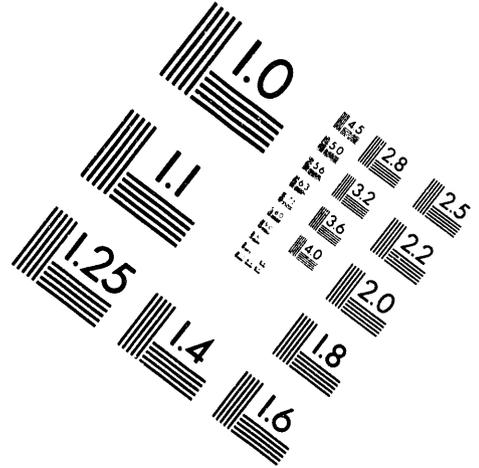
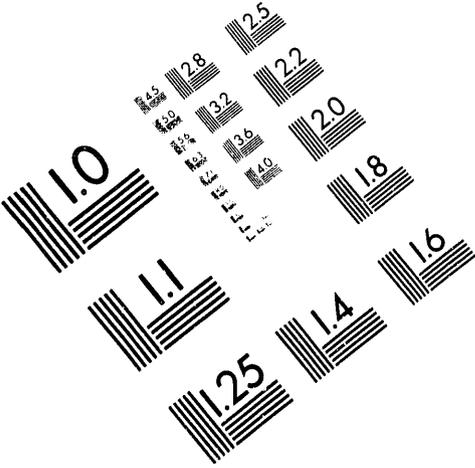




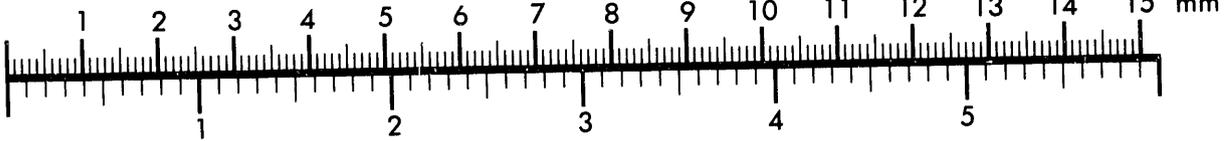
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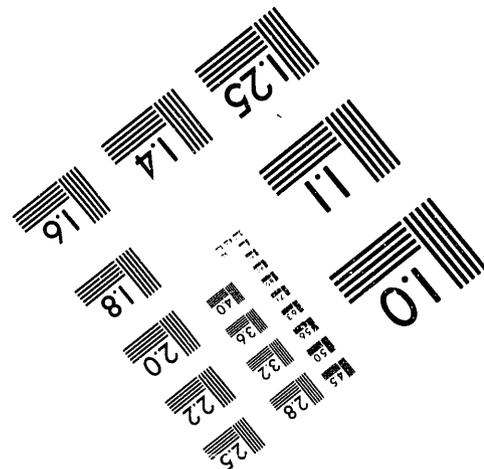
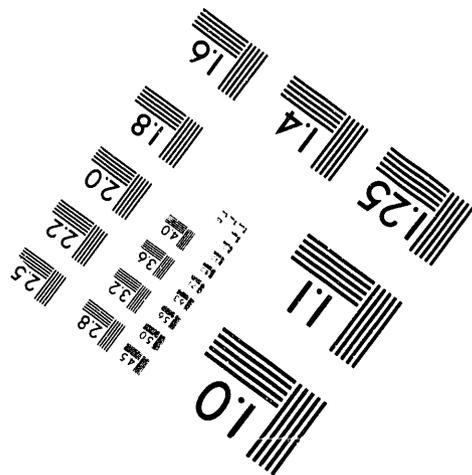
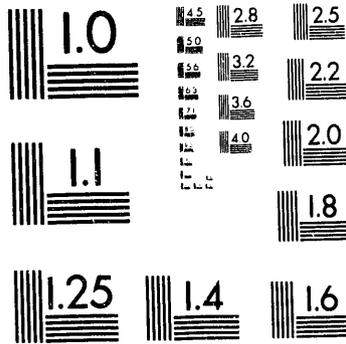
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ABSTRACT

We have optimized the ferroelectric properties and microstructural characteristics of sol-gel PZT thin films used in a CMOS-integrated, 256 bit ferroelectric non-volatile memory. The sol-gel process utilized in our work involved the reaction of Zr n-butoxide, Ti isopropoxide, and Pb (IV) acetate in a methanol/acetic acid solvent system. A 10-factor screening experiment identified solution concentration, acetic acid addition, and water volume as the solution chemistry factors having the most significant effects on the remanent polarization, coercive field, ferroelectric loop quality, and microstructural quality. The optimal values for these factors were determined by running a 3-factor uniform shell design, modelling the responses, and testing the models at the predicted optimal conditions. The optimized solution chemistry generated 3-layer, 300-400 nm thick films on RuO₂ coated silicon substrates with coercive fields of less than 25 kV/cm (a 40-50 % improvement over the original solution chemistry), a remanent polarization of 25-30 $\mu\text{C}/\text{cm}$, and a reduction in the pyrochlore phase content below observable levels.

INTRODUCTION

PZT thin films are being investigated for an increasing number of diverse applications, including non-volatile memories, decoupling capacitors, optical storage devices, and DRAMs [1-4]. Sol-gel processing is proving to be a powerful technique for generating these films with the required tailored properties. However, there is still a very large gap in our understanding of the cause and effect relationships between the solution chemistry and the resulting ferroelectric properties. This is due, in large part, to the complexity of the sol-gel chemistry as well as the complexity of the physical transformation of the sol to the crystalline film. Studies of the solution chemistry effects in our system utilizing alkoxide/acetate precursors in methanol/acetic acid have provided a better understanding of what reactions are occurring and how reaction byproducts are an important factor in controlling reaction equilibria and rates [5,6]. Yet even with this information, we are not yet able to accurately predict how to manipulate the processing factors or chemical reactions to produce desired ferroelectric properties.

One approach to building this understanding is to systematically evaluate the solution chemistry factors and develop models relating ferroelectric properties to these factors. The work described below is in support of a program to build a 256 bit ferroelectric non-volatile memory. The sol-gel process employed in this work utilized Zr and Ti alkoxides and Pb(IV) acetate in a methanol/acetic acid solvent system. An improvement in coercive field (to meet voltage operating requirements) and in PZT microstructure (to achieve the required yield for $5\mu\text{m} \times 5\mu\text{m}$ capacitors) was the goal of this study.

The initial phase of the study involved screening a number of solution chemistry and processing factors to identify those having the greatest impact on properties. This was followed by a statistical experimental design which generated data for modelling the various responses. The models were then tested and an optimized solution chemistry was identified.

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EXPERIMENTAL

Solution Synthesis, Film Fabrication, and Electrical Property Characterization

The Inverted Mixing Order process, employed in this study, is a modification of the process of Yi, Wu, and Sayer [7] in which the order of precursor addition has been reversed. All films were 53:47 compositions with 10% excess Pb. The process flow diagram is shown in Figure 1. PZT films were deposited on silicon substrates with RuO₂ bottom electrodes by spin coating for 30 sec. Film thicknesses varied from 0.1 to 0.8 μm, depending on the number of layers, the solution concentration, and the spinner speed. Individual layers were heat treated at 310°C for 3 min to decompose the residual organics. The films were crystallized at 675°C for 30 min (50°C/min ramp rate) in ambient air. Ferroelectric properties were measured on a Radiant Technologies RT66A operated in virtual ground mode with an applied field of 250 kV/cm.

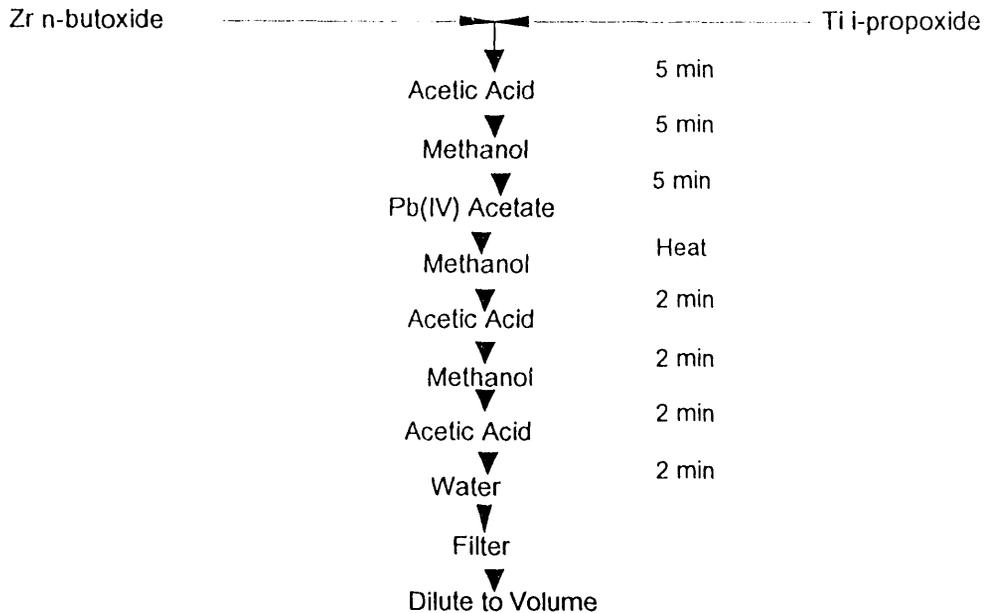


Figure 1. The IMO Process

Plackett-Burman Screening Study

Ten factors (eight solution chemistry, two film deposition) were initially identified as potentially having significant effects on material properties. To fully model this number of factors would require well over 100 experiments. To reduce this task to a manageable level it was necessary to screen the factors to identify those having the greatest impact on the desired responses. A modified Plackett-Burman screening design, requiring only 15 experiments, was employed [8]. Table I lists the factors, the range of factor levels, and for comparison, the nominal values. The range of design values was chosen to be as wide as technically reasonable, and if possible, to bracket the nominal values.

Response Surface Modelling

From the screening study three factors were identified as having significant effects on several of the measured responses. A three-factor uniform shell design was chosen (see Figure 2 for a graphical representation) [9]. This allowed for either a Main Effects + Interactions (ME+I) model or a Quadratic model to be fitted to the data. The center point of the design was run in triplicate. All other factors were set to their nominal values.

Table I. Plackett-Burman Screening Design Factors

Variable	Screening Values (Low or High)	Nominal Value
Zr/Ti Reaction Time	0 or 15 min	5 min
Acetic Acid Amount	¼ or 2 times nominal	4:1 HOAc to Zr+Ti
Acetic Acid Reaction Time	0 or 15 min	5 min
Solution Concentration	0.4 or 0.8 M	0.4 M
Pb Dissolution Temperature	75 or 100°C	75°C
Refluxing	No or Yes	No
Post-dissolution Acetic Acid	0 or 10 mL	10 mL
Water Volume	0.5 or 5 mL	2 mL
Number of Film Layers	2 or 4	4
Spinner Speed	1000 or 6000 rpm	3000 rpm

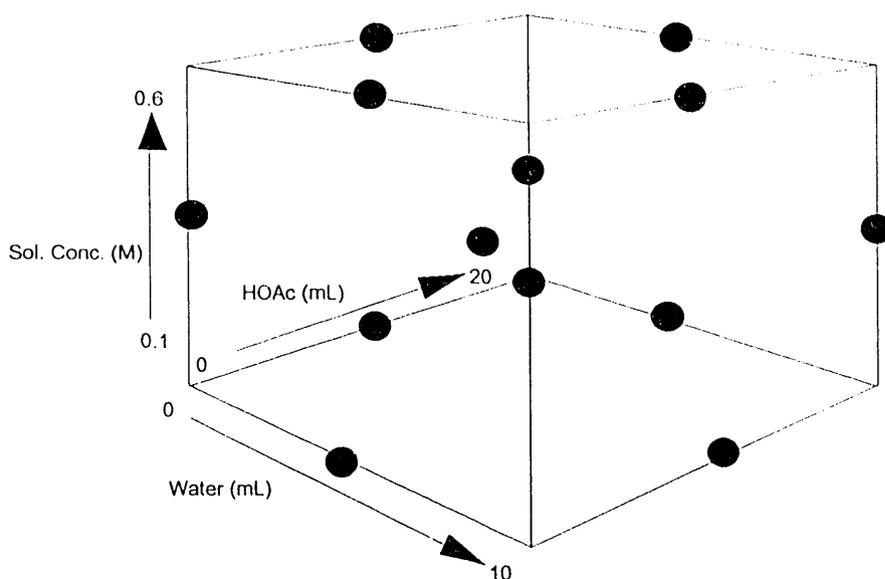


Figure 2. Uniform Shell Design for 3 Factors

RESULTS AND DISCUSSION

Plackett-Burman Screening Study

The value of a screening design is that the effects of a large number of factors can be evaluated with relatively few experiments. However, there is a trade-off. The results from the screening design are confounded; that is, the main effect (the effect of a single factor) and interactions (effects produced by the synergism or antagonism of two or more factors) are combined. The simplifying assumption invoked (and it is generally valid) is that main effects will dominate.

Table II summarizes the results of the screening study. Six of the ten factors had statistically significant effects on one or more of the responses. Several of the responses showed no measurable dependence on any of the factors. However, several factors exhibited strong effects on coercive field, the ferroelectric response we were most interested in improving. Three factors (post-dissolution acetic acid, solution concentration, and water volume) were chosen for further study. These factors also exhibited statistically significant effects on several of the other responses. Looking at the direction of effects for the three major factors it can be seen that the desired direction of change is antagonistic among the responses. For example, to improve coercive field (i.e., lowering the value) the model requires increasing the solution concentration. However, the models for loop quality (higher values are associated with higher quality), P_r , and capacitor yield all require decreasing solution concentration to improve those properties. Clearly the optimized

conditions will be a compromise and therefore are not readily predictable without a more detailed examination of their effects and possible interactions.

Table II. Summary of the Plackett-Burman Screening Study

Decreasing Fit to the Model →

Decreasing Importance of Factor ↓	Coercive Field	Loop Quality	Remanent Polar.	Capacitor Yield
	Post HOAc (-)	Post HOAc (-)	Post HOAc (-)	Sol'n Conc. (-)
	Sol'n Conc. (-)	Sol'n Conc. (-)	# of Layers (+)	
	Water Vol. (-)	Spinner Speed (+)	Sol'n Conc. (-)	
	Initial HOAc (+)	Water Vol. (-)		
	Spinner Speed (+)	Initial HOAc(-)		

Note: The sign associated with the factor indicates the direction of the effect from the low level to the high level (e.g., a "Sol'n Conc. (-)" indicates that the numerical value of the response decreases from 0.4 M to 0.8 M).

Response Surface Modelling

A three-factor uniform shell design was performed to study the effects of solution concentration, the post-dissolution acetic acid amount, and the water volume in more detail. Table III lists the range of values measured for the responses. The bottom row of the table gives the values for the nominal composition. No individual design run had the best value for all responses, but several compositions yielded responses that were each individually superior to those of the nominal composition.

Table III. Summary of the 3-Factor Uniform Shell Design Results

	P_r ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	V_c (V)	Capacitor Yield (%)	Microstruc. Quality (0-5)*	Loop Quality**
Design Runs	0 - 47.2	0 - 78.9	26.1 - 200+	0.96 - 4.97	0 - 100	0 - 5	0 - 105
Nominal	23 - 30	45 - 50	40 - 45	1.5 - 2.0	90 - 100	3	40

* 0 (poorly defined) to 5 (fully dense microstructure with 1-5 μm rosettes)

** A figure of merit to quantify hysteresis loop quality using P_r , P_s , and E_c .

Two models were fitted to the data. An ME+I model allows for simple response surfaces. The quadratic model allows for more complex response surfaces, including curvature. As an illustrative example, the coercive field models are presented below. All the other models had similar shaped response surfaces.

Main Effects + Interactions Model

$$E_c = 102.1 + 35.6 * X_1 - 86.0 * X_2 + 4.4 * X_3 + 9.6 * X_1 * X_2 + 0.8 * X_1 * X_3 - 9.7 * X_2 * X_3 \quad (1)$$

Quadratic Model

$$E_c = 31.7 + 35.6 * X_1 - 86.0 * X_2 + 4.4 * X_3 + 9.6 * X_1 * X_2 + 0.8 * X_1 * X_3 - 9.7 * X_2 * X_3 + 36.1 * X_1^2 + 42.9 * X_2^2 + 44.1 * X_3^2 \quad (2)$$

Where X_1 = Acetic Acid; X_2 = Solution Concentration; X_3 = Water Volume in normalized design units (-1 to +1).

From inspection of the models it can be seen that solution concentration is the dominant factor in determining E_c . Solution concentration is the dominant term in all of the other response models

as well. To determine the optimal composition a grid search program was run with criteria set for each response. A "sweet spot", a composition or compositions meeting all criteria, was identified from each model (see Table IV).

Table IV. Criteria and "Sweet Spots" for Each Model

Criteria for selecting "sweet spots":

$P_r \geq 25 \mu\text{C}/\text{cm}^2$ $P_s \geq 40 \mu\text{C}/\text{cm}^2$ V_c 0.5 to 1.5 V E_c 10 to 40 kV/cm
 Capacitor Yield $\geq 99\%$ Microstructural Quality ≥ 4 Loop Quality ≥ 50

	Main Effects + Interactions	Quadratic
Post Dissolution Acetic Acid	0 - 4 mL	5 - 10 mL
Solution Concentration	0.50 - 0.54 M	0.56 M
Water Volume	0 - 6 mL	9 - 10 mL

Common between the models is the higher solution concentration, but as might be expected, it is not at the maximum value of the modelled space. Acetic acid ranged from zero up to the nominal composition volume. The water volume covered the entire design space, but both "sweet spot" regions favored water volumes greater than nominal. To test the models three compositions were run; one from the ME+I model and two from the Quadratic model. The compositions and property results are presented in Table V along with the nominal composition for comparison.

Table V. Comparison of the Nominal Composition with the "Sweet Spots"

	Acetic Acid (mL)	Sol'n Conc. (M)	Water Vol. (mL)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	V_c (V)	Micro. Quality	Loop Quality
Nominal	10	0.40	2	27	43	1.7	3	40
ME+I	0	0.50	5	26.9	23.9	1.0	4	105.2
Quad. 1	10	0.56	10	25.0	33.2	1.2	4	50.0
Quad. 2	5	0.56	10	29.6	33.0	1.2	3	41.4

All three "sweet spot" runs met the predicted criteria and were an improvement over the nominal composition, particularly with respect to E_c . The ME+I "Sweet Spot" was the superior composition, showing improvements over the nominal composition in every measured response except for P_r where it maintained the nominal value. Comparison of actual values to the model is of limited value. Several of the samples in the original design had extremely poor properties and the measured values for polarization and coercive field were quantitatively meaningless. However, these values qualitatively represented the responses. Therefore, the models generated were successfully used to predict compositional areas to investigate, rather than to quantitatively predict actual film properties.

As for using the information from this study to develop a more fundamental understanding of the solution chemistry, some cautious conclusions can be drawn. The compositions that represented improved properties were consistent with a solution chemistry that generates a denser, perhaps more highly crosslinked structure. Increasing the water volume would be expected to increase hydrolysis, generating more species for condensation. However, water is a byproduct of some of the condensation reactions, and therefore excess water could inhibit condensation. Similar effects have been noted in the PbTiO_3 system [10]. With solution concentration, a higher concentration should promote condensation and aid film densification by reducing the amount of organic removal required. But too high of a concentration leads to film cracking and organic removal problems. The role of acetic acid following the Pb dissolution is not well understood. Sufficient acetic acid is added prior to the lead acetate to completely chelate the Zr/Ti alkoxides. However, the post-dissolution acetic acid may be more than a simple solvent. It may be acting as a

weak acid catalyst. Acid catalysis leads to linear polymerization rather than crosslinkages in many sol-gel systems, whereas base catalysis generally promotes crosslinking [11].

Some preliminary work has been done to test these ideas. If crosslinking is important, substituting a base for the acetic acid at the back end of the process would be expected to yield improved films. When ammonium hydroxide was used in place of the post-dissolution acetic acid, a dense film microstructure with no observable pyrochlore was generated. However, the ferroelectric properties were only comparable to the nominal composition. The role of solution concentration remains to be resolved. It may be a physical effect; a denser gel/film as a result of less solvent/organics. Or the sol may have a different polymeric structure due to concentration effects on reaction equilibria. Additional experimentation will be required to resolve this, possibly by studying dilution and viscosity effects.

CONCLUSION

A sol-gel process utilizing alkoxide and acetate precursors in an acetic acid/methanol solvent system was optimized to generate 53/47 PZT thin films with improved microstructure and ferroelectric properties. Ten solution chemistry and film processing factors were screened for their ability to measurably impact a variety of responses. The three most statistically significant factors with respect to coercive field (post-dissolution acetic acid, solution concentration, and water volume) were evaluated in greater detail using 3-factor uniform shell design. Models generated from the data identified several compositions predicted to be superior to the nominal composition. Testing of these models confirmed these compositions as superior. Coercive field was reduced from over 40 kV/cm to less than 25 kV/cm. Pyrochlore phase clearly visible in the nominal composition films was no longer observable in the optimized composition films.

ACKNOWLEDGMENTS

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