278 Materials for Nonvolatile Memory Devices: Magnetoelectric Multiferroics and Resistive Switching Oxides

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Multiferroics, which display simultaneous magnetic, electric, and ferroelastic orderings, have drawn increasing interest in recent years due to their multi-functionality for a variety of device applications, especially in energy efficient non-volatile memory devices and weak magnetic field sensors. These materials are, however, rare at room temperature. We have, therefore, successfully designed a few novel room temperature multiferrics that showed magnetoelectric (ME) behavior. Such properties were observed in bilayers and superlattices of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) with half-metallic oxide $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), fabricated by pulsed laser deposition (PLD) technique. The piezoforce microscopy (PFM) measurements revealed switching of polarization under external bias field confirming ferroelectric behavior. Frequency dependent dielectric anomaly was observed near room temperature suggesting dynamic magneto (resistance)-dielectric coupling. The polarization flop in the presence of magnetic field of merely 0.34 T in bilayers was observed that was explained due to excessive voltage across the PZT layer, causing short-circuiting. This behavior was reversible. Even though the polarization disappearance is not intrinsic, it has potential in many magneto-electronic applications.

Single phase multiferroics were also fabricated by preparing solid solutions of lead zirconate-titanate (PZT) with $Pb(Zr_{0.46}Ti_{0.34}Fe_{0.13}W_{0.7})O_3$ (PFW), $PbFe_{0.5}Ta_{0.5}O_3$ (PFT), or $PbFe_{0.5}Nb_{0.5}O_3$ (PFN). One such compound is $(PbZr_{0.53}Ti_{0.47}\ O_3)_{(1-x)}$- $(PbFe_{0.5}Ta_{0.5}O_3)_x$ (PZTFT) with x=0.3 to 0.4. The resulting material had ultra-low losses (1% or less), which is extremely important for GHz phase-shifters (for which the important device parameter is insertion loss), and these exhibit both ferromagnetic switching and ferroelectric switching up to about 400 K, even though neither PZT nor PFT are magnetic above room temperature. Interestingly this system shows four different crystal phases from 4 K to ~1300 K which are confirmed by x-ray structural studies, dielectric spectroscopy, and Raman spectra. The ME coupling was measured on conducting LSMO coated PZTFT (x= 0.4) ceramic at room temperature, moderate electric control of remanent magnetization and coercive filed was observed. The applied electric field also modified the magnetic coercive field by (50 -100 Oe) which enabled us to compute the ME coefficients as 1.3 x $10e^{-11}$ s/m. The present ME value is comparable to the value obtained for single phase Cr_2O_3, $\alpha \sim 4.1 \times 10^{-12}$ s/m and also for other single phase materials. Interestingly, this material also showed the switching of piezoelectric hysteresis with merely ~ 0.1 tesla of magnetic field, thereby showing large magneto-electric coefficient in this material.

Among all nonvolatile memory device concepts currently being explored to overcome the problems associated with existing charge storage based nonvolatile memories, resistive memory devices based on switching of the resistance between the two or more states (high and low) of resistances through external electrical stimulus has recently gained tremendous attention for the development of next generation low power, high speed, rugged, high density, and nonvolatile resistive random access memory (RRAM) devices. The memory effect in RRAM devices is realized through switching of the resistance of device between the two states (high and low) of resistances. Based on whether the switching characteristic depends on the voltage polarity, resistive switching is generally classified as unipolar and bipolar switching. Switching is termed as unipolar when it is independent of the polarity of the applied voltages. We have studied resistive switching phenomenon in mixed oxides, namely amorphous thin films of Lanthanum based turnery oxides $LaGdO_3$ and

$LaLuO_3$, poly-crystalline thin films of multi-ferroic $BiFeO_3$ and graphene oxide thin films. In case of amorphous lanthanum based ternary oxides and polycrystalline $BiFeO_3$, we observed unipolar resistive switching with well defined and non- overlapping switching voltages although an initial forming process was essential to start repeatable switching. On the other hand, forming free bipolar switching was observed in case of graphene oxide thin films. The switching mechanism in case of Lanthanum based ternary oxides and $BiFeO_3$ was found to follow formation of metallic filaments between the electrodes through the agglomeration of oxygen vacancies and metal atoms in films and their subsequent rupture on application of suitable bias bringing the low and high resistance states. While in case of graphene oxide thin films two resistance states were formed by movement of oxygen ions from the bottom oxide electrode tin-doped indium oxide (ITO) into graphene oxide film and vice versa. The ratio of high (HRS) and low (LRS) resistance states was found to be much higher in case of unipolar switching compared to the case of bipolar switching. However in both the cases the resistance of LRS and HRS showed no obvious degradation for up to $\sim 10^4$ s indicating good data retention.

Recently, we have observed multilevel resistive switching in trilayer stacked geometry composed of graphene nano flakes sandwiched between organic ferroelectric polyvinylidene fluoride layers fabricated by spin coating method, which are expected to fullfill the need of high density data storage memories. External parameters, such as current compliance and induced voltage pulse imposed on the devices provided an aid to tune the inherent resistance states. As fabricated devices exhibited multilevel switching with stable resistance ratios between different resistance states and excellent data retention and endurance. Space charge limited conduction and Fowler-Nordheim (F-N) tunneling were found to be responsible for the switching mechanism. Graphene enriched with trapping sites provides the adequate environment for F-N tunneling process to occur, resulting in multi-bit resistance states. Detailed results of these studies will be presented.