Theoretical study of the reaction mechanism Ba, Ti, O in the early growth of BTO thin films

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Abstracts: We use the $DMol^3$ program based on density functional theory(DFT) to clarify the processes of microcosmic reactions and the particle states in the early growth of $BaTiO_3$ (BTO) thin films. This research is important for optimal preparation and structure control of BTO thin films. After designing and optimizing some possible intermediate states, we find that the molecules may serve as nucleation sites for BTO growth. This occurs by combining TiO_2 with BaO molecules to form $BaTiO_3$ with the G conformation, which is similar to a quarter of a BTO unit cell. By virtue of understanding these mechanisms, perovskite-structured BTO thin films are formed.

Keywords: Barium Titanate, Reaction Mechanism, Thin Films Growth, Density Functional Theory, Activation Energy

1. Introduction

A revolution is occurring in science and technology based on the recently developed ability to measure, manipulate, and organize matter on ferroelectric thin films. These thin films are widely exploited for microwave phase shifters and dynamic random access memory due to their advantageous physical properties (piezoelectricity, ferroelectricity, pyroelectricity, and photoelectricity—the latter is used in nonlinear optics). As a typical representative of the perovskite structure thin films, $BaTiO_3$ thin films are used not only to make microelectronic devices, but also to develop ferroelectric/superconductor devices by combining them with superconducting thin films[1-3]. As a result, progress in understanding BTO thin films will have a very far-reaching impact.

Currently, $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) thin films are prepared primarily by Laser Molecular Beam Epitaxy (LMBE), not only because it allows *in situ* monitoring, but also because the chemical composition of thin films can be controlled. Using LMBE to prepare BTO and STO thin films, Li, et al[4-6] demonstrated the feasibility of unit cell migration with surface self-diffusion by *in situ* reflective high energy electron diffraction and atomic force microscopy. The experiments revealed "unit cell migration", which formed the basis for a growth model for films. In addition, they measured the activation energy of unit cell migration in BTO and STO thin films to be 0.29 ± 0.01 eV[4,5].

However, these experimental investigations are inadequate to describe physical chemistry data such as interface structure, adsorption, diffusivity, and particle trajectories in the growth of thin films. Additionally, experimental information is lacking regarding the formation of the BTO perovskite structure unit cell and the physicochemical processes involving Ba, Ti, and O atoms. Thus, developing a theoretical picture is very important for advancing research in this area. We had investigated possible reaction mechanisms in initial growth process of $SrTiO_3$ (STO) by a first-principles calculation in previous research [7]. To this end, we present a first-principles calculation using density functional theory (DFT)[8,9] to investigate both the possible combination reactions and the initial process of migration growth of BTO to the cell stage.

Regarding unit cell formation with Ba, Ti, and O microcosmic particles formed by flash evaporation in the unit cell migration growth of BTO thin films, we hypothesize two cases. The first is that Ba, Ti, and O atoms form intermediates (O_2, BaO, BaO_2, TiO, TiO_2) by colliding, after which the unit cell is formed. The second is the formation of a perovskite structure unit cell by direct deposition of Ba, Ti, and O atoms on the surface of the substrate.

This paper is organized as follows, a brief introduction about the calculation method shows in section 2, the main results and discussion of the paper are described in section 3 and the end of the paper is conclusion.

2. Methodology

We use the local orbital density functional method DMol^3 program[10,11], which evolved from a gas phase molecular method to a method that allows for state-of-the-art calculations on non-conducting and metallic solids[12,13]. We used the PW91 function of the Generalized Gradient Approximation[14,15] and convergence conditions with a large basis set and high accuracy to optimize each structure of this system. During the calculations, the wave function of the valence electrons is expanded using the Double Numeric Polarization basis set in DFT, which is similar to 6-311++G** of Gaussian theory, but more precise. Its self-consistent convergence precision is set above 10^{-6} a.u. The energy convergence accuracy reaches 10^{-5} a.u., and the convergence accuracy of grads and displacements surpassed 10^{-4} a.u./nm and 5×10^{-4} nm, respectively. In the DMol^3 program, all the electrons of atoms with atomic number less than 21 are involved in the calculation. Thus, all the electrons of O atoms and the valence electrons of Ba and Ti atoms are treated explicitly, but the core electrons of Ba and Ti atoms are replaced with effective core potential approximations[15]. Besides, we chose the most accurate transient state (TS) search methods to obtain the TS structure, namely the complete linear synchronous transit and the complete quadratic synchronous transit[17,18]. The activation energy of reactions can then be obtained after analyzing the energy difference between the intermediate state and the TS[19,20]. Incidentally, the TS can be confirmed easily if it has a higher energy than that of the reactants or intermediates and if it exists only at an imaginary frequency[21-23].

3. Results and Discussion

Generally, in an atmosphere containing Ba, Ti, and O atoms, Ba and Ti are easily oxidized by O atoms of higher activity, so that O_2, BaO, BaO_2, TiO, TiO_2, and $BaTiO_3$ molecules are formed preferentially prior to formation of the unit cell. Based on our analysis, we present some reaction models and their initial conditions, assuming a vacuum and non-equilibrium states with high-density reactants.

3.1. The Formation of Molecular TiO$_2$

In vacuum, O atoms and O_2 molecules may oxidize Ti atoms to form TiO_2 molecules. We present two models to describe this process. Model IA (IB) involves O atoms (O_2 molecules) reacting directly with Ti atoms to form TiO_2 molecules.

Within Model IA, the stabilization energy $E_s = E_{TiO_2} - E_{Ti} - 2E_O$ of the TiO_2 molecule is 1,429.59 kJ/mol, using the energies given in Table 1. This reaction proceeds very easily because of the gradual reduction of the total energy. For model IB, however, the situation is more complicated. There are few O_2 molecules in the vacuum, although some are formed when O atoms are vaporized by the laser. Ti atoms and O_2 molecules may form TiO_2 molecules upon colliding. In the process of TiO_2 formation, we find a barrier with one unique imaginary frequency, implying that an activation energy is needed to overcome the barrier. To analyze the reaction mechanism that yields TiO_2, we optimize the conformations of the reactants (Ti atoms and O_2 molecules), resultant (TiO_2 molecules), intermediate state (M1), and transient state (TS1) and find the reaction channel shown in Figure 1.

Table 1. *The energies for particles of BTO thin films in the early growth.*

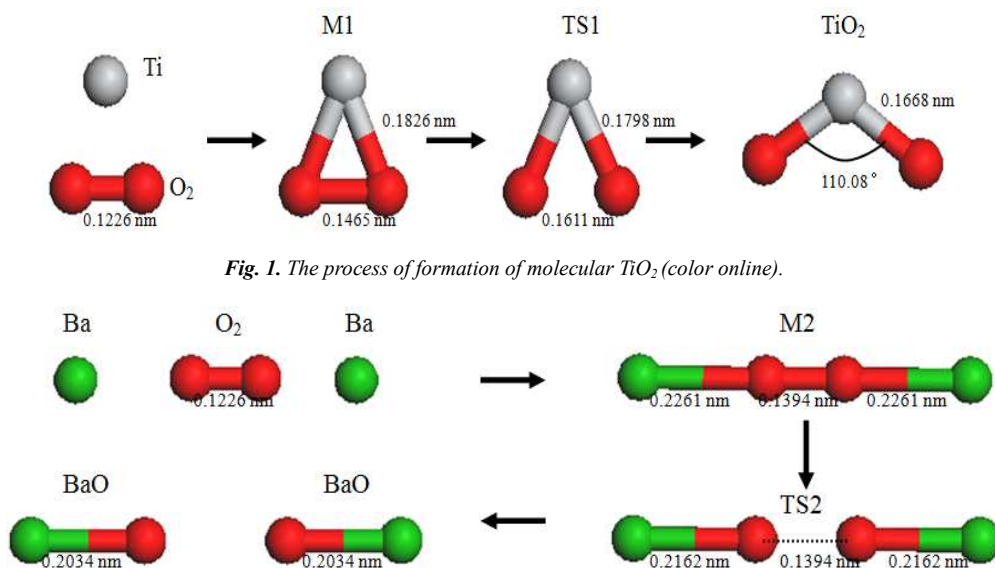|	Energy (kJ/mol)		Energy (kJ/mol)
O	-197073.44	Ti	-153099.73
O_2	-394760.13	TiO_2	-548676.20
M1	-548267.41	TS1	-548255.60
Ba	-66817.44	BaO	-264463.67
M2	-528746.82	TS2	-528691.81

Fig. 1. *The process of formation of molecular TiO₂ (color online).*

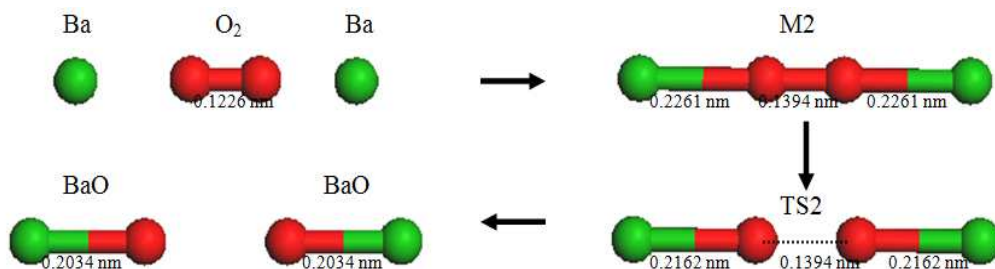**Fig. 3.** *The process of formation of molecular BaO (color online).*

Ti atoms form a coordination bond with the O_2 lone-pair electrons, instantly (on the time scale of interest) transforming into an M1 compound. Due to the vibration of the O-O bond, TiO_2 molecules form only after passage through the transient state TS1. We calculate that the energy of the reactants (Ti atom and O_2 molecule), intermediate state (M1), transient state (TS1), and resultant (TiO_2) is -547859.86 kJ/mol, -548267.41 kJ/mol, -548255.60 kJ/mol and -548676.20 kJ/mol, respectively, as shown in Fig. 2. From these values we find the stabilization energy M1 is 407.55 kJ/mol, and the activation energy $E_A = E_{TS1} - E_{M1}$ of formation of TS1 is 11.81 kJ/mol. The O-O and Ti-O bond lengths and the O-Ti-O bond angles change during the formation of the TiO_2 molecule, as shown in Fig. 1. This indicates that forming the Ti-O bonds weakens the O-O bond in M1, so that it is easily broken, leading to the formation of TiO_2 via the transient state TS1. The changes in bond lengths, bond angles, and stabilization energies thus lead us to conclude that the reaction always favors the formation of TiO_2.
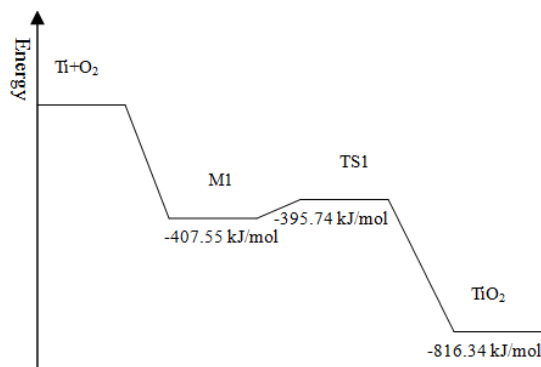

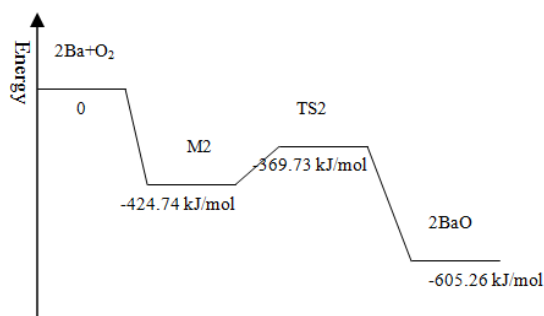*Fig. 2.* The reaction energies of the formation of TiO_2.

Fig. 4. The reaction energies of the formation of BaO.

3.2. The Formation of Molecular BaO

The same analysis may be applied to Ba atoms, which are oxidized and form BaO molecules due to interactions with O atoms or O_2 molecules. Here, we likewise use two models, model IIA (IIB) where the Ba and O atoms (O_2 molecule) interact to form BaO. The reaction process is quite simple within model IIA—our calculation indicates that there is no energy barrier in this process. Using the energies given in Table 1, we find that the stabilization energy of the BaO

molecule is 572.03 kJ/mol, which is consistent with values reported in the literature; *i.e.* $E_s \geq 562.8 \pm 14.6$ kJ/mol[24]. In addition, the bond length of BaO is 0.2034 ± 0.0053 nm[24].

Within model IIB, two Ba atoms form coordination bonds with the lone-pair electrons of an O_2 molecule, instantly (on the time scale of interest) transforming into an M2 compound. The formation of the Ba-O bond weakens the O-O bond, and it is gradually broken resulting in the decomposition of M2 toward the BaO molecule via the transient TS2 state. By analyzed the transient TS2 state, we find that the stabilization energy of M2 is 424.74 kJ/mol and that the activation energy of the reaction is 55.01 kJ/mol. These results imply that the reaction always favors the formation of BaO molecules.

3.3. The Formation of Molecular BTO

After BaO and TiO_2 molecules are formed, they may interact to form $BaTiO_3$. BaO, TiO_2, and $BaTiO_3$ molecules, providing precursors for forming the BTO unit cell.

To be sure of the geometric conformations of $BaTiO_3$, we built seven different possible structures according to the principle of molecular symmetry. As shown in Fig 5, after optimization of the seven structures, we find that the A, B, and C conformations are similar to the F conformation and that the D and E conformations are similar to the G conformation. Furthermore, the system energies of the F and G conformations are the lowest, at -813585.88 kJ/mol and -813587.18 kJ/mol, respectively, indicating that these conformations are more stable.

To study the components and structures of BTO thin film crystals, we create a 2×2 BTO super-cell with four BTO molecules, corresponding to $BaTiO_3$ molecules. The total energy of the super-cell is -3257201.00 kJ/mol, and the average energy of the BTO molecule is -814300.25 kJ/mol, making it 714.37 and 713.07 kJ/mol less than the F and G conformations, respectively. In addition, we note that the most stable conformation, G, is similar to a quarter-corner of the BTO unit cell, so that a BTO molecule with the G conformation, formed by BaO and TiO_2 molecules, will be shaped into the BTO unit cell with a perovskite structure. Put another way, the G conformation, which is a BTO molecule, may be regarded as one component of a BTO unit cell.

To form a BTO molecule (see Figs. 6 and 7), the F conformation is first formed by collision between BaO and TiO_2 molecules, which is a barrierless reaction. Immediately thereafter, the Ba atoms moves toward the center of the three O atoms until the G conformation is formed because of the attractive forces of the lone-pair electrons of the three O atoms. This process involves a barrier. Upon optimization and frequency analysis, we find a new transient state TS3. The characteristic parameters of TS3 are given in Table 2, and indicate that the reaction favors the G conformation and that it occurs easily due to the low activation energy (10.55 kJ/mol).

Our calculation and optimization indicate that there is little probability that Ba, Ti, and O atoms form a BTO unit cell directly but that some intermediates (such as BaO, TiO_2, and

BTO molecules) need to be formed beforehand. The activation energies for the formation processes of BaO, TiO$_2$, and BTO are 55.01 kJ/mol, 11.81 kJ/mol, and 10.55 kJ/mol, respectively, with the lower value indicating that the reaction occurs more easily.

Table 2. *The differences between F, G conformations and BTO molecule on the atomic structures.*

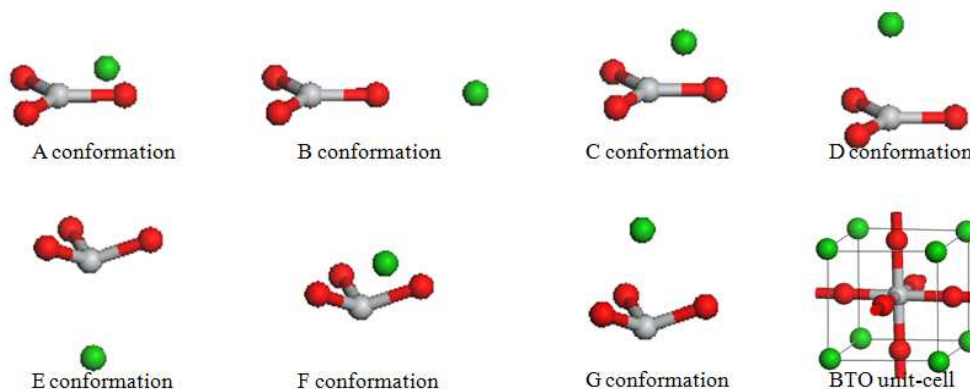|	Bond length (nm)			Bond angle (°)			The distance from Ba to O (nm)			Energy (kJ/mol)
	O1-Ti	O2-Ti	O3-Ti	O1-Ti-O2	O2-Ti-O3	O3-Ti-O1	Ba-O1	Ba-O2	Ba-O3	
F conformation	0.1831	0.1841	0.1679	95.7	112.2	111.3	0.2367	0.2362	0.4171	-813585.88
TS3	0.1814	0.1816	0.1703	96.3	101.8	101.9	0.2406	0.2396	0.3193	-813575.33
G conformation	0.1779	0.1779	0.1779	96.8	96.8	96.8	0.2522	0.2522	0.2522	-813587.18
BTO unit cell	0.2015	0.2015	0.2015	90.0	90.0	90.0	0.2849	0.2849	0.2849	-814300.25

Fig. 5. *The conformations of BTO molecule and the structure of BTO unit cell (color online).*
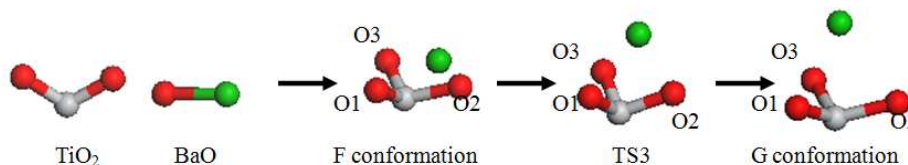

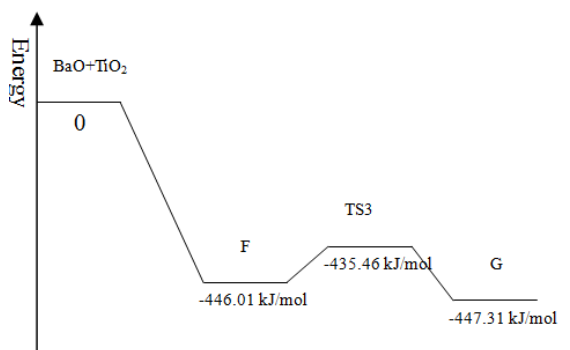**Fig. 6.** *The process of formation of BTO molecule (color online).*

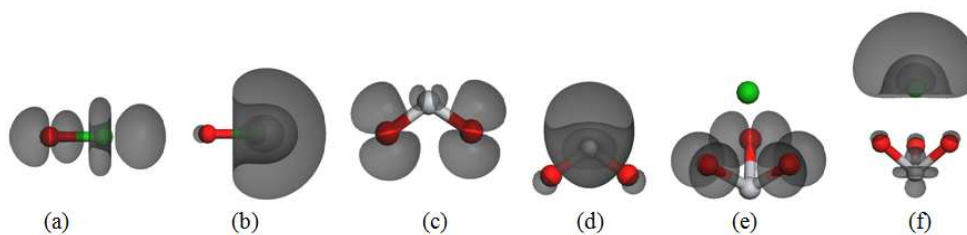**Fig. 7.** *The reaction energies of formation of BTO molecule.*

Fig. 8. *The HOMO and LUMO orbits of BaO, TiO$_2$, and BaTiO$_3$ molecules (color online).*

(a) The HOMO of BaO; (b) The LUMO of BaO; (c) The HOMO of TiO$_2$;
(d) The LUMO of TiO$_2$; (e) The HOMO of BaTiO$_3$; (f) The LUMO of BaTiO$_3$

3.4. Analysis Using the Frontier Orbital Theory

The Frontier Orbital Theory considers that molecular orbitals (the highest occupied molecular orbital, or HOMO, and the lowest unoccupied molecular orbital, or LUMO) play a pivotal role during the chemical reaction. For lower E_{HOMO}, the electronic capacity to offer molecules is lower because the electrons in the orbital are steadier. We use E_{LUMO} to describe the ability of a molecule to accept electrons. The lower it is, the better electron-acceptor it is.

Our calculations indicate that the energy of the BaO HOMO is -288.44 kJ/mol and its LUMO energy is -154.02 kJ/mol. For TiO_2 the HOMO and LUMO energies are -558.31 kJ/mol and -352.97 kJ/mol, respectively, so that $E_{HOMO}(BaO) > E_{HOMO}(TiO_2)$, and the $E_{LUMO}(BaO) > E_{LUMO}(TiO_2)$. As a result, the LUMO of TiO_2 can react with the HOMO of BaO because BaO can offer electrons and TiO_2 can accept electrons. As shown in Figure 8, the main HOMO of BaO comes from the lone-pair electrons of the O 2p orbital, and the main part of the TiO_2 LUMO comes from the 3d orbital of the Ti atom, indicating that the O atoms of BaO molecules will combine with the Ti atoms of TiO_2 molecules. This conclusion is the same as the conclusion reached above. In addition, the calculated BTO HOMO and LUMO orbits are shown in Figure 8. The BTO HOMO distributed around the O atoms mainly form its lone-pair electrons in the 2p orbital, and the LUMO distributed around the Ba and Ti atoms mainly form their 5s and 3d orbital.

4. Conclusion

In our calculation, we find that BaO, TiO_2, and $BaTiO_3$ molecules are the primary particle states in the early growth of BTO thin films by LMBE, with activation energies of 55.01 kJ/mol, 11.81 kJ/mol, and 10.55 kJ/mol, respectively. We find that TiO_2 molecules are formed first in vacuum where Ba, Ti, and O atoms coexist and become nucleation sites for BTO unit cell growth. Furthermore, the $BaTiO_3$ molecule, a part of the BTO unit cell, is formed by TiO_2 and BaO molecules. The BTO primary unit cell with a perovskite structure then evolves and grows with BTO unit cell migration growth on the substrate surface.

Acknowledgements

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