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Growth optimization and characterization of ferroelectric properties of Aurivillius thin film

Aurivillius 박막의 증착 조건과 강유전성에 관한 연구

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이 논문을 이학석사 학위논문으로 제출함

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Abstract

Ferroelectric thin film is applied to many aspects of electromagnetic devices, especially to non-volatile memory, because of there spontaneous electric polarization. For more denser memory, the thinner film with strong ferroelectricity is needed. However, this challenge is facing difficulty by the depolarizing filed which hinders c-axis ferroelectric polarization more as a film is getting thinner. To overcome this problem, a material with pure a-axis or b-axis ferroelectricity is needed. Bi_2WO_6 (BWO) is the simplest member of the Aurivillius family, with one WO_6 octahedron sandwiched between two Bi_2O_2 layers. BWO has a high Curie temperature around 950 °C and exhibits a large, spontaneous, pure in-plane polarization of about 50 $\mu C/cm^2$ at room temperature. The robust ferroelectricity combined with the in-plane polarization, thereby makes BWO an attractive candidate for non-volatile memory devices that could overcome the "size-effect" problem by depolarizing field of canonical ferroelectrics like BaTiO3 or PbTiO3. Despite this advantage, most of the study about BWO is focusing on the photocatalyst effect and a systematic study focusing on the growth optimization, structural, and ferroelectric characterization of BWO thin films is not done yet. Using the pulsed laser deposition (PLD) technique, we have grown epitaxial BWO thin films on (001)-oriented $SrTiO_3$ substrates and optimized growth conditions based on the X-ray diffraction (XRD) and atomic force microscopy (AFM) data. In this paper, the best growth condition of BWO films grown by PLD method will be presented. Also, the ferroelectric property of the optimized BWO film probed by the piezoresponse force microscopy (PFM) technique and scanning transmission electron microscopy (STEM) will be presented.

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Chapter 1

Introduction

1.1 Ferroelectricity

Ferroelectricity indicates phenomena of certain material that have a spontaneous electric polarization and can be reversed by an external electric field. Dielectric materials and paraelectric materials also have electric polarization under an electric field. However, the difference which distinguishes ferroelectric materials from dielectric and paraelectric one is that ferroelectric material still shows remaining electric polarization when an external electric field is gone while the dielectrics and the paraelectrics are not. As shown in Fig. 1.1., we can schematically see the difference of the dielectric, the paraelectric and the ferroelectric. The coercive field (E_C) refers to the electric field at which electric polarization begins to be switched. Electric polarization approaches saturated polarization (P_S) if an electric field is larger than E_C, while it approaches remnant polarization (P_R) when an electric field becomes zero. By this non-volatile property of ferroelectric polarization, the ferroelectrics are used in various applications. For instance, reversible ferroelectric polarization with two opposite-direction has been used for non-volatile memory like ferroelectric tunnel junction [1]. Another example is a microactuator, using the piezoelectric properties of the ferroelectrics [2, 3].

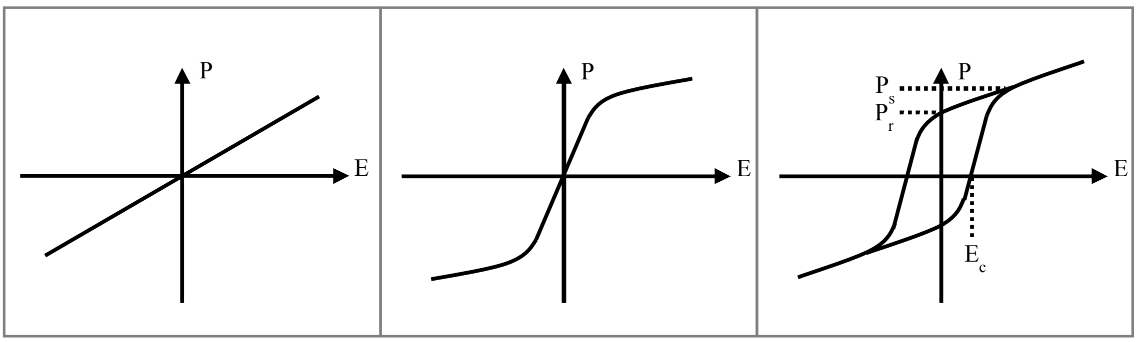

Figure 1.1

Polarization–voltage *(P–E)* hysteresis loop for the dielectric (left), paraelectric (middle) and ferroelectric (right).

1.2 Pure in-plane polarization of Bi_2WO_6

By spontaneous electric polarization, ferroelectric materials are used in various applications, especially in non-volatile memory and magnetoelectric devices [1]. For this application, researches on the ferroelectric thin film are essential. Many studies for traditional ferroelectric thin films like $BiFeO_3$ (BFO), $PbTiO_3$ (PTO) are done. However, those materials have out-of-plane (OP) components of the ferroelectric domain direction, which is restricted by substrate clamping [4]. Furthermore, to apply ferroelectric thin film for denser memory, thinner films are needed. Unfortunately, if we make films thinner and thinner with (OP) component of the ferroelectric domain, opposite surface charges by electric polarization getting closer and closer, enhancing the depolarization field like Fig. 1.2. For this reason, there is a critical thickness which means minimum thickness to have ferroelectricity. If the film's thickness is thinner than that, the film will not possess ferroelectricity.

Under this situation, a material with pure in-plane (IP) ferroelectricity is needed, so that there will be no or less critical thickness and effect from substrate clamping. For this reason, Bi_2WO_6 (BWO) is chosen in this work. BWO is one of the simplest aurivillius family, which is a form of layered perovskite structure like Fig. 1.3., with a general formula, $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$, and n = 1, B = W for this case, and WO_6 octahedral layer is sandwiched by $(Bi_2O_2)^{2+}$. It shows strong spontaneous polarization, Curie temperature is 950° C, spontaneous polarization about 50 μC/cm^2 due to WO_6 perovskite like part. BWO has pure IP ferroelectric domain direction along (100) and it can rotate by 90° degrees, total in 4 directions. Therefore, BWO is expected to be able to provide a new filed for the application of the ferroelectric thin film.

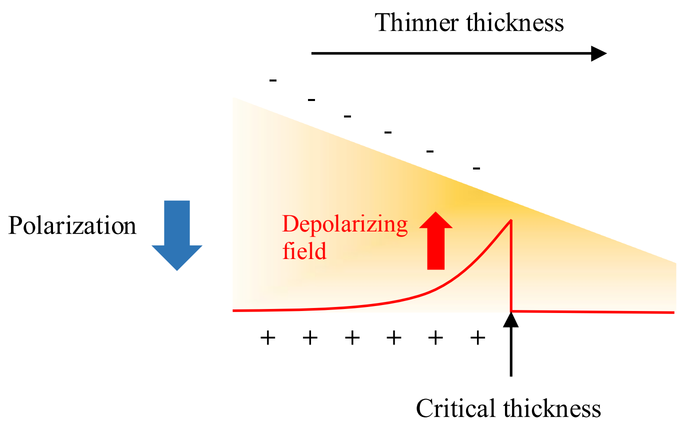

Figure 1.2

Schematic of depolarizing field dependence on thickness. If thickness is lower than critical thickness, ferroelectricity will be gone.

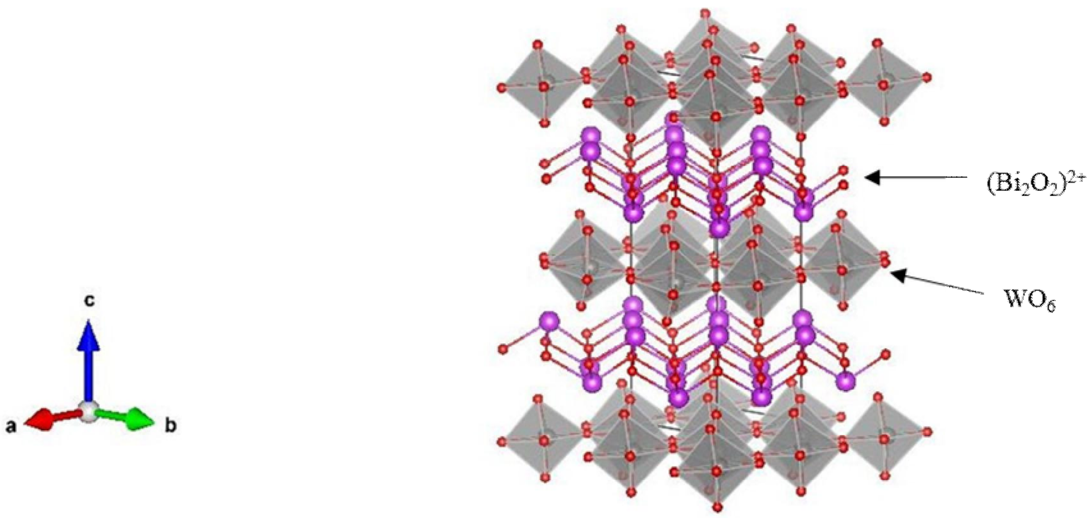

Figure 1.3

Layered perovskite structure of Bi_2WO_6 crystal.

1.3 Previous Studies on Bi_2WO_6 thin films

Although BWO has strong and unique ferroelectric properties mentioned before, most of the previous work on BWO paying attention to the photocatalyst effect, but there are some researches on ferroelectric BWO thin film. M. Hamada at al. and V. I. Utkin at al. reported dielectric properties of BWO [5, 6], H. Takeda at al. reported piezoelectric properties [7], Y. Ahn at al. measured the ferroelectric hysteresis loop of BWO thin film along the c-axis [8]. Recently, a new method to switch pure IP ferroelectric domain of BWO by trailing electric field by Piezoresponse Force Microscopy (PFM) tip is discovered, promising reversible switching without additional electrode [4].

Despite those interesting researches, there is no systematic, detail research about growth condition optimization and ferroelectric characterization. There are some examples of BWO thin film with uniform crystallinity and growth condition [6-8], but no information about the quality of thin film if growth condition is changed. Moreover, previous theoretical, indirect researches indicate that the origin of ferroelectricity of BWO is atomic displacement of W cations from the center of oxygen octahedral and it should be around 30~40 pm [9, 10], but there is no experimental proof about this.

References

[1] D. Lu, S. Crossley, R. Xu, Y. Hikita, H.Y. Hwang, Nano Lett, 19 (2019) 3999-4003.
[2] L.W. Martin, A.M. Rappe, Nature Reviews Materials, 2 (2016).
[3] P. Zubko, G. Catalan, A.K. Tagantsev, Annual Review of Materials Research, 43 (2013) 387-421.
[4] C. Wang, X. Ke, J. Wang, R. Liang, Z. Luo, Y. Tian, D. Yi, Q. Zhang, J. Wang, X.F. Han, G. Van Tendeloo, L.Q. Chen, C.W. Nan, R. Ramesh, J. Zhang, Nat Commun, 7 (2016) 10636.
[5] V. Utkin, Y.E. Roginskaya, V. Voronkova, V. Yanovskii, B. Sh. Galyamov, Y.N. Venevtsev, physica status solidi (a), 59 (1980) 75-82.
[6] M. Hamada, H. Tabata, T. Kawai, Thin Solid Films, 306 (1997) 6-9.
[7] H. Takeda, J.S. Han, M. Nishida, T. Shiosaki, T. Hoshina, T. Tsurumi, Solid State Communications, 150 (2010) 836-839.
[8] Y. Ahn, J.Y. Son, Journal of Crystal Growth, 462 (2017) 41-44.
[9] R. Wolfe, R. Newnahm, M. Kay, Solid State Communications, 7 (1969) 1797-1801.
[10] H. Okudera, Y. Sakai, K. Yamagata, H. Takeda, Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials, 74 (2018) 0-0.

Chapter 2

Experimental details

2.1 Pulsed Laser Deposition

There are various methods to fabricate thin film in nanometer scale. In order to reveal the best condition for the crystallinity of BWO thin film, an experimental setup which can change the various condition is needed. For this reason, pulsed laser deposition (PLD) method is chosen for this research. PLD has many advantages: (1) the laser system, which supplies energy to ablate the target, is separated from temperature controller and vacuum system. This means flexibility in controlling growth conditions like pressure, energy of laser pulse, substrate temperature separately. (2) The use of a pulsed laser beam enables precise control over the growth rate, growth amount can be controlled to the desired one. This makes PLD be a suitable method for research in the laboratory than other methods like sputtering or chemical vapor deposition [1].

Figure 2.1 is a schematic diagram of PLD with reflectance high energy electron diffraction (RHEED). First, the substrate must be set upside down and fixed in vacuum chamber, and the substrate temperature must be maintained to the desired one because the surface temperature has a large effect on the nucleation density. In most cases, as the temperature is increased, the nucleation density decreases. So, the substrate must be heated, generally more than 400°C. Background pressure is also an important parameter. Especially in depositing oxide thin film, oxygen is much lighter than other elements so base oxygen (or ozone) pressure is needed, which can be controlled by input by gas inlet and exhaust through the vacuum pump. For example, if the oxygen pressure is too low, stoichiometry will not fit and there may be oxygen vacancies in crystal structure or it can increase nucleation density. If the substrate temperature and base pressure are set to be desired ones, the target is ablated by excimer laser pulses to create plasma with a form of plume. That ablated plasma propagates upward in a vacuum chamber and can be deposited on the surface of the substrate. During a deposition, electrons are shot from electron gun and make diffraction patterns from the surface of the film. RHEED system can measure the diffraction pattern on the screen and precisely know the thickness of the film.

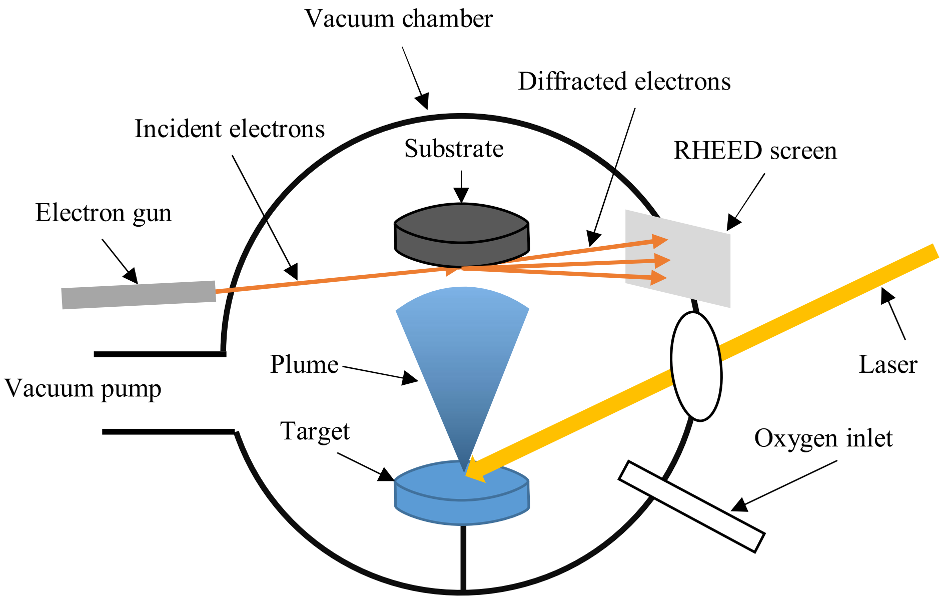

Figure 2.1

Schematic diagram of pulsed laser deposition with reflectance high energy electron diffraction system.

In this work, we used commercial $SrTiO_3$ (STO) substrate [Crystech GmbH, AMS korea, Korea] and $SrRuO_3$ (SRO)as a bottom electrode for PFM measurement. The bare STO was put in pure water and sonicated for 35 seconds to clean the surface and make SrO layer react with water to $Sr(OH)_2$. After sonication, the substrate was dipped into buffered oxide etch for 30 seconds to get rid of $Sr(OH)_2$ layer, only TiO_2 termination remaining. Finally, the substrate was annealed in 1050°C for 1hour to make TiO_2 terminated surface atomically flat.

After atomically flat, TiO_2 terminated substrate is ready, SRO buffer layer for PFM measurement is grown on a substrate by PLD. Here is condition for SRO growth; substrate temperature: 730 °C, base oxygen pressure: 100 mTorr, laser spot size: 2.42 mm^2, laser fluence: 2.07 J/cm2, laser frequency: 2Hz. Since the growth condition of BWO is one of the results of this paper, it will be discussed later.

2.2 X-Ray Diffraction measurement

The crystal structure can be observed by high-resolution X-ray diffraction (HRXRD). Analyzing HRXRD result with Bragg's law, the lattice constant and thickness of the film can be obtained. By *θ-2θ* scan, the orientation of film, c-axis lattice parameter and the film's thickness can be determined. Moreover, crystal quality also can be observed. If the crystal quality of the film is good, peaks and thickness fringes in *θ-2θ* scan will be sharp, otherwise, peaks and fringes will be broad and blur. By analyzing reciprocal space mapping (RSM), a-axis or b-axis lattice parameter can be obtained.

Figure 2.2. shows *θ-2θ* data of BWO thin film grown on Nb-doped STO substrate by M. Hamada *at al* [2]. Like Fig 2.2., *θ-2θ* scan is mainly used to see the crystal quality of films grown under different conditions. *θ-2θ* scan result for each condition will be plotted in result session to compare crystal quality and orientation of films and figure out the best growth conditions.

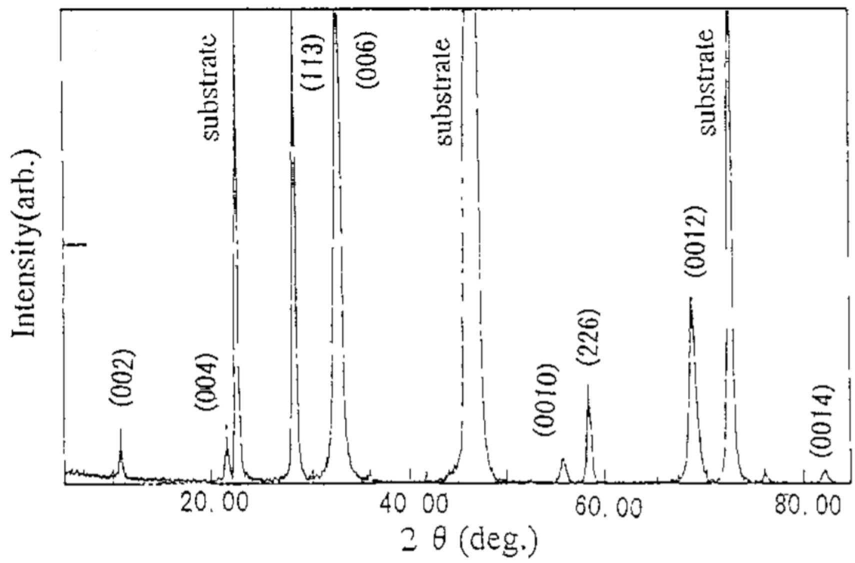

Figure 2.2

***θ–2θ* scan of X-Ray Diffraction for Bi_2WO_6 crystal on $SrTiO_3$ substrate. (001) and (113) orientations are mixed. Adapted by M. Hamada *at al.* [2].**

2.3 Piezoresponse force microscopy

Piezoresponse force microscopy (PFM) is a special type of atomic force microscopy (AFM). This is designed to directly image the ferroelectric domain on the surface of the film. PFM is based on the piezoelectricity, which means a linear coupling between mechanical strains and electric fields. All the ferroelectrics exhibit piezoelectricity. If mechanical stress is applied to the ferroelectric, not only mechanical displacement and but also the electric field will be generated. On the contrary, when an electrical field is applied to ferroelectric materials, mechanical displacement will occur. This effect is called *"converse piezoelectric effect"*.

Interestingly, there is a dependence of the piezoelectric effect on the ferroelectric domain. Fig 2.3. shows a schematic setup of PFM experiment, showing a conductive tip and a bottom electrode are needed. Tip touches the surface of ferroelectric material, and ac electric bias, $V_{\mathrm{tip}} = V_0 \sin\omega t$, is applied to the tip. The amplitude V_0 must be lower than coercive voltage or ferroelectric domain will be switched and this will not give any physical meaning. If the ferroelectric domain parallels with the electric field, the domain expands, resulting upward mechanical deformation of the surface by converse piezoelectric effect. On the other hand, when the ferroelectric domain is antiparallel with the electric field, domain contracts and there will be downward deformation on the surface. PFM equipment detects that deformation to determine the ferroelectric domain on the surface by measuring reflected light from the tip.

PFM equipment also can be used to switch the ferroelectric domain by applying voltage on tip more than the coercive voltage on purpose. If we want to switch the ferroelectric domain in OP direction, we can switch it simply by applying positive or negative voltage on the tip. However, if we want to switch in IP direction, some tricky technique is needed. Fig 2.4. shows schematic of the technique invented by C. Wang *at al* in paper published in 2016 [3]. If we apply electric voltage on tip there will be a radial field from the tip, giving some IP components. When tip moves on the surface while the electric voltage is applied, there will be trailing electric field along the IP direction. This trailing field switches the ferroelectric domain. By adjusting the route of moving tip, we can select the region where we want to switch. This method is used to confirm that BWO thin film shows the ferroelectric domain has 4 IP directions and can be switched among them freely. The result of this technique will be mentioned in result session.

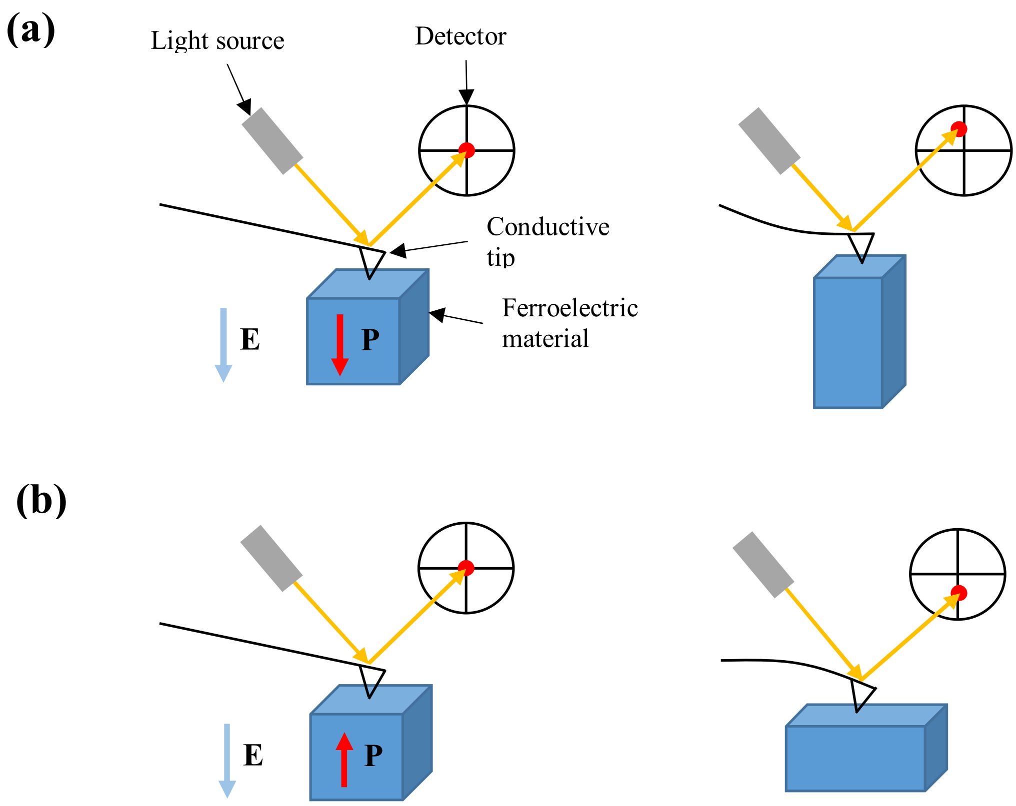

Figure 2.3

Schematic diagram of how piezoresponse force microscopy works. Ferroelectric polarization and electric field are parallel in (a) and antiparallel in (b)

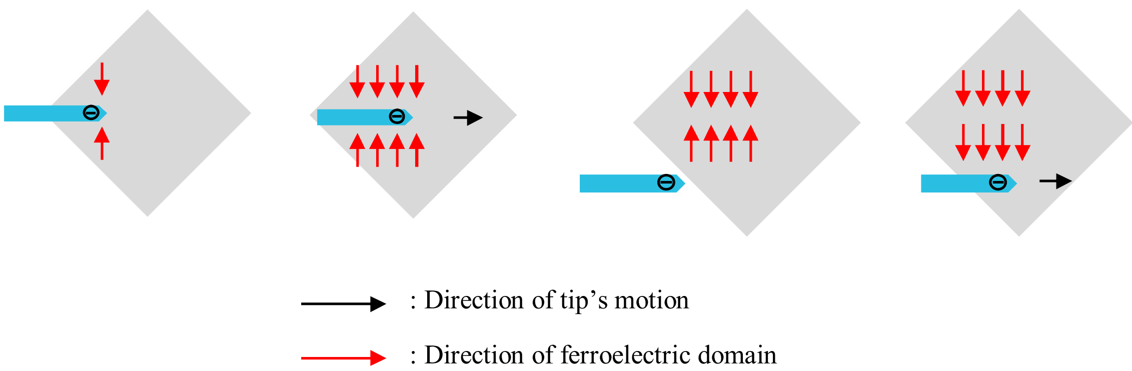

Figure 2.4

Schematics of the in-plane polarization switching process under the application of electric voltage to a conductive tip. Adapted by C. Wang *at al.* [3].

References

[1] P. Willmott, J. Huber, Reviews of Modern Physics, 72 (2000) 315.

[2] M. Hamada, H. Tabata, T. Kawai, Thin Solid Films, 306 (1997) 6-9.

[3] C. Wang, X. Ke, J. Wang, R. Liang, Z. Luo, Y. Tian, D. Yi, Q. Zhang, J. Wang, X.F. Han, G. Van Tendeloo, L.Q. Chen, C.W. Nan, R. Ramesh, J. Zhang, Nat Commun, 7 (2016) 10636.

Chapter 3

Results and Discussion

3.1 Growth phase diagram

In growing oxide thin film, substrate temperature and base oxygen pressure are the most important condition to determine the quality of a sample. To figure out the effect of one factor, we must fix all the other factors. Likewise, to find the best substrate temperature, all the other conditions like pressure and laser frequency so on, are fixed. Best base oxygen pressure is also found in the same way. By comparing XRD pattern with an already known pattern, we can distinguish the orientation of crystal and uniformity [1]. In Fig 3.1., we plotted XRD θ-2θ scan data of 20 nm thick BWO thin film grown under different conditions. First, we fixed substrate temperature and varied base oxygen pressure. Those many samples were grown at the same temperature but different pressures are plotted together in Fig 3.1. (a) to compare. When the pressure is increased larger than 125 mTorr, we can see clear BWO thin films peak and sharp substrate fringes, meaning high crystal quality. Moreover, all peaks are pure (001) oriented peaks. However, if pressure is decreased lower than 125 mTorr, peaks and fringes began to disappear. Also, many 20 nm thick samples grown on the same pressure but different temperatures are plotted in Fig 3.1. (b). Unlike the former case, all samples showing significant pure (001) oriented peaks. The only difference is thickness fringe, sharpest at 600 °C and disappeared at 800 °C.

It looks like only XRD θ-2θ scan is not enough to figure our best combination of substrate temperature and base oxygen pressure. Exactly, we can clearly know that pressure must be around or lager than 125 mTorr, but in the case of temperature, the only difference in thickness fringe does not look like enough clue. So, AFM experiments to check the flatness of the surface are done. Fig 3.2. shows AFM image of BWO thin film grown on the same pressure but different temperatures. 500 °C shows fluctuating but quite uniform steps, and 600 °C shows most uniform steps and pm scale height retrace, while 700 °C and 800 °C shows uneven steps and nm scale height retrace.

By combining additional XRD θ-2θ data and AFM data, we concluded that the best combination of temperature and pressure is around 600 °C and 125 ~ mTorr. Fig 3.3. final growth phase diagram based on XRD and AFM data. If the temperature is larger than 700 °C or pressure is lower than 125 mTorr, pure (001) orientation phase began to disappear and there will be a mixed phase. If the pressure is lower than 50 mTorr, BWO film is not deposited at all and there is no phase.

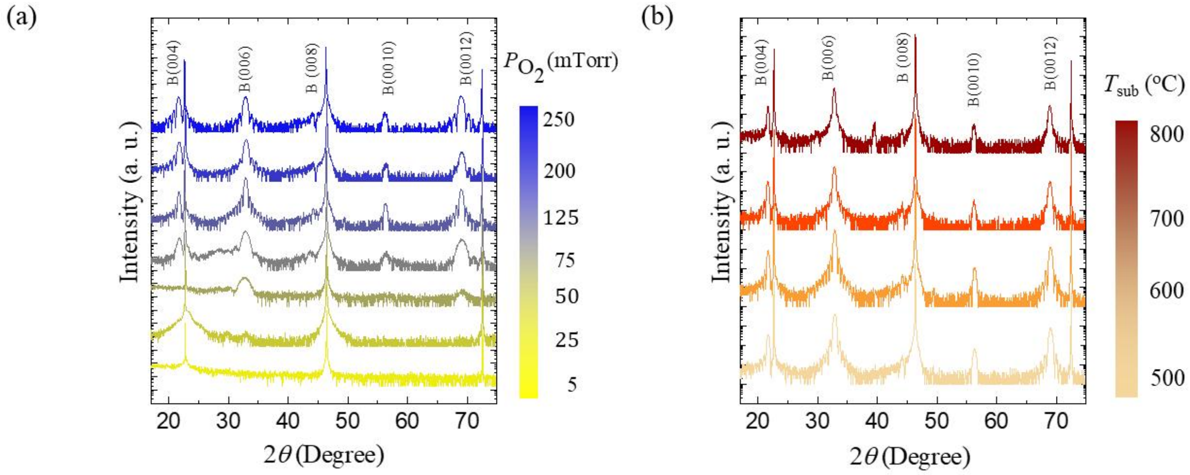

Figure 3.1

(a) XRD plots of Bi_2WO_6 thin films grown at the same temperature (600 °C) but different partial oxygen pressure. (b) XRD plot of Bi_2WO_6 thin films on the same partial oxygen pressure (125 mTorr) but different temperatures.

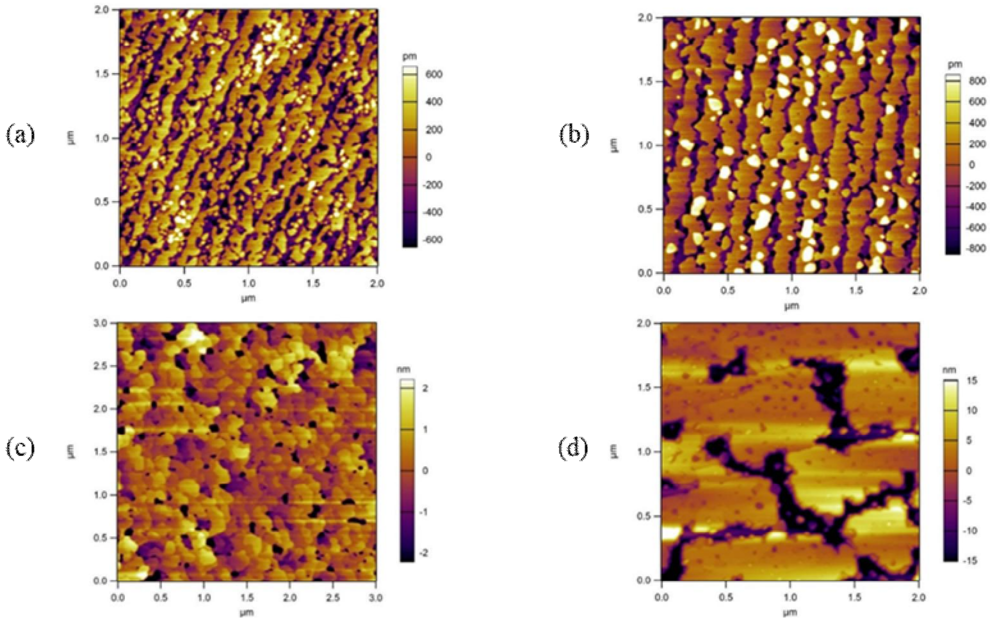

Figure 3.2

AFM images of Bi_2WO_6 thin film grown at same P_{O2} = 1.25 mTorr but different T = (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C.

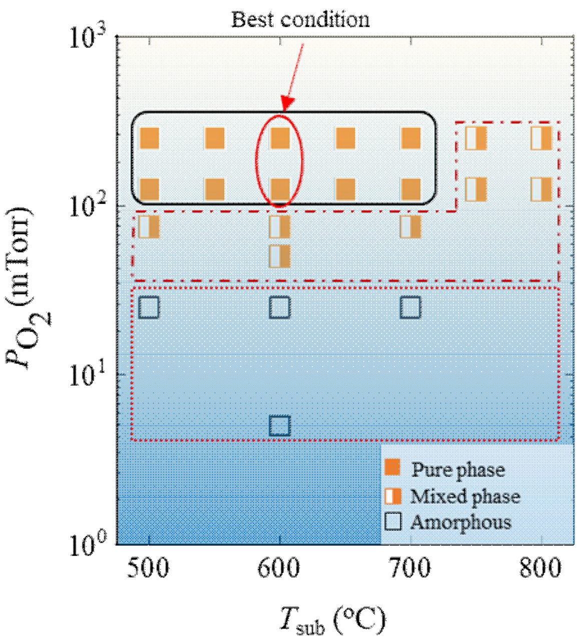

Figure 3.3

Growth phase diagram of Bi_2WO_6 growth by PLD. Pure phase, mixed phase and amorphous are distinguished by a solid line and dotted line based on XRD data. Red ellipse means the best growth condition based on XRD and AFM data.

3.2 In-plane ferroelectric switching

As we discussed in Chapter 2.3, we can switch IP ferroelectric domain by PMF tip. In this way, the ferroelectric domain of BWO thin film which has thickness around 20 nm is switched in all 4 directions. Fig 3.4. (a) shows PFM image before applying voltage, (b) after applying a voltage and moving the tip to switch ferroelectric domain to the downward direction, (c) after applying the same voltage but opposite slow scan axis to switch in the upward direction. That clear phase contrast indicates the ferroelectric domain can be switched freely. Since PFM can only detect IP direction perpendicular to tip, cannot detect parallel one, we rotated sample 90 ° and did the same PFM experiment. Fig 3.4. (b) shows the result of the rotated sample, in the same way as (a). All PFM image desired phase contrast, meaning we can selectively switch the ferroelectric domain among 4 directions as we want.

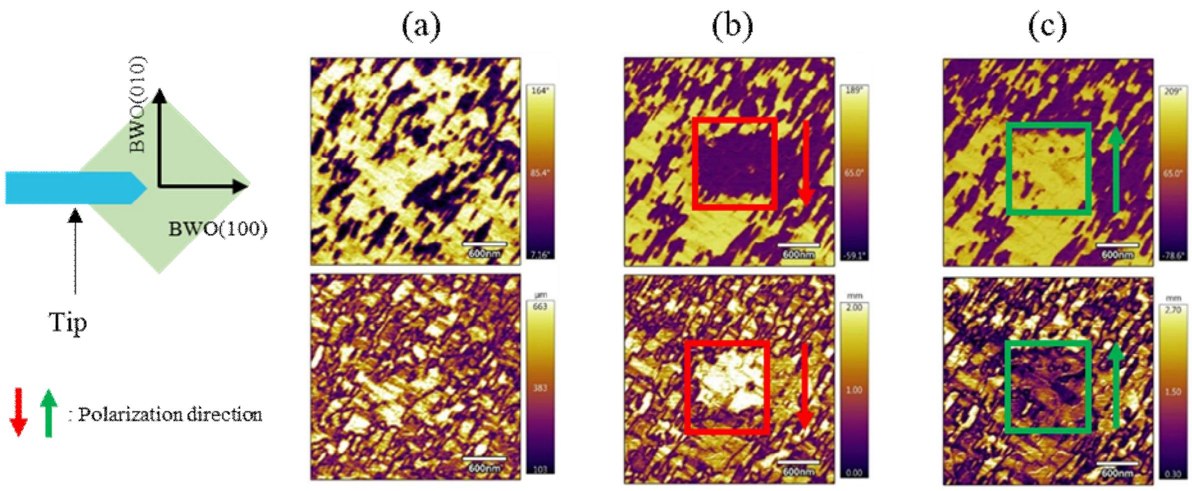

Figure 3.4

PFM image of Bi_2WO_6 thin film before applying a voltage (a), after applying voltage to switch polarization to downward direction by the way of Fig 2.4 (b), and after applying voltage to reverse the polarization to the upward direction (c).

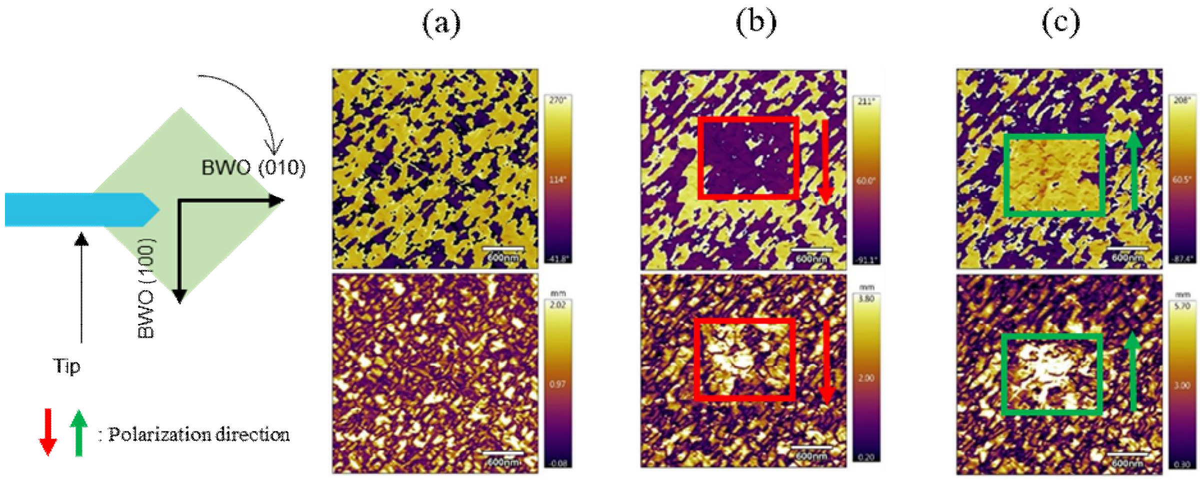

Figure 3.5

PFM image of Bi_2WO_6 thin film after we rotated film 90 °. PFM image is gained by the same way as Fig 3.4.

3.3 Ferroelectric origin of Bi_2WO_6 crystal

As we discussed before, there are some theoretical, indirect studies proving that the origin of ferroelectricity of BWO is atomic displacement of W cations from the center of oxygen octahedral and it should be around 30~40 pm [2, 3], but there is no experimental proof about this. However, there are some studies that directly measured atomic displacement by using scanning transmission electron microscopy (STEM) [4, 5]. To directly see atomic displacement, STEM is done to one of our samples. Fig 3.5. shows high resolution STEM data and average atomic displacement of W cations. Most of the atomic displacements are around 20 pm. We can see there is clearly atomic displacement which affects ferroelectric polarization. However, theoretical studies indicate it must around 30 pm, which is definitely larger than the experimental one. This implies that atomic displacement may not be the only origin of ferroelectric polarization. To figure out all detail origin of ferroelectricity more research is needed.

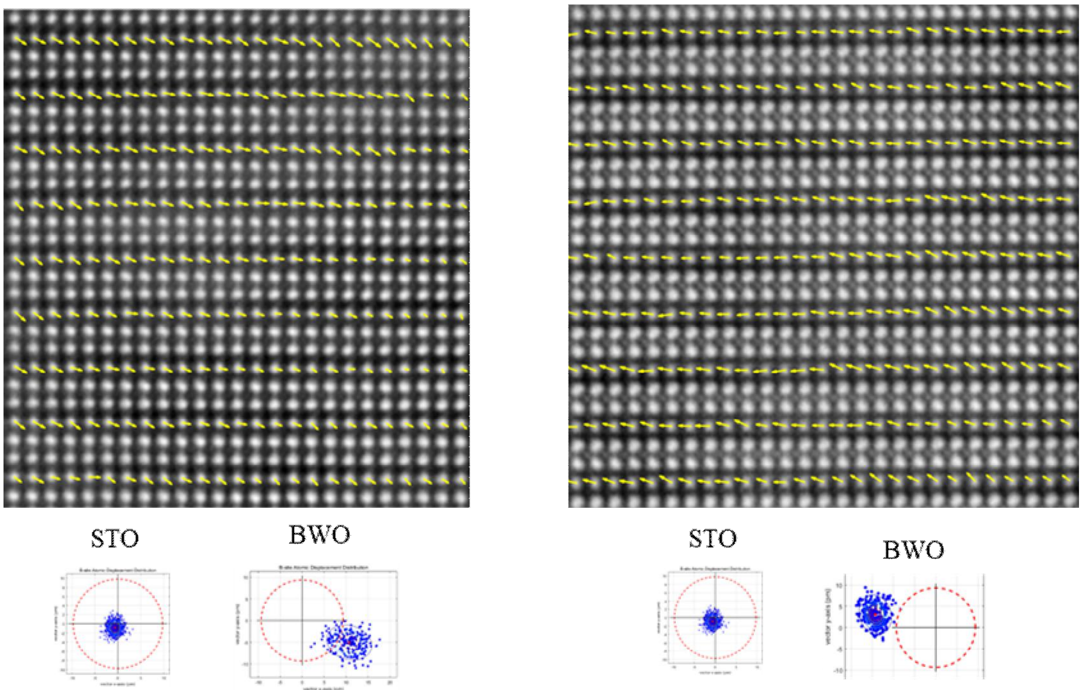

Figure 3.6

STEM image of Bi_2WO_6 thin film and averaged atomic displacement of Ti cations from paraelectric $SrTiO_3$ and W cations from Bi_2WO_6. Ti cations are not displaced much from the center of oxygen octahedral but W cations displace around 20 pm.

References

[1] M. Hamada, H. Tabata, T. Kawai, Thin Solid Films, 306 (1997) 6-9.

[2] R. Wolfe, R. Newnahm, M. Kay, Solid State Communications, 7 (1969) 1797-1801.

[3] H. Okudera, Y. Sakai, K. Yamagata, H. Takeda, Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials, 74 (2018) 0-0.

[4] R.B. Comes, S.R. Spurgeon, S.M. Heald, D.M. Kepaptsoglou, L. Jones, P.V. Ong, M.E. Bowden, Q.M. Ramasse, P.V. Sushko, S.A. Chambers, Advanced Materials Interfaces, 3 (2016) 1500779.

[5] M. Campanini, M. Trassin, C. Ederer, R. Erni, M.D. Rossell, ACS Applied Electronic Materials, (2019).

Chapter 4
Conclusion

We investigated the growth phase diagram by XRD and AFM. By checking the crystal quality of series of samples, we figured our best growth conditions for growing BWO are 600 ~ 700 °C for substrate temperature and 125 mTorr for base oxygen pressure. The only drawback of this growth phase diagram is that BWO is grown on the SRO buffer layer, which means additional research is needed to grow BWO on a different substrate, like bare STO. Even so, this result can give some clues about the growing BWO thin film with PLD. Also, some ferroelectric characterization is done. We confirmed our BWO thin film shows 4 IP ferroelectric domain and that domain can be selectively switched. Moreover, we observed atomic displacement by STEM to check the origin of ferroelectricity. We can see the atomic displacement of W cations generate ferroelectricity but it may not be the sole origin.