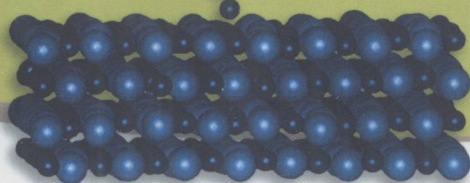
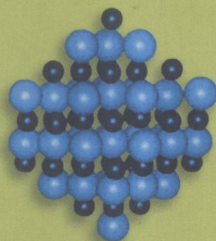
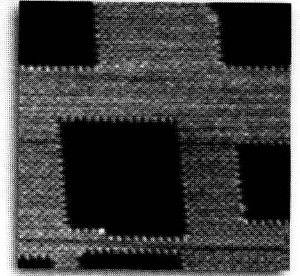
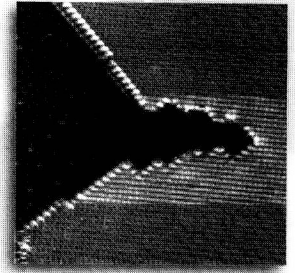


Nanoscale Processes on Insulating Surfaces

Enrico Gnecco ■ Marek Szymonski



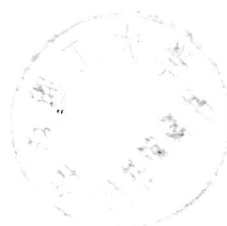
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Nanoscale Processes on Insulating Surfaces

About the authors

Dr. Enrico Gnecco was awarded his Ph.D. from the University of Genova in 2000. He started his research activities as an undergraduate student with investigations of current noise in Hg and Tl based high-temperature superconductors. His Ph.D. thesis focused on nanotribology, i.e. the study of friction and wear processes occurring on the nanometer scale. Within the group of Prof. Ugo Valbusa he characterized the growth of amorphous carbon films by scanning probe microscopy, and studied the relationship between friction and self-affine properties of these films. In the second part of his Ph.D. studies, he joined the group of Prof. Ernst Meyer in Basel, where he investigated friction processes on alkali halide surfaces in ultra high vacuum (UHV). The main result was the observation of a logarithmic velocity dependence of atomic friction, which was interpreted within a combination of the classical Tomlinson and Eyring models.

After his Ph.D. he joined the Swiss National Center of Competence of Research in Nanoscale Science, where he studied other basic nanotribological phenomena, such as abrasion wear on ionic crystals in UHV, various forms of superlubricity onset transitions, and electromechanical methods to reduce friction on the atomic scale. Most of these experiments were performed on insulating surfaces, and have found promising applications in the development of micro- and nano-devices. He also investigated self-assembly of organic molecules on insulators, using an original technique to trap molecules in rectangular nanopits produced by electron irradiation. He is also interested in surface nanomanipulation on different systems (from metal clusters to single molecules) with the goal of evaluating the dissipative forces accompanying the manipulation process.

E.G. has co-authored more than 40 scientific publications, including articles on Science, Nanoletters, Nanotechnology, and Physical Review. He was also awarded a diploma in piano from the Conservatory of Music of his hometown, Genova.

Prof. Marek Szymonski was awarded his Ph.D. from the Jagiellonian University, Krakow, in 1978. He joined the Physics Department of the Jagiellonian University in 1973, he was awarded a higher doctoral degree (so called 'habilitation') in 1982, and he was appointed to the full professor position at this University in 1991. He held several positions during his academic carrier, such as Vice-Rector of the Jagiellonian University (1993-1999), Chairman of the Supervisory Board for the 'Krakow Center for

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His scientific record includes over 130 scientific publications and several dozens of invited lectures at scientific conferences. He was Ph.D. thesis supervisor for 12 Ph.D. students and for many M.Sc. graduates. He organized several national and international research workshops and conferences, among them the 20th European Conference on Surface Science (ECOSS-20), 2001, and the 12th International Conference on Organized Molecular Films (LB 12), 2007.

His research activities are concentrated on those topics of materials research which are related to properties of nano-size materials with particular focus on scanning probe methods, to design and characterization of functional materials with emphasis on semiconductors, dielectrics and molecular structures, to quantum phenomena in mesoscopic systems, to manufacturing and characterization of self-assembling structures, and to research on biomedical materials. His interest in ionic insulators dates back to 1977 when he participated in the pioneering experiments on electron-stimulated desorption of alkali halides together with Hans Overeijnder and Dolf de Vries from the FOM Institute of Atomic and Molecular Physics in Amsterdam.

Preface

The rapid development of scanning probe microscopy (SPM) has made possible investigations of morphological and physical properties of insulating surfaces with unprecedented resolution. Since the ‘father’ of the SPM family — the scanning tunneling microscope (STM) — can only be applied to image ultrathin insulating films grown on conducting surfaces, most of the SPM investigations on insulators have been performed using the atomic force microscope (AFM). The principle of AFM is simple: an ultrasharp tip is driven over a surface, and the tip-surface interaction is reconstructed by monitoring the deflection of a flexible cantilever supporting the tip. Thanks to the extraordinary sensitivity of the piezo-elements used for positioning the tip with respect to the surface, atomically resolved images of several insulating crystal surfaces can be readily obtained in such a way.

Before introducing the AFM and STM techniques, we briefly discuss the crystallographic structures and preparation methods of various insulating surfaces in the first two chapters. Our attention will be limited to alkali halide surfaces and to oxide surfaces with large band gaps. We will not address other insulating surfaces, such as those of polymers, plastics, glasses and minerals like mica, where the interpretation of the SPM results is often not so conclusive. We will also not cover issues like chemical reactivity of the surfaces except when they become relevant to interpret SPM images.

Alkali halide surfaces have a simple structure and can be easily prepared and characterized in an ultra high vacuum environment (UHV). For these reasons, they have quickly become reference models to investigate crystal growth processes on the nanometer scale. Alkali halide surfaces are also important playgrounds for nanoscale phenomena such as self-assembly of metal clusters and large organic molecules, or friction and wear processes.

Insulating oxide surfaces find a broad use in several applications, ranging from interfaces for electronic ceramics to chemical catalysis. Even if they are more difficult to characterize, these surfaces are still amenable to fundamental investigations on the nanoscale, and high-resolution SPM images can be obtained after the surfaces have been carefully prepared.

The central part of the book begins with Chapters 4 and 5. Here we will focus on bulk and ultrathin insulating surfaces as imaged by SPM. Atomic resolution is unquestionable when single defects are imaged, which is now commonly achieved on several structures studied by AFM. Some defects like vacancies can be even created and subsequently imaged by the same AFM tip, which gives important information on the scanning process itself. Several experimental results have been also complemented by theoretical simulations of the imaging process, which allowed to identify the main forces responsible for atomic resolution.

Chapters 6, 7 and 8 introduce the interaction of ions, electrons and photons with halide surfaces, with special emphasis on the nanostructures created by the interaction processes. The discussion of the basic mechanisms responsible for crystal erosion and large surface nanopatterning with nanometer precision is supplemented by recent experimental results obtained by means of high resolution AFM imaging.

Chapters 9 and 10 deal with self-assembly of metals and organic molecules on bare and nanopatterned insulating surfaces. Once again the discussion of the experimental results is complemented by theoretical interpretations of the imaging process. Since the ordering of metal and molecular adsorbates is often hindered by the weak interaction between adsorbate and substrate, nanopatterns play an important role in improving the stability of the adsorbed species. For instance, self-assembly can be readily achieved along monatomic step edges or inside nanometer-sized pits produced by electron irradiation. As a further step, connecting well-defined molecular assemblies to external electrodes via metal nanowires grown on insulating surfaces might become feasible in the near future.

In Chapter 11 we discuss force spectroscopy measurements on insulating surfaces. In such cases, the response of the SPM tip is monitored at different separations between tip and surface, which gives important information on the tip-surface interaction. If a current flow between tip and sample can be established, by decreasing the band gap in the material, scanning tunneling spectroscopy (STS) is also possible. With this technique metals and organic molecules deposited on thin insulating films can be also investigated, and different electronic states of single molecules have been even identified.

The last two chapters deal with mechanical phenomena induced and observed using SPM on insulating surfaces. These processes include friction, wear, indentation and manipulation of tiny nano-objects. While several important results have been obtained in the first three topics — last but not least the achievement of superlubricity — nanomanipulation on insulating surfaces is still in its embryonic phase. However, nanomanipulation has such potential applications to molecular electronics and nanomechanics that exciting experiments are on sight, once again driven by theoretical models.

This book could have not been written without the collaboration of several people who supported us during the time of writing. Even if it is not possible to cite all of them, a special thanks goes to Jacek J. Kolodziej, Franciszek Krok, Bartosz Such, Piotr Cyganik, Piotr Goryl, Piotr Piatkowski, Janusz Budzioch and Salah Raza Saeed from the Jagiellonian University of Krakow, and Ernst Meyer, Roland Bennewitz, Luca Ramoino, Sabine Maier, Laurent Nony, Anisoara Socoliuc, Alexis Baratoff, Thilo Glatzel, Lars Zimmerli, Oliver Pfeiffer, Akshata Rao, Pascal Steiner and Raphael Roth from the University of Basel. We also thank Urszula Lustofin for administrative assistance and Tim Ashworth for carefully reviewing parts of the book. E.G. would like to thank his wife Tatiana for her patience and for continuous encouragement while writing this book. Financial support from the European Community under the Maria Curie Host Fellowship for Transfer of Knowledge (contract no. MTKD-CT-2004-003132), the Polish Foundation for Science (contract for subsidy no. 11/2007), and the Swiss National Science Foundation and NCCR Nanoscale Science is also gratefully acknowledged.

E. Gneco and M. Szymonski

Contents

<i>Preface</i>	vii
1. Crystal Structures of Insulating Surfaces	1
1.1 Halide Surfaces	1
1.1.1 Alkali halide surfaces	1
1.1.2 Alkaline earth halide surfaces	2
1.2 Oxide Surfaces	2
1.2.1 True insulating oxide surfaces	3
1.2.2 Mixed conducting oxide surfaces	4
2. Preparation Techniques of Insulating Surfaces	9
2.1 Ultra High Vacuum	9
2.2 Preparation of Bulk Insulating Surfaces	10
2.2.1 Halide surfaces	10
2.2.2 Oxide surfaces	11
2.2.3 Nanostructuring of insulating surfaces	12
2.3 Deposition of Insulating Films, Metals and Organic Molecules	13
2.3.1 Thin insulating films	14
2.3.2 Metal adsorbates on insulators	14
2.3.3 Organic molecules on insulators	15
3. Scanning Probe Microscopy in Ultra High Vacuum	17
3.1 Atomic Force Microscopy	17
3.1.1 Relevant forces in AFM	19
3.1.2 Contact AFM	21

3.1.3	Non-contact AFM	21
3.1.4	Kelvin probe force microscopy	24
3.2	Scanning Tunneling Microscopy	24
3.2.1	Scanning tunneling microscopy	24
3.2.2	Scanning tunneling spectroscopy	26
3.3	Atomistic Modeling of SPM	26
4.	Scanning Probe Microscopy on Bulk Insulating Surfaces	29
4.1	Halide Surfaces	29
4.1.1	Alkali halide surfaces	29
4.1.2	Alkaline earth halide surfaces	32
4.2	Oxide Surfaces	34
4.2.1	True insulating oxide surfaces	34
4.2.2	Mixed conducting oxide surfaces	37
4.3	Modeling AFM on Bulk Insulating Surfaces	42
4.3.1	Halide surfaces	42
4.3.2	Oxide surfaces	44
5.	Scanning Probe Microscopy on Thin Insulating Films	47
5.1	Halide Films on Metals	47
5.1.1	Carpet-like growth	47
5.1.2	Restructuring and patterning of vicinal surfaces	51
5.1.3	Fractal growth at low temperatures	53
5.2	Halide Films on Semiconductors	55
5.3	Heteroepitaxial Growth of Alkali Halide Films	58
5.4	Oxide Films	59
5.5	Modeling AFM on Thin Insulating Films	63
6.	Interaction of Ions, Electrons and Photons with Halide Surfaces	65
6.1	Ion Bombardment of Alkali Halides	65
6.2	Electron and Photon Stimulated Desorption	68
6.2.1	Electron stimulated desorption	69
6.2.2	Photon stimulated desorption	70
7.	Surface Patterning with Electrons and Photons	77
7.1	Surface Topography Modification by Electronic Excitations	77

7.1.1	Layer-by-layer desorption	77
7.1.2	Coexcitation with visible light	81
7.2	Nanoscale Pits on Alkali Halide Surfaces	83
7.2.1	Diffusion equation for F-centers	85
8.	Surface Patterning with Ions	89
8.1	Ripple Formation by Ion Bombardment	89
8.1.1	Linear continuum theory for ripple formation	91
8.1.2	Beyond the continuum theory	93
8.2	A Case Study: Ion Beam Modifications of KBr Surfaces	94
9.	Metal Deposition on Insulating Surfaces	101
9.1	Metals on Halide Surfaces	101
9.1.1	Metals on plain halide surfaces	102
9.1.2	Metals on nanopatterned halide surfaces	105
9.2	Metals on Oxide Surfaces	107
9.2.1	Metals on true insulating oxide surfaces	107
9.2.2	Metals on mixed conducting oxide surfaces	109
9.3	Metals on Thin Insulating Films	110
9.3.1	Metals on halide films	111
9.3.2	Metals on oxide films	111
9.4	Modeling AFM on Metal Clusters on Insulators	113
10.	Organic Molecules on Insulating Surfaces	115
10.1	Chemical Structures of Organic Molecules	115
10.1.1	Fullerene molecules	115
10.1.2	Porphyrin molecules	116
10.1.3	Phthalocyanine molecules	116
10.1.4	Perylene molecules	116
10.2	Organic Molecules on Halide Surfaces	117
10.2.1	Self-assembly of fullerene molecules	117
10.2.2	Nanoscale pits as molecular traps	121
10.2.3	Molecular nanowires	123
10.3	Organic Molecules on Oxide Surfaces	125
10.4	Organic Molecules on Thin Insulating Films	127
10.4.1	Organic molecules on halide films	127
10.4.2	Organic molecules on oxide films	128
10.5	Modeling AFM on Organic Molecules on Insulators	129

11. Scanning Probe Spectroscopy on Insulating Surfaces	131
11.1 Force Spectroscopy on Insulating Surfaces	131
11.1.1 Alkali halide surfaces	131
11.1.2 Alkaline earth halide surfaces	135
11.1.3 Oxide surfaces	137
11.2 Tunneling Spectroscopy on Thin Insulating Films	137
11.3 Tunneling Spectroscopy on Metal Clusters	138
11.3.1 Alkali halide films	138
11.3.2 Oxide films	139
11.4 Tunneling Spectroscopy on Organic Molecules	139
12. Nanotribology on Insulating Surfaces	141
12.1 Friction Mechanisms at the Atomic Scale	142
12.1.1 The Tomlinson model	142
12.1.2 Superlubricity	143
12.1.3 Velocity dependence of atomic friction	144
12.2 Friction on Halide Surfaces	144
12.2.1 Friction on bulk halide surfaces	144
12.2.2 Friction on halide films	146
12.3 Nanowear Processes on Insulating Surfaces	147
12.3.1 Abrasion wear on alkali halide surfaces	147
12.3.2 Nanoindentation processes	149
12.4 Modeling Nanotribology on Insulating Surfaces	152
13. Nanomanipulation on Insulating Surfaces	155
13.1 Nanomanipulation Experiments on Insulating Surfaces . .	155
13.1.1 Manipulation on halide surfaces	156
13.1.2 Manipulation on oxide surfaces	158
13.2 Modeling Nanomanipulation on Insulating Surfaces	159
13.2.1 AFM imaging of surface diffusion	159
13.2.2 Nanomanipulation of adatoms and vacancies	160
<i>Bibliography</i>	163
<i>Index</i>	183

Chapter 1

Crystal Structures of Insulating Surfaces

This chapter introduces the crystal structures and the main properties of several insulating halide and oxide surfaces that have been addressed by scanning probe microscopy on the nanometer scale. In the first part of the chapter we distinguish between alkali and alkaline earth halides. In the second part we introduce oxides surfaces, and divide them into true insulators and mixed conductors. The preparation methods of these surfaces are discussed in Chapter 2.

1.1 Halide Surfaces

1.1.1 *Alkali halide surfaces*

Alkali halides result from the binding of alkali metal to halogen ions. In standard room conditions alkali halides are white or transparent crystals. The most representative among them is *sodium chloride* (NaCl). Apart from being a material of obvious importance in several aspects of everyday life, NaCl plays a vital role in chemistry, biology, and several other scientific disciplines. Sodium chloride crystallizes in the *rock salt* structure shown in Fig. 1.1(a), which is common to all alkali halide crystals with the exceptions of CsCl, CsBr, and CsI [Ashcroft and Mermin (1976)]. Only very few facets of the NaCl structure are stable, in particular the (001) surface. This is due to the arrangement of the Na^+ and Cl^- ions, which makes such a facet electrically neutral. It is also well established that the ions at the surface undergo only small relaxations with respect to their bulk-truncated positions [Tasker (1979)].

In general, stable alkali halide surfaces are obtained by *cleavage*, i.e., by splitting a crystal along a definite plane. This process is always

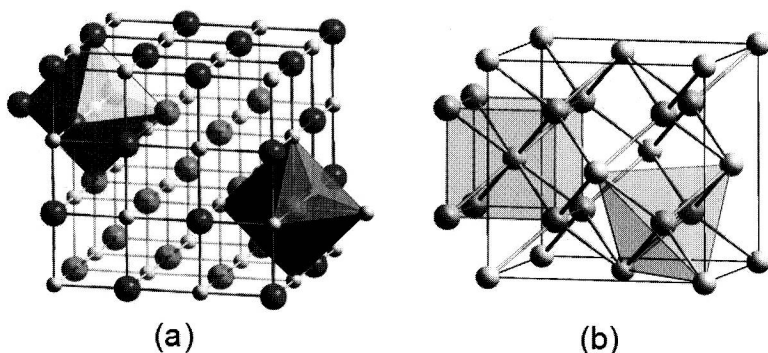


Fig. 1.1 Crystal structures of (a) sodium chloride and (b) calcium fluoride. Brighter spheres in (b) represent Ca^{2+} and darker spheres correspond to F^{-} ions.

accompanied by the formation of *steps*, which play an important role in many physical and chemical processes such as self-assembly of metal clusters and of large organic molecules. Characteristic nanopatterns can also be obtained by photon or electron irradiation or by ion bombardment of the surfaces, as discussed in details in Chapters 7 and 8.

1.1.2 Alkaline earth halide surfaces

Alkaline earth halides are other ionic materials of great interest in nanoscience. These crystals are formed by alkaline earth metal and halogen ions. The most studied among alkaline earth halides is *calcium fluoride* (CaF_2). Calcium fluoride crystallizes in the *fluorite* structure, which is shown in Fig. 1.1(b). In the fluorite structure each F^{-} ion is surrounded by four Ca^{2+} ions. Although the pure material is colorless, the mineral is often deeply colored due to the presence of *F-centers*, i.e. crystallographic defects in which a halogen vacancy in the crystal is filled by an electron. The most stable facet of the CaF_2 crystal is the (111) surface. This surface has a small lattice misfit of 0.6% with respect to Si(111), which makes calcium fluoride quite attractive as epitaxial insulator (Sec. 5.2).

1.2 Oxide Surfaces

Oxides are chemical compounds of oxygen with more electropositive elements or groups. Oxides have heterogeneous and complicated surfaces,

which makes their fundamental properties quite difficult to recognize. In the following we will distinguish between *true insulating oxides* and *mixed conducting oxides* [Fu and Wagner (2007)]. While true insulating oxides are characterized by very large band gaps making their electric conductivity practically negligible, mobile electronic and ionic defects can be generated in mixed conducting oxides, according to distinct reactions, so that these solids can exhibit a certain electric and ionic conductivity.

1.2.1 True insulating oxide surfaces

1.2.1.1 Aluminum oxide

Aluminum oxide or *alumina* (Al_2O_3) has a band gap of 8.8 eV. Aluminum oxide has a narrow range of stoichiometry, and bulk defects do not increase its electronic conductivity. For these reasons Al_2O_3 is widely used as a catalyst support and as a substrate for growth of metal films. The most common way by which aluminum oxide crystallizes is the *corundum* structure shown in Fig. 1.2, which is also known as *α -aluminum oxide*. In this structure each unit cell contains six formula units of Al_2O_3 and the oxygen atoms nearly form a hexagonal close-packed substructure with aluminum atoms filling two thirds of octahedral interstices. *Rubies* and *sapphires* are gem-quality forms of corundum with their characteristic colors due to impurities in the crystal structure. The most stable among the unreconstructed alumina surfaces is the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface terminated by a single Al layer. This surface undergoes a series of reconstructions upon annealing at high temperatures in vacuum and oxygen desorption [French and Somorjai (1970)].

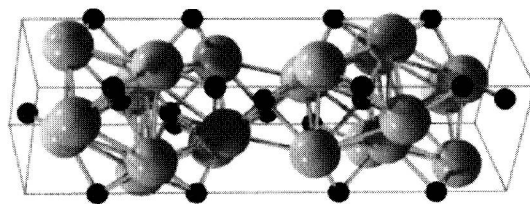


Fig. 1.2 Unit cell of α -aluminum oxide (corundum). Black spheres represent aluminum and gray spheres correspond to oxygen atoms. Reprinted from [Al-Abadleh and Grassian (2003)], Copyright 2003, with permission from Elsevier.

1.2.1.2 Magnesium oxide

Magnesium oxide or *magnesia* (MgO) has an energy gap of 7.8 eV and, similar to aluminum oxide, is widely used as a substrate for epitaxial growth of metal films and as a catalytic support. Magnesium oxide is a white solid mineral, which appears in nature in the form of *periclase*. The crystal structure of MgO is the same of NaCl . The $\text{MgO}(001)$ surface is one of the most studied oxide surfaces due to its simple structure, stable stoichiometry, and easy preparation by cleavage. Furthermore, this surface is non-polar, which makes it a good model system for theoretical studies of insulating oxide surfaces.

1.2.1.3 Silicon dioxide

Silicon dioxide or *silica* (SiO_2) has a very large band gap of about 9.0 eV, which makes this material a superior electric insulator with high chemical stability. As well as being a major component in earth's crust, SiO_2 plays an important role in many technological applications, for example as a dielectric layer in microelectronics and as a catalyst support. One of the most common structures of silica is the α -*quartz*. This structure is formed by spirals of SiO_4 tetrahedra (Fig. 1.3) and is stable over a broad range of temperatures and pressures. In general, surfaces of α -quartz have very complicated structures, which makes their investigations on the nanoscale quite challenging.

1.2.2 Mixed conducting oxide surfaces

1.2.2.1 Titanium dioxide

Titanium dioxide or *titania* (TiO_2) has a band gap of 3.2 eV. Titanium dioxide has a wide range of applications. It is used in catalysis, in solar cells, as white pigment, as anti-corrosion coating, in ceramics, as well as in electric devices. Titanium dioxide usually crystallizes in the *rutile* structure, which consists of octahedra with a titanium atom in the center and oxygen atoms at the apices. *Anatase* and *brookite* are other known stable structures of titanium dioxide.

Bulk-truncated $\text{TiO}_2(110)$ surfaces (the most stable ones) reveal two kinds of termination: polar surfaces terminated with either Ti or O atoms, and a non-polar surface containing both undercoordinated Ti and O atoms. More precisely, on the non-polar surface coexist six-fold coordinated