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DELIVERABLE REPORT

WP11 JA1 - Real-time observation and control in microscopy and spectroscopy of nano-objects

D11.6

Introducing near-ambient pressure measurements in conventional STM microscopes

Due date

M30

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

PROJECT DETAILS

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Prof. Giovanni De Ninno (UNG)

DELIVERABLE DETAILS

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D11.6	Introducing near-ambient pressure measurements in conventional STM microscopes

DELIVERABLE DESCRIPTION

Upgrade of an existing UHV commercial STM setup to perform measurements in near-ambient pressure conditions.

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M30 31/08/2023	09/10/2023

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NATURE

☐ R - Report

☒ P - Prototype

☐ DEC - Websites, Patent filing, Press & media actions, Videos, etc

☐ O - Other

DISSEMINATION LEVEL

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☐ PP - Restricted to other programme participants & EC:

☐ RE - Restricted to a group

☐ CO - Confidential, only for members of the consortium

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CONTENTS

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INTRODUCTION

The investigation of ultra-fast phenomena and metastable systems strongly interacting with their environment often requires dedicated instruments characterized by a low degree of interoperability. In this context, one of the objectives of JA1 is to extend the range of scanning probe microscopy (SPM) experiments to multiphase environments. Specifically, sub-task 11.1.1 is devoted to extend the real-time capabilities of SPM-based measurements in NFFA-Europe to realistic environments, in particular near-ambient pressures (NAP) conditions. To this purpose, a protocol to modify a commercial scanning tunneling microscopy (STM) setup to routinely perform NAP-STM experiments has been conceived. Instrumentation and hardware for the setup has been purchased, with particular focus on the critical technical issues (pumping stages, purification of the sample environment, high-pressure ultra-pure gases, materials for holders and STM tips). Practices and protocols to achieve this goal have been firstly designed and implemented at TUM on a dedicated system already intended for NAP measurements, with the aim to transfer the conceived approach to the commercial ultra-high vacuum (UHV) STM system located at CNR-IOM.

SETUP UPGRADE

Design of the NAP-STM protocol

The NAP-STM setup at TUM has been adapted and used as benchmark to implement protocols and practices to be transferred on a commercial UHV STM setup at CNR-IOM.

The conceived protocol to perform NAP measurements is schematically represented in Figure 1.

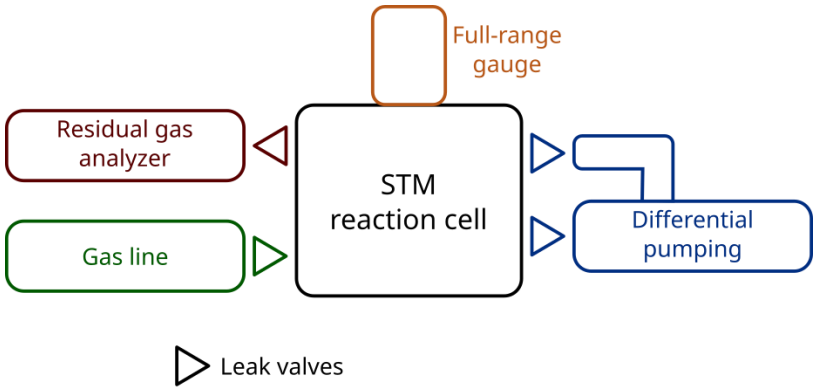

Figure 1 Schematic representation of the dedicated NAP setup implemented at TUM.

The gas line is connected to the STM reaction cell through a precision leak valve and a residual gas analyzer is employed to precisely monitor the gas concentration and the product formation occurring during in-situ STM experiments. This allows monitoring in real-time the gas composition in the STM

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chamber. The pumping system of the reaction cell has been designed and routines to perform near-ambient pressure experiments have been developed. Based on this approach, the reaction cell system can be evacuated without severely affecting the base pressure of the UHV chamber, avoiding frequent bake out of the experimental system, and maximizing the uptime of the instrument. Sample holders made of stainless steel have been purchased and successfully tested for STM experiments. Compared to Molybdenum (typically used for such purposes), the choice of stainless steel allows circumventing issues with the formation of volatile Mo oxide species which can contaminate the sample surface during NAP experiments in oxidative environment. A MATLAB script was written to plot and analyze composition and time evolution of gases measured by a dedicated mass spectrometer. This approach enables also the adjustment of the composition of gas mixture during the experiment, as well as the detection of reaction products, providing information complementary to atomic scale microscopy.

Transfer to the commercial UHV STM

The approach conceived at TUM has then been readily adapted and transferred to the UHV STM setup at CNR-IOM, originally not designed for NAP measurements. In this case the reaction cell is absent, so the inlet valves, pressure measurement and pumping system have been installed to perform near-ambient pressure experiments using the whole UHV chamber hosting the STM. Figure 2 schematically represents the setup implemented at CNR-IOM.

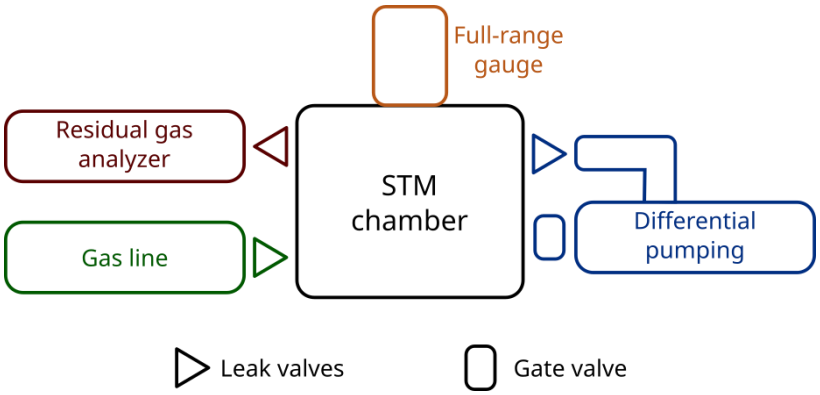

Figure 2 Schematic representation of the NAP setup implemented on the commercial UHV STM at CNR-IOM.

A gas-line has been mounted to the chamber through a valve which allows to change or purge the dosed gases without breaking the UHV of the STM chamber (Figure 3d). To conveniently evacuate the chamber at the end of the gas dosing, a two-stage differential pumping system has been installed, constituted by a first stage leak-valve and a second stage gate-valve (Figure 3a). This configuration is necessary to guarantee both the static conditions (no pumping during exposure) during the high-pressure gas dosing and the correct gas evacuation towards the turbo pumps: the first stage allows to evacuate the near-ambient pressure gas down to approximately 1E-3 mbar and the second stage permits to achieve UHV conditions in a reasonable amount of time.

On the basis of the practices conceived at TUM, a strategy to use the residual gas analyzer (RGA) already available in the existing setup was implemented to monitor gas mixtures concentration and purity, even at high pressures, thanks to a leak valve connected to an adjacent chamber (Figure 3c). This solution allows to use the low-pressure RGA to monitor the partial (high-)pressure of each dosed

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gas by letting a small amount of gas mixture through the leak valve, which is mandatory to properly control the relative ratio and pressure stability during exposure, particularly important in high-pressure experiments. On the other hand, in this case, the configuration does not allow to monitor any possible product formation occurring during the reaction. A digital full-range cathode has then been installed for continuous pressure reading from UHV to atmospheric pressure inside the STM chamber (Figure 3b).

Finally, the choice of using reducing gases (H_2, CO_2, CO), which prevents the formation of Mo oxide, did not require any modification in the material composition of the STM head or the sample holder.

The NAP-STM, with the given limitations on the possible gas usage and product monitoring, is expected to be added to the NFFA-Europe Pilot offer to users starting from Call 12 at the latest.

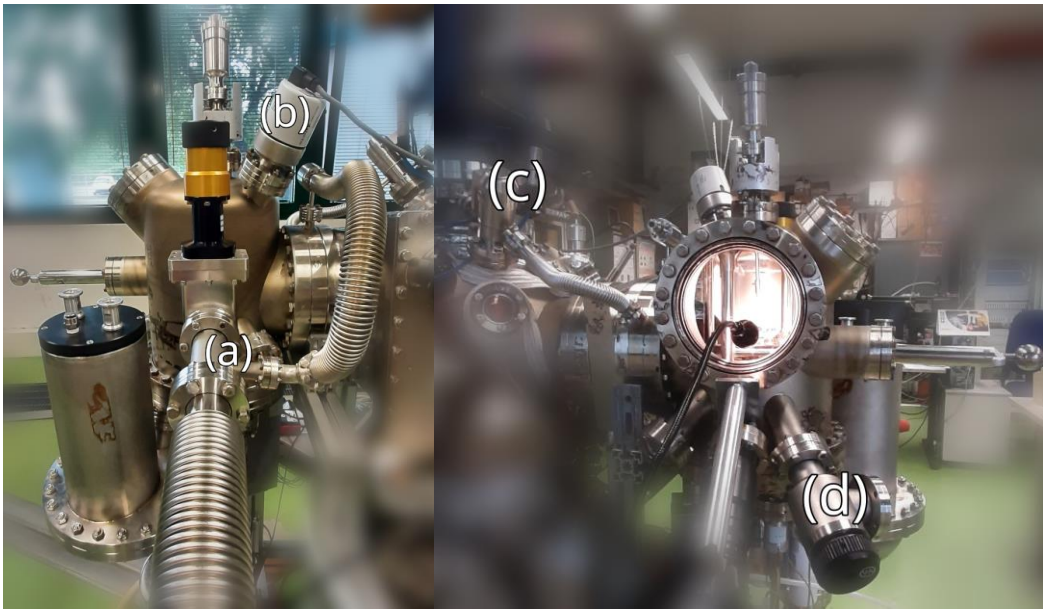

Figure 3 Pictures of the NAP setup implemented on the commercial UHV STM present at CNR-IOM. (a) Two-stage differential pumping system, constituted by a first stage leak-valve and a second stage gate-valve. (b) Digital full-range cathode for continuous pressure reading from UHV to atmospheric pressure. (c) Leak valve connected to an adjacent chamber to monitor dosed gas mixtures concentration and purity. (d) Valve for gas line connection.

Test measurements

The implementation of the NAP capability in the commercial UHV STM has been tested by reproducing a similar NAP experiment previously conducted in a dedicated high-pressure cell in the same system, with the aim of assessing the success of the in-situ implementation.

In this test experiment, in particular, we exposed a B-doped graphene layer, previously grown on Ni(111), to 10 mbar of carbon monoxide (CO) directly in the STM chamber, using the newly implemented NAP setup. Based on similar experiments on pristine and N-doped graphene on Ni(111) [1, 2], we expect CO to intercalate between the graphene layer and the Ni substrate. Figure 4a shows an atomic resolution STM image of the surface before any gas exposure, where the typical triangular pattern of the epitaxial graphene on Ni(111) is clearly visible, with only the carbon atoms

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of the fcc sublattice appearing bright. In the image, several defects in the graphene layer can also be identified, appearing as darker features, that correspond to carbon vacancies (darker and circular, encircled in blue) and substitutional B defects (triangular depressions, encircled in green) in fcc position.

The grown layer has then been exposed to 10 mbar of CO for 20 minutes, in-situ within the STM chamber. Figure 4b represents an STM image, right after gas evacuation, showing a drastic change in the appearance of the graphene layer. Now, in particular, both carbon atoms sublattices are visible and electron scattering occurs within the layer, especially in proximity of graphene defects (white circle). These are clear fingerprints of a quasi-free standing graphene layer, indicating that the intercalation of CO between the layer and the substrate occurred [1], as schematically represented in the inset model. Also, the graphene defects appear now as bright protrusions due to the reduced interaction of the layer with the substrate and the electron scattering.

In conclusion, this preliminary measurement demonstrated the successful implementation of NAP capability in a commercial UHV STM and allowed to verify for the first time the CO in-situ intercalation underneath a B-doped graphene layer grown on Ni(111).

The next step will be to repeat these test experiments focusing on performing the measurements in operando conditions, i.e. by acquiring the STM images during the gas exposure at high pressure, in order to characterize the real time evolution of the surface during the intercalation process.

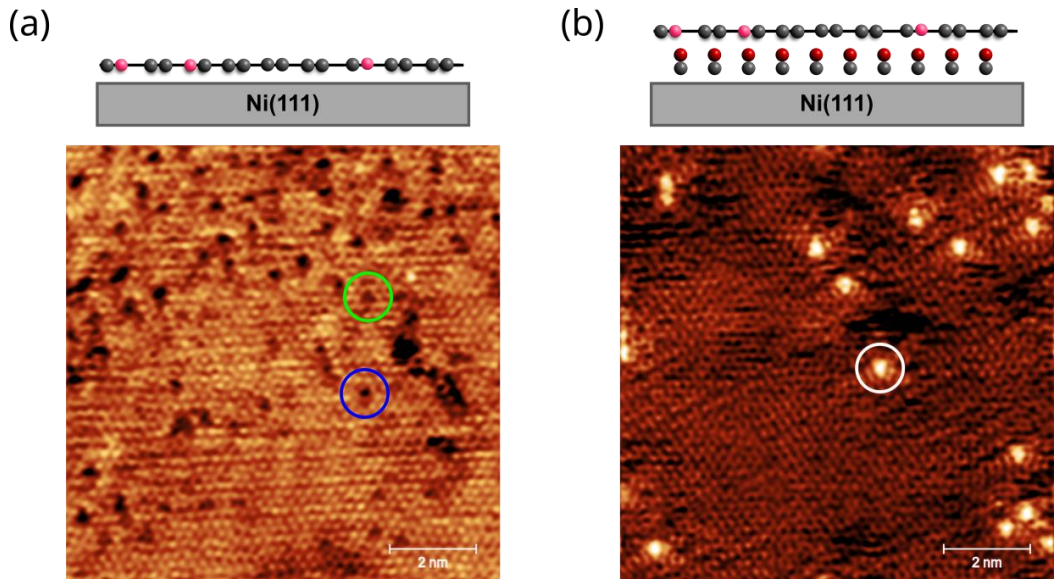

Figure 4 (a) Atomic resolution STM image of B-doped Gr on Ni(111) before any gas exposure. The typical triangular pattern of the epitaxial graphene on Ni(111) is clearly visible. (Scanning parameters: V = -0.2V, I = 1.2 nA) (b) Atomic resolution STM image of B-doped Gr on Ni(111) after exposure to CO at 10 mbar for 20 minutes. Carbon atoms sublattices are visible and electron scattering occurs within the layer, indicating that the intercalation of CO between the layer and the substrate (Scanning parameters: V = -0.07V, I = 4.8 nA). The models on top represent the layer before and after intercalation.

References

[1] Del Puppo et al. Carbon 176, 253-261 (2021). DOI: 10.1016/j.carbon.2021.01.120

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[2] Perilli et al. J. Phys. Chem. Lett. 11, 8887–8892 (2020). DOI: 10.1021/acs.jpclett.0c02447

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