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\textsuperscript{1} and Falko P. Netzer\textsuperscript{2}

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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 accommodation 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), Sweden (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**

<table>
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<tr>
<th>Time</th>
<th>Session I: Models of metal-oxide catalysts and inverse catalysts</th>
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<tr>
<td>09:00</td>
<td>Welcome and opening remarks</td>
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<td>Convenors</td>
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<td>The European Science Foundation</td>
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<td>C. Afonso, ESF Standing Committee for Physical and Engineering Sciences</td>
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<td>09:15</td>
<td>H.-J. Freund: Sites, edges and corners on nanoclusters deposited on oxide surfaces: selectivity in model catalysis</td>
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<td>09:45</td>
<td>C. Henry: Nucleation and growth of gold on MgO single crystals and thin films</td>
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<td>10:15</td>
<td>S. Bourgeois: Reactivity of molybdenum oxide nanodeposits on TiO$_2$ (110) surfaces</td>
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<td>10:45</td>
<td>Coffee break</td>
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**Session II: Reactivity and catalysis on oxide surfaces**

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<tr>
<th>Chair: Preben Møller</th>
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<td>11:45</td>
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<td>12:15</td>
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</table>
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 
   -Al2O3(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 CrO2 Layers on Nanocrystalline 
   TiO2 and MnO2

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*

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**Sunday 18th May 2003  Morning**

**Session IX**  
**Chair:** Claude Henry

**Oxide and metal nanoparticles**

09:30  
M. Bäumer:  
Vanadia particles on oxides

10:00  
P. Møller:  
Metal-, metaloxide- and conjugated molecular deposits on to ordered ZnO, TiO₂, MgO and SrTiO₃ 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
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 indispensable 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 enigmatic 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 reactivity for hydrogenation reactions. In the following session II on *Reactivity 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$_2$O$_3$ films and the adsorption of simple gas molecules thereon. The Topical Discussion on catalysis related problems (discussion leaders F.P. Netzer, P. Móller) 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. Sambó, Universita degli Studi di Padova), and V-oxides on Cu$_3$Au 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, Universitat 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 SiO₂ 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 Al₂O₃. 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\textsubscript{2}, ZrO\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2} impregnated TiO\textsubscript{2} and MnO\textsubscript{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 dangerous 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 VO₂ on TiO₂ as a powerful potential chemical gas sensor system for O₂ and NO₂ 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*

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