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Coupling scanning tunneling microscope and supersonic molecular beams: A unique tool for in situ investigation of the morphology of activated systems

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I. INTRODUCTION

Supersonic molecular beams (SMB) are a precious tool in surface science, especially for the investigation of activated systems and of the dynamics of gas-surface interaction. In fact, being monochromatic and highly directional, they have been employed for the determination of the adsorption probability and of all the related parameters (coverage, adsorption energy, lifetime of metastable species, etc.) as a function of translational and internal energy of the gas molecules and of their angle of incidence. The energy parameters may just influence the adsorption kinetics by varying the sticking probability, or they may affect the final adsorption state of the impinging molecules. Although most SMB investigations in surface science have dealt so far with the former effect, some paradigmatic examples of the latter have also been reported.

More recently state selected experiments, i.e., experiments employing gas molecules in a given rotational, vibrational or helicity state, were performed, while interesting applications in the growth of better-ordered organic and oxide films have been demonstrated.

In the study of surface science phenomena, SMBs must be coupled with surface sensitive characterization methods to provide exhaustive information. The complementary detection technique may be a quadrupole mass spectrometer (QMS) to investigate the molecule-surface interaction dynamics with the retarded reflector method of King and Wells, if the interest is focused on the kinetics and/or dynamics of the reaction. On the contrary, it can be a spectroscopic or diffractive tool, if the attention is put on the final products of the reaction or on the composition and structure of the grown layer. However, scrolling the literature in this field, it is evident that topographic investigations of systems prepared by SMBs are scarce, especially if one considers in situ characterizations. For example, the morphological analysis of organic films grown by SMB deposition was performed

II. EXPERIMENTAL: THE DESIGN OF THE SMB+STM APPARATUS

A scheme of the SMB+STM apparatus is reported in Fig. 1. Before proceeding with an accurate description, we underline that the innovative idea behind our design is to combine a pre-existing, home-made SMB evacuated by turbo-molecular pumps with a commercial (Createc) low
temperature STM. Since the scanner is completely shielded by a double screen at liquid N2 and liquid He temperature, inside which the vacuum is much better than the \(1 \times 10^{-10}\) mbar value typical of UHV chambers, the sample remains frozen and clean for a prolonged time once inserted into the STM immediately after its preparation. Typically, at least one week is necessary to complete the STM characterization of the surface; in this period the turbo-molecular pumps are switched off and the SMB is left in rest vacuum.

The SMB used in the present experiments is the one already employed for several investigations.\(^{10,27-30}\) It consists of three differentially pumped stages (see Fig. 1(a)), separated by copper skimmers S1 (470 \(\mu\)m diameter) and S2 (1 mm diameter). A third collimator S3, of variable diameter, is placed at the exit of the third stage and determines the spot diameter on the sample and the extension of the penumbra region. In this configuration the angular divergence of the beam is strongly limited, being \(\sim 0.4^\circ\) and \(\sim 0.1^\circ\) when employing S3 collimators with 3.1 mm and 1.0 mm diameter, respectively. The first stage, reaching pressures as high as \(1 \times 10^{-3}\) mbar under working conditions, is pumped by two turbo-molecular pumps in parallel (1000 l/s and 500 l/s, indicated as T1 in Fig. 1), connected to the same raw pump (64 m\(^3\)/h, R1) to provide fore-vacuum. A 360 l/s turbo-molecular pump (T2) evacuates the second stage, characterized by a typical pressure of \(\sim 1 \times 10^{-6}\) mbar under gas flow, while a 300 l/s one (T3) is mounted on the third stage (reaching a maximum pressure of \(\sim 1 \times 10^{-8}\) mbar with the beam on). Both pumps are connected to the same raw pump (16 m\(^3\)/h, R2). The SMB is coupled to the main chamber through, in order, a CF40 bellows, a rigid fourth stage (pumped by a 70 l/s turbo-molecular pump, T4) and a gate valve.

The SMB was upgraded by installing it on a mobile support of variable height (90 cm < h < 160 cm from ground), which hosts both the SMB, the raw pumps, the pumps control units and the oxygen bottles. This setup allows to have an instrument as compact as possible and thus easier to move.

The mobile support consists of a commercial single pantograph lifter mounted on four wheels, which guarantee the possibility to displace the system from one UHV chamber to another without the need of auxiliary tools. Once positioned, the top platform is fixed to the ground with four massive legs (see Figs. 1 and 2) and the weight is removed from the oleodynamic lifter. After the SMB is approached to the desired UHV chamber and the bellows is connected, fine adjustment of the SMB position is required to align the beam on the sample. This is possible since a home-designed and home-made fine displacement mechanism allowing controlled XYZ translations (±50 mm, ±50 mm, and ±25 mm, respectively), rotation (∼5°, +90°) and tilt (±5°) of the whole SMB chamber is mounted over the platform (see Fig. 2). A 20 mm thick rectified stainless steel (SS) plate is fixed on the top of the platform and acts as a basis for the fine tuning system. X and Y movements are then achieved by superimposing to it two other rectified SS plates of identical thickness, sliding on ball bearings rollers in orthogonal directions. A disk of the same material and of 500 mm diameter is placed over the plates and allows for rotation (a teflon sheet reducing the friction between sliding metal surfaces). Finally, the Z coordinate is fine-tuned by acting on the three vertical rods holding the SMB chamber. These rods are formed by two parts screwed into each other and with a ball joint at their top, so that their length can be varied independently, resulting in a change of height and in
a moderate tilt of the beam trajectory. With this system the SMB can be easily moved and rapidly connected to different UHV apparatuses. To further reduce the installation time, the SMB is provided with a fast alignment system consisting of a laser beam shining light through the skimmers onto the sample (L in Fig. 1(b)). We underline that the ceramic nozzle (100 μm diameter, heatable up to 1000 K) is mounted on a XY translator with maximum excursion of 25 mm and that it is located on the SMB chamber axis in operation conditions. During the alignment procedure, the nozzle is moved away from the beam path so that the laser can pass through the skimmers. The SMB chamber position is then adjusted until the laser beam illuminates the sample. Once the SMB is aligned, the nozzle is brought back to the SMB axis and its position is optimized by maximizing the gas signal into the main chamber with a QMS.

The STM chamber is the one already described in Ref. 31. It is equipped with valves for gas inlet, a QMS, an ion gun, and all other typical vacuum facilities. The sample holder is mounted on a four degrees of freedom, He-coolable manipulator and can be transferred from the manipulator into the STM. The sample can be resistively heated up to \( T = 800 \) K and cooled down to 7 K (90 K) by liquid He (liquid N2) flux. Before each experiment, the Ag(110) surface is prepared by sputtering followed by annealing to 740 K. O2 exposure was performed either by SMB or by backfilling the chamber. In the former case an O2/He mixture (4% O2) was employed to reach a translational energy \( E_t = 0.39 \) eV. After the exposure the sample is cooled down below 120 K before transferring it into the STM. The adsorbate coverage was determined \textit{a posteriori} from the periodicity of the superstructures observed by STM. Using the coverage vs. exposure curves published in literature\textsuperscript{29} a beam flux \( \phi = (0.05 \pm 0.02) \) ML/s can be roughly estimated for the O2 beam seeded in He.

STM measurements were performed with the instrument cooled at liquid N2 temperature (77 K), which is low enough to guarantee that the adsorbate mobility is completely frozen, at least for dissociatively adsorbed moieties. Surface contamination remains negligible for several days after insertion of the sample inside the cryostat. The STM tip is a 0.2 mm diameter Pt-Ir wire cut under strain; while measuring, the tip apex was re-shaped by controlled crashes into the Ag sample, so that tunnelling occurs effectively through a silver tip. The piezo constants are calibrated on the basis of the Ag lattice parameter from atomically resolved images of the clean surface. Images are acquired in constant current mode, using typical currents between 0.1 nA and 2.0 nA and bias voltages between \(-1.20 \) V and 1.20 V applied to the sample. STM analysis was performed with the help of WSxM software.\textsuperscript{32}

III. RESULTS

A. The O/Ag(110) surface

For a careful control of the performances of the SMB+STM apparatus the very well-known O/Ag(110) system was used as reference. O2 exposures performed with the sample between \( T = 200 \) K and room temperature result in the formation of added rows with periodicity depending on oxygen coverage. This reconstruction, well described in literature,\textsuperscript{31,33} implies a massive movement of Ag atoms and consists in the creation of additional Ag-O chains along the \langle 001 \rangle direction with Ag adatoms sitting in fourfold hollows. (n \times 1) overlayers with n = 1, \ldots, 8 were reported depending on the initial O2 dose and hence on the achieved O coverage. It is believed that the same structures form both when using thermal and hyperthermal oxygen, but this comparison was possible, so far, only by diffractive means.\textsuperscript{29} Fig. 3 shows for the first time a comparison between STM images of the O/Ag(110) added row superstructure achieved by dosing thermal oxygen (backfilling – panel a) or hyperthermal oxygen (SMB – panels b and c). From inspection of the images in Fig. 3 and of the height profiles measured along the \langle 1\overline{1}0 \rangle direction, it is evident from the added rows, it is evident that the final layer produced upon O2 adsorption is qualitatively the same both for backfilling and for the SMB experiments even if the final coverage, and hence the (n \times 1) periodicity, is different. All images show indeed well-defined rows aligned along \langle 001 \rangle. However, we underline that:

1. When adsorption is performed by the beam, it is highly more efficient. In fact 300 ML of thermal O2 produce a (3 \times 1) pattern (\( \Theta = 0.33 \) ML) while a 32 ML exposure gives a mixed (6 \times 1) and (5 \times 1) overlayer

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{STM images of the O/Ag(110) added row reconstructed surface produced: (a) by dosing 900 L (\sim 300 ML) of O2 by backfilling the chamber with the sample at 300 K; (b) by dosing 0.7 ML of O2 with \( E_t = 0.39 \) eV on Ag(110) at 250 K; (c) same as (b) for a 27 ML dose. The line scans cut along the dashed lines in panels a-c show the different periodicity of the three structures: a (3 \times 1) and (2 \times 1) overlayers formed, respectively, in preparations (a) and (c), in perfect agreement with the increased sticking efficiency of hyperthermal O2. Preparation B is characterized, on the contrary, by a mixed \( (6 \times 1) \) to \( (4 \times 1) \) periodicity in view of the very limited exposure. An atomically resolved image of added rows produced by SMB exposure is reported in the inset of panel b. (Size of all panels: 210 Å \times 210 Å, (a) I = 4.4 \times 10^{-10} A, V = 0.29 V. (b) I = 1.0 \times 10^{-10} A, V = 0.40 V. (c) I = 1.6 \times 10^{-10} A, V = 0.63 V. Inset of (b): image size 70 Å \times 35 Å, I = 1.5 \times 10^{-10} A, V = 0.74 V.)}
\end{figure}
(average surface coverage 0.16 ML < Θ < 0.20 ML – image not shown35). On the other hand, only 0.7 ML of O2 seeded in He (Ei = 0.39 eV) lead to the formation of a mixed overlayer with (4 × 1) to (6 × 1) periodicity (Θ ~ 0.2 ML), and 27 ML at the same energy generate a full (2 × 1) superstructure (Θ = 0.5 ML). This is expected and in perfect agreement with the known kinetic energy dependence of the sticking coefficient of O2 on Ag(110).29 The slightly different crystal temperature set in the two experiments is not significant on this scale since the variation of the adsorption probability between 250 K and 300 K is less than 20%.29

(2) Besides being more efficient, and as a consequence of that, SMB exposure allows also for the formation of a cleaner and more ordered reconstruction. Fig. 3, which is the representative of a statistical analysis performed over several images recorded upon different preparations, shows indeed that the (2 × 1) overlayer produced with hyperthermal O2 has evenly spaced rows and almost no defects/contaminants in-between them. On the contrary, no good (2 × 1) superstructures were achieved by backfilling the chamber with the sample below room temperature, as it will be discussed in Sec. III B.

(3) The quality of the STM images recorded with the SMB connected (Figs. 3(b) and 3(c)) to the STM apparatus is as good as the one obtained without the SMB (Fig. 3(a)). Indeed, atomic resolution on the added rows could be achieved under appropriate scanning conditions, as witnessed by the inset of panel b. The high resolution and low noise characteristic of our microscope were proved to be limited by other factors (especially the tip shape and the presence of electronic disturbance), totally uncorrelated with the presence of a mechanical connection between the STM chamber and the SMB.

B. Hydroxylation of the O/Ag(110) surface

It is already well known that, in the temperature range between 200 K and 300 K, water adsorption on the O/Ag(110) surface leads to surface hydroxylation. The reaction consumes between 200 K and 300 K, water adsorption on the O/Ag(110) surface leads to surface hydroxylation. The reaction consumes between 200 K and 300 K (Ref. 35) or by annealing a molecular O2 layer to T = 300 K.34 When the added rows formation was observed below room temperature, extreme care was necessary to avoid water contamination and experiments were usually limited to short exposures.37

The amount of unwanted surface hydroxylation is thus a good probe to test the advantages of SMB preparation. Figure 4(a) reports a STM image relative to 33 ML of O2 by backfilling at T = 250 K. Water contamination, leading to the formation of the characteristic OH stripes, is evident (I = 4.1 × 10−10 A, V = 0.25 V). For both images, image size: 420 Å × 325 Å.

FIG. 4. (a) Ag(110) surface after exposure to 98 L (~33 ML) of O2 by backfilling at T = 250 K. Water contamination, leading to the formation of the characteristic OH stripes, is evident (I = 4.1 × 10−10 A, V = 0.25 V), (b) Corresponding experiment performed dosing 0.7 ML of O2 by SMB (Ei = 0.39 eV) (I = 2.1 × 10−10 A, V = 0.37 V). For both images, image size: 420 Å × 325 Å.
in He ($E_i = 0.39$ eV). The periodicity of the added row reconstruction varies between $(6 \times 1)$ and $(4 \times 1)$, so that an average coverage $\Theta \sim 0.20$ ML can be estimated. The reason of the much better result obtained in preparation (b) lies in the higher sticking coefficient of the hyperthermal oxygen molecules ($S_0 \sim 0.32$ at $E_i = 0.39$ eV) with respect to thermal ones ($S \sim 10^{-3}$), and hence on the ratio between O adatoms and water molecules available for the hydroxylation reaction. In fact, water comes from the rest vacuum inside the preparation chamber and either from the O$_2$ gas line (in preparation (a)) or from the 4th stage of the SMB (in preparation (b)). By a careful QMS analysis of the composition of the vacuum inside the chamber before and during the dose, we can roughly estimate a maximum undesired water exposure of $\sim 0.001$ L/s in both cases, corresponding to $\sim 3 \times 10^{-4}$ ML/s of water molecules sticking on the O/Ag surface ($S = 1$).

In the backfilling experiment, performed at $P_{O_2} \sim 1 \times 10^{-6}$ mbar ($\sim 0.75$ L/s), the accumulation rate for O ($\Delta \Theta_O/\Delta t$) is only slightly higher than the one of water due to the low O$_2$ sticking coefficient. The generated O adatoms have therefore a significant probability to react with a H$_2$O molecule producing 2 OH radicals even before organizing into added rows. Only a few and often isolated O/Ag rows are indeed detected on the surface. When using the SMB, on the contrary, $\Delta \Theta_O/\Delta t \sim 3 \times 10^{-2}$ ML/s in the initial stages of O$_2$ adsorption. Only a minor fraction of O adatoms are therefore consumed by hydroxylation, while the majority of them organizes into the added row superstructure.

Some OH contamination is nonetheless visible also upon long exposure by SMB (see Fig. 5). In view of the above discussion, however, it is reasonable that a complete $(2 \times 1)$ added rows reconstruction has formed and that oxygen has reacted with water only eventually. It seems also reasonable that the corrosion has started from the edges of the added rows, since no free sites for water adsorption are available in the middle of the $(2 \times 1)$ O/Ag(110) overlayers. To corroborate this hypothesis we observe that the OH/Ag(110) and the O/Ag(110) covered areas form extended islands of $(1 \times 2)$ and $(2 \times 1)$ periodicity, respectively, with very little intermixing.

Finally, we mention that no evidence of monoatomic Ag islands, formed by clustering of Ag ad-atoms released during dissolution of the added rows, was observed either for thermal or hyperthermal O$_2$ exposure.

IV. CONCLUSIONS AND PERSPECTIVES

We have reported here the first images recorded in a newly built apparatus combining a SMB and a low temperature STM. The setup was tested on the well-established O/Ag(110) system proving its capability to provide direct space images of the morphology of a layer generated by SMB deposition. Such information had so far been retrieved only indirectly by inverting scattering experiments or by performing ex situ analysis. The possible applications are huge. In the frame of gas-surface interaction, e.g., a combined SMB+STM equipment can offer precious topographic information on the adsorption state reached by hyperthermal molecules, which may be different from the one reached by slow molecules. As an example we mention that for O/Ag(410) several adsorption sites, characterized by different adsorption paths and energy barriers, were identified by vibrational spectroscopy and confirmed by DFT calculations, but no topographic investigation was feasible. Besides the study of activated systems, SMBs allow to select gas phase molecules in defined rotational, vibrational, and helicity states. Varying this last parameter we demonstrated that dissociation of helicoptering or cartwheeling O$_2$ molecules leads to the population of different adsorption sites on Pd(100). This conclusion was based on the quite different chemical activity of these oxygen moieties and on the different photoelectron diffraction patterns generated by them. If a SMB+STM apparatus had been available, the same information could have been retrieved directly and probably with less effort. The same holds for the different arrangement reached by O atoms generated by cartwheeling and helicoptering O$_2$ molecules on CO precovered Pd(100).

Concerning the production of thin organic films, they were proved to grow more ordered if the molecules are deposited by SMB at hyperthermal energy. In particular, translational energy has a relevant role in the determination of the critical island size and density. The capability of performing in situ morphological analysis opens new perspectives in the production and characterization of thin organic films, since it eliminates possible contaminations and modifications of the layer connected to exposure to air or controlled atmosphere in the so far used ex situ analysis. Finally, we mention the possibility of performing scanning tunneling spectroscopy and inelastic electron tunneling spectroscopy with our setup, thus to record the valence band density and the vibrations of single adatoms/admolecules and to correlate them with the adsorption site and with the local environment. This information, quite common at present for non-activated systems, would be precious for the complete characterization of adlayers deposited by SMB.

FIG. 5. (a) STM image of the Ag(110) surface covered by O/Ag(110) and OH/Ag(110) domains. The surface was prepared by dosing 27 ML of O$_2$ with $E_i = 0.39$ eV on Ag(110) at 250 K. Some water contamination originating in the fourth stage of the SMB is present. Image size 840 Å × 630 Å, $I = 3.8 \times 10^{-10}$ A, $V = 0.31$ V.
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