Invited Talks
NEW MAGNETIC MATERIALS BASED ON DEFECTS, INTERFACES AND DOPING

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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.

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-dimensional 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.

SIGNIFICANCE OF SOLID STATE IONICS FOR TRANSPORT AND STORAGE

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The role of ionic point defects and their impact on electronic charge carriers are considered from 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.

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

Figure 2: Conductivity versus oxygen partial pressure $P$ measured at $544$ $^\circ$C for microcrystalline (open squares) and nanocrystalline SrTiO$_3$ (filled squares: $30$nm) 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 multilayers of CaF$_2$ and BaF$_2$ (as well as composites) are investigated as a function of layer thickness ranging from $\sim 1 \mu\text{m}$ (semi-infinite conditions) to $\sim 1 \text{ nm}$ (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].](image)

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$_2$O/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$_2$O/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]](image)

The reason lies in this novel “job-sharing” storage at the interface: Li$_2$O stores Li$^+$, Ru stores e$^-$. This mechanism forms the bridge between an electrostatic and chemical capacitor [6,7].

ELECTROCHEMICAL DOPING OF OXIDE HETEROSTRUCTURES

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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 expected1, 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 data2. Pristine systems will likely require changed growth conditions or modified 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 observed3. 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.

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

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 ferroelectric 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.

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.

![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.](image)

EXPLORATION OF ELECTRON SYSTEMS AT OXIDE INTERFACES

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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 LaAlO3-SrTiO3 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 LaAlO3-SrTiO3 interface as drain-source channels and the LaAlO3 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]).

THE INFLUENCE OF IMPERFECTIONS ON THE 2DEG TRANSPORT PROPERTIES IN THE LaAlO3-SrTiO3 SYSTEM

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Within this contribution, I will focus on the creation and annihilation of oxygen vacancies in LaAlO3/SrTiO3 heterostructures, as well as their influence on the transport properties of the 2DEG created at the interface between LaAlO3 and SrTiO3. 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 LaAlO3-SrTiO3 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 SrTiO3 heterostructures. As an example, metallic conducting interfaces are observed in such heterostructures with various overlayers of amorphous LaAlO3, SrTiO3 and yttria-stabilized zirconia (YSZ) films. Whereas, an insulating heterointerface is found when the overlayer is an amorphous La7/8Sr1/8MnO3 film. I will present evidence that the interfacial conductivity results from the oxygen vacancies on the SrTiO3 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 SrTiO3-based oxide heterostructures.

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 SrTiO3-LaAlO3 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.

CORRELATED ELECTRONIC MATERIALS: COMPUTATIONAL STUDIES OF MULTIORBITAL MODELS FOR BULK COMPOUNDS AND INTERFACES OF MAGNETIC AND SUPERCONDUCTING MATERIALS

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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 $T/t_{aa}=0.09$ 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 photoemission 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 Heisenberg models with localized spins provide an accurate representation of the physics. The presentation will continue by addressing next the case of superlattices made of strongly correlated materials, as in the figure shown on the left, with emphasis on results for magnetic compounds, 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 computational technique in quasi one dimensional systems will also be discussed. They correspond to the propagation of excitons, as those created in photovoltaic devices, in the framework 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 metallic 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.


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

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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$_2$.](image-url)
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.

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].

Complex crystal structures that enable relatively low thermal conductivity have lead to several new classes of thermoelectric materials. Ca$_3$AlSb$_3$, Ca$_3$AlSb$_2$, 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$_4$Sb$_3$ [3] and Cu$_2$Se [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].

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

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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. Ge2Sb2Te5 – 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 devices1. 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.

ELECTRONIC PHASE CHANGE AND ENTROPIC FUNCTIONS IN TRANSITION METAL OXIDES

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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\textsubscript{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\textsubscript{x}CoO\textsubscript{2}, can be viewed as a realization of such scenario. Other possible application of the large electronic entropy will be discussed.

DISORDER INDUCED METAL-INSULATOR TRANSITION IN PHASE CHANGE MATERIALS

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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\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{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).

Other phase change materials along the pseudo-binary (GeTe)-(Sb\textsubscript{2}Te\textsubscript{3}) line exhibit the same behavior, with a critical resistivity of 2-3 mΩcm 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.

ELECTRONIC PROPERTIES OF THE INTERFACIAL LaAlO\textsubscript{3} / SrTiO\textsubscript{3} SYSTEM

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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\textsubscript{3} and SrTiO\textsubscript{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\textsuperscript{13} electrons/cm\textsuperscript{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].

EMERGENT PHENOMENA IN TWO-DIMENSIONAL ELECTRON GASES AT OXIDE INTERFACES

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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 SrTiO₃ 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 SrTiO₃ films and that these oscillations are much more pronounced than those currently observed in structures with SrTiO₃ substrates.

In the second half of the presentation, we will discuss emergent phenomena at interfaces between band insulators, such as SrTiO₃, and strongly correlated (Mott) materials, such as the rare earth titanates (R̅TiO₃, where R is a trivalent rare earth ion), or the rare earth nickelates (R̅NiO₃). SrTiO₃/R̅TiO₃ 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 GdTiO₃ and SrTiO₃, grown by molecular beam epitaxy. The sheet carrier densities of all GdTiO₃/SrTiO₃ heterostructures containing more than one unit cell of SrTiO₃ are approximately ½ electron per surface unit cell (or 3×10¹⁴ cm⁻²), independent of layer thicknesses and growth sequences. Unlike the more commonly studies LaAlO₃/SrTiO₃ 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 SrTiO₃ 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 SrTiO₃. 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

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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 BaTiO₃ 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].

REVISITING THE HEXAGONAL MANGANITES

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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.

STUDY OF MAGNETOELECTRIC EFFECTS DUE TO MULTI-SPIN VARIABLES

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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 ferroelectricity 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 toroidal 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., $t \propto \sum_i r_i \times S_i$. 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$_3$Co$_2$Fe$_{24}$O$_{41}$ [1], ferromagnetic and ferroelectric nature in an olivine compound Mn$_2$GeO$_4$ [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.

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

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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 TaOx). Our model was able to successfully predict the I-V characteristics of these resistive switching materials.

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 Ta2O5 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.

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.

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.

SELF-ORGANIZATION IN ADAPTIVE, RECURRENT, AUTONOMOUS MEMRISTIVE CROSSNETS

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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 $g >> g_t$, 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.](image-url)
Analysis of the equations describing firing-rate CrossNets has confirmed that at $g >> g_c$, 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 $g < g_c$.

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 $\tau$) close to 0.3 at $x_t \rightarrow x_c$, 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 $\langle r \rangle << 1$) 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.

The work was supported in part by NSF and AFOSR. Useful discussions with D. Hammerstrom, R. O’Reilly, C. Segal, and D. Strukov are gratefully acknowledged.

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 ($l = 10\%$ of max).

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 (≤ 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 – BiFeO₃ and a ferromagnetic metal - Co₀.₉₀Fe₁₀ in the light of BiFeO₃ domain structure, magnetometry and X-ray PEEM studies (b,c). How this coupling is used to demonstrate a reversal of the magnetization of the Co₀.₉₀Fe₁₀ 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 BiFeO₃ 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.
Invited Talks

(a) [Image of a schematic diagram]

(b) [Images of PEEM and IP PFM]

(c) [Graph showing Magnetization vs. H(Oe) for different angles]

(d) [Graph showing $g_r$ vs. Angle with different electric fields]

MAGNETIC SWITCHING OF FERROELECTRIC DOMAINS AT ROOM TEMPERATURE IN A NEW MULTIFERROIC

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We have prepared sintered ceramic specimens of ball-milled ceramics of formula Pb(Fe,Ta,Zr,Ti)O₃ and measured their electrical and magnetic properties.[1] This perovskite oxide is prepared by mixing 30-40% PbFe₁₂Ta₁₂O₃ [“PFT”] with 70-60% PbZr₁₂Ti₁₂O₃ [“PZT”] and gives a single-phase crystal with very high-temperature ferroelectricity. Although pure PFT exhibits long-range magnetic ordering only up 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 that 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.

CONTROL OF CORRELATED ELECTRONS IN METAL-OXIDE SUPERLATTICES

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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.

METAL-INSULATOR TRANSITIONS OF CORRELATED ELECTRONS IN OXIDE HETEROSTRUCTURES

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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 $4 \times 10^{19} \text{ cm}^{-3}$, 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 Mott 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.](image-url)
If one can design a hetero-junction that can generate photocurrent from a narrow charge-gap ($\Delta$) 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].

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.

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.

[10] M. Nakano et al., submitted
THEORETICAL DESIGN OF TOPOLOGICAL PHENOMENA

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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, M. S. Bahramy, S. Nakosai, D. Isobe, D. Asahi and R. Arita.

MAGNETIC RECONSTRUCTIONS IN PEROVSKITE HETEROINTERFACES AND ULTRATHIN FILMS

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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 LaAlO₃/SrTiO₃ [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. LaAlO₃/SrTiO₃ heterostructure [3]. (b) Thickness phase diagram of ultrathin La₀.7Sr₀.3MnO₃ thin films [5].


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.](image)

The atomic switch was first developed as a nanoscale, two-terminal, nonvolatile switch with a nanoscale vacuum gap between a solid-electrolyte (Ag$_2$S) 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$_2$S 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], suggesting 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$_2$O$_5$) [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$_2$S) [22, 23] or an ion-transport layer (Ta$_2$O$_5$) [24, 25]. Interestingly, an atomic transistor using Ta$_2$O$_5$ 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 intermediate 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].
