Invited Talks

NEW MAGNETIC MATERIALS BASED ON DEFECTS, INTERFACES AND DOPING

__George A. Sawatzky__, **Ilya Elfimov, Bayo Lau and Mona Berciu**

Physics dept and Max Planck-UBC Centre for Quantum Materials
University of British Columbia Vancouver Canada

Ideas based on theory and some experiments will be presented regarding possible new magnetic materials based on extended and point defects (1), interface engineering (2), anion substitution in oxides and hole and electron doping of oxides. The concentration will be on rather ionic oxides mostly not involving conventional magnetic elements. Special attention will also be placed on surface and interface effects involving polar surfaces as well as on the role of doped holes in O 2p in charge transfer gap oxides. O 2p holes play an extremely important role in the magnetism and superconductivity of oxides and new results will be presented regarding the ferromagnetic exchange coupling they introduce in transition metal oxides(3) and the interplay between transport properties, magnetic order and the general phase diagrams of materials involving O 2p holes either in the so called self doped case of stochiometric oxides or in chemically substituted systems and cation or anion vacancies. We also present exact results on the spin polaron formation(4) and charge propagation of doped Fermions in Ferromagnetic lattices and the pairing interaction due to the magnetic background.

1. I. S. Elfimov, S. Yunoki, and G. A. Sawatzky PRL 89, 216403, (2002)
2. N. Pavlenko, T. Kopp, E.Y. Tsymbal, G.A. Sawatzky, and J. Mannhart PRB 85, 020407, (2011)
3. Bayo Lau, Mona Berciu and George A. Sawatzky, PRL 106, 036401 (2011)
4. Berciu and G. A. Sawatzky, PRB 79, 195116 (2009)

INV 2

ATOMIC-RESOLUTION ELECTRON SPECTROSCOPY OF INTERFACES AND DEFECTS IN COMPLEX OXIDES

D. A. Muller[1], J. A. Mundy[1], L. Fitting Kourkoutis[1], M. P. Warusawithana[2], J. Ludwig[2], P. Roy[2], A. A. Pawlicki[2], T. Heeg[3], C. Richter[4], S. Paetel[4], M. Zheng[5], B. Mulcahy[5], W. Zander[6], J. N. Eckstein[5], J. Schubert[6], J. Mannhart[4], D. G. Schlom[3]

[1]School of Applied and Engineering Physics, Cornell University,
[2]Department of Physics and NHMFL, Florida State University,
[3]Department of Materials Science and Engineering, Cornell University,
[4]Experimentalphysik VI, University of Augsburg,
[5]Department of Physics, University of Illinois at Urbana – Champaign,
[6]Inst. of Bio and Nanosystems IBN1-IT and JARA-FIT, Research Centre Jülich

Electron energy loss spectroscopy (EELS) in a new generation of aberration-corrected electron microscopes provides direct images of the local physical and electronic structure of a material at the atomic scale [1]. The sensitivity and resolution can extend to imaging single dopant atoms or vacancies in their native environments. The detection and control of interface defects using EELS, closely-coupled with atomically-precise growth methods, has enabled the realization of interface-stabilized emergent ground states, including a 2D metal at the $LaTiO_3/SrTiO_3$ interface; a 2D superconductor between a $LaAlO_3$ and $SrTiO_3$; and, by eliminating extended 2D defects, ferromagnetic manganites a few unit cells thick - well below the widely-assumed critical thickness for ferromagnetism and conductivity in manganite systems. In each case, the detection and control of defects has proven crucial to distinguishing between intrinsic and extrinsic interface effects. This is well illustrated at the $LaAlO_3/SrTiO_3$ interface. After controlled experiments effectively eliminate the extrinsic effects that have been suggested as possible mechanisms of conductivity, electron microscopy reveals that defect compensation at the interface is different for A-site vs B-site rich systems, and the stoichiometry is key to the existence of the interface 2-dimentional electron gas.
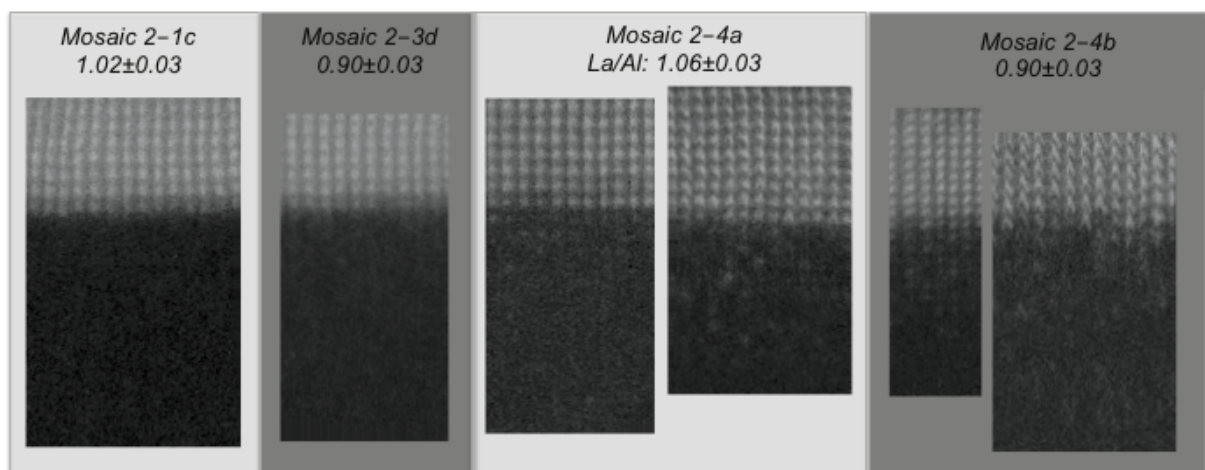

Figure 1: Spectroscopic maps of La at $LaAlO_3/SrTiO_3$ interfaces. The maps are arranged in order of apparent La interdiffusion and labeled by the La/Al ratio. Samples with La/Al > 1 (light grey) showed insulating interfaces while La/Al<1 (dark grey) were conducting. As shown, there is no correlation between the La interdiffusion and the transport properties.

[1] D. A. Muller, L. F. Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby, O. L. Krivanek, *Science* 319, 1073 (2008).

SIGNIFICANCE OF SOLID STATE IONICS FOR TRANSPORT AND STORAGE

Joachim Maier

Max Planck Institute for Solid State Research, Stuttgart, Germany

The role of ionic point defects and their impact on electronic charge carriers are considered form a thermodynamic point of view. Particular emphasis is laid on the influence of interfaces. The thermodynamic correspondence between ionic and electronic excitations is highlighted by Fig. 1.
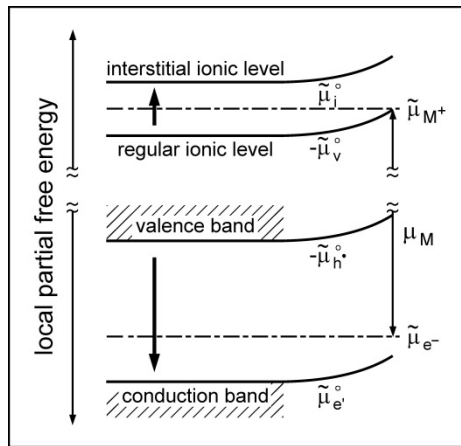

Figure 1: Ionic and electronic disorder in bulk and at boundaries. According to Ref. [1].

The relations are set out using four examples. Example 1 discusses ionic and electronic transport in the bulk for typical transition metal oxide under full equilibrium at high temperatures and links the situation to a typical low temperature situation where the ionic point defects are frozen. This example highlights the significance of point defects and preparation conditions for electronic transport at room temperature [2,3].

Example 2 refers to the effect of grain boundaries on the ionic and electronic charge carrier distribution. The effects can be well understood by ionically dominated space charge phenomena. The mixed conductor $SrTiO_3$ is considered here. Such space charge effects culminate in giant variations of n-, p- and oxygen ion conductivity in nanocrystalline $SrTiO_3$ (see Fig. 2) solely due to the small grain size. The effect can be well explained as fully mesoscopic phenomena as a function of temperature and oxygen partial pressure [4].
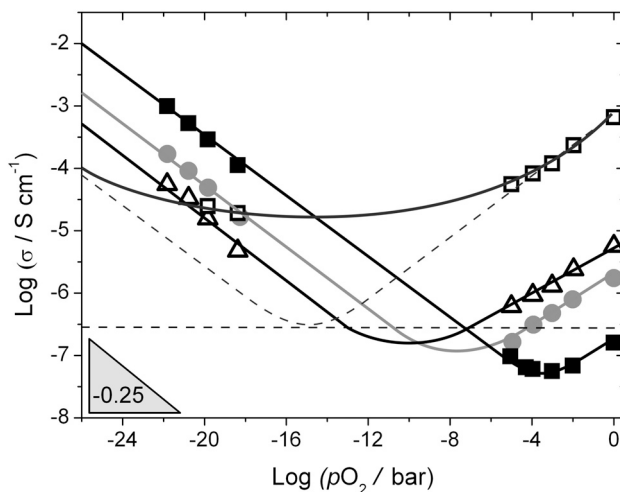

Figure 2: Conductivity versus oxygen partial pressure P measured at 544 °C for microcrystalline (open squares) and nanocrystalline $SrTiO_3$ (filled squares: 30nm) as a function of oxygen partial pressure. The p-type (n-type) conductivity is decreased (increased) by 3 orders of magnitude and the ion conductivity decreased by 6 orders of magnitude. According to Ref. [4].

Example 3 refers to an ionic conductor system and treats heterophase contacts [6]. MBE-grown multi-layers of CaF_2 and BaF_2 (as well as composites) are investigated as a function of layer thickness ranging from $\sim 1\,\mu$m (semi-infinite conditions) to ~ 1 nm (mesoscopic conditions) (see Fig. 3).
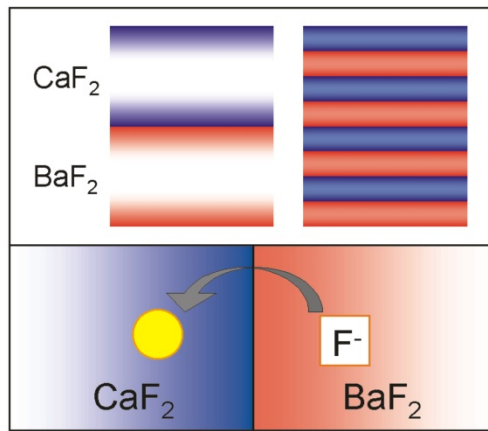

Figure 3: In CaF_2-BaF_2-heterostructures thermodynamic contact equilibrium demands fluorine ion redistribution (bottom).This leads to charge carrier accumulation in semi-infinite space charge zones (top, l. h. s.) or for very small spacings to a fully mesoscopic situation (top, r. h. s.). According to Ref. [5].

The greatly increased F^- conductivity on size reduction can be well understood in terms of ionic charge transfer at the boundaries and shows the significance of "nanoionics" as a field of fundamental importance for energy research. The consideration of the full interfacial thermodynamics paved the way for "composite electrolytes" as a new class of solid electrolyte [6].

Example 4: Space charge effects do not only lead to drastically altered transport properties, they can also lead to drastically altered storage properties. As an example we consider the nano-composite Li_2O/Ru in which quite an amount of lithium can be stored even though none of the individual phases can do this (Fig. 4).
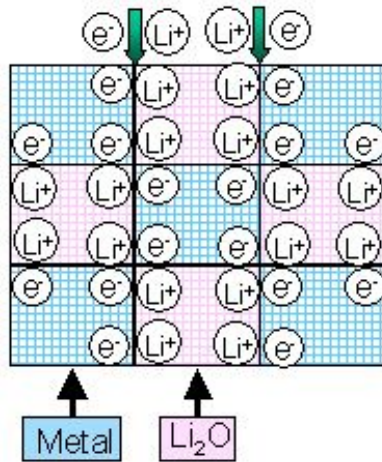

Figure 4: The Li_2O/M stores Li via job-sharing. This mechanism forms the bridge between an electrostatic composite and a battery electrode if the space charge profiles overlap. According to Ref. [7]

The reason lies in this novel "job-sharing" storage at the interface: Li_2O stores Li^+, Ru stores e^-. This mechanism forms the bridge between an electrostatic and chemical capacitor [6,7].

[1] J. Maier, *Physical Chemistry of Ionic Materials. Ions and Electrons in Solids*, Wiley, 2004.
[2] R. Waser, J. Am. Ceram. Soc.**74**, 1934 (1991).
[3] J. Maier, Phys. Chem. Chem. Phys. **5**, 2164 (2003).
[4] P.Lupetin, G. Gregori, and J. Maier, Angew. Chem. Int. Ed. **49**, 10123 (2010).
[5] N. Sata, K. Eberman, K. Eberl, and J. Maier, Nature **408**, 946 (2000).
[6] J. Maier, Nature Materials **4**, 805 (2005); J. Maier, Prog. Solid St. Chem.**23**, 171 (1995).
[7] J. Maier, Faraday Discussions **134**, 51 (2007).

ELECTROCHEMICAL DOPING OF OXIDE HETEROSTRUCTURES

E. Artacho[1,2,6,7] , N.C Bristowe[1,2], P.B. Littlewood[5], J.M. Pruneda[8], M. Stengel[3,4]

[1]Theory of Condensed Matter, Cavendish Laboratory,University of Cambridge, Cambridge CB3 0HE, UK;
[2]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK;
[3]ICREA - Institució Catalana de Recerca i Estudis Avan¸cats, 08010 Barcelona, Spain;
[4]Institut de Ciéncia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain;
[5]Physical Sciences and Engineering, Argonne National Laboratory, Argonne, Illinois 60439, USA;
[6]CIC Nanogune, and Donostia International Physics Center DIPC, Tolosa Hiribidea 76, 20018 San Sebastian, Spain;
[7]Basque Foundation for Science Ikerbasque, 48011 Bilbao, Spain;
[8]Centre d'Investigación en Nanociéncia i Nanotecnologia (CSIC-ICN), Campus UAB, 08193 Bellaterra, Spain

Heterostructure oxides have emerged as a promising avenue to control electronic functionality by precise control of chemistry on the atomic scale. In particular, the possibility of utilising built-in electric fields in polar structures presents the possibility of modulation doping of two- dimensional electron gases (2DEG) in oxides. A case in point is the generation of carriers at the polar interface between LaAlO3 (LAO) and SrTiO3 (STO).

To progress, the origin of the 2DEG must be understood. While in pristine materials, electron transfer to counter the polar catastrophe would be expected[1], often defects, non-stoichiometry and in particular surface O vacancies are the source. We find that surface redox reactions, in particular surface O vacancies, are thermodynamically stable under most growth conditions, using a phenomenological model supported by first principles calculations which is in agreement with spectroscopic data[2]. Pristine systems will likely require changed growth conditions or modifed materials with a lower vacancy free energy.

In a related problem, but against expectations, robust switchable ferroelectricity has been recently observed under open-circuit electrical boundary conditions in nm thick ferroelectric films. First-principles calculations show that the pristine system does not polarize and instead we propose electrochemical ferroelectric switching as the phenomenon being observed[3]. If not exceeding its bulk value, the ferroelectric polarization of the film adapts to the bound charge generated on its surface by redox processes when poling the film.
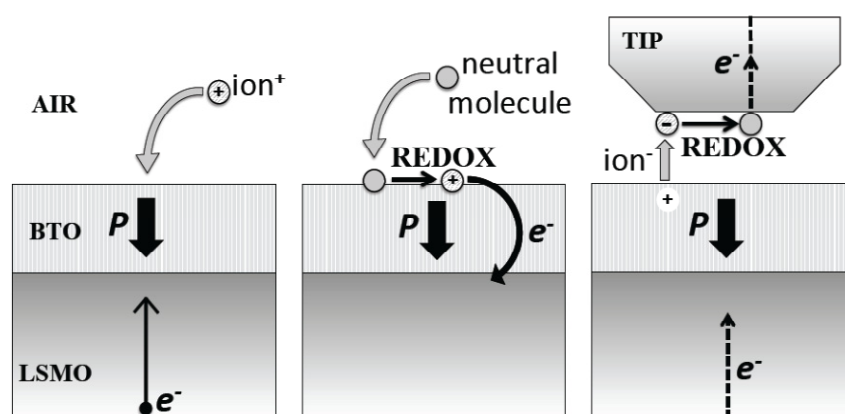

FIG. 1: Schematic illustration of the conventional (left) and redox (center) mechanisms for ferroelectric screening in the absence of a top electrode. The presence of a biased tip can promote an alternative redox mechanism that provides an external circuit for the screening electrons (right). (From Ref 4)

The interplay of electrochemistry and modulation doping offers opportunities to speculate about novel nanoscale electrochemical and storage applications.

1   N.C. Bristowe, E. Artacho, and P.B. Littlewood, Phys. Rev. B 80 045425 (2009)
2   N. C. Bristowe, P. B. Littlewood, Emilio Artacho, Phys. Rev. B 83, 205405 (2011)
3   V. Garcia, S. Fusil, K. Bouzehouane, S. Enouz-Vedrenne, N. Mathur, A. Barth_el_emy, and M. Bibes, Nature 460, 81 (2009).
4   N. C. Bristowe, Massimiliano Stengel, P. B. Littlewood, J. M. Pruneda, Emilio Artacho, Phys. Rev. B 85, 024106 (2012)

SWITCHABLE PHOTODIODE EFFECT IN FERROELECTRIC BiFeO₃

S-W. Cheong, H. T. Yi, T. Choi, and A. Hogan

Rutgers Center for Emergent materials and Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854, USA

Using photodiodes and solar cells, solar energy can be converted directly into electric current flow and light illumination can modulate the current. The rectification at a p-n junction originates from carrier diffusion across the p-n barrier, associated with an internal electric field. Recently, to enhance the optical device and solar energy harvest functionalities, other types of photovoltaic cells have been widely researched. For example, the bulk photocurrent flow created in ferroelectrics such as $LiNbO_3$ by UV light illumination depends upon the direction of ferroelectric polarization, leading to a ferro-electric photovoltaic (FPV) effect [1,2]. The main drawback of this fascinating FPV effect is the tiny magnitude of photocurrent in typically-insulating ferroelectrics. A recent breakthrough has been made in ferroelectric $BiFeO_3$ (BFO) in which large FPV current is induced by visible light illumination [3]. On the other hand, the mechanism for this remarkable FPV effect in BFO is largely unknown, and technical exploitation has to be pursued.
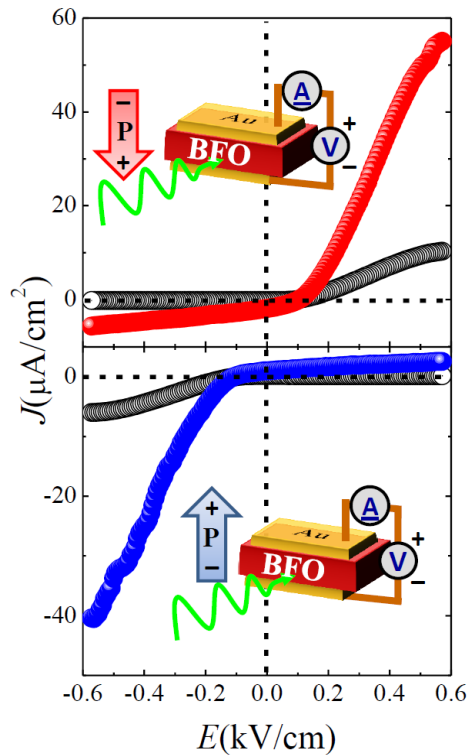

Figure 1: I-V curves with downward polarization (top) and upward polarization (bottom). Black open circles are for the I-V curves in dark, and red and blue filled circles indicate current under green laser illumination. Cartoon shows the schematic of our experiment setup.

From comprehensive investigation of the photodiode effect in BFO, we found that significant rectification and ferroelectric photovoltaic effects exist in BFO, and the direction of the rectification and photovoltaic current is reversely switchable by large external voltages (Fig. 1). The forward bias direction is along the ferroelectric polarization direction while the photovoltaic current direction is against the polarization direction (Fig. 2). The polarization clearly plays an essential role on the rectification and photovoltaic effects. On the other hand, we unveiled that polarization flipping at low temperatures is not sufficient to switch the rectification direction and near-room-temperature poling is necessary for the switching, indicating that electromigration of defects such as oxygen vacancies is important for the switching [4]. The rectification effect is consistent with the presence of Schottky-to-Ohmic contacts, and the Schottky-to-Ohmic contacts appear to be switchable with external voltages. The switching of Schottky-to-Ohmic contacts results from a combined effect of polarization flipping and electromigra-

tion of defects (oxygen vacancies) from one contact to the other contact. We also found that the bulk absorption across the bulk band gap determines the photovoltaic effect, and external quantum efficiency of our simple device can be as large as ~1.5 % at ~2.9 eV. By engineering the band gap, carrier concentration, and device configurations, this fascinating switchable photovoltaic effect needs to be further exploited for novel technologies such as fast readout of ferroelectric state, ferroelectric solar cells, or ferroelectric sensors.
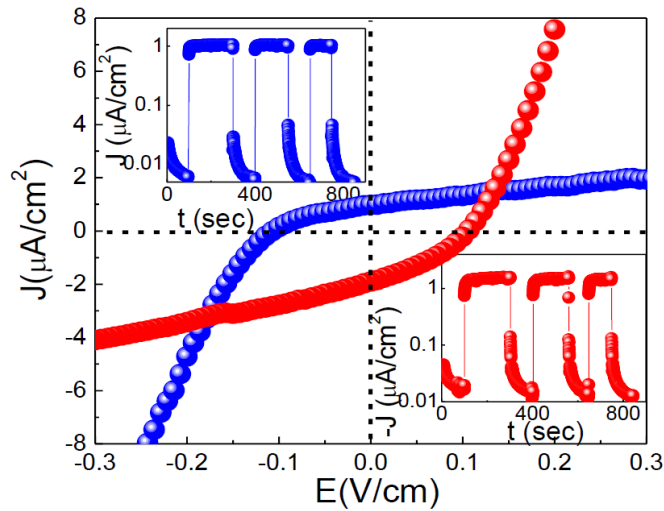

Fig. 2 Expanded view of the *I-V* curves for two different polarization orientations. Insets show zero-bias photocurrent with repetition of light on and off. Blue and red colored data are for upward and downward polarizations, respectively.

[1] A. M. Glass, D. von der Linde, and T. J. Negran, Appl. Phys. Lett. **25**, 233 (1974).
[2] G. Dalba *et al*., Phys. Rev. Lett. **74**, 988 (1995).
[3] T. Choi *at al*., Science **324**, 63 (2009).
[4] H. T. Yi *et al*., Adv. Mater. **23**, 3403 (2011)

INV 6

EXPLORATION OF ELECTRON SYSTEMS AT OXIDE INTERFACES

Werner Dietsche[1], Benjamin Förg[2], Cameron Hughes[1], Carsten Woltmann[1], Thilo Kopp[2], Florian Loder[2], <u>Jochen Mannhart</u>[1], Natalia Pavlenko[2], Christoph Richter[1], Ulrike Waizmann[1], Jürgen Weis[1]

[1]Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany
[2]Experimental Physics VI, Augsburg University, 86135 Augsburg, Germany

Induced by quantum phenomena, oxide interfaces offer a fascinating potential to create novel electron systems. In this presentation, we will report on recent progress we have made in exploring the fundamental properties of the 2D electron liquid at $LaAlO_3$-$SrTiO_3$ interfaces.

Furthermore, we will analyse the potential of such 2D systems for use in future electronic devices. We have fabricated, for example, field-effect devices that utilize the two-dimensional electron liquid generated at the bilayers' *n*-type $LaAlO_3$-$SrTiO_3$ interface as drain-source channels and the $LaAlO_3$ layers as gate dielectrics (Fig. 1). With gate voltages well below 1V, the devices are characterized by voltage gain and current gain [1].
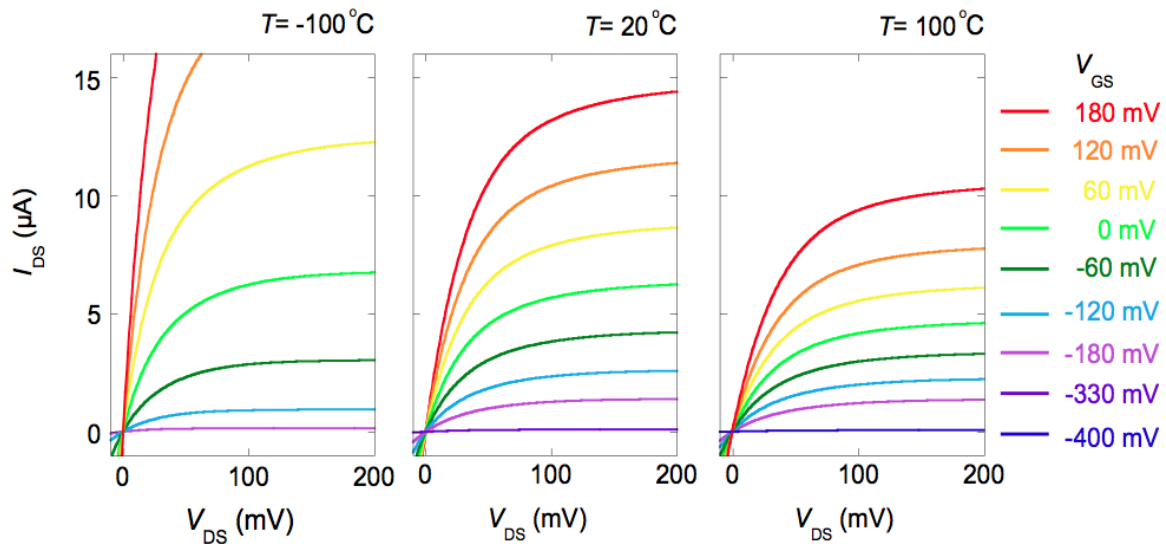

Figure 1: I_{DS} (V_{DS})-characteristics of a device measured in four-point configuration at -100, 20, and 100 °C. The measurement was done on a device with a channel length of 40 μm and a channel width of 1600 μm (from Ref. [1]).

[1] B. Förg, C. Richter, and J. Mannhart, Appl. Phys. Lett. **100**, 053506 (2012).

THE INFLUENCE OF IMPERFECTIONS ON THE 2DEG TRANSPORT PROPERTIES IN THE LaAlO$_3$-SrTiO$_3$ SYSTEM

Guus Rijnders[1]

[1]University of Twente, MESA+ Institute for Nanotechnology, Enschede, the Netherlands

Within this contribution, I will focus on the creation and annihilation of oxygen vacancies in LaAlO$_3$/SrTiO$_3$ heterostructures, as well as their influence on the transport properties of the 2DEG created at the interface between LaAlO$_3$ and SrTiO$_3$. The manifestation of quantum behavior in two dimensional electron gases in semiconducting heterostructures and their progressive complexity towards fractional quantum Hall effect went hand-in-hand with the efforts to remove the effect of impurity scattering. For oxide materials, history is repeating itself and to date sample quality is reaching levels where quantum behavior starts to become accessible. To really understand the ground state of two dimensional electron gases in oxide LaAlO$_3$-SrTiO$_3$ systems, the influence of imperfections on the 2DEG should be investigated and minimized.

I will show that, due to redox reactions, oxygen vacancies can be created within SrTiO$_3$ heterostructures. As an example, metallic conducting interfaces are observed in such heterostructures with various overlayers of amorphous LaAlO$_3$, SrTiO$_3$ and yttria-stabilized zirconia (YSZ) films. Whereas, an insulating heterointerface is found when the overlayer is an amorphous La$_{7/8}$Sr$_{1/8}$MnO$_3$ film. I will present evidence that the interfacial conductivity results from the oxygen vacancies on the SrTiO$_3$ substrate side due to the exposure of the substrate surface to reactive species of film growth, see figure 1. Although the energy of the arriving species has been suggested to be responsible for the creation of defects, the chemical reactivity of these species at the substrate surface has not been considered yet. Our results [1] show that the latter mechanism is an important source for the creation of mobile charge carriers in SrTiO$_3$-based oxide heterostructures.
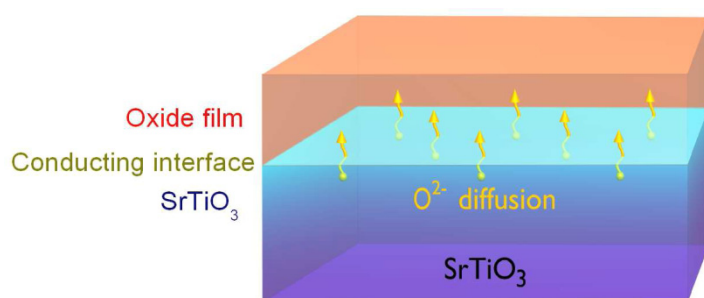

Figure 1: Schematic representation for the oxygen ions outward diffusion induced interfacial conduction in SrTiO$_3$-based heterostructures during growth of the oxide films at room temperature.

On the other hand, impurity scattering can heavily reduce the carrier mobility in epitaxial heterostructures. I will show that the impurity level can be significantly suppressed by defect engineering, resulting in an increase of the carrier mobility, allowing, for instance, the observation of quantum transport. We used SrTiO$_3$-LaAlO$_3$ heterostructures with epitaxial capping layers, in which the latter plays an important role in the suppression of defect scattering.

Within the contribution, growth and properties of the complex oxide heterostructures will be presented, with a focus on the underlying mechanism of defect engineering.

[1] *Nanoletters* **11** (9), (2011) 3774–3778

INV 8

CORRELATED ELECTRONIC MATERIALS: COMPUTATIONAL STUDIES OF MULTIORBITAL MODELS FOR BULK COMPOUNDS AND INTERFACES OF MAGNETIC AND SUPERCONDUCTING MATERIALS
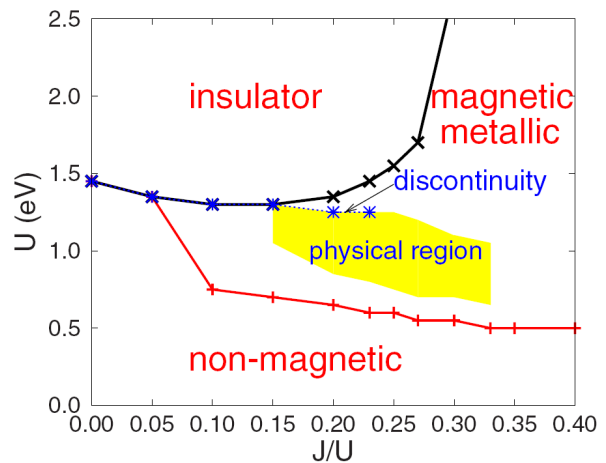
Elbio Dagotto[1]

[1]Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA, and Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
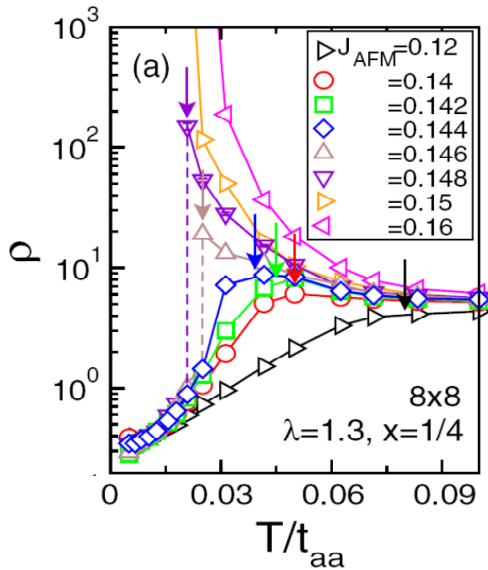
The current status of computer simulations of model Hamiltonians for correlated electronic materials will be reviewed. The focus will be on the Mn-oxides with the colossal magneto-resistance (CMR) and the novel Fe-based high critical temperature superconductors. It will be shown that state-of-the-art computer simulations involving Monte Carlo studies of double-exchange models with Jahn-Teller phonons do display the CMR effect. This is exemplified in the figure on the right, reproduced from [1], where the calculated resistivity vs. temperature (in units of the hopping amplitude t_{aa}) is shown (with $T/t_{aa} \sim 0.09$ being room temperature). Varying the super-exchange coupling J_{AFM}, the results interpolate between those of a ferromagnetic metallic state to those corresponding to a competing insulator [1]. The interpolation, with an increasing resistivity that abruptly drops to a metallic state with decreasing temperature, is in excellent agreement with experiments carried out for a variety of rare-earth elements in the perovskite chemical formula, as discussed in [1].

In addition, it will be argued that multiple-orbital Hubbard models for pnictides and chalcogenides have magnetic order with the correct wavevector in the undoped-limit ground state, and pairing tendencies in several competing channels upon doping. For example the figure on the left shows the phase diagram of a three-orbital Hubbard model obtained via a mean-field approximation, reproduced from [2]. Shown are three regions: a non-magnetic metallic state at small Hubbard repulsion U, an insulator (with orbital order) at large U, and an intermediate phase with magnetic

and metallic characteristics that seem to fit nicely the properties of the pnictides. In fact, the region shown in yellow, centered at a Hund coupling J which in units of U is approximately 0.25, corresponds to a regime where the theoretical results agree quantitatively with those of neutron and photo-emission scattering, as discussed in [3]. A combination of localized and itinerant features appears to be needed for properly describing these exotic high-Tc superconductors that are in the "intermediate" coupling range between the weak and strong coupling limits, as exemplified in the sketched shown on the right reproduced from [3]. In this sketch, the yellow region is a magnetically ordered state that starts at small U (bandwidth W units) in a regime where Fermi surface nesting works, followed by an

intermediate region where the pnictides
may be located, and then ending in a
large U insulating region where Heisen-
berg models with localized spins provide
an accurate representation of the physics.

The presentation will continue by ad-
dressing next the case of superlattices
made of strongly correlated materials, as
in the figure shown on the left, with em-
phasis on results for magnetic com-
pounds, such as large- and low-
bandwidth manganites (i.e. LMO/SMO, LMO/CMO), and also manganites/ferroelectrics. The focus
will be on the states that are stabilized at the interfaces, some of which do not have an analog in the
materials that form the superlattice when in bulk form, as reported in [4].
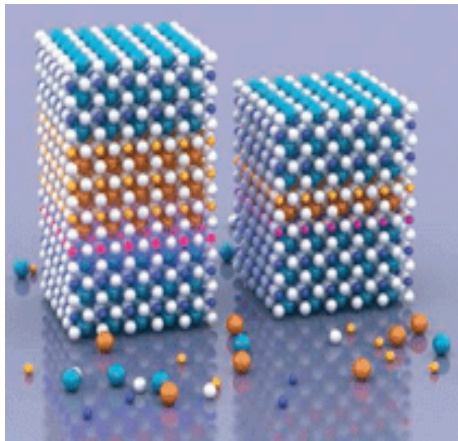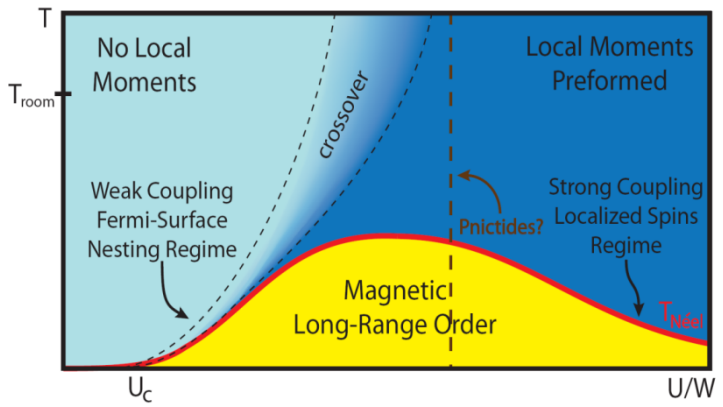
Time allowing, interesting results obtained using computa-
tional technique in quasi one dimensional systems will also
be discussed. They correspond to the propagation of exci-
tons, as those created in photovoltaic devices, in the frame-
work of Hubbard insulators, as exemplified in the figure on
the right that is reproduced from [5]. A real-time analysis
can follow the "holon" and "doublon" as they propagate and
eventually cross the boundary from the insulator to the me-
tallic leads.

It is concluded that the use of computational techniques
applied to model Hamiltonian systems is crucial for the
analysis of a variety of interesting materials, with magnetic,
superconducting, and multiferroic properties.
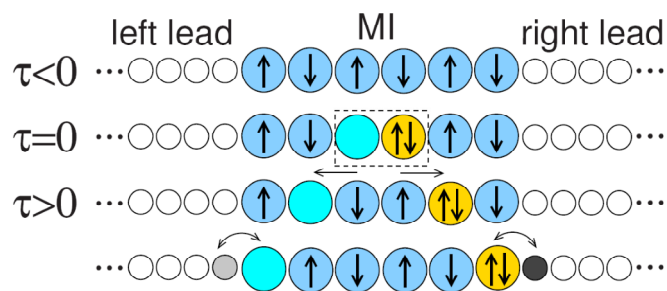
[1] C. Sen et al., Phys. Rev. Letters **105**, 097203 (2010).
[2] Q. Luo et al., PRB **82**, 104508 (2010).
[3] P. Dai, J. Hu, and E. Dagotto, Nature Physics (submitted).
[4] R. Yu et al., Phys Rev B **80**, 125115 (2009).
[5] L. Dias et al., Phys. Rev. B **81,** 125113 (2010).

ELECTROLYTE GATE INDUCED METALLIZATION OF SEVERAL FACETS (101, 001, 110 and 100) OF RUTILE TiO$_2$ AND (001) SrTiO$_3$

Stuart S.P. Parkin[1], Thomas D. Schladt[1], Tanja Graf[1], Mingyang Li[1,2], Nagaphani Aetukuri[1,3], Xin Jiang[1] and Mahesh Samant[1]

[1]IBM Almaden Research Center, San Jose, California, USA;
[2]Department of Physics, Stanford University, Stanford, California, USA; [3]Department of Materials Science and Engineering, Stanford University, Stanford, California, USA

The electric field induced metallization of insulating oxides is a powerful means of exploring and creating novel electronic states. Recently large internal electric fields from polar surfaces have been used to create emergent metallic, superconducting and magnetic states at interfaces between two insulating oxides[1]. However, the origin of the metallicity is a subject of considerable debate. Moreover, relying on the interface polar discontinuity to create the electric field restricts the interface orientation to that in which the surface of the polar material has an uncompensated charge. Electrolyte gating, on the other hand, can be applied to any crystal facet, and allows for varying electric fields and associated induced carrier densities. We have used electrolyte gating to study four different facets of rutile TiO$_2$. Two of these, namely (101) and (001), show clear evidence of metallization, with a disorder-induced metal-to-insulator transition at low temperatures, whereas two other facets, (110) and (100), show no substantial effects (see Figure 1). This facet-dependent metallization can be correlated with the energy of formation of oxygen vacancies on the respective facet[2], thereby clearly showing that gate induced charge transfer effects are not the sole origin of the metallicity. The orientation dependence of electrolyte gating is a novel way of distinguishing purely electrostatic field effects from electric field induced modifications of the surface structure and stoichiometry.
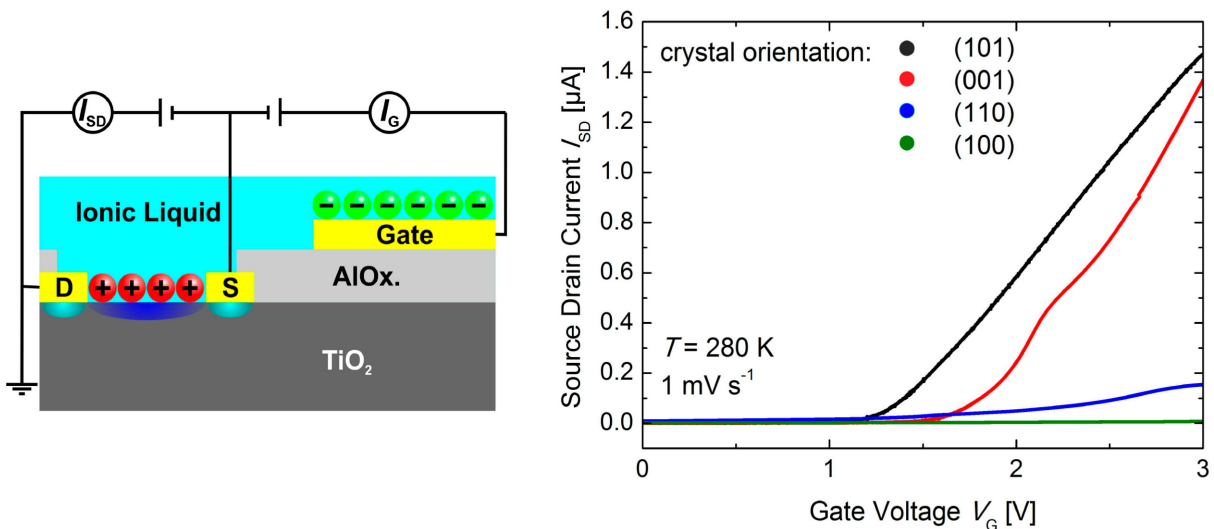

Figure 1: Left: Schematic diagram of the EDLT device configuration, showing the lateral gate electrode and the source and drain contacts to the surface of the TiO$_2$. Right: Source-drain current I_{SD} as a function of gate voltage V_G for four crystal orientations of TiO$_2$.
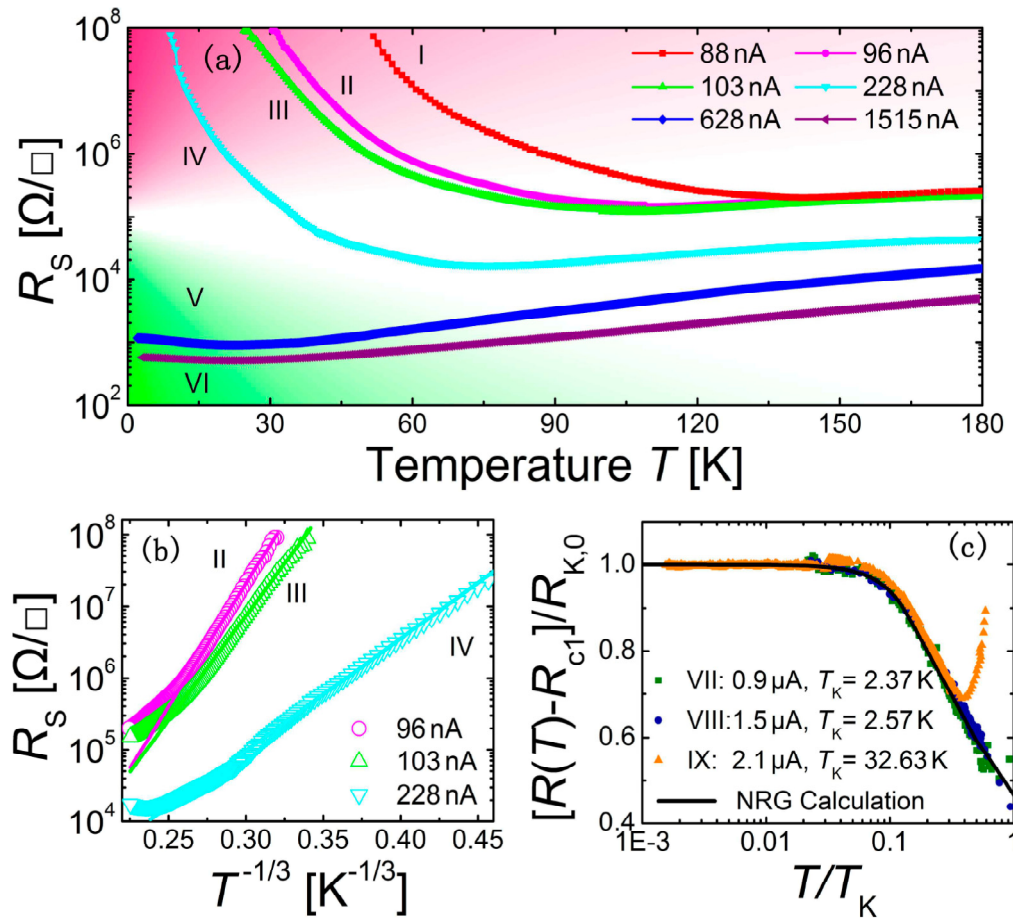
Figure 2: Top: Sheet resistance versus temperature curves for various gate voltages V_G corresponding to the source-drain currents I_{SD} shown in the inset to the figure. Bottom: Left: Sheet resistance plotted versus $1/T^{1/3}$ in the non-percolative regime, and Right: Normalized sheet resistance versus temperature normalized to the Kondo temperature T_K showing a resistance upturn and a temperature independent resistance as T→ 0.

The role of disorder in the structure of the gated electrolyte is explored in studies of the electrolyte gate-induced conductance at the surface of single crystalline $SrTiO_3$ (001). By varying the gate voltage and, thereby, the induced carrier density, we find two distinct transport regimes. At high carrier densities, a percolative, metallic state is induced in which, at low temperatures, signatures of a Kondo effect are clearly observed. Specifically, an upturn in resistance saturates to a constant value from below ~10% of the Kondo temperature down to the lowest temperatures measured (20 mK). At lower carrier densities, the resistance decreases from below the freezing temperature of the ionic liquid dielectric to a broad minimum below which the resistance diverges to very high values at low temperatures. In this regime the resistance increase can be well described by a variable range hopping model in two dimensions. We speculate that this results from non-percolative transport that likely results from inhomogeneous electric fields due to imperfect ordering of the ions at the frozen liquid/ oxide interface. Further evidence of the non-percolative and percolative regimes is provided by their non-linear and linear current versus voltage behaviours, respectively, as well the much larger magneto-conductance in the non-percolative regime.

[1]   H. Y. Hwang et al. Nat. Mater. **11**, 103 (2012).
[2]   B. J. Morgan and G. W. Watson, J. Phys. Chem. C **113**, 7322 (2009).

INV 10

COMPLEX THERMOELECTRIC MATERIALS

G. Jeffrey Snyder

California Institute of Technology, Pasadena, California 91125 USA

The widespread use of thermoelectric generators has been limited by the low material efficiency of the thermoelectric material. A number of strategies for *Complex Thermoelectric Materials* [1] with higher Thermoelectric figure of merit, *zT*, are being actively studied at Caltech.

Complex electronic band structures provide mechanisms to achieve high *zT* in thermoelectric materials through *band structure engineering*. High *zT* is obtained p-type PbTe and PbSe which contains both light and heavy valence bands that can be engineered to achieve high valley degeneracy which leads to an extraordinary peak *zT* of nearly 1.8 at 750K [2].
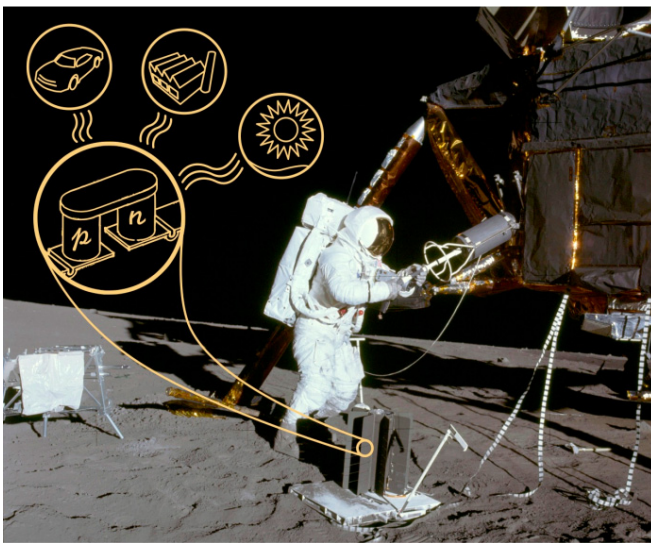

Figure 1: A thermoelectric generator directly converts heat into electricity with no moving parts. The long term reliability of these systems has encouraged NASA to use thermoelectric generators in many space probes since the 1960s (up to 35 years unattended). Today, thermoelectrics are being considered for terrestrial applications such as automotive and industrial waste heat recovery as well as solar-electricity generation.

Complex crystal structures that enable relatively low thermal conductivity have lead to several new classes of thermoelectric materials. Ca_3AlSb_3, Ca_3AlSb_3 and $Yb_{14}AlSb_{11}$ are complex Zintl compounds containing differently connected $AlSb_4$ tetrahedra that obtain *zT* near 1 at high temperatures. Fast diffusing or 'liquid-like' elements in the complex materials Zn_4Sb_3 [3] and Cu_2Se [4] provide additional mechanisms to scatter and otherwise inhibit phonon heat conductivity. The principles of Zintl chemistry facilitates the search for new complex materials and the tuning of known thermoelectric materials with earth abundant, non-toxic elements [5]

Finally, the incorporation of nanometer sized particles reduces thermal conductivity from long mean-free-path phonons. This principle has been successfully demonstrated in PbTe with large nanoscale precipitates (>100nm) that can be independently doped with La (n-type) or Na (p-type). The synthesis of nanoscale composites can be controlled with the aid of equilibrium phase diagrams (experimental or theoretically determined) to produce microstructure of varying composition and length scale [6].

[1] G. J. Snyder, E. S. Toberer. "Complex thermoelectric materials" *Nature Materials* **7**, p 105 - 114 (2008)
[2] Y. Z. Pei, G. J. Snyder, et al. "Convergence of Electronic Bands for High Performance Bulk Thermoelectrics"*Nature* **473**, p 66 (2011)
[3] H. Liu, X. Shi, G. J. Snyder, et al. "Liquid-like Copper Ion Thermoelectric Materials" *Nature Materials*, doi:10.1038/nmat3273 (2012)
[4] G. J. Snyder, et al., "Disordered Zinc in Zn_4Sb_3 with Phonon Glass, Electron Crystal Thermoelectric Properties" *Nature Materials*, **Vol 3**, p. 458 (2004)
[5] E. S. Toberer. A. F. May, G. J. Snyder, "Zintl Chemistry for Designing High Efficiency Thermoelectric Materials" *Chemistry of Materials* **22**, p 624 (2010)
[6] D.L. Medlin and G.J. Snyder "Interfaces in Bulk Thermoelectric Materials" *Current Opinion in Colloid & Interface Science* **14,** 226 (2009)

PCRAM OPERATION AT DRAM SPEEDS: EXPERIMENTAL DEMONSTRATION AND COMPUTER-SIMULATIONAL UNDERSTANDING

D. Loke,[1,2,3,*] T. H. Lee,[1,*] W. J. Wang,[2] L. P. Shi,[2,†] R. Zhao,[2] Y. C. Yeo,[4] T. C. Chong,[5] and S. R. Elliott,[1,†]

[1]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.
[2]Data Storage Institute, A*STAR, DSI Building, 5 Engineering Drive 1, Singapore 117608.
[3]NUS Graduate School for Integrative Sciences and Engineering, 28 Medical Drive, Centre for Life Sciences #05-01, Singapore 117456.
[4]Department of Electrical and Computer Engineering, National University of Singapore, 1 Engineering Drive 3, Singapore 117576.
[5]Singapore University of Technology & Design, 20 Dover Drive, Singapore 138682.

Phase-change random access memory (PCRAM) is one of the leading candidates for next-generation, non-volatile electronic data-storage devices, in which data bits are stored in terms of different structural states of a memory material (e.g. $Ge_2Sb_2Te_5$ – GST), i.e. either crystalline or amorphous, each having a different electrical resistivity. Switching between these two metastable memory states is achieved by the application of suitable voltage pulses. This new non-volatile memory technology is scalable beyond the current size limitations of silicon MOSFET-based 'flash' memory, and is now starting to appear in consumer products, e.g. Samsung smart-phones. However, the present writing (crystallization) speed of GST (ca 10ns) has been insufficiently fast to enable PCRAM to replace volatile DRAM with a *non-volatile* equivalent, for which switching speeds of less than 1ns are required.

We have controlled the crystallization kinetics of a phase-change material (GST) by the application of a constant low voltage, via pre-structural ordering (incubation) effects. An ultrafast crystallization speed of 500 ps was achieved, the first time that the 1ns barrier has been broken for PCRAM devices[1]. High-speed reversible switching using 500 ps pulses has also been demonstrated. *Ab initio* molecular-dynamics simulations have been performed to reveal the phase-change kinetics in PCRAM devices, and the structural origin of the incubation-assisted increase in crystallization speed has been identified. This paves the way to achieve a "universal electronic memory", capable of non-volatile operations at GHz data-transfer rates.

[1] D. Loke *et al.,* Science (to be published).

INV 12

ELECTRONIC PHASE CHANGE AND ENTROPIC FUNCTIONS IN TRANSITION METAL OXIDES

Hidenori Takagi[1,2] and Seiji Niitaka[2]

[1]Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0022, Japan;
[2]RIKEN Advanced Science Institute, Wako, Japan

The electric and magnetic properties of transition metal oxides (TMO) are often dominated by electrons in d-orbitals. Large Coulomb repulsion between electrons accommodated in the spatially constrained d-orbitals tends to block the motion of electrons from one atom to another, and the electrons are highly entangled. Just like interacting atoms and molecules, the entangled electrons, called correlated electrons, form solid (insulator), liquid (metal), and superfluid (superconductor) states inside the solid. The presence of the three degrees of freedom attached to electrons – charge, spin and orbital, enrich these electronic phases further. These rich electronic phases compete with each other in a delicate balance. Even a minute perturbation can induce a phase change, giving rise to a dramatic response to external fields. This is the hallmark of phase change functions in transition metal oxides, useful as sensors, memories and for signal conversion [1].

In this talk, we would like to discuss the application of phase change concept to entropic functions rather than the long discussed functions mentioned above. Partly because of the multiple degrees of freedom, the complicated electronic phases in transition metal oxides are often highly entropic. The high entropy can manifest itself in a large entropy (enthalpy) change associated with the electronic phase change. VO_2 is known to show a paramagnetic metal (liquid) to a nonmagnetic insulator (solid) transition around room temperature, where we indeed observed a large entropy change per volume, comparable to that of water-ice transition. This can be utilized as a "solid" electronic ice pack of which melting temperature is "tunable" upon doping. We can construct electronic icepack working at 10 C, which for example may be used to preserve human tissues during surgery. The large electric entropy coupled with electric current can be utilized for thermoelectric conversion. The oxide thermoelectrics, Na_xCoO_2, can be viewed as a realization of such scenario. Other possible application of the large electronic entropy will be discussed.

[1] H.Takagi and H.Y.Hwang, Science 327 (2010) 1601.

DISORDER INDUCED METAL-INSULATOR TRANSITION IN PHASE CHANGE MATERIALS

T. Siegrist[1,2]

[1]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, USA; [2]1. Physikalisches Institut (IA), RWTH Aachen, Aachen, Germany

Phase change materials that reversibly switch between amorphous and crystalline states show large optical and electronic property contrasts. Rewritable DVDs and Blu-ray discs are based on such materials, while the large change in electronic transport properties with resistivity contrast of up to six orders in magnitude is used in a new class of non-volatile data storage devices. Such devices hold great potential for future miniaturization, and with fast read/write operations, they may find applications as universal data storage devices in mobile applications.

While the amorphous state is characterized by saturated covalent bonds, the crystalline phase forms resonant bonds. This bonding mechanism can account for the high electronic polarizabilities which characterize crystalline phase change materials. Interestingly, the relevant electronic states also govern the charge transport in the crystalline phase, leading to unique transport properties including a high degree of electronic localization, in those phase change materials, which are characterized by a high degree of disorder. An initially amorphous thin film of $Ge_1Sb_2Te_4$ that is annealed in steps up to 340°C shows a transition to a crystalline phase with a high degree of disorder at 145°C, where the sheet resistance drops by two orders of magnitude. Even though the crystalline material is a degenerate semiconductor, its temperature dependence of the resistivity shows a non-metallic behavior. Stepwise annealing to higher temperatures changes the temperature coefficient of the resistivity from negative to positive, indicative of a metal-insulator transition (MIT) (Figure 1)
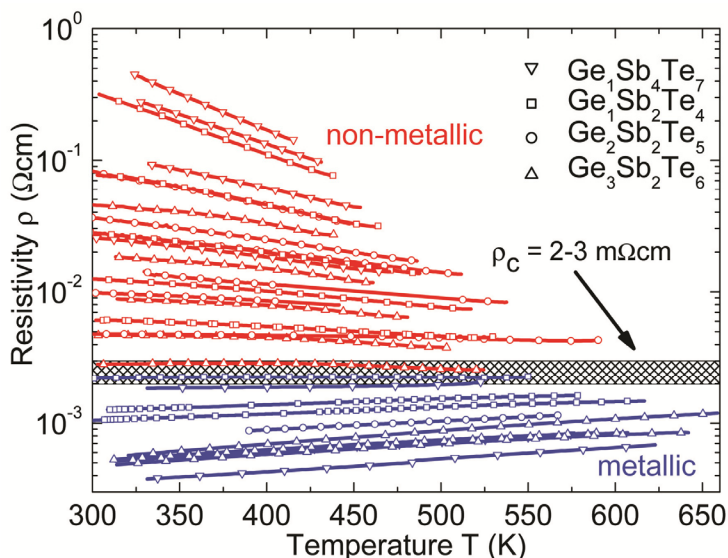

Figure 1: Systematic change of resistivity for four different Ge-Sb-Te phase change alloys annealed in steps of 20°C: $Ge_1Sb_4Te_7$, $Ge_1Sb_2Te_4$, $Ge_2Sb_2Te_5$, and $Ge_3Sb_2Te_6$. Only cooling data are shown, as obtained from the step annealed samples. All Ge-Sb-Te phases display the same behavior, with a critical resistivity of about 2-3 mΩcm where the temperature coefficient changes sign for all four alloys.Ref. [1].

Other phase change materials along the pseudo-binary (GeTe)-(Sb$_2$Te$_3$) line exhibit the same behavior, with a critical resistivity of 2-3mΩcm where the temperature coefficients of the resistivity change sign. The phase change materials therefore represent a unique system that is governed by localization effects induced by strong disorder and weak electron correlations. This universal behavior seems to be responsible for the high level of reproducibility of the resistance switching crucial to the application in non-volatile memory devices.

[1] T. Siegrist et al., Nature Mater. 10(3), 202-208 (2011).

ELECTRONIC PROPERTIES OF THE INTERFACIAL LaAlO$_3$ / SrTiO$_3$ SYSTEM

J.-M. Triscone[1], A. Fête[1], S. Gariglio[1], A. Caviglia[1], D. Li[1], D. Stornaiuolo[1], M. Gabay[2], B. Sacépé[1], A. Morpurgo[1], M. Schmitt[3], C. Cancellieri[3], P. Willmott[3]

[1]DPMC, University of Geneva, 24 quai E.-Ansermet, CH-1211 Geneva 4, Switzerland;
[2]Laboratoire de Physique des Solides, Université de Paris Sud, 91405 Orsay, Cedex, France;
[3]Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Oxide materials display within the same family of compounds a variety of exciting electronic properties ranging from ferroelectricity to ferromagnetism and superconductivity. These systems are often characterized by strong electronic correlations, complex phase diagrams and competing ground states. This competition makes these materials very sensitive to external parameters such as pressure or magnetic field. An interface, which naturally breaks inversion symmetry, is a major perturbation and one may thus expect that electronic systems with unusual properties can be generated at oxide interfaces [for reviews, see 1-3]. A striking example is the interface between LaAlO$_3$ and SrTiO$_3$, two good band *insulators*, which was found in 2004 to be conducting [4], and, in some doping range, superconducting with a maximum critical temperature of about 200 mK [5]. The characteristics observed in the normal and superconducting states are consistent with a two-dimensional electronic system. The thickness of the electron gas is found to be a few nanometers at low temperatures. This electron gas with low electronic density, typically 5 10^{13} electrons/cm^2, and naturally sandwiched between two insulators is ideal for performing electric field effect experiments allowing the carrier density to be tuned. Such an approach revealed the sensitivity of the normal and superconducting states to the carrier density. In particular, the electric field allows the tuning of the critical temperature between 200 mK and 0 K and thus the on-off switching of superconductivity. The system phase diagram reveals a superconducting pocket with an underdoped and an overdoped regime [6]. A large, interfacially generated, tunable spin-orbit coupling and a remarkable correlation between the spin-orbit coupling strength and the system phase diagram are other hallmarks of this fascinating system [7].

Here I will describe recent experiments aiming at determining the origin of the electron gas. I will then discuss superconductivity and the phase diagram of the system, magnetotransport in "standard" and in recently obtained high mobility samples that display Shubnikov de Haas (SdH) oscillations [8].

[1] J. Heber, Nature **459**, 28 (2009).
[2] J. Mannhart and D. Schlom, Science **327**, 1607 (2010).
[3] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, Annual Review : Condensed Matter Physics **2**, 141 (2011).
[4] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).
[5] N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone and J. Mannhart, Science **317**, 1196 (2007).
[6] A. Caviglia, S. Gariglio, N. Reyren, D. Jaccard, T. Schneider, M. Gabay, S. Thiel, G. Hammerl, J. Mannhart, and J.-M. Triscone, Nature **456**, 624 (2008).
[7] A.D. Caviglia, M. Gabay, S. Gariglio, N. Reyren, C. Cancellieri, and J.-M. Triscone, Physical Review **104**, 126803 (2010).
[8] A.D. Caviglia, S. Gariglio, C. Cancellieri, B. Sacépé, A.Fête, N. Reyren, M. Gabay, A.F. Morpurgo, J.-M. Triscone, Physical Review Letters **105**, 236802 (2010).

EMERGENT PHENOMENA IN TWO-DIMENSIONAL ELECTRON GASES AT OXIDE INTERFACES

<u>Susanne Stemmer</u>[1], Pouya Moetakef[1], Daniel Ouellette[2], and S. James Allen[2]

[1]Materials Department, University of California, Santa Barbara, California, 93106-5050, USA
[2]Department of Physics, University of California, Santa Barbara, California, 93106-9530, USA

Two-dimensional electron gases at oxide interfaces have attracted significant attention because they can exhibit unique properties, such as strong electron correlations, superconductivity and magnetism. In the first half of the presentation we will highlight the importance of materials quality and deposition methods in achieving the desired control over these phenomena, as needed for novel electronic devices: similar to what has long been accepted in the semiconductor device community, only low-energetic deposition techniques, such as molecular beam epitaxy (MBE), can produce electronic device-quality materials. For example, we demonstrate record electron mobilities in $SrTiO_3$ thin films grown by MBE, which exceed even those of single crystals. We show that these high-quality MBE films allow for the study of quantum oscillations in two-dimensional electron gases in $SrTiO_3$ films and that these oscillations are much more pronounced than those currently observed in structures with $SrTiO_3$ substrates.

In the second half of the presentation, we will discuss emergent phenomena at interfaces between band insulators, such as $SrTiO_3$, and strongly correlated (Mott) materials, such as the rare earth titanates ($RTiO_3$, where R is a trivalent rare earth ion), or the rare earth nickelates ($RNiO_3$). $SrTiO_3/RTiO_3$ interfaces are particularly interesting, because both the oxygen and Ti sublattices are continuous across the interface. An interfacial fixed polar charge arises because of a polar discontinuity at the interface. This interfacial charge can be compensated by a two-dimensional electron gas, residing in the bands of the Mott and/or band insulator and bound to the interface by the fixed interface charge. In this presentation, we report on intrinsic electronic reconstructions, of approximately 1/2 electron per surface unit cell at a prototype Mott/band insulator interface between $GdTiO_3$ and $SrTiO_3$, grown by molecular beam epitaxy. The sheet carrier densities of all $GdTiO_3/SrTiO_3$ heterostructures containing more than one unit cell of $SrTiO_3$ are approximately ½ electron per surface unit cell (or 3×10^{14} cm^{-2}), independent of layer thicknesses and growth sequences. Unlike the more commonly studies $LaAlO_3/SrTiO_3$ interface, these carrier densities closely meet the electrostatic requirements for compensating the fixed charge at these polar interfaces. We will report on electron correlation effects, such as magnetism, in the extremely high carrier density $SrTiO_3$ quantum wells that can be obtained using these interfaces. We will discuss the coexistence of emergent phenomena, in particular ferromagnetism and superconductivity, in electron gases in $SrTiO_3$. Models of the charge distribution and measurements of transport coefficients, such as the Seebeck effect, and of the optical conductivity provide insights into the nature of the two-dimensional electron gas, the importance of band alignments, background doping and the occupancy of subbands that are derived from the Ti d-states. We will also discuss new experimental approaches to probe the Mott insulating state, using modulation doping with heterointerfaces for electrostatic control of large carrier densities in Mott materials. Finally, we will discuss the potential for new device applications of complex oxide heterostructures.

GIANT TUNNEL ELECTRORESISTANCE IN FERROELECTRIC TUNNEL JUNCTIONS

A. Chanthbouala[1], V. Garcia[1], K. Bouzehouane[1], S. Fusil[1], X. Moya[2], S. Xavier[3], H. Yamada[4], C. Deranlot[1], N.D. Mathur[2], J. Grollier[1], A. Barthélémy[1] and <u>M. Bibes</u>[1]*

[1] Unité Mixte de Physique CNRS/Thales, 1 Av. A. Fresnel, Campus de l'Ecole Polytechnique, 91767 Palaiseau (France) and Université Paris-Sud, 91405 Orsay (France)
[2] Department of Materials Science, University of Cambridge, Cambridge, CB2 3QZ, UK
[3] Thales Research and Technology, 1 Av. A. Fresnel, Campus de l'Ecole Polytechnique, 91767 Palaiseau (France)
[4] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562 (Japan)

Because it is spontaneous, stable and electrically switchable the polarization of ferroelectrics is an excellent state variable for non-volatile data storage. In addition, polarization reversal can be as fast as tens of ps [1] and only dissipates the modest power associated with polarization charge switching (with current densities typically lower than 10^4 A/cm²). When ferroelectrics are made as thin as a few nm, they can be used as tunnel barriers and the tunneling current is influenced by the polarization direction [2] enabling a simple non-destructive readout of the polarization state.

In this talk, we will show how the tunnel resistance can vary by more than two orders of magnitude upon polarization switching in highly-strained ultrathin $BaTiO_3$ tunnel barriers. This strong electroresistance effect can be probed using a conductive AFM tip as the top electrode [3], or using solid-state submicron pads. Such ferroelectric tunnel junctions show large, stable, reproducible and reliable tunnel electroresistance, with resistance switching related to ferroelectric polarisation reversal [4]. They thus emerge as an alternative to other resistive memories, with the additional advantage of not being based on voltage-induced migration of matter at the nanoscale, but on a purely electronic mechanism. Importantly, switching can be as fast as a few ns, and I will present data on the dynamical response of ferroelectric junctions, and their analysis with standard models of polarization reversal [5].
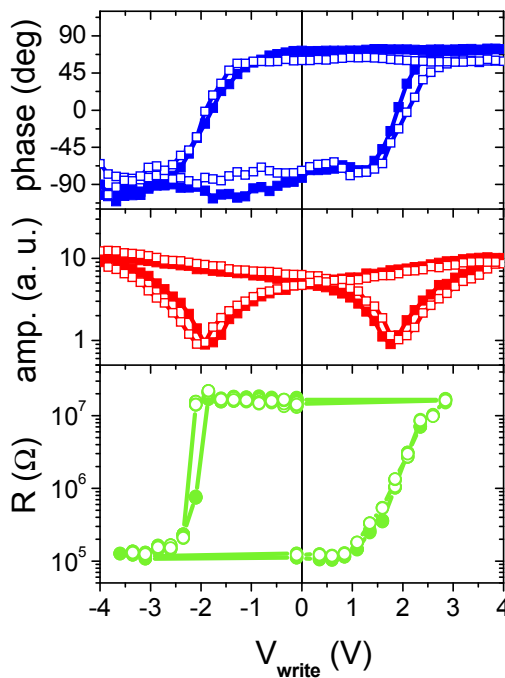

Figure 1: Ferroelectric switching versus resistive switching. Out-of-plane PFM phase (top) and amplitude (center) measurements on a typical gold/cobalt/BTO/LSMO ferroelectric tunnel junction. Bottom: Dependence of the junction resistance on the amplitude of the write voltage pulse measured in remanence (V_{read} ~100 mV) after applying successive write voltage pulses of 100 μs. The open and filled circles represent two different scans to show reproducibility. Adapted from Ref. [4].

[1] D.S. Rana et al. *Adv. Mater.* **21**, 2881 (2009)
[2] E.Y. Tsymbal and H. Kohlstedt, *Science* **313** (2006)
[3] V. Garcia et al, *Nature* **460**, 81 (2009)
[4] A. Chanthbouala et al, *Nature Nanotech.* **7**, 101 (2012)
[5] Y. Ishibashi & Y.N. Takagi, *J. Phys. Soc. Jpn.* **31**, 506 (1970) ; H. Orihara et al, *J. Phys. Soc. Jpn.* **63**, 1601 (1994)

REVISITING THE HEXAGONAL MANGANITES

Nicola Spaldin

Materials Theory, ETH Zurich, Wolfgang-Pauli-Strasse 27, 8093 Zurich, Switzerland
nicola.spaldin@mat.ethz.ch

The hexagonal manganite multiferroics, of which $YMnO_3$ is the prototype, have recently been shown to exhibit a fascinating ferroelectric domain structure [1] which is a consequence of their improper geometric ferroelectricity [2,3]. Here we discuss how this results in topologically protected ferroelectric vortices providing a model system to test theories of cosmic string formation in the early universe. We show how first-principles electronic structure calculations are contributing to the design of test experiments, as well as understanding the coupling between ferroelectricity and magnetism, and the behavior of the ferroelectric domain walls.

[1] Fennie, C. J. & Rabe, K. M., *Ferroelectric transition in YMnO₃ from first principles*. Phys. Rev. B 72, 100103 (2005).
[2] Van Aken, B. B., Palstra, T. T. M., Filippetti, A. & Spaldin, N. A., *The origin of ferroelectricity in magnetoelectric YMnO₃*. Nature Mater. 3, 164-170 (2004).
[3] Choi, T. et al. Insulating interlocked ferroelectric and structural antiphase domain walls in multiferroic YMnO₃. Nature Mater. 9, 253-258 (2010)

INV 18

STUDY OF MAGNETOELECTRIC EFFECTS DUE TO MULTI-SPIN VARIABLES

Tsuyoshi Kimura

Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 506-8531, Japan

Interest in the study of magnetoelectric (ME) effects, magnetic control of electric polarization P or electric control of magnetization M has been reinvigorated since the discovery of spin driven ferro-electricity and giant ME effects in some spin-spiral magnets. Usually, the ME effect can exist in crystals with ordered spin structures having peculiar magnetic symmetries. In ME materials, additional multi-spin variables often play an important role in their ME properties. A well-known multi-spin variable which couples spins with P is "vector spin chirality", defined as $\kappa = (S_i \times S_j)$ where S_i and S_j denote spins at the sites i and j. The most successful microscopic mechanisms for the contribution of the vector spin chirality to the spiral-spin driven ferroelectricity are the so-called "spin current" and "inverse Dzyaloshinskii-Moriya" mechanisms. Another known ME active multi-spin variable is tor-oidal moment t which is described as the outer product of the displacement of magnetic ions from the center position r_i and their spins S_i; i.e., $t \propto \Sigma_i r_i \times S_i$. The sign of t changes under time reversal and space inversion operation, and ME effects in several compounds such as $LiCoPO_4$ have been discussed in terms of the toroidal ordering.

In this presentation, I show recent progress on the study of ME effects in several magnetoelectrics in which the above-mentioned multi-spin variables play important roles. (For example, low-field ME effect at room temperature in hexaferrite compounds such as $Sr_3Co_2Fe_{24}O_{41}$ [1], ferromagnetic and ferroelectric nature in an olivine compound Mn_2GeO_4 [2], and antisymmetric off-diagonal ME effects in a spin-glass system, ilmenite $(Ni,Mn)TiO_3$ [3].)

This work has been done in collaboration with Y. Hiraoka, Y. Yamaguchi, T. Honda, T. Ishikura, K. Okumura, Y. Kitagawa, H. Nakamura, Y. Wakabayashi, M. Soda, T. Asaka, T. Nakano, Y. Nozue, Y. Tanaka, S. Shin, J. S. White, and M. Kenzelmann.

[1] T. Kimura, Annu. Rev. Condens. Matter Phys. 3, 93 (2012).
[2] J. S. White, T. Honda, K. Kimura, T. Kimura, Ch. Niedermayer, O. Zaharko, A. Poole, B. Roessli, and M. Kenzelmann, Phys. Rev. Lett. 108, 077204 (2012).
[3] Y. Yamaguchi, T. Nakano, Y. Nozue, and T. Kimura, Phys. Rev. Lett. 108, 057203 (2012).

BI-LAYERED RERAM: MULTI-LEVEL SWITCHING, RELIABILITY AND ITS MECHANISM FOR STORAGE CLASS MEMORY AND RECONFIGURATION LOGIC.

U-In Chung[1], **Young-Bae Kim**[1], **Seung Ryul Lee**[1], **Dongsoo Lee**[1], **Chang Bum Lee**[1], **Man Chang**[1], **Kyung min Kim**[1], **Ji Hyun Hur**[1], **Myoung-Jae Lee**[1], **Chang Jung Kim**[1]

[1] Samsung Advanced Institute of Technology, San 14-1, Nongseo-dong, Giheung-gu, Yongin-si Gyeonggi-do, 446-712, South Korea, E-mail) uin.chung@samsung.com

The age of fast-moving information and computer technology is driven by silicon CMOS technology. Even though there seems to be no fundamental limit to scaling current devices to below 10 nanometers, there has been a shift toward functional diversification. Among several devices that could add more function, oxide based devices have been kept in focus because of its possibility of emulating organic brain functions and reconfigurable functions on Si circuits in addition to basic storage operations. Although research on ReRAM has continued to be reported [1-2], a reliable memory performance has not yet been presented, because of lacking material architecture and an insufficient understanding of the switching mechanism. In this presentation, a new model and architecture will be proposed based on the movement of oxygen vacancies in a bi-layered metal oxide.

Figure 1 shows the basic device structure with the equivalent bi-layered switching element ReRAM circuit architecture. The oxygen concentration of the oxygen exchange layer (OEL), was controlled by plasma oxidation of the TaOx surface. We propose a model [3-5] in which resistance varies through the movement of oxygen vacancies into or out of the conductive paths formed in the OEL. Figure 2 demonstrates the experimental and the calculated DC voltage sweep properties of typical ReRAM materials (SZO, PCMO and TaO_x). Our model was able to successfully predict the I-V characteristics of these resistive switching materials.
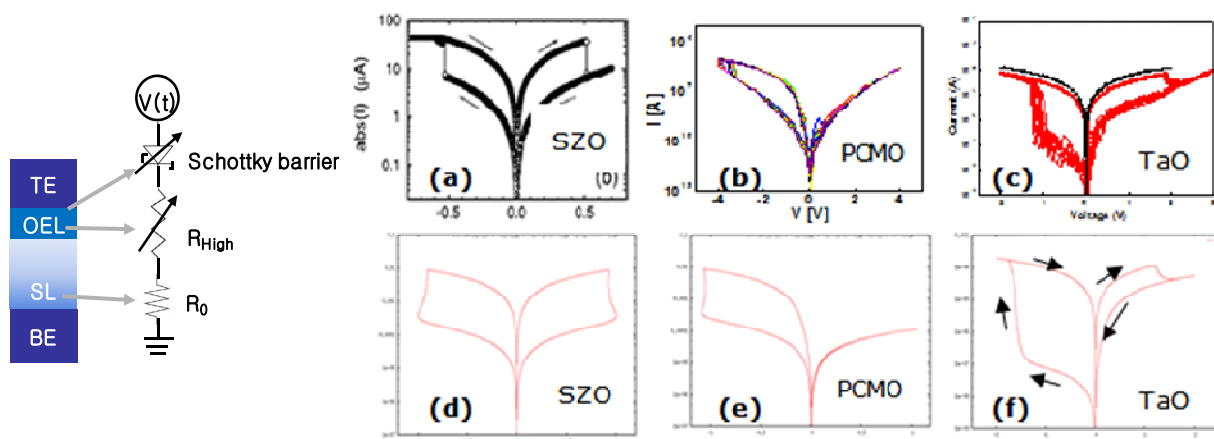

Figure 1: A bi-layered TaOx/Ta2O5 ReRAM structure with an equivalent circuit. The basic device structure is composed of bottom electrode (BE)/ self-compliance layer (SL)/oxygen exchange layer (OEL)/top electrode (TE).

Fig. 2. Experimental [(a), (b) and (c)] and calculated [(d), (e) and (f)] results for SZO, PCMO and TaO system, respectively.

Figure 3 indicates that the resistive switching is originated from the formation and rupture of conducting path which is consisted of nano-sized Ta-rich oxide clusters in Ta_2O_5 layer.
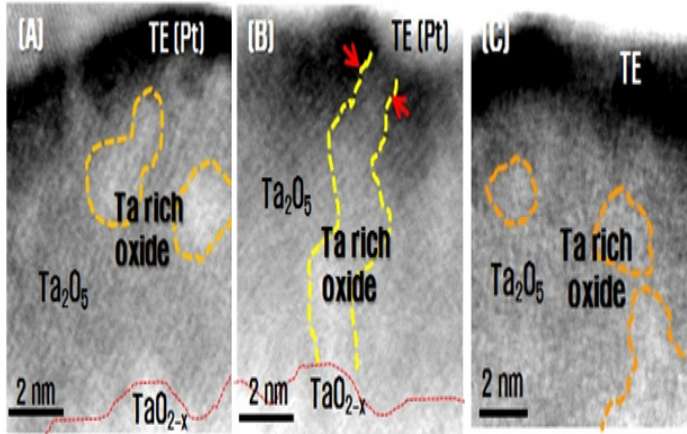
Figure 3 : (A), (B) and (C) display the in-situ high resolution scanning transmission electron microscopy (HR-STEM) images at pristine state, low resistance state (LRS) and high resistance state (HRS), respectively, in which, the LRS and HRS are formed in TEM apparatus, sequentially.

Figure 4 shows that the cell stably operates over 1E7 cycles for all the resistance levels.
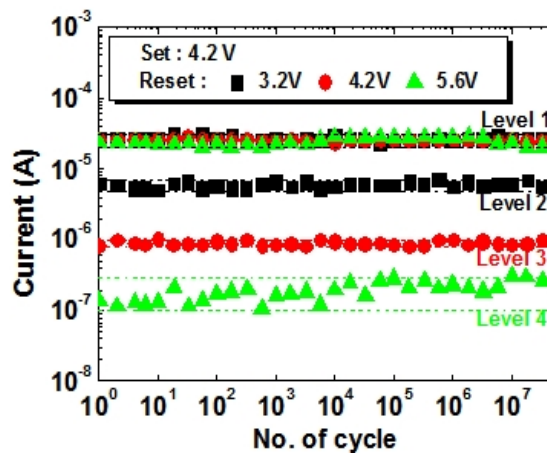

Figure 4: Endurance performance in 2 bits/cell operation using Constant Signal Pulse Programming (CSPP).

To realize bi-layered ReRAM as a storage, another bit selection switch is necessary. Among many selection methods, the antiserial connection is one of the many solutions for bit selection [6]. Figure 5 shows antiserial connection and its switching result.
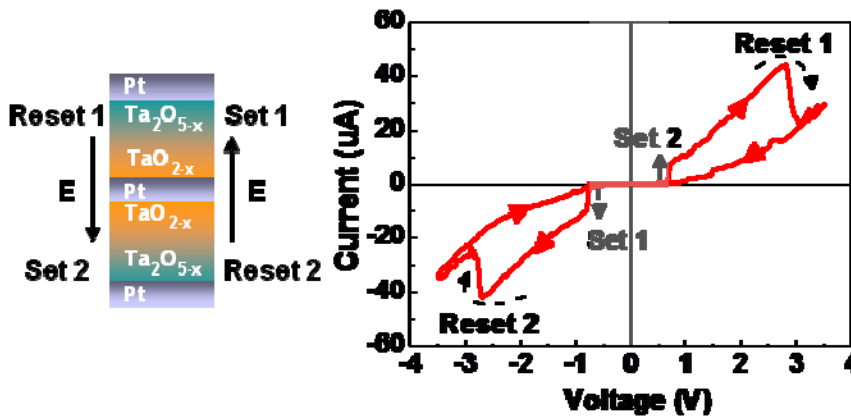

Figure 5: The structure of an antiserial architecture and its operation. It shows the required switching region in between -0.7 and +0.7 volt which inhibits unwanted switching.

In conclusion, the bi-layered switching element can provide the key element for the future of next generation non-volatile storage class memory, reconfigurable logic and neuromorphic circuit toward very high speed and extremely low energy information processing.

[1] C. H. Ho, et al, Symp. VLSI Tech., p. 228-229 (2007).
[2] M. J. Lee, et al, Nano Lett., 9, 1476-1481 (2009).
[3] J. H. Hur, et al, Phys. Rev. B, 82, 155321 (2010).
[4] Y. B. Kim, et al, Symp. VLSI Tech., p. 52-53 (2011).
[5] M. J. Lee et al., Nature Mater. 10, 625 (2011)
[6] Eike Linn, et al., Nature Mater. 9, 403(2010)

SELF-ORGANIZATION IN ADAPTIVE, RECURRENT, AUTONOMOUS MEMRISTIVE CROSSNETS

Konstantin K. Likharev[1], Dmitri N. Gavrilov[1], Thomas J. Walls[1]

[1]Stony Brook University, Stony Brook, NY 11794-3800, U.S.A.

CrossNets [1-3] are analog neuromorphic networks based on hybrid CMOS/nano-crossbar circuits with two-terminal memristive devices at each crosspoint. Such networks are believed to be the first plausible hardware basis for overcoming the mammalian cortical circuitry in density per unit area (at comparable connectivity $M \sim 10^4$), while far exceeding them in speed, at manageable power consumption [2, 3]. However, reaching a comparable cognitive functionality of CrossNets is a grand challenge, toward which only the first humble steps have been made so far [3].

Two crucial aspects of neuromorphic networks are their adaptation (plasticity) and recurrency (internal feedback). In this work we have addressed a simple problem which is a natural background for network interaction with incoming information: what happens to a recurrent, adaptive network if it is left alone (is autonomous)? The problem was considered within two most prominent neural network models:

(i) a firing-rate model with quasi-Hebbian weight adaptation which may be implemented in CrossNets using the stochastic multiplication technique [3, 4], and

(ii) a spiking model with spike-time-dependent plasticity (STDP) which may be also simply implemented in CrossNets, with very small area overhead [3, 5].

Previous work [1] had shown that in recurrent firing-rate CrossNets with fixed, random synaptic weights, an increase of somatic gain g beyond certain threshold value g_t leads to self-excitation of random localized spots – some of them static, some oscillatory (at $g \gg g_t$, chaotic). In this work we demonstrate that quasi-Hebbian plasticity leads to the transformation of the excitation spots into self-contained domains with static, periodic internal structure. (The structure is the same within one domain, but may be different between the domains.) Domain boundaries gradually expand into the passive CrossNet regions (Fig. 1a). Running into each other, the domains compete for space, the largest of them (and those with the simplest internal structure) suppressing others (Fig. 1b).
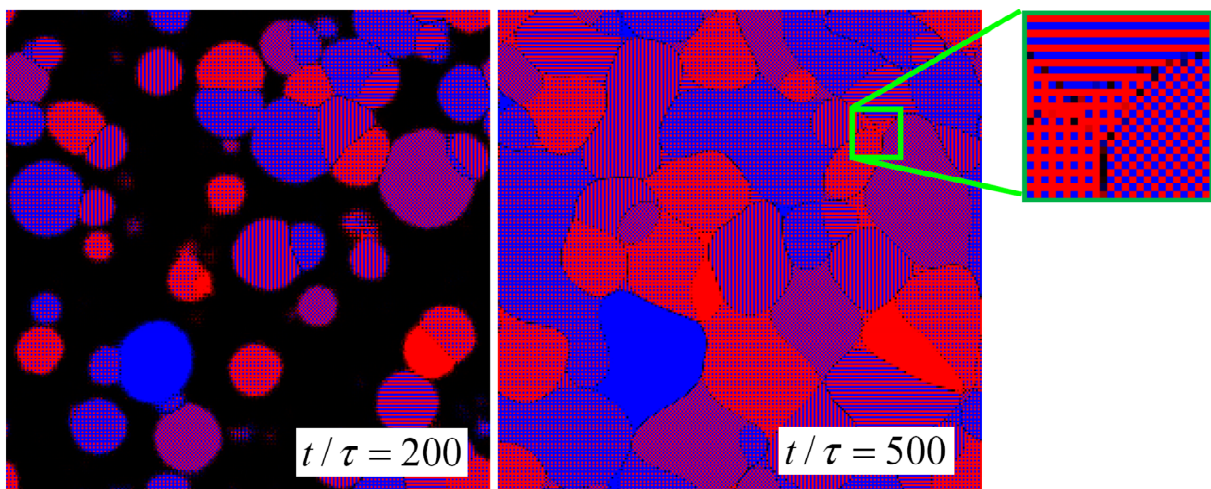

Figure 1: Domain growth and competition in firing-rate CrossNets of size $N = 256 \times 256$ with $M = 24$ at (a) an early stage, and (b) a late stage of time evolution.

Analysis of the equations describing firing-rate CrossNets has confirmed that at $g \gg g_t$, the network can sustain stable domains with *any* periodic internal structure. This feature hardly bodes well for possible information processing by such networks, so that the future development of cognitive functionality should probably focus on systems with $g < g_t$.

For spiking CrossNets the picture is rather different. Here the regulating role of somatic gain is played by the spiking threshold x_t for the action potential $x(t)$ of each soma. Our simulations have shown that spiking CrossNets with random, fixed weights w (either positive or negative, enabling both excitation and inhibition) may sustain self-excitation if x_t is below certain critical value x_c, with the average spiking rate $\langle r \rangle$ (per cell per relaxation time τ) close to 0.3 at $x_t \to x_c$, and gradually increasing with the further decrease of x_t. Both the minimum rate and the critical value x_c have been found to be in reasonable (~15%) agreement with an approximate analytical theory (asymptotically exact at $\langle r \rangle \ll 1$) based on the Smoluchowski equation. This fact, as well as essentially flat auto- and cross-correlation functions, confirm the hypothesis of essentially random spiking in the absence of adaptation (Fig. 2a).

Turning on STDP adaptation, with a global stabilization of the average firing rate, leads to a noticeable change of the synaptic weight distribution (Fig. 2b) and the auto- and cross-correlation functions. However, more specific correlation function(s) still need to be defined and evaluated to understand the exact nature of the observed self-organization. Our hope is to report more definite results at the meeting.
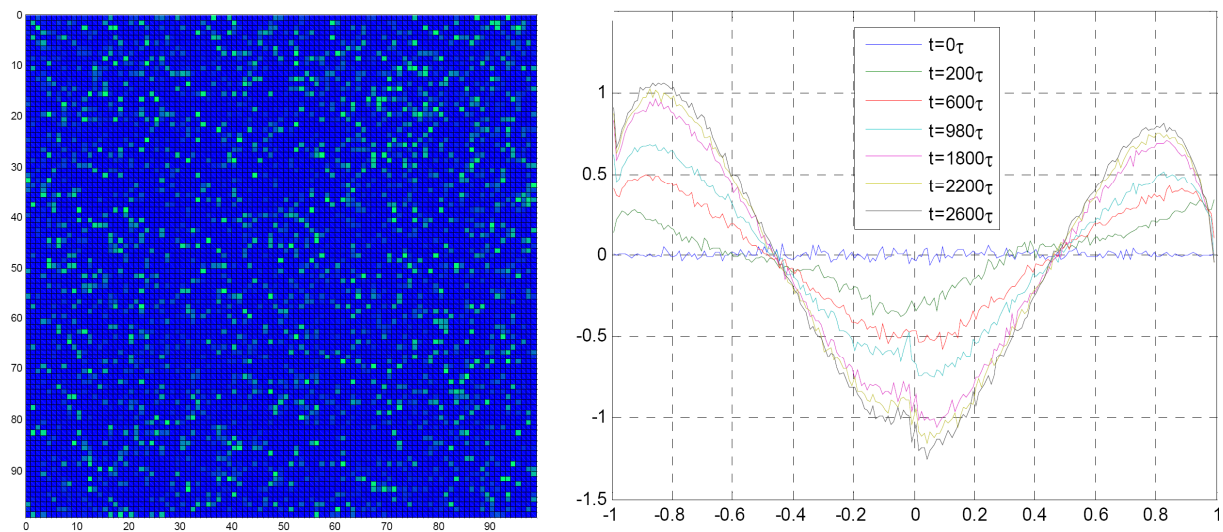
Figure 2: (a) A snapshot of spiking in a CrossNet of size $N = 100 \times 100$ with connectivity $M = 960$, and (b) change of the synaptic weight histogram with time at STDP adaptation (1 = 10% of max).

[1] Ö. Türel and K. Likharev, Int. J. Cir. Theory & Appl. 31, 37 (2003).
[2] J. H. Lee et al., in: Adv. *in Neural Inf. Proc. Syst.* **18**, MIT Press, 2006, pp. 755-762.
[3] K. K. Likharev, Sci. Adv. Mater. **3**, 322 (2011).
[4] J. H. Lee and K. K. Likharev, in: *Proc. WCCI/IJCNN*, IEEE Press, 2006, pp. 5026-5034.
[5] K. K. Likharev, J. Nanoel. & Optoel. **3**, 203 (2008).

ELECTRIC FIELD CONTROL OF MAGNETIZATION

R. Ramesh

University of California, Berkeley

Complex oxides have fascinated the scientific community for years due to the rich physics and the often unique phenomena displayed by these materials. More specifically, complex perovskite oxides have been studied intensively as of the past few decades due to the vast collection of functional electronic phases observed in this class of materials (magnetism, ferroelectricity, superconductivity, highly correlated electron behavior). There is a set of complex oxide perovskites, known as multiferroics, which possess both a ferroelectric polarization and a (anti)ferromagnetic order. Furthermore, a multiferroic is deemed magnetoelectric when these two orders are coupled together. Due to the ability to use an electric field to switch the remnant states of the ferroelectric and magnetic orders, magnetoelectric multiferroics have been proposed as a potential solution to the energy losses faced by field of spintronics.

The energy dissipation in spintronics applications is the result of resistive losses that come during the writing of the magnetic state (i.e. a reversal of the magnetization direction). Writing of the magnetic state is done with either an externally applied magnetic field or injecting a large current density into a magnetic tunnel junction. Recent developments have shown that an applied voltage to a magnetic tunnel junction with an MgO barrier can reduce the energy needed to reverse a magnetization by modulating its anisotropy. However a biasing magnetic field is still needed to make this assisted switching possible and would be required to change sign in order to make this assisted switching reversible. In contrast, a reversal of magnetization requiring only the application of an electric field can lead to the low-power writing of magnetic devices. Using multiferroics, this idea becomes possible. To support both a magnetic order and a ferroelectric polarization, magnetoelectric multiferroics are typically antiferromagnetic insulators and thus cannot serve as a standalone spintronic material. We circumvent this issue by exchange coupling a ferromagnetic metal to a multiferroic in a heterostructure which then enables the low-power control of a magnetic layer using only an applied electric field, (a). Previous approaches based on this concept have seen limited success by only achieving rotations ($\leq 90°$) of the magnetization upon applying an electric field. To pave the way to new low-power devices, the more desirable electric-field driven magnetization reversal must be achieved and read out with a small current.

In this presentation we will discuss our work that investigates the magnetic coupling heterostructures of the room temperature multiferroic – $BiFeO_3$ and a ferromagnetic metal - $Co_{.90}Fe_{.10}$ in the light of $BiFeO_3$ domain structure, magnetometry and X-ray PEEM studies (b,c). How this coupling is used to demonstrate a reversal of the magnetization of the $Co_{.90}Fe_{.10}$ layer using only an in-plane applied electric field at room temperature in a magnetotransport-based device is also discussed. Using magnetotransport measurements (AMR), this electrically-driven 180° reorientation of the magnetization is non-volatile and reversible, (d). In an effort to further demonstrate the potential for low-power consumption spintronics, a vertically applied electric field is used to reverse the magnetization; requiring only 7 volts.

With these results, we push towards the realization an all electrical magnetoelectric memory device. By pinning the bottom layer of a GMR device with $BiFeO_3$ we work towards establishing the electric field control of resistance state of the GMR device. Contrary to the contemporary method of controlling the resistance state of a GMR device (magnetic field switching of the free layer), our approach envisions the purely electrical control of a spin valve by manipulating the magnetization that is coupled to a magnetoelectric multiferroic.

(a)

(b)

(c)

(d)

J. T. Heron et al., Phys. Rev. Lett. 107, 217202 (2011)
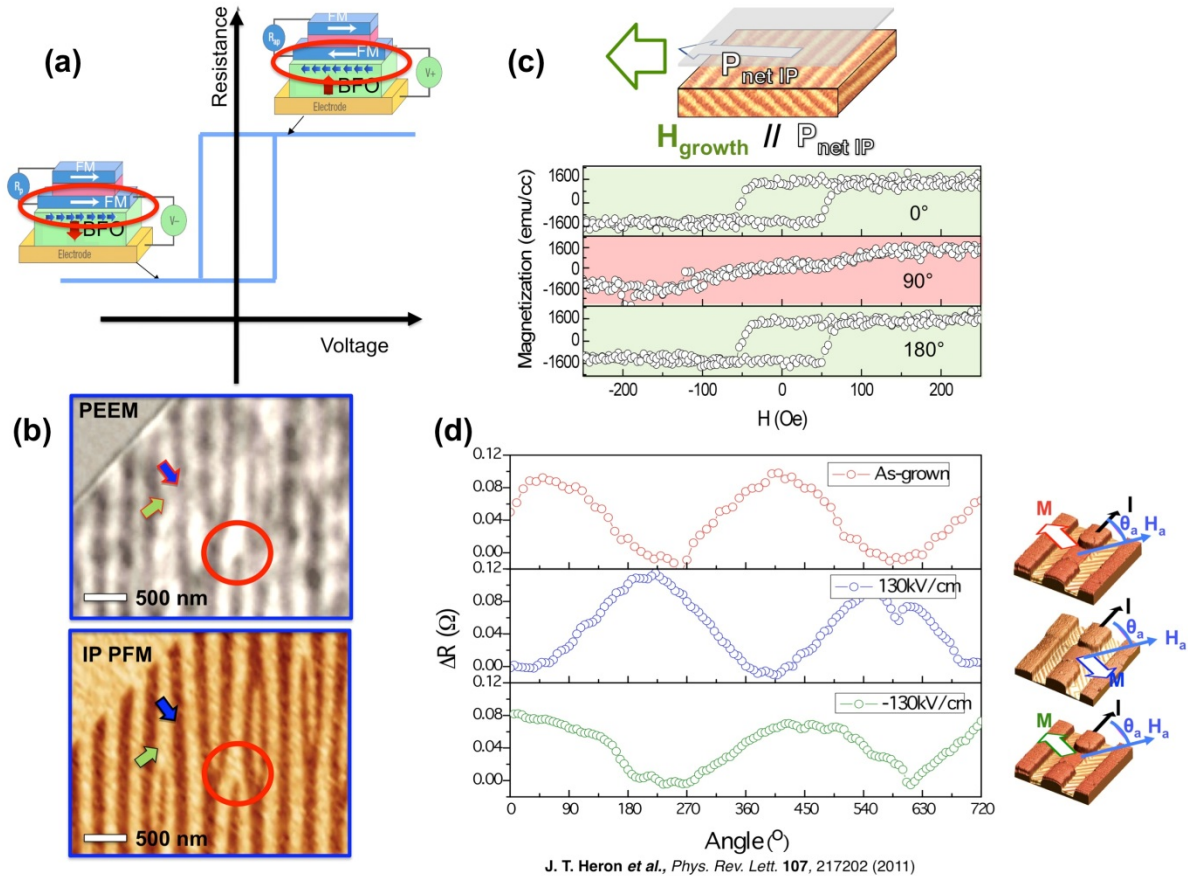
MAGNETIC SWITCHING OF FERROELECTRIC DOMAINS AT ROOM TEMPERATURE IN A NEW MULTIFERROIC

J. F. Scott[1], D. M. Evans[2], J. M. Gregg[2], Ashok Kumar[3,4], D. Sanchez[3], N. Ortega[3], and R. S. Katiyar[3]

[1]Dept. Physics, Cavendish Lab., Cambridge University, Cambridgem UK
[2]Dept. of Physics, Queen's University, Belfast, Northern Ireland, UK
3 Speclab, Dept. Physics, University of Puerto Rico, San Juan, P.R., USA

We have prepared sintered ceramic specimens of ball-milled ceramics of formula $Pb(Fe,Ta,Zr,Ti)O_3$ and measured their electrical and magnetic properties.[1] This perovskite oxide is prepared by mixing 30-40% $PbFe_{1/2}Ta_{1/2}O_3$ ["PFT"]with 70-60% $PbZr_{1/2}Ti_{1/2}O_3$ ["PZT"] and gives a single-phase crystal with very high-temperature ferroelectricity. Although pure PFT exhibits long-range magnetic ordering onlyup to 150K, it is known to have weak ferromagnetism due to Fe clustering up to ca. 400K. As a result, single-phase mixtures of PFT/PZT are multiferroic at room temperature. There is only one other known room-temperature multiferroic – BiFeO3 – and our new material exhibits far lower electrical conductivity and dielectric loss (ca. 1%) for device applications. Several other materials such as CuO are multiferroic slightly below room temperature, sometimes requiring a small dc field.

We have carefully analyzed our specimens via EDX (Fig.1), TEM (Fig.2), Raman spectroscopy, and other techniques and confirm than any second phase must be in amounts << 1%. This is too small to explain the measured magnetization at 295K and cannot explain the switching results below. In our initial work we were unable to see either a linear magnetoelectric effect or magnetoelectric switching, due to the measurement area extending over many domains. However, in the present work (Fig.3) we demonstrate good magnetoelectric switching at room temperature: In particular the ferroelectric domains measured via PFM are switched using a very small bar magnet (rare earth, ca. 0.1 Tesla). The direction of H was normal to the plane of the domains.
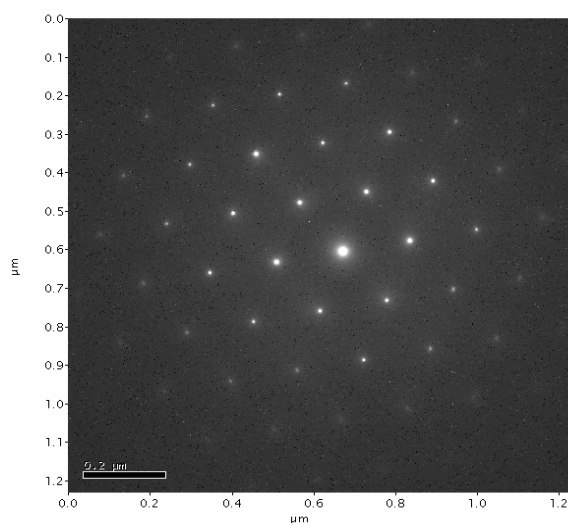

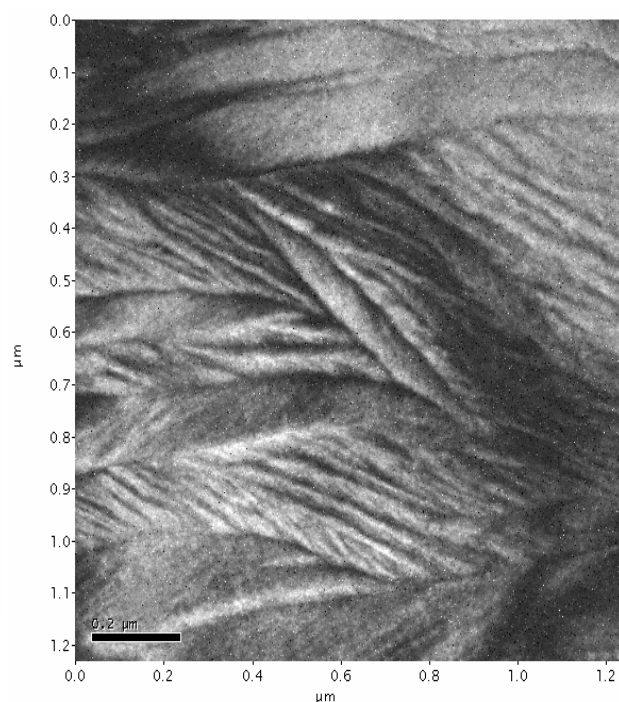Fig. 1. X-ray diffraction pattern.   Fig.2. TEM pattern.
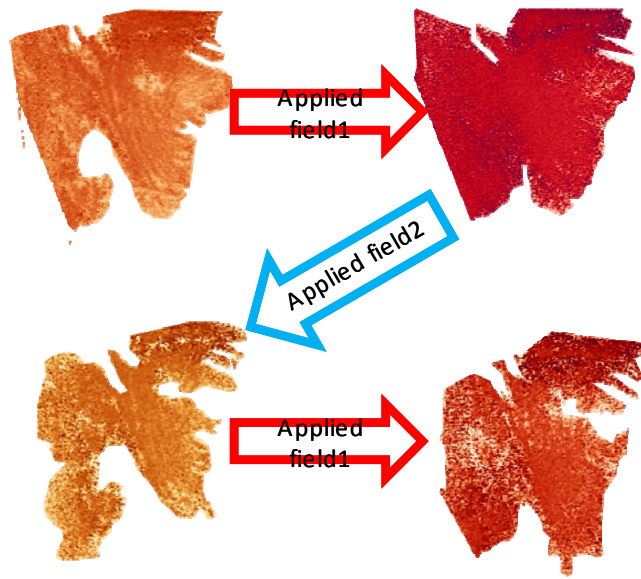
Fig.3: Magnetic switching:

Dark areas of PFM images. Apply field 1 and cause dark area to grow

Apply opposite field to cause dark area to shrink

Can cause 'switching' of dark area by using different magnetic field.

[1] D. Sanchez, N. Ortega, A. Kumar, R. S. Katiyar, J. F. Scott, AIP Adv. 1, 042169 (2011) .

CONTROL OF CORRELATED ELECTRONS IN METAL-OXIDE SUPERLATTICES

Bernhard Keimer

Max Planck Institute for Solid State Research, Stuttgart, Germany

We will outline recent results of an experimental program aimed at controlling the phase behavior of correlated electrons through the synthesis and characterization of metal-oxide superlattices, with particular emphasis on copper and nickel oxides. Control parameters include the occupation of transition-metal d-orbitals [1] and the dimensionality of the electron system [2]. In particular, we will demonstrate control of the electron-phonon interaction in cuprate superlattices [3], and of the spin density wave polarization in nickelate superlattices [4]. These results also highlight the power of resonant x-ray scattering [1,4], spectral ellipsometry [2], and Raman scattering [3] as microscopic probes of the electron system in metal-oxide heterostructures and superlattices.

[1] E. Benckiser, M. W. Haverkort, S. Brück, E. Goering, S. Macke, A. Frañó, X. Yang, O. K. Andersen, G. Cristiani, H. U. Habermeier, A. V. Boris, I. Zegkinoglou, P. Wochner, H. J. Kim, V. Hinkov, and B. Keimer, Nature Mater. **10**, 189 (2011).
[2] A. V. Boris, Y. Matiks, E. Benckiser, A. Frano, P. Popovich, V. Hinkov, P. Wochner, M. Castro-Colin, E. Detemple, V. K. Malik, C. Bernhard, T. Prokscha, A. Suter, Z. Salman, E. Morenzoni, G. Cristiani, H.-U. Habermeier, and B. Keimer, Science **332**, 937 (2011).
[3] N. Driza, S. Blanco-Canosa, M. Bakr, S. Soltan, M. Khalid, L. Mustafa, K. Kawashima, G. Christiani, H.-U. Habermeier, G. Khaliullin, C. Ulrich, M. Le Tacon, and B. Keimer, submitted.
[4] A. Frano, E. Schierle, M. W. Haverkort, Y. Lu, M. Wu, S. Blanco-Canosa,Y. Matiks, A. V. Boris, P. Wochner, G. Cristiani, G. Logvenov, H.U. Habermeier, V. Hinkov, E. Benckiser, E. Weschke, and B. Keimer, in preparation.

METAL-INSULATOR TRANSITIONS OF CORRELATED ELECTRONS IN OXIDE HETEROSTRUCTURES

Masashi Kawasaki[1,2]

[1]Quantum Phase Electronics Center (QPEC) and Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan
[2]Correlated Electron Research Group (CERG) and Cross-Correlated Materials Research Group (CMRG), RIKEN Advanced Science Institute, Wako 351-0198, Japan

There have been numbers of examples where metal-insulator transition is induced at the interfaces of correlated oxides by tiny stimuli such as electric field, photo-irradiation, and magnetic field [1]. These phenomena provide potential functionalities for the application of non-volatile memories, switches, sensors, and photovoltaics. In addition, these interfaces are excellent playground to explore new physics. We have studied numbers of heterostructures comprised of transition metal oxides and found some similarities to but also limitations for the rigid band model to describe the connection of two different electronic structures [2]. Examples of carrier accumulation or depletion at the interfaces by electric field, charge transfer, and photo irradiation are discussed to elucidate characteristics of each oxide. The system includes half-doped manganites [3], robust Mott insulators of manganites and cuprates [4], spin-peierls vanadium oxide [5] and correlated electrons in band insulators [6,7].

Figure 1 shows an example of the rigid band view of hetero-junctions. Photocurrent, optical absorption, and capacitance-voltage measurements enabled us to map out the band lineup [2]. From the bias dependence of photocurrent, one can readily extract an acceptor concentration of 4×10^{19} cm^{-3}, depletion layer width of 3 nm, and minority carrier diffusion length of 3 nm in $LaMnO_3$ [4].
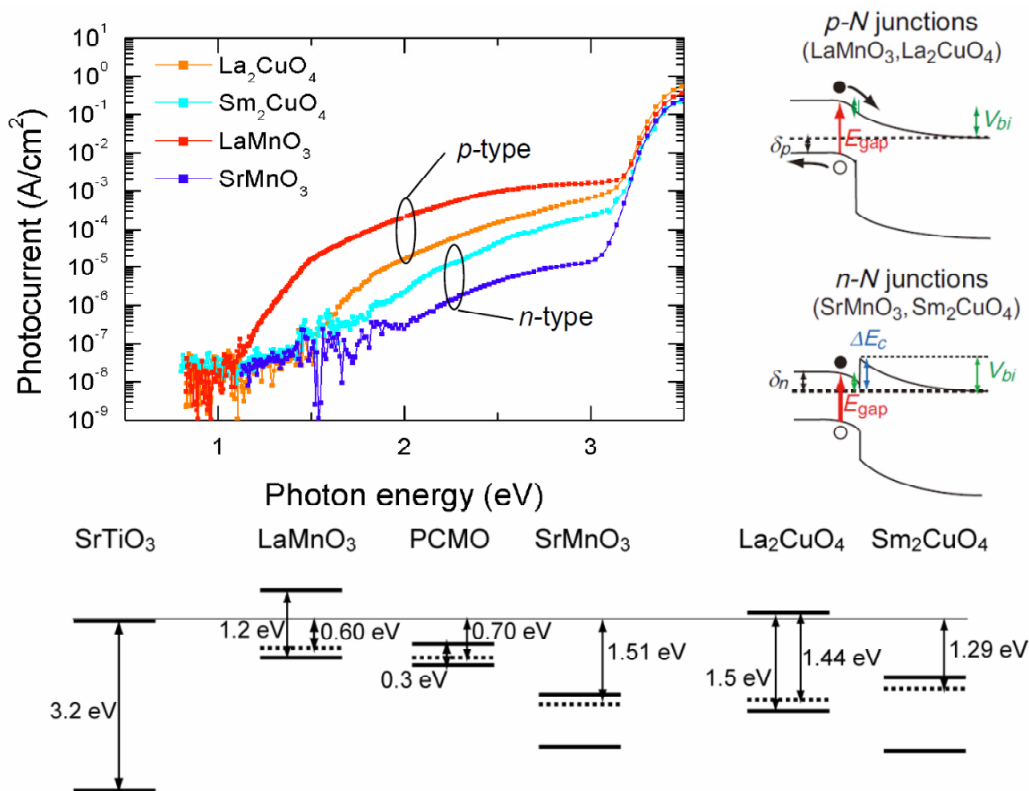

Figure 1: Photocurrent spectra (upper left) of hetero-junctions of Mot insulators and a doped band insulator ($SrTiO_3$). The band diagrams can be classified as *p-N* and *n-N* junctions (upper right). From the analysis, band lineup (bottom) is drawn.

If one can design a hetero-junction that can generate photocurrent from a narrow charge-gap (Δ) insulator such as half-doped manganites with charge-orbital ordered structure, one may be able to construct a multiple-carrier generation solar cell. The concept of the solar cell is given in Figure 2. Photo-induced insulator-metal transition could be regarded as a sort of multiplication process. Theoretically, this process is verified to occur [8].
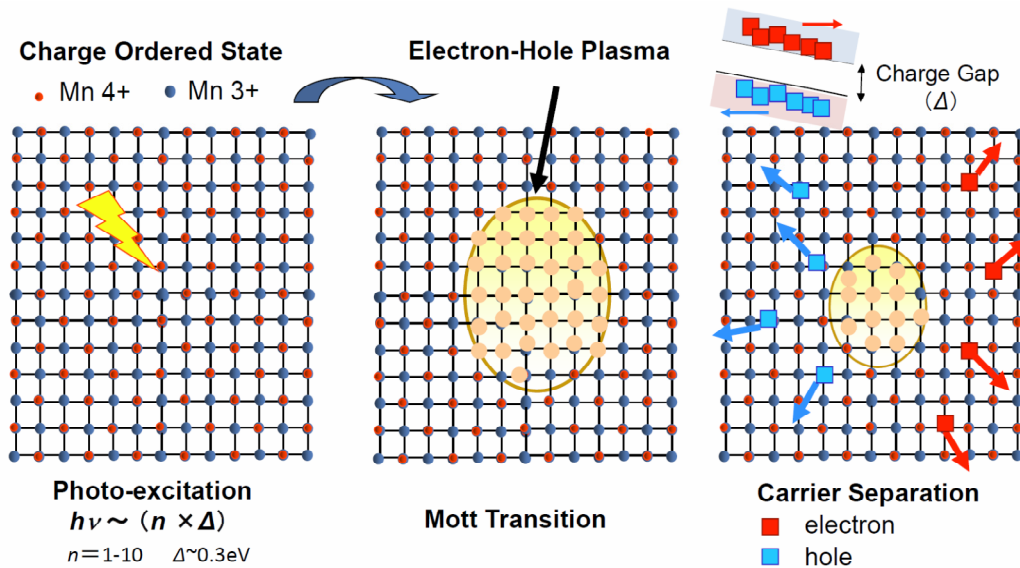

Figure 1: Schematic representation of the concept of correlated electron solar cell. There are many cases, in which multiplication of photo-generated carriers occurs in Mott insulators. If the carriers can be extracted, it may be possible to devise a high efficiency solar cell.

Vanadium oxide is another material that is promising for possible devices. The insulator metal transition can be easily tuned by doping [9], photo-irradiation [5] and electric field [10]. On the other hand it is elucidated to be very robust against quantum confinement [11]. The band lineup of VO_2 and other materials are also discussed in view of solar cell and transistor application.

[1] As a review see for example, H. Y. Hwang et al., Nature. Mater. **11**, 103 (2012).
[2] M. Nakamura et al., Phys. Rev. B **82** 201101 (2011)
[3] M. Nakamura et al., Adv. Mater **22**, 500 (2011)
[4] J. Fujioka et al., J. Appl. Phys. **111**, 016107 (2012)
[5] K. Shibuya et al., Phys. Rev. B **84**, 165108 (2011)
[6] Y. Kozuka et al., Phys. Rev. B **84**, 033304 (2011)
[7] D. Maryenko et al., Phys. Rev. Lett. in press. arXive 1203.3349
[8] W, Koshibae et al., Phys. Rev. Lett. **103**, 266402 (2009); Euro. Phys. Lett. **94**, 27003 (2011)
[9] K. Shibuya et al., Appl. Phys. Lett., **96**, 022102 (2010)
[10] M. Nakano et al., submitted
[11] K. Shibuya et al., Phys. Rev. B **82**, 205118 (2010)

INV 25

THEORETICAL DESIGN OF TOPOLOGICAL PHENOMENA

Naoto Nagaosa[1,2]

[1]Department of Applied Physics, The University of Tokyo, Japan
[2]Cross-Correlated Materials Research Group (CMRG), and Correlated
Electron Research Group (CERG), RIKEN-ASI, Japan

The topological classification of the electronic states in solids has recently revealed the rich possibilities of materials and phenomena, and attracts much attention both from the scientific and technological viewpoints. Especially the topological insulator (TI) and topological superconductor (TSC) are the new states of matter characterized by the topological invariants and reveal their novel properties at the edge/surface. Topological periodic table is now established to classify all the possible topologically nontrivial states including at the textures such as dislocations. Based on these recent developments, the next step is to design theoretically the materials and their functions using for example the artificial structures.

In this talk, I will present the principles for this design, and show some of the examples which include (i) the correlated TI and TSC at oxide super-lattice [1,2,3], (ii) noncentrosymmetric TI and their quantum critical phenomena in Bi-based compounds [4,5], and (iii) correlated Majorana fermion in TSC [6,7]. Especially, the role of dimensional reduction is stressed, which enhances the topological singularity and also the electron correlation. These works have been done in collaboration with Y. Tanaka, A. Yamakage, S. Okamoto, X. Di, Y. Ran, W. Zhu, S. Bahramy, S. Nakosai, D. Isobe, D. Asahi and R. Arita.

[1] Di. Xiao et al., Nature Communications 2, 596 (2011).
[2] S. Nakosai et al., Phys. Rev. Lett. In press (2012)
[3] H. Hwang et al, Nature Materials. 11, 103 (2012).
[4] K. Ishizaka et al., Nature Materials, 10, 521 (2011).
[5] M. S. Bahramy et al., Nature Communications 3, 679 (2012)
[6] Y. Asano et al., Phys. Rev. Lett. 105, 056402 (2010).
[7] A. Yamakage et al., Phys. Rev. Lett. 106, 246601 (2011)

MAGNETIC RECONSTRUCTIONS IN PEROVSKITE HETEROINTERFACES AND ULTRATHIN FILMS

Harold Y. Hwang[1]

[1]Departments of Applied Physics and Photon Science, Stanford University and SLAC National Accelerator Laboratory

Complex oxides are fascinating systems which host a vast array of unique phenomena, such as high temperature (and unconventional) superconductivity, 'colossal' magnetoresistance, all forms of magnetism and ferroelectricity, as well as (quantum) phase transitions and couplings between these states. In recent years, there has been a mini-revolution in the ability to grow thin film heterostructures of these materials with atomic precision. With this level of control, the boundary conditions at oxide surfaces and interfaces can be used to form new electronic phases [1]. Between two insulators, for example, metallic, superconducting, and magnetic states can be induced. Here we focus on two examples of magnetic reconstructions we observe in perovskite heterostructures (Figure 1); the inhomogeneous ferromagnetic patches which occur in $LaAlO_3/SrTiO_3$ [2-4], and the thickness evolution of the magnetic structure in ultrathin manganite films [5].
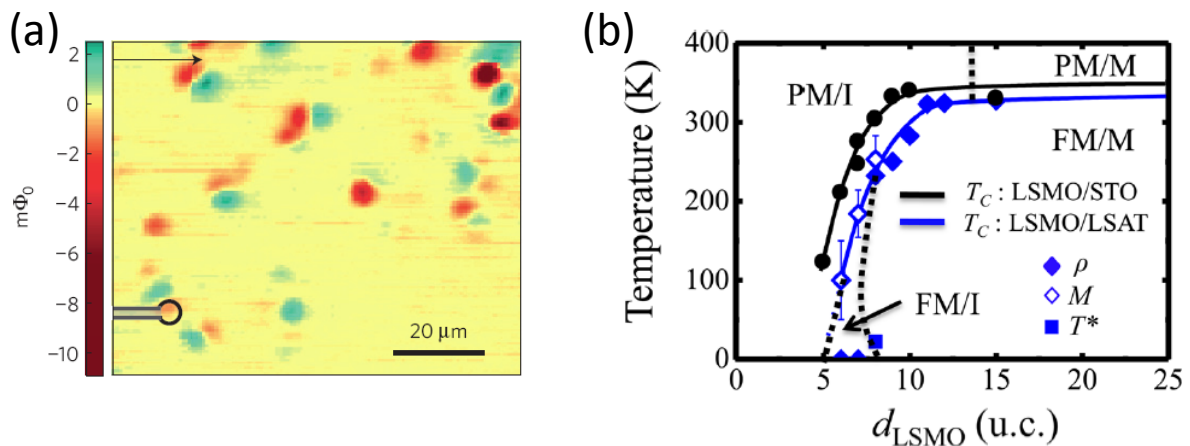

Figure 1: (a) Scanning SQUID magnetometry image of a 10 u.c. $LaAlO_3/SrTiO_3$ heterostructure [3]. (b) Thickness phase diagram of ultrathin $La_{0.7}Sr_{0.3}MnO_3$ thin films [5].

[1] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nature Mater., 11 (2012) 103.
[2] A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nature Mater., 6 (2007) 493.
[3] J. A. Bert, B. Kalisky, C. Bell, M. Kim, Y. Hikita, H. Y. Hwang, and K. A. Moler, Nature Phys., 7 (2011) 767.
[4] B. Kalisky, J. A. Bert, B. B. Klopfer, C. Bell, H. K. Sato, M. Hosoda, Y. Hikita, H. Y. Hwang, and K. A. Moler, arXiv:1201.1063.
[5] B. Kim, D. Kwon, T. Yajima, C. Bell, Y. Hikita, B. G. Kim, and H. Y. Hwang, Appl. Phys. Lett., 99 (2011) 092513.

PROGRESS IN THE ATOMIC SWITCH

Masakazu Aono[1], Tsuyoshi Hasegawa[1], Kazuya Terabe[1], Tohru Tsuruoka[1], Takeo Ohno[1], and Toshitsugu Sakamoto[2]

[1]WPI Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan; [2]Low-power Electronics Association and Project (LEAP), Tsukuba, Japan

The atomic switch is generally known as such nanoscale switching devices that make ON/OFF switching by the growth and shrinkage of a conduction path composed of metal atoms (in contrast with other nanoscale switching devices collectively called the resistive switch in which a conduction path is formed by anion [e.g. oxygen ion] vacancies, etc.). Actually, the atomic switch has many more interesting functionalities depending on its structure and constituent materials (see Fig. 1).
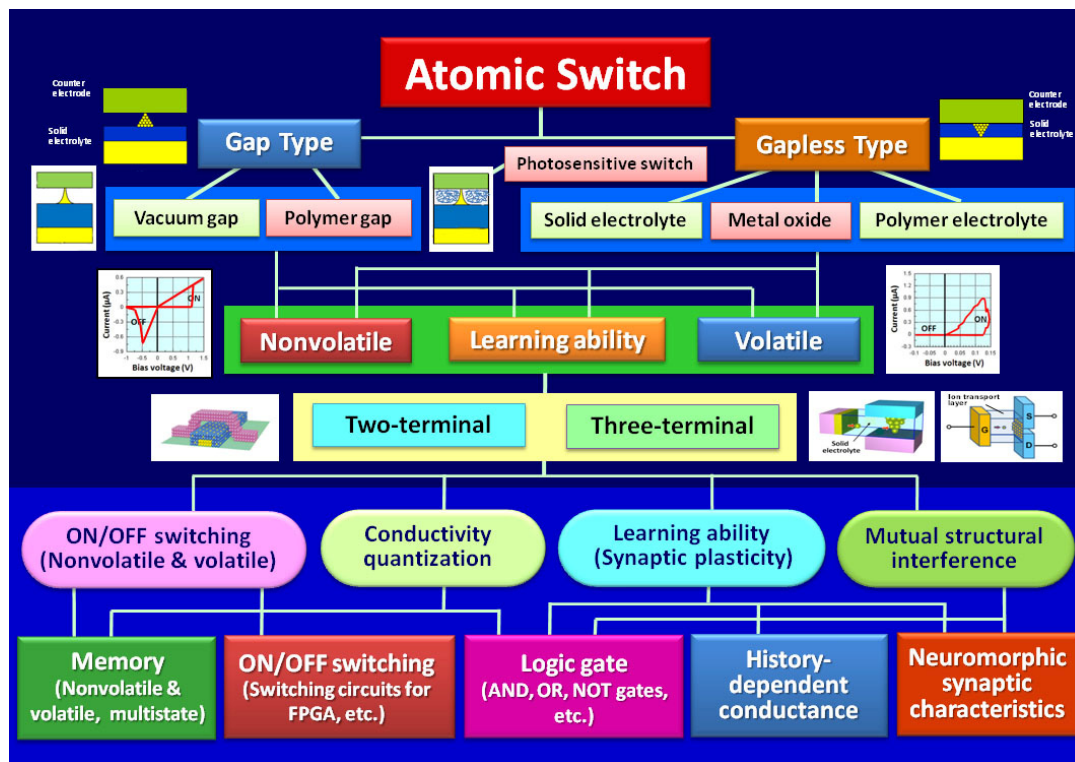

Figure 1: Various types of the atomic switch, which have different structures and constituent materials.

The atomic switch was first developed as a **nanoscale**, **two-terminal**, **nonvolatile** switch with a nanoscale vacuum gap between a **solid-electrolyte** (Ag_2S) electrode and a simple-metal counter electrode, i.e. a **gap-type** atomic switch [1, 2]; if necessary, a **volatile** atomic switch can be made [3]. It has been found later that the vacuum gap can be filled with soft organic molecules [4] and if the molecules are photoconductive, a photosensitive atomic switch can be made, where ON/OFF switching is controlled by photons [4]. The switching mechanism of the gap-type atomic switch has been studied in detail [5-7].

Soon after the development of the gap-type atomic switch, we developed a **gapless- type** atomic switch without a gap between a solid-electrolyte electrode (Cu_2S was used) and a simple-metal counter electrode [8-11]; this gapless-type atomic switch is advantageous for practical application. We have also found that the solid electrolyte in the gapless-type atomic switch can be a **polymer-based electrolyte** (e.g. poly-ethylene + $AgClO_4$) [12], suggestinh that a flexible two-dimensional atomic switch array can be fabricated. Moreover, it has been found that the electrolyte in the gapless-type atomic

switch can be replaced by a **metal oxide** (e.g. Ta_2O_5) [13-17]; the metal oxide is not a solid electrolyte but works as an **ion transport layer**. The switching mechanism of this ion-transport-layer atomic switch has been studied in detail [18-21].

We have succeeded to develop **three-terminal atomic switches (transistors)** using a solid electrolyte (Cu_2S) [22, 23] or an ion-transport layer (Ta_2O_5) [24, 25]. Interest-ingly, an atomic transistor using Ta_2O_5 can be operated in **either volatile or non-volatile modes** by simply controlling applied voltage [24].

Interestingly, we have revealed that the two-terminal gap-type atomic switch exhibits **learning ability** [26, 27]; namely, the conductivity of the switch can have inter-mediate values between the OFF and ON conductivities, depending on the history of input signals. More interestingly, the atomic switch show interesting **characteristics similar to a synapse** in neural network [28-30]; such characteristics are also observed in a certain gapless-type atomic switch [31]. On the basis of these results, we have been developing **neuromorphic circuits** made of atomic switches [28, 31, 32].

The studies described above have been partially reviewed in Refs. [33-37].

[1] K. Terabe et al., *Riken Review* No. 37 (July, 2001) 7.
[2] K. Terabe et al., *Nature* 433 (2005) 47.
[3] T. Hasegawa et al., to be published.
[4] T. Hino et al., *Small* 6 (2010) 1745.
[5] A. Nayak et al., *J. Phys. Chem. Lett.* 1 (2010) 604.
[6] A. Nayak et al., *Appl. Phys. Lett.* 98 (2011) 233501.
[7] I. Valov et al., *Nature Mater.*, in press.
[8] T. Sakamoto et al., *Appl. Phys. Lett.* 82 (2003) 3032.
[9] S. Kaeriyama et al., *IEEE J. Solid-State Circuits* 40 (2005) 168.
[10] N. Banno et al., *IEICE Trans. Electron.* E89-C (2006) 1492.
[11] N. Banno et al., *IEEE Trans. Electron* Devices 55 (2008) 3283.
[12] S.-W. Wu et al., *Adv. Func. Mater.* 21 (2011) 93.
[13] T. Sakamoto et al., *Appl. Phys. Lett.* 91 (2007) 092110.
[14] N. Banno et al., *Appl. Phys. Lett.* 97 (2010) 113507.
[15] M. Tada et al., *IEEE Trans. Electron Devices* 57 (2010) 1987.
[16] Y. Tsuji et al., *Appl. Phys. Lett.* 96 (2010) 023504.
[17] N. Banno et al., *Jpn. J. Appl. Phys.* 50 (2011) 074201.
[18] T. Tsuruoka et al., *Nanotechnology* 21 (2010) 425205.
[19] T. Tsuruoka et al., *Nanotechnology* 22 (2011) 379502.
[20] T. Tsuruoka et al., *Adv. Func. Mater.* 22 (2012) 70.
[21] A. Nayak et al., *Nanotechnology* 22 (2011) 235201.
[22] T. Sakamoto et al., *IEDM Technical Digest* (2005) 475.
[23] T. Sakamoto et al., *Appl. Phys. Lett.* 96 (2010) 252104.
[24] T. Hasegawa et al., *Appl. Phys. Express* 4 (2011) 015204.
[25] H. Kawaura et al., *Electronics and Communications in Japan* 94 (2011) 55.
[26] T. Hasegawa et al., *Adv. Mater.* 22 (2010) 1831.
[27] T. Hasegawa et al., *Appl. Phys. A* 102 (2011) 811.
[28] T. Ohno et al., *Nature Mater.* 10 (2011) 591.
[29] T. Ohno et al., *Appl. Phys. Lett.* 99 (2011) 203108.
[30] A. Nayak et al., submitted. [31] R. Yang et al., submitted.
[32] A. Stieg et al., *Adv. Mater.* 24 (2012) 286.
[33] R. Waser, M. Aono, *Nature Mater.*, 6 (2007) 833.
[34] T. Hasegawa et al., *MRS Bulletin* 34 (2009) 929.
[35] M. Aono, T. Hasegawa, *Proc. IEEE* 12 (2010) 2228.
[36] T. Hino et al., *Sci. Technol. Adv. Mater.* 12 (2011) 013003.
[37] T. Hasegawa et al., *Adv. Mater.* 24 (2012) 252.