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The goal of this research program is to develop atomically smooth, nanostructured, single crystalline, epitaxial complex oxide thin films as the basic building block for a nonvolatile, ultrahigh density, fast, low voltage, radiation-hard memory. Oxide materials exhibit a broad diversity of behavior: transport properties that include superconducting, metallic, semieonducting and insulating ground states; magnetic properties ranging from ferromagretism and colossal magnetoresistance to antiferromagnetism; and dielectric properties ranging from high-k insulating behavior to ferroelectricity, piezoelectricity, and pyroelectricity. The chemical and structural similarity of perovskite oxides makes it possible to combine these various functionalities into epitaxial heterostructures. In this work, the crystallinity and surface quality of epitaxial films and the quality of the interfaces between different oxides are important factors determining device performance.

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The goal of this research program is to develop atomically smooth, nanostructured, single crystalline, epitaxial complex oxide thin films as the basic building block for a nonvolatile, ultrahigh density, fast, low voltage, radiation-hard memory. Oxide materials exhibit a broad diversity of behavior: transport properties that include superconducting, metallic, semiconducting and insulating ground states; magnetic properties ranging from ferromagnetism and colossal magnetoresistance to antiferromagnetism; and dielectric properties ranging from high-k insulating behavior to ferroelectricity, piezoelectricity, and pyroelectricity. The chemical and structural similarity of perovskite oxides makes it possible to combine these various functionalities into epitaxial heterostructures. In this work, the crystallinity and surface quality of epitaxial films and the quality of the interfaces between different oxides are important factors determining device performance.

For this project, we focus on ferroelectric oxides as the underlying component to achieve nonvolatility for memory applications. In particular, we use the permanent, bi-stable polarization (dipole moment) of these materials to represent the on and off states of the memory. Ferroelectric materials are characterized by a spontaneous polarization that is switchable by an applied external electric field. The fast switching times (sub-ns) and small domain sizes (<10 nm) of the polarization are attractive properties for the development of a fast, ultrahigh density, nonvolatile memory. In this project, we examine a variety of issues that affect device capabilities. In particular, we investigate ferroelectric domain size, which will determine device density; we explore the feasibility of ferroelectric field effect transistor architectures using multifunctional metallic oxides; and we examine the possibility of making three dimensional circuits using vertical integration for greatly increased device density.

Using RF magnetron sputtering, we have fabricated high quality, single-crystalline, epitaxial ferroelectric lead zirconate titanate (PZT) thin films on single crystal (001) $SrTiO_3$ (STO) substrates. The crystal structure has been characterized by x-ray diffraction. θ-2θ scans taken along the 001 reflection show c-axis oriented PZT, with the polarization pointing along the surface normal. The high crystalline quality of these films is reflected in the narrow x-ray diffraction rocking curves that have been observed; typical full width at half maxima (FWHM) are ~0.04°. The surface properties have been studied using atomic force microscopy (AFM). Figure 1 shows an AFM image taken on a 300 Å PZT film, revealing a root-mean-square (RMS) surface roughness of 2 Å. Films have been grown with thicknesses ranging from 100 Å to 4000 Å.

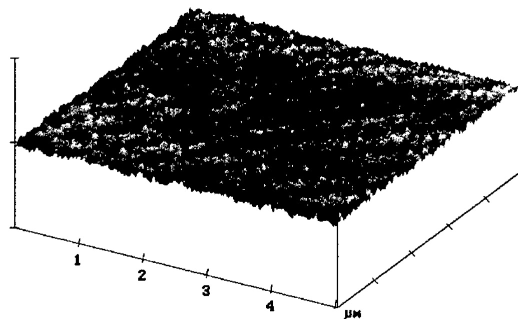

Fig. 1 AFM image taken on a 300 Å PZT film. It has an RMS surface roughness of 2 Å, with atomically smooth terraces separated by 4 Å steps. These steps are due to the slight miscut of the STO substrate.

Atomic force microscopy can also be used to examine domain structure in ferroelectric films. Using an atomic force microscope equipped with a conducting tip, we have carried out studies to polarize and image small ferroelectric domains in PZT films. Voltages larger than the coercive voltage of PZT were applied between the conducting AFM tip and the film substrate to switch the polarization. We imaged the resulting domain structures by applying a voltage smaller than the coercive voltage to the tip while scanning the area of interest, sensing the piezoelectric response [1]. Using this approach, we have written and imaged sub-100 nm domains in ferroelectrics. Figure 2 shows an AFM image of a 5 by 5 array of ferroelectric domains that have been written in a PZT film, with domain sizes as small as 40 nm having been obtained (Figure 2). The corresponding areal density for this bit size is ~100 Gbit/in^2. We have also performed retention time studies of these domains. Dot-shaped, line-shaped, and square-shaped domain structures have been written and imaged, with the resulting structures remaining stable for periods of weeks, the length of the measurements. Currently, the minimum domain size that can be achieved is limited by the radius of curvature of the AFM tip and the length of the voltage pulse applied to the tip.

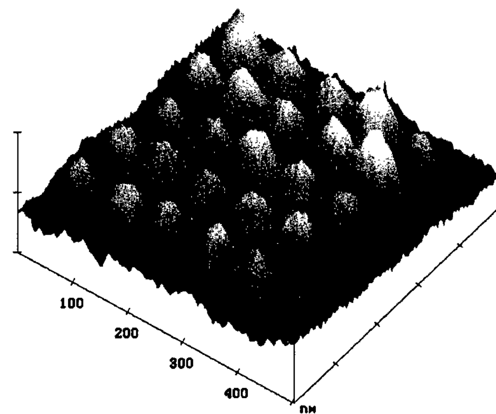

Fig. 2 Piezoelectric image of 25 domains written on a 1000 Å PZT film. The average domain diameter is 40 nm, and the areal density is ~100 Gbit/in^2.

We have also investigated the possibility of making nonvolatile field effect transistors, using the nonvolatile polarization field of PZT to induce an electrostatic field effect in an all-oxide transistor structure. As the conducting medium for the field effect device, we have examined correlated oxide materials, whose diverse electronic behavior, such as superconductivity, ferromagnetism, and colossal magnetoresistance, can be tuned by changing their carrier concentration (Figure 3) [2-8]. Using the field effect approach preserves the field effect device architecture that is ubiquitous in electronic applications; this approach also allows one to integrate the multifunctionality of correlated systems with mainstream semiconductor devices. One challenge in applying this approach to correlated materials, however, is the nearly metallic carrier density at which various phase transitions occur in those materials. The sheet charge modulation required to observe a substantial field effect is on the order of 10^{14} charges/cm^2, an order of magnitude larger than the breakdown field of SiO_2. It has been shown that the

polarization field of ferroelectric materials such as PZT is ~15-45 μC/cm^2 (1-3 x 10^{14} charges/cm^2), which is what is required for field effect studies in correlated oxides. By changing the carrier concentration using the polarization field of PZT, for example, the PI has tuned a high temperature superconductor reversibly between superconducting and insulating behavior [9].

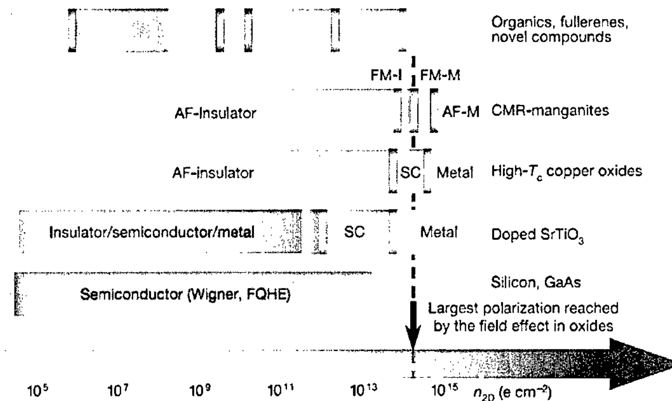

Fig. 3 Schematic illustration of the diverse behavior displayed by correlated materials as a function of carrier concentration. The vertical line is drawn as a reference to show the largest polarization reached by the field effect in oxides [8].

For this project, we have used the colossal magnetoresistance (CMR) materials (manganites) as the conducting medium of the field effect structures. The electronic properties of these materials are sensitive to changes in carrier concentration, as seen in the (La,Sr)MnO_3 system [10]. At low temperatures, $LaMnO_3$ is an antiferromagnetic insulator. When hole doped by Sr via chemical substitution, transitions to ferromagnetic insulating and ferromagnetic metallic phases occur. The carrier concentrations at which this transition occurs are relatively close to those of metals, resulting in a screening length (depletion region) on the order of 1 nm or less. This small depletion width allows for scaling of field effect devices beyond what is possible with silicon technology. It also requires ultrathin CMR films with atomically smooth surfaces to achieve a substantial field effect.

Using RF magnetron sputtering, we have grown epitaxial LSMO films with RMS roughnesses of ~2 Å. The film surfaces consist of atomically smooth terraces, separated by 2 Å high steps. These steps are due to atomic steps on the $SrTiO_3$ substrate used to nucleate epitaxial growth. X-ray diffraction scans show (001) oriented growth of LSMO with a pseudo-cubic lattice constant of ~3.85 Å. No other impurity phases are detected. CMR films as thin as 4 nm have been grown, exhibiting the colossal magnetoresistance effect. Such ultrathin films are required to observe substantial field effects because of the small screening length in these materials.

On top of these LSMO films, we have grown epitaxial PZT layers *in situ* for ferroelectric field effect experiments. X-ray measurements show c-axis oriented PZT. The typically surface roughness of the bi-layer is 4 Å. These PZT/LSMO heterostructures have been patterned into four-point resistivity paths for transport measurements. The

structures are stable, with transport and surface properties having been measured on devices for periods of a year.

Nonvolatile, reversible switching of the transport properties of the LSMO layer has been induced by applying voltage pulses of a few volts across the PZT layer [11]. In Figure 4, a sequence of voltage pulses with alternating positive and negative polarities has been applied to the PZT/LSMO heterostructure. The observed resistivity on/off ratio is ~100, and the interval between each switching is 1 hour. Devices have also been measured after ~1 year, showing that the materials properties are robust.

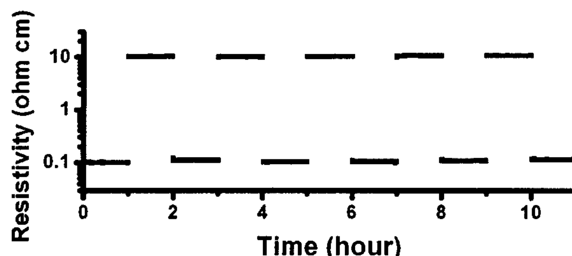

Fig. 4 Resistivity of a PZT/LSMO heterostructure as a function of the polarization state of the PZT layer. To switch the PZT polarization, voltage pulses of alternating polarity have been applied across the PZT layer. The measured on/off ratio is ~100. The interval between each switching is 1 hour.

We have also investigated the switching times of these devices. Voltage pulses with widths ranging from milliseconds to 100 nanoseconds have been applied across the PZT layer, and the resulting conductivity changes have been measured. For large devices (typical feature sizes of several tens of microns), the switching time is several microseconds, consistent with the calculated RC time constant of the circuits. Smaller RC time constants can be achieved by reducing the device dimensions. Using ferroelectric $SrBi_2Ta_2O_9$/Si capacitor structures that have smaller RC time constants, we have observed switching times of less than 10 nanoseconds. Cycling of the capacitors also shows that the ferroelectric maintains its polarization after $>10^{10}$ switching cycles.

Because the complex oxides discussed in this project possess very similar crystal structures, one can consider the growth of epitaxial heterostructures composed of multiple conducting layers separated by insulating buffer layers, which can lead to three-dimensional integrated circuits (3-D ICs). By fabricating high quality conductors and insulators that are all epitaxial, one can acquire the essential elements for a 3-D IC, consisting of multiple layers of planar ICs that are all interconnected, as one proceeds towards a much higher degree of integration than planar ICs can offer.

For the 3-D IC study, we have grown epitaxial heterostructures composed of two layers of ultrathin LSMO sandwiched around a ferroelectric PZT layer [12]. The structural properties of the heterostructures have been examined using x-ray diffraction (Figure 5). Rocking curves taken around the 001 reflection of PZT before and after the deposition of the top LSMO layer have a FWHM of ~0.5°, showing no appreciable degradation after the top LSMO layer has been deposited. The transport properties of the top and bottom LSMO layers have been investigated, with both layers showing similar temperature dependencies of the resistivity and the CMR effect. The magnitude of the CMR effect is consistent with what is observed in single layer LSMO films of this

thickness. Studies of the ferroelectric field effect modulation of the transport properties of the LSMO layers are currently underway.

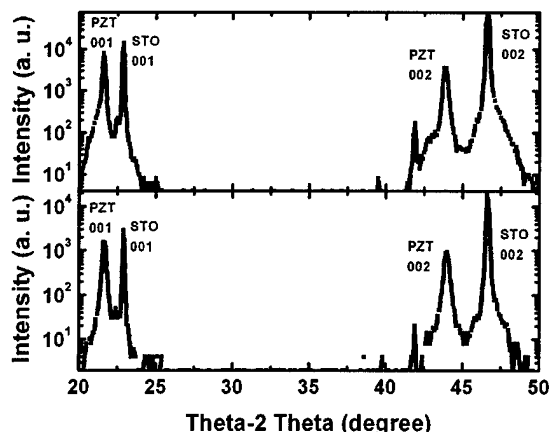

Fig. 5. θ-2θ diffraction scans taken on a 2000 Å PZT/50 Å LSMO film (upper graph); the same film with a 50 Å LSMO film on top (lower graph) [12].

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