experimental ($\sigma_O = 20 \text{ Å}^2$) and MD ($\sigma_O = 32.6 \text{ Å}^2$) results.

As apparent from (5) the removed amount $\Theta_S$ depends on the product of $\sigma_S$ and $\Theta_O$. The latter quantity is exponentially dependent on $\sigma_O$ as apparent from (A.4) in the appendix. Therefore the rise of $\Theta_S$ in our fit is rather sensitive to $\sigma_O$ and the experimental value of $\sigma_O$ should be a reasonable estimate. However, in experiment we measure essentially the removal of O from the surface; hence the experimental desorption cross section of 20 Å² not only includes O desorption, but also O incorporation into the target. The experimental $\sigma_O$ therefore overestimates the true value for systematic reasons. In the MD simulation the fate of the adsorbate under irradiation is followed and only trajectories leading to desorption were counted for $\sigma_O$. The MD cross section for implantation (43.9 Å²) is even larger than that for desorption (32.6 Å²). However, from an inspection of the depth distribution of implanted O atoms we find that 77% are ‘implanted’ into the first layer, 9% into the second layer, and the remainder form a highly skewed distribution extending deep into the Pt crystal. We feel that our potential cannot safely predict the fate of the shallow implanted O atoms; many of them may actually return to the surface in the course of time and will thus not be removed from the surface.
The overall agreement for the sputtering cross section $\sigma_S$ in the presence of oxygen is rather good with 10.7 and 11.3 Å$^2$ for the experiment and simulation, respectively. Also here it is necessary to consider possible systematic errors in experiment and simulation. In (5), $\sigma_S$ is just a multiplier determining the magnitude of $\Theta_S$. As pointed out already in section 5, our experimental $\sigma_S$ not only includes the additional sputtering at the locations of the adsorbed oxygen adatoms. The damage created by the presence of oxygen (adatoms, adatom clusters surface vacancy clusters) itself enhances $\Theta_S$, as the damage is illuminated by the ion beam and allows for large-angle scattering events. This positive feedback mechanism is not included in our MD simulation. In the simulation, always a single oxygen atom on a perfect surface is investigated. Thus $\sigma_S$ as derived in experiment overestimates the true $\sigma_S$ and thus should also overestimate the value obtained in the MD simulations. This is not the case, most likely due to the general overestimation of sputter yields on Pt(111) through MD simulations [12].

It may be asked, how realistic are the experimental values for $\Theta_{S,\text{clean}}$ in the light of our results on adsorbate enhanced sputtering. Indeed for $\vartheta > 83^\circ$ the MD simulations predict the absence of any surface damage [12]. Even when considering the MD simulations with proper skepticism, it appears unlikely that for $\vartheta = 87^\circ$ 5 keV Ar$^+$ ions are able to induce surface damage. Let us consider for instance the case of CO adsorption described in section 4. Using the data of Poelsema et al [14] and a rough estimate for the sputtering cross section of adsorbed CO based on our data shown in section 4, we find a partial pressure of $P_{\text{CO}} \approx 3 \times 10^{-10}$ mbar to be sufficient to induce the observed $\Theta_{S,\text{clean}} = 0.04$ ML after 1 MLE at 400 K. Although the CO partial pressure in the absence of the ion beam is in the low $10^{-11}$ mbar range, turning on the ion beam results in a considerable increase of the CO background by about $1 \times 10^{-10}$ mbar. It is thus nothing but plausible that the removed material $\Theta_{S,\text{clean}}$ at very large angles $\vartheta$ is mainly due to adsorbate-induced sputtering resulting from the adsorption prior to the onset of ion exposure and the adsorption induced by the pressure rise of the ion beam itself.

The adsorbate enhanced erosion is relevant in a number of situations. Among them is pattern formation under grazing incidence conditions, which might be accelerated under poor vacuum conditions. Also ion scattering experiments under grazing incidence conditions are always in danger of being obscured by the effects of unwanted adsorption.

9. Conclusion

STM experiments demonstrate that sputtering on terraces in grazing incidence ion erosion is dominated by adsorbed particles. MD simulations reveal that the mechanism responsible for adparticle-induced sputtering are adsorbate knock off impacts. The energized adsorbates in turn transfer energy to substrate atoms, which eventually become sputtered. At extreme grazing incidence we found an enhancement of the initial erosion rate by a factor of 40 through adsorbed oxygen atoms. A similar enhancement of the initial erosion rate is found for adsorbed CO. This is particular important since CO adsorbs with a high sticking probability at room temperature on many metal surfaces and it is at the same time a major component of the background gas in UHV systems. The desorption cross section and the related and adsorbate-induced sputtering cross section for oxygen are extracted from experiment and MD. They agree within the uncertainties. The obtained desorption cross section also agrees reasonably with the one derived for knock off desorption within the Winters and Sigmund theory. Our results show that a reliable measurement of the sputtering yield of perfect crystalline terraces at grazing incidence is difficult due to hardly avoidable minute amounts of adsorbed particles. However, as soon as a significant number of
vacancy and adatom clusters are present on the substrate, the presence of adsorbates will be less important for the erosion rate.

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Appendix. Calculation of the oxygen coverage during ion exposure

The oxygen coverage \( \Theta_O(t) \) at a time \( t \) results from the balance of adsorption from the background and desorption through the ion beam and is dependent on the adsorption and desorption history. To calculate the increase in the oxygen coverage \( \Theta_O \) due to adsorption we assume simple Langmuir adsorption kinetics resulting in

\[
\frac{d\Theta_O}{dt} = \frac{2}{\Theta_{sat,O}} \Omega \cdot \phi \cdot S_O (\Theta_{sat,O} - \Theta_O).
\]

(A.1)

Here \( \phi \) is the flux of impinging oxygen molecules. The product \( \Omega \cdot \phi \) is the particle flux in units of ML s\(^{-1}\) and the factor of \( \frac{2}{\Theta_{sat,O}} \) = 8 in (A.1) takes into account that oxygen adsorbs dissociatively resulting in two adsorbed oxygen atoms and that the saturation coverage of oxygen \( \Theta_{sat,O} \) is 0.25 ML with respect to the Pt surface sites. The flux of molecules \( \phi \) is given by Knudsen equation \( \phi = P / \sqrt{2 \pi m k_b T} \), with \( P \) being the pressure, \( m \) the molecular mass, \( k_b \) the Boltzmann constant and \( T \) the temperature. The sticking coefficient \( S_O \) in (A.1) is assumed to be coverage independent for simplicity (identical to the initial one of 0.03 [17]). The decrease of \( \Theta_O \) due to the ion impingement is given by

\[
\frac{d\Theta_O}{dt} = -f \cdot \sigma_O \cdot \Theta_O.
\]

(A.2)

In total the change of \( \Theta_O \) is thus

\[
\frac{d\Theta_O}{dt} = 8\Omega \cdot \phi \cdot S_O (\Theta_{sat,O} - \Theta_O) - f \cdot \sigma_O \cdot \Theta_O.
\]

(A.3)

Experimentally, adsorption and ion erosion both start at \( t = 0 \). With this boundary condition the solution of this differential equation results in

\[
\Theta_O(t) = \frac{8\Omega \cdot \phi \cdot S_O}{8\Omega \cdot \phi \cdot S_O + \sigma_O \cdot f} (1 - \exp[-(8\Omega \cdot \phi \cdot S_O + \sigma_O \cdot f)t]).
\]

(A.4)

References

[1] Boers A L 1977 Surf. Sci. 63 475–500
[2] Hupkens T M and Fluit J M 1984 Surf. Sci. 143 267–86
[3] De Wit A G J, Bronckers R P N, Hupkens T M and Fluit J M 1979 Surf. Sci. 90 676–87
[4] Algra A J, Surrmeijer E P T M and Boers A L 1983 Surf. Sci. 128 207–23
[5] Van Dijken S, de Bruin D and Poelsema B 2001 Phys. Rev. Lett. 86 4608
[6] Hansen H, Redinger A, Messlinger S, Stoian G, Rosandi Y, Urbassek H M and Michely T 2006 Phys. Rev. B 73 235414
[7] Redinger A, Hansen H, Linke U, Rosandi Y, Urbassek H M and Michely T 2006 Phys. Rev. Lett. 96 106103

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[8] Stepanova M and Dew K 2006 J. Vac. Sci. Technol. B 24 592
[9] Toma A, Chiappe D, Setina Batic B, Godec M, Jenko M and Buatier de Mongeot F 2008 Phys. Rev. B 78 153406
[10] Winter H 2002 Phys. Rep. 367 387
[11] Pfandzelter R, Bernhard T and Winter H 2003 Phys. Rev. Lett. 90 036102
[12] Redinger A, Rosandi Y, Urbashek H M and Michely T 2008 Phys. Rev. B 77 195436
[13] Hansen H, Polop C, Michely T, Friedrich A and Urbashek H M 2004 Phys. Rev. Lett. 92 246106
[14] Poelseifma B, Palmer R L and Comsa G 1993 Surf. Sci. 136 1–14
[15] Steininger H, Lehwald S and Ibach H 1982 Surf. Sci. 123 264–82
[16] Nagasaka M, Kondoh H, Nakai I and Ohta T 2005 J. Chem. Phys. 122 044715
[17] Elg A P, Eisert F and Rosen A 1997 Surf. Sci. 382 57–66
[18] Gland J L 1980 Surf. Sci. 93 487–514
[19] Campell C T, Ertl G, Kuipers H and Segner J 1981 Surf. Sci. 107 220–36
[20] Gades H and Urbashek H M 1994 Phys. Rev. B 50 11167
[21] Gland J L, Sexton B A and Fisher G B 1980 Surf. Sci. 95 587
[22] Kirchner E J J, Baerends E J, van Slooten U and Kleyn A W 1992 J. Chem. Phys. 97 3821
[23] Feibelman P J, Esch S and Michely T 1996 Phys. Rev. Lett. 77 2257
[24] Materer N, Starke U, Barbieri A, Döll R, Heinz K, Van Hove M A and Somorjai G A 1995 Surf. Sci. 325 207
[25] Ziegler J F, Biersack J P and Littmark U 1985 The Stopping and Range of Ions in Solids (New York: Pergamon)
[26] Rosandi Y, Redinger A, Michely T and Urbashek H M 2009 Surf. Sci. 603 320
[27] Kalff M, Comsa G and Michely T 1998 Phys. Rev. Lett. 81 1255
[28] Michely T and Comsa G 1993 Nucl. Instrum. Methods B 82 207–19
[29] Winters H F and Sigmund P 1974 J. Appl. Phys. 45 4760–6
[30] Taglauer E 1990 Appl. Phys. A 51 238–51
[31] Winters H F and Taglauer E 1987 Phys. Rev. B 35 2174–87

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