공학석사 학위논문

Observation of Ferroelectric Critical Thickness of $BaTiO_3$ Thin Film by Cs-corrected STEM

구면수차보정 투과전자현미경을 이용한 $BaTiO_3$ 산화물 박막의 강유전성 임계두께 관찰 연구

2018년 8월

서울대학교 대학원

재 료 공 학 부

김 윤 구

Abstract

Observation of Ferroelectric Critical Thickness of $BaTiO_3$ Thin Film by Cs-corrected STEM

Yoonkoo Kim
Department of Materials Science and Engineering
College of Engineering
Seoul National University

$BaTiO_3$ is well known for its ferroelectricity. However, its ferroelectricity can be changed under various external conditions. Particularly, the critical thickness that retains ferroelectricity have attracted continuous attention. Thus, it is very important to reveal critical elements that determine the ferroelectricity of $BaTiO_3$ in thin film structure to apply $BaTiO_3$ for electronic devices. In this study, we investigate the possibility of reducing the critical thickness of $BaTIO_3$ of 3.5 unit cell by introducing dielectric

$SrTiO_3$ layers, for which, 1unit cell and 10unit cell of $SrTiO_3$ on 2.5unit cell $BaTiO_3$ between $SrRuO_3$ electrodes are compared. Using high-resolution HAADF-STEM imaging, we measured displacements of cations to examine the existence of ferroelectricity for each samples. We extracted atomic peak positions from HAADF-STEM images and calculated ionic displacements of B cations (Ti, Ru), $\delta_{A\text{-}B}$. From this $\delta_{A\text{-}B}$, we found that there is ferroelectricity in 1unit cell $SrTiO_3$ sample, however, ferroelectricity disappears 10 unit cell $SrTiO_3$ sample. Ferroelectricity in 1 unit cell SrTiO3 sample was also measured in piezoresponce force microscopy. This difference could be originated from theoretically expected, polarization penetration into electrodes. This result demonstrates that the thickness of the dielectric $SrTiO_3$ layer on $BaTiO_3$ can affect the critical thickness of $BaTiO_3$ ferroelectricity.

Keywords: Ferroelectricity, ionic polarization, Cs-corrected STEM, Piezoresponce Force Microscopy, $BaTiO_3$ thin film

Student Number: 2015-20810

Contents

List of Figures

Chapter 1. Introduction

Perovskite transition metal oxide heterostructures have attracted extensive research interests because these oxide materials show various novel properties.[1] Espcially, $BaTiO_3$ is one of the typical example of transition metal oxide which show strong ferroelecricity due to its simultaneous ionic polarization and have large dielectric constants compared to other various paraelectric and ferroelectric oxide materials.[2] Bacause of this high dielectric constant, Barium titanate is promising candidate material for many electronic devices such as capacitor, non-volatile memory(Fe-RAM) and piezoelectric actuator.[3-5]

Ferroelectric perovskite oxide materials like $BaTiO_3$ show their ferroelectricity as its unit cell structure changes.[6] As described in Fig. 1, ions moves from their original position and these displacements generates polarization and ferroelectricity. This polarization makes $BaTiO_3$ have strong ferroelectricity. However, its ferroelectricity depends on many factors such as stoichiometry, crystal morphology, growth methodology and so on.[2]

Many researchers have interested in the ferroelectricity of $BaTiO_3$ in its thin film form. Because thin film structure is very general in device fabrication and attracts much industrial interests. Especially, ferroelectricity in oxide thin films degrade when the film thickness going thinner and interesting physical issues such as depolarization field and polarization penetration are related to here.[7] We will talk about these issues later.

Because of these reasons mentioned, researchers performed many studies to find ferroelectric critical thickness of $BaTiO_3$ thin film sandwiched in two metal electrodes, especially $SrRuO_3$ or Pt.[7-8] However, there were relatively small number of researches for $BaTiO_3$ thin film attached to dielectric material such as $SrTiO_3$.[2,9] Ferroelectricity of $BaTiO_3$ on the dielectric material is quite important problem in the viewpoint of industry. Because most of practical electric devices use Si for substrate and Si substrate require dielectric buffer layer to grow ferroelectrics like BaTiO3 on top of that.

In this paper, we grow $BaTiO_3/SrTiO_3$ thin film between $SrRuO_3$ electrodes to reproduce metal/dielectric/ferroelectric heterostructure and we performed Cs-corrected STEM observation using high angle annular dark field imaging to directly observe its ferroelectricity with varying thickness of dielectric layer, that is, $SrTiO_3$. Also we performed piezoresponce force microscopy to crosscheck the swiching property of ferroelectricity.

Here, we demonstrate that extremely thin $BaTiO_3$ thin film can show ferroelectricity with sufficiently thin dielectric $SrTiO_3$ thin film. However, when dielectric $SrTiO_3$ goes thicker, this ferroelectricity cannot be stabilized and disappear. We think that this phenomenon can occur because of polarization penetration into dielectric layer.

Chapter 2. Literature Studies

2.1 BaTiO3 and Its Ferroelectricity

$BaTiO_3$ is a typical example of ferroelectric transition metal oxide. Among many oxide materials, $BaTiO_3$ attracts much research interest because of its strong dielectric constant and moderate Curie temperature(~120℃).[6] As known before, $BaTiO_3$ have much higher dielectric constant compared to many other materials such as $PbZrO_3$.[2] The origin of this strong dielectric constant is change of lattice constants. Paraelectric $BaTiO_3$ have cubic unit cell, however, ferroelectric $BaTiO_3$ have tetragonal unit cell in which Ti cation and oxygen anion move from its body center and face centers respectively.[10] These ionic displacements generate ionic polarization. The schematic description of these ionic displacements are shown in Fig. 1. This strong polarization effect makes $BaTIO_3$ promising candidate material for various device applications such as field effect transistor, non-volatile memory.[1]

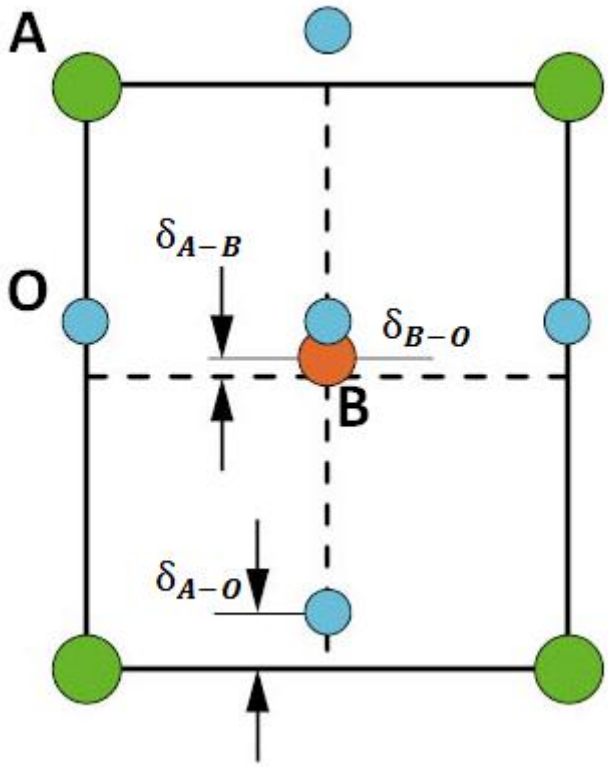

Figure 1 Schematic description of tetragonal ABO_3 ferroelectric materials and ionic displacemetns.

2.2 Studies on BaTIO3 thin film heterostructure

As we mentioned, tetragonal $BaTiO_3$ has strong ferroelectricity. The electrical properties like ferroelectricity are affected by many factors such as chemical composition, crystal morphology.[2] Even fabrication method can affect to the ferroelectricity. Especially, because of continuing miniaturization of electric devices, stabilization of ferroelectric polarization at the nanometer scale become more and more important. Moreover, atomic scale growth techniques have advanced significantly recently, ones are able to control the number of unit cell, stacking sequence of nanometer scale oxide thin film. Therefore, many researchers have interests in the critical thickness of ferroelectricity of $BaTiO_3$ thin film.

Even though miniaturization tendency makes possible achieve high electric fields from low-voltage, but it also generates size effect and following degradation phenomena.[12] That is, the ferroelectricity of $BaTiO_3$ thin film going unstable as its thickness being thinner.

In general, there are two kind of explanations for this size effect. The first one is related to the free charges in the electrodes. As described in Fig. 2, because of polarization in the ferroelectric, free charges in electrodes approach to the interface to screen the electric field due to bound charges. This accumulated free charges generate new electric field which direction is opposite to the original electric field. This is called depolarization field which is described red arrow in Fig. 2.

This phenomenon is also known as Thomas-Fermi screening.[13] Based on this depolarization field theory, Junquera et al studied ferroelectric critical thickness of $SrRuO_3/BaTiO_3/SrRuO_3$ thin film heterostructure.[8] Using first-principle calculation, they calculated stability of ferroelectric polarization as a function of various $BaTiO_3$ thicknesses. From their calculation, Junquera et al found that until four unit cell, ferroelectricity in BaTiO3 can be stabilized.

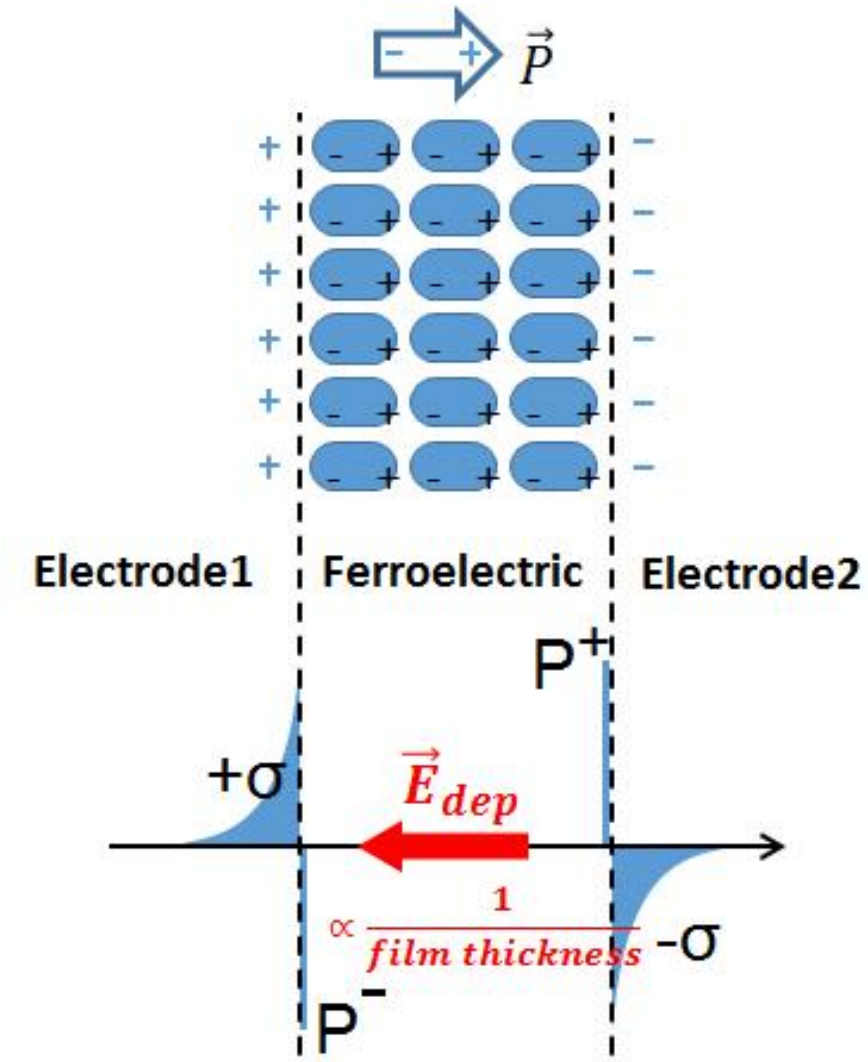

Figure 2 Schematic description of bound charges in ferroelectrics and depolarization field.

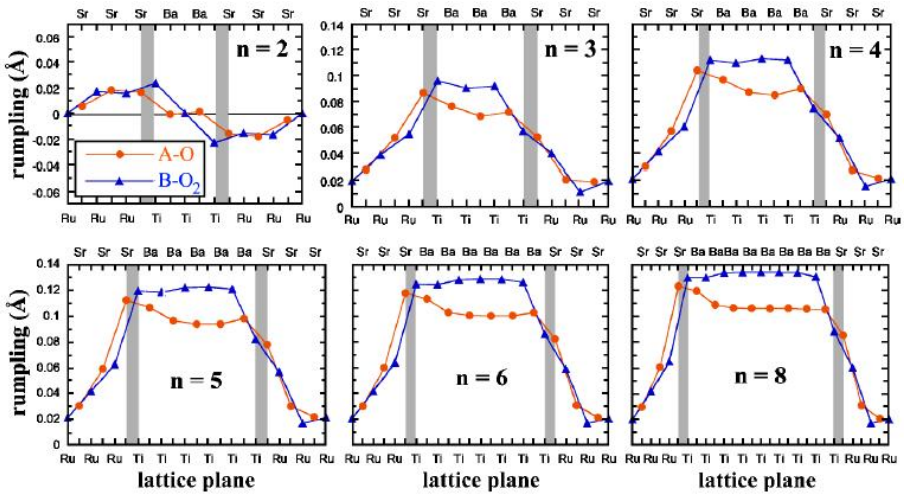

Figure 3 First-principle calculated ferroelectirc displacemetns in $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructure.[7]

The second explanation for the size effect is continuity effect. The polarization can't drop abruptly at the ferroelectric-electrode interface. Thus small polarization can be exist in the electrode region. This is so-called Kretschmer-Binder effect.[14] Gerra et al also performed first-principle calculation study to investigate the effect of this ferroelectric polarization penetration into the electrodes.[7] They also used $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructure with various $BaTiO_3$ thicknesses. For their calculation, they considered not only free charges but also ionic relaxation in the $SrRuO_3$ electrodes. Under these conditions, they found that 3.5u.c $BaTiO_3$ can show stable ferroelectric displacements as described in Fig. 3. In the Fig. 3, we can notice that there are stable ferroelectric displacements larger than 10pm in 3.5unit cell and more thick $BaTiO_3$ samples. However, in 2.5u.c samples, the magnitude of ferroelectric displacements in 2.5u.c $BaTiO_3$ is very small. This result implies that ferroelectric polarization can be stabilized till 3.5u.c $BaTiO_3$ thin film which have thinner thickness compared to result of Junquera et al.[7-8]

There is another issue for the ferroelectricity of $BaTiO_3$ thin film. The stacking sequence of the thin film is that. In the Fig. 4, there are two cases of $SrRuO_3/BaTiO_3/SrRuO_3$ thin film heterostructure. Both of Fig. 4(a) and (b) have three Ba layers between $SrRuO_3$ layers. However, at the top interfaces situation is different. Fig. 4(a) have Ru layer and Fig. 4(b) have Ti layer between Ba and Sr layers. These interfacial layers are called 'termination

layers' and Fig. 4(a) and (b) have different symmetry in their termination layers.

Lu et al studied the relation between these termination layers and ferroelectricity of $BaTiO_3$ thin film.[15] They also performed first-principle calculation for $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructure with varying $BaTiO_3$ thicknesses. However, to compare the effect of termination layer, they implemented one $SrTiO_3$ layer in one structure. Their structure and calculation results are shown in Fig. 5. A structure in Fig. 5(a) have asymmetric termination layers and Fig. 5(d) have symmetric termination layers. Other four figures show energetic stability of polarizations. Fig. 5(b) and (c) show that when $BaTiO_3$ have asymmetric termination layers, one of the two polarization direction is more stable than one another. However, when $BaTiO_3$ have symmetric termination layers, two polarization direction are all stable and makes ferroelectric swiching possible.[15]

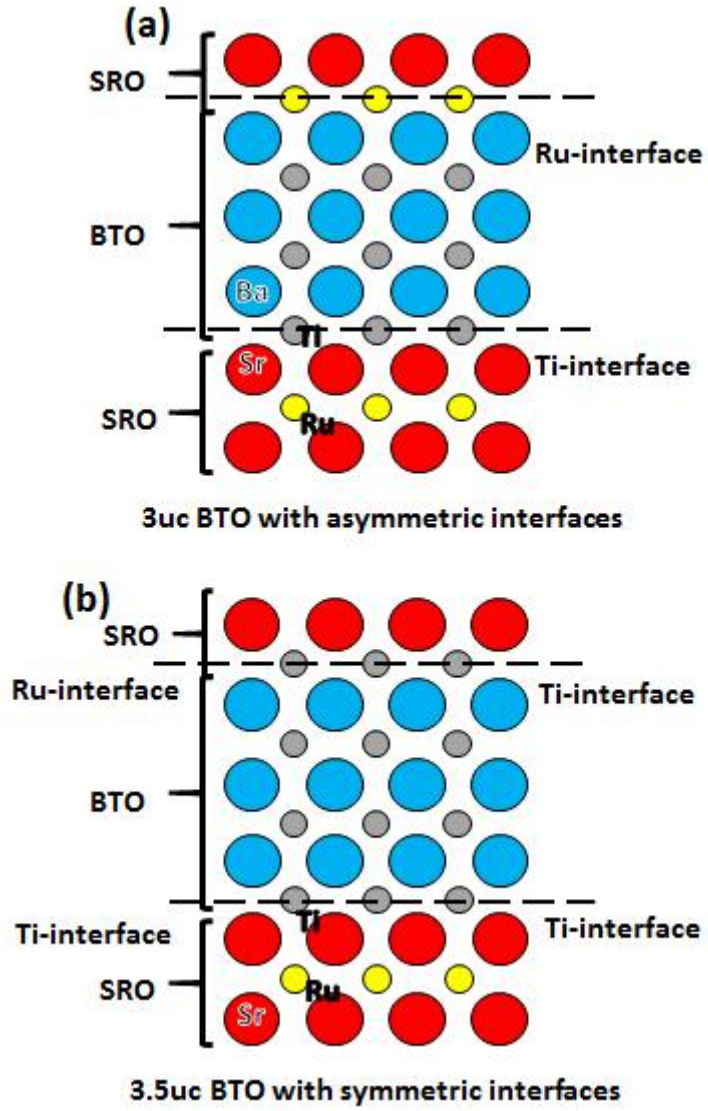

Figure 4 Schematic description for (a) asymmetric Ru and Ti termination layers and (b) symmetric Ti termination layers.

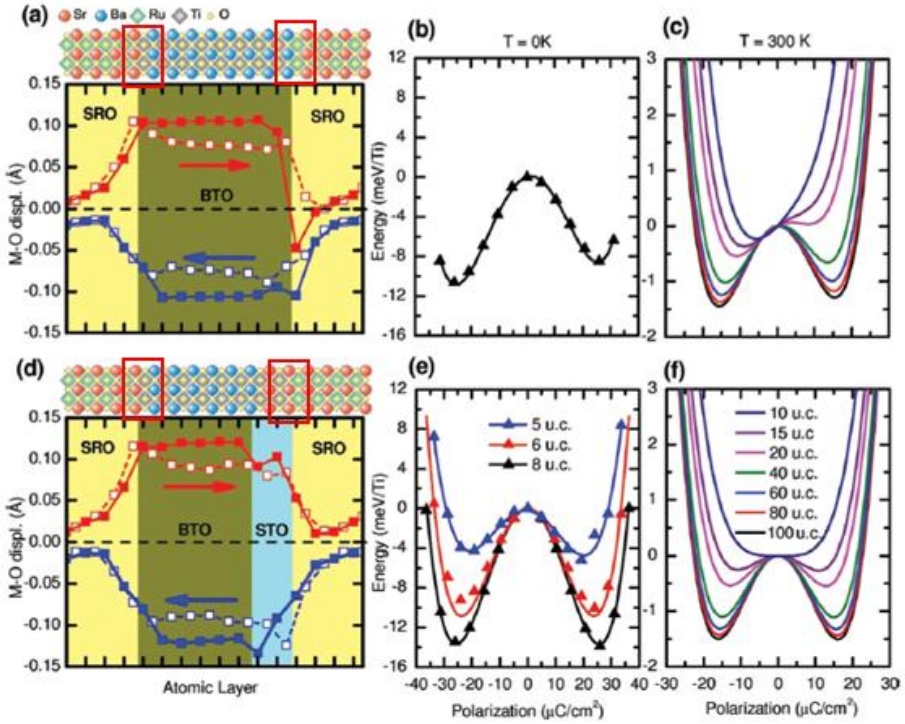

Figure 5 Energetic stability of ferroelectricity of $BaTiO_3$ thin film according to film thickness and symmetry of termination layers.[15]

The research of Lu et al show that symmetric termination layers are very important to embody swichable ferroelectricity. However, many studies on $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructure have shown that atomic scale interface control is very difficult obstacle to approach theoretical limit, 3.5unit cell $BaTiO_3$.[16-17] Shin et al succeeded in growth 3.5u.c $BaTiO_3$ between $SrRuO_3$ electrodes using pulsed laser deposition with atomically sharp symmetric Ti termination layers.[11] They controlled oxygen partial pressure and found that with low oxygen partial pressure condition Ti termination layer can be stabilized. Fig. 6 shows high angle annular dark field image of 3.5u.c $BaTiO_3$ heterostructure and we can observe that atomically sharp Ti termination layer in large region.

Fig. 7 shows Ti ionic displacements in 3.5u.c $BaTiO_3$ thin film. B cation displacement, δ_{A-B} in Fig. 1. The plot in Fig. 7(b) shows ferroelectric displacements of Ti cations and their penetration into $SrRuO_3$ electrode. These displacements are direct evidence of ferroelectric displacements in 3.5u.c $BaTiO_3$ thin film, that is, theoretical limit thickness of stable ferroelectricity in $BaTiO_3$ thin film structure.

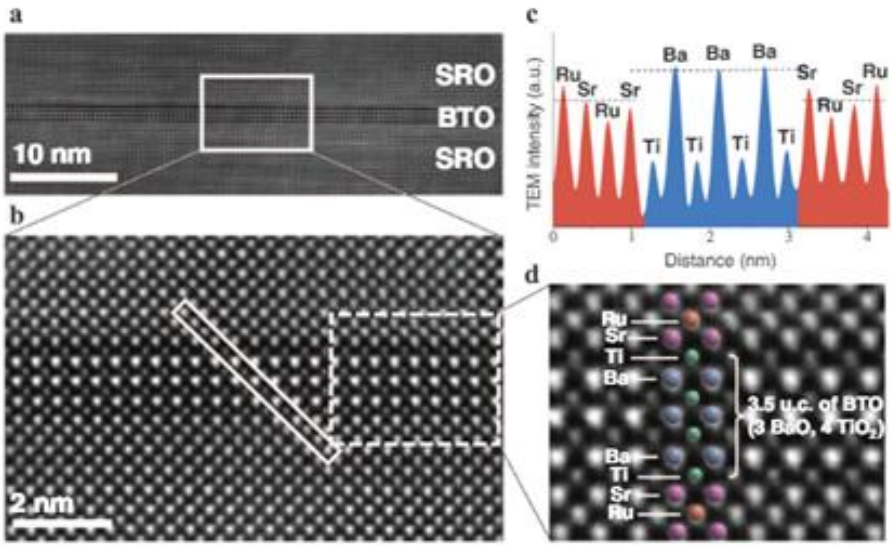

Figure 6 (a) HAADF image of 3.5u.c BaTiO3 between SrRuO3 electrodes, (b) same sample with more magnified image, (c) intensity profile of long, diagonal white box in (b), (d) much more magnified image in white dashed box in (b) and atomic model.[11]

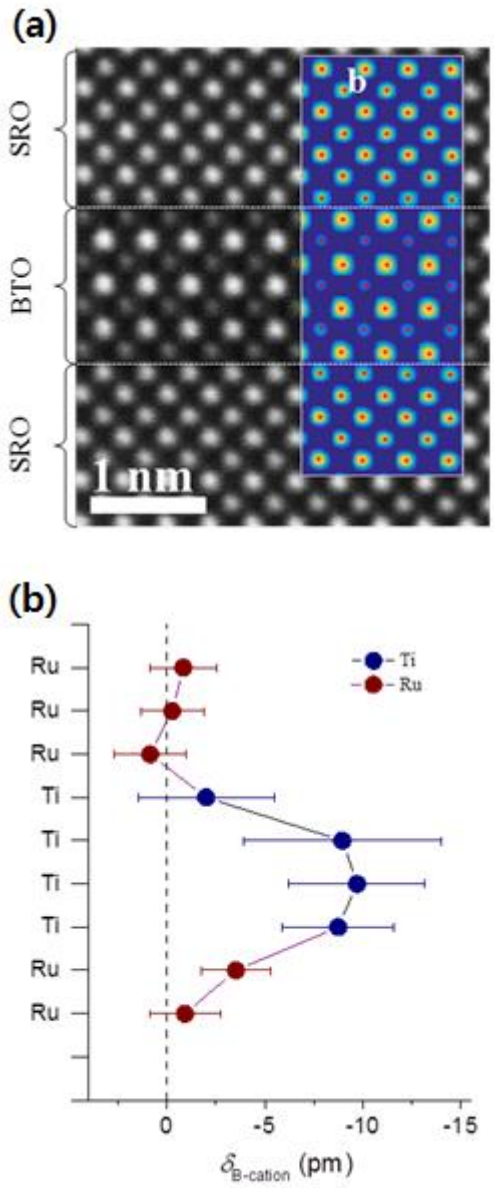

Figure 7 (a) HAADF image of 3.5u.c $BaTiO_3$ between $SrRuO_3$ electrodes, (b) plot of B site cation displacements.[11]

2.3 Critical thickness of BaTiO3 in FE/Dielectric structure

We introduced many researches dealing with critical thickness of ferroelectricity of $BaTiO_3$ thin film. However, all those researches required metallic $SrRuO_3$ electrodes. Of course, $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructure is great model system to investigate ferroelectric critical thickness. However such metal/ferroelectric/metal structure is somewhat different from real device structure. In real industry, most of electric devices use Si substrate. It is very important issue to grow $BaTiO_3$ thin film on top of Si substrate directly.[18] Therefore, one grow $SrTiO_3$ on the Si substrate first and then grow $BaTiO_3$ film on the $SrTiO_3$ film. In this $Si/SrTiO_3/BaTiO_3$ structure, doped Si have metallic property and $SrTiO_3$ is dielectric. Consequently, this structure has metal/dielectric/ferroelectric properties respectively. This is quite different compared to $SrRuO_3/BaTiO_3/SrRuO_3$ structure, which have metal/ferroelectric/metal properties.

Dubourdieu et al tried to grow mentioned thin film system.[6] Fig. 8(a) shows high angle annular dark field image of $Si/SiO_2/SrTiO_3/BaTiO_3$ system. High resolution STEM image shows highly crystalline $BaTiO_3$ film can grow on $SrTiO_3$. Then how about the ferroelectricity of such system? To measure ferroelectricity in this metal/dielectric/ferroelectric structure, Dubourdieu et al and Mazet et al performed piezoresponce force microscopy(PFM).[9] Fig. 8(b) and (c) shows PFM amplitude and phase

respectively. Fig. 8(b) shows typical 'butterfly curve' which implies the existence of ferroelectric swiching.[19] Such researches say that $BaTiO_3$ film on $Si/SrTiO_3$ can exhibit ferroelectricity. However, the critical thickness of ferroelectricity in these model system is unknown.

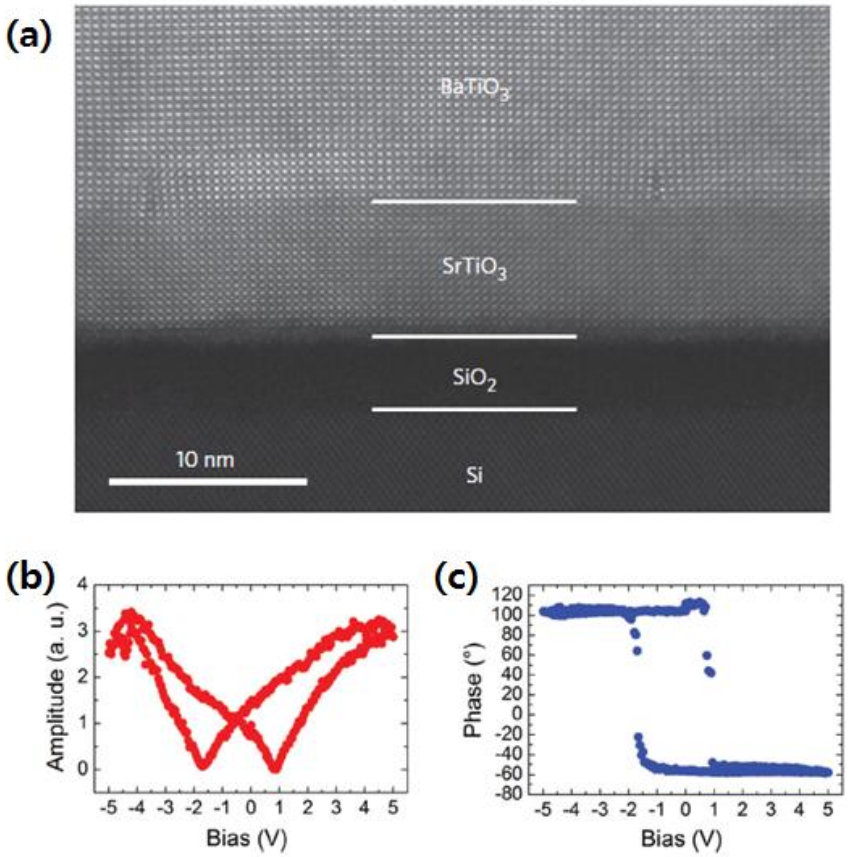

Figure 8 (a) HAADF image of $Si/SiO_2/SrTiO_3/BaTiO_3$ heterostructure, (b),(c) PFM amplitude and phase of $Si/SiO_2/SrTiO_3/BaTiO_3$[6,9]

Chapter 3. Experimental Details

3.1 Growth and Characterization of BaTiO3 films

Our perovskite thin films were fabricated by a pulsed laser deposition(PLD) system with a KrF excimer laser(λ =248nm). Before deposition, $SrTiO_3$(001) substrates were etched using buffered hydrofluoric acid and annealed at 1000℃ in an ambient oxygen flow to create atomically smooth TiO_2-terminated surfaces. The temperature of the substrate was 700 during deposition and the laser fluence repetition rate were set at 1.5Jcm-2 and 2Hz, respectively. The $SrRuO_3$ electrodes were grown at on oxygen partial pressure (Po_2) of 100mTorr and ultrathin $BaTiO_3$ layers were subsequently deposited at Po_2 = 5mTorr. The heterostructures were ex-situ annealed at 600 in an ambient oxygen flow for 1 hour to minimize the oxygen deficiency.[20] Following above processes, two heterostructure films samples were fabricated. In the first sample, 20nm $SrRuO_3$ bottom electrode was deposited on top of $SrTiO_3$ substrate. On the bottom electrode, 2.5u.c $BaTiO_3$, 1u.c $SrTiO_3$, 20nm $SrRuO_3$ top electrode are deposited consequtively. For second sample, on top of 20nm bottom electrode, 2.5u.c $BaTiO_3$, 10u.c $SrTiO_3$, 20nm top electrode are deposited in the same manner. Schematic description of these two samples are given in Fig. 9.

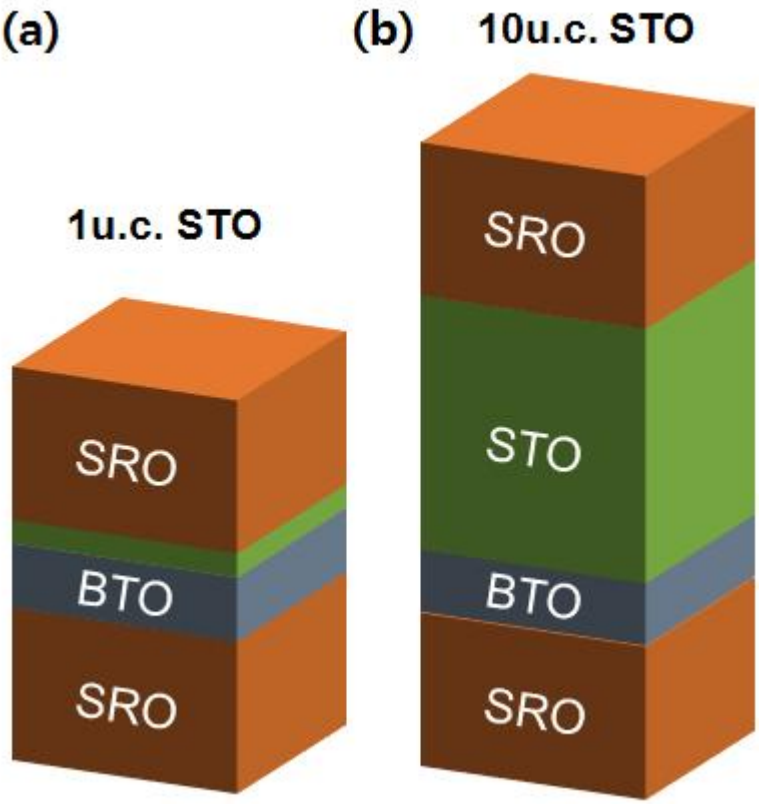

Figure 9 Schematic description of our heterostructures. (a) 1u.c $SrTiO_3$/2.5u.c $BaTiO_3$ and (b) 10u.c $SrTiO_3$/2.5u.c $BaTiO_3$ between $SrRuO_3$ electrodes.

High resolution XRD and atomic force microscopy(AFM) observations were followed after film fabrication processes to investigate surface morphology and crystalline quality of heterostructure film system.[20] AFM and XRD results are given in Fig. 10.

3.2 Cs-corrected STEM observation and analysis

After the film sample deposition, TEM specimens were made by focused ion beam(FIB). When sample prepared, fine milling is following using nanomill. Cs-corrected STEM observation was performed.

Cs-corrected STEM observation was performed by JEOL ARM-200F in National Center for Interuniversity Research Facility(NCIRF), Seoul National University. Acceleration voltage was 200kV. When we obtain high angle annular dark field image(HAADF), JEOL STEMMeister software integrated 30 images to correct sample drift effect.

Using HAADF images, we investigated peak position of each atomic columns by two dimensional fitting. For this, we used peak pairs analysis algorithm developed by Ishizuka et al.[21]

3.3 Piezoresponce Force Microscopy(PFM)

The swiching properties of ferroelectric ionic polarization were measured by an piezoresponce force microscopy using atomic force microscopy at room temperature. A Cr/Pt-coated probe tip with a 40N/m

spring constant and a resonant frequency of 400kHz was used. The high spring constant and contact resonance frequency minimized possible effects of nonpiezoelectric response, such as electrostatic force.[11]

Chapter 4. Results and Discussion

4.1 Growth and Characterization of BaTiO3 films

The characterization of two samples with different $SrTiO_3$ thickness described in Fig. 9 was performed by atomic force microscopy and high resolution XRD. Fig 10 below show AFM image and XRD scan of our heterostructure film system.

As shown in Fig 10(a), AFM image show typical step-terrace surface morphology. Its wide terrace regions show that $SrRuO_3$ top electrode have atomically smooth surface roughness under 1nm. Each terrace area is up to in hundreds nm region. It means that our film system have atomically flat structure in wide region.

Next, in Fig 10(b), HRXRD image show 2θ-ω scan result. It shows two major peaks which are $SrTiO_3$ (002) and $SrRuO_3$(220) respectively. High and sharp $SrTiO_3$ (002) peak come from $SrTiO_3$ substrate. $SrRuO_3$(220) peak show that $SrRuO_3$ electrodes are well stabilized on top of $SrTiO_3$ substrates. Because there were no any other major peaks, there were not other secondary phases in scanning range. Therefore, we confirmed that $SrRuO_3$ films were deposited on substrates epitaxially. We cannot observe XRD peak for $BaTiO_3$ because 2.5u.c $BaTiO_3$ layers are too thin to be measured in XRD scan. High crystallinity of our samples can be confirmed again in our high resolution STEM images.

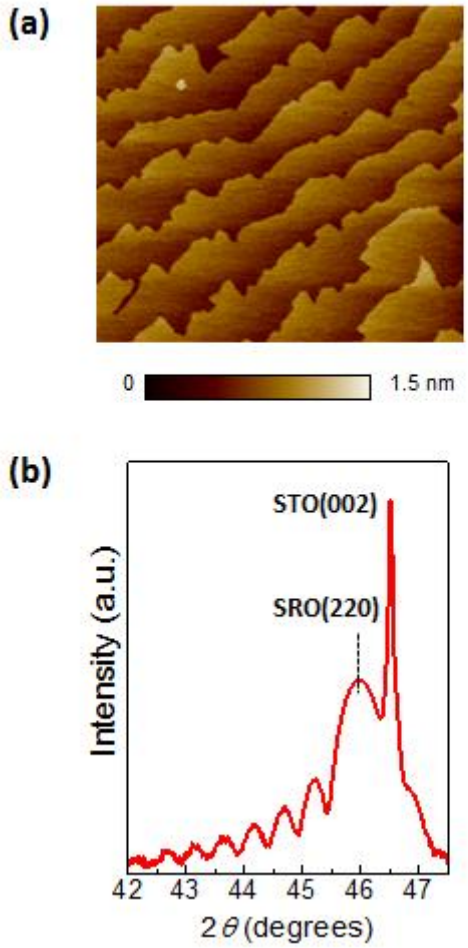

Figure 10 (a) AFM imaging of film heterostructure, (b) HRXRD **2θ-ω** sacn data.

4.2 Cs-corrected STEM observation and analysis

As described in Fig 9, we observed two samples with different $SrTiO_3$ thicknesses, 1u.c and 10u.c respectively. In this section, we will discuss Cs-corrected STEM observation images and analysis results for each samples.

4.2.1 1u.c SrTiO3 on 2.5u.c BaTIO3 films

Fig 11 shows the high resolution annular dark field image of our heterostructure film system of 1u.c $SrTiO_3$ on the 2.5u.c $BaTiO_3$ between two $SrRuO_3$ electrodes. Fast Fourier transform of HAADF image in Fig. 11(b) shows typical perovskite (100) zone axis and there are no any half-integer peaks which imply the existence of supercell structure. This result corresponds with the XRD result in Fig. 10 which shows no any other secondary phase of $SrRuO_3$ and $BaTiO_3$. It means that our $SrRuO_3$ and $BaTiO_3$ film structure deposited epitaxially on top of $SrTiO_3$ substrate and have stable pseudo-cubic structure.

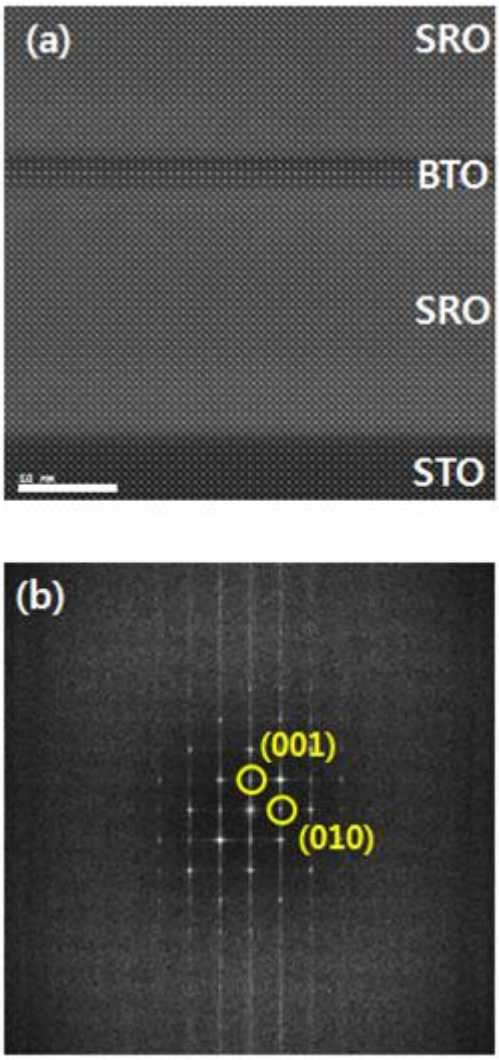

Figure 11 (a) HAADF image with low magnification, (b) FFT image of HAADF image of 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$.

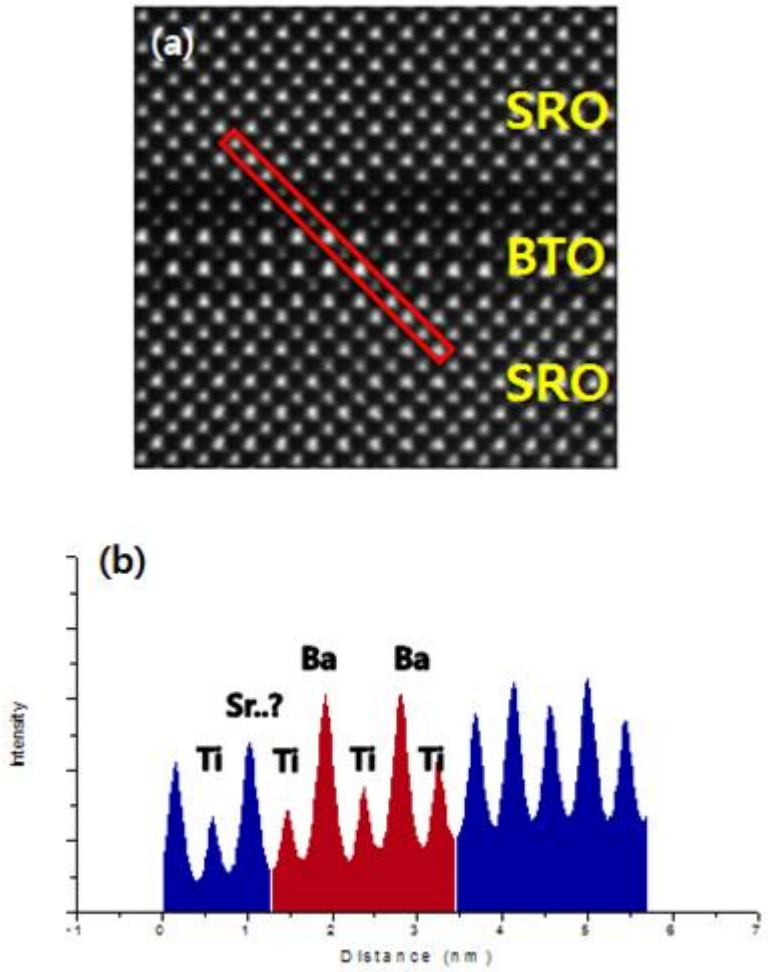

Figure 12 (a) HAADF image of 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ with high magnification, (b) intensity profile of long, red box region.

Fig. 12(a) is more magnified HAADF image of 1u.c $SrTiO_3$ and 2.5u.c $BaTiO_3$ sample. Between top and bottom SrRuO3 electrodes, we can easily observe two A site cation layer and three B site cation layers. Even in bare eyes, we can see two A site cation layers are brighter than one other A site cation layer. Fig. 12(b) shows intensity line profile of red box in Fig. 12(a). we can see intensity peaks for each A and B site cations alternatively. We know (Sr and Ba) for A site and (Ru and Ti) for B site cations respectively. Therefore, among three A site cation peaks between $SrRuO_3$ electrodes, two peaks have higher intensities than one another peak. In HAADF STEM image, peak intensity is proportional to the square of atomic number[], so we can expect that this smaller peak is a Sr atomic column and other two peaks with higher intensities are Ba respectively.

To confirm the film structure and the existence of 1u.c $SrTiO_3$ layer between top electrode and 2.5u.c $BaTiO_3$, we performed energy dispersive spectroscopy(EDS) measurement for elemental analysis. Fig 13 shows two dimensional elemental mapping images. Fig. 13(e), that is, Sr elemental map apparently shows that there are one Sr layer on top of Ba layers. Therefore, we confirmed that one unit cell of $SrTiO_3$ layer between top $SrRuO_3$ electrode and $BaTiO_3$ thin film.

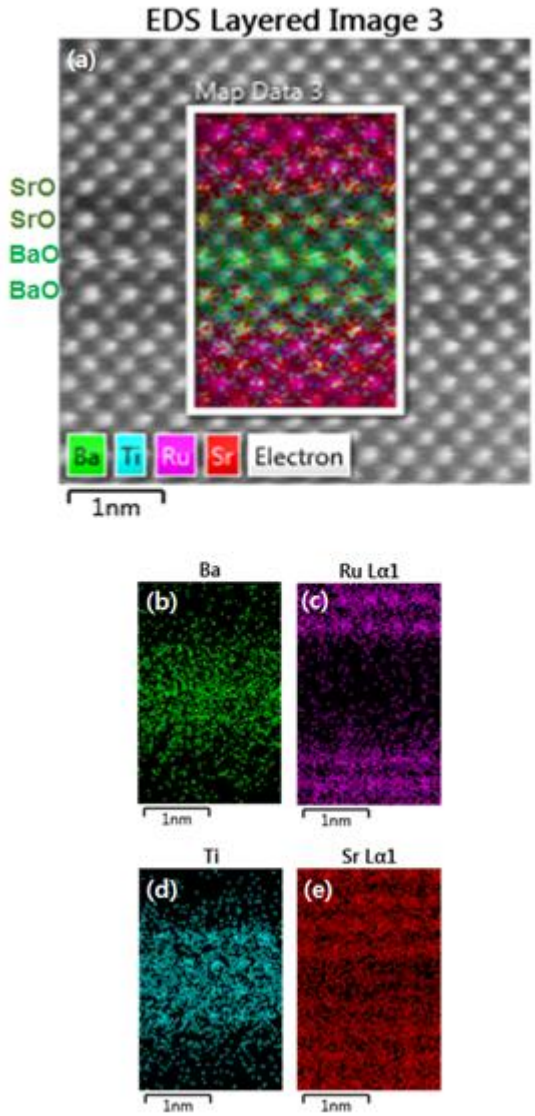

Figure 13 (a) HAADF image and integrated EDS signal mapping, (b)~(e) Each elemental maps for Ba, Ru, Ti and Sr in 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ respectively.

Next, to measure the ferroelectric displacement of B site cations in $BaTiO_3$ region, we measured atomic peak positions by two dimensional fitting of atomic columns. We used peak finding tool implemented in peak pairs algorithm software package developed by Ishizuka et al.[21] As explained in Fig. 1, we calculated difference between real B site cation position and midpoint of four A site cation positions for each unit cell. Fig. 14 shows the result from this image analysis for 1u.c $SrTiO_3$ sample. As legend shows, red dots mean cation displacements of Ru ions. Green and blue dots mean Ti displacements. Especially, blue dots mean Ti displacements in 2.5u.c $BaTiO_3$ layers and green do mean Ti displacement in termination layer between $SrRuO_3$ electrode and $SrTiO_3$ layer. These four Ti layers show more than 10pm displacements, this is the direct evidence of ferroelectricity and polarization penetration expected in Gerra et al's study.[7] Moreover, among many images, more than 70% of images (26 images from total 36 images) shown ferroelectric displacements like Fig. 14(a).

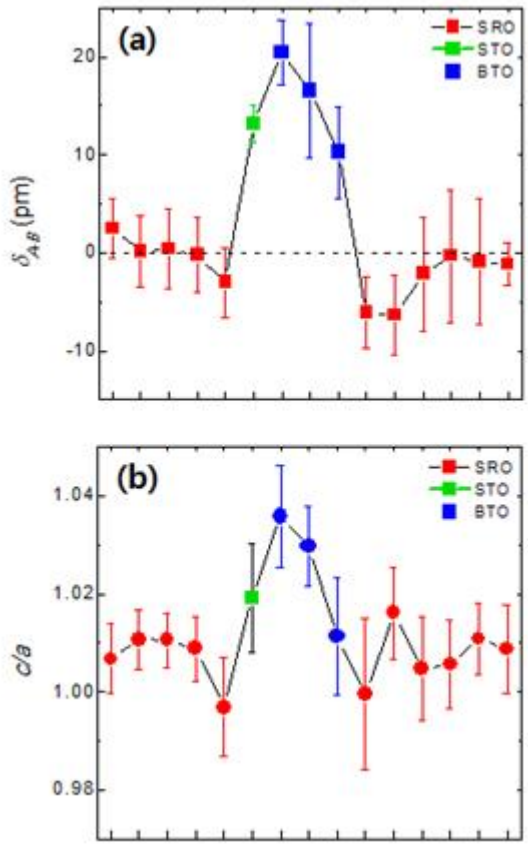

Figure 14 (a) Ferroelectric displacements, (b) c/a ratio in 1u.c $SrTiO_3$ and 2.5u.c $BaTiO_3$

4.2.2 10u.c SrTiO3 on 2.5u.c BaTiO3

Same as 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample, we observed 10u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample. Low magnification high angle annular field image and its fast fourier transform image are given in Fig 15. As shown in Fig 15(a), on Top of $SrRuO_3$ bottom electrode, 2.5u.c $BaTiO_3$, 10u.c $SrTiO_3$ and $SrRuO_3$ top electrode are deposited consequtively. Fig. 15(b), fast fourier transform image of Fig. 15(a) shows perovskite (100) zone axis same as Fig. 14(b). It implies that our 10u.c $SrTiO_3$ sample have epitaxial film structure similar with 1u.c $SrTiO_3$ sample.

Same as 1u.c $SrTiO_3$ sample, Fig. 16 shows magnified image of 10u.c $SrTiO_3$ on top of 2.5u.c $BaTiO_3$ film. We can observe two bright Ba layers below $SrTiO_3$ layer in the Fig 16(b), the intensity profile. Therefore, we can expect that there are only two Ba layers on top of bottom $SrRuO_3$ electrode. To confirm this, we performed EDS measurement for elemental mapping. Sr and Ti elemental maps, Fig. 17(d) and (e) show that $SrTiO_3$ exist on top of 2.5u.c $BaTiO_3$. It confirms that there are two Ba layers under the $SrTiO_3$ film.

Next, Fig. 18 shows ionic displacements and c/a ratio for 10u.c $SrTiO_3$ sample. In contrast to Fig. 14(a), 10u.c sample do not show any ionic displacements in all regions. It means that there is no ferroelectricity in this 10u.c $SrTiO_3$ and 2.5u.c $BaTiO_3$ sample. As we did for 1u.c. SrTiO3 sample, we investigated many images and found that more than 70% of images (20 imags from 27 images) do not have any sign of ferroelectricity. Especially,

the magnitude of Ti displacements was smaller than 5pm. Moreover, other 7 images, Ti cations move ~5pm in average. The pixel size of our STEM images is 6.505pm per pixel. Thus this 5 pm displacement is not meaningful and we can demonstrate that in the 5pm scale level, there are no displacements in 10u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample. Therefore, we concluded that in 10u.c SrTiO3 sample, ferroelectric displacement is not stable and moreover, no polarization penetration exists.

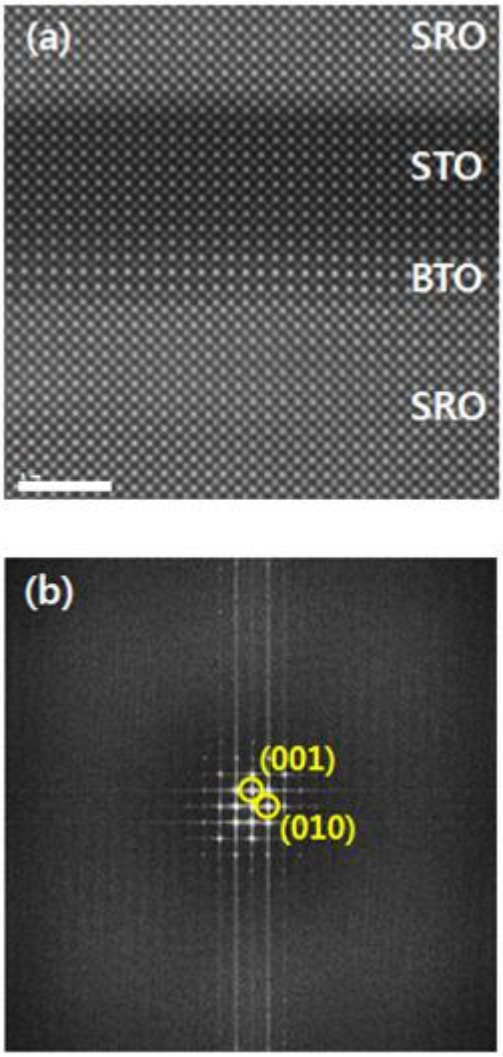

Figure 15 (a) HAADF image with low magnification, (b) FFT image of HAADF image of 10u.c SrTiO3 on 2.5u.c BaTiO3.

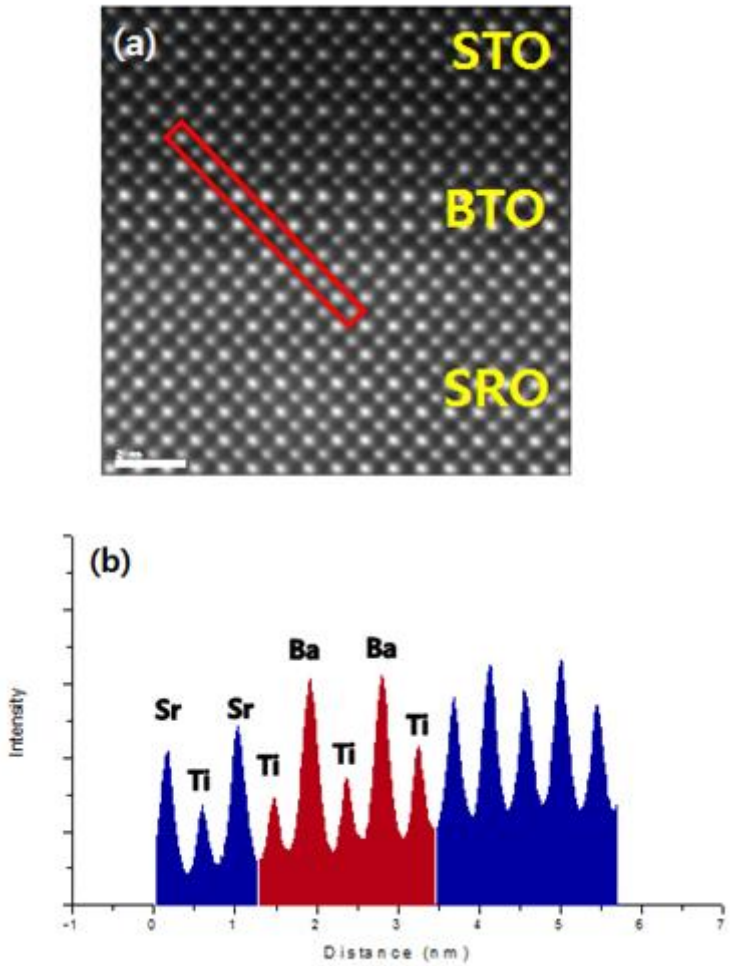

Figure 16 (a) HAADF image of 10u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ with high magnification, (b) intensity profile of red box region.

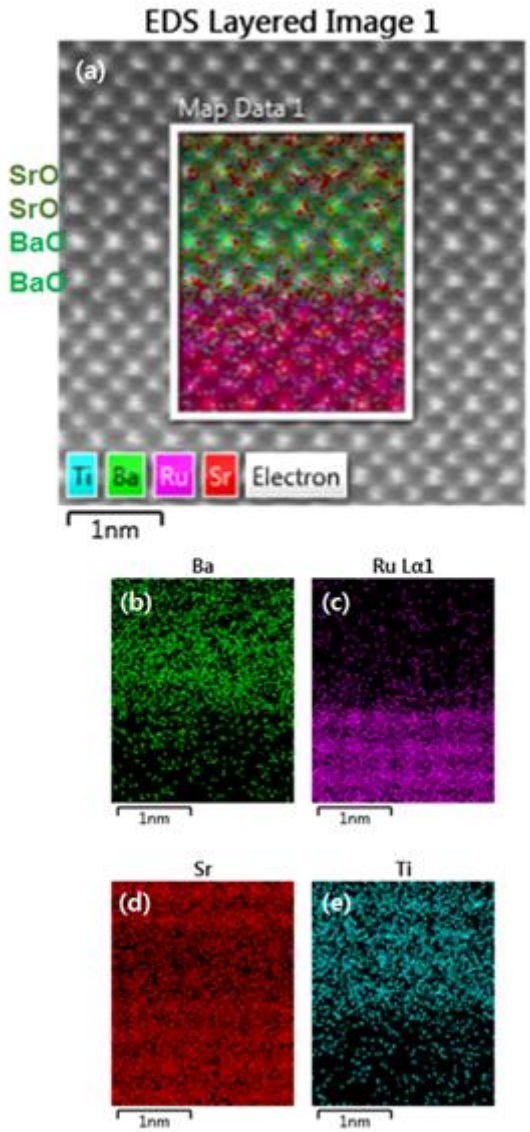

Figure 17 (a) HAADF image and integrated elemental signal mapping, (b)~(e) Each elemental maps for Ba, Ru, Ti and Sr in of 10u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ respectively.

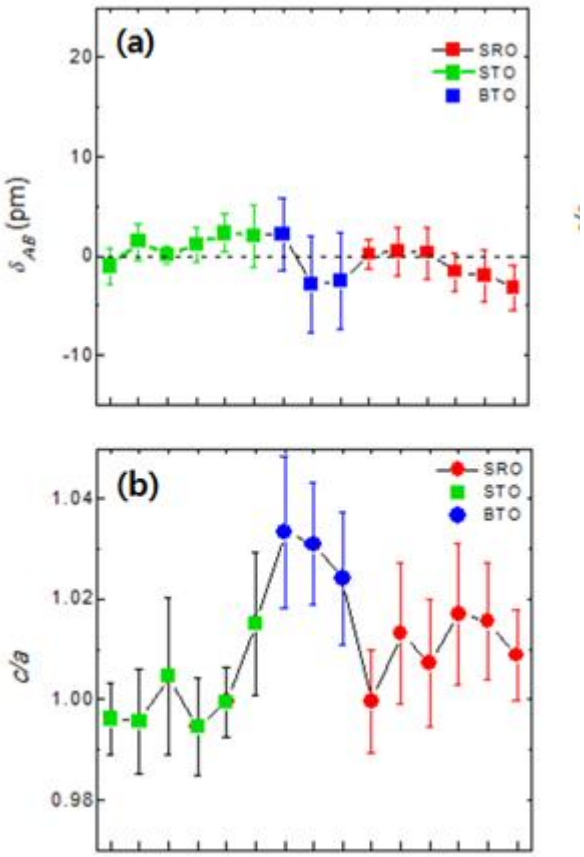

Figure 18 (a) Ferroelectric displacements, (b) c/a ratio in 10u.c $SrTiO_3$ and 2.5u.c $BaTiO_3$

4.3 Piezoresponce Force Microscopy(PFM)

PFM measures an expansion and contract of lattice constant using atomic force microscopy. If an oxide film had swichable ferroelectricity, PFM amplitude and phase should have butterfly curve and 180° phase difference respectively, as described in Fig. 19. Fig. 19 is experimental PFM result for 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample. Two vertical axis are PFM phase(left, blue) and amplitude(right, red) respectively. PFM amplitude shows apparent butterfly curve and 180° phase difference. This is another evidence of ferroelectricity correspond to the Ti displacements shown in Fig. 14(a).

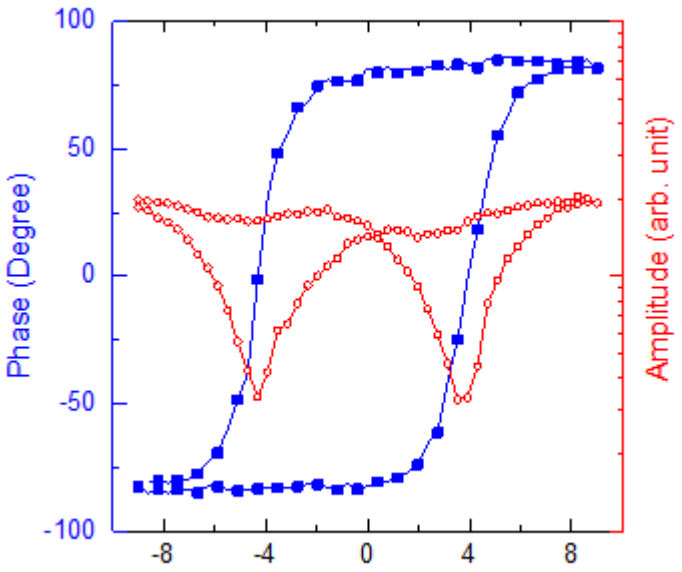

Figure 19 PFM result for 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$.

Chapter 5. Conclusion

To investigate ferroelectric critical thickness of $BaTiO_3$ thin film in metal/dielectric/ferroelectric heterostructure, we observed two samples, 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ and 10u.c $SrTiO_3$ on 2.5u,c $BaTiO_3$ using high angle annular dark field imaging by Cs-corrected STEM and measured ionic displacements using peak position finding. Using this image processing technique, we calculated δ_{A-B} in Fig. 1 to observe ferroelectric ionic displacements.

In 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample, Ti cations show ferroelectric displacements as displayed in Fig. 14. This is direct evidence of Ferroelectricity. However in 10u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ sample, Ti cations do not show significant ferroelectric displacements. It means there are no spontaneous polarization in this sample.

We also performed PFM measurement for 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$. PFM amplitude and phase show typical butterfly curve and hysteresis like loop. These curves are general in ferroelectric materials. Thus PFM result also supports the stable ferroelectricity in 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ structure.

We think that this stable ferroelectric polarization in 2.5u.c $BaTiO_3$ is closely related with 1u.c $SrTiO_3$ layer. Like Gerra et al's study,[7] polarization

penetration into very thin $SrTiO_3$ may stabilized the polarization. However, unlike Gerra et al's result, polarization penetration in our sample is limited only one unit cell of $SrTiO_3$. In $SrRuO_3$ region, almost no polarization penetration was observed. Therefore, though we observed ferroelectric polarization in 1u.c $SrTiO_3$ on 2.5u.c $BaTiO_3$ heterostructure, much more studies including first-principle calculation are necessary to complete understanding of ferroelectricity in metal/dielectric/ferroelectric system.

References

[1] M.B. Salamon et al., Rev. Mod. Phy. 73, 583(2001)

[2] R. Ulrich et al., The International Journal of Microcircuits and Electronic Packaging, 23, 2, (2000)

[3] J. F. Scott, Ferroelectric Memories, Springer, (2000)

[4] O. Auciello et al., Phys. Today 51, No, 7, 22 (1998)

[5] N. Setter, Electroceramic-Based MEMS, Springer (2005)

[6] C. Dubourdieu et al., Nature Nanotechnology, 8, 748, (2013)

[7] G. Gerra et al., PRL, 96, 107603 (2006)

[8] J. Junquera et al., Nature, 422, 506, (2003)

[9] L. Mazet et al., J. Appl. Phys. 116, 214102 (2014)

[10] C.L. Jia et al., Nature Materials 6, 64 (2007)

[11] Y.J Shin et al., Adv. Mater, 29, 1602795 (2017)

[12] A. K. Tagantsev, J. Appl. Phys. 90, 1387 (2001)

[13] R. D. Tilley et al., Ferroelectrics, 134, 313 (1992)

[14] R. Kretschmer et al., phys. Rev. B, 20, 1065 (1979)

[15] H. Lu et al., Adv. Mater. 24, 1209 (2012)

[16] J. Shin et al., ACS Nano, 4, 4190, (2010)

[17] G. Rijnders et al., Appl. Phys. Lett. 84, 505 (2004)

[18] S. Salahuddin et al., NaNo let, 8, 405 (2008)

[19] www.ntmdt-si.com/resources/applications/piezoresponse-force-microscopy-in-its-applications

[20] L. Wang et al., Adv. Mater, 29, 1802001 (2017)

[21] P.L. Galindo et al., Ultramicroscopy, 107, 1186 (2007)

초 록

$BaTiO_3$는 특유의 강유전성으로 인해 주목받고 있는 물질이지만 그 강유전성은 다양한 외부 조건들로 인해 크게 변화할 수 있다. 따라서 실제 소자에서 널리 사용되는 박막 구조로 제작되었을 때 어떤 메커니즘이 BaTiO3의 강유전성에 영향을 미치는지를 이해하는 것은 $BaTiO_3$를 이해하고 실제 소자에 적용하기 위해 필수적이라 할 수 있다. 본 연구에서 우리는 $SrRuO_3$ 전극과 2.5 유닛 셀의 극히 얇은 $BaTiO_3$ 박막 사이에 각각 1유닛 셀과 10유닛 셀 두께의 $SrTiO_3$ 층을 갖는 박막 구조 샘플들을 제작하였고 고배율 HAADF-STEM 이미징 기법을 사용하여 원자 수준에서 양이온들의 움직임을 측정, 각각의 샘플에서의 강유전성의 유무를 관찰하였다. HAADF-STEM 이미지에서 얻은 원자 피크 위치 정보로부터 B 위치 양이온(Ru, Ti)들의 위치 변화량인 $\delta_{A\text{-}B}$ 값을 계산할 수 있었고 이로부터 1유닛 셀 두께의 $SrTiO_3$를 가지는 $BaTiO_3$ 샘플에서 강유전성이 관찰되지만, 10유닛 셀 $SrTiO_3$ 샘플에서는 강유전성이 관찰되지 않음을 확인하였다. 이러한 차이는 이론적으로 예측된, 이온 분극이 전극 안으로 뚫고 들어가는 현상으로 설명될 수 있다. 또한 1유닛 셀 $SrTiO_3$ 샘플에서의 강유전성은 압전현미경 실험 결과와 일치하였다. 본 연구로부터 $SrTiO_3$와 같은 유전체의 두께가 강유전성 임계 두께에 영향을 줄 수 있음을 확인할 수 있다.

주요어: 강유전성, 이온 분극, 구면수차보정 주사투과전자현미경,

압전현미경, BaTiO3 박막

학 번: 2015-20810

Observation of Ferroelectric Critical Thickness of BaTiO3 Thin Film by Cs-corrected STEM

2018

김윤구