LOW COVERAGE PHASE OF 1,4 BENZENEDIMETHANETHIOL ON Au(111) and Ag(111)

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Self-assembled monolayers (SAMs) of organothiols on metal surfaces have been investigated in detail due to their promising properties: corrosion inhibition, fabrication of sensors, new electronic devices, lithography [1]. In particular, aromatic thiols and dithiols (for example 1,4 benzenedimethanethiol (BDMT)) have been proposed for use in a number of applications and studied from both experimental and theoretical approaches [2]. Depending on the type of substrate, on its reactivity, it may be advantageous the use of a vacuum approach to form the SAM instead of its counterpart of solution growth [3]. In this case, a clean surface is exposed to the vapours of the corresponding thiol in high vacuum. During growth the system may undergo different phases prior to attaining the final SAM, and in some cases the system may grow continuously forming multilayers. The knowledge of all the phases formed during SAM preparation can help to optimize the preparation method in order to obtain films of better quality. Here we studied the growth of BDMT under ultra-high vacuum conditions on Au(111) and Ag(111), and characterized the phases formed by different techniques including: low energy electron diffraction (LEED), scanning tunnelling microscopy (STM), and ion scattering. Calculations within the functional density model (VASP code) were also performed to help the interpretation of the STM images. Ion scattering provided information on the formation of different phases as a function of BDMT exposure. In Fig. 1 we recognized two phases: for very low exposures the molecules are lying down, while for very high exposures a standing up configuration is formed on the surface. Surprisingly, it is seen that due to the higher reactivity of Ag, the initial phases formed are better defined and more ordered than on Au. The LEED pattern of Fig.2 shows a well-defined arrangement for BDMT/Ag while it is blurred for BDMT/ Au (not shown). The STM images acquired on BDMT/Ag (Fig.2) show that for very low exposures the surface is covered with a single layer of BDMT molecules forming a long range and very well ordered arrangement. A close inspection of the STM images shows that the molecules are tilted with respect to the surface. The molecular arrangement looks very complex, so a DFT calculation is very useful to provide extra information. The simulation was performed by putting the molecules in the lying down phase with the orientation of the molecules as shown in the STM images. If all the Ag atoms are left on the surface, the STM simulations did not agreed with experimental ones, showing BDMT parallel to the surface. The only way to reproduce the experimental molecular arrangement with tilted molecules was after including in the calculation Ag vacancies. The results of the DFT calculation together with a comparison with the experiment are shown in Fig. 3. In the presentation we emphasize the convenience of using spectroscopic, theoretical and STM techniques to achieve a full characterization of the surface.

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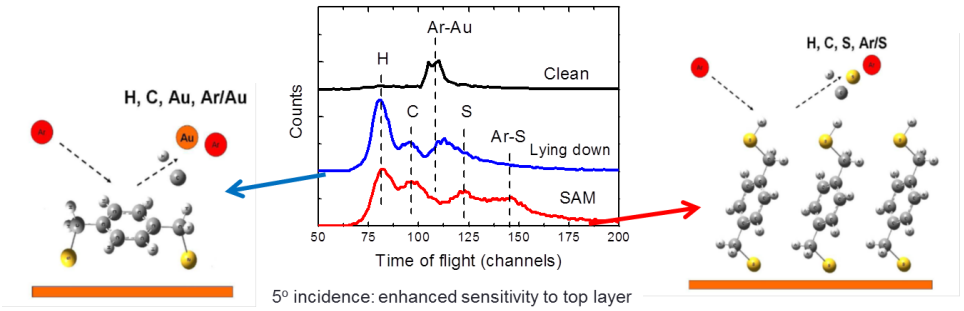

Fig.1: Schematics of molecule orientation. Left: lying down phase, Center: corresponding ion scattering spectra, Right: standing up phase.

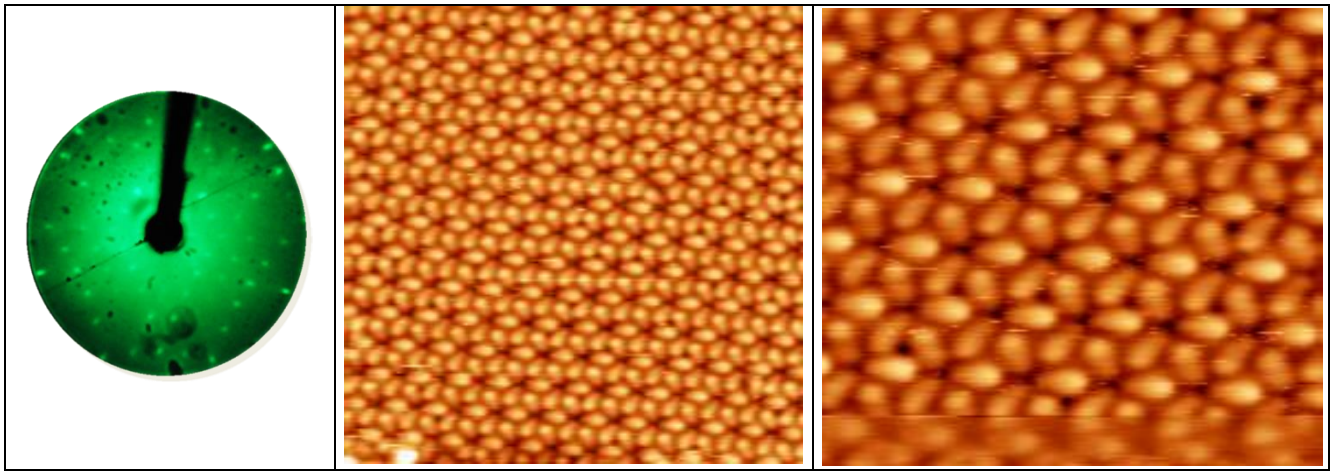

Fig.2: Left panel: LEED pattern for the low coverage lying down phase of BDMT on Ag (111). Center and right panels: STM images of the corresponding molecular arrangement in 20x20 nm^2 and 10x10 nm^2 areas, respectively.

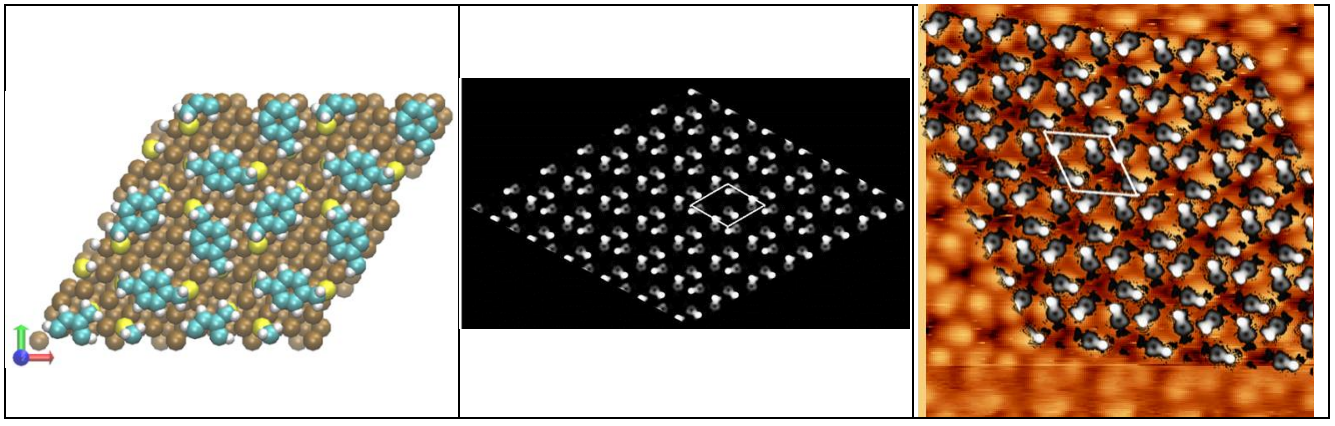

Fig. 3: Left panel: molecular arrangement obtained by DFT calculations with Ag vacancies on the top most layer. Center panel: simulation of the corresponding STM image. Right panel; comparison between the experimental and calculated 10x10 nm^2 STM images.