

International Technology Roadmap for Semiconductors
Emerging Research Materials
Strongly Correlated Electron Materials for Beyond CMOS Logic Workshop
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Workshop Summary by Kos Galatsis

Introduction

The Semiconductor Research Corporation (SRC) & National Science Foundation sponsored the Emerging Research Materials Workshop titled “Strongly *Correlated Electron Materials for Beyond CMOS Logic*”. The workshop aimed at exploring the complex nature of strongly correlated electron (SCE) material functionality for possible information processing use. SCE materials incorporate physical interactions such as spin, charge, lattice and orbital hybridization being simultaneously active. As such, complex interactions between electric and magnetic properties and ferromagnetic, anti-ferromagnetic phase transitions occur. Even potentially more interesting is that heterointerfaces formed between correlated materials have new state properties and interfaces to ferromagnetic materials has enabled coupling between ferroelectric properties and ferromagnetic properties in these structures. Most of the existing applications of these materials utilize relatively slow processes for High Tc superconductors, Colossal Magnetoresistance for hard disk read applications, and ferroelectric memories. The challenge is to determine whether these complex interactions can be controlled at high enough speeds and densities to enable new logic device functionality at the nanometer scale. Parameters such as energy, phase switching speed, field required to switch the state, dynamics of the states, and size dependencies need to be quantified to determine if SCE materials could indeed be employed as a building block for an information processing system.

1.0 Beyond CMOS Logic Device Challenge, G. Bourianoff, Intel

The need for new functional materials for beyond CMOS device concepts is considered to be paramount to advance information processing beyond current CMOS functionality. A framework that effectively describes the “beyond CMOS” challenge is described within the research vectors that form the basis of the Nanoelectronics Research Initiative (NRI) program and the guiding principles of ITRS logic devices. These are:

1. **Energy** – explore other state variables other than electronic charge
2. **Noise** - non-equilibrium systems - thermally isolated from the environment bath
3. **Interconnection** – new energy transfer mechanisms
4. **Heat** – thermal management – looking at complex phonon heat transport mechanisms beyond diffusive (too slow)
5. **Manufacturing Cost** – directed self assembly opportunities

Various classes of materials that provide opportunity with respect to the aforementioned research vectors are ferroelectric, ferromagnetic, multiferroics together with their coupling regimes [1] and strongly correlated materials. SCE materials are characterized by spatial complexity, multiple spatially correlated ferroic phases and complex phase stability relationships. Not only are these materials complicated in a bulk regime, but also provide another dimension of complexity (opportunity) at interfaces. In context of the research vectors outlined above, these material offer the following opportunities:

1. **Energy** – Store state in ferroic phase of nanodomain structures
2. **Noise** - Self correcting phase stability may isolate noise

3. **Interconnection** – Utilize conjugate response functions to induce phase change in neighboring nanodomains.
4. **Heat** – Energetics of dynamic phase change unknown
5. **Manufacturing Cost** – directed self assembly opportunities - Multiple competing order parameters (long range – short range) in complex oxides.

The grand challenge of employing such materials for logic is the need to understand dynamics of phase change in multiferroics and SCE materials. Energy, time scales, response functions, conjugate functions, phase diagrams are all critical elements. One prime near term achievement required is to demonstrate conditional phase change induced in adjacent unit cells or across interfaces and programmable phase change sequences in spatially complex arrays.

2.0 Material & Hetero-interface Properties & Phases, M. Kawasaki, Tohoku University

SCE materials exhibit correlated functions via their charge, spin and orbital symmetry [2]. These materials have complex phases that include anti-ferromagnetic or ferromagnetic states which are often coupled to insulating or metallic conducting states and in some cases superconductivity. The key is to create **a phase change through a external stimulus** that will result in a dramatic change in electrical or magnetic properties [2]. **Ionic radius can also be controlled to tune the phase transition and behaviors in oxides such as manganites.** In doing so, it has been shown that phase transition of charge order, spin glass and ferromagnetic phases [3] can be controlled which could induce colossal magnetoresistance (CMR) and colossal electroresistance (CER) [4].

An interesting proposal is for “*orbitronics*” which aims at controlling the electric current and possibly spin by triggering changes in d-electron orbital hybridization that propagate as a wave. This orbital wave could potentially transfer information and is called an “*orbiton*”. Orbital waves are characterized by peaks in orientation dependent Raman spectra that occur at approximately a few times the phonon frequency in LaMnO_3 [5]. Experimental evidence of orbitons being controlled by an electric field **is still required as is the understanding of orbiton dynamics and the energy required to generate an orbiton.**

An important parameter that comes from spin-orbit interactions is the toroidal moment which is the product of polarization and magnetization. For instance, a material such as Ga_2FeO_3 has been shown to possess magnetoelectric properties also in an optical frequency region as revealed by nonlinear Kerr rotation detection [6]. This may have value in electro-magneto-optical devices. This optical technique has also been shown to be applicable for detecting interface magnetism of SCE heteroepitaxial structures [7].

Lastly, a technique to create colossal magnetoresistance is possible via electric control of a frustrated spin-structure. Competition between ferromagnetic, paraelectric, antiferromagnetic and ferroelectric **phases causes phase change at a bi- or multi-critical point by applying electric or a magnetic field on a multiferroic material** [8]. TbMnO_3 exhibits gigantic-magnetoelectric and magnetocapacitance effects, which can be attributed to switching of the electric polarization induced by magnetic fields. Frustrated spin systems therefore provide a new area to search for magnetoelectric media.

Generally, however, it has been acknowledged that speed and kinetics of phase transitions, ordering and state changes requires further investigation. In order to detect these mechanisms, an optical technique is the only available option that allows the capture of fast transitions. In addition, such materials require MBE or PLD and clean interfaces, so that the quality of interfaces are also an key issue. In addition, scaling is a challenge, e.g., how small can the material be scaled to maintain such effects? And how sensitive are they towards strain in the material? Thermal stability is also a key factor with respect to room temp devices, since Curie temperature limitations dictate function of SCE materials.

3.0 Modeling of Dynamic Correlated Electron State Materials, A. Millis, Columbia University

Correlated materials are a broad array of materials that show interesting behaviors based on their correlated electron-electron interactions. Material examples are a) colossal magnetoresistance manganites, b) high temperature superconductors, c) Mott Insulators d) Heavy electron compounds and e) Organic conductors. These materials show functionality associated with many phases and most of these phase transitions are present at low temperature $T_c < T_{\text{room}}$.

The theoretical challenge in tackling correlated electron systems migrates from a) the inherent complexity of solving Schrodinger's equation with a complex wave function, i.e. 1cm^3 solid has 10^{23} particles (co-ordinates) making it extremely difficult to write down and solve such an equation and b) the wave function of electrons are impossible to solve since electrons are fermions and their wave function is antisymmetric – straightforward numerics are not practical. This is known as the fermion sign problem. The density functional based band theory approaches which have been very successful in predicting properties of wide classes of materials have not worked well for correlated electron systems. Density functional methods work well for the ground state and for states with a few particles excited from the ground state into basically free-electron like states. In correlated electron materials the important behavior involves phase transitions involving large numbers of excitations above the ground state. Also the excitations are not band (free-electron) like.

To circumvent these shortfalls we need to identify new kinds of ground states or better methods of calculation. One method is dynamical mean field theory by Metzner/Vollhardt; Mueller Hartmann Kotliar which can now model simple correlated systems [9, 10]. This model is able to calculate local effects, but is not currently capable of modeling the longer range interactions that occur in correlated electron states, which is the next problem to be solved.

Modeling aspects of SCE material behavior such as speed and understanding the dynamics is still under development. Because the potentially important behavior is connected with novel electronic phases and with the transitions between them, this modeling requires control over both the atomic size scales which control the basic physics and over the longer scales associated with the domains of different phases. The frontier research questions relate to the length scales associated with the different phases, the nature of the domain walls between them, and the factors governing the nucleation and motion of phases.

4.0 Dynamic Magneto-electric Coupling at Ferroelectric-Ferromagnetic Interfaces, E. Tsymbal, University of Nebraska

The interplay between ferroelectricity and magnetism allows magnetic control of ferroelectric properties and an electric control of magnetic properties and could yield new device concepts, such as ferroelectric and multiferroic tunnel junctions [11]. A Fe/BaTiO₃ multilayer is a representative composite multiferroic that has been investigated. This choice is motivated by the fact that Fe and BaTiO₃ are two “classical” ferroic materials which have well-known properties in the bulk. It has been shown that a sizable difference exists between magnetic moments of Fe and Ti atoms at the two interfaces, dissimilar by the orientation of the local electric dipole moments exists. The predicted magnetoelectric effect is comparable in magnitude with that observed in elastically coupled composites and opens a new direction to control magnetic properties of thin-film layered structures by electric fields. With increasing BaTiO₃ thickness, the net polarization of the ferroelectric film grows and gradually approaches its bulk value. Since this phenomenon is primarily due to the electronic hybridization between the transition metal elements with less than half occupied d bands (Ti) and more than half occupied d bands (Fe), any ferromagnetic-ferroelectric multilayer with such a combination of elements is predicted to have the magnetoelectric coefficient similar to that found for Fe/BaTiO₃. Also by using a magnetoelectric material instead of antiferromagnetic material, an applied electric field changes the interface magnetic moment through magnetoelectric effect altering the exchange bias field. An example of this is Co/Pt with Cr₂O₃ [12] that shows a passive control and Py with YMnO₃ [13] showing active control.

Ferroelectric tunnel junctions (FTJ) are also interesting since they employ ferroelectric materials between two metal electrodes. It has been shown that a giant electroresistance (GER) is present [14]. The existence of ferroelectricity at such a small film thickness makes it possible to use ferroelectrics as tunnel barriers in metal-ferroelectric-metal (M-FE-M) junctions. Recent experiments indicate that the electrical resistance in M-FE-M junctions with ultrathin barriers depends on the orientation of the electric polarization which can be switched by an applied electric field. It has been shown that the reversal of the electric polarization in the ferroelectric produces a change in the electrostatic potential profile across the junction. This leads to the resistance change which can reach a few orders of magnitude for metal electrodes with significantly different screening lengths. This is the giant electroresistance (GER) effect. The mechanism of FTJ resistance change consists of an a) electrostatic effect, b) interface effect and c) strain effect [15].

Multiferroic Tunnel Junction (MFTJ) is another interesting structure [16]. This method is used for the switching of the spin polarization of the electric current injected into a semiconductor, based on injecting spins from a diluted magnetic semiconductor through a ferroelectric tunnel barrier. It has been shown that the reversal of the electric polarization of the ferroelectric results in a sizable change in the spin polarization of the injected current, thereby providing a two-state electrical control of this spintronic device. It has also been predicted a possibility of switching of tunneling magnetoresistance in magnetic tunnel junctions with a ferroelectric barrier and coexistence of tunneling magnetoresistance and giant electroresistance effects in multiferroic tunnel junctions [17].

Based on the aforementioned effects different memory devices can be implemented such as MRAM, FTJ RAM, MFTJ RAM and electrically controlled MRAM. Oxygen vacancies may affect the operating principle of these device concepts, which require further investigation.

5.0 Hetero-interface properties, G. Koster, Stanford University, and J. Mannhart, Augsburg University

Recent studies of electronic structure at interfaces between perovskite oxides was discussed. Modern atomic-scale growth and probe techniques enable the formation and study of new artificial interface states that are quite distinct from the bulk state. For example, the interface between two insulators, LaAlO_3 and SrTiO_3 , sustains a metallic phase with high carrier mobility for an appropriate atomic arrangement of the interface. Reports show that this interface can be dynamically tuned across a metal-insulator transition by applying an external gate field. The result is a system that can be switched from highly insulating to highly conducting for a wide range of potential device applications [18]. The switching has been demonstrated to have a seven order of magnitude change in resistivity and has a hysteretic effect.

Maintaining pristine growth conditions with control of oxygen vacancies to determine the origin of high mobilities is a challenge. Even with some vacancies within the LaAlO_3 and SrTiO_3 system large mobilities in the range of $10^4 \text{ cm}^2/\text{V}\cdot\text{sec}$ are reported. In addition there is a critical thickness of interface conductance vs the number of LaAlO_3 unit cells. It has been shown that a critical separation distance of six perovskite unit cell layers, corresponding to approximately 23\AA , below which a decrease of the interface conductivity and carrier density occurs. Interestingly, the high carrier mobilities characterizing the separate conducting interfaces are found to be maintained in coupled structures down to subnanometer interface spacing [19]. Theorists have not been able to model such an effect.

By growing precise structures incorporating an external gate, the interface can be statically and dynamically tuned over many orders of magnitude - $R_{\text{on}}/R_{\text{off}} 10^7$ [20]. Due to the long time constant, it was hypothesized that this may be controlled by creation and migration of defects such as oxygen defects. At the high end, the doping levels should allow access to phase transitions that have not been previously reachable. These phase transitions can be precisely traversed and studied. Control of the interface electronic structure is central to the function and improvement of virtually all existing oxide device characteristics. The switching voltages used were very high (60-100V) [20] due to the thick insulating substrate, but it is important to understand the local fields required to cause the formation and elimination

of the conductive interface. It will also be important to determine the fundamental mechanism that enables this switching and determine the role of oxygen related defects or other effects.

6.0 Scanning Probe Characterization of Dynamic Properties, S. Kalinin, Oak Ridge National Laboratory

Coupling between multiple order parameters including ferroelectric polarization, magnetization, and strain, and lattice properties underpins the beautiful physics of multiferroic materials and strongly-correlated oxides. The knowledge of local *static* and *dynamic* coupling between dissimilar order parameters on the nanometer and atomic levels holds the promise of understanding the driving forces behind the phase separation, stripe, spin, charge, and orbital ordering behaviors, and will be the key to future device applications. Recent progress in static and dynamic order parameter measurements in ferroelectric and multiferroic materials on the nanoscale was discussed on an example of Piezoresponse Force Microscopy (PFM). PFM is based on the detection of local piezoelectric deformation in a ferroelectric sample induced by an external electric field [21-27]. The linear coupling between the piezoelectricity and polarization infers that the local polarization can be determined from the sign and amplitude of the field-induced strain. A problem of low sensitivity of a static piezoresponse mode has been circumvented by employing a dynamic piezoresponse imaging method based on the voltage modulation approach, which allows sensitivity to be increased by three orders of magnitude, and development of band excitation method for determination of resonance-enhanced response.

Scanning force microscopy provides a pathway for controlling the ferroelectric properties at the nanoscale and direct studies of the domain structure evolution under an external electric field, temperature, and other stimuli, which cannot be matched by previously available techniques. Furthermore, a conductive probing tip can be used for modification of the initial domain structure. Application of a small dc voltage between the tip and bottom electrode generates an electric field of several hundred kilovolts per centimeter, which is higher than the coercive voltage of most of ferroelectrics, thus inducing local polarization reversal. One of the most important applications of PFM is local piezoelectric spectroscopy, i.e., measurements of local hysteresis loops at the 10 nm level. The vector PFM approach in conjunction with the local switching experiments can be used to analyze the effect of grain crystallographic orientation on the local hysteresis loop parameters, visualize the relationship between switching activity and local microstructure including dislocations, grain boundaries, and domain wall junctions, (switching centers), and presence of long-range correlations in the ferroelectric material. These developments contribute to understanding of the nanoscale functionality of ferroelectric-based devices such as FeRAM and ferroelectric data storage, as well as emerging device concepts such as tunneling barriers, ferroelectric-nanotube hybrid FETs, and self assembled multiferroic heterostructures.

Application of piezoresponse force microscopy to ferroelectrics has opened new possibilities not only for high-resolution imaging of domain structures, but also for quantitative characterization and control of ferroelectric properties at the nanoscale. However, more work is still required to (a) obtain quantitative dynamic switching information of multiferroic materials, (b) achieve sub-nanometer spatial resolutions, (c) high (ideally, nanosecond and below) bandwidth measurements, (d) perform quantitative reproducible measurements, and (e) correlate PFM with other local structural and property probes.

7.0 Nanoscale coupling of dynamic properties, R. Ramesh, U.C. Berkeley

Materials that have coupled electric, magnetic, and structural order parameters that result in simultaneous ferroelectricity, ferromagnetism, and ferroelasticity are known as multiferroics [28]. These compounds present opportunities for potential applications for information storage. However the understanding of ferroelectricity in materials such as BiFeO_3 is still limited, especially when the vertical and lateral dimensions decrease in thin films.

Structure analysis of BiFeO_3 indicates that the crystal structure of the films is monoclinic in contrast to the bulk, which is rhombohedral. The films display a room-temperature spontaneous

polarization (50 to 60 microcoulombs per square centimeter) almost an order of magnitude higher than that of the bulk (6.1 microcoulombs per square centimeter). The observed enhancement is corroborated by first-principles calculations and found to originate from a high sensitivity of the polarization to small changes in lattice parameters. The films also exhibit enhanced thickness-dependent magnetism compared with the bulk. These enhanced and combined functional responses in thin film form present an opportunity to create and implement thin film devices that actively couple the magnetic and ferroelectric order parameters [29].

The first observation of electrical control of antiferromagnetic domain structure in a single-phase multiferroic material at room temperature has been demonstrated [30]. High-resolution images of both antiferromagnetic and ferroelectric domain structures of (001)-oriented multiferroic BiFeO₃ films show a clear domain correlation, indicating a strong coupling between the two types of order. The ferroelectric structure was measured using piezo force microscopy, whereas X-ray photoemission electron microscopy as well as its temperature dependence was used to detect the antiferromagnetic configuration. Antiferromagnetic domain switching induced by ferroelectric polarization has been achieved, in agreement with theoretical predictions. [31]

8.0 Conclusions

It is clear that the complex nature of SCE materials provides a rich source of opportunity in employing phase states for potential memory applications, but a more detailed understanding of the dynamic properties of these materials and the physical mechanisms that enable these is needed before their applicability to logic applications can be assessed. Colossal magnetoresistance and colossal electroresistance are some electronic behavior examples of SCE materials and have found application in memory devices such as MRAM, FTJ RAM, MFTJ RAM and electrically controlled MRAM. The recent progress in developing hetero-interfaces with complex properties may enable control of spin and charge properties, but more understanding of the role of oxygen vacancies and stress at these interfaces is needed.

Beyond CMOS logic needs to have low energy dissipation processes for changing and communicating state information and it is critical to understand the dynamic processes that occur in state changes including the energy dissipated and speed at which they occur. If changes in orbital hybridization can propagate spin and charge state, this could enable reduction in power consumption, but these proposed mechanisms need to be validated in their ability to change and propagate electric and spin state.

It is clear that the complex interplay between charge, spin, lattice and orbitals of SCE materials and their interfaces provide degrees of complexity beyond traditional materials, particularly in engineering and understanding mechanisms at critical points between phases and at interfaces. Specific challenges in context of the 5 research vectors can be summarized as follows:

- **Modeling:** A more mature theoretical understanding of dynamics, temperature influence and size dependencies is required. Current progress is challenged by identifying new kinds of ground states and better methods of calculation such as dynamical mean field theory.
- **Metrology:** More advanced experimental tools to probe magnetic and charge order of these materials and interfaces at the nanometer scale and their dynamic processes is critically needed to assess their potential applicability to logic technologies. Improvements are proceeding via optical and physical probing methods, but more effort is needed to characterize the speed of and mechanisms of transition.
- **Interfaces** are critical and the complexity at interfaces needs to be better understood. Heterointerfaces have enabled new properties and more understanding of the role of structure, composition, defects, and orbital hybridization on interface state and properties is needed

along with the factors that control them. As was shown, the control of the interface electronic structure is central to the function and improvement of virtually all existing oxide device characteristics.

- **Size Dependency:** A key aspect to SCE materials is the dependency of certain domain or smallest element size whilst retaining desirable SCE properties. Such a dependency will limit the potential scalability of this material system.
- **Speed:** Understanding the dynamics from both a theoretical and experimental (metrology) aspect is still needed and currently lacking.

It should be reiterated that SCE materials are complex materials and do indeed provide a rich source of functionality. How such functionality can be usefully captured for information processing still requires more development.

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