COST CM 1104 “Reducible Oxides”
WG4 meeting
April 10-11, 2014
Riga, Latvia
Scientific Programme

Meeting location: ground zero, meeting room, Wellton Old Riga Palace Hotel, 8/10 Minsterejas Street, Riga, LV-1050, Latvia

All talks 25 min + 5 min discussion

Thursday, April 10

12.00 Lunch, coffee

12.50 Welcome (A. Shluger, E. Kotomin)

Session 1. Advanced methods for materials characterization, Discussion leader E. Kotomin

13.00 Aleksandr Lushchik -- Defects creation mechanisms in wide-gap metal oxides

13.30 Yuri Dekhtyar-- Weak electron emission to characterize nanomaterials with energy gap

14.00 Alexei Kuzmin --- X-ray absorption spectroscopy: probing local structure and beyond

14.30 Ilja Makkonen--- Oxygen vacancies in oxides: can positrons detect them?

15.00 Coffee break

Session 2. Surfaces/Interfaces, Discussion leader Yildiz

15.30 Claudine Noguera -- Conditions of occurrence of electron reconstructions at polar surfaces and polar-polar interfaces

16.00 Aleksandro Fortunelli -- Novel phases and processes in ultrathin oxides: Ternary CuWO₄ & electric field effects

16.30 Ladislav Kavan --- Electrochemical characterization of dense titania layers for dye sensitized solar cells

17.00 Mårten Björketun -- Ab initio thermodynamic modeling of electrified metal-oxide interfaces: consistent treatment of electronic and ionic chemical potentials

17.30-18.00 Discussion

19.30 Dinner
Friday, April 11

Session 3. Hafnia, Discussion leader V. Afanasiev

9.00 Alexander Shluger -- Electron-induced formation of Frenkel defect pairs in monoclinic HfO₂

9.30 Florin Cerbu --- Spectroscopy of gap states in amorphous and crystallized HfO₂

10.00 Oreste Madia -- Si P₀₀ defects at interfaces of Si-passivated SiGe channels with HfO₂

10.30 Coffee break, placing posters

Session 4. Processes in oxides. Discussion leader A. Lushchik

11.00 Jeremy Allen--- Doping CeO₂ with trivalent cations: Defect structures and reducibility

11.30 Oliver Diwald -- Combined Electron Paramagnetic Resonance and FT-IR Spectroscopic Evidence for Reversible O₂ Adsorption on In₂O₃₋ₓ Nanoparticles

12.00-13.30 Lunch and poster session

Session 5. Titania. Discussion leader D. Gryaznov

13.30 Keith McKenna-- Grain Boundary Controlled Electron Mobility in Polycrystalline Titanium Dioxide

14.00 Geoff Thornton -- Electron Beam and Scanning Tunneling Microscope Tip Induced Defects on TiO₂(110) Surfaces

14.30 Peter Deák -- The oxygen vacancy in TiO₂: a defect with phase-, site- and concentration-dependent properties

15.00 Coffee break, discussion of posters

Session 6. Fuel cells, Discussion leader A. Shluger

15.30 Leonarda Liotta -- Structural and redox properties of La₁₋ₓ SrₓCo₁₋ₓFe₀.₉₃Pd₀.₀₇O₃₋₉ perovskites as cathode materials

16.00 Denis Gryaznov -- First principles calculations on oxygen vacancy behaviour in Sr-doped complex perovskites for permeation membranes and solid oxide fuel cells

16.30 General discussion and Conclusion
**Posters**

1. **C. Slouka, G. Holzlechner, H. Hutter, J. Fleig**  
   Ion transport in DC-polarized donor-doped lead zirconate titanate (PZT)

2. **B. Laskova, M. Zukalova**  
   Electrochemical behavior of nanocrystalline TiO$_2$ (anatase) with exposed (001) facets

3. **T. Musso, Teemu Hynninen, Adam S. Foster**  
   Dynamic Charge Transfer Potential For Modeling Oxide Interfaces

4. **Chen Wu, Matthew S. J. Marshall, Xiao Hu and Martin R. Castell**  
   Surface structures of ultrathin TiO$_x$ and BaO films on Au (111)

   Nanolinelstructures on the SrTiO$_3$(001) surface

6. **Yu. A. Mastrikov and E. A. Kotomin**  
   First-principles modeling of oxygen transport in complex perovskites

7. **A. Popov, A. Lushchik, Ch. Lushchik and E.A. Kotomin**  
   Analysis of Excitonic Mechanism of Defect Formation in Insulating Materials - Generalization of Rabin-Klick diagram for a whole family of alkali halides

   (La,Sr)(Co,Fe)MO$_3$ as cathodes for IT_SOFC: structure-properties relationship
Defects creation mechanisms in wide-gap metal oxides

Aleksandr Lushchik
Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia
aleksandr.lushchik@ut.ee

The radiation resistance of various construction and functional materials is one of the "hottest" problems of various applications and modern technology. Many wide-gap metal oxides (WGMOs) proved to be highly resistant against radiation. In WGMOs, Frenkel pairs of radiation defects (RDs) are formed due to fast impact mechanisms, while the processes of RDs creation at the decay of electronic excitations are weakened. The formation energy of a Frenkel pair exceeds the energy gap \( E_{RD} > E_g \) thus impeding defect creation in the bulk via the recombination of relaxed electrons (\( e \)) and holes (\( h \)) or the decay of excitons, i.e. the dominant mechanisms of radiation damage in materials with \( E_{RD} < E_g \), for instance, in the majority of alkali halides. However, the energy released at the recombination of hot \( e \) with already localized \( h \) can be sufficient for the creation of RDs even in WGMOs. The probability of such hot \( e - h \) recombination significantly increases under irradiation conditions providing extremely high density of electronic excitations, e.g., in the cylindrical tracks of ~GeV heavy ions of \(^{197}\text{Au} \) (LET > 20 keV/nm).

The efficiency of defect creation via hot \( e - h \) recombination can be decreased to some extent due to the solid state analogue of the Franck-Hertz effect – the direct excitation of luminescent impurity centers by hot conduction electrons that is rival to defect creation. Such "luminescent protection" against nonimpact mechanisms of radiation damage has been revealed in some complex WGMOs containing single and isovalent RE impurity ions: \( \text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+} \) and \( \text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+} \). In many WGMOs with \( E_{RD} > 3E_g \) the situation is more complicated and the presence of various impurities just decreases the radiation resistance. Both reversible and irreversible (do not undergo a complete thermal annealing) defects are formed at the periphery of ion tracks at fluences about \( \Phi = 10^{11} \) ions/cm², while a sharp rise of the relative number of irreversible defects is detected after irradiation with \( \Phi \geq 10^{12} \) ions/cm² when a considerable overlapping of neighbouring tracks takes place. The last fact agrees well with theoretical predictions of the collective creation of 3D defects (rearrangement of many host atoms) under the dense irradiation of metal alloys predisposed to anharmonic interactions. The experimental manifestations of this mechanism of radiation damage have been revealed in some WGMOs as well.

Even the traces of calcium (important feature is the presence of 3d⁰ states) cause a sharp increase of the creation efficiency of RDs, especially of irreversible ones in WGMOs, which did not undergo specific procedures of a deep purification. According to recent theoretical calculations, complex metal oxides (in particular, \( \text{CaSO}_4 \)) possess a complex conduction band where d-subband is located ~1.5 eV above the bottom formed by s-states. A long-lived conduction d-electron participates in a slow hopping diffusion resulting in the appearance of a tunnel luminescence and increased recombination probability between a d-electron and a radiation-induced hole within the core electron shells of a WGMO. The energy released at such
recombination is sufficient for the formation of polyatomic 3D defects via collective creation mechanisms. In closely packed WGMOMs, the creation of such complex defects is energetically more profitable than the creation of several Frenkel pairs. It is worth noting that polyatomic impurity centres serve as seeds for the creation of radiation damage via collective creation mechanisms of RDs under high-dense irradiation of WGMOMs.
Weak electron emission to characterize nanomaterials with energy gap

Yuri Dekhtyar
Riga Technical University

Biomedical Engineering and Nanotechnologies Institute

1 Kalku str, Riga LV-1658, Latvia

Nanomaterials characterization requires nondestructive measurement technologies to identify imperfections. This could be achieved because of detection of the electron that escapes the nanoobject, a mean free path of the electron being not more that the tested object dimensions. Such the mode is available, when the electron has a kinetic energy \( \leq 1 \) eV. For this a prethreshold photoelectron emission (PPE) could be employed.

The physical fundamentals of conventional as well as exo- and dual- PEE are considered. Soft ultraviolet radiation (UV) is suitable to excite PEE. When temperature (T) of the tested object is a constant, UV induces conventional PPE, energy of the photons (hv) are close to the electron work function. When T = var, modulation of density of the electron states and/or surface potential is provided and photothermostimulated exoelectron emission (PTSE) is achievable. If high intensity photons having an energy close to the energy gap are supplied alongside with UV to the doped material, electrons and holes are intensively excited resulting a shift of the Fermi level and recharging of the surface electrically. By this way dual emission mode (DE) is provided.

The examples to employ PPE modes for characterization of nanoobjects (surface layers, nanoparticles, nanofilms) are reviewed (surface electrical potential, local states). The conventional PPE is demonstrated to recognize size depended electrical charge at the nanoparticles surface, characterization of the engineered surface charge of the materials, etc. The formal kinetic approach has been applied to correlate PTSE current with defect kinetics. PTSE provides knowledge on the point type imperfection concentration, interaction length, reconstruction, annealing (activation energy, frequency factor), diffusion (activation energy). DE confirms a capability to identify the energy gap and the surface electrical potential. PTSE is demonstrated also to identify phase transitions, polarization of the nanofilms and their interface with the substrate.

Some PPE specific applications like characterization and engineering of the bone properties, functionalized biomaterials, as well as nanodosimetry are considered, too.
X-ray absorption spectroscopy: probing local structure and beyond

A. Kuzmin
Institute of Solid State Physics, University of Latvia, Riga, Latvia
a.kuzmin@cfi.lu.lv

The popularity and possibilities of x-ray absorption spectroscopy (XAS) have been significantly grown during the last decades with the rapid progress in synchrotron radiation sources. Being element-selective and short-range order sensitive technique, XAS is well suited for an investigation of complex crystalline, nanostructured and disordered materials. Moreover, time-resolved XAS experiments can be realized to follow in-situ modifications of the materials structure under extreme conditions at time scales down to femtoseconds [1]. At the same time, the analysis of the extended x-ray absorption fine structure (EXAFS), containing structural information on the local environment around absorbing atom, is usually limited to a few nearest coordination shells due to the difficulties associated with shell overlap, structural and thermal disorder as well as many-atom contributions. Therefore, a significant amount of structural information contained in the experimental EXAFS spectra often gets lost.

This challenging problem can be successfully addressed using the advanced approach, based on classical molecular dynamics (MD) simulations [2-4]. The MD-EXAFS method allows one to perform (i) an interpretation of the experimental EXAFS spectra and (ii) a validation of the available force-field (FF) models. In this report recent advances in the development of the MD-EXAFS method will be presented on the example of several oxide materials.

This study was supported by the ESF project 2013/0015/1DP/1.1.1.2.0/13/APIA/VIAA/010.

Oxygen vacancies in oxides: can positrons detect them?

Ilja Makkonen, Esa Korhonen, Janne Heikinheimo, Vera Prozheeva, and Filip Tuomisto
Department of Applied Physics, Aalto University School of Science, Espoo, Finland

Oxygen vacancies in oxide semiconductors have been a widely debated topic over the past decades. The properties attributed to oxygen vacancies include the inherent $n$-type conduction, poor $p$-type dopability, coloration (absorption), deep level luminescence and non-radiative recombination. However, the only direct experimental evidence of their existence has been obtained on the crystal surface, e.g., on the TiO$_2$ (110) surface [1].

Positron annihilation spectroscopy is a method sensitive to neutral and negatively charged open volume defects. The decreased electron density in a vacancy manifests itself as an increase of positron lifetime and the narrowing of the 511 keV photo-peak in the annihilation gamma spectrum, compared to a defect-free crystal. Positron lifetime spectroscopy provides information on the atomic structure, the charge state and often the concentration of the vacancies while the Doppler broadening of the photopeak allows the identification of atoms surrounding the vacancy defects. The combination of positron annihilation spectroscopy and supporting first-principles modeling of the measured annihilation parameters has been efficiently used to identify and quantify technologically important vacancy-related defects in, for example, group IV semiconductors, III-nitrides and ZnO [2].

We present developments leading to the possibility of detecting oxygen vacancy-related defects in oxide semiconductors. Our data consists of both experimental results and computational predictions. The examples cover such materials systems as ZnO, In$_2$O$_3$, SnO$_2$, ZrO$_2$, SrTiO$_3$ and spinel MgAl$_2$O$_4$. We show that O vacancies may be directly detected in these oxides, in cases where they are complexed with cation vacancies. The detection is based on the modification of the positron annihilation signal of the cation vacancies when one or more oxygen vacancies are attached, similar as observed for nitrogen vacancies in InN [3].

Conditions of occurrence of electron reconstructions at polar surfaces and polar-polar interfaces

C. Noguera, J. Goniakowski
Institut des NanoSciences de Paris, Paris, France

Oxide-oxide interfaces have recently focused the attention of the research community, due to the entirely new properties they display, compared to their parent materials, and their much wider variety of behaviors compared to traditional semiconductor-semiconductor interfaces. The possibility of producing a confined two-dimensional electron gas (2DEG), subject of enhanced correlation effects, magnetic or even superconducting instabilities, represents a particularly exciting issue. In the past and more recently, 2DEG have been invoked at non-stoichiometric or hydrogenated oxide surfaces, and also evidenced and thoroughly studied at polar/non-polar interfaces between two insulating oxides.

Much less work has been devoted to interfaces between two oxides which are both oriented along a polar direction. While a number of polar-polar interfaces between conventional semi-conductors have been studied in the past, and compensation mechanisms, such as nonstoichiometric reconstructions or intermixing, have been proposed, there exists no general classification of the scenarios which can be encountered.

Relying on first principles simulations of ZnO(0001)/MgO(111), MgO(111)/CaO(111) and AlN(0001)/GaN(0001) interfaces and with the help of a simplified microscopic description of the electronic structure, we have built a general framework to assess the polar character of an interface. We have highlighted the key parameters which determine the polarization discontinuity at a stoichiometric polar/polar interface, and its three contributions: structural discontinuity, valence discontinuity, and electronic term. From this analysis which allows to generalize our ab initio results to any other stoichiometric polar/polar interface, we deduce various scenarios that such an interface may display, leading or not to an electronic reconstruction.
The field of nanostructured oxides is enjoying a period of great interest in the surface science community. Especially the combination of advanced experimental and theoretical tools continuously produces new information and fascinating developments. In this presentation I will focus on two topics which may have a bright perspective in future research.

Ultrathin ternary oxides represent novel materials with very appealing features. Multi-elemental oxide combination at the nanoscale opens completely new possibilities in terms of structure and properties. Here I will present a recent example of a CuWO₄ 2-D phase, which belongs to ternary tungsten oxides, such as metal tungstates (MWO₄), a class of functional materials at the cutting edge of fundamental science and with a high potential for applications. We recently unveiled [1] the structure of this novel phase via a combined experimental and theoretical investigation, and thoroughly characterized its spectroscopic properties. The structure corresponds to a CuWO₄ monolayer arranged in three sublayers with stacking O-W-O/Cu from the interface. The resulting bidimensional arrangement forms a robust framework with localized regions of anisotropic flexibility, thus exhibiting features which are very unusual in ultrathin binary oxide and may be appealing e.g. in catalytic applications. Electronically it displays a reduced band gap and increased density of states close to the Fermi level with respect to the bulk compound, which is also interesting e.g. in the optics field. Its fabrication route, via a two-dimensional solid-state reaction, is also novel and potentially generalized to a wide set of ternary oxides.

Manipulation of chemistry and film growth via external electric fields is a longstanding goal. Numerous systems have been predicted to show such effects but experimental evidence is sparse. Here we report evidence of field-induced reduction of a polar oxide surface by applying spatially-extended, homogeneous, very high (> 1 V/nm) DC-fields. We achieve such high fields in a setup resembling a plate capacitor where a Ag(100) substrate (with a deposited ultrathin NiO polar film) acts as the cathode with a counter electrode placed 800 nm apart. In a proof-of-principle test case, the well characterized ultrathin NiO/Ag(100) gets reduced to supported Ni clusters under fields exceeding the threshold of +0.9 V/nm: oxygen atoms are torn away from the surface, while the remaining Ni atoms are highly mobile and cluster together. The external field thus not only changes the system energetics but triggers dynamic processes which become important much before static contributions appreciably modify the potential energy landscape. Using an effective model based on density functional theory, we trace the observed interfacial redox process down to a dissociative electron attachment resonant mechanism. The proposed approach can be easily implemented and generally applied to a wide range of interfacial systems, thus opening new opportunities for the manipulation of film growth and reaction processes at solid surfaces under strong external fields.


Work supported by the ERC Advanced Grant SEPON
Compact thin films of TiO$_2$ are required for recombination blocking in the solid-state dye-sensitized solar cells, such as the state-of-art perovskite-based solar cells achieving up to 15% efficiency. [1] The compact dense titania layer can be grown on top of F-doped SnO$_2$ (FTO) by spray pyrolysis, atomic layer deposition (ALD), electrochemical deposition from solutions of TiCl$_3$ or by sol-gel dip-coating from solutions containing poly(hexafluorobutyl methacrylate) as the structure-directing agent. [2,3] The films are quasi-amorphous, but crystallize partly to anatase upon heat treatment. Electrochemical techniques are particularly suitable for the characterization of titania layers. [4] Cyclic voltammetry using ferri/ferrocyanide, methylviologen or 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as the model redox probes indicates selectively the pinholes, if any, in the layer. The pinhole-free films on FTO represent excellent rectifying interface, at which no anodic Faradaic reactions occur in the depletion state. The flatband potentials of the electrodeposited films, determined from Mott-Schottky plots, are comparable to those of anatase single crystal. The values of sol-gel films are upshifted by ca. 0.2-0.4 V, yet still follow the Nernstian pH dependence. The optimized buffer layer embodies interplay of quasi-amorphous morphology, responsible for the electrochemical blocking function, and the calcination-induced crystallinity, responsible for the fast electron injection and transport in the conduction band. The latter manifests itself by reversible charging of chemical capacitance and band-gap trap states of TiO$_2$ in its accumulation state. The solution-processed layers are outperforming those made by standard methods, i.e. spray pyrolysis and ALD.

This work was supported by the COST Action CM 1104 and by the Czech National Foundation, contract No. 13-07724S.

Ab initio thermodynamic modeling of electrified metal-oxide interfaces: consistent treatment of electronic and ionic chemical potentials

Mårten E. Björketun\textsuperscript{1}, Zhenhua Zeng\textsuperscript{2}, Martin Hangaard Hansen\textsuperscript{1}, Jeffrey P. Greeley\textsuperscript{2} and Jan Rossmeisl\textsuperscript{1}

\textsuperscript{1}CAMD, Department of Physics, Technical University of Denmark, 2800 Lyngby, Denmark
\textsuperscript{2}School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, United States
E-mail: martebjo@fysik.dtu.dk

The structure of the metal-oxide interface in a solid-oxide-based electrochemical cell depends sensitively on the electrode potential and the chemical activity of ions in the electrolyte. Up until now there has been no computational method that considers both these effects at the atomic level. This is unfortunate as the rates of energy conversion and polluting reactions taking place across the interface can be strongly affected by the interface structure, in particular at lower operating temperatures [1,2].

Here we present a method to determine the ground state interface structure at a given electrode potential, chemical potential of oxygen ions, temperature and set of gas pressures. The method uses thermodynamic arguments and draws extensively on schemes recently developed for electrified metal-water interfaces [3,4]. As an illustration we determine the structure and stoichiometry of a Ni-YSZ anode as a function of electrode potential at 0 and 1000 K. More specifically, we demonstrate how the oxygen deficiency, or excess, changes with potential and temperature. We find that a given electrode potential can be set up by a variety of interfacial structures; a critical insight from this work is then that the chemical activity of the electrolyte ions picks out the relevant structure. Finally, we describe how the structural information can be used as a starting point for accurate calculations of the kinetics of electrochemical fuel oxidation reactions.

Electron-induced formation of Frenkel defect pairs in monoclinic HfO$_2$

Samuel Bradley, Matthew B. Watkins, and Alexander L. Shluger

Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, Gower Street, London, WC1E 6BT, United Kingdom

The dielectric breakdown of transistors and setting of memory cells using HfO$_2$ films as a dielectric is manifested in the formation of metal filaments on application of voltage across the oxide film. The formation mechanisms of such filaments, which may be several nm in diameter, are based on the assumption of oxygen deficiency of the oxide film and aggregation of oxygen vacancies near pre-existing grain boundaries. We use *ab initio* calculations to demonstrate that an electron injection into the conduction band of HfO$_2$ from metallic electrodes can lead to formation of pairs of oxygen vacancies and interstitial oxygen ions, which separate efficiently via fast diffusion of oxygen interstitials.

Trapping of two extra electrons at pre-existing neutral oxygen vacancies in the 3-coordinated oxygen sublattice leads to formation of neighbouring oxygen vacancies with formation energies reduced to about 0.5 eV and activation barriers of about 1.2 eV. The neutral vacancy aggregation in the 3-coordinated oxygen sublattice proceeds with a small energy gain of about 0.1 eV per vacancy. These vacancies form a wide band in the middle of the HfO$_2$ band gap. The energies of these processes in 4-coordinated oxygen sublattice of monoclinic HfO$_2$ are generally higher. We discuss the relevance of this process to the mechanism of conductive filament formation in resistive random access memory devices.
Spectroscopy of gap states in amorphous and crystallized HfO$_2$

F. Cerbu$^1$, V. Afanasiev$^1$, A. Stesmans$^1$, M. Houssa$^1$, W. C. Wang$^1$

$^1$Department of Physics and Astronomy, University of Leuven, 3001 Leuven, Belgium

Energy distribution and density of defect energy levels inside the bandgap of insulating HfO$_2$ were evaluated using photoionization/photodepopulation experiments. The studied samples were prepared by atomic layer deposition of 19 nm HfO$_2$ or Hf$_{0.8}$Al$_{0.2}$O$_X$ films on top of 7.5 nm thick SiO$_2$ layer thermally grown on (100)Si surface. By observing the illumination – induced oxide charge variations in the pristine and the electron-injected samples we were able to evaluate the density of donor and acceptor states, respectively. The density of donor states appears to be below the detection limit ($\sim 1 \times 10^{11}$ cm$^{-2}$). By contrast, energy levels of trapped electrons are found in the wide energy range [fig. 1.] (1.3 eV $\leq$ $E_t$ $\leq$ 4 eV) below conduction band bottom in the 5.6-eV wide HfO$_2$ bandgap. Upon crystallization to cubic phase by annealing at 1000$^0$C, a band of deep electron traps emerges at (3 eV $\leq$ $E_t$ $\leq$ 4 eV). In the amorphous Hf$_{0.8}$Al$_{0.2}$O$_X$ layers more shallow trap distributions are found at (1.8 eV $\leq$ $E_t$ $\leq$ 3 eV). Typical trap acceptor densities lie in the range of $10^{12}$ – $10^{13}$ cm$^{-2}$ eV$^{-3}$ which corresponds to volume concentrations in the range. These results reveal two important features of defects in HfO$_2$: First, the dominant presence of acceptor centers as opposed to the commonly invoked O-vacancy centers. Second, the 1-2 eV wide energy distributions of electron states in the HfO$_2$ gap indicate large site-to-site structure variations rather than well reproducible defect configurations and associated with them, discrete levels predicted by theory. These observations are consistent with previous results obtained in amorphous and crystallized Al$_2$O$_3$ and rare-earth aluminates suggesting general relevance of these conclusions to high-k oxide insulators.

Fig. 1.
Negative bias temperature instability (NBTI) has become a major reliability issue for ultra-scaled metal-oxide-semiconductor transistors (MOSFETs), since it causes significant shift in the threshold voltage of p-MOSFETs and degradation of the mobility. Recently, high-k metal-gate p-FETs with SiGe channel have been shown to exhibit superior reliability as compared to the Si-channel devices. This finding may pave the way to solve the NBTI problem in highly-scaled (sub-1nm equivalent oxide thickness, EOT) p-FETs.

Although it is commonly accepted that NBTI originates from the bulk oxide defects (the recoverable component) and the interfacial traps (the permanent component), a better understanding of the physical mechanism behind the enhanced performances of SiGe channels is still missing. By analyzing the Si reference samples and the SiGe-channel structures with different Ge concentration, we will try to fill this gap and address the open question regarding the influence of germanium on the interface dangling bond density.

The major methodological challenge consists in the electrical characterization in MOS capacitor structures, which fails in assessing the defect densities. The valence band offset between the buried SiGe channel and the passivating Si capping layer is responsible for the formation of a quantum well structure. The conductance response of this well overwhelms the signal related to re-charging of the interfacial defects. At the same time, quantification of the interface defect density by using electron spin resonance (ESR) spectroscopy requires several challenging sample preparation steps, including removal of the metal gate stack, which is needed to avoid loading the ESR cavity, while preserving the ultra-thin (1.8nm) high-k dielectric below it.

ESR analysis of the (100)Si/HfO2 reference structures confirms the previous results by revealing the presence of Si Pb0 dangling bond defects with densities around $3.5 \times 10^{12}$ cm$^{-2}$. Experiments performed on SiGe-channel structures show the presence of the same Si Pb0 defects probably originating from the interface between Si capping layer and the insulating oxides. The density of these defects is seen to decrease as more Ge is introduced into the SiGe channel region, reaching $1 \times 10^{12}$ cm$^{-2}$ level for the maximal studied Ge concentration (55%). This observation explains the reduced permanent component of NBTI evaluated on p-MOSFET devices [1]. Although further experimental analysis is needed to establish the mechanism of the dangling bond density variation, one may suggest that a local strain relaxation occurs in the SiGe channel during post-fabrication anneal, required to reach the desirably low EOT (0.6 nm in our samples). This would result in tensile strain in the Si capping layer, leading to the low interface defect density. Thus, with increasing the Ge fraction in the SiGe layer, it appears possible to reduce the defect density by reducing the network mismatch between the Si cap and the insulating oxide (HfO2).

Doping CeO$_2$ with trivalent cations: Defect structures and reducibility

Jeremy P. Allen,$^1$ Patrick R. L. Keating,$^1$ David. O. Scanlon,$^2$ and Graeme W. Watson$^1$*

$^1$School of Chemistry and CRANN, Trinity College Dublin, Dublin 2, Ireland
$^2$University College London, Kathleen Lonsdale Materials Chemistry, Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, UK

*E-mail: allenje@tcd.ie; watsong@tcd.ie

CeO$_2$ has received considerable interest as an electrolyte for intermediate temperature solid oxide fuel cells. [1] Unfortunately, within this temperature range (~500-1000K), CeO$_2$ displays poor ionic conductivity, while high temperatures and low oxygen partial pressures can reduce Ce(IV), due to facile oxygen vacancy formation, [2] and cause electronic conductivity. To improve the ionic conductivity, aliovalent doping is commonly employed, with trivalent species (e.g. Y) a particular focus due to their creation of charge compensating vacancies, forming an O$^{2-}$ diffusion pathway without Ce(III). Experimental evidence [3] has corroborated the increased ionic conductivity from trivalent dopants, however a detailed understanding on the effect of the dopant on the electronic structure of CeO$_2$ and a full exploration of the range of trivalent dopants has been lacking.

This study considers two aspects of trivalent doping using density functional theory simulations: (i) the formation of charge compensating vacancies and their role in O$^{2-}$ conductivity, and (ii) their effect on the reducibility of CeO$_2$. These aspects are explored for a range of $p$-, $d$- and $f$-block ions. The first part of the study focusses on the position of the dopant ions to the vacancies, as dopant-vacancy association can limit ionic diffusion. The results indicate a clear relationship between the dopant species ionic radius and its position relative to the vacancy. In addition, some rare earth dopants (e.g. Dy, Nd) are found to have low dopant-vacancy association energies, suggestive of better ionic conductivity. The second aspect of the study, which is largely ignored in the literature, shows that the reduction energy correlates with the defect structure, therefore being only indirectly influenced by the ionic radius.

Combined Electron Paramagnetic Resonance and FT-IR Spectroscopic Evidence for Reversible O$_2$ Adsorption on In$_2$O$_{3-x}$ Nanoparticles

Nicolas Siedl$^1$, Philipp Gügel$^1$, Daniel Thomele$^2$ and Oliver Diwald$^{1,2}$

1) Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg, Cauerstraße 4, 91058 Erlangen, Germany
2) Department of Materials Science and Physics, University of Salzburg, Hellbrunnerstrasse 34/ III, A-5020 Salzburg, Austria

Adsorption-induced electronic property changes determine the performance of nanostructured transparent conductive oxides and sensor materials. For the study of O$_2$ adsorption on electron rich In$_2$O$_{3-x}$ nanoparticles we used transmission FT-IR spectroscopy in combination with electron paramagnetic resonance (EPR). The reversible emergence and annihilation of conduction band electrons is subject to O$_2$ adsorption and was tracked at different oxygen pressures via IR active Drude absorptions. Corresponding results were related to EPR measurements that were performed under identical experimental conditions. For the first time we identified a weak adsorption complex between O$_2$ and the surface of In$_2$O$_{3-x}$ nanoparticles in the temperature range between $T = 90$ K and $T = 298$ K. Complementing and supporting our FT-IR observations, this evidence opens the way to study sensing relevant adsorption processes at room temperature with spectroscopy.
Grain Boundary Controlled Electron Mobility in Polycrystalline Titanium Dioxide

Suzzane K. Wallace and Keith P. McKenna
Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom.
e-mail keith.mckenna@york.ac.uk

The trapping and mobility of electrons in nanocrystalline oxide materials underpins a diverse range of applications in areas such as solar energy generation, catalysis, gas sensing and nanoelectronics [1-5]. Grain boundaries, one of the most pervasive defects in these materials, are widely believed to be critical in controlling electron mobility but probing their effects directly has proved extremely challenging. Here, we provide atomistic insight into this important issue through first principles based modeling of the interaction of electrons with grain boundaries in TiO₂. We show that perturbations in electrostatic potential are responsible for high concentrations of strong electron trapping sites at grain boundaries which hamper electron transport between grains. However, this effect is partially ameliorated at high current densities (>0.01 mAcm⁻²) as a result of a highly nonlinear trap filling effect (see Figure 1 below) pointing to ways to help improve the performance of materials for applications such as dye-sensitized solar cells and photocatalysts [1,6].

Fig. 1: a) The (210)[001] tile grain boundary in rutile. Ti ions are coloured according to the magnitude of the onsite electrostatic potential (green=low, blue=high). The deepest electron trapping sites correspond to the highest electrostatic potential. b) Variation of the average electron transit time on the electronic current density.

Electron Beam and Scanning Tunneling Microscope Tip Induced Defects on TiO$_2$(110) Surfaces

D. S. Humphrey$^1$, C. L. Pang$^1$, Q. Chen$^{1,2}$, and G. Thornton$^1$

$^1$Department of Chemistry and London Centre for Nanotechnology, University College London, London, WC1H 0AJ, UK
$^2$Department of Chemistry, University of Sussex, BN1 9QJ, UK

g.thornton@ucl.ac.uk

Previously, we removed individual H-adatoms from a TiO$_2$(110) surface using +3 V electrical pulses from a scanning tunneling microscope (STM) tip [1]. More energetic pulses, between 5-10 V, created approximate ovals of the 12 reconstruction, 6-10 nm in diameter [2]. Electron bombardment from a filament (75 V) led to desorption of H-adatoms from the surface and an increase in bridging oxygen vacancy (O$_b$-vac) density. Bombardment at 300 V led to the formation of a 1$n$ (n ≥ 2) reconstructed surface.

Here, we focus on the combined effect of irradiation from an electron gun and electrical pulses from an STM tip. A defocused electron beam (3 kV, ~0.65 mA cm$^{-2}$) was directed at the surface, irradiating an area a few mm wide. We used STM to image the inner and outer beam-irradiated regions of the surface. The inner region has lost 1×1 ordering and is rough with features elongated in [001]. Some of the features display 1×$n$ periodicity, including 1×2 regions. Figure 1 shows an STM image following a +7 V pulse, which reconstructs an area ~50 nm wide, an order of magnitude wider than for similar pulses on the non-irradiated surface. Annealing this surface to ~850 K partially recovers the surface structure: 1×1 and 1×2 areas are both present but the surface is very rough. Annealing to ~1000 K returns the surface to a typical 1×1 morphology.

In the outer beam-irradiated area where the electron density was lower, a different morphology is observed in STM. The surface is essentially 1×1, but modification in the form of well-resolved atomic scale surface “cracking” is observed. When the final anneal step of a typical sputter/anneal sample preparation is dropped from ~1000 K to ~570 K a similar structure is also formed. Annealing the cracked surface to ~850 K leads to a surface with well-defined 1×1 and 1×2 areas. Annealing to ~1000 K returns the surface to a typical 1×1 morphology as with the inner region.

The oxygen vacancy in TiO$_2$: a defect with phase-, site- and concentration-dependent properties

Peter Deák, Bálint Aradi, and Thomas Frauenheim
University of Bremen, BCCMS, PoB 330440, D-28334 Bremen, Germany
deak@bccms.uni-bremen.de

TiO$_2$ is one of the most studied reducible oxides but, despite decades of research, experimental and theoretical results on its oxygen vacancy (V$_O$) remained controversial. Usage of the HSE06 functional, which is free of the electron self-interaction error of standard DFT functionals, has allowed us to reproduce measured infrared absorption, photoluminescence and thermal ionization data of V$_O$ within ~0.1eV [1]. From our calculations a consistent and quantitative interpretation of the conflicting experiments emerges. In rutile, where native Ti$^{3+}$/Ti$^{4+}$ traps in the bulk can capture electrons, the behavior of V$_O$ depends on its concentration. In oxidized samples these traps passivate V$_O$, and only one gap level, related to trapped electrons, is observed. Electrons localized to the vacancy can only be observed after illumination at very low temperature, as proven by magnetic resonance experiments. In strongly reduced samples electrons may stay localized in the vacancy and even the neutral state gives rise to two vertical electronic transitions in infrared. In contrast to that, Ti$^{3+}$/Ti$^{4+}$ electron traps occur only at the surface of anatase, while in the bulk only holes are self-trapped by O$^{2-}$/O$^{1-}$ transitions. Therefore, V$_O$ in bulk anatase can retain both of its electrons in an antiferromagnetic singlet state, much shallower than in bulk rutile. At the surface, however, V$_O$ behaves similarly in both phases. The carrier self-trapping also influences the doping behavior of TiO$_2$ [2].

Structural and redox properties of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$-0.03Pd$_{0.03}$O$_{3-\delta}$ perovskites as cathode materials

F. Puleo$^1$, L.F. Liotta$^1$, Valeria La Parola$^1$, Dipanjan Banerjee$^2$, C. Paoletti$^3$, E. Simonetti$^3$, Antonino Martorana$^{1,4}$ and Alessandro Longo$^{1,5}$

$^1$Istituto per lo Studio di Materiali Nanostrutturati (ISMN)-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy
$^2$Dutch-Belgian Beamline (DUBBLE), European Synchrotron Radiation Facility (ESRF), B.P. 220, F-38043 Grenoble, France.
$^3$ENEA, Centro Ricerche Casaccia, Via Anguillarese 301, 00123 Roma, Italy.
$^4$Dipartimento Fisica e Chimica Università di Palermo, Viale delle Scienze Ed., 17, 90128 PALERMO, Italy.
$^5$Netherlands Organization for Scientific Research (NWO), 6 rue Jules Horowitz, BP220, 38043 Grenoble CEDEX, France.
E-mail: liotta@pa.ismn.cnr.it

Due to their high mixed ionic and electronic conductivity, perovskite oxides based on lanthanum strontium cobalt ferrite (LSCF) are the most studied mixed ionic and electronic conducting materials for cathode applications in solid oxide fuel cells. Recently, it has been reported that the performance of LSCF cathodes can be further enhanced by adding nano-sized noble metals such as Cu, Ag and Pt [1,2]. In this work nanostructured La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$-0.03Pd$_{0.03}$O$_{3-\delta}$ perovskites with fixed La-Sr composition ($x=0.4$) and two different Fe contents ($y=0.2$ and 0.8), labelled as LSCF02-Pd and LSCF0.8-Pd, were prepared. The incorporation of Pd cations into the perovskite lattice was evidenced by solving the local environment of Pd using EXAFS spectroscopy. In Fig.1 the Fourier Transform of EXAFS signals for the two samples LSCF08-Pd and LSCF0.2-Pd is displayed and compared with Pd foil and PdO signals as reference. XPS analyses showed that introduction of Pd in the B-site of the perovskite caused an increase of oxygen vacancies, the variation being much more pronounced in the LSCF02-Pd. By looking at the relative percentages of the lattice and surface components, a decrease in the lattice component with respect to the surface was evidenced in the Pd doped samples indicating an increase of oxygen vacancies (Fig. 2) Moreover, ionic Pd$^{4+}$ was detected as the only palladium species on the perovskite surfaces. EIS measurements evidenced the best electrochemical properties for LSCF02-Pd with respect to the corresponding un-doped perovskite, in agreement with higher oxygen vacancies content and improved reducibility of Co ions (as detected by TPR analysis).

First principles calculations on oxygen vacancy behaviour in Sr-doped complex perovskites for permeation membranes and solid oxide fuel cells

Denis Gryaznov, Jevgenijs Begens, Eugene Kotomin

Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063, Latvia
gryaznov@mail.com

La$_{1-x}$Sr$_x$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$ perovskite solid solutions containing reducible transition metals is known as one of the best cathode materials for permeation membranes and solid oxide fuel cells. The key properties controlling the quality of cathode materials are the concentration of oxygen vacancies and their migration energies. The first principles calculations were used in this study, in order to understand properties of oxygen vacancies in

La$_{1-x}$Sr$_x$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$ and La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ at two concentrations of Sr dopant, namely 12.5 and 50%. The standard GGA-type PBE exchange-correlation (ex-corr) functional and the DFT+U method, as implemented in plane wave code VASP [1], and hybrid ex-corr functional PBE0, as implemented in Gaussian basis set code CRYSTAL [2], were used for better comparison and analysis of obtained results. The calculations were spin polarized in supercells with full structure relaxation. The analysis also included the phonon contribution to the formation energies using direct method in supercells and, thus, temperature dependence of formation energies [3].

We compare the calculated formation energies with those obtained in thermogravimetric measurements [3] as well as the calculated migration energies with permeation measurements. In particular, we emphasize the important role of a proper ex-corr functional for the calculated formation energies, especially for high concentrations of Sr which requires PBE0 or DFT+U for their better agreement with the experiments. The magnitude of the phonon contribution to the Gibbs free formation energy increases not only with temperature, but, also with Sr content.

[1] www.vasp.at
[2] www.cryst.unitio.it
Despite donor doping, lead zirconate titanate (PZT), one of the most prominent ferroelectric materials may exhibit a significant oxygen vacancy concentration, which can be attributed to the only partially controllable loss of lead oxide during the sintering process. Already at moderate temperatures (above 350°C) these oxygen vacancies are sufficiently mobile and enable tracer diffusion. Oxygen isotope exchange experiments can therefore be used to get a detailed mapping of oxygen tracer motion and thus indirectly of the oxygen vacancy distribution, also under DC field load.

In this contribution, we present results of oxygen tracer diffusion experiments on polarized Nd-doped PZT, monitored by spatially resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS). Electrode material, temperature and DC field load were varied and corresponding spatially resolved and time-dependent information of the oxygen vacancy redistribution under the influence of electric fields could be obtained. An enhanced oxygen tracer concentration is measured near the cathode and interpreted in terms of field-driven oxygen vacancy accumulation at an oxide ion blocking electrode. The near anode area shows a significant dependence of the oxygen tracer concentration on the electrode material. Furthermore, a field driven change of the grain boundary diffusion was observed soon after applying a DC load, resulting in a significantly better ionic conductivity in the grain boundaries compared to the virgin sample. These fast grain boundaries are compared to those with thermally induced fast ionic conduction found above ca. 600°C.
Electrochemical behavior of nanocrystalline TiO$_2$ (anatase) with exposed (001) facets

B. Laskova, M. Zukalova, M. Bousa, L. Kavan
J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, CZ-18223 Prague 8, Czech Republic

The electrochemical behavior of TiO$_2$ anatase with a predominant (001) face (ANA001) was studied by cyclic voltammetry of Li insertion and chronoamperometry$^1$. Both methods proved its higher activity toward Li insertion compared to that of reference materials.

The lithium diffusion coefficient of ANA001 calculated from cyclic voltammetry is by 1 order of magnitude higher than those of reference materials with a dominating (101) face. The same tendency, although not so large difference, exhibited the chronoamperometric diffusion coefficients and rate constants of ANA001 and reference samples. The enhanced activity of the anatase (001) face for Li insertion stems from synergic contributions of a faster interfacial charge transfer at this surface and a facile Li transport within a more open structure of the anatase lattice in the direction parallel to the c-axis. In addition to this, the solar conversion efficiency of the dye-sensitized solar cell employing ANA001 sensitized with C101 was measured and compared with that of standard nanocrystalline TiO$_2$ anatase (101) sensitized with the same dye$^2$. The (001) face adsorbs a smaller amount of the used dye sensitizer (C101) but provides a larger open-circuit voltage of the solar cell. The negative shift of flatband potential is suggested to be responsible for the observed enhancement of $U_{oc}$.

Figure 1: TEM image of nanocrystalline TiO$_2$ anatase with a predominant (001) face.

Acknowledgement: This research was supported by the COST Action CM1104.

MoS₂/Graphene Oxide As Novel Semiconductor/Oxide Interfaces For Electronics

Tiziana Musso,¹ Priyank V. Kumar,² Adam S. Foster¹ and Jeffrey C. Grossman²

¹ Department of Applied Physics, Aalto University School of Science, Finland
² Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
tiziana.musso@aalto.fi

The excellent physical and semiconducting properties of transition metal dichalcogenide (TMDC) monolayers make them promising materials for many applications, particularly electronic devices. In current TMDC-based electronics, SiO₂ is usually used as a substrate for various TMDCs [1], either to support them or to form semiconductor/oxide junctions. However, substrate induced modulation of the TMDC properties is rather difficult, and generally requires external control [1, 2].

In this work, we investigate the role of graphene oxide (GO) as a substrate for TMDC monolayers, using MoS₂ as an example, and show substrate induced property modulation. GO has many advantages over silica, thanks to its flexibility and easier fabrication protocols [3]. We have used ab-initio simulations to investigate the effects of GO oxygen concentration and type of functional groups on the overall interface with MoS₂. From the density of states and band structure analysis, we discover that by increasing the oxygen concentration in GO, the n-type Schottky barrier increases, indicating that the MoS₂ becomes p-doped. This result suggests a new and considerably easier way to tune and control the MoS₂ doping level directly by designing appropriate GO layers, without having to externally dope MoS₂. Overall we suggest a new, more affordable design of CMOS devices based on MoS₂/GO structures as novel semiconductor/oxide interfaces.

Fig. 1. Top and side view of GO/MoS₂ interface. GO has epoxy functional groups in concentration 28.57%

Surface structures of ultrathin TiO\textsubscript{x} and BaO films on Au (111)

Chen Wu, Matthew S. J. Marshall, Xiao Hu and Martin R. Castell
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
chen.wu@materials.ox.ac.uk; martin.castell@materials.ox.ac.uk

Following the discovery of enhanced catalytic properties of oxide supported nanoparticles of noble metals, especially Au, interactions between the two have become a focus in research [1-3]. The growth of oxides on Au(111) surfaces serves as an inverse model and provides insights into their interactions. Well-ordered TiO\textsubscript{x} and BaO layers were grown on (22\times\sqrt{3})-reconstructed Au(111) surfaces by Ti and Ba deposition and oxidation.

In the growth of TiO\textsubscript{x} thin films on Au(111), three different structures were observed with increased amounts of Ti deposited [4]. The first structure occurs for Ti surface coverages of <0.5 monolayer (ML), and exhibits a (2\times2) -reconstructed structure resembling a honeycomb pattern. The second structure arises after depositing 0.5 ML - 1.8MLs of Ti and exhibits a pinwheel shape. The pinwheel structure forms a ($\sqrt{67}\times\sqrt{67}$)R12.2° Moiré pattern. The third structure occurs for >0.5 ML Ti depositions and forms triangular shaped islands. Film growth continues via the coalescence of triangular islands with further increased Ti coverage.

For BaO ultrathin film growth on Au(111), coexistence of a honeycomb (4\times4) and a hexagonal ($4\sqrt{3}\times4\sqrt{3}$)periodicity were observed. Both structures lift the Au herringbone reconstruction [5]. Using the sub-monolayer TiO\textsubscript{x} structures on Au(111) as templates, new reconstructions were created following Ba deposition which were not observed when BaO was grown on Au directly. Consequently, we demonstrate the possibility of creating novel epitaxial oxide structures on both metal substrates and other oxide templates.

Nanoline structures on the SrTiO$_3$ (001) surface


1. Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, U.K.

2. Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, U.S.A.

Atomic resolution scanning tunnelling microscopy (STM) of the SrTiO$_3$ (001) surface reveals that certain surface treatments give rise to the formation of a variety of nanostructures including nanodots and nanolines. 0.5wt% Nb doped SrTiO$_3$ (001) single crystals were used in this experiment. Samples were introduced into an ultra-high vacuum (10$^{-8}$ Pa) STM chamber followed by argon ion sputtering (10 mins, 2-5μA ion current, 1keV beam energy) and direct current annealing in the temperature range 875 – 900 °C. This surface preparation produced three types of linear nanostructures named as nanolines on the SrTiO$_3$ (001) surface.

These three types of nanolines are dilines, trilines and tetralines. All these nanolines consist of parallel rows that assemble into domains that are oriented in the $<$001$>$ directions. Auger electron spectroscopy (AES) and X-ray photoemission (XPS) show that surfaces decorated with nanolines are TiO$_x$ rich. XPS spectra obtained from these three types of nanolines reveals significant Ti$^{2+}$ peak on trilines compared with a small amount on dilines and no Ti$^{2+}$ peak on tetralines.
FIRST-PRINCIPLES MODELLING OF OXYGEN TRANSPORT IN COMPLEX PEROVSKITES

Yu. A. Mastrikov and E. A. Kotomin

Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, Latvia

Reducible cobaltates in the form of complex $\text{ABO}_3$-perovskite solid solutions exhibit a perceptible ionic conductivity, leading to their promising use as oxygen permeation membranes, electrolytes, and solid oxide fuel cells (SOFC) cathodes ($\text{(La,Sr,Ba)}(\text{Mn,Fe,Co})\text{O}_3$). Oxygen stoichiometry strongly affects transport properties of the materials, which, in turn, defines suitability of the material for targeted applications.

The oxygen migration in those perovskites occurs via the vacancy mechanism, in which the vacancy moves through a bottleneck formed by the "critical triangle" of one $B$-site cation and two $A$-site cations. In addition to their influence on bulk transport properties, the concentration and mobility of oxygen vacancies are two major factors determining the surface oxygen incorporation rate. Although oxygen vacancies are being extensively studied in perovskites, our understanding of their effects on behavior of the materials and the corresponding performance of practical devices is far from complete.

Using first-principles parallel GGA-level calculations (VASP 5.3 computer code) in large (40-320 atoms) supercells, we simulated migration of oxygen in $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF) and $(\text{Ba,Sr})(\text{Co,Fe})\text{O}_3$ (BSCF) perovskites. The atomic relaxation, charge redistribution, migration barrier, and the structure of transition states for oxygen ion migration are obtained. We explore the differences between BSCF perovskites [1], which exhibit considerably lower migration barriers for oxygen than other perovskites, and LSCF [2]. We discuss relevant implications for the oxygen surface and bulk reaction and hence for energy conversion in real devices, such as SOFC [3,4].

Analysis of Excitonic Mechanism of Defect Formation in Insulating Materials
- Generalization of Rabin-Klick diagram for a whole family of alkali halides

A.I. Popov\textsuperscript{a} , A. Lushchik\textsuperscript{b} , Ch. Lushchik and E.A. Kotomin\textsuperscript{a,c}

\textsuperscript{a} Institute for Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV-1063, Latvia
\textsuperscript{b} Institute of Physics, University of Tartu, Ria 142, 51014 Tartu, Estonia
\textsuperscript{c} Max Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany

In this presentation, the efficiency of excitonic mechanism of radiation-induced defects formation in insulating solids is discussed. We analyze the condition for the nonradiative exciton decay into stable Frenkel point defects and compare experimental and theoretical values of primary defect formation energies, band gap and absorption energies including wide class of materials (halides, binary and ternary oxides etc).

In materials containing $F$ centers, the relation between the stable $F$ center (anion vacancy with trapped electron) formation yield vs material structural parameters under irradiation (known as Rabin-Klick diagram) is widely used. We demonstrate in this talk, how this diagram could be generalized for a whole family of alkali halides (both NaCl and CsCl–type structures). For this reason, experimental data on the $F$ center production efficiency (eV/center) vs. S/D parameter (the ratio of the separation between halogen ions and diameter of the halogen ion) for cesium halides are collected and analysed. We discuss also current understanding of the $F$-type center formation process in alkali halides and oxides with a special attention to self-trapping of electron/holes.
La$_{0.6}$Sr$_{0.4}$Co$_{1-x}$Fe$_{x}$O$_{3-\delta}$ (x=0.2-0.8; M=Ni, Pt, Rh) as cathodes for IT-SOFCs: structure-properties relationship

S. Guo$^{1,2}$, A. Longo$^{1,3}$, F. Puleo$^1$, V. La Parola$^1$, G. Pantaleo$^1$, D. Banerjee$^4$, A. Martorana$^5$ and L.F. Liotta$^1$.

$^1$Istituto per lo Studio di Materiali Nanostrutturati (ISMN)-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy
$^2$Northwestern Polytechnical University, Xi’an 710072 PR China.
$^3$Netherlands Organization for Scientific Research (NWO), 6 rue Jules Horowitz, BP220, 38043 Grenoble CEDEX, France.
$^4$Dutch-Belgian Beamline (DUBBLE), European Synchrotron Radiation Facility (ESRF), B.P. 220, F-38043 Grenoble, France.
$^5$Dipartimento Fisica e Chimica Università di Palermo, Viale delle Scienze Ed., 17, 90128 PALERMO, Italy.

E-mail:guoshaoili@mail.nwpu.edu.cn

Thanks to their mixed ionic/electronic conductivity and high catalytic activity for oxygen exchange reaction, La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ (LSCF) perovskites have received much attention as cathode materials for intermediate solid oxide fuel cells (IT-SOFCs) operating at relatively low-temperature, 600-800 °C [1]. Lowering the operating temperature, however, decreases the electrode kinetics. So, new materials composition and/or controlling the cathode properties through new syntheses are required in order to improve oxygen reduction and both, electronic and ionic conductivities. LSCF cathodes with metal substitution in B-site prepared by different methods, such as solid-state reaction or by impregnation of the perovskite with the metal dopant precursor, have been extensively investigated as new materials [2,3]. We have recently evidenced by EXAFS analysis the promotion of La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ by incorporation of palladium in the B-site of the perovskite structure through one pot synthesis by citrate method [4]. A dual effect of Pd in promoting the electrical and ionic conductivity of La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ perovskite was found. On these bases, the present study aims to investigate the structural and reduction properties of LSCF oxides with different Co/Fe content doped by Ni, Pt and Rh. Special attention to the effect of the doping metal insertion on the perovskite oxygen vacancies formation was paid.

S. Guo thanks COST Action CM 1104 for supporting her STSM (COST-STSM-ECOST-STSM-CM1104-010414-042095). The CHINA SCHOLARSHIP COUNCIL is also acknowledged for supporting Guo’s scholarship.