

CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter will be divided into three sections. The first section is detailed description of the sol-gel process for PZT thin films, including the preparation of the stock solutions and the fabrication of thin films. The second section is detailed description of thick film or sol-gel based composites, including the preparation of sol-gel based composites and the fabrication of thick films. The last section discusses characterization techniques, including room temperature X-ray diffraction (XRD) and the Field Emission Scanning Electron Microscope (FESEM). Moreover, this section discusses a description of the electrical characterization, using standard measurements for the polarization hysteresis and dielectric constant.

3.1 Sol-gel Process and Thin Film Preparation

3.1.1 Preparation of Stock Solution

In this study, the preparation of stock solution was carried out by a method similar to that reported by Budd et al. (1985), Udayakumar (1992) and Aungkavattana (1996). Thin ferroelectric films of lead zirconate titanate, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, were prepared from metal alkoxide precursors. Lead acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_3\cdot 3\text{H}_2\text{O}$, titanium (IV) isopropoxide, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, and zirconium (IV) n-propoxide, $\text{Zr}(\text{OCH}(\text{CH}_3)_2)_4$, were used as the precursors. These chemicals were purchased from Fluka Chemica, Switzerland.

2-methoxyethanol, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, was used as a solvent. It was purchased from Carlo Erba Reagenti. Figure 3.1 shows a schematic chart of sol-gel processing and the PZT thin film preparation.

Lead acetate trihydrate was dissolved and distilled in 2-methoxyethanol in a three-neck flask at 125°C for approximately 3 hours to get rid of residual water under flowing argon gas. In order to compensate for lead loss on heat treatment during sintering state, addition of excess Pb in the solution was used. For this study, amount of mole% excess Pb was varied in the range of 0 to 10 mole%. After that, the dehydrated solution was cooled to room temperature and subsequently mixed with zirconium (IV) n-propoxide and titanium (IV) isopropoxide under the ambient air. The mixture was then refluxed at 90°C for 4-5 hours under flowing argon gas in order to promote dissolution and reaction of the lead acetate. The final concentration of obtained solution was 0.88 mol/l of 2-methoxyethanol. Upon cooling, the solution was then diluted to form a 0.3M stock solution. Since the solution was prepared under the ambient air, the stock solution provided partial hydrolysis by no added H_2O and 4 vol% of formamide was mixed in order to obtain crack-free films.

3.1.2 Thin Film Fabrication

The substrates used in this study were Pt-coated Si substrates (Nova electronic Materials, Inc., Richardson, TX, USA). The Pt-coated Si substrates were 3-inch Si wafers coated with 1 micron of thermally oxidized layer and a 200 \AA Ti interlayer to promote bonding of the top $1000\text{-}1500 \text{ \AA}$ layer of sputtered platinum. The Pt-coated Si substrates were cleaned by immersion in 2-methoxyethanol. Thin films were deposited on the substrates by spin-coater

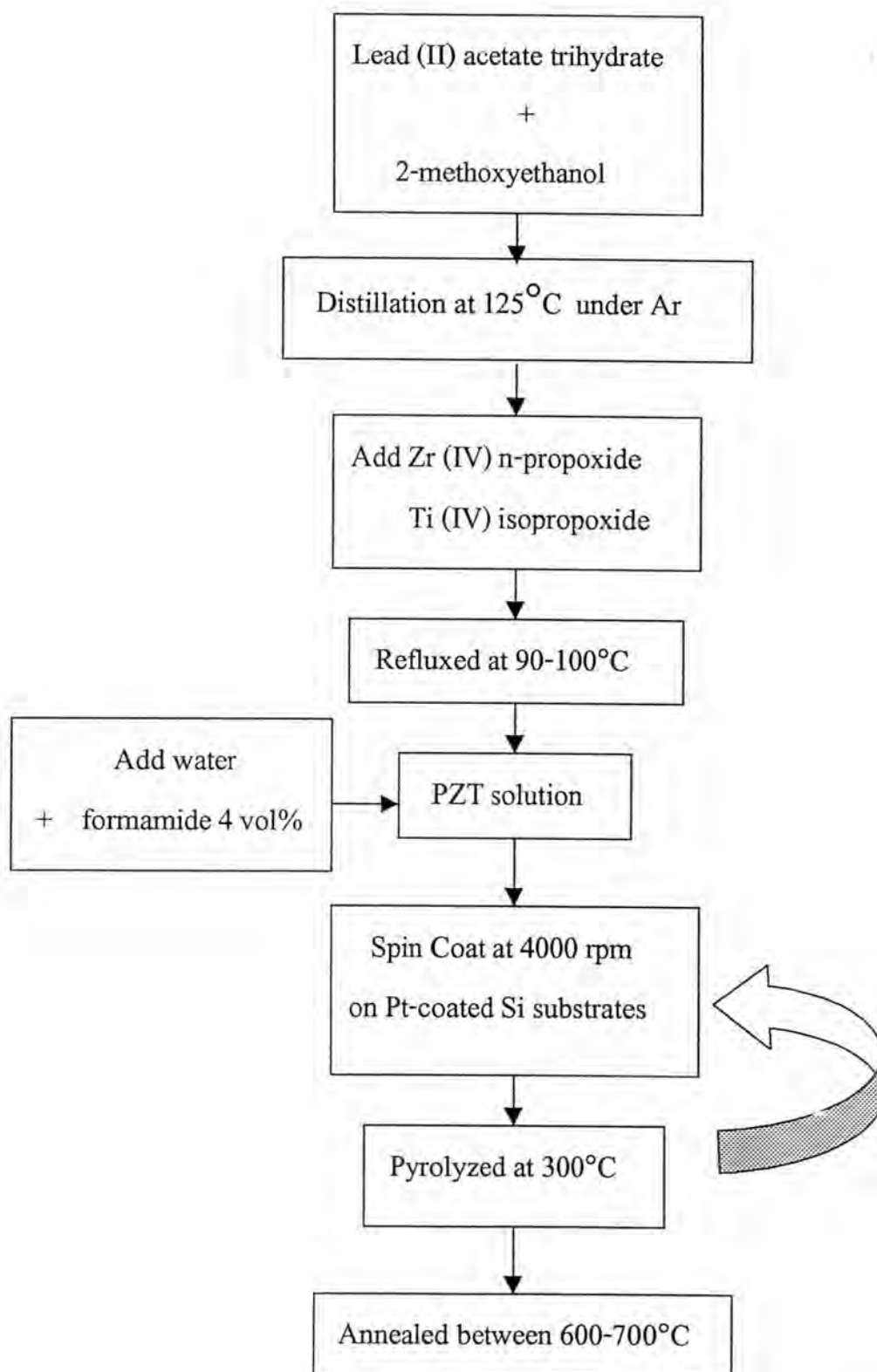


Figure 3.1 A schematic chart of sol-gel processing and the PZT thin film preparation.

(Model No.P6206 Indianapolis. In. USA). The precursor solution was spin-coated at 4000 rpm for 30 seconds. Then, the films were pyrolyzed on a heating hot plate for 2 minutes in air at 300°C in order to remove water and the residual organics. The deposition-pyrolysis cycle was repeated until the desired thickness was obtained. In this study, 5 layers of solution were deposited onto the substrates in order to achieve film thickness approximately 3000 Å. After that, films were annealed at 600°C to 700°C for 30 to 60 minutes in an electric box furnace at 5°C/minute.

3.2 Powder and Thick Film Preparation

The thick PZT films were fabricated by preparing sol-gel based composites which composed of PZT powders and PZT sol-gel solution. PZT powders were fabricated by mixed oxides or conventional method. PZT sol-gel solution was fabricated by using the recipe of Budd et al. (1986).

3.2.1 Powder Preparation

Figure 3.2 shows a flow diagram of PZT powder preparation. PZT (52/48) powders were prepared by mixing oxides from reagent grade (purity \geq 99%) lead oxide yellow, PbO, Zirconium (IV) oxide, ZrO₂, and Titanium dioxide, TiO₂. These chemicals were purchased from Fluka Chemica, Switzerland. The weighed oxides were homogenized by wet-ball milling for 24 hours (using partial stabilized ZrO₂ media with diameter of 10 mm and deionized water). Then, the mixed oxide powders were dried at 120°C for 24 hours. After that, the dried powders were calcined at 800°C for 4 hrs. In order to decrease in size of PZT powders, the calcined powders were milled by

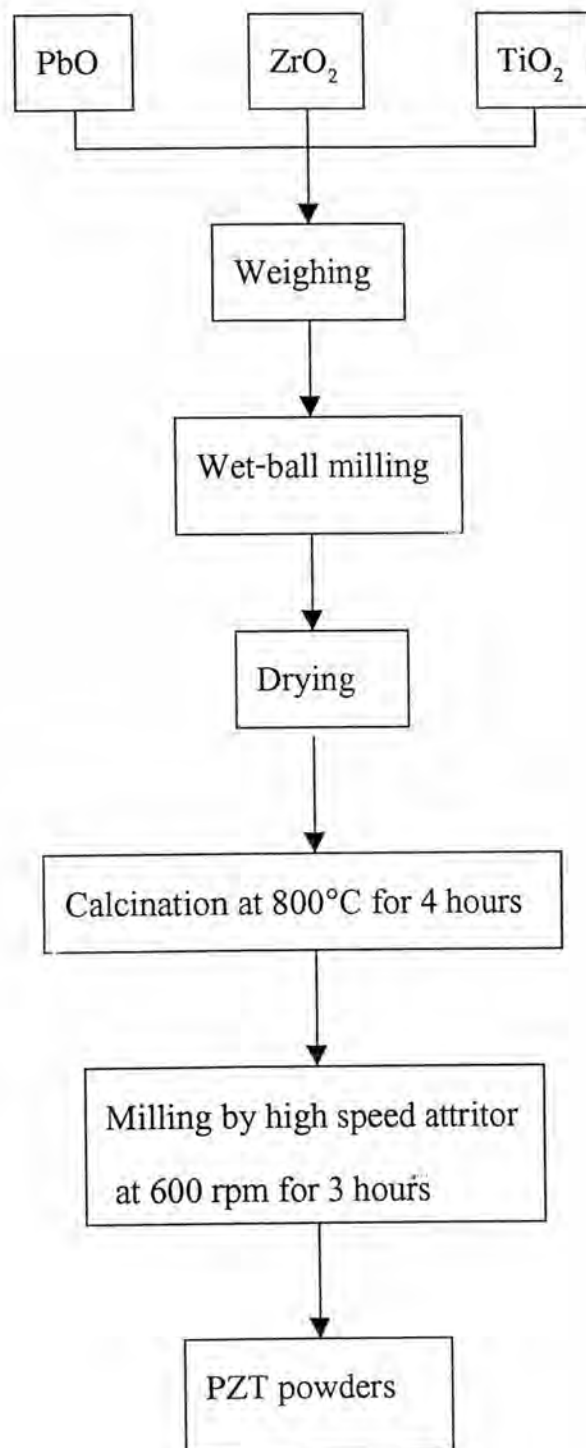


Figure 3.2 A flow diagram of PZT powder preparation.

attritor (Szegvari attritor Model 01-HD Series) at 600 rpm for 3 hours (using Y_2O_3 media with diameter of 3 mm and deionized water). Then, the particle size distribution of PZT powders was characterized by using laser light scattering technique (Mastersizer S Ver. 2.11, Malven Instruments Ltd.,UK)

3.2.2 Thick Film Preparation

To produce sol-gel based composites, PZT powders were dispersed in PZT sol-gel acted as an organic vehicle. After that, the mixture was milled for 24 hours (using partial stabilized ZrO_2 media with diameter of 5 mm). Then, the resulting paste can be printed onto Pt-coated Si substrate using a screen printing method. The mesh count of 77 strands per cm was used in this study.

3.3 Characterization

Phase was monitored by X-ray diffractometer. The thickness of the film deposited on a substrate and the microstructure were determined by the Field Emission Scanning Electron Microscope. For electrical characterization of the annealed PZT thin films, ferroelectric measurement was done using RT66A standardized ferroelectric test system. The capacitance and dielectric loss were measured by using HP 4192A Impedance analyzer. The dielectric constant was calculated from the obtained capacitance.

3.3.1 Structural Characterization

The structure of PZT powders and PZT films were identified using room temperature X-ray Diffractometer (JEOL: JDX-3530) with monochromatic

CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). XRD patterns were recorded at a scan rate of 0.5 sec^{-1} . The 2-theta range scanned was from 20° to 60° . Step scan with a sampling interval is 0.02° . XRD systems utilized Bragg-Brentano (Cullity 1978) diffractometer (2θ - θ mode) and glancing angle method were used in this study.

3.3.2 Microstructural and Chemical Composition Characterization

The microstructure of the PZT films was studied using Field Emission Scanning Electron Microscope (FE-SEM). A JEOL JSM-6301F which is operated with a cold cathode field emission electron gun (FEG) as an electron source. This source is up to five orders of magnitude greater in brightness than conventional thermionic tungsten or lanthanum boride guns. The other advantages of FE-SEM are the followings:

- provide a high resolution scanning electron microscopy image;
- enhance signal-to-noise ratios for a smaller probe size;
- give an ultimate spatial resolution of 1.5 nm at an operating potential of 30 KeV and magnification of 10 to 500,000X;
- minimize charging problems in poorly conducting specimens.

Moreover, when a specimen is irradiated with an electron probe, x-rays are generated from the specimen. Detection of x-rays by energy dispersive detection system (EDS) was used to analyze chemical composition in the electron microscope.

3.3.3 Electrical Characterization

For electrical characterization, gold top electrodes with an area of $7.065 \times 10^{-4} \text{ cm}^2$ were sputtered onto the film surfaces using a shadow mask method. One corner of films was etched away using hydrofluoric acid (HF) until the platinum bottom electrode was exposed. Sample configuration for electrical measurements of the PZT films was shown in Figure 3.3. At least 10 capacitance measurements and 10 Polarization-Electric field (P-E) measurement were performed on different dot capacitors for each sample.

P-E hysteresis was measured using standardized RT66A ferroelectric tester. RT66A test system was fully automated and controlled by a personal computer. RT66A test unit block diagram is shown in Figure 3.4. Hysteresis measurements were run at the frequency of 60 Hz and applied voltage of 7 volts under the virtual ground mode as seen in Figure 3.5.

To measure the capacitance and dielectric loss of the films at room temperature, a Hewlett Packard multi-frequency LCR meter (HP 4192A Impedance analyzer) was used at 1kHz. The dielectric constant (K) can be calculated from the following equation:

$$K = C t / \epsilon_0 A$$

Where K represents the dielectric constant, C is the capacitance, t is the film thickness, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-14} \text{ F/cm}$) and A is the area of electrode which $7.065 \times 10^{-4} \text{ cm}^2$ is used in this study.

Sample configuration for electrical measurements

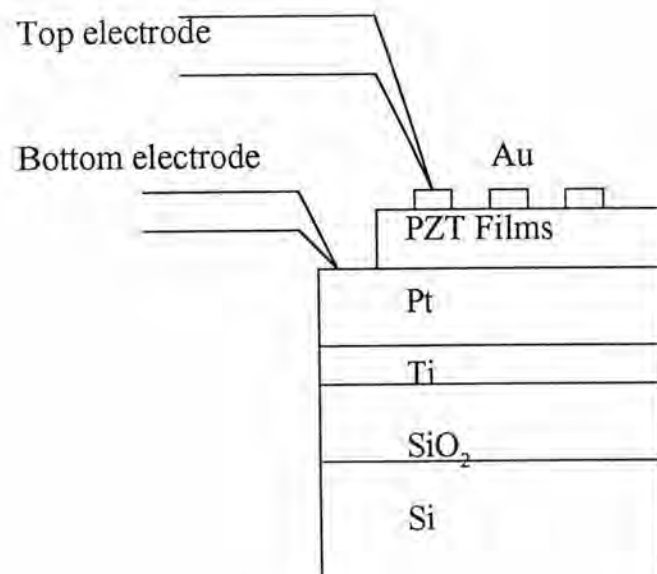


Figure 3.3 Cross-section of the test capacitor.

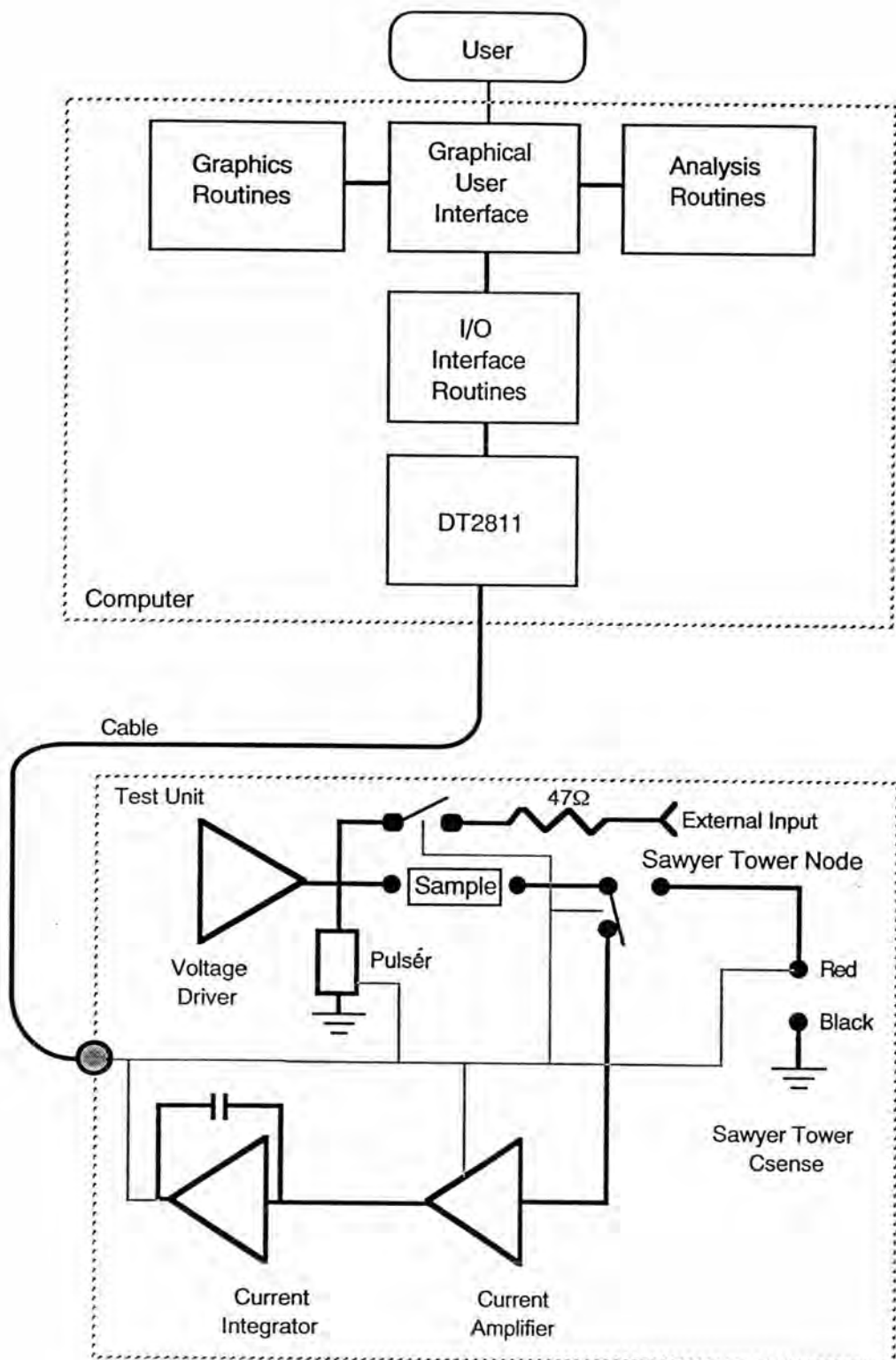


Figure 3.4 RT66A test unit block diagram.

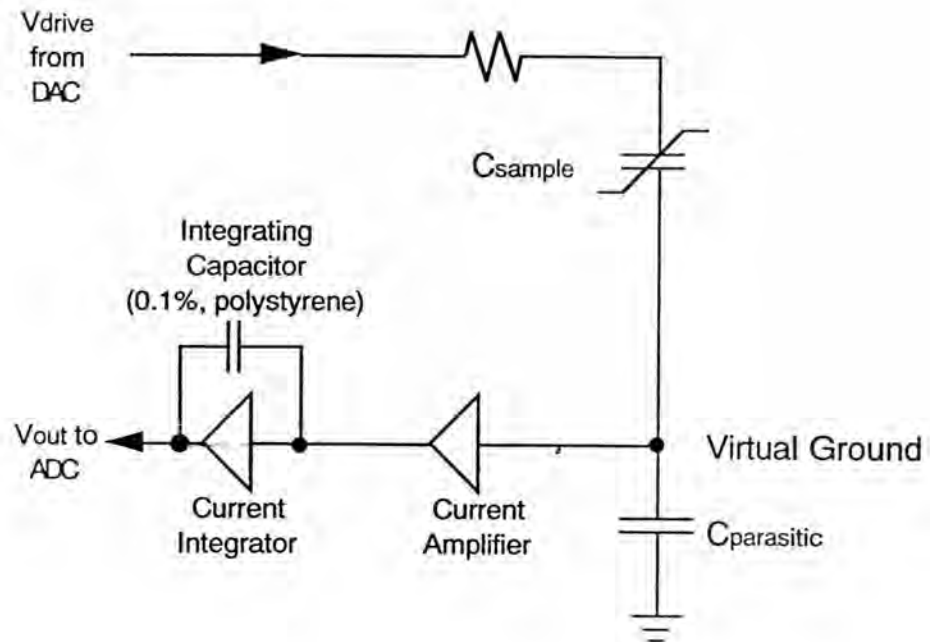


Figure 3.5 Equivalent circuit, Virtual ground Mode.