Tuning surface reactivity by \textit{in situ} surface nanostructuring


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As recently demonstrated, the morphology of a surface can be modified on the mesoscopic scale by ion sputtering. Here we show by microscopy and spectroscopy that the chemical properties of the surface are strongly affected by nanostructuring and that surface reactivity can be tuned by changing surface morphology. For the otherwise inert Ag(001) surface significant O\textsubscript{2} dissociation takes place on the nanostructured surface, thus allowing us to control the relative coverage of admolecules and adatoms. The dissociation probability is determined by the experimentally tunable density of kinks.

Growing attention has been recently devoted to the possibility of modifying the chemical reactivity of surfaces by changing their morphology, e.g., by controlling the density and kind of the defects present on them. It has been, in fact, found that surface structure strongly affects the reaction barrier for relevant chemical processes: let us mention here as examples C–H bond activation of ethane on Ir(111),\textsuperscript{1,2} defect-induced CO dissociation on polycrystalline Pd,\textsuperscript{3} and CO adsorption on stepped Pd surfaces.\textsuperscript{4} Recently defect-induced oxidation of graphite was reported by Lee \textit{et al.}\textsuperscript{5} who showed that vacancies induced by ion bombardment are active for exothermal O\textsubscript{2} dissociation. A further step would be to produce in a \textit{controlled} and reproducible way a surface with a certain density of defects of a well-defined type in order to modify surface reactivity. This can be achieved by nanostructuring the surface with ion bombardment, as recently demonstrated by some of us for Ag(110),\textsuperscript{6} Cu(110),\textsuperscript{7,8} and Ag(001).\textsuperscript{9} The temperature of the substrate and the angle of incidence of the ions can be used to select the final surface morphology as they affect the balance between the erosion action due to the impinging ions and the healing action due to defect diffusion.\textsuperscript{10} When sputtering at normal incidence, diffusion dominates and the surface achieves a morphology that resembles the crystallographic symmetry of the underlying substrate: ripples thus form on Ag(110) and Cu(110) and a checkerboard structure of pits and hills on Ag(001). On the contrary, when sputtering at grazing incidence and low substrate temperature, erosion dominates over diffusion, resulting in the formation of ripples aligned along the ion beam direction, independently on surface symmetry.

In the present paper we demonstrate that the chemical properties of a surface can be controlled by nanostructuring. The dissociation probability of O\textsubscript{2} on Ag(001) was monitored by high resolution electron energy loss spectroscopy (HREELS) while the morphology and the defect density were characterized by scanning tunneling microscopy (STM). This system was chosen because on the flat surface at 105 K only molecular chemisorption of O\textsubscript{2} occurs.\textsuperscript{11} The experiments were performed in two different apparatuses equipped, respectively, with HREELS and supersonic molecular beam\textsuperscript{12} and with a variable temperature STM.\textsuperscript{13} All setups are in UHV and have an ion gun for sputtering and a quadrupole mass spectrometer (QMS) for residual gas analysis. In a paradigmatic experiment, after cleaning the sample by Ne\textsuperscript{+} sputtering and annealing it to 750 K, the surface is exposed to a Ne\textsuperscript{+} beam at a defined crystal temperature, \textit{T}\textsubscript{sput}. The Ne\textsuperscript{+} beam impinges normally (or at a grazing incidence angle of 70° along the (100) azimuth) onto the surface, at an energy of 1 keV, with an ion flux of 2.1 \textmu A cm\textsuperscript{-2} at the sample. The latter is exposed to the beam for 20 min, corresponding to a dose of 13.5 ML [doses are expressed in ML units for Ag(001), 1 ML=1.18\times10\textsuperscript{15} atoms/cm\textsuperscript{2}]. After sputtering, the crystal is cooled and reaches temperatures lower than 130 K within typically a few minutes. With the STM apparatus the morphology of the surface is investigated, recording the images in the constant current mode with typical conditions of \textapprox 1 nA tunnelling current and \textapprox 1 V bias voltage.

In the HREELS apparatus oxygen is dosed by the supersonic molecular beam with the sample at 105 K. The oxygen molecules are seeded in helium while the nozzle is at room temperature in order to take advantage of the enhanced sticking probability (about 0.3) of oxygen at hyperthermal energy (\textapprox 0.4 eV). Small O\textsubscript{2} doses were used in order to study the limit of O\textsubscript{2} interaction with a bare surface. The molecular beam flux is calibrated by a spinning rotor gauge. After each dose a HREEL spectrum is recorded in order to monitor the status of the adsorbates and their coverage. Vibrational spectroscopy easily discriminates between molecular and dissociative oxygen chemisorption, characterized, respectively, by vibrations at 80 meV and around 34 meV (the exact value depending on coverage). The spectrometer was operated at a resolution of 8 meV in order to improve the count rate for the damaged surfaces.

In Fig. 1 we show HREEL spectra recorded after sputtering at normal and grazing incidence at \textit{T}\textsubscript{sput}=250 K followed by an exposure of 0.1 ML of O\textsubscript{2} at 105 K. Such nanostructuring conditions correspond indeed to two differ-
FIG. 1. HREELS spectra recorded for the same oxygen dose (0.1 ML) deposited on surfaces sputtered with the same ion dose and at the same sputtering temperature $T_{\text{spu}}=250$ K but for different angles of incidence $\theta_{\text{spu}}$. The spectrum corresponding to adsorption on the flat surface is also shown for comparison and coincides with our previous result. The spectra were recorded in specular with the electron beam impinging onto the surface at 1.8 eV energy and at an angle of 63°. Adsorption of oxygen is performed by means of a supersonic molecular beam. The sample is kept at 105 K during the O 2 exposure and the subsequent HREELS analysis.

In the range from 180 to 380 K. When $T_{\text{spu}}$ increases, the intensity of the O–O stretch grows while the atomic oxygen peak has the opposite behavior, indicating that less O 2 dissociates.\(^{15}\)

In order to determine quantitatively the concentration of atomic and molecular oxygen, we exploit the proportionality of the intensity of the vibrational loss to the coverage of the corresponding moiety, which at low coverage reads\(^{16}\) as

$$\Theta_{O_2} = \frac{c_{O_2} I_{80}}{I_0},$$

(1)

$$\Theta_{O} = \frac{c_{O} I_{34}}{I_0},$$

(2)

where $I_{80}$, $I_{34}$, and $I_0$ are the intensities of the losses at 80 meV (molecular oxygen), 34 meV (atomic oxygen), and of the elastic peak, while $\Theta_{O_2}$ and $\Theta_{O}$ are the corresponding molecular and atomic coverages, respectively. $\Theta_{O_2}$ can be determined for the flat surface case by measuring the total O 2 uptake by the direct method of King and Wells,\(^{17}\) thus allowing us to determine $c_{O_2}$. For the sputtered surface case, $\Theta_{O}$ comes out as the difference between the measured total uptake and the molecular coverage estimated from $I_{80}$ by Eq. (1). We can thus safely convert the intensities of the losses Ag–O and O–O into $\Theta_{O}$ and $\Theta_{O_2}$, provided that surface roughness does not affect the dynamic dipole moment of the O–O stretch. This assumption is reasonable as the admolecules are in a chemical state quite similar to the flat surface case, as no frequency shifts are observed. The dissociation probability $P_{\text{diss}}$, accounting for the relative amount of atomic and molecular oxygen on the surface, is then given by

$$P_{\text{diss}} = \frac{\Theta_{O}}{\Theta_{O} + 2 \Theta_{O_2}},$$

(3)

which, for 200 K < $T_{\text{spu}}$ < 300 K, reads as $\approx 3\%$ at $\theta_{\text{spu}} = 0^\circ$ and $\approx 9\%$ at $\theta_{\text{spu}} = 70^\circ$. Such values are two orders of magnitude larger than for the flat surface case.

The relevant kind of defects was investigated by STM. Typical images are shown in Fig. 2. Let us focus first on the image obtained at normal ion incidence and $T_{\text{spu}}=350$ K, i.e., for the diffusion-dominated sputtering regime when the surface is characterized by a checkerboard of pyramids or truncated-pyramid-like pits (Fig. 2, upper panel). By a careful inspection (see the inset) of the STM topographies, it turns out that the straight edges of these almost square structures are running along [110] directions that are the thermodynamically preferred step orientations. Such [110] steps expose (111) microfacets that are known to be unreactive toward oxygen and thus cannot be the relevant defect. The rounded corners interconnecting the straight steps, on the other hand, present a large density of kinks, which were suggested as active sites for thermal dissociation.\(^{14}\) It is not possible to count such defects directly, as no atomic resolution could be obtained over these connection regions because of the high step density. Nevertheless, the rounded corners continued to appear as continuous features, even for the highest magnification obtained, which means that these regions are not formed by (110) segments but rather by a sequence of very rough (001)-like steps that are exposing a sequence of kinks. An estimate of the kink density could thus be ex-
tracted from the relative amount of rounded to straight steps and from the total step density on the sides of the pyramids. These quantities have been measured by analyzing a large statistics of STM topographies and were confirmed by spot profile analysis low-energy electron diffraction (SPA-LEED) measurements done on the same system. In the erosion-dominated regime, ripples elongated along the ion beam direction dominate the surface morphology. Since in the present experiment we oriented the ion beam along \( ^{110} \), the edges of the ripples are forced to run along the thermodynamically unfavored direction, i.e., parallel to the diagonal of the surface unit cell, and are therefore necessarily highly indented. Contrary to the normal sputtering case, high resolution images, as that shown in the inset of Fig. 2(b), demonstrate that the indentation does not occur at each lattice site but that steps are characterized by a sawtooth shape with straight \([110]\) segments, having an average extension of 20 Å at \( T_{\text{sp}} = 250 \) K. We can therefore evaluate the kink density from the average step density on the sides of the ripples.

Dissociation probability and kink density \( \rho_{kink} \) (the number of kinks for a unit cell) are reported in Fig. 3 for normal (upper panel) and grazing ion incidence (lower panel). We can see the following.

(a) \( P_{\text{diss}} \) remains about constant up to 300 K and decreases then rapidly to zero. The behavior is similar for both normal and grazing sputtering conditions.

(b) For \( T_{\text{sp}} \) between 200 and 300 K, the dissociation probability is higher for \( \theta_{\text{sp}} = 70^\circ \) than for normal incidence.

(c) The kink density nearly coincides with \( P_{\text{diss}} \) and follows closely its behavior versus \( T_{\text{sp}} \). A better agreement of \( P_{\text{diss}} \) and \( \rho_{kink} \) can be achieved by multiplying the latter by \( \approx 1.5 \). This discrepancy can be attributed to an underestimation of the kink density and/or to the conversion of HREELS intensities into coverage. In both cases a systematic error of some 25% appears more than reasonable.

It is in any case evident that there is an excellent correlation between the nonthermal dissociation probability of molecular oxygen and the density of kink sites on the surface produced by sputtering. These results demonstrate therefore that the control of the defect density by properly changing the sputtering geometry and the substrate temperature, allows us to tune the chemical activity.

In conclusion, we can summarize our findings as follows. With increasing \( T_{\text{sp}} \), surface diffusion leads to the formation of better and better ordered nanostructures, whose
morphology depends on the sputtering geometry and on crystal temperature. This nanostructuring allows us to change the dissociation probability of O₂ molecules chemisorbed on Ag(001) from less than 10⁻³ on a flat surface to 0.1 on the rippled surface. In perspective, this straightforward result opens up the possibility to control the chemical properties of a surface by modifying \textit{in situ} its morphology, i.e., by creating different amounts and different kinds of defects on which the reactivity of the chemisorbed species can be enhanced.

18. The dipole moment of atomic oxygen comes out to be enhanced reading now 0.22 Debye, compared to about 0.075 Debye for the flat Ag(110) surface [L. Vattuone, M. Rocca and U. Valbusa, Surf. Sci. Lett. 369, 336 (1996)]. Such an enhancement is in accord with a stronger charge transfer, which is reasonable for adatoms at defect sites.