Investigation for the Thermodynamic Polarization Degradation of the BaTiO₃ Crystal Thin Films

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Abstract. According to the latest development of memory, it is found that the motion of ferroelectric domain wall is very important for the high-density non-volatile devices of ferroelectric materials. This paper mainly studies the microstructure of barium titanate (BaTiO₃) crystal films with the molecular dynamics of crystal domain motion and then models the polarization degradation with the conservation of the nucleation energy-focusing and free energy thermodynamic processes in the crystalline domains. First, by the means of XRD diffractometer and JADE software, the crystal axis orientation of BaTiO₃ thin film is analysed, and then the crystal axis orientation is determined by referring the published measurement results. Further, for the ferroelectric crystal BaTiO₃ thin film, the thermodynamic process is studied and the temperature dependences of the polarization ratio with respect to the spontaneous polarization is modelled. Numerical simulations have shown the much higher temperature dependence on the nucleation energy than on the free energy in a domain wall system, leading to the possibility to reach a high polarization ratio with the optimal deposition conditions to control the local energy and the nucleation energy cost of crystalline domains.

1. Introduction

The premise of producing high performance modulator is the signal processing with high performance optical waveguide modulation. Both the current research results and applications of barium titanate (BaTiO₃) thin film material have shown that it has the advanced electro-optic (EO) and ferroelectric properties. Since the current trend is toward the miniaturization of equipment, the basic mechanism of domain wall motions in ferroelectrics has practical significance for the applications of high-density memory and other technologies in the field of material performance. So, it has laid a foundation for the development of high-performance waveguide EO modulators and other equipment[1-3].

In the past decade, the crystalline structures of BaTiO₃ crystal thin films and EO functional devices have attracted much more interests owing to its extremely high EO effect. As a result, the prestigious establishments have been made and then the dramatic studies of the ferroelectric and electrooptic properties have been promoted[4-6]. However, up to now, no adequate efforts have been made to the studies of the thermodynamic process of the crystal domains in BaTiO₃ crystal thin films. In this work, by using XRD instrument and the JADE software, the BaTiO₃ crystal thin-film diffraction spectrum is analysed to determine the BaTiO₃ crystal axis orientation, thus to study the BaTiO₃ crystal film microstructure of molecular dynamics theory, and then the crystal film formation process of domain walls is studied and the temperature dependence of polarization ratio in the crystal domain walls is modelled with the energy conversion theory. Numerical simulations have shown the polarization ratio is strongly dependent on temperature. Finally, a conclusion that the polarization ratio model is sustainable to improving the ferroelectric properties and developing the substantial applications of BaTiO₃ crystal films is given.
2. Device Processing and Theoretical Modelling

2.1. Crystal Domain Motion Concept

![Schematic diagram of crystal domain](image)

Figure 1. Schematic diagram of crystal domain from the formation process to the stabilization state during epitaxial growth of the crystal thin film: (a) is the distribution of all the atoms in a molecule of BaTiO₃ crystal material; (b) is a process of crystalline domain formation from molecules during deposition and then form a film on the surface of the substrate material.

Figure 1(a) shows the schematic structure of BaTiO₃ crystal molecule where the large dark spots indicate the atoms of barium (Ba), the white spots indicate the atoms of oxygen (O), and the small dark spots indicate the atoms of titanium (Ti). Figure 1(b) shows the schematic deposition process, in which a set of BaTiO₃ molecules form a domain first and then drop onto the crystal substrate. Any BaTiO₃ crystal domain has a random normal direction, then under the effect of energy conservation in the crystalline system where the molecule domains are separated by an interface of two categories of crystal domains[6-8]. The interface between two crystal domains is called domain boundary that makes its structural consistency and continuity with both of two categories of crystal domains, but some features also show no consistency and continuity with the domains. Before and after a crystal domain azimuth shift reaches the stable state, the domain deposition stability so far is still uncontrollable.

2.2. Analysis for the Theoretical Model with Experimental Measurements

![XRD spectrum](image)

Figure 2. XRD spectrum of BaTiO₃ film grown on MgO crystal for identifying the crystal orientation. First, a 450nm thick BaTiO₃ film was grown by using PLD technique on a 0.5mm thick with the material of magnesium oxide (MgO) crystal substrate. Based on the first principle of the tetragonal type of ferroelectric crystal, the growing process of the crystal film is an energy transferring process with a crystal unit cell - the crystal domain from the dynamic energy of target material to the chemical energy of the thin film on substrate. At the high temperature condition of film growing process, the film formation is a process of the domain movement that can have both the linear and rotary motions to create a kinetic energy. The domain orientation is defined at the stable state, so the average orientation of the domains is defined as the axis orientation of the crystal, which is also called the local polarization direction and the different positions of film can have different local orientations. As a result, the domains in one layer can have different polarizations and the adjacent layers at the same position can have different polarization directions[8,9]. In one layer, the interface of the two adjacent domains having the different polarization directions is an important identification of the crystal system. Some researchers call the crystal domain itself as the domain wall, but some call the interface between two domains as the domain wall. With an XRD instrument the diffraction spectrum of this BaTiO₃ crystal film was obtained.
as shown in figure 2, which was further analysed by the software JADE based on the peak positions and the orientation of the film was determined to be c-axis oriented.

2.3. Derivations for the Theoretical Models of the Kinetic Energy

Since the 1950s until the end of the last century, a theory of the tetragonal crystalline membrane of BaTiO3 crystal in the process of epitaxial growth domain theory had been formed, and the domain was recognized to be the triangle shape, and meanwhile a theory for explaining the domain movement of 180°-spinning principle was proposed by Merz and an essential Miller-Weinreich’s theory on the excitation electric field was proposed, namely, the kinetic energy of domains is changed to the potential energy after the formation of the excitation electric field[4-6].

Since the begin of this century, the studies of the lattice structures and EO properties of BaTiO3 crystal films have enjoyed some prestigious establishments. At this direction, Shu, Potnis and Choudhury still held the point of view that the domain walls have the triangle shapes[7-9]. But, in 2007 Shin et al. changed the shape of the triangle crystal domains into squares[10]. However, the nucleation process of the domain walls is the key source causing the polarization degradation of crystalline domains irrespective of the domain wall shape. Namely, the local nucleation effect of domain walls relaxes the polarization orientation during epitaxial growth of a BaTiO3 crystal film and then transfers the domain wall potential to the free energy of the crystalline system. Landau-Ginzberg-Devonshire (LGD) is the most accurate theoretical model for the transformation of internal energy of the crystal domains from the motion state to a stability state, and it is later known as the LGD theoretical model. From figure 2, we have confirmed the BaTiO3 film sample has a c-axis orientation, so the polarization degradation dependence on temperature is determined by the ratio of the c-axis polarization state to the spontaneous polarization state as $P_c / P_s$. If the local energy cost density $U_{loc}(P_c)$ is for the polarization to deviate from the spontaneous polarization $P_s$, there is a relationship between the $P_c / P_s$ and the local energy cost in one crystalline domain as defined by equation (1)[7,10]

$$U_{loc}(P_c) = A_{loc} \left[1 - \left(\frac{P_c}{P_s}\right)^3 \right]^{\frac{1}{2}}$$

(1)

where the direction of spontaneous polarization $P_s$ is also dependent of temperature, $A_{loc}$ is a constant, which is $2.41 \times 10^7$ J/m$^3$ at 0K for BaTiO3 crystal. From the LGD model, the working temperature dependences of the two parameters in equation (1), $P_s$ and $A_{loc}$, have the following relationships as

$$A_{loc}(T) = \frac{1}{4} BT_s^4$$

(2)

$$P_s^4 = [-A_{loc}(T - T_c) / B]$$

(3)

where $T$ and $T_c$ are the working and the Curie temperatures, respectively, $A_0 \neq A_{loc}(T = 0)$. Equations (2) and (3) meet: $A_0 > 0$ and $B > 0$, which can be obtained with the values of $P_s$ and $A_{loc}$ at $T=0$.

If $W_{loc}$ is the local energy, and $W_{gs}$ and $W_{gz}$ are the energy gradients of the electric dipoles at the x-axis and z-axis, respectively, then they are defined as[10]

$$W_{loc} = \int_0^\mu dz \int_0^\mu dy \int_0^\mu dx U_{loc}(x,y,z) = \frac{2}{3} A_{001} A_{loc} \delta_z$$

$$W_{gs} = \int_0^\mu dz \int_0^\mu dy \int_0^\mu dx \frac{dP}{dx} = \frac{8A_{001} P_s g_s}{3\delta_x}$$

$$W_{gz} = \int_0^\mu dz \int_0^\mu dy \int_0^\mu dx \frac{dP}{dx} = \frac{8A_{001} P_s g_z}{3\delta_z}$$

(4)

where $g_s$ and $g_z$ are the energy gradient coefficients of the electric dipoles at the x-axis and z-axis, respectively, which can be obtained with the values of $A_{001}$ and $A_{010}$ in the areas of the a-axis and c-axis oriented crystal domains, respectively, and $\delta_x$ and $\delta_z$ are their corresponding effective delta functions.
2.4. Derivations for the Theoretical Models of the Potential Energy

In the forming process of the crystal axis orientation before and after the stabilization of domains, a potential energy inside the material lattice is generated\cite{11-14}. So, the total free energy $F_{crys}$ in a crystal domain can be calculated from the arithmetic sum of four energy density components - the bulk free energy density $f_{bulk}$, the ferroelectric energy density $f_{elas}$, the gradient energy density $f_{grad}$ and the electrostatic energy density $f_{elec}$\cite{11,12}. Then, the total free energy in a volume $V$ is defined by

\begin{equation}
F_{crys} = \int (f_{bulk} + f_{elas} + f_{grad} + f_{elec})dV
\end{equation}

(5)

In the crystalline domain walls, $f_{grad}$ just exists when an external electric field is applied and nonzero around domain wall. So, for the static state without external electric field, $f_{grad}$ and $f_{elec}$ do not need to be considered. In this work, among the four contribution factors in equation (5), only $f_{elas}$ and $f_{bulk}$ need to be taken into account. In a BaTiO$_3$ crystal film, the elastic energy density is calculated by\cite{12,13}

\begin{equation}
f_{elas} = \frac{1}{2} C_{ijkl} e_{ij} e_{kl} = \frac{1}{2} C_{ijkl} (e_{ij} - e_{ij}^0)(e_{kl} - e_{kl}^0)
\end{equation}

(6)

where $C_{ijkl}$ is the elastic stiffness tensor, $e_{ij} = e_{ij} - e_{ij}^0$ is the elastic strain, $e_{ij}$ is the total strain of the crystal compared to the parent paraelectric phase, and $e_{ij}^0$ is the stress-free strain. In the general case of a ferroelectric BaTiO$_3$ crystal film, the strain is relaxed\cite{15}, namely, $e_{ij}$ is supposed to be zero, further the $f_{elas}$ defined by equation (6) is zero.

For the stress-free state of the ferroelectric BaTiO$_3$ crystal, the stress components can be eliminated, then the formula for defining the bulk energy density can be changed from the $f_{bulk}$ form of the bulk material defined by Ref.\cite{14} to the crystal film with the Legendre transformation formula of the well-known expressions for the elastic Gibbs function of a quasi-cubic style ferroelectric crystal as

\begin{equation}
f_{film} = \alpha_1^*(P_1^2 + P_2^2) + \alpha_3^*P_3^2 + \alpha_{11}^*(P_1^4 + P_2^4) + \alpha_{33}^*P_3^4 + \alpha_{12}^*P_1^2P_2^2 + \alpha_{13}^*P_1^2P_3^2 + \alpha_{23}^*P_2^2P_3^2 + \alpha_{44}^*P_4^2 + \alpha_{111}^*[P_1^2P_2^2 + P_3^2] + \alpha_{112}^*[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] + u_m^2 / (s_{11} + s_{12})
\end{equation}

(7)

Further, the other transformation parameters are defined by the following set of equations:

\begin{equation}
\begin{align*}
\alpha_1^* &= \alpha_1 - u_m (Q_{11} + Q_{12}) / (s_{11} + s_{12}) \\
\alpha_3^* &= \alpha_3 - u_m (2Q_{12}) / (s_{11} + s_{12}) \\
\alpha_{11}^* &= \alpha_{11} - (1/2) [(Q_{11}^2 + Q_{12}^2) s_{11} - 2Q_{11}Q_{12}s_{12}] / (s_{11} - s_{12}) \\
\alpha_{12}^* &= \alpha_{12} - [(Q_{11}^2 + Q_{12}^2) s_{11} - 2Q_{11}Q_{12}s_{12}] / (s_{11}^2 - s_{12}) + Q_{44}^2 / 2s_{44} \\
\alpha_{33}^* &= \alpha_{33} + Q_{12}^2 / (s_{11} + s_{12}) \\
\alpha_{13}^* &= \alpha_{13} + Q_{12}^2 (Q_{11} + Q_{12}) / (s_{11} + s_{12})
\end{align*}
\end{equation}

(8)

Where $u_m$ is a uniform misfit strain in the film plane at the film/substrate interface under the condition of the lattice matching between film and substrate for the c-axis oriented BaTiO$_3$ crystal, which is defined as $u_m = (b - a_0) / b$ with the lattice constants of the film and substrate, $b$ and $a_0$, respectively.

In the case of a single-crystalline single-domain film, the internal elastic fields are homogeneous so that the above conditions hold through the film volume. For the BaTiO$_3$ crystal films, the values of the
thermodynamic expansion parameters used in equation (7) are listed in table 1 where the temperature unit is °C [14]. Further, all the transformation parameters defined in equation (8) are listed in table 2.

Table 1. Thermodynamic expansion parameters of BaTiO3 crystal film.

| Units for α’s (m⁵/FC²) | α₁ | α₁₁ | α₁₂ | α₁₁₁ | α₁₁₂ | α₁₁₃ |
|-------------------------|----|-----|-----|-------|-------|-------|
| Expressions             | 3.3(T-110) ×10⁵ | 3.6(T-175) ×10⁶ | 4.9×10⁸ | 6.6×10⁹ | 2.9×10⁹ | 7.6(T-120) ×10⁷+4.4×10¹⁰ |

Table 2. Transformation parameters of expansion for BaTiO3 crystal film.

| Units For α’s (m⁵/FC²) | Q₁₁ | Q₁₂ | Q₄₄ | S₁₁ | S₁₂ | S₄₄ |
|-------------------------|-----|-----|-----|-----|-----|-----|
| Expressions             | 0.11 | -0.043 | 0.059 | 8.3×10⁻¹² | -2.7×10⁻¹² | 9.24×10⁻¹² |

3. Derivation of the Formula for Defining the Polarization Degree of Domain Wall

As mentioned above, the polarization ratio is determined by the thermodynamic process of the domain motions. So, based on the conservation law of the total energy in the crystal domains, we have

\[ W_{loc}(P_z) - U_{loc}(P_z) = F_{crys} \] (9)

Consequently, with equation (1) the polarization ratio of the crystalline at c-axis can be expressed as

\[ \left( \frac{P_z}{P_s} \right)^2 \approx 1.0 - \left\{ \left[ W_{loc}(P_z) - F_{crys} \right] / A_{loc} \right\}^{1/2} \] (10)

With the above theoretical models defined by the equations (1)-(10), we can calculate the polarization ratio \( (P_z / P_s) \), in which the conservation in the polarization stabilization process plays the key role.

4. Numerical Simulations for the Polarization Degree of Domain Wall

The study of molecular dynamics enables to accurately model the nucleation phenomenon of domain wall motion. So, by selecting the constant values of BaTiO₃ crystal domain density as \( a = 3.900 \) Å and \( c = 4.150 \) Å, with equations (2)-(4), we first obtain the temperature dependence of the total local kinetic energy \( W_{loc} \) of one crystalline domain as shown in figure 3(a). Note that the total local energy increases with temperature at a high-order, and illustratively at the temperature \( T = 60°C \) the free energy of one domain is \( W_{loc} = 2.50 \times 10^{-3} \) J. Further, for the free energy of one crystalline domain \( F_{crys} \), with the set of equations (5) through (8) and the parameter values given in tables 1 and 2, we obtain the numerical simulation results of the temperature dependence of the total free potential energy \( F_{crys} \) of one crystalline domain in BaTiO₃ crystal film as shown in figure 3(b). Note from figure 3(b) that \( F_{crys} \) linearly increases with the temperature, and illustratively, at the temperature \( T = 60°C \), the free energy of one domain is \( F_{crys} = 3.92 \times 10^{-4} \). Consequently, we analyze the distributions of the local kinetic energy shown in figure 3(a) and the free potential energy shown in figure 3(b) and then find the total local kinetic energy \( W_{loc} \) is averagely higher than the free energy \( F_{crys} \) in a crystalline domain by one order in the temperature range of simulation, resulting in a conclusion that the polarization ratio defined by equation (10) is only dependent on the total local kinetic energy and the energy cost in the nucleation process of crystalline domains, while is independent of the free energy.
Figure 3. (a) Numerical simulation for the temperature dependence of the total local energy of c-axis BaTiO₃ crystal domain wall switching process; (b) Numerical simulation for the temperature dependence of the free energy of c-axis BaTiO₃ crystal domains grown on MgO crystal. With equations (2)-(4) and (7)-(10), we obtain the numerical simulation result of the polarization ratio \( P/P_s \) as shown in figure 4. Note that the polarization ratio presents the linear degradation with temperature and there is a degradation of 8% in the range of 80°C. The linear degradation with temperature is only determined by the local kinetic energy as analyzed above. For instance, when the working temperature increases from the room temperature 20°C to 100°C, the polarization ratio degraded from 54% to 46%, leading to an inefficiency of a functional device in the operations. As an EO property, the EO coefficient will decrease to some extent.

Figure 4. Numerical simulation for the temperature dependence of the polarization ratio of c-axis BaTiO₃ crystal domains grown on MgO crystal.

5. Conclusion

By means of XRD diffractometer with JADE software, the crystal axis orientation of BaTiO₃ thin film was analysed, and by referring the measurement results that were published in our previous work, the crystal axis orientation was determined to be c-axis\(^{[15]}\). By means of molecular dynamic theory and the numerical simulations, we obtained the temperature dependence of both the kinetic and potential domain energies of BaTiO₃ crystal. The final numerical simulation results for the polarization ratio lead to the conclusion is that, in the growth process, the local energy and the energy cost of polarization switching process in the nucleation process of a crystalline domain co-determine the polarization ratio of a BaTiO₃ crystal film. Such a new finding is very sustainable to the research and development of the functional devices based on the tetragonal type ferroelectric crystals. As a promising ferroelectric material, the BaTiO₃ crystal thin-film has been attracting increasing interests in both the high bandwidth EO modulators and the high-capacity electrical-energy memories, thus this work is of importance to the
product developments and applications of ferroelectric devices in both modern computers and fiber-optic telecommunications.

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