FERROELECTRIC THIN FILM RESEARCH AT RIT

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ABSTRACT

At RIT, a sol-gel method is being used to synthesize lead zirconate titanate (PZT). Techniques available to characterize these films include scanning electron microscopy , ellipsometry, energy dispersive analysis using X-rays (EDAX), and X-ray diffraction (XRD) to determine crystallinity. After heating above the Curie temperature, XRD indicated that a perovskite structure, known to be ferroelectric, was obtained for a PZT film.

INTRODUCTION

Of the 32 crystal classes, some are unique in that their structure provides for two different stable polarization states [1]. This effect is known as ferroelectricity and can be utilized to create a nonvolatile memory cell. Hence, concerns, such as power loss, which are inherent in the volatile nature of DRAMs and SRAMs may be eliminated. Additionally, ferroelectrics can achieve high density like DRAMs, but without the need for three dimensional fabrication of trench capacitors. Ferroelectrics also offer the promise of radiation hardness and also better endurance than EEPROMs [2]. Hence, the potential of ferroelectrics has led to a surge in reasearch and development.

A diagram of a crystal which exhibits ferroelectricity is shown in Figure 1. When an electric field is applied the domains, ordered parallel electric dipoles, can be switched from one direction of polarization of alignment to another.

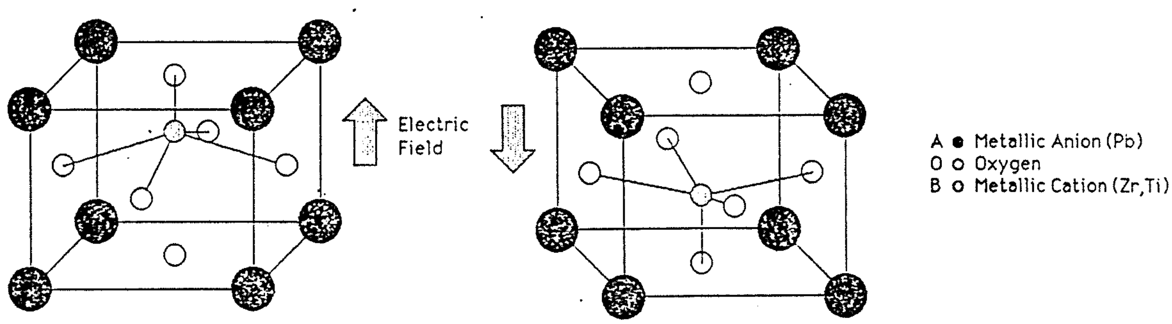


Figure 1: Crystal structure exhibiting ferroelectricity.

The perovskite structure is one type of crystal which exhibits ferroelectric behavior and is compatible with semiconductor standards. The crystal has the form ABO_3 where A metallic ions are situated at the corners of the cell, and a B metallic ion at the center. The arrangement gives rise to an octahedral cage, from which the middle metallic ion can be displaced into either two different positions. Various elements have been utilized, notably barium and titanium ($BaTiO_3$) [3], however the perovskite containing lead with zirconium and titanium (PZT) has proven to have better characteristics [2].

The relationship between applied voltage and resulting polarization charge exhibits a hysteresis behavior as shown in Figure 2. In 1921, this phenomenom was inaccurately termed ferroelectric because of its resemblance to behavior found in magnetic materials. As voltage is increased the ferroelectric will reach a point, known as saturation polarization, where almost all of the domains have been aligned. Any further increase will result in a negligible increase; however, too much voltage may result in breakdown. Once saturated, upon removal of the electric field a significant number of domains will retain their state. The two zero-field points are referred to as remanent polarization. Thus, binary application can be achieved by defining one state to be a "0" and the other a "1". The amount of voltage necessary to switch the polarization state is known as the coercive field. In order to be assimilated into microelectronics, the magnitudes of these parameters need to meet current specification, such as a 5 V power supply.

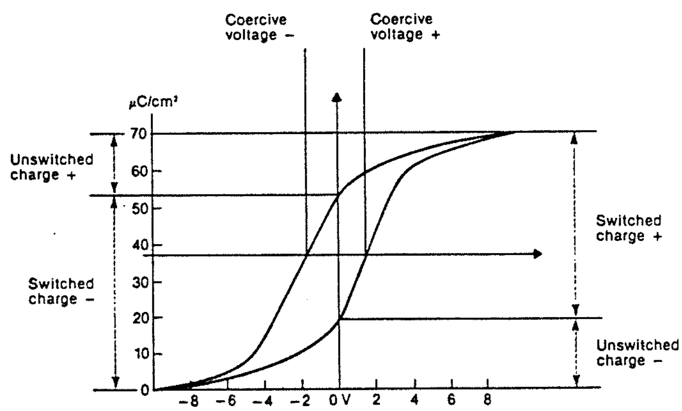


Figure 2: Polarization vs. Electric Field [2].

Perovskites have been made utilizing familiar techniques such as sputtering and CVD, as well as more exotic techniques like sol-gel, laser ablation. Sol-gel is considered the most feasible method for college research since only a basic chemistry set up is needed - no expensive machines [4]. Coincidentally, as it turns out the sol-gel process has become a leading method because more uniform films can be obtained. In this work, preliminary studies were begun in sol-gel preparation and material characterization. Long range goals involve development of a ferroelectric thin film for applications in ferroelectric RAMs (FRAMS).

Currently two companies market FRAMs; Ramtron of Colorado Springs utilizes sputtering of ferroelectric material in creating a cell which is used for back up of SRAMs; the polarization occurs within 10-20ns, well before the RAM loses its state. Krysalis of Albuquerque reportedly uses a sol-gel process in order to fabricate a cell which is used as the primary storage element, like that of a DRAM [5]. Figure 3 illustrates a possible implementation of a ferroelectric memory cell.

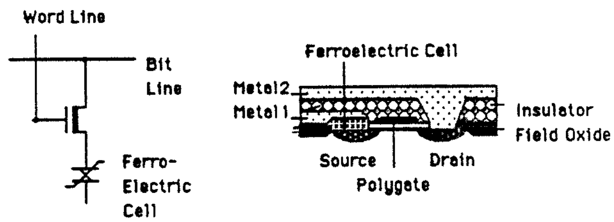


Figure 3: Memory Cell (FRAM) Realization.

It should be emphasized that although ferroelectrics have high dielectric constants, from 1000-1500 [2], the cells, though sometimes termed capacitors and whose symbol resembles a capacitor are not such - their nonvolatility is possible due to its bistable nature. A true capacitor has inherent lossy characteristics which, besides requiring refresh, render it volatile.

EXPERIMENT

The method of sol-gel preparation, derived from Gurkovich and Blum [6] and annealing information from Budd, Dey, and Payne [7], was used to obtain $(Pb_{1.1}Zr_{0.5}Ti_{0.5})O_3$. During the synthesis the solution and vapor temperature were monitored. Distillate was captured after each distillation to aid in quantifying the process. Due to their moisture sensitivity, the isopropoxides were handled in a nitrogen ambient.

The complex was coated onto glass slides. At this juncture, the components are in an amorphous state. In order to facilitate crystal formation, the complex must be heated in order to give the components sufficient energy to crystallize. This threshold is known as the Curie temperature. The heat treatment of the films consisted first of an initial softbake in an oven at 185°C for 20 minutes to drive off solvents, then an anneal in a furnace in nitrogen at 650°C for 10 minutes.

PZT thin films on bare silicon and on glass were studied using an ellipsometer, SEM, and EDAX and XRD. Ellipsometry was used to obtain refractive index and thickness inforamtion. A Nanometrics Cwikscan/100 SEM and an optical microscope were utilized in order to study surface morphology. EDAX was performed to determine the composition of the film. X-ray diffraction was performed on a Riguka machine with a copper K-alpha source in order to determine the crystallinity.

RESULTS/DISCUSSION

Figure 4 is the liquid and vapor temperatures recorded during synthesis of the PZT complex. A three-neck flask containing 25ml of 2-methoxyethanol anhydrous was heated to distill off any water. The linear rise in temperature between times 0 and 8 minutes confirmed the solvent's purity. Upon cooling to 56°C, 11.48g (0.03026 mol) of lead (II) acetate trihydrate was added. The solution was reheated to the boiling point of 2-methoxyethanol (124-125°C), in order to remove the water, which would otherwise react with the isopropoxides. The kink in the temperature plot at 112°C is evidence of water. Upon cooling to 77°C, it was rediluted with 15ml of solvent. The rapid rate of temperature between times 70 to 75 minutes indicated most of the water had been removed.

The solution cooled to 73°C, at which time 4.1ml (0.01378 mol) of titanium (IV) isopropoxide and 5.39g (0.01375 mol) of zirconium (IV) isopropoxide isopropanol complex were added. At this time the color of the solution went from a light opaqueness to a golden yellow. The complex was again heated and at approximately 95°C the isopropanol distilled off. Afterwards the temperature of the solution, now unimpeded, rose quickly to the b.p. of 2-methoxyethanol. After about 5 minutes at this level the heating was stopped and the solution was left to cool. The complex was filtered through glass wool during which 10ml of solvent was used to aid in the recovery of the complex.

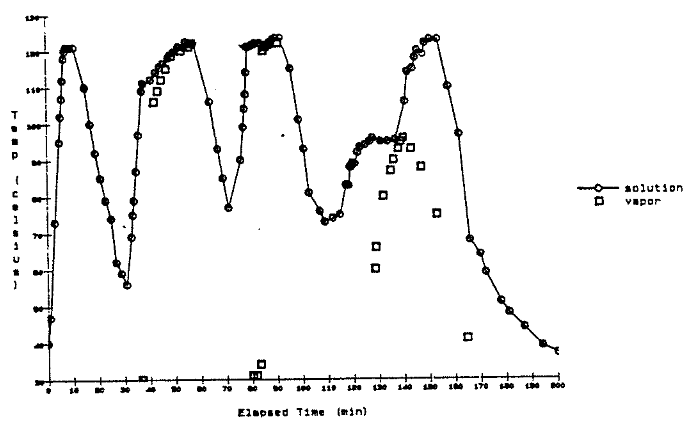
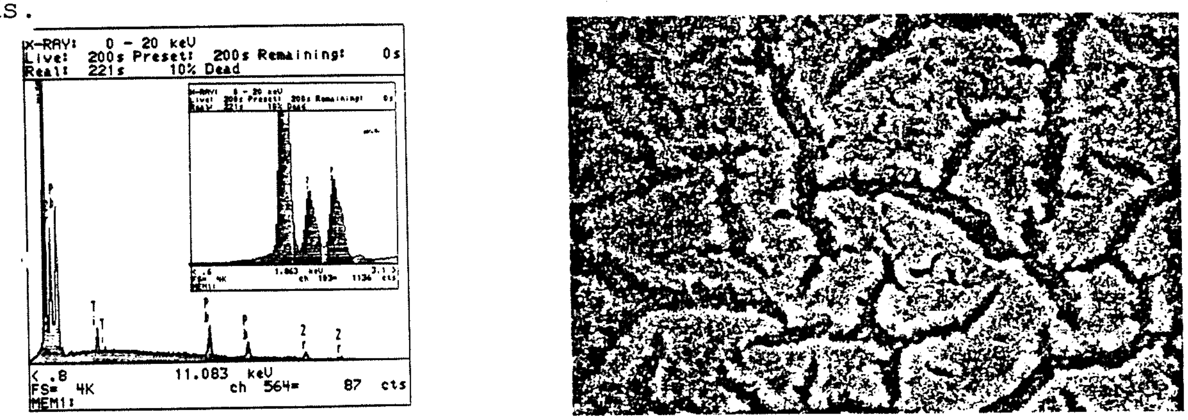


Figure 4: Sol-gel temperature monitoring.

From ellipsometry measurements on three films with different compositions it was observed that as the nominal percent of zirconium increased from 25-100%, the real refractive index of the film varied from 2.0 to 2.6. Results indicated that the films were about 2000Å. After firing a 100Å decrease was observed.

For some spin-coated films, an optical scope revealed that density of material decreased radially. Hence, the current coating method using a static dispense needs to be optimized or an an alternative method such as dipping may be needed. In general, proper control of the viscosity of the solution along with a smooth heating procedure will be needed to form uniform films.

EDAX information is shown in Figure 5a. The spectrum shows all elements to be present. No quantitative analysis was attempted.The scanning electron micrograph in Figure 5 gives insight into the film's uniformity and porosity. Obviously, cracking is a concernthat must be addressed if these films are to be used as FRAMs.



(a) (b)

Figure 5: a) EDAX b) SEM of PZT.

From the XRD spectrum in Figure 6, the atomic plane spacings in Table 1 were found by solving Bragg's Law. They are characteristic of the perovskite phase which is a known ferroelectric [8]. In addition to the annealed slice, a film which had been dried at room temperature was analyzed and found to be amorphous.

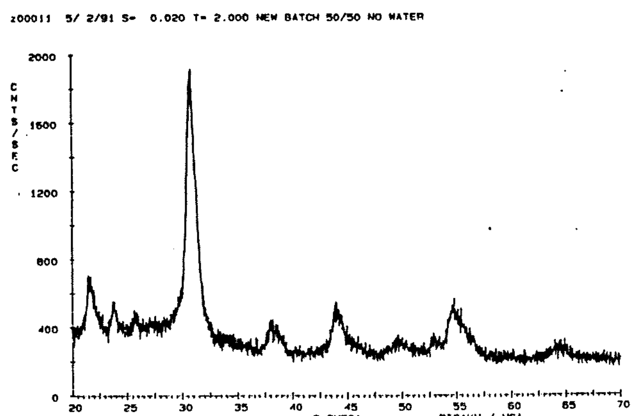


Figure 6: X-ray diffraction on $Pb_{1.1}Zr_{0.5}Ti_{0.5}O_3$.

Table 1: Plane Computations Using Bragg's Law

			d(Å)	
2(Θ)	Θ	Sin(Θ)	RIT	Okada
21.5	10.3	0.179	4.30	4.10
30.5	15.3	0.264	2.92	2.90
38.0	19.0	0.326	2.36	2.33
44.0	22.0	0.375	2.05	2.05
49.5	24.8	0.419	1.84	1.84
54.5	27.3	0.459	1.68	1.67

A capacitor has yet to be fabricated, but before building one it will be necessary to find suitable electrodes which can withstand the annealing of PZT while also promoting uniform crystal growth. Aluminum, which with silicon has a eutectic of 577°C, can be deposited as one of the electrodes provided the anneal temperature is below 550°C. The perovskite structure is obtainable at a minimum temperature of about 500°C, however a lower temperature may result in a pyrochlore phase which is not ferroelectric. Therefore anneal studies will be necessary.

CONCLUSION

A sol-gel process has been developed to produce the PZT complex. An anneal procedure at 650°C for 10 minutes successfully formed the perovskite structure needed for ferroelectric applications. Refinement of both film formation and analysis is needed.

ACKNOWLEDGEMENTS

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