Chapter 3
Experimental and Characterization Details

3-1. Preparation of SBT, BNT, STO, STSO precursor solutions

Sol-gel technology arose as a method of fabrication of high quality ceramics, glasses and has been extended to the fabrication of thin films or coatings on different substrates. In early time, there are essentially two different kinds of sol-gel technology. The first or "colloidal" method involves the dispersion of colloidal particles in a liquid to form a sol and then the destabilization of the sol to produce a gel. The second method involves the polymerization of organometallic compounds such as alkoxides to produce a gel with a continuous network. In recent years, the SBT thin films directly used sol made by organic or inorganic metal salts of solution to coating on substrates. This also called the metalorganic deposition method (MOD). We also used this method to prepare the SBT precursor solution. Two kinds of chemical reagents are selected to prepare the SBT precursor solution. One kind of chemical reagents are strontium acetate, $Sr(CH_3COO)_2$, Bismuth acetate, $Bi(CH_3COO)_3$, tantalum pentaethoxide, $Ta(OCH_2CH_3)_5$, and acetic acid as a solvent, we call this as acetate system. Another are strontium nitrate, $Sr(NO_3)_2$, Bismuth nitrate, $Bi(NO_3)_3$, tantalum pentaethoxide, $Ta(OCH_2CH_3)_5$, and 2-methoxyethanol as a solvent, we call that as nitrate system. In order to obtain a stable solution in air and multi-component homogeneous system, we add a chelating organic ligand into the solution. Several additives are added into solution including the surfactants and drying control chemical additives. A surfactant acts to reduce the capillary force so that it will

reduce the stress concentration. Fig.3-1 shows the method of preparing solution of SBT precursors. First, strontium nitrate and bismuth nitrates are dissolved into 2-methoxyethanol at 75°C, respectively. Then they are mixed together and stirred for two hours at 75°C in order to evaporate the water. After that, tantalum pentaethoxide is added to the solution with chelating agents and refluxed for 2hr at 75°C.

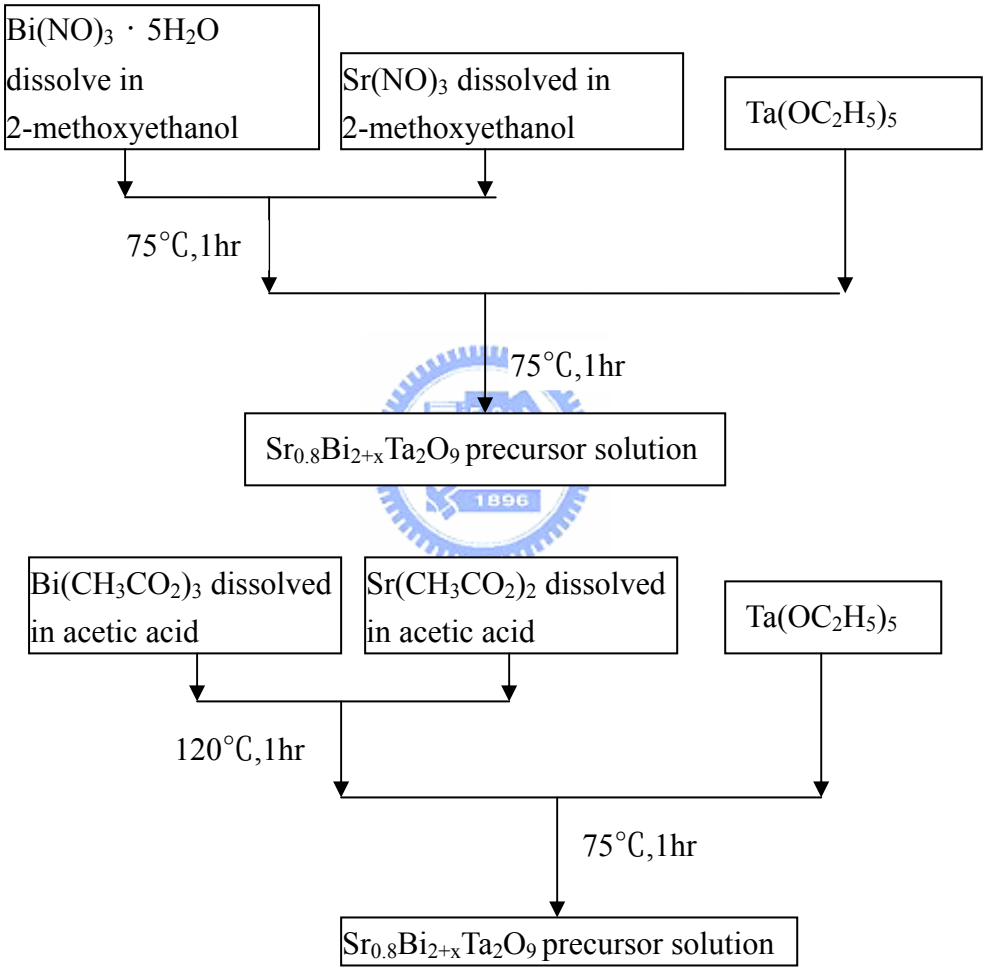


Fig.3-1 The preparation of the precursors solution

Another SBT precursor solution was prepared similar to that of the nitrate system. Strontium acetate and bismuth acetate were dissolved in

acetic acid at 120°C, respectively, then mixed together and stirred for two hours. After that, tantalum pentaethoxide is added to the solution with chelating agents, together refluxed for 2hr at 75°C.

The BNT precursor solution is fabricated by high purity $Bi(OOCCH_3)_3$, $Ti(OCH_2CH_3)_4$, $Nd(OOCCH_3)_3$ chemical compound as the Bi, Ti, Nd sources, acetic acid and ethylene glycol as a solvent. The mole ratios of Bi:Nd:Ti in the MOD solution are 3.25:0.75:3 in order to obtain good electrical characteristics.

The STO precursor solution is prepared from $Sr(CH_3COO)_2$, $Ta(OCH_2CH_3)_5$, and acetic acid as a solvent. The mole ratios of S:Ta in the precursor solution are 1:1 in order to obtain good electrical characteristics.

The $SrTiSi_xO_{3\pm2y}$ (STSO) thin film with x value from 0 to 0.45 was prepared on $Pt/Ti/SiO_2/Si$ substrate by a chemical solution deposition method. The precursor solution is made by alkoxide-carboxylate complexes. Strontium acetate [$Sr(CH_3COO)_2$], Silicon ethoxide [$Si(OC_2H_5)_4$] and titanium ethoxide [$Ti(OC_2H_5)_5$] are selected as starting materials, acetic acid and ethylene glycol were selected as solvent. Strontium acetate is initially dissolved into dehydrated acetic acid and ethylene glycol solution which is sealed in a reflux flask under nitrogen gas. The solution is heated to 120°C for 1 hour, and then titanium ethoxide and Silicon ethoxide are added to the solution to form a clear and stable precursor solution at 70°C for 1 hour.

3-2. Preparation of bottom electrodes

The structure of SBT thin films in integrated design used for

electrical measurement is MIM (metal-Insulator-metal) structure. The SBT thin films are deposited on M/SiO_2/Si substrate. We also deposit the SBT films on various bottom electrode materials. First the 100 nm thick SiO_2 layer was thermally grown on Si substrate at 1050℃ in a furnace under dry oxidation condition. Then , the Pt, Ir and IrO_2 were selected as a bottom electrode, respectively, which are sputter on it at a fixed power of 50W (power density is 2.55W/cm_2), constant pressure of 5 mTorr and substrate temperature of 350℃. The IrO_2 films are formed by magnetron sputtering with Ar and O_2 mixture in the mixing ratio of 4:1. The resistivity of Pt, Ir, and IrO2 are determined to be about 17, 27 and 67 μΩ-cm at room temperature, respectively.

3-3. Formation of SBT, BNT, STO, STSO thin films

Thin films of SBT gels are spread on Pt (100nm)/Ti (50nm)/SiO_2/Si, Ir(100nm)/ SiO_2/Si, IrO_2/ SiO_2/Si substrates by a spin-coating technique with prepared SBT precursors solution. The gel films are preheated by conventional furnace at 150℃ for 10 min in order to evaporate the solvent, then heated at 400℃ for 30min to remove other organic compound. After repeating the process of spin coating and preheating can obtain a desire thickness, the thin films are crystallized by conventional furnace with different heating rate in ambient oxygen atmosphere. This process is called as two steps method. Another was one step process, that is the SBT gel films preheated at 150℃ for 10 min to evaporate the solvent then directly sintered by rapid thermal annealing (RTA) furnace with a heating rate of 600℃/min at different temperature from 10 to 30 min in O_2 atmosphere. The flow chart shows in Fig.3-2.

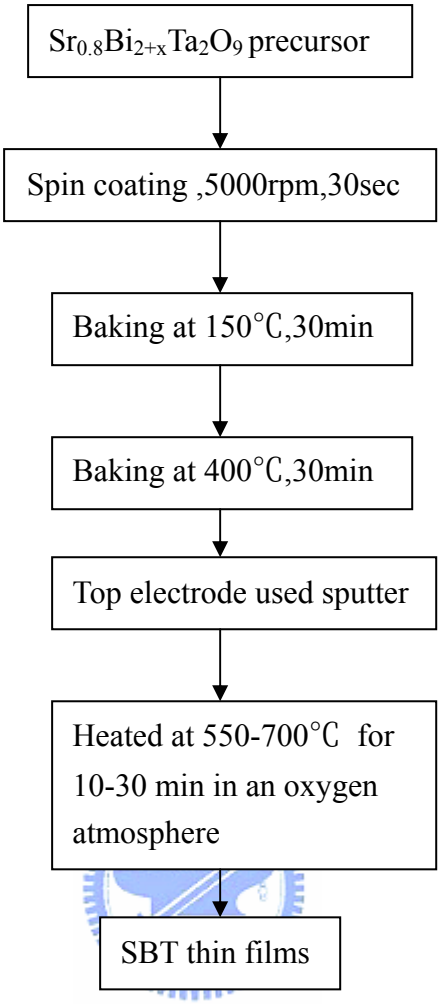


Fig.3-2 The preparation of SBT thin films.

The $Bi_{3.25}Nd_{0.75}Ti_3O_5$ (BNT) thin films are deposited on SRO/STO/Si substrates by spin-coating at 5000 rpm for 30 sec followed by pyrolysis at 150℃ for 10 min to evaporate the solvent, then heated at 400℃ in air for 30 min to eliminate other organic compound. The $SrTiO_3$ (STO) thin films are deposited on CeO_2/Si, substrates by spin-coating at 5000 rpm for 30 sec followed by pyrolysis at 150℃ for 10 min to evaporate the solvent, then heated at 400℃ in air for 30 min to eliminate other organic compound. The precursor solution of $SrTiSi_xO_{3+2\delta}$ (STSO) with a concentration of 0.25mol/L is spin-coated on Pt/Ti/SiO_2/Si

substrates. The coated thin film is dried at 150℃ for 10 min, and then 400℃ for 30 min in conventional furnace to remove organic complex. This step was repeated several times until the desired thickness was obtained.

3-4. X-ray diffraction analysis (XRD)

The formation of SBT thin film was characterized by X-ray diffraction using a Hitachi S2000 X-ray diffractometer with CuKα radiation at 30kV and 20mA. The 2θ powder method was employed and the detected X-ray beams were diffracted from the lattice planes, which was parallel to the substrate. The grains size can be calculated by the full width at half maximum of the dominant (115) peak and Scherrer's equation, as followings:

$$D_{hkl}=0.9\lambda/(\beta\times\cos\theta)$$

$$B_{hkl}^2=B_m^2-B_s^2$$

Where D is the grain size, λ is the wavelength of the X-ray, β is the FWHM of the XRD peak and θ is the diffraction angle, B_{hkl} is efficient breadth in radian, B_m is measured breadth, B_s is standard breadth.

The XRD profile can compare with table 3-1 to define the SBT phase.

3-5. DTA and TG measurements

The precursor of SBT solution was heated in conventional furnace for several days at 120℃, until all the solvent was evaporated and the SBT powder was obtained. Then the powder was analyzed by the Seiki TG/DTA 200 with a heating rate of 10℃/min from 100℃ to 1000℃. This analysis gives temperature-dependent the weight loss, exothermic

and endothermic behaviors for the powder.

Table 3-1 Calculated XRD data for SBT [87]

$(hkl)_{tet}$	$(hkl)_{orth}$	d spacing (Å)	2θ (degree)	I/I_0 (%)
004	004	6.2650	14.136	≪1
006	006	4.1767	21.272	3
101	111	3.8492	23.106	4
103	113	3.5304	25.225	9
008	008	3.1325	28.493	5
105	115	3.0757	29.031	100
110	200	2.7545	32.504	39
112	202	2.6903	33.303	1
107	117	2.6359	34.010	≪1
114	204	2.5215	35.603	<1
0010	0010	2.5060	35.831	15
$10\bar{9}$	$11\bar{9}$	2.2653	39.792	1
0012	0012	2.0883	43.325	1
$11\bar{8}$	$20\bar{8}$	2.0685	43.761	7
3114	217	2.0295	44.647	≪1
$10\bar{11}$	$11\bar{11}$	1.9666	46.158	2
$20\bar{0}$	$22\bar{0}$	1.9477	46.630	22
202	222	1.9246	47.224	<1
204	224	1.8599	48.973	≪1
$11\bar{1}0$	$20\bar{1}0$	1.8537	49.149	23
$00\bar{1}4$	$00\bar{1}4$	1.7900	51.020	<1
$20\bar{6}$	$22\bar{6}$	1.7652	51.788	1
211	311	1.7379	52.664	1
$10\bar{1}3$	$11\bar{1}3$	1.7277	52.999	7
$21\bar{3}$	$31\bar{3}$	1.7054	53.748	2
$11\bar{1}2$	$20\bar{1}2$	1.6641	55.193	<1
$20\bar{8}$	$22\bar{8}$	1.6541	55.558	3
215	315	1.6455	55.871	34
217	317	1.5665	58.960	≪1
$00\bar{1}6$	$00\bar{1}6$	1.5662	58.969	<1

3-6. SEM measurement

The thickness, microstructure, cross-section and the surface morphology of SBT thin films were examined by FESEM (Field emission scanning electron microscopy) using Hitachi model S4700.

3-7. TEM measurement

The thickness of thin layer and micrograph analysis was

investigated with field emission of the Philips JEM9110 Transmission Electron Microscopy (TEM) at 200kV accelerating voltage.

3-8. AFM measurement

The surface roughness and root mean square value of thin films were examined by Digital Instruments Nano-Scope Ⅲ atomic force microscopy (AFM).

3-9. XPS measurement

The electron affinities and chemical states of the deposited thin films were analyzed by photoelectron spectroscopy (XPS) with Al Kα x-ray at a constant pass energy by using a Physical Electronics ESCA PHI 1600 spectrometer under a chamber base pressure of ~1×10^{-8} Torr. An Ar^{+} ion beam was used to etch the films to obtain the depth profiles of the films. The total power applied to the x-ray source was 300 W.

3-10. Polarization measurement

The ferroelectric properties of the SBT thin films are measured using RT-66A ferroelectric tester from Radiant Technologies. An automatic measurement system combined with PC, RT-66A and a probe station are used to measure the SBT thin films. The structure used for electrical measurement is MIM (Metal-Insulator-Metal) structure (see Fig.3-4). In order to observe the hysteresis loop of SBT thin films in P-E curve, the module of Sawyer-Tower circuit is set to measure ferroelectricity in Fig.3-3.

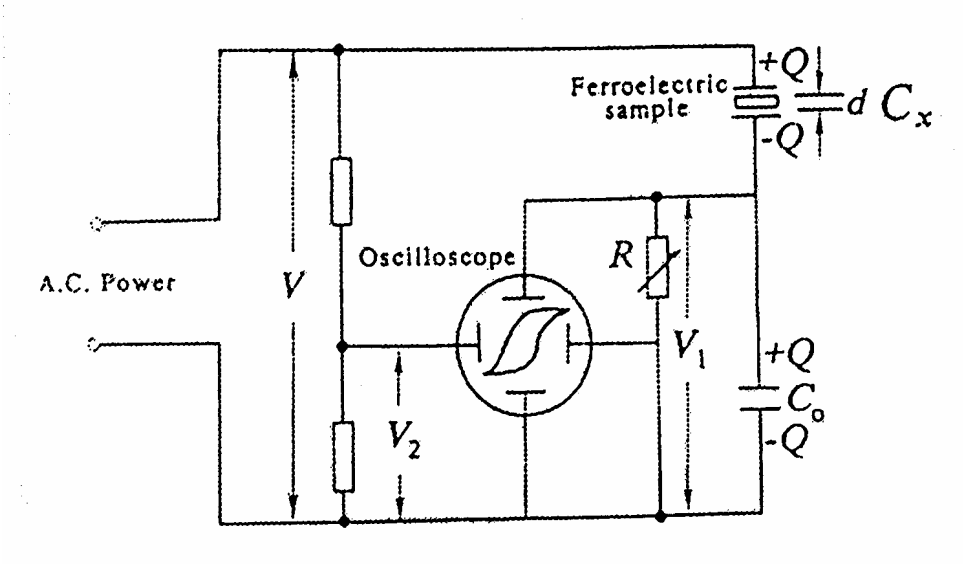


Fig.3-3 The schematic circuit of Sawyer-Tower Bridge.

3-11. Capacitance-Voltage (C-V) measurements

An automatic measurement system combined with personal computer, HP4145A, HP8142 and a probe station is used for the C-V measurement of SBT thin films. The dielectric properties of the SBT thin film capacitors is measured at 100k Hz with 0.025 oscillation level and sweep rate of 0.1V/s from negative to positive bias. We can obtain the dielectric constant and loss tangent from the C-V measurement. The measurement for MIM and MFMIS structure is shown in Fig.3-4.

The dielectric constant was calculated from the following relation:

$C=k\times\varepsilon_o\times A/d$

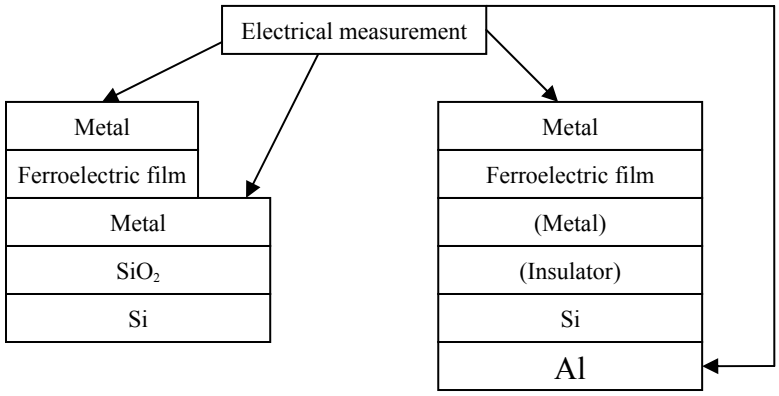
Where A: capacitor area (the area of the top electrode)

d: thickness of the insulator(SBT thickness)

k: dielectric constant

C: the insulator capacitance

ε_o: the permitivity in vacuum



(a) MIM structure (b) MFMIS, MFIS or MFS structure

Fig.3-4 Electrical measurement for MIM and MFMIS structure.

3-12. Current-Voltage (I-V) measurements

An automatic measurement system also combined with personal computer, HP4145 and a probe station is used to measure current-voltage characteristics. A suitable delay time is selected to measure the true leakage current. When voltage is applied to a dielectric thin film, the current response is composed of polarization contribution (comprising charges which are stored in the system) and leakage contribution (comprising charges which transported from one electrode to the other) [88]. Conduction mechanisms are analyzed by measuring the I-V curves on the basis of electrode-limited Schottky emission and bulk-limited Poole-Frenkel models.

3-13. Fatigue measurements

The fatigue test is measure by RT-66A used to change of polarization in SBT thin films. The cycling signal is a square wave with bias from -3V to +3V at 100 kHz. Fatigue is measured as a function of cycling.

3-14. Retention measurements

Retention is simply the loss of polarizability with time of an idle capacitor. Retention tests are a time consuming measurement and used the RT66A analyzer performs completely the retention time of SBT films in the MFM structure or the HP4284A meter accomplishes the retention time of MFIS and MFMIS structure.