Chapter 2

Experiment Detail

2.1 Experiment Process Flow

We sorted our experiments into two parts: sample preparation and property analyses as showed in Fig. 2-1. There are several sample preparation steps as showed in Fig. 2-2. First, 4 inch boron-doped (100) silicon substrates were cleaned by standard RCA clean and then, a 200 nm thick SiO_2 layer was thermally grown on the silicon substrates, which acts as the isolation layer to prevent the leakage current from the substrate. Second, the Pt/Ti bottom electrodes are deposited by electron-beam evaporation. Then, the synthesis of the $LaNiO_3$ powder has been prepared previously. The powders are made into the disk-shaped target for sputtering. Next, the 140nm $LaNiO_3$ (LNO) buffer layer is deposited on the Pt bottom electrode by radio frequency (RF) magnetron sputter. Then, the structure of the LNO/Pt bottom electrode is treated by rapid temperature annealing (RTA). After degassing for two hours, the BTO film is deposited on the LNO/Pt bottom electrode by spin-coating. Finally, the Pt top electrodes (80nm) are evaporated on the BTO film by electron-beam evaporation. The memory device is accomplished as shown in Fig. 1-1. The scanning electron microscope system (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and x-ray diffraction system (XRD) are used to obtain the micro-structure and the crystallization of the films, respectively. SEM analysis could help us to understand the

surface roughness and thickness of the LNO and the BTO films. This analysis will help us to discover whether the switching conductivity phenomenon is related with phase changing, and help us understand whether the degree of crystallization affect the characteristics of the memory devices. Otherwise, x-ray photoelectron spectroscopy system (XPS) is used to identify the components of memory device to conform the binding energies. An Agilent 4155C semiconductor parameter analyzer is used to record the current - voltage (I-V) characteristics. Based on the results of electrical measurement, we could modify the manufacturing process to improve the performance of the memory device.

2.2 RF Magnetron Sputter System

In this study, we utilized a set of RF magnetron sputter system to deposit LNO thin films. The figure of the sputter system is displayed in Fig. 2-3. The components of the sputtering system are illustrated as followed:

● Vacuum system:

It includes a mechanism pump and a diffusion pump. The chamber base pressure is evacuated to 10^{-5} torr before deposition process. There are several valves to control the atmosphere and the pressure in chamber and in tubes.

● Pressure system:

There are two digital gauges in the system to show the chamber pressure in various working conditions. One is Granville-Phlips Co.'s product with a display range from 1 ATM to 0.1m torr to show the higher chamber pressure for rough vacuum and sputtering condition. The other one is an ion gauge with an accurate display of a high vacuum from 10^{-3} to 10^{-7} torr. Accordingly, we can precisely control the vacuum situation under

sputtering and ensure the diffusion pump working in the safe pressure.

● **Temperature controlling system:**

It contains two thermal couples sensor, a set of four quartz lamps used as heater, and a temperature controller. During the heating process, the lamps just located above the wafer holder could heat the sample directly by radiation in lower pressure. At the same time, the change of the thermal couple could be detected and sent back to temperature controller to modify the heating power. Further, we could setup the temperature rising time, holding time, and falling time by temperature program.

● **Gas flow controlling system:**

In general, the percentage of oxygen in the sputtering atmosphere played an important role in oxide ceramics. We used Gas MFC (mass flow meter) to control the flow rate and atmosphere contents during the sputtering process. So we could find out that the dependence of the mass ratio for the device performance by tuning recipe.

● **Plasma controlling system:**

This system consists of a RF power generator, a network-matching box, and a 3-inch magnetron gun. The RF power generator has only one working frequency 13.56 MHz, and the network-matching box could minimum reflection power by adjusting the capacitance of the whole circuit. We were able to gain the stable plasma by the controlling system.

● **Cooling system:**

There was cooling water which flows in the pipe welded on the chamber and in the magnetron gun. During the sputtering process, the heating lamps and plasma always produced a lot of redundant heat energy in the chamber. We needed cooling water to prevent from mechanical breakdown and maintain the sample uniformity.

2.3 Thin Film Deposition

Choosing sol-gel method to deposit BTO memory thin film is not only to decrease the producing costs but also to increase the variety and convenience of procedure. We choose acetic acid (CH_3COOH) and acetylacetone ($C_5H_8O_2$) as solvents. Then, we choose bismuth acetate [$Bi(OOCCH_3)_3$] and titanium isopropoxide $Ti[OCH(CH_3)_2]_4$ as the solutes. The method about how to prepare the precursor solution and to coat the BTO thin films on LNO/Pt bottom electrode is introduced as followed.

2.3.1 Precursor Solution

The process of solution process is listed on Fig. 2-4. In Fig. 2-5, we dropped acetic acid into the triangle bottle and put it on the hot plate for ten minutes to decrease the moisture content at the beginning. The temperature of hot plate was $80^{O}C$. Then we added bismuth acetate into the acetic acid. Bismuth acetate was dissolved in the acetic acid by stirring and heating to $80\,^{O}C$. The speed of stirring was 400 rpm. Thirty minutes later, acetylacetone, which had the same content of acetic acid, was dropped into the solution. After adding acetylacetone, titanium isopropoxide was mixed with the solution immediately. In order to dissolve solute and mix completely, the solution had been stirred and heated continuously for one hour at least.

2.3.2 Thin Film Coating

Before coating the BTO thin film, the wafer is cut into 2.2x2.2 cm^2 pieces. Then, we stick the adhesive tape on the side of LNO/Pt in order to avoid BTO precursor solution coating on it and, further to cover the bottom electrode. The tape which is made by NITTO whose model is NO.973UL with the ability to prevent from etching. In order

to coat a uniform and flat BTO thin films on the LNO/Pt bottom electrode. We use a spinner made by Synrex which model is 1-PM101D-R790.

Two spin-coating steps are used to improve the degree of uniformity and control the thickness of BTO thin films. The first step is 1000rpm and for 5 seconds. The second step is 3500rpm for 60 seconds. After 0.04 M precursor solution is spin-coated on the $LaNiO_3/Pt/Ti/SiO_2/Si$ substrates, the sample is put on the hot plate for soft baking and the temperature of the hot plate is set for 125 ^{O}C. The model of the hot plate, made by Fargo, is HMS-530. At the same time, we put a glass cup to cover the sample and to avoid dust falling on the samples. In this way, we can increase the quality of BTO thin films and decrease the occurrence of the defects. After 10 minutes, the samples are put on a board which is made by Al_2O_3. Then, the samples are loaded into a furnace and treated at 200 ^{O}C for 10 min and then 400 ^{O}C for 30 min. The coating and heating steps are repeated three times to obtain the desired film thickness. From TG and DTA analysis diagrams (Fig. 2-6 and 2-7), we can find that the first pyrolysis temperature is 200 ^{o}C. Because of this, we adopt two steps of pyrolysis process. At First, we raise the temperature to 200 ^{o}C during 20 minutes and hold at the temperature for 10 minutes. Then, the temperature is further raised to 400 ^{o}C during 20 minutes and hold at 400 ^{o}C for 30 minutes. The pyrolysis temperature profile is shown in Fig. 2-8.

2.4 Top Electrode Deposition

We utilize the shadow mask to define top electrode area with pattern diameters are 350um, 250um, and 150um. The areas of this shadow mask are around 9.61x10^{-4}, 4.91 x10^{-4}, and 1.76 x10^{-4} cm^2. We adopt Pt as top electrode. The deposition instrument is electron-beam evaporation. The thickness of the Pt top electrode is 80nm.

2.5 Thermal Treatment Process

There are two functions for us to use rapid thermal annealing system (RTA) and thermal treatment system. One is that we want to enhance conductivity of the LNO buffer layer as a result to from better crystallization. The other is that we use thermal treatment system atmosphere (nitrogen) and temperature (from 400 ^{O}C to 700 ^{O}C) to modify our BTO thin films (Fig. 2-9). The RTA model is FE-004A made by JETFIRST and thermal treatment model is BF51732BC made by Lindberg/Blue M.

2.6 Measurements and Analysis

In order to analyze the quality of BTO thin films and measure the memory effects, we use many kinds of measurement and analysis instruments. In the following section, the instruments for physical property analyses and electrical properties measurement are introduced.

2.6.1 Physical Properties

We can find out the characteristics of BTO thin films such as the components, crystallization, surface roughness, orientation, bonding energies. From those analysis data, we can modify our manufacturing parameters to improve thin film qualities.

●**Thermal analyzers**

The thermal analyzer is manufactured by Seiko (SSC 5000). From the thermal analysis, we can realize the degree of weight loss, phase change, degree of purity, and content mist as raised temperature. We put the sol-gel solution in the oven at the temperature of 80 ^{O}C for one week to become dried-gel BTO precursor power. Then, we

put the powder into the Pt dish and raise the temperature form 25 ^{O}C to 910 ^{O}C at the rate of 2 ^{O}C/min in atmosphere. The measurement of differential thermal analysis (DTA) which references sample is Al_2O_3 in the same temperature raising rate and atmosphere. The physical property of those data will be explained in the next section.

● **X-ray diffraction (XRD)**

X-Ray Diffraction analysis (Fig. 2-10) is used to investigate the crystal structure of our samples. Furthermore, we can identify the crystallization dependence and the thin film stress dependence of on our samples. Follow Scherrer's formula, we can calculate the average grain size from XRD illustration:

$$D = \frac{0.9 \times \lambda}{B \times \cos\theta}$$

The background information of our XRD analysis is that $\lambda = 1.5405$ Å (K_α), B is the full width at half maximum (FWHM) of the XRD peak, and θ is the diffraction angle. In this analysis, X-ray is made with 0.02 degree beam divergence and operation configuration at 30KV, 20mA.

● **Scanning electron microscopy (SEM)**：

We acquired the information of planar and cross section views of thin films by using the High-Resolution Scanning Electron Microscope & Energy Dispersive Spectrometer (Hitachi, S-4700I, with the resolution 15Å (at 15kV) or 25Å (at 1kV) in the Semiconductor Research Center.

● **Atomic force microscope (AFM)**

The atomic force microscopy (AFM) is a very good tool to research the surface roughness and surface morphology. We use an AFM made by digital instruments whose model is Nano-Scope III. The root mean square (RMS) value of roughness of the film is

automatically calculated by the AFM software.

● **Transmission electron microscopy (TEM)**

Electrons from an electron gun are accelerated by high voltages and focused on the sample by the condenser lenses. The sample is placed on a small copper grid a few mm in diameter. The static beam has a diameter of a few microns. The sample must be sufficiently thin to be transparent to electrons. The transmitted and forward scattered electrons form a diffraction pattern in the back focus plane and a magnified image in the image plane. In order to study the interface mechanics and determine the interface thickness, Philips JEOL JEM9100 transmission electron microscopy (TEM) is used to observe the interface. Furthermore, the TEM can be used to characterize the crystallized status of the films. The maximum magnification is 900000.

● **X-ray photoelectron spectroscopy (XPS)**

The X-ray spectroscopy is used to characterize the binding energy and the compositions of the thin film. The electron binding energy is influenced by its chemical surroundings making binding energy suitable for determining chemical states. XPS is a surface-sensitive method because the emitted photoelectrons originate from the upper 0.5~5 nm of the sample, just as Auger electrons do, despite the deeper penetration of the primary X-rays compared to a primary electron beam.

2.6.2 Electrical Properties

To investigate the quality of the memory films for RRAM is not only from the physical properties but also from the electrical properties measurement. We use a system which consists of a probe station, an Agilent E5250A low leakage switch, an Agilent 4155C semiconductor parameter analysis, an Agilent 8110A pulse generator,

and a personal computer with the software of Agilent VEE to characterize the electrical properties of our experiment samples (Fig. 2-11). The electrical properties test included I-V sweep test, endurance test, stress test, and retention test. Those analysis properties will be introduced in the following sections.

●DC sweep voltage

The bistable resistive switching memory device can be switched between high resistance and low resistance states when applying a sweep voltage on the device. In order to measure the resistive switching, Agilnet 4155C and probe station are used to measure leakage current with the DC sweep voltage applied on our experiment samples. The various kinds of bistable resistive switching phenomena or materials will show significantly different I-V curves. Differing from the duration time of the applied voltage, the bistable resistive switching phenomenon can be separated into two kinds of characteristics: dc properties and transient properties. The resistive states of the device can be changed by applying a dc voltage or a pulse voltage within specific period range. In order to measure the dc properties, we utilize the double voltage sweep function of Agilent 4155C. By adjusting the magnitude of the positive voltage and negative voltage, we can get an I-V curve with Fig. 2-12, that is the dc bistable resistive switching phenomenon.

●Pulse voltage

When we apply not only sweep voltage but also by pulse voltage pulse to the device, the bistable resistive switching memory device can be switched and detected between high resistance state and low resistance state .We use a write-erase cycle to measure the memory property which is switched by pulse voltage. We use Agilent 4155C to perform

the read process and the current is measured by the VPULSE mode with pulse width of 5ms and period of 9ms for protecting the sample from damage during the read process. The pulse generator, which is Agilent 8110A, is used to generate write and erase process. The parameters of the pulse width will divide into nine periods, 10ns, l00ns, 1us, 10us, 100us, 1ms, 10ms, 100ms, 1s. We use the different pulse width to measure the switching speed, and the cycle delay is adjustable as well. In the write process, we apply a positive pulse voltage on the top electrode to switch the conductivity to a high conductivity state. Besides, a negative pulse voltage is applied on the top electrode that it will switch the device to a low conductivity state and this is the erase process. We apply a tiny voltage by Agilent 4155C to do the read process and measure the current between the write and erase process as indicated in Fig. 2-13. The read process will be repeated for five times to judge the memory states.

●Stress

In the stress test, we use Agilent 4155C to stress the device by applying a dc bias voltage for a long time. At the same time, the Agilent 4155C will measure the leakage current of the sample in a period time. The measure function what we use is SAMPLING mode. The individual period time of sampling is 30 seconds.

●Retention

When we switch the experiment sample to high resistance or low resistance state, we need to measure that how long the resistive states can be hold to record the data. Because the resistance can be hold for a long time, we use a heating instrument to perform the accelerating test. The set up parameter of heating instrument will raise the temperature from 20°C to 150°C in 50 mins and keep the temperature at 150°C for 1 hour. Then the temperature will lower to 20°C in 50mins. After that, we will measure

the leakage current again by Agilent 4155C to observe if the experiment can stay in the same conductivity state.

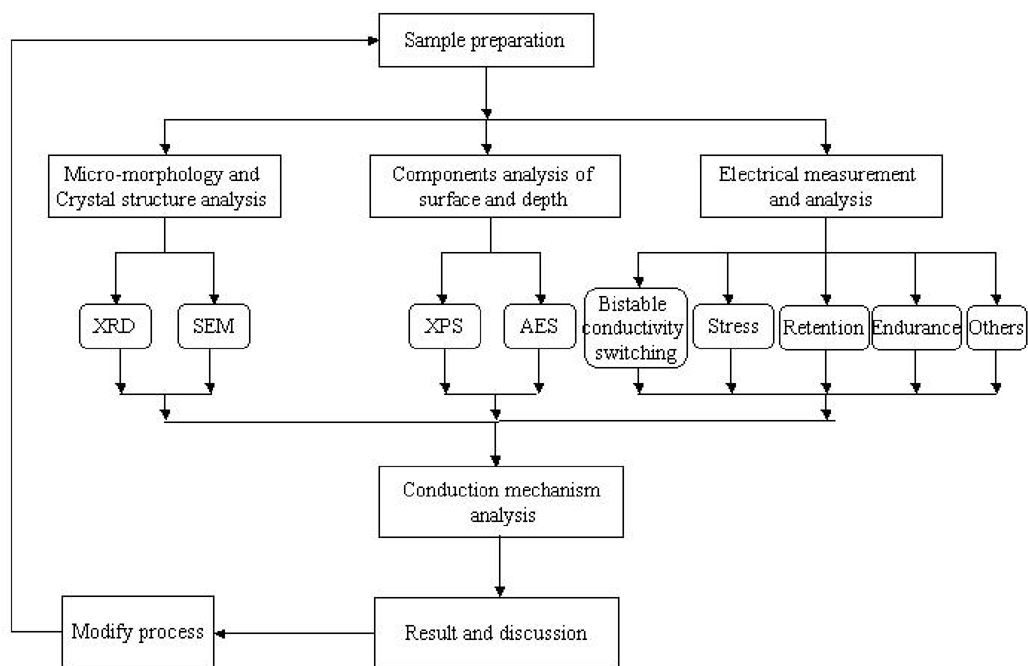


Fig. 2-1 Illustration of the experiment flow

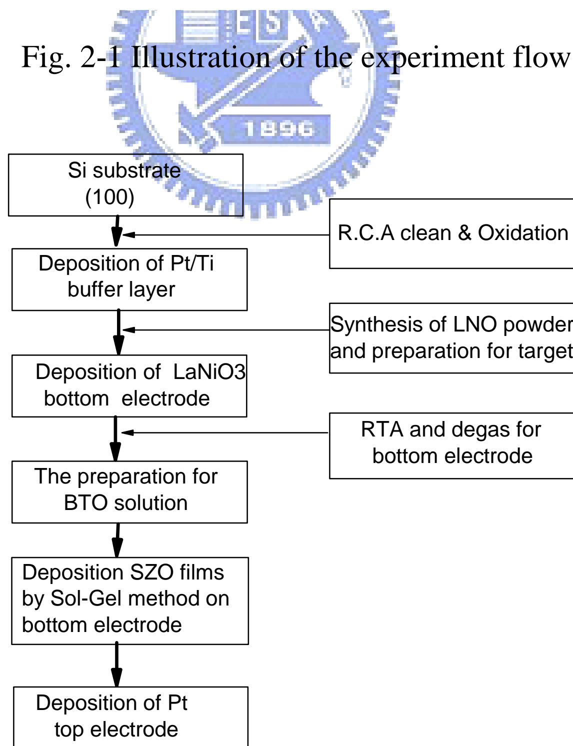


Fig.2-2 Sample preparation steps

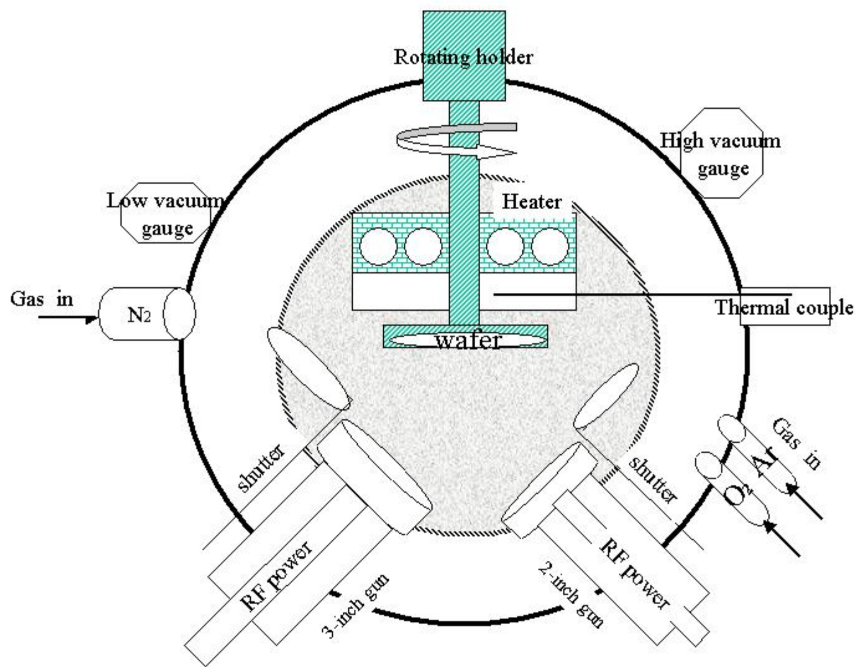


Fig.2-3 Sputter system

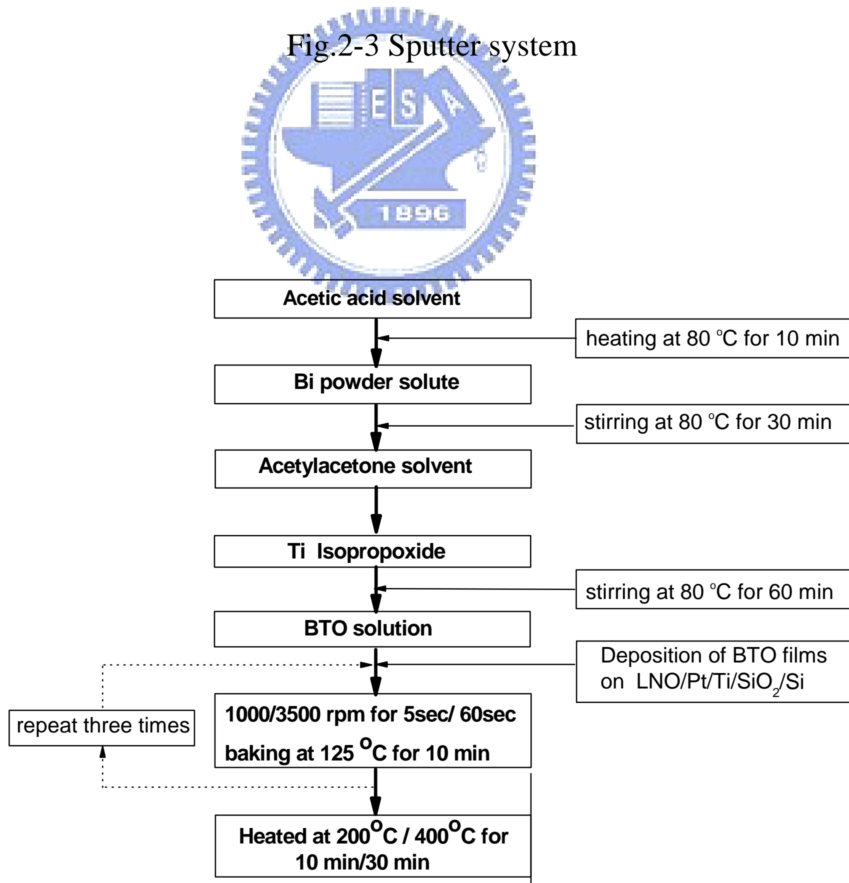
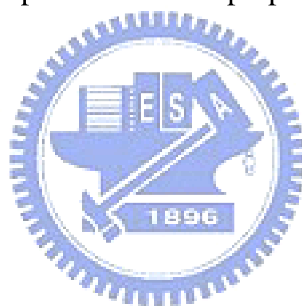


Fig.2-4 Process of solution preparation

	Scientific name	**Chemical formula**	**Purity**	**Supplier**
Solute	Bismuth acetate	$Bi(OOCCH_3)_3$	99.999%	Alfa Aesar
	Titan-isopropylate	$C_{12}H_{28}O_4Ti$	97%	ALDRICH
Solvent	Acetic acid	CH_3COOH	>99.8%	FLUKA
	Acetylacetone	$C_5H_8 0_2$	>99.5%	FLUKA

Fig.2-5 Specifications of preparation materials



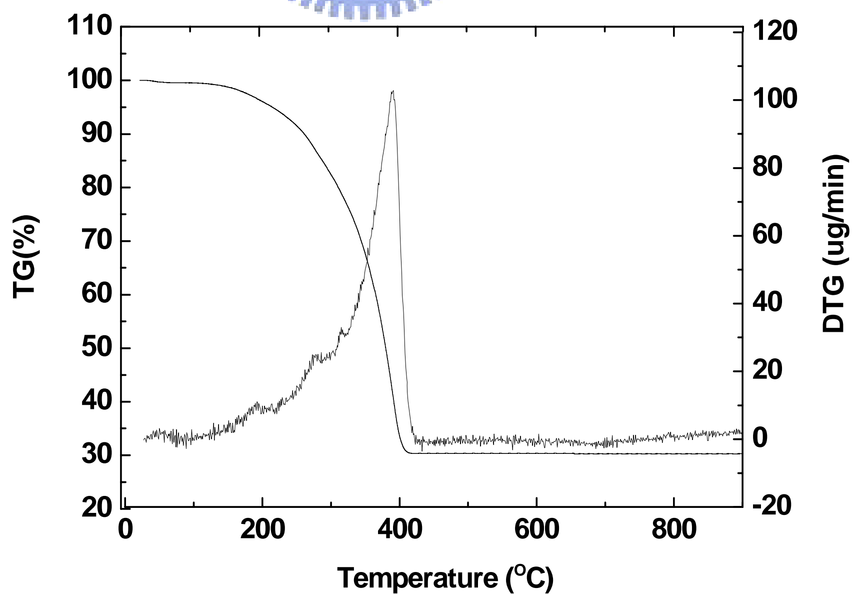


Fig.2-6 TG & DTG analyses of 0.04M BTO thin film

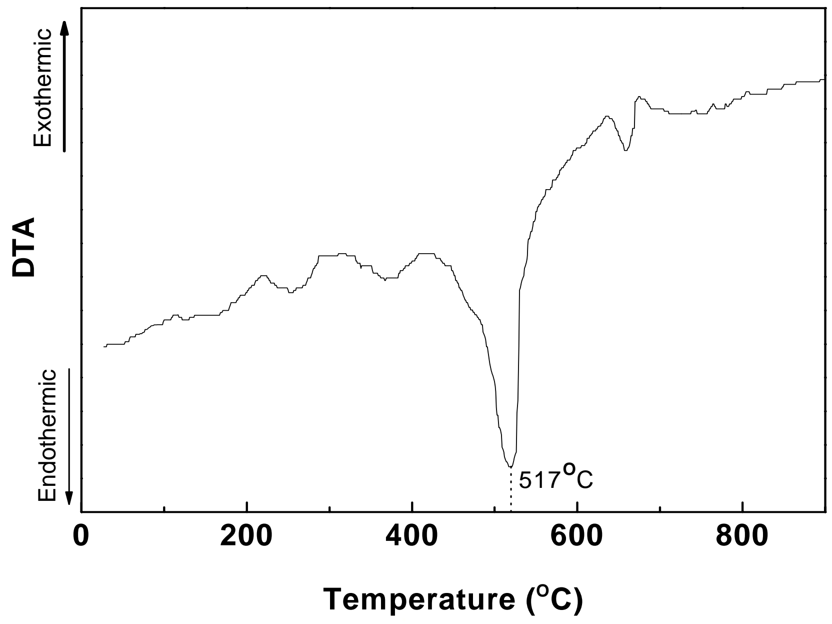


Fig.2-7 DTA analysis of 0.04M BTO thin film

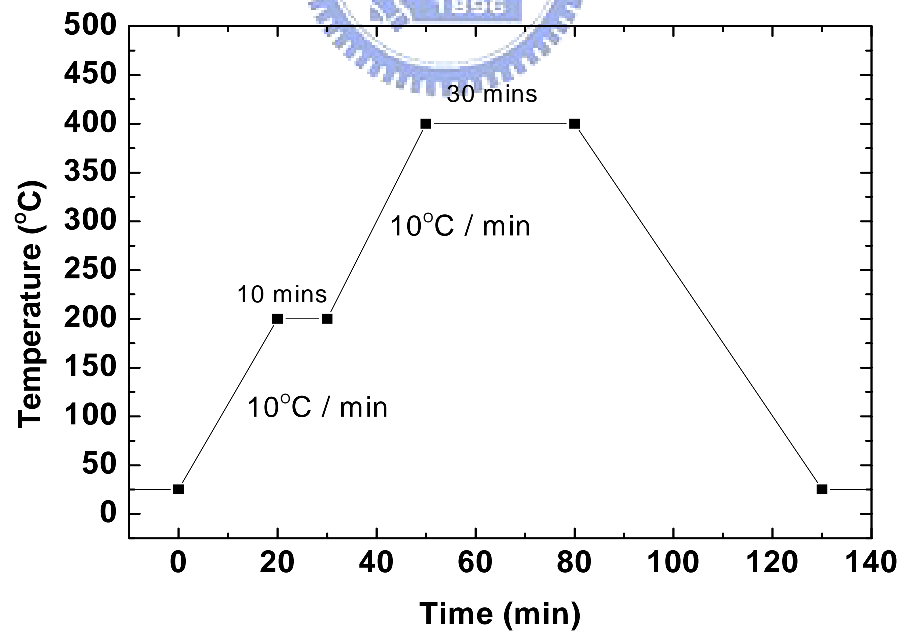
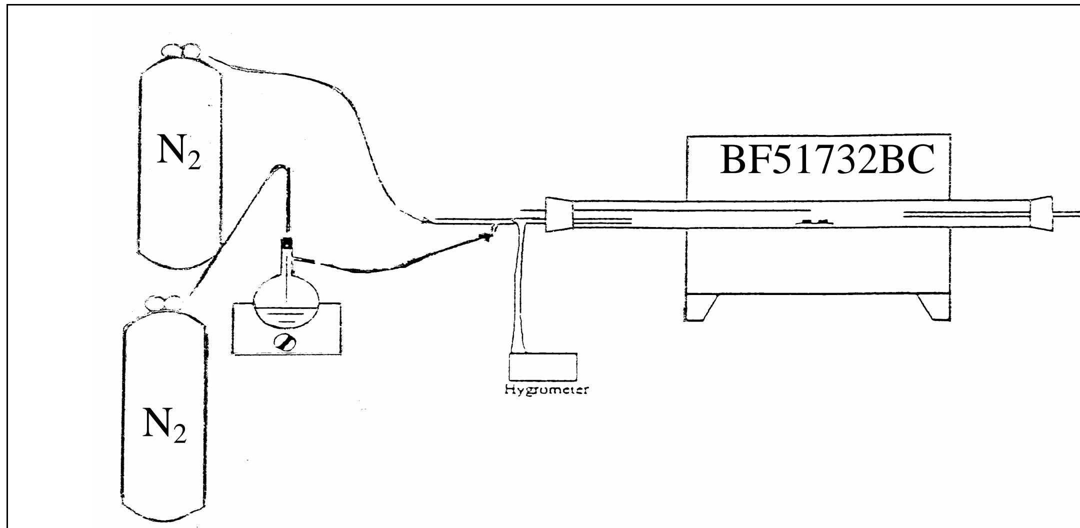


Fig.2-8 Pyrolysis temperature profile of BTO thin film



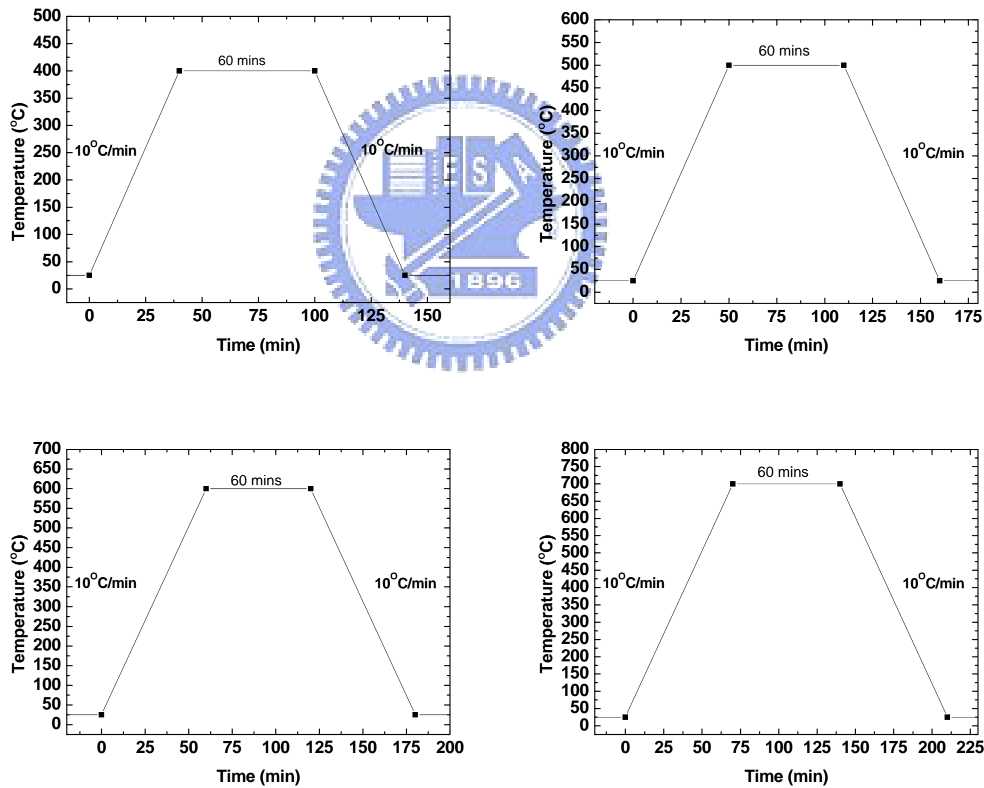


Fig.2-9 (a)Thermal treatment system and thermal treatment profiles at (b) 400 ^{O}C. (c) 500 ^{O}C (d) 600 ^{O}C (e) 700 ^{O}C

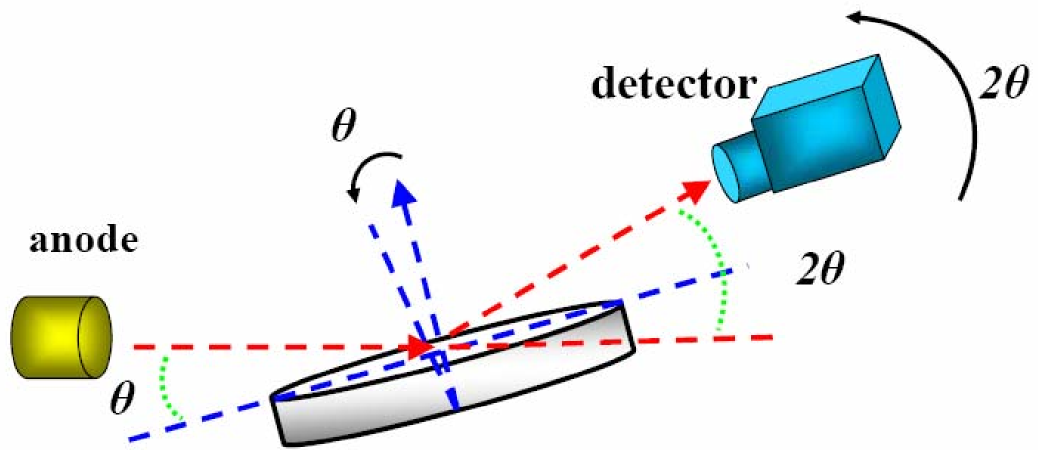


Fig. 2-10 X-ray diffraction analysis

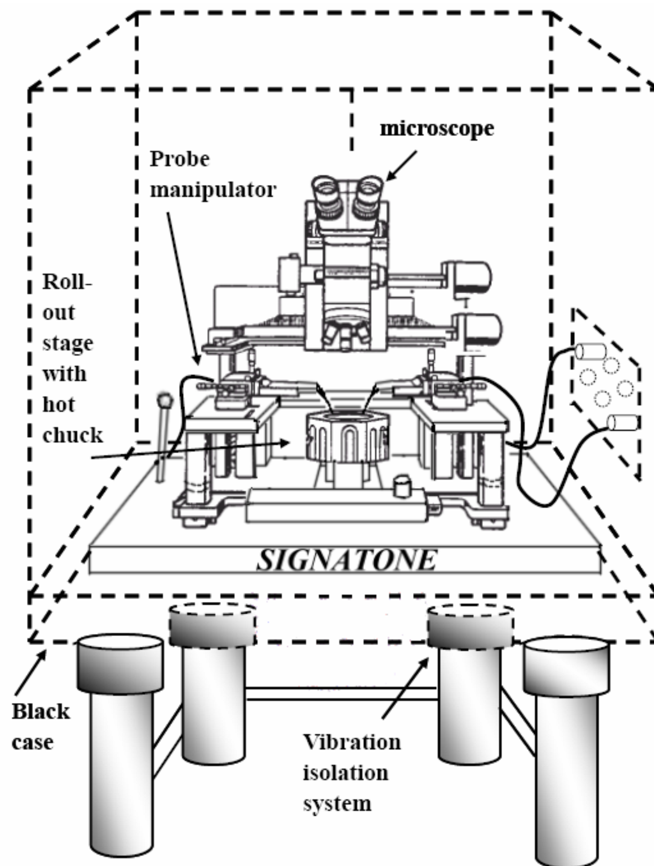


Fig. 2-11 Schematic drawing of the probe station

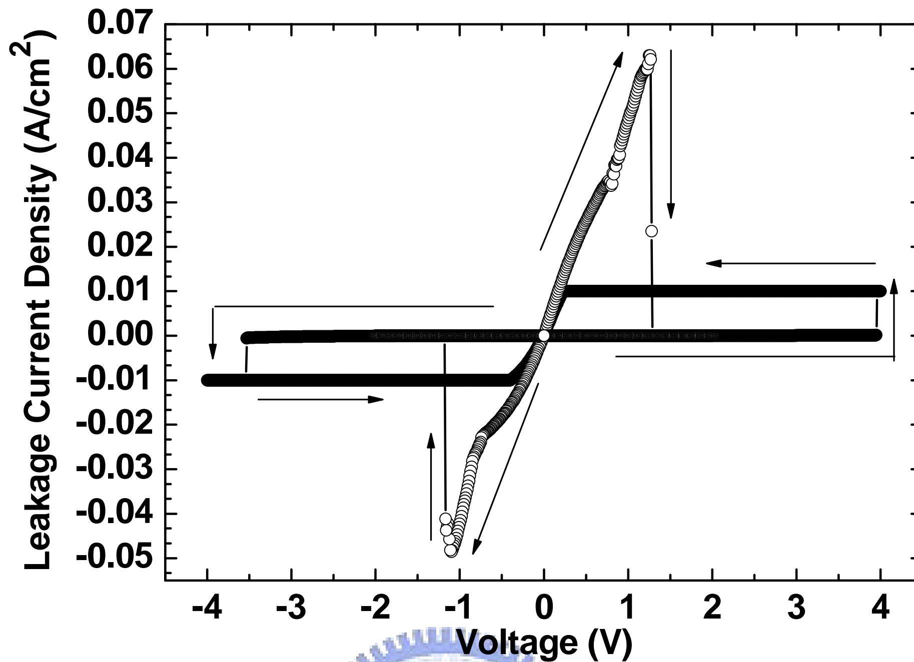


Fig. 2-12 Bistable resistive switching phenomenon by dc voltage

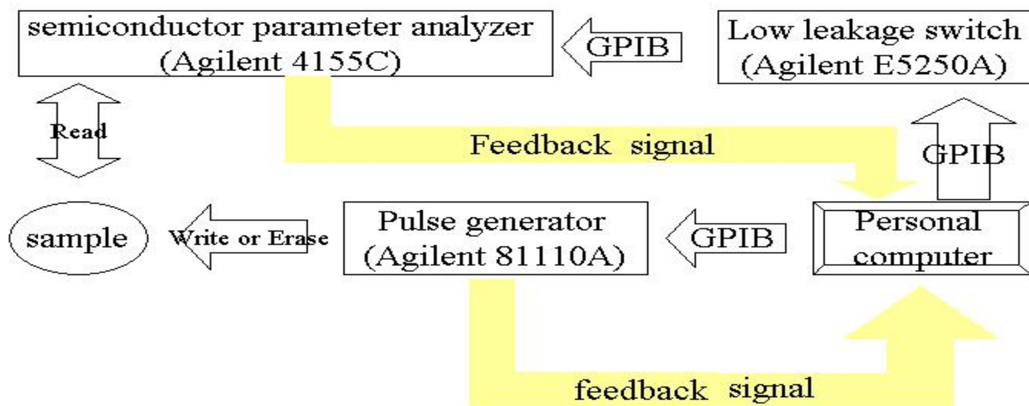


Fig. 2-13 Measuring system of transient resistive switching