



Investigation of surface reactions by means of scanning probe techniques and electron spectroscopies

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Ph.D. Thesis

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ABBREVIATIONS

AES	A uger E lectron S pectroscopy
AFM	A tom F orce M icroscopy
DFT	D ensity F unctional T heory
PES	P hoto E lectron S pectroscopy
SPM	S canning P robe M icroscopy
STM	S canning T unneling M icroscopy
SMSI	S trong M etal- S upport I nteraction
TDS	T ermal D esorption S pectroscopy
UHV	U ltra- H igh V acuum

INTRODUCTION

The development of surface science as a specific field of chemistry and physics had a strong connection with the rapid and versatile evolution of heterogeneous catalysis [1]. This latter field served as one of the most important cornerstones of modern industry. The strategic steps in the history of the surface science were unequivocally accompanied by introducing new experimental techniques that can characterize the atomic and molecular composition of adsorbate/surface systems. Furthermore, the discovery and rapid spread of scanning probe microscopies (SPM), which allowed real-space atomically resolved imaging of surfaces and made atomic and molecular recognition possible, had an extraordinary impact on our level of understanding of surface chemistry [2, 3].

For a proper usage, these revolutionarily new techniques required ultrahigh vacuum (UHV) systems in which the base pressure falls even below 10^{-8} Pa. SPM operation under UHV conditions opened up the possibility to study atomically clean surfaces and to comprehend isolated surface processes such as phase transitions, single molecule adsorption and manipulation, growth and nucleation of nanoclusters. The strong enthusiasm about new surface phenomena triggered the start of producing and studying more and more two-dimensional (2D) systems. These model materials are important not just from catalytic point of view but also for development of state-of-the-art nanoelectronic devices.

In this work the main interest is directed towards the investigation of the adsorption of metals and molecules on oxide and semiconductor surfaces. Among the huge variety of suitable oxide supports, as a model material, $\text{TiO}_2(110)$ was chosen to investigate in detail the adsorption of metals. This topic derives from the fact that the metal/ TiO_2 systems have already made, and will continue to have, an impact on the development of catalysts of high performance, moreover, that of solar and hydrogen fuel cell fabrication [4].

By deposition of potassium and investigation of thermal treatments, we characterized the morphological effects of a typical alkali additive used widely in the heterogeneous catalysis. Interesting results will be presented in connection of decorated/encapsulated Rh nanoparticles supported on $\text{TiO}_2(110)$ surface by atomic scale scanning tunneling microscopy (STM) studies. In this latter topic, there is an internationally strong activity for the better understanding of the formation of oxide ultrathin films on noble metal nanocrystallites supported on reducible oxides (the phenomenon called decoration and/or strong metal-support

interaction, SMSI) [4, 5].

The SiC surface has a strong technological significance in production of electronic devices and catalysts [6, 7]. Ethylene can act as a source of carbon for the production of SiC. In accordance to this, it will be shown by a complex surface investigation (involving many methods) how the scanning atom probe techniques can contribute to the elucidation of the proper adsorption mechanism of C_2H_4 molecule on Si(111)- 7×7 substrate. In addition, it will be made obvious that in contrast with STM, AFM can successfully be used to identify the adsorbed molecule on the surface.

The usage of piezoelectric sensors with the capability of self-sensing made combined AFM/STM measurements available. However, this setup requires special attention to avoid the so-called cross-talk effect between the current signal and the deflection channels. The basics of the cross-talk phenomena will be briefly introduced and several methods for its elimination will be also be discussed.

APPLIED EXPERIMENTAL TECHNIQUES

The experimental results presented in this thesis has been collected using two UHV systems equipped with STM/AFM heads and several other surface analyzing tools. In addition, there were several possibilities to perform research at the Materials Science Beamline at the Elettra synchrotron light source in Trieste, Italy. The photoelectron spectroscopy results were obtained in that beam-line. Scanning tunneling microscopy (STM) was applied in this work as a main characterization method. In some cases, STM was combined with atomic force microscopy (AFM) to gain further information about the chemical nature of the adsorbate (molecular identification). The recent development of the qPlus AFM technique enabled simultaneous acquisition of interaction forces and tunneling current opening a new horizon for surface investigations [8]. While SPM technologies can provide crucial information about surface structure, they provide only limited information about the chemical composition and bonding configuration of the surface/adsorbate system. In order to have more complete picture about surface processes, electron and mass spectroscopies were also utilized. For the interpretation of observed SPM images and recorded PES spectra, DFT calculations will be presented for the adsorption of ethylene.

RESULTS

Adsorption of potassium on $\text{TiO}_2(110)$

Alkali metal compounds are extensively applied as promoter additives for the preparation of catalysts and gas sensors for integrated humidity detection [9,10]. During the last decades, most of the studies in connection of the effects of alkali metals have been focused on metal and semiconductor surfaces GaAs [11]. Much less attention has been given to the interaction between alkali metals and oxide surfaces, although this type of experimental and theoretical works are very important for elucidating some important issues in the fine tuning of catalytic performance. By the application of two-dimensional metal-oxide model systems (planar catalysts), the complex effects of the additives can be efficiently studied [4].

I have studied the effect of coverage and annealing temperature on the morphology of K deposited $\text{TiO}_2(110)$ surface mainly by scanning tunneling microscopy (STM). In addition, some thermal desorption spectroscopy (TDS) and Auger-electron spectroscopy (AES) were measurements were also carried out.

Theses:

- 1.1 I found that the adsorption of potassium leads to the formation of dark protrusions visible on empty state STM images. This observation can be explained by a partial charge transfer from K atoms to the substrate. Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) measurements have shown that the desorption energy of K decreases with the coverage via the decrease in the heat of adsorption.
- 1.2 I showed that annealing of the K covered surface to 900 K leads to the formation of the reduced 1×2 reconstruction and to the presence of terrace decoration, depending on the initial K coverage. This observation strongly suggest that potassium may create both K-O_x and $\text{K-Ti}_x\text{O}_y$ compounds and leaves the surface also in this form.

- 1.3 I observed that annealing further near to 1100 K results a back transformation to the original 1×1 reconstruction with slightly increased concentration of strings. This latter process may be connected to the segregation of oxygen from the subsurface region.

Surface characterization of TiO_2 supported Rh crystallites

The so-called strong metal-support interaction (SMSI) appeared as the effect of an appropriate thermal treatment of noble metals supported on reducible oxides in a reductive atmosphere [12]. Furthermore, the SMSI phenomenon appeared also in vacuum as the effect of annealing at high temperatures (600–1000 K) and it seemed to have a connection with the defect concentration in the bulk of the support oxide [13–15]. This phenomenon was recently reviewed by Fu and Wagner, and a more complete theory was given for its driving force. In their model operating with the Schottky barrier formed at the particle/support interface, it was successfully explained why certain metals supported on reducible oxides exhibit decoration phenomenon [5]. Importantly, the main feature of the SMSI phenomenon is the suppression of CO chemisorption ability of the catalysts [13, 14]. This behavior can be explained by a simple site-blocking effect in which the coverage of the decoration oxide is proportional to the inhibited amount of adsorbed carbon-monoxide [16].

I have investigated the formation of ordered and quasi-ordered TiO_x phases on the top facets of Rh crystallites supported on a $\text{TiO}_2(1\ 1\ 0)$ by using the combination of STM and AES. Moreover, I evaluated the effect of soft Ar^+ bombardment and restoration of the decoration layer by thermal treatments in the light of the proposed structure of the decoration layer.

Theses:

- 2.1 I detected first an ordered decoration TiO_x layer on Rh nanoparticles supported on TiO_2 as a result of annealing a Rh deposited $\text{TiO}_2(1\ 1\ 0)$ surface at 1050 K. This finding reveals that the formation of ordered 2D oxide films on topfacet of noble metal nanocrystallites supported on reducible oxides is a quite general behavior.

2.2 High resolution STM scans proved that the encapsulation layer at saturation coverage exhibits a “wheel” structure with a hexagonal unit cell of $\sim 1.5 \text{ nm} \times 1.5 \text{ nm}$. The wheels are determined by three triangles consisting of 5 atoms in a distance of 0.31 nm. This complex wheel structure can be attributed to a moiré-like pattern formed by the slight misfit between the atomic lattice of the metal particles and the overlayer oxide.

A “worm-like”, partially saturated layer was also detected which exhibited 1D stripes (nanostripes) oriented in the close-packed direction of the (1 1 1) facet of Rh nanoparticles. The characteristic sizes of these latter features are the following: width of 0.5 nm and length of 2–3 nm. The “worm-like” structure can be regarded as an initial state for the formation of the “wheel” arrangement.

2.3 With a quite new approach, I proved that it is possible to selectively remove the “wheel-like” decoration layer by Ar^+ sputtering (0.5 keV, $3 \mu\text{A}/\text{cm}^2$) and to subsequently restore it by a short thermal treatment at 1000 K. At 600 – 700 K the surface of the Rh nanoparticles becomes flat but it is not yet covered by TiO_x layer. Apparently, the decoration process starts at 800 – 850 K.

Ethylene Attachment to $\text{Si}(1\ 1\ 1)\text{--}7\times 7$

Ethylene serves as an excellent probe molecule in the study of adsorption on metal and semiconductor surfaces because it is a simple unsaturated, nonaromatic molecule. One of the first studies of ethylene adsorption on $\text{Si}(1\ 1\ 1)\text{--}7\times 7$ was performed by Klimesch and coworkers [17]. They proposed that the ethylene most probably adsorbs without dehydrogenation and found that compared with metal surfaces the dehydrogenation takes place at much higher temperature suggesting a strong and stable adsorption (chemisorption) mechanism. Piancastelli *et al.* reported a scanning tunneling microscopy (STM) experiment where ethylene exposures caused surface atoms to “disappear” and also introduced change in the local density of states around the Fermi level [18]. On the basis of their observations, they proposed an adsorption model, where the molecule bridges an adatom and an adjacent restatom. However, Rochet and coworkers disagreed with the suggested adsorption process described above [19]. On the basis of their combined LEED and PES experiment, an alternative adsorption mechanism was proposed involving the reconstruction of the 7×7 unit cell. The idea of adsorption-induced

reconstruction was supported later also by Kim *et al.* [20].

Because of the recent discussion about the validity of the adatom–restatom model for the adsorption of ethylene on the Si(1 1 1)–7×7 surface, we examined the adsorption of ethylene from low coverage unto the saturation coverage where all bridging sites are occupied. For this study different techniques (STM, AFM, PES, DFT) were used.

Theses:

- 3.1 I have concluded from STM measurements that the reaction between the Si(1 1 1)–7×7 surface and C₂H₄ molecules leads to a decrease in the number of observable Si adatoms. In addition, by recording of high resolution images, it is clear that the restatom neighbors must also be directly involved in the reaction, and the simulated STM images suggest exactly the same behavior.
- 3.2 By the application of the combined AFM/STM mode, I could distinguish between adatom vacancy and adsorbed molecule that sits in fact exactly in the supposed position. This result gives rise to a possible new way for following surface reactions in a direct manner.
- 3.3 On the one hand, in the valence band PES spectra I also saw quenching of the corresponding surface states in good agreement with previous studies. On the other hand, I verified on base of low temperature, angle-resolved photoemission spectra that it is clear that the S₁ surface components corresponding to center adatoms quench much faster than the S'₁ component (corner adatoms), especially at low coverage. Although there is no significant energy difference between the adsorption sites, the center adatoms preferentially react during the adsorption process because the population of the central adatom–restatom adsorption configuration is two times higher than that of the corner adatom–restatom configuration. I clarified that the remaining electronic states close to the Fermi level originate from unsaturated adatoms. This observation comes from the fact that there are more adatoms available than rest atoms in a unit cell and the STM results clearly showed unreacted adatoms after all possible bridge positions had been filled by ethylene.
- 3.4 I pointed out the existence of the peak clearly correlated with the formation of the Si–C bond in the Si 2p core levels and I found good agreement for

the C–H stretching loss feature in C 1s core level with the possibility of the existence of higher harmonic modes.

Simultaneous current, force and dissipation measurements using an optimized qPlus AFM/STM technique

In frequency-modulation (FM)-AFM mode, a sensor (mostly cantilever) vibrates with a constant oscillation amplitude a . The cantilever has f_0 resonant frequency, k stiffness and it has m^* effective mass (that includes the tip as well). Decreasing the tip-sample distance $k_{ts} = -\partial F_{ts}/\partial z$ force gradient appears between the tip and the sample. As a result of the acting force(s) the value of f_0 is changed by Δf . At the beginning, mainly silicon-based cantilevers oscillating with large amplitudes (tens of nanometers) were used, because they possess the important oscillation stability [21–23]. However, low amplitude operation appeared to be beneficial, especially for parallel detection of interaction forces between the tip and the sample and tunneling current. So far the most popular and reasonable way to reach the desired small amplitudes is replacing the micro-fabricated (Si) cantilevers by stiff, piezoelectric quartz tuning forks similar to those used as frequency etalons in watches. The configuration when one of the prongs is attached to a solid substrate and the free prong acts as a cantilever with the capability of self-sensing, is called qPlus, named by Giessibl [8]. One of the largest benefits of this design is that it has nearly the optimal stiffness for operating FM-AFM with low amplitudes but keeping the force sensitivity high enough [24]. Not surprisingly, qPlus design presented high potential for outstanding atomic scale imaging from its early stages [25].

Unfortunately, in the case of quartz based sensors with self-sensing, the presence of the tunneling current may introduce an undesired interference (cross-talk) between the current and the deflection channel. Therefore special attention has to be paid to minimize the impact of this phenomena to a negligible level.

I investigated the origin of the coupling between the deflection and the tunneling current channel by means of circuit simulations and by experimental measurements. I carried out simultaneous STM/AFM measurements on the Si(1 1 1)– 7×7 surface with the modified setup to prove that the cross-talk has nonsignificant impact on the measured quantities. In addition, I compared these simultaneously measured force, tunneling current and dissipation to theoretical predictions [26] and with measurements done by optical interferometric deflection [27].

Theses:

- 4.1 As a result, I proved that the cross-talk is the outcome of the speed limit of the current to voltage converter used for tunneling current detection and the stray capacitance between the internal connections of the microscope.
- 4.2 I presented a modification of Omicron qPlus VT system, made to avoid the crosstalk between the deflection and the tunneling current channels. In the new design of the sensor, the current to voltage converter of STM is connected directly to the tip with a gold wire. Beside separating the tunneling current signal, it was necessary to replace the original ceramic support by a metal one in order to reduce the capacitive coupling between the channels.
- 4.3 With site-specific force/tunneling current measurements on the Si(111)-7×7 surface I showed an excellent agreement with the published results obtained with the optical beam deflection system. The sudden decrease of the tunneling current caused by the formation of a covalent bond between the tip and the sample was clearly repeated, as in the previous work.
- 4.4 From the analysis of the dissipation signal, I clearly demonstrated that the tunneling current does not induce artificial damping up to 100 nA at room temperature. The dissipation detected by the amplitude regulator is the result of mainly two contributions. The first one, which has long range characteristic, is related with the instrumentation and it can be subtracted. The second one appears only above the adatom site after the tip approach exceeds the positions of the short range attractive force maxima. The latter one can be attributed to the adhesion hysteresis.

LIST OF PUBLICATIONS

Publications relevant to this thesis:

- i. Z. Majzik, N. Balázs, and A. Berkó. Ordered SMSI decoration layer on Rh nanoparticles grown on $\text{TiO}_2(110)$ surface. *Journal of Physical Chemistry C*, 115:9535–9544, 2011, IF: 4.805.
- ii. Z. Majzik, N. Balázs, and A. Berkó. Thermally activated reconstruction of $\text{TiO}_2(110)$ - 1×1 surface in the presence of potassium: an STM study. *Catalysis Today*, 181:89–94, 2012, IF:3.407.
- iii. Z. Majzik, W. Kamiński, A. J. Weymouth, M. Vondráček, V. Zobač, M. Švec, A. Berkó, A. B. McLean, K. C. Prince, P. Jelinek, and V. Cháb. An investigation of ethylene attachment to $\text{Si}(111)$ - 7×7 in the restatom-atom bridging geometry: electronic and vibrational properties. *Journal of Physical Chemistry C*, 115:21791–21799, 2011, IF:4.805.
- iv. Z. Majzik, M. Setvín, A. Bettac, A. Feltz, V. Cháb, and P. Jelinek. Simultaneous current, force and dissipation measurements on the $\text{Si}(111)$ - 7×7 surface with an optimized qPlus AFM/STM technique. *Beilstein Journal of Nanotechnology*, 3:249–259, 2012, IF:0.789.

Other publications:

- i. J. Berger, M. Švec, M. Muller, M. Ledinský, A. Fejfar, P. Jelínek, and Z. Majzik. Characterization of the mechanical properties of qPlus sensor using different methods. *Beilstein Journal of Nanotechnology*, 2012, IF:0.789 (Submitted).
- ii. A. Berkó, Z. Majzik, and A. Kiss. Low temperature CO oxidation on differently prepared $\text{TiO}_2(110)$ supported Au catalysts. *Journal of Physics: Conference Series*, 61:110, 2007, IF: Not rated.
- iii. Z. Majzik, N. Balázs, L. Robin, M. Petukhov, B. Domenichini, S. Bourgeois, and A. Berkó. Tunneling induced decomposition of $\text{Mo}(\text{CO})_6$ onto $\text{TiO}_2(110)$ surface. *Vacuum*, 86:623–626, 2012, IF:1.317.

- iv. P. Mutombo, N. Balázs, Z. Majzik, A. Berkó, and V. Cháb. Theoretical study of the adsorption of rhodium on a $\text{TiO}_2(110)\text{-}1\times 1$ surface. *Applied Surface Science*, 258:4478–4482, 2012, IF:2.103.
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- vii. M. Setvín, J. Javorský, Z. Majzik, P. Sobotík, P. Kocán, and I. Ošťádal. Competition between thermally activated and tip-induced hopping of indium atoms on $\text{Si}(100)$. *Physical Review B*, 85:081403, 2012, IF:3.691.
- viii. M. Setvin, P. Mutombo, M. Ondracek, Z. Majzik, M. Švec, V. Cháb, I. Ost’adal, P. Sobotik, and P. Jelinek. Chemical identification of single atoms in heterogeneous III-IV chains on $\text{Si}(100)$ surface by means of NC-AFM and DFT calculations. *ACS Nano*, 6:6969–6976, 2012, IF:10.774.

$$\sum \text{IF} = 40.144$$

In cases of publications that were published in the year of the submission of this dissertation, the impact factor for the previous year is presented.

PRESENTATIONS AT INTERNATIONAL CONFERENCES

1. Z. Majzik, A. J. Weymouth, M. Vondráček, M. Švec, K. C. Prince, A. B. McLean and V. Cháb: The thermal conversion of ethylene/Si(111)-7×7 → SiC studied with photoemission and STM. **ECOSS 26**, Parma, Italy – 2009, *Oral*
2. M. Setvín, Z. Majzik, V. Cháb, P. Jelínek: Simultaneous STM and NC-AFM measurements on silicon surfaces. **NC-AFM 13**, Kanazawa, Japan – 2010, *Poster*
3. Z. Majzik, N. Balázs and A. Berkó: Atomically resolved STM detection and tunneling current spectroscopy of wagon-wheel-like decoration layer on Rh nanocrystallites supported on TiO₂(110). **IVC 18, ICN+T**, Beijing, China – 2010, *Poster*
4. Z. Majzik, W. Kaminski, M. Vondráček, M. Švec, A. Berkó, V. Cháb, P. Jelínek: Discrimination of single ethylene molecules adsorbed on the Si(111)-7×7 surface by means of Atomic Force Microscopy. **ECOSS 28**, Wrocław, Poland – 2011, *Oral*
5. Z. Majzik, W. Kaminski, M. Vondráček, V. Cháb, P. Jelínek: Experimental and theoretical investigation of the adsorption of ethylene on Si(111)-7×7 surface. **AAFMT**, Karlsruhe, Germany – 2011, *Poster*
6. Z. Majzik, W. Kaminski, M. Vondráček, V. Cháb, P. Jelínek: Experimental and theoretical investigation of the adsorption of ethylene on Si(111)-7×7 surface. **ICFSI 13**, Prague, Czech Republic – 2011, *Oral*
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9. Z. Majzik, M. Ondráček, J. Berger and P. Jelínek: Relation between the apparent height barrier, the chemical force and the local contact potential difference in atomic scale. **NC-AFM 15**, Český Krumlov, Czech Republic – 2012, *Oral*
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 11. Z. Majzik, M. Ondráček, J. Berger and P. Jelínek: Understanding the influence of the tunneling current and the chemical force on the contrast formation in KP-AFM. **AVS 59**, Tampa, FL, USA – 2012, *Oral*

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