European Science Foundation
Standing Committee for Physical and Engineering Sciences (PESC)

ESF PESC EXPLORATORY WORKSHOP

NANO-OXIDES: perspectives and applications of oxide-based ultrathin films and nanoparticles

SCIENTIFIC REPORT

Brixen (South Tyrol), Italy
15-18 May 2003

Convened by: Gaetano Granozzi[1] and Falko P. Netzer[2]

[1] Dipartimento di Chimica Inorganica, Università degli Studi di Padova, Italy
[2] Institut für Experimentalphysik, Karl-Franzens-Universität Graz, Austria

EXECUTIVE SUMMARY

The ESF-PESC Exploratory Workshop on "*NANO-OXIDES: perspectives and applications of oxide-based ultrathin films and nanoparticles"* has been held in Bressanone (Brixen), Italy, in the period from **15 to 18 May 2003.**

The workshop has been hosted without charge in the Casa della Gioventù, the summer residence of the University of Padova, located in Via Rio Bianco 1 Brixen.

The accomodation of the participants was at the Hotel Best Western Grüner Baum, Stufels 11, Brixen.

The participants (see the list reported at the end of this document) were 25 people from the following European countries: Italy (5), Austria (3), Germany (6), France(5), Denmark (1), Sweeden(1), United Kingdom(3) and Spain (1). In addition an ESF representative from Spain (Prof. Carmen Afonso) has been present and participated actively for the whole workshop.

The Workshop has been organised to assess the current status of scientific research in the field of nano-oxides, to investigate the perspectives for the potential applications of nano-oxides in existing and future technologies, and to develop visions for the most promising areas of nano-oxide research. Moreover, the possibilities for setting up an ESF Scientific Network in the field of nano-oxides was intended to be explored.

The workshop was organised in 9 sessions, two per half day which were followed by a Topical Discussion. The Topical Discussions were centred on key questions, which arose during the foregoing sessions, and were moderated by two discussion leaders, the chairpersons of the foregoing two sessions. In addition, three General Discussions were held on *Applications and Perspectives, European Networks and Programmes,* and on *Where are*

we going?; the latter was intended as the concluding discussion to decide on a future ESF Network activity.

The final programme of the workshop is reported below while the scientific content of each session is outlined in the next paragraph. The assessment of the results and a discussion on the contribution to the future direction of the field is the argument of the final paragraph.

FINAL PROGRAMME

Friday 16th May 2003 — Morning

09:00	**Welcome and opening remarks** Convenors
	The European Science Foundation C. Afonso, ESF Standing Committee for Physical and Engineering Sciences
Session I: **Chair:**	**Models of metal-oxide catalysts and inverse catalysts** *Falko Netzer*
09:15	H.-J. Freund: Sites, edges and corners on nanoclusters deposited on oxide surfaces: selectivity in model catalysis
09:45	C. Henry: Nucleation and growth of gold on MgO single crystals and thin films
10:15	S. Bourgeois: Reactivity of molybdenum oxide nanodeposits on TiO_2 (110) surfaces
10:45	*Coffee break*
Session II: **Chair:**	**Reactivity and catalysis on oxide surfaces** *Preben Møller*
11:15	K. Schierbaum: Ultrathin cerium oxide on Pt(111): Structure, Phase transitions and implications for solid-electrolyte sensors
11:45	H. Kuhlenbeck: Spectroscopy of V_2O_3(0001) films: termination and adsorbate interactions
12:15	**Topical discussion.**

Discussion leaders: F. Netzer and P. Møller

12:45 *Lunch*

Friday 16th May 2003 Afternoon

Session III: **Growth and characterization of ultrathin films**
Chair: *Hajo Freund*

14:30 G. Thornton:
Thin films and nanostructures of TiO_2

15:00 M. Sambi:
Epitaxial oxide ultrathin films and nanoclusters: preparative strategies and structural characterisation

15:30 H. Niehus:
Preparation and Characterization of thin epitaxial Vanadium Oxide Layers

16:00 *Coffee break*

Session IV: **Nanostructured oxides**
Chair: *Jacques Jupille*

16:30 S. Surnev:
Oxide nanostructures on metal surfaces: growth, structure, and reactivity

17:00 P. Varga:
Structure of a Surface Oxide on Pd(111)

17:30 **Topical discussion**
Discussion leaders: H. Freund and J. Jupille

18:00 **General discussion:**
Applications and perspectives of oxide nanostructures in nanotechnology
Coordinators: F. Netzer and G. Granozzi

19:30 *Dinner*

Saturday 17th May 2003 Morning

Session V: **Electronic structure of oxide nanostructures**
Chair: *Alex Shluger*

09:00 G. Pacchioni:
Electronic structure and properties of metal-oxide interfaces

09:30 C. Noguera:
Growth, structure and electronic properties of small unsupported oxide clusters

10:00 F. Illas:
The interaction of Pd atoms and clusters supported with □-Al_2O_3(0001)

10:30 *Coffee break*

Session VI: **Defectivity of oxide surfaces**
Chair: *Gianfranco Pacchioni*

11:00 K. Hermann:
Electronic structure and Spectroscopy from Transition Metal Oxide Surfaces with and without defects: theoretical DFT studies on Vanadium Oxide Surfaces

11:30 A. Shluger:
Defects in nanostructured oxides: models, spectroscopy and Atomic Force Microscopy

12:00 **Topical discussion**
Discussion leaders: A. Shluger and G. Pacchioni

12:30 *Lunch*

Saturday 17th May 2003 Afternoon

Session VII: **Metal-oxide interfaces**
Chair: *Geoff Thornton*

14:00 S. Valeri:
Oxidation-reduction processes at epitaxial metal/oxide interfaces

14:30 E. Lundgren:
The initial oxidation of some late transition metals

15:00 J. Jupille:
Adhesion at metal/oxide interface

15:30 *Coffee break*

Session VIII: **Magnetic oxides**
Chair: *Claudine Noguerra*

16:00 F. Ciccacci:
Interface effects in epitaxial magnetic oxides

16:30 R. Egdell:
Magnetic Properties of Ultrathin CrO_2 Layers on Nanocrystalline TiO_2 and MnO_2

17:00 A. Barbier:
Magnetically exchange coupled metal/oxide interfaces

17:30 **Topical discussion**

Discussion leaders: G. Thornton and C. Noguerra

18:00 **General discussion:**
European Networks and Programmes
Coordinators: F. Netzer and G. Granozzi

19:30 *Workshop dinner*

Sunday 18th May 2003 Morning

Session IX **Oxide and metal nanoparticles**
Chair: *Claude Henry*

09:30 M. Bäumer:
Vanadia particles on oxides

10:00 P. Møller:
Metal-, metaloxide- and conjugated molecular deposites on to ordered ZnO, TiO_2, MgO and $SrTiO_3$ surfaces: synthesis and characterisation

10:30 **Topical discussion**
Discussion leader: C. Henry

11:00 **Closing General discussion**
"Where are we going ? Operative decisions"
Coordinators: F. Netzer and G. Granozzi

SCIENTIFIC CONTENT

The first session I on *Models of metal-oxide catalysts and inverse catalysts* was opened by H.-J. Freund (Fritz-Haber Institut Berlin), who addressed the problem of the complexity gap between research on catalytic model systems and the catalytic industrial reality. In order to move towards the desired 100% selectivity for a given reaction product it will be necessary to identify the active centres for steering the reaction into a particular direction, while blocking the pathways into other directions. To assess these reaction centres model studies will remain indispensible also in the future. The next speaker, C. Henry from CNRS Marseille, focussed his presentation on the preparation and characterisation of Au nanoparticles on MgO and on their egnimatic catalytic activity, while S. Bourgeois (Université de Bourgogne, Dijon) reported on Mo nanodeposits on TiO_2, with a view towards the oxidation of the Mo overlayers and their special reactvity for hydrogenation reactions. In the following session II on *Reactvity and catalysis on oxide surfaces* K. Schierbaum (Universität Düsseldorf) addressed the use of ultrathin Ce-oxide layers in gas sensor technology and the growth of Ce-oxide nanoparticles on Pt surfaces. H. Kuhlenbeck (Fritz-Haber Institut Berlin) discussed novel surface terminations of V_2O_3 films and the adsorption of simple gas molecules thereon. The Topical Discussion on catalysis related problems (discussion leaders F.P. Netzer, P. Møller) developed around the question of particle size and shape effects, e.g. why are Au nanoparticles catalytically active while bulk Au is not, and on particular sites for chemisorption/reaction at the metal-oxide interface.

The next two sessions were on *Growth and characterisation of ultrathin oxide films* and on *Nanostructured Oxides*. Here, growth strategies of TiO_2 layers on Ni (G. Thornton, University of Manchester), NiO films on Pd(100) (M. Sambi, Universita degli Studi di Padova), and V-oxides on Cu_3Au surfaces (H. Niehus, Humboldt Universität Berlin) have been reported and

discussed. The presence of different oxide structures, depending on the growth conditions, has been emphasised. S. Surnev (Karl-Franzens Universität Graz) discussed the properties of novel oxide phases in the limit of nanoscale layer dimensions and developed ideas for future research directions, while P. Varga (Technische Universität Wien) reported on a comprehensive structure determination of the elusive Pd surface oxide. In the subsequent Topical Discussion (discussion leaders H.-J. Freund, J. Jupille) the need for the combination of different methods, both experimental and theoretical, has been stressed to obtain reliable converging structure results of complex oxide layers. Novel diffraction methods for nanostructure determination have been pointed out. Another topic of interest concerned the connection between work function changes and chemical reactivity at surfaces and the question of global versus local work function concepts.

The third half day (sessions V and VI) was devoted to contributions from theory. Electronic structure calculations of metal-oxide interfaces (G. Pacchioni, Universita degli Studi di Milano; F. Illas, Universitad de Barcelona) and of oxide clusters (C. Noguera, Universite de Paris Sud) were treated in session V, whereas the electronic structure and spectroscopy of surface defects in nanostructured oxides were investigated by K. Hermann (Fritz-Haber Institut) and A. Shluger (University College London). G. Pacchioni discussed the bonding and adhesion of Pd and Ag adatoms on 1-2 layers of MgO and SiO_2 films on metal substrates, and F. Illas tested the validity of different theoretical methods in the determination of adsorption energies on the example of Pd on Al_2O_3. The physical properties of unsupported oxide nanoclusters were described by C. Noguera, who also discussed the future challenges of oxide nanocluster fabrication and characterisation. This latter topic was also carried over to the subsequent Topical Discussion: size control, stoichiometry control, and local morphology characterisation were identified as major issues. K. Hermann reported calculations of V-oxide surfaces and defect formation energies thereon and emphasised in his outlook the need to

tackle more complex oxide materials, e.g. vanadyl pyrophosphates, which are catalytically most relevant. A. Shluger addressed novel fabrication procedures for high k dielectric layers (HfO_2 , ZrO_2) by atomic layer deposition and examined theoretically the influence of defects at the interface to Si on band offsets. He also pointed out the fundamental scientific and industrial interest in the so-called cage oxides (silicates, Al-earth alkali-O systems), which could be a new field for controlled surface science studies. The Topical Discussion led by Pacchioni and Shluger then focussed on fundamental aspects of the dimension – property relationship of nano-oxides, e.g. the existence of a characteristic length for a given property which determines the size – property relation. The surface as a technical tool to allow the preparation and characterisation of oxide nanostructures at the atomic level has been highlighted in the discussion: surface science is thus inherently a major discipline of nanoscience.

In the session VII on *Metal-oxide interfaces* S. Valeri (Universita di Modena e Reggio Emilia) introduced the concept of abrupt versus reactive interfaces and reported results of NiO growth on Ag(100) and Fe on NiO. In the same session E. Lundgren (University of Lund) showed synchrotron radiation core level spectroscopy results on the oxidation of Pd and Rh single crystal surfaces under high oxygen pressures, emphasising the differences between high and low oxygen pressure oxidation. J. Jupille (Universités Paris 6 et 7) discussed the metal-oxide contact problem and the adhesion of Ag and Ti layers on Al_2O_3 (0001) substrate surfaces. The *Magnetic oxide* session VIII had F. Ciccacci (Politecnico di Milano), R. Egdell (University of Oxford), and A. Barbier (CEA Saclay) as speakers. Ciccacci introduced spintronics as a major application field for nanometric oxide layers and concentrated on linear magnetic dichroism measurements on the NiO/Fe(001) system and spin-resolved inverse photoemission photoemission experiments on LaSrMn perovskite structures. R. Egdell showed results from CrO_2 impregnated TiO_2 and MnO_2 ferromagnetic powders, while A. Barbier gave an

impressive overview of new surface magnetic scattering experiments at the ESRF. He assessed the high potential of magnetic oxides for spin valve and giant magnetoresistance devices and emphasised the interplay between magnetic properties and micro(nano)structure. The subsequent Topical Discussion (discussion leaders C. Noguera, G. Thornton) was started with the provocative question: where is theory going – can codes be given as "black boxes" to experimentalists? The theoreticians in the audience pointed out the limitations and dangereous pitfalls of this "Ansinnen" ,
arguing vividly against such an endeavour, but eventually the general agreement was reached that because of the progress of effective theoretical tools the interactions between experimentalists and theoreticians have much improved in the last decade and will further improve. Finally, interfaces were discussed again and their dominant role in nanotechnology was underlined.

The last session IX had *Oxide and metal nanoparticles* as major topics on the programme. M. Bäumer (Universität Bremen) discussed V and vanadia nanoparticles on alumina as model systems for catalysis and P. Møller (University of Copenhagen) addressed a number of different problems, ranging from thin overlayers of VO_2 on TiO_2 as a powerful potential chemical gas sensor system for O_2 and NO_2 recognition to the interaction of water with MgO nanolayer surfaces.

The three general discussions were moderated by the convenors (G. Granozzi, F.P. Netzer) and concentrated, on the one hand, on the more general scientific questions and perspectives for industrial applications which had arisen during the Topical Discussions, and on the other hand, on European Networking procedures and strategies for future pan-European initiatives.

In the closing discussion *Where are we going?* the participants decided unanimously that this group should attempt to set up an ESF Scientific Network on *NANO-OXIDES: Surfaces and Interfaces.*

ASSESSMENT OF THE RESULTS, CONTRIBUTION TO THE FUTURE DIRECTION OF THE FIELD

The scientific results of the workshop have been summarised in the section on the scientific content. The presentations of the participants gave an impressive overview of the activities of the major groups in Europe working in the area of nano-oxide surface science and this was an important contribution to assess future trends and possible new directions in this field. A number of topics have been identified as important areas for future research with high prospective potential. On a more general level it became clear that fundamental basic science to develop the physical principles of nanostructure growth and properties is still a major issue, which is a necessary prerequisite before more applied science and technological applications can be realised on a broader scale. The assembled "surface science oxide group" identified the ability to obtain atomic-level control during the formation and characterisation of oxide nanostructures as a particular strength of this community. It was clear that this capacity is a stronghold which has to be maintained. The ability to extract fundamental physical and chemical principles from atomically controlled experiments with model nano-systems as presented during this workshop is an important aspect of the surface science approach to nano-science. The transfer of this basic knowledge to more technologically applied and inherently less well-controlled systems and processes is a further step, which will be necessary to broaden the scientific data base on which future nano-technologies can emerge. However, it was the opinion of this group that the atomic-level control of the surface science approach must not be lost in the attempt of tackling industrially applied problems. But, it was

also recognised that the connection to applied research in the physics and chemistry of nano-science and to technologically relevant themes should be emphasised and strengthened.

The participants decided that the setting up of an ESF Scientific Network on *Nano-oxides: Surfaces and Interfaces* should be attempted, with the attendees acting as a core group. Moreover, the need to broaden the community by including e.g. members of the interface to biologically motivated and geoscience oriented research areas has been fully recognised. Attempts in this direction will be undertaken.

A subgroup of persons has been selected to act as a coordination committee for the preparation of an application for an ESF Network:

G. Granozzi (chairman), F.P. Netzer, C. Henry, F. Illas, E. Lundgren, P. Moller, C. Noguera, G. Thornton

List of Participants

ESF/PESC Exploratory Workshop:

NANO-OXIDES:

perspectives and applications of oxide-based ultrathin films and nanoparticles

Brixen (South Tyrol), Italy, 15-18 May 2003

Gaetano GRANOZZI
Università di Padova
Dipartimento di Chimica Inorganica
via Loredan 4
35131 Padova
Italy
Email: gaetano.granozzi@unipd.it

Falko P. NETZER
Karl-Franzens-Universität Graz
Institut für Experimentalphysik
Universitätsplatz 5
8010 Graz
Austria
Email: falko.netzer@uni-graz.at

Carmen N. A FONSO
(ESF OFFICER)
Consejo Superior de Investigaciones Cientificas
Instituto de Optica
Serrano 121
28006 Madrid
Spain
Email: cnafonso@io.cfmac.csic.es

Antoine BARBIER
CEA Saclay, DRECAM / SPCSI
Bâtiment 462
91191 Gif-Sur-Yvette
France
Email: abarbier@cea.fr

Marcus BÄUMER
Universität Bremen
Institut für Angewandte und Physikalische Chemie,
Fachbereich 2, NWII
Postfach 33 04 40
28334 Bremen
Germany
Email: baeumer@fhi-berlin.mpg.de

Sylvie BOURGEOIS
Université de Bourgogne
Laboratoire de Recherches sur la Réactivité des
Solides, UFR Sciences et Techniques
UMR 5613 CNRS
BP 400
21011 Dijon Cedex
France
Email: sbourg@u-bourgogne.fr

Franco CICCACCI
Politecnico di Milano
Dipartimento di Fisica
Piazza Leonardo da Vinci 32
20133 Milano
Italy
Email: franco.ciccacci@fisi.polimi.it

Russel EGDELL
University of Oxford
Inorganic Chemistry Laboratory
Parks Road
Oxford OX1 3PH
United Kingdom
Email: russ.egdell@chem.ox.ac.uk

Hans-Joachim FREUND
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Abteilung Chemische Physik
Faradayweg 4-6
14195 Berlin
Germany
Email: freund@fhi-berlin.mpg.de

Claude R. HENRY
CRMC 2 - CNRS
Campus de Luminy
Case 913
13288 Marseille Cedex 09
France
Email: henry@crmc2.univ-mrs.fr

Klaus HERMANN
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Abteilung Theorie
Faradayweg 4-6
14195 Berlin
Germany
Email: hermann@fhi-berlin.mpg.de

Francesc ILLAS
Universitat de Barcelona
Centre de Recerca en Química Téorica (CeRQT),
Departament de Química Física
Parc Cientific de Barcelona
Martí i Franquès 1
8028 Barcelona
Spain
Email: f.illas@qf.ub.es

Jacques JUPILLE
Universités Paris 6 et Paris 7
Groupe de Physique des Solides
UMR CNRS 7588
Tour 23
2 place Jussieu
75251 Paris Cedex 05
France
Email: jupille@gps.jussieu.fr

Helmut KUHLENBECK
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Abteilung Chemische Physik
Faradayweg 4-6
14195 Berlin
Germany
Email: kuhlenbeck@fhi-berlin.mpg.de

Edvin LUNDGREN
University of Lund
Institute of Physics
Department of Synchrotron Radiation Research
Box 118
221 00 Lund
Sweden
Email: edvin.lundgren@sljus.lu.se

Preben J. MØLLER
University of Copenhagen
Department of Chemistry
Kemisk Laboratorium IV
Universiteitsparken 5
2100 Copenhagen
Denmark
Email: pjm@kiku.dk

Horst NIEHUS
Humboldt Universität zu Berlin
Institut für Physik
Invalidenstr. 110
10115 Berlin
Germany
Email: niehus@physik.hu-berlin.de

Claudine NOGUERA
Université Paris Sud
Laboratoire de Physique des Solides
Bâtiment 510
91405 Orsay Cedex
France
Email: noguera@lps.u-psud.fr

Gianfranco PACCHIONI
Università degli Studi di Milano Bicocca
Dipartimento di Scienza dei Materiali
Via R. Cozzi 53
20125 Milano
Italy
Email: Gianfranco.Pacchioni@mater.unimib.it

Mauro SAMBI
Università degli studi di Padova
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica
Via Loredan 4
35131 Padova
Italy
Email: mauro.sambi@unipd.it

K.-D. SCHIERBAUM
Heinrich-Heine Universität Düsseldorf
Institut für Physik der kondensierten Materie
Abteilung Materialwissenschaft
Universitätsstr. 1
Geb. 25.23
40225 Düsseldorf
Germany
Email: schierb@uni-duesseldorf.de

Alexander SHLUGER
University College London
Department of Physics and Astronomy
London WC1E 6BT
United Kingdom
Email: a.shluger@ucl.ac.uk

Svetlozar SURNEV
Karls-Franzens-Universität Graz
Institut für Experimentalphysik
Universitätsplatz 5
8010 Graz
Austria
Email: svetlozar.surnev@uni-graz.at

Geoff THORNTON
Manchester University
Surface Science Research Centre and
Chemistry Department
Manchester M13 9PL, UK
e-mail: geoff@ssci.liv.ac.uk

Sergio VALERI
Università di Modena e Reggio Emilia
Istituto Nazionale per la Fisica della Materia (INFM)
Dipartimento di Fisica
Via Campi 213/A
41100 Modena
Italy
Email: valeri@unimo.it

Peter VARGA
Technische Universität Wien
Institut für Allgemeine Physik
Wiedner Hauptstr. 8-10/134
1040 Wien
Austria
Email: varga@iap.tuwien.ac.at