Ultramicroscopy 182 (2017) 233–242

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Simultaneous scanning tunneling microscopy and synchrotron X-ray measurements in a gas environment

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ARTICLE INFO

Article history:
Received 25 November 2016
Revised 17 May 2017
Accepted 9 July 2017
Available online 14 July 2017

Keywords:
Scanning tunneling microscopy
Synchrotron radiation
High-pressure surface science
Operando catalysis research

ABSTRACT

A combined X-ray and scanning tunneling microscopy (STM) instrument is presented that enables the local detection of X-ray absorption on surfaces in a gas environment. To suppress the collection of ion currents generated in the gas phase, coaxially shielded STM tips were used. The conductive outer shield of the coaxial tips can be biased to deflect ions away from the tip core. When tunneling, the X-ray-induced current is separated from the regular, 'topographic' tunneling current using a novel high-speed separation scheme. We demonstrate the capabilities of the instrument by measuring the local X-ray-induced current on Au(1 1 1) in 800 mbar Ar.

1. Introduction

The synchrotron-based techniques developed over the last decades provide a powerful toolbox for the study of interface phenomena. The weak interaction of X-rays with matter makes these methods particularly suitable for *operando* studies, which are indispensable in research areas such as catalysis [1], environmental science [2], and film growth [3]. However, most X-ray techniques make use of a large beam spot compared to the features studied, thereby averaging out possibly important structural and chemical variations. For techniques that use a highly focused beam on the other hand, finding the feature of interest can be a tedious process as searching based on reciprocal-space images or absorption features is non-trivial.

Scanning probe microscopy can supplement X-ray measurements by providing local structural information in real space. Inspired by this potential, several atomic force microscopes (AFM) [4–9] and scanning tunneling microscopes (STM) [10–14] have been installed on beamline end stations. In the AFM studies, it was shown that the AFM tip can be used to align the X-ray beam with features of interest [6]. Once aligned, the tip can be used for nanomanipulation or the application of local stress [15,16].

Using the combination of STM and X-rays, it was shown that the current collected by the STM tip can be used to measure local X-ray absorption, with a spatial resolution as small as 2 nm [11,17–19]. Thus, local chemical information can be obtained and coupled to the local structure. This combination is highly desirable for the understanding and design of materials and chemical processes.

So far, all synchrotron X-ray assisted STM (SXSTM) studies have been performed in vacuum. Under these conditions, the signal collected by the tip consists of three principal components: the photo-electron current, the regular, 'topographic' tunneling current, and an X-ray-induced increase of the tunneling current. While both the photo-electron current and the X-ray-induced increase of the tunneling current are related to X-ray absorption, only the latter

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http://dx.doi.org/10.1016/j.ultramic.2017.07.011
0304-3991/

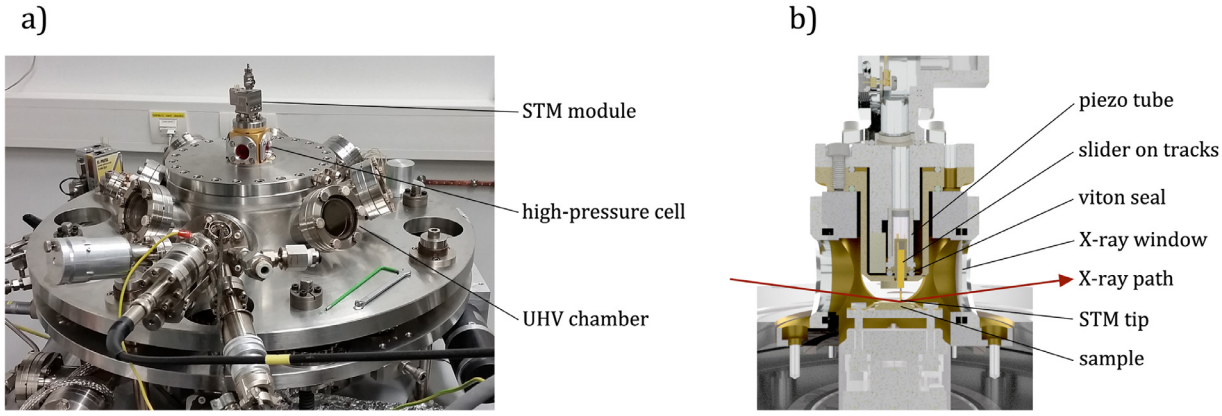

Fig. 1. Overview of the set-up. a) Assembly of ID03's ReactorSXRD chamber [25], our new high-pressure cell and the recently developed STM module [14]. b) Cross-section of the STM module and high-pressure cell.

provides local information [11,17–19]. To improve the ratio between this local signal and the photo-electron current, most SXSTM experiments employ coated STM tips, leaving only the tip apex uncoated [17,20–23]. This effectively reduces the number of photo-electrons that the tip collects. Besides this background reduction, the X-ray-induced part of the tunneling current needs to be separated from the topographic tunneling current. Several experimental schemes employing a beam chopper and lock-in amplification have been developed for this purpose [11,24].

To use SXSTM in *operando* studies at elevated pressures, two challenges need to be addressed: i) Inhibitively large ion currents are generated in the gas phase. We show that the insulator-coated tips used in most SXSTM studies are inadequate to suppress these. ii) Most interesting systems for *operando* studies require elevated temperatures and have some degree of roughness in their morphology. To cope with thermal drift and to follow the surface morphology accurately, fast response in the height feedback is necessary. However, the current separation schemes for the topographic and the X-ray-induced tunneling current limit the height feedback in the STM to response frequencies below roughly 1 kHz.

Here, we describe an instrument that can perform SXSTM measurements in a gas environment using hard X-rays, overcoming the barriers for performing *operando* studies. Our methodology includes the following: i) A quick method for aligning tip and beam with micrometer precision. ii) An electronics scheme to separate X-ray-induced current and topographic tunneling current that enables fast height feedback at frequencies up to the chopper frequency. iii) A coaxially shielded STM tip following the approach of ref [17] and a mounting configuration that effectively suppresses the ion current background. As a proof of concept, we have collected the local, X-ray-induced tunneling current on a Au(1 1 1) sample at a gas pressure of 800 mbar.

2. Instrument design

2.1. High-pressure cell

The starting point for our experiments was the high-pressure scanning probe and surface X-ray scattering instrument developed earlier in collaboration between our group and the ID03 beamline staff at the ESRF [14], which we modified for the SXSTM measurements. In short, this system consists of an ultrahigh vacuum (UHV) chamber with a high-pressure cell on top (see Fig. 1) [25]. The UHV chamber allows for surface preparation by ion bombardment, annealing, controlled gas exposure, and metal evaporation onto the sample. The high-pressure cell can be operated as a flow reactor, providing a controlled gas atmosphere at pressures up to 1.1 bar. The cell is exchangeable, allowing for a versatile combination of experiments.

In our recent work, we fitted a high-pressure scanning probe module on the system [14,26]. Similar to the design of the ReactorSTM and ReactorAFM [27,28], it uses a single piezo tube both for the coarse approach of the tip to the sample and for generating the scanning motion. The coarse approach is achieved by a stick-slip motion of the tip holder (slider) on two tracks. The piezo tube is separated from the gas environment by a polyimide cap and a viton seal, as depicted in Fig. 1b. In our previous design, the reactor wall was a dome-shaped aluminum piece of 1 mm thickness, providing homogeneous and satisfactory X-ray transmission over a large range of angles at photon energies above 18 keV. While this made the system excellent for surface X-ray diffraction measurements, the X-ray transmission was insufficient in the lower energy range relevant to X-ray absorption spectroscopy.

To allow for measurements at energies down to 8 keV, we designed a new cell that uses four thin, exchangeable windows (see Fig. 1) sealed on both sides by viton O-rings. In our first test measurements, we used a stack of three 75 µm thick Kapton sheets for each window. In the energy range from 10 keV to 12 keV, the Kapton stack provides an excellent X-ray transparency of 91%–95% [29]. However, the permeability of Kapton towards gases [30] limits the base pressure of the UHV chamber to the 10^{-6} mbar range. Aluminum foil windows provide a lower transmission (59% for 100 µm thick foil at 11 keV [29]), yet do not suffer from any gas permeability. Beryllium windows were not preferred here for safety reasons, as the reactor needs to be handled frequently for tip exchanges.

The reactor walls and the part of the microscope head that are exposed to gases are gold coated. This prevents undesirable side reactions from occurring on these surfaces. Furthermore, charge collected on the walls from photo-electrons and ions is immediately neutralized. Charging of the native oxide of materials such as aluminum and stainless steel may cause memory effects in the background signal of the SXSTM measurements. This could adversely affect the reproducibility of the data.

2.2. Coaxial tips and mounting scheme

In a gas environment, the X-ray-induced current collected by the STM tip behaves differently as compared to the vacuum situation. Photo-electrons emerging from the sample cause a cascade of ionization processes in the gas. This effect is particularly pronounced for the high-energy Auger electrons produced during hard X-ray absorption [31,32]. Furthermore, the plasma created in the gas environment helps the charge transport to and from insulating surfaces [33–35]. Hence, when a beam chopper is employed,