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Nanometer-Scale Characteriazation by Scanning Tuneling Microscopy

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1. Introduction

The scanning tunneling microscope (STM) opened up new fascinating possibilities for the development of atomic scale technologies. The force between the STM-tip and a single adsorbate can be used to laterally position atoms/molecules with atomic precision (lateral manipulation). This allows the buildup of small nanostructures in an atom by atom way. By exploiting electric field and inelastic tunneling effects individual molecules can be desorbed, transferred to the STM-tip (vertical manipulation), dissociated or even synthesized. Morevoer inelastic tunneling spectroscopy can be used to identify adsorbates and to investigate the details of their binding to the substrate. For future applications the basic physical mechanisms controlling these techniques have to be investigated first [1,2].

2. Lateral Manipulation of Atoms/Molecules

In the case of lateral manipulation we have studied as model systems single metal adatoms (Cu, Pb), small molecules (CO) and large molecules (CuTBPP) adsorbed on a metal surface. The experiments were performed with a low temperature STM operated in a temperature range between 6 and 60K. By recording the signal of the STM feedback loop or the tunneling current during the manipulation sequence, the movement behavior of the atom/molecule can be characterized. In the case of atoms and small molecules a simple pushing/pulling behavior is observed, depending on whether repulsive or attractive forces between the tip apex and the adsorbate are used [3].

In the case of larger molecules (CuTBPP: a porphyrin molecule equipped with four legs), i.e. molecules which have additional internal degrees of freedom, a more complicated movement behavior involving changes of the internal conformation during the lateral movement can be determined from the experimental data. To extract from the measured signal the intramolecular mechanics occuring during a manipulation sequence, detailed molecular mechanics and STM-ESQC calculations have been performed. Moreover the internal conformation of molecules can be reversibly changed in a controlled way by the STM tip realizing a molecular switch [4].

As an application in the area of surface science the lateral manipulation can be used to determine binding sites of isolated adsorbates by positioning marker atoms close to the adsorbate and exploiting registry information. In the case of ordered structures small domains can be formed in a molecule by molecule way. This opens up an alternative way to solve the problem of the complicated contrast mechanisms arising in these ordered structures. The lateral manipulation can be also extended to the extraction of substrate atoms and therefore to the atomic scale structuring of the underlying substrate [5].

3. Breaking and Forming of Chemical Bonds

Inelastic tunneling can be used to break individual bonds in molecules. Moreover it has been shown recently that also the formation of chemical bonds can be induced. This technique might be used in the future to synthesize molecules. As an example we will present the formation of a biphenyl molecule from two phenyl groups. The process starts with two iodobenzene molecules adsorbed at a monoatomic step edge of a Cu(111) surface. These are first dissociated into individual phenyl groups and iodine atoms by applying a short voltage pulse of about 1.5V. Using lateral manipulation the iodine atoms are then removed from the step edge, which allows the phenyl groups to be positioned close together at the step edge. The final association step, the formation of a bond between the two phenyl groups, is performed again by applying a short voltage pulse of now 0.5V, exploiting the excitation of the molecule by inelastic tunneling. To prove the successful association of the two phenyl groups, the lateral manipulation technique is applied again [6]. The molecule is pulled from one end along the step edge. If a bond has been established between the phenyl groups the whole molecule will follow, otherwise the two phenyl groups will be taken apart again. The formation of biphenyl from iodobenzene is a well known catalytic chemical reaction, the Ullmann reaction.

4. Manipulation on/of Insulators

An outlook will be given on the manipulation of individual atoms and molecules on thin insulating films. This will allow the formation of metallic nanostructures which are electronically decoupled from the substrate. As a substrate we have used ultra thin layers of NaCl grown on a metal surface. NaCl films with a thickness of up to four layers can be investigated with the STM.

We have observed that vicinal metal surfaces represent a class of useful substrates for the growth of polar insulator films. This can be attributed to a strong binding between the polar insulator film and the underlying regularly stepped metal surface (NaCl/Cu(311), NaCl/Cu(211)), which is laterally charge modulated due to the Smoluchowski effect [7]. While flat and defect free insulator films have been grown, also a self organized patterning of the insulator on metal system can be induced by faceting of the metal substrate with a selective growth of the insulator film on only specific facet orientations [8].

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