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Temperature-Dependent Electrical Characterization of Multiferroic $BiFeO_3$ Thin Films

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The polarization hysteresis and current leakage characteristics of bismuth ferrite, $BiFeO_3$ (BFO) thin films deposited by pulsed laser deposition was measured while varying the temperature from 80 - 300 K in increments of 10 K, to determine the feasibility of BFO for capacitive applications in memory storage devices. Data is compared to the performance of prototypic ferroelectric barium strontium titanate, $Ba_xSr_{1-x}TiO_3$ (BST) under similar conditions. Finding contacts on the BFO samples that exhibited acceptable dielectric properties was challenging; and once identified, the polarization characteristics between them varied greatly. However, the non-uniformity among the contact points within each sample suggests that either the samples were defective (by contamination or growth process), or that the deposition process of the contacts may have undermined the functionality of the devices. Subjected to increasing temperatures, BFO's polarization improved, and though its polarizability was shown to be inferior to BST, the dielectric loss was less.

Introduction

Multiferroic materials have lately been a subject of interest in material science due to the unique properties that they can possess simultaneously; in fact, a material is called "multiferroic" if it exhibits two or more of the following characteristics: ferroelectricity, ferromagnetism, or ferroelasticity. Multiferroics are rare, and rarer still is a multiferroic that performs at room temperature. The potential applications that exist if one is found that could also be made cheaply and compatible with existing technology make multiferroics worthy of further investigation.

The desire to improve upon the existing technology that enables our everyday devices such as smart cards, flash drives, and computers has led to the investigation of higher-performance materials with regard to memory storage capacity and write/erase efficiency.[1] Ferroics are uniquely capable of adapting to a variety of tasks within information storage technology due to their ability to exhibit hysteresis-a quality by which they are able to retain a switchable, permanent polarization (ferroelectric), magnetization (ferromagnetic), or deformation (ferroelastic) when once exposed to an electric or magnetic field, or mechanical stress. The polarization that can be induced in the material can function as binary for storage in a non-volatile memory device that can easily be rewritten when exposed to another field, or stored indefinitely.

Ferroelectric devices can be tuned, or adjusted, simply by subjecting them to an electric field-a very precise, cheap, and contact-less technology.[2] There is a remarkable range of applications in addition to information storage that exploit the piezoelectric and pyroelectric qualities that all ferroelectric materials possess.[3] Microactuators and transducers can be created because mechanical stress induces charge in the material (piezoelectric), and infrared sensors as well as thermal sensors and images are possible because ferroelectrics detect heat (pyroelectric).

Bismuth ferrite, $BiFeO_3$ (BFO), a perovskite crystal that is multiferroic at room temperature[4], has been identified as a possible alternative to barium strontium titanate, $Ba_xSr_{1-x}TiO_3$ (BST), a known ferroelectric that is currently used in industry. Though BST has the advantage of a higher polarizability at room temperature than BFO, it is not multiferroic, and researchers are hoping to cultivate BFO's ferromagnetic properties to produce a higher-performance device. However, it is the ferroelectric properties of BFO that are the concern of the present study, in particular its pyroelectric qualities. BFO's ability to induce charge under varying thermal and electric fields is the chief object of this research, and is what makes bismuth ferrite a valuable material, and possible alternative to BST, for a wide range of commercial applications.

Synthesis of Bismuth Ferrite

There are several ways to grow thin-film BFO, one of which is by a pulsed laser deposition process, in which a laser is focused onto the surface of a solid body to remove the material by evaporation or sublimation processes, after which the particles organize onto a substrate.[5] Chemical vapor deposition is another method to deposit thin films in which the constituent elements of the desired material are introduced as gases in the vicinity of a heated substrate, onto which they combine. Finally, there is the molecular-beam epitaxy process, in which "beams of atoms or molecules in an ultra-high vacuum environment are incident crystal that as previously been processed to

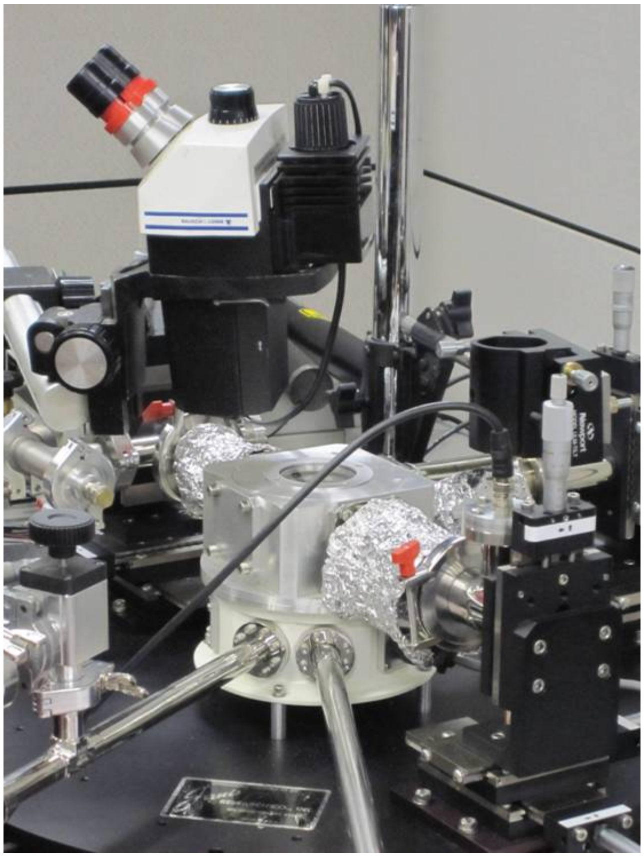
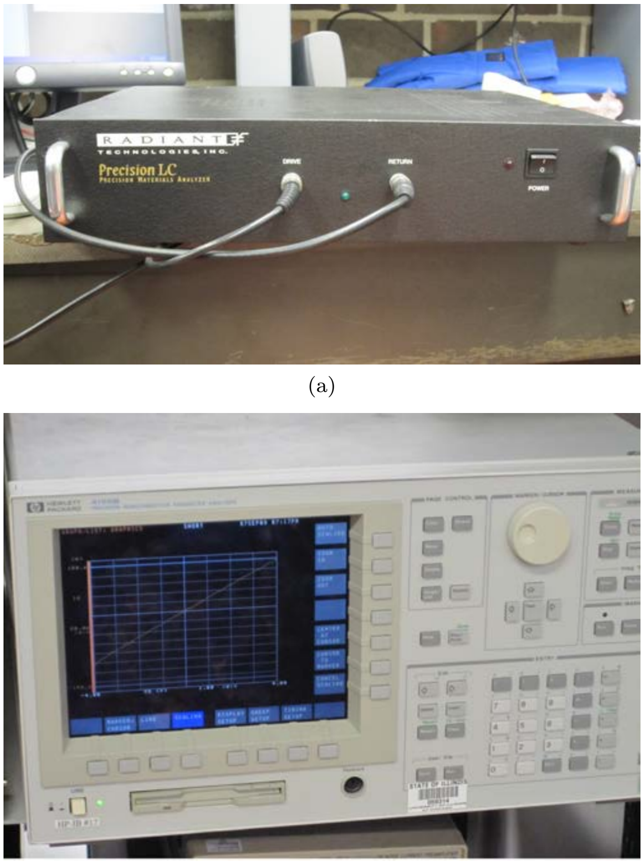


FIG. 1: The probe station houses our sample in a pressure and temperature-controlled chamber.



(a)

(b)

FIG. 2: The probe station: a) material analyzer; b) semiconductor parameter analyzer.

produce a nearly atomically clean surface. The arriving constituent atoms form a crystalline layer in registry with the substrate. . . ."[6]

Our BFO was grown by pulsed laser deposition to a thickness of 300 nm on a substrate of strontium titanate, a material that was chosen because its lattice structure is a close match to most perovskite crystals. During fabrication, gold and platinum contacts (thickness of 100 nm and 50 nm respectively) with an area of 0.25 cm^2 were deposited on the sample by an electron beam using a shadow mask. Before measurements could begin it was necessary to ground our sample on a solid gold plate using a silver paste adhesive to ensure that proper conduction would occur between the sample and the ground.

Procedure

To observe the variations in polarizability and current leakage characteristics of BFO while changing temperature, it was necessary to house our samples in a pressure and temperature-controlled probe station. Liquid nitrogen was used to vary the temperature between 80 K and 300 K in increments of 10 K. Pressure was kept at 4 mTorr.

The probe station was connected to a material analyzer which provided information about polarization (input parameters being contact area and material thickness), while supplying a voltage varying between -4 and 4 V to the sample.

A semiconductor parameter analyzer, also connected to the probe station, was used to plot current as a function of electric field in order to evaluate the current leakage characteristics of the sample. Before any temperature measurements could begin, it was necessary that all of the contacts on each sample be probed to discover their polarizability at room temperature. Because we were interested in the dielectric behavior of BFO, only contacts exhibiting a hysteresis were selected for our measurements (see Figures 3 and 4). Realizing that any significant pressure from the probe onto the sample could influence polarity due to BFO's piezoelectric properties, it was important that undue pressure be avoided while probing. However, while too much pressure on the sample was undesirable, too little pressure would not ensure sufficient conduction to the probe. As a result, much care was taken to avoid both extremes.

Each of the gold contacts on the BFO samples was sus-

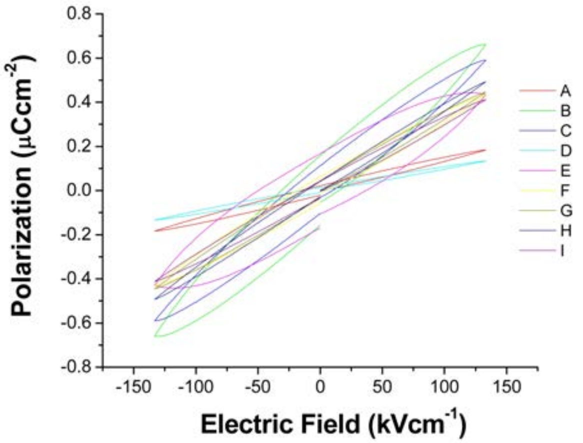


FIG. 3: Polarization versus electric field curves for nine capacitive contacts on BFO sample. They displayed widely varying polarization at room temperature.

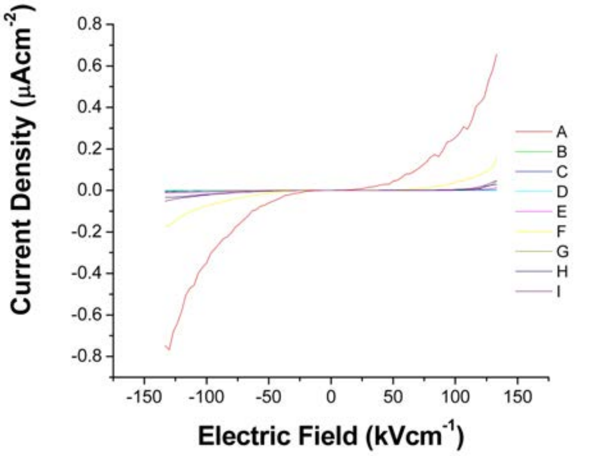


FIG. 4: Current density versus electric field curves for nine capacitive contacts on BFO sample. The nine contacts display similar current leakage characteristics, excepting one particularly leaky device (shown in red).

ceptible to scratching by the probe. Much of this could not be helped; in fact, it was not possible to tell that contact had been with the probe unless a small scratch was visible on the gold. Over the course of the experiment, however, too much of the gold was scratched from the surface of the contacts, altering the area of each contact, and thus the software parameters of the material analyzer. This necessitated a redeposition of the contacts, but it was discovered that the redeposited contacts did not behave on the sample as they had previously.

Expectations

It has been documented that the crystalline structure of bismuth ferrite undergoes a phase change at 140 K and 200 K [7] possibly due to spin-reorientation transitions;[8] however it is unknown exactly how the temperature-induced phase shift influences polarity and dielectric leakage. Leakage current is expected to improve at lower temperatures due to the smaller number of charge carriers available. In semiconducting materials, whose lattice structure is not altered by temperature, this should also improve the polarity of our material: less current leaking into the circuit means that more charge is kept separate and contained in the capacitor. However, because BFO's lattice does change, it is unknown how polarizability is affected after these critical temperatures.

Ideally, relative uniformity in dielectric performance is expected between contacts; however, some variation can be explained by the crystal's morphology. A single crystal sample should be uniform throughout because of its homogenous arrangement. If our sample is polycrystalline, there will be groupings of similar contacts within an area that are distinguishable from its neighbors; whereas an amorphous sample will not appear to have any particular unity among its contact points.

Experimental Results

We have examined two samples of bismuth ferrite, each of which has approximately twenty-three contacts. Only nine contacts exhibited a capacitive hysteresis on one sample, and two in the other. The other sites were purely resistive. The nine capacitive contacts were not similar in their polarization, however, as exhibited by the hysteresis loops in Figure 3. It is clear that some of the devices have a much larger polarization under the same electric field than others, as evidenced by their wider loops. Both Figures 3 and 4 are measurements taken at room temperature, and the colored loops in both graphs represent the same contact point.

Because several of the capacitive contacts appeared in spatial proximity to each other on the sample, this might indicate a polycrystalline lattice structure in our BFO; however, the predominance of resistive over capacitive contacts is a puzzling find that could possibly be attributed to defects in the samples resulting from inefficiencies in the laser fluence during fabrication, or in the deposition of contact points that fail to achieve proper conduction with the material.

Current leakage characteristics are summarized in Figure 4. There does not appear to be any correlation between polarization and current leakage in the data. Only two of the nine capacitive contacts on the first sample retained a capacitive hysteresis after redeposition of the contacts. The others exhibited purely resistive behavior. The second sample lost both of its capacitive sites, and functioned purely as a resistor.

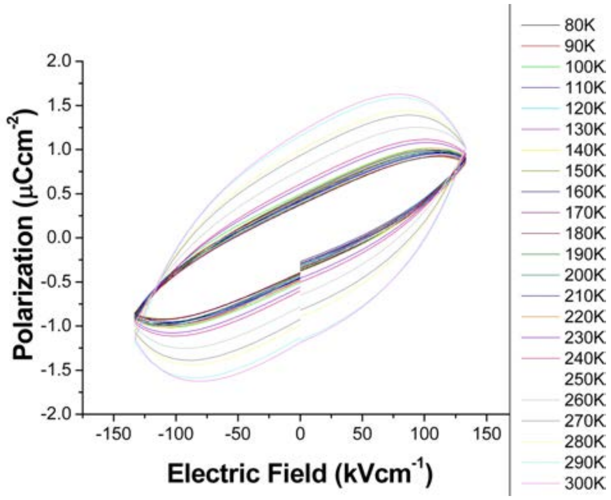


FIG. 5: Polarization versus electric field curves for one BFO contact described over ranging temperatures. Higher temperatures are associated with wider hysteresis loops.

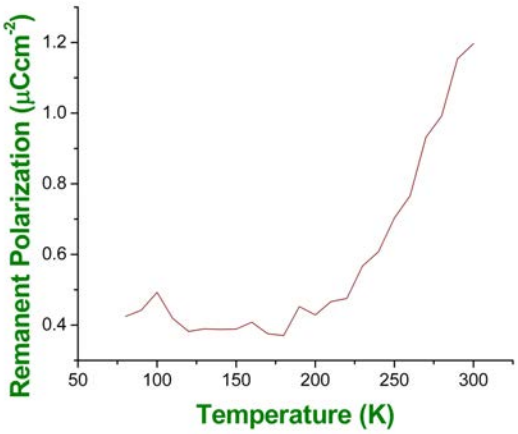


FIG. 6: Remanent polarization versus temperature for one BFO contact at -1.5 V. Polarization markedly increases after 200 K.

Figure 5 is temperature-controlled data taken from one of the two capacitive sites. The hysteresis loops shown there seem to suggest a correlation between increasing temperatures and greater polarizability. This occurrence may be explained by the predicted lattice structural changes at 140 K and 200 K. Further research that details the changing lattice of the crystal should be conducted on BFO samples under a high-resolution electron microscope in order to better understand this phenomenon.

In comparison to current data of BST (composed as $Ba_{0.75}Sr_{0.25}TiO_3$) grown by pulsed laser deposition and of the same thickness as our samples (300 nm),[9] it is clear that our BFO's dielectric performance is inferior. At approximately 300 K (25° C) the BST thin film's hysteresis loop ranges between -5 and 5 $\frac{\mu C}{cm^2}$, while the loop in Figure 5 is roughly between -1.5 and 1.5 $\frac{\mu C}{cm^2}$. It should be noted that while the polarization of BST was measured between -5 and 5 V (as opposed to -4 and 4 V for our BFO), the comparison still demonstrates a more effective polarizability in BST within the same parameters.

In order to better illustrate the association of BFO's polarizability with temperature, the remanent polarization was plotted for data associated to -1.5 V (see Figure 6). A fairly constant polarization is visible between 0.4 $\frac{\mu C}{cm^2}$ and 0.5$\frac{\mu C}{cm^2}$ until approximately 200 K, at which it sharply increases. The current leakage characteristics behave as expected over a varying temperature. The influx of charge carriers that exists at higher temperatures allow more current to leak from the device, an occurrence which Figure 8 appears to confirm.

Compared to current data[10], BFO is considerably less leaky than $Ba_{0.6}Sr_{0.4}TiO_3$ (BST). This is evidenced where non-annealed BST's leakage at room temperature is shown to be in the order of milliamps, while BFO's leakage is a fraction of a microampere.

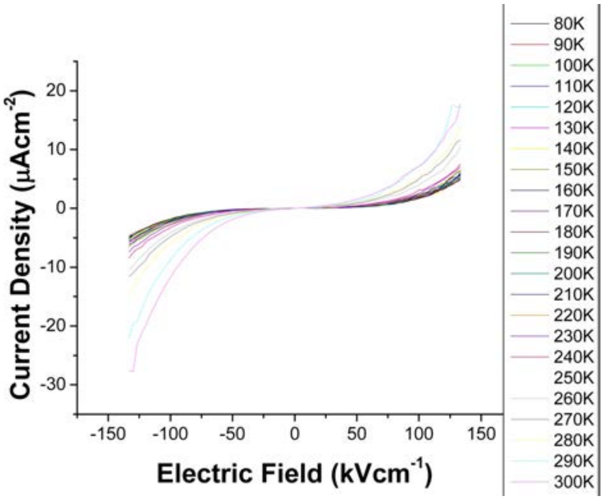


FIG. 7: Current density versus electric field for one BFO contact described over ranging temperatures. Current leakage in the dielectric increases at higher temperatures.

Conclusion

The samples of BFO that were used in this research were not characterized by dielectric behavior. Selecting contacts that displayed appropriate capacitive characteristics was difficult; careful probing was necessary due to the piezoelectricity of the material, and upon redeposition of the contacts most of their capacitive func-

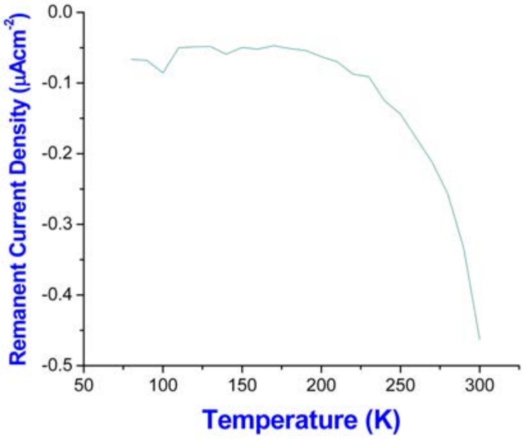


FIG. 8: Remanent current density versus temperature field for one BFO contact at -1.5 V. The absolute value of the current increases with increasing temperatures.

tionality was lost. Prior to redeposition, there were approximately nine capacitive contacts whose polarizability at room temperature varied greatly. However, the contact that was selected for the temperature-varying measurements displayed a marked increase in polarization with increasing temperatures. While more experiments utilizing high-resolution electron microscopy should be conducted to observe the structural changes that occur within the lattice of the crystal, it appears that there is a discernable change in dielectric as well as leakage characteristics after approximately 200 K. Under similar growth and testing conditions, BFO does not appear to polarize as effectively as $Ba_{0.75}Sr_{0.25}TiO_3$), and its dielectric loss was less than $Ba_{0.6}Sr_{0.4}TiO_3$.

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