CHAPTER III
RESERCH METHODOLOGY

This chapter covers preparation of the sample ranging from the preparation of the substrate, thin film deposition and nanopatterning to basic characterization. Both nano-grid patterned by FIB and gold nanohole array patterned by EBL are well defined. Additionally, the principal information and procedures from each experimental technique are described.

3.1 Substrate preparation

3.1.1 Substrate Cleaning

In this work, Nb-$SrTiO_3$ (NSTO) substrates (10 x 10 x 1.0 mm^3, [010],[001] orientation, one side polished from Crystal Base Co., Ltd) and Fluorine-doped Tin Oxide glass (FTO) were used. The NSTO and FTO were cut into sizes of 5.5 x 1.0 mm^2 and 10 x 10 x 2.2 mm^3, respectively. The cleaning process involved 4 steps. First, the substrates were cleaned with acetone to remove organic impurities. Then, they were rinsed with isopropanol (IPA) to get rid of any acetone residue, preventing streaks. After that, a rinse with DI water was performed. For each step, ultrasonic cleaning was applied to the NSTO and FTO for 15 minutes. After cleaning, the substrates were thoroughly dried. Nitrogen gas was used for drying. Water molecules, usually present due to cleaning process and air humidity, were removed by heating at 120°C for 1 hour. Finally, oxygen plasma cleaning (electronic diener plasma-surface technology) was used to clean the surfaces for removing organic and carbon contaminants, using 300 watts for 30 minutes at a pressure of 0.8 mbar.

3.2 Thin film deposition and nanoscale patterning

3.2.1 $BiFeO_3$ thin film deposition

The BFO films (a two-inch-diameter BFO target from Kurt J. Lesker Company, USA) were deposited on an NSTO substrate and FTO glass, each with a thickness of about 100 nm, using RF magnetron sputtering. Argon and oxygen gases flowed during the entire deposition process at a ratio of 4:1. The deposition was carried out under base and operated pressures of 3.6 and 6.0 mTorr, respectively. The RF power was set at 100 watts. The BFO film deposition began after 5 minutes of pre-sputtering, and the entire coating process was completed in 3 minutes without heating the substrate. Thermal annealing was performed in an air environment at a temperature of 600°C. The muffle furnace's heating rate was 5°C per minute. Once the temperature of each sample reached the target temperature, it was maintained for 30 minutes, and then the samples were allowed to cool down naturally at a rate of 5°C per minute to room temperature.

3.2.2 Nanoscale patterning of Metal oxide thin film.

3.2.2.1 Nano-grid pattern BFO/NSTO with Focus Ion Beam (FIB)

FIB technology is a key tool in nanotechnology for machining materials with high precision at the nanoscale (Orloff et al., 2003). FIB is mainly used for imaging, milling, deposition, and creating patterns on a very small scale (Yao, 2007). This technology enables the creation of tiny features, making it vital in fields like materials science, semiconductor research, and nanofabrication (Giannuzzi et al., 2005). FIB can produce nano-patterns as small as 5-10 nanometers, providing the precision and control needed for making advanced nanoscale devices and structures (Yao, 2012). The principle of FIB involves the use of a focused beam of ions, typically gallium ions, to interact with the surface of a sample (Orloff et al., 2003). The ions are accelerated and focused into a narrow beam, which can be directed with high precision onto the sample's surface. The interaction between the ions and the sample material results in the sputtering of atoms from the surface, allowing for the removal or deposition of

material with nanometer accuracy (Yao, 2007). This process can be controlled to create intricate patterns, such as grid patterns, by scanning the ion beam across the sample according to a predefined design (Giannuzzi et al., 2005).

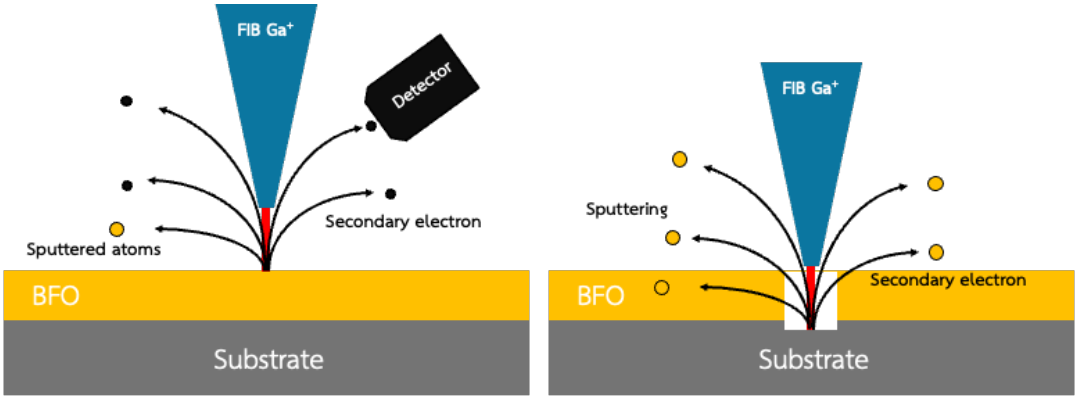

Figure 3.1 Diagram illustrating the principle of FIB operation.

In this study, FIB was chosen for creating grid patterns ranging from 200 to 2000 nm because of its accuracy and flexibility (Yao, 2012). Our system has both electron and ion beams, allowing real-time monitoring of the etching process. The acceleration voltage was set at 30 kV, and the ion current was 200 pA (matching a 30 nm spot size), based on the grid size. The ion beam was angled at 90° to the etched surface. After the FIB process, the sample was annealed again under the same conditions as the initial annealing. This step was to remove Gallium ions and restore the crystallinity of the structures (Orloff et al., 2003).

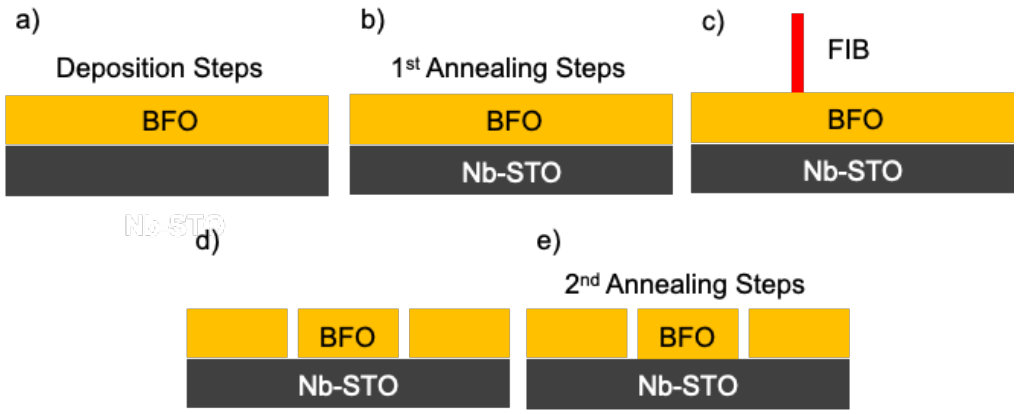

Figure 3.2 Schematic of the BFO film on NSTO fabrication procedure. (a) Deposition BFO thin film by RF-sputtering, (b) The Annealing with temperature at 600 °C, (c) the process of patterning, d) structures are acquired (e) Thermal treatments are designed to restore the crystalline nature of the structures and Gallium ion removal.

3.2.2.2 Au-Nanohole Array/BFO/FTO by Electron beam lithography (EBL)

EBL is a widely used technique in nanotechnology for creating very small patterns on a substrate. It is a key method in the fabrication of nanoscale devices due to its high precision and flexibility (Chen et al., 1993). EBL is commonly used in research and industry for producing intricate structures that are essential in various fields, including semiconductor manufacturing, materials science, and nanoelectronics (Rai-Choudhury, 1997). The principle of EBL involves using a focused beam of electrons to draw patterns on an electron-sensitive film called resist, which is coated on the substrate (Tseng, 2005). The electron beam changes the chemical structure of the resist in the exposed areas. This alteration makes the exposed areas either more or less soluble in a developer solution, depending on whether a positive or negative resist is used. This selective solubility allows for the precise creation of patterns at the nanoscale (Chen et al., 1993).

In this work, the process of creating nanostructures using EBL can be broken down into several steps. The first step is to apply a thin, even layer of electron beam resist onto the substrate using a spin coater. The negative electron beam resist (AR-N 7520 new e-beam resists). The spin coat condition is 4000 rpm for 45 seconds. This step ensures a uniform and thin layer of resist across the substrate. Soft bake on hotplate at 85℃ for 1 minute. Next, the sample is placed in an EBL system where a focused electron beam is used to write the desired pattern onto the resist. The e-beam changes the solubility of the resist layer in the exposed areas, defining the pattern. After exposure, post-bake at 85 ℃ for 1 minute on the hotplate. After exposure and post-bake, the sample is immersed in a developer solution. This step removes the resist in the unexposed area out, revealing the pattern (Chen et al., 1993). A thin layer of Chromium and gold are deposited over the entire substrate using methods like electron beam evaporation with the thickness 20 and 150 nm, respectively. This layer forms the needed structure. Then, the sample undergoes a lift-off process where the resist, along with the material deposited on top of it, is removed. This leaves behind the material only in the patterned areas. Finally, the sample is annealed at a specific temperature at 120℃ for 1 hour to improve the adhesion and quality of the deposited material, ensuring the stability and functionality of the nanostructures.

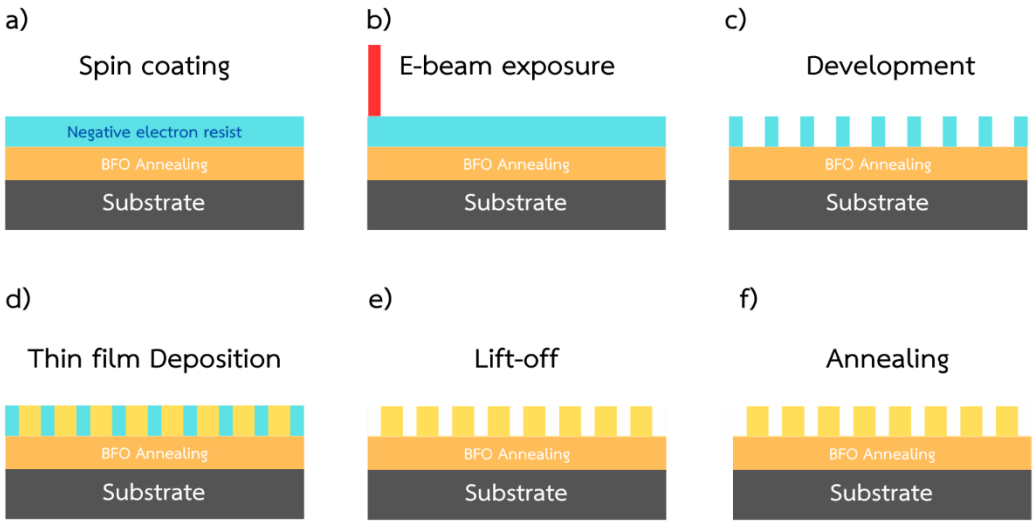

Figure 3.3 The process for direct writing using EBL: (a) The electron beam resist is applied to the surface of the substrate using spin coating. (b) A pattern is designed and then exposed onto the resist layer using an electron beam. (c) The sample undergoes a development process where the resist layer in the unexposed areas is removed, leaving behind the desired nanostructure pattern on the sample. (d) A thin layer of gold is deposited onto the patterned resist layer by electron beam evaporation. (e) The resist, along with the unwanted gold, is lifted off from the sample, revealing the gold pattern on the sample. (f) The sample is annealed at 120°C for 1 hour. This step helps to improve the crystallinity and adhesion of the gold layer to the substrate.

3.3 Basic characterization

3.3.1 X-ray diffraction (XRD)

XRD is a technique that is used to analyze the structure and composition of materials. Many researchers in materials science, chemistry, geology, and biology use it (Cullity et al., 2001). XRD works by shining X-rays onto a crystal sample. The X-rays are made in an X-ray tube, where a heated metal filament makes electrons. These electrons are shot at a target, making the target give off X-rays (Klug

et al., 1974). When the X-rays hit the sample, they bounce off in different directions depending on the crystal's atomic arrangement. We can look at this pattern to understand the crystal structure (Pecharsky et al., 2003).

The angle at which the X-rays bounce is important. We can use it to find the space between atomic planes. We do this using Bragg's law as shown in Figure 3.4 and equation (3.1):

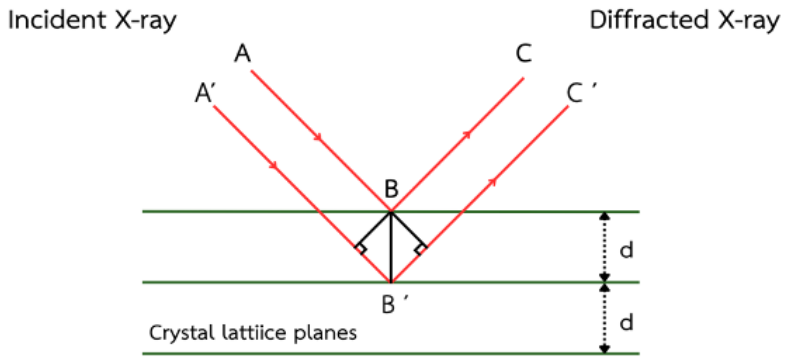

Figure 3.4 The illustration presents principal of X-ray diffraction.

$$\sin\theta = \frac{n\lambda}{2d} \tag{3.1}$$

where λ is the wavelength, θ is the angle of diffraction, and d is the distance between atomic planes.

The result of an XRD measurement is a graph of signal intensity against angles of diffraction, known as two theta positions. These positions show specific spacings between crystals or atoms in the sample (Cullity et al., 2001). By converting the diffraction peaks to d-spacings, we can identify minerals, as each mineral has unique d-spacings. This is usually done by comparing the d-spacings with standard patterns (Klug et al., 1974). XRD provides a lot of information. It tells us about chemical composition, crystal structure, crystal orientation, crystallite size, lattice strain, preferred orientation, and layer thickness. For larger crystals, XRD can find the atomic structure. For small crystals, XRD can determine the sample's composition, crystallinity,

and phase purity (Pecharsky et al., 2003). In this study, XRD was used to find out the crystal structure of different samples. These samples were: NSTO substrate, BFO on NSTO, BFO on NSTO and then annealed, FTO glass, BFO on FTO glass, BFO on FTO glass and then annealed. The XRD results were shown as intensity against a 2θ range from 20° to 80°.

3.3.2 Scanning electron microscope (SEM)

SEM is a method that helps us look closely at the surface of materials at the micro and nano scale. It is used in many research fields like materials science, chemistry, geology, and biology (Burany, 2003; Egerton, 2005). The basic idea of SEM is to use a strong beam of high-energy electrons that hit the atoms in the sample. As these electrons move across the sample's surface, they scatter. The slower secondary electrons are collected by a detector and used to create a magnified image of the sample. This gives a detailed view of the sample's surface (Reimer, 1998; Williams et al., 2013). In our research, SEM is used to compare the surface of different samples. Here are some general observations we might make as demonstrated in Table 3.1.

Table 3.1 Sample's condition list for SEM measurement.

Name	Substrate	Deposited Thin Film	Annealing process (°C)
NSTO substrate	NSTO	-	-
BFO on NSTO	NSTO	BFO	-
BFO on NSTO annealed	NSTO	BFO	600
FTO glass	FTO	-	-
BFO on FTO	FTO	BFO	-
BFO on FTO annealed	FTO	BFO	600

3.3.3 Optical profilometer

The optical profilometer is an important tool in surface metrology. It uses light to measure a surface's topography without touching it (De Groot, 2015). The optical profilometer works based on light interference. Light from a source is split into two paths by a beam splitter. One path goes to the test surface, and the other goes to a reference mirror. The reflections from these surfaces are combined and sent to a digital camera. When the path lengths are within a few light wavelengths, interference patterns form. These patterns show details about the sample surface's shape. The data from the profilometer gives detailed information about the surface's topography. This includes surface roughness, flatness, warpage, and step-height (Thomas, 1999). The data can also be used for advanced measurements of critical dimensions. The information from the profilometer helps us understand the sample surface's geometric features, such as height differences, slopes, curvature, and irregularities.

In this research, an optical profilometer was used to measure the thickness of thin films after coating and the electron beam resist during nanoscale sample preparation (Bhushan, 2010). The profilometer's non-contact, high-resolution measurements are important for controlling film and resist thickness, which affects their properties and the success of electron-beam lithography. Therefore, the optical profilometer is essential for both the coating process and nanoscale sample preparation.

3.3.4 Energy-Dispersive X-ray Spectroscopy (EDS)

EDS is a method used to find the chemical composition of a material. Each element has a unique atomic structure, which creates distinct peaks in its emission spectrum (Burany, 2003). The process starts when a beam of X-rays hits the sample. This beam can knock an electron out of one of the inner shells of an atom, creating a vacancy. An electron from an outer shell then fills this vacancy, and the energy difference is released as an X-ray (Egerton, 2005). The emitted X-rays have energy that is characteristic of the element they came from. These X-rays are detected,

and their energy is measured, allowing us to identify and measure the elements in the sample (Reimer, 1998). The main parts of an EDS system include the excitation source (either an electron or X-ray beam), the X-ray detector, the pulse processor, and the analyzer. The type of excitation source depends on the application: electron beam excitation can be found in electron microscopes, including scanning electron microscopes (SEM) and scanning transmission electron microscopes (STEM) (Williams et al., 2013). EDS is a non-destructive technique, making it valuable in many research fields. It is often used with SEM to give detailed information about the elemental composition of materials (Fultz et al., 2008). In our thesis, we used EDS to find the elements and their percentages composition in the thin film sample.

3.3.5 Piezoresponse Force Microscopy (PFM)

PFM is a specialized scanning probe microscopy technique used to study the piezoelectric properties of materials at the nanoscale. It is especially useful for examining ferroelectric domains and their dynamics, which are important in materials science, electronics, and nanotechnology (Kalinin et al., 2006). PFM works by applying an AC voltage to a conductive tip that is in contact with the sample's surface. This voltage causes the material to deform due to its piezoelectric properties. The deformation is detected by the AFM cantilever, which is used to map the piezoelectric properties of the sample (Alexe et al., 2004). PFM relies on the inverse piezoelectric effect, where an applied electric field causes a mechanical strain in the material. The amplitude measures the magnitude of the sample’s deformation in response to the applied voltage, indicating the strength of the piezoelectric response (Gruverman et al., 2006). The phase measures the phase difference between the applied AC voltage and the resulting mechanical response, providing information on the orientation of ferroelectric domains (Neumayer et al., 2020). Additionally, the topography maps the surface topography of the sample simultaneously with the PFM measurements using the AFM. We can use the simultaneously obtained topographical data to correlate surface features with piezoelectric properties, helping to understand how structural characteristics influence piezoelectric behavior (Kalinin et al., 2006).

3.3.5.1 Sample configurations for PFM measurement

Proper sample preparation is crucial for obtaining reliable and accurate PFM measurements. This section outlines the steps taken to prepare BFO thin films on a NSTO substrate and FTO glass for PFM analysis.

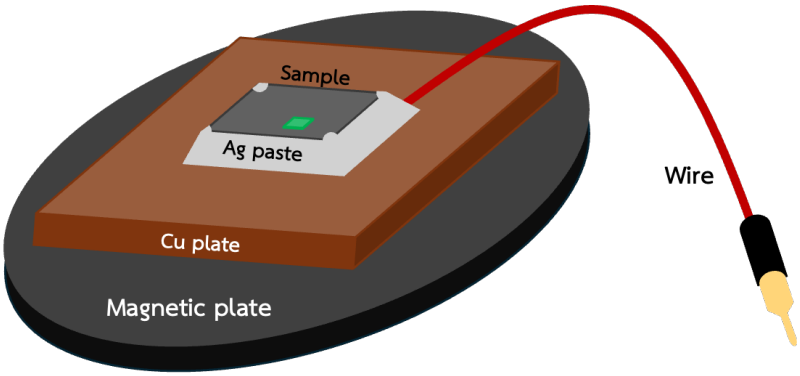

Figure 3.5 The sample preparation for PFM measurement.

Firstly, the sample was cleaned to remove any surface contaminants. This can be done using solvents such as acetone and isopropyl alcohol (IPA) rinsing the sample sequentially in acetone and IPA. Then, it was dried using nitrogen gas flow. Secondly, mounting the sample to secure the sample on a copper plate using conductive adhesive. This step ensures that the sample is firmly attached and has a good electrical connection with the copper plate. To ensure good electrical contact, a small region of the sample is painted with silver paste. Applying the silver paste to a corner of the sample will act as an electrode to facilitate the application of an electric field during PFM measurements. Then, the electrical wires were attached to copper plate to establish an electrical connection to the external voltage source during PFM measurements. Also, another wire should be connected to the silver-painted conner to complete the electrical circuit. Lastly, samples need to be held on the magnet plated for connecting with the PFM sample state. The complete look of the sample which is ready for PFM measurement is illustrated in Figure 3.5.

3.3.5.2 PFM amplitude and phase measurement

In this study, Piezoresponse Force Microscopy (PFM) was employed to investigate the ferroelectric properties of BFO thin films deposited on a NSTO substrate and FTO glass. PFM is a powerful technique for characterizing ferroelectric property on a nanoscale level, offering insights into domain structures and their dynamics. Using PFM, we measured both the phase and amplitude responses of the BFO thin films. The conductive AFM tip (Multi75E-G from budgetsensors) was used to apply an AC voltage (17 kHz, 2.5 Vpp) to the sample surface, inducing a piezoelectric response. The AFM cantilever detected the resulting deformation, allowing us to map the phase and amplitude across the sample. The phase response provided information on the orientation and polarity of the ferroelectric domains.

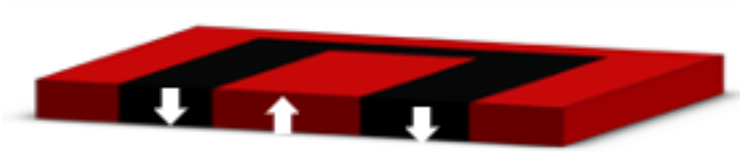

Figure 3.6 The phase image shows different polarization direction when voltage is applied to the sample surface.

By analyzing the phase data, we were able to identify regions with different domain orientations. The amplitude response indicated the magnitude of the piezoelectric effect, reflecting the strength and uniformity of the ferroelectric properties across the sample (Gruverman et al., 2006). To further investigate the ferroelectric behavior, a DC voltage was applied to the surface of the BFO/NSTO and BFO/FTO sample. This application allowed us to study the switching behavior of the ferroelectric domains. By applying a series of positive and negative voltages, we induced domain switching and observed the changes in both phase and amplitude responses. This experiment was crucial for understanding the stability and reliability of the ferroelectric properties under an applied electric field.

3.3.5.3 PFM amplitude and phase measurement under UV

In this study, we utilized a modified PFM setup to measure the piezoelectric properties of the sample under UV irradiation. The setup is based on the standard PFM configuration with an additional blue laser to illuminate the sample during measurements. The blue laser with a wavelength of 405 nanometers was used and the beam spot was focused on the area being scanned by the AFM tip. The intensity of the blue laser was set at 4.5 volts. PFM measurements were conducted with and without UV irradiation which can be compared later to ensure the effect of UV irradiation.

3.3.5.4 PFM hysteresis measurement

PFM hysteresis loop measurements are essential for investigating the ferroelectric properties of materials, especially their polarization switching behavior.

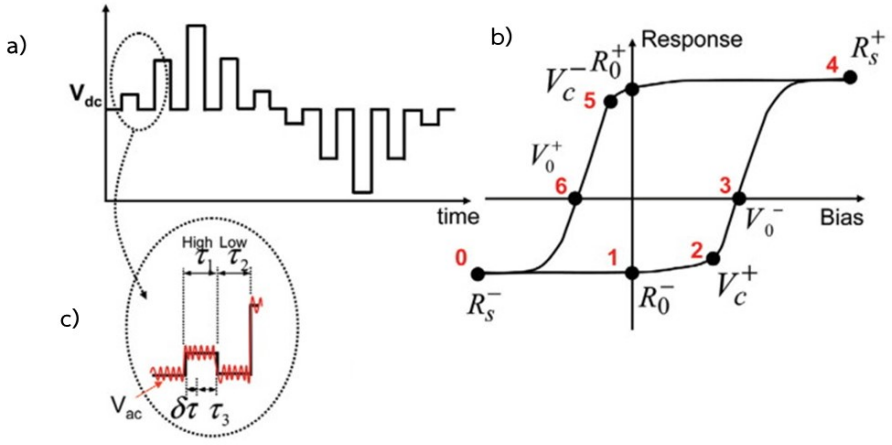

Figure 3.7 The switching spectroscopy PFM: (a) DC triangle waveform, (b) local hysteresis loop result, and (c) the zoomed-in view of triangle waveform (Kalinin et al., 2008).

The hysteresis loop provides valuable information about the material's coercive field, remanent polarization, and domain dynamics (Kalinin et al., 2008). The experimental setup is also based on conventional PFM with external data

acquisition (DAQ) and waveform generator to operate switching spectroscopy PFM as shown in Figure 3.7.

For the measurement procedure, the PFM system was used to map the position of the area of interest on the sample. This ensures precise targeting of the region where the hysteresis loop will be measured. The DC triangular waveform from the waveform generator was set with the maximum of +10V and minimum of -10V, then it applied to the AFM tip. The AC reference signal of 17 kHz frequency with 2.5 V peak-to-peak (V_{pp}) was applied to the sample. The combined external voltage bias is illustrated in Figure 3.7(a) and Figure 3.7(c). The amplitude and phase of the piezoresponse were detected by the system and passed through a lock-in amplifier. Then, external DAQ was used to record the amplitude, phase, and applied voltage signals. To clearly demonstrate the data, only the average of signals on the DC off-field region were selected. Amplitude and applied voltage plot show the amplitude of the piezoelectric response as a function of the applied DC voltage, revealing the characteristic butterfly loop which indicates polarization switching. Phase and applied voltage plot show the phase response as a function of the applied DC voltage, forming a hysteresis loop that provides insights into the polarization direction and switching dynamics. In addition, with the result of amplitude and phase, the piezoresponse can be calculated by equation (3.2) (Neumayer et al., 2020).

$$PR = A\sin\emptyset \tag{3.2}$$

where (A) is the amplitude of the response and (ϕ) is the phase angle. This calculation is performed for each data point as a function of the applied voltage.

The calculated piezoresponse values were plotted against the applied voltage to generate the hysteresis loop as illustrated in Figure 3.5(b). From the hysteresis loops, ferroelectric properties such as coercive field, the voltage at which

polarization switching occurs, remanent polarization, the polarization after removing the applied field, and other domain switching behaviors were analyzed.

The PFM hysteresis loop measurement setup, enhanced with an external Data Acquisition (DAQ) system, allows for precise and detailed investigation of the ferroelectric properties of materials. By mapping the area of interest, applying controlled waveforms, and utilizing a lock-in amplifier in conjunction with a DAQ system, we can accurately measure and analyze the piezoresponse of the sample under varying applied voltages. This approach provides comprehensive insights into the material's polarization switching behavior and ferroelectric characteristics.