

# A review of processing dependences of microstructure and orientation of ferroelectric thin films

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The ferroelectric thin film was widely investigated in detail in recent years. The ferroelectric properties of the thin films are obviously dependent on the microstructure of the film, which were influenced by some processing parameters for preparing the films, including precursor solution chemistry, nature of substrate, film thickness, and condition of heat treatment etc. In this paper, these processing dependences of the films were reviewed.

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## 1. Introduction

Ferroelectric materials having the perovskite structure are of great interest in electronics and microelectronics, finding application in pyroelectric and piezoelectric devices, nonvolatile memories, multilayer capacitors and positive temperature coefficient resistors (PTCR), and optical waveguides. Especially, substituted bismuth-containing layered perovskite films have been recently found to be ferroelectric properties and very high Curie temperature and good fatigue resistance, and to be very suitable for potential applications in nonvolatile random-access memories (NVRAM) and dynamic random-access memories (DRAM). These ferroelectric films should be carefully prepared to utilize their remarkable anisotropy-dependent physical characteristics. Thin film growth techniques can be advantageous in achieving the order state since atomic ordering can be manipulated in the process of film growth.

Fabrication of ferroelectric thin films has usually been accomplished by the sputtering technique, producing oriented or epitaxial films for high-efficiency devices. In the last few years, sol-gel and chemical solution deposition techniques, with its advantages of strict compositional control and low fabrication costs, have been extensively utilized to produce ferroelectric films mainly for memory applications. Most of the work has focused on the dielectric and ferroelectric properties. Consequently, the control of film orientation with sol-gel and chemical solution deposition processes had been widely investigated. It has been demonstrated that the microstructure that evolves during heat treatment can be affected by the nature of the substrate, the precursor solution chemistry, the film thickness, and heat treatment approach utilized. In present paper we review these processing dependences of microstructure and orientation of the thin film.

## 2. Processing dependence of microstructure

### 2.1. Chemistry of Precursor Solution

The chemical properties of precursor solutions can be altered by modifying the organic ligands attached to the metal cations or using different stabilizers and/or solvents to form complex precursor solutions. The differences in the nature of precursors affect the gelation behavior after deposition, and thereby, influence physical properties of the film during subsequent heat treatment. Many approaches have been used to prepare stable precursor sols for making perovskite thin films with high-quality electric properties. Most of the work has been involved effects of precursor solution on the electric properties of the film. It is apparent from the existing literature report that the precursor solution significantly impacts the densification, orientation, and crystallization behavior, as well as the optical and electric properties of the deposited thin films [1-3].

Lead zirconium titanate (PZT) ferroelectric thin films, having higher remanent polarization, were fabricated on electroded silicon wafers using chemical solution deposition by Schwartz *et al* [2]. In this study, two different chelating agents, acetic acid and acetylacetone, were used in the synthesis of the precursor solutions. The microstructure of the acetylacetone-derived film was characterized by nucleation at the platinum electrode and a columnar growth morphology (~100–200 nm lateral grain size). In contrast, the acetic acid-derived film was characterized by both columnar grains nucleated at the electrode, and larger (~1 μm) grains nucleated at the surface of the film. Schwartz *et al* [2] demonstrated that the observed changes may be closely related to changes in film pyrolysis behavior induced by changes in solution preparation condition, i.e. water: metal cation ratio or use of chelating agents, and concluded that the precursor

chemistry basically affects the pyrolysis temperature, which in turn controls the crystallization behavior, degree of orientation, and surface morphology of the deposited PZT thin films. Similar influence of precursor solution on the ferroelectric properties of  $\text{Pb}_{0.85}\text{La}_{0.15}\text{TiO}_3$  thin films was reported by Bhaskar *et al* [4]. This PLT thin films were prepared with sol-gel method using different precursor sources for lanthanum, namely, lanthanum acetate dissolved in acetic acid (LAA) and lanthanum 2-methoxyethoxide in 2-methoxyethanol (LMM). The PLT film processed through the LAA route exhibit relative larger crystallite size and were, essentially, randomly oriented, whereas films prepared by the LMM route showed a relatively smaller grain size and strong tendency toward a (100) preferred growth orientation. The LMM-derived PLT films had lower dielectric constants, poorer polarization hysteresis characteristics, and higher leakage current densities. However, when the pyrolysis temperature is increased from 450 °C to 550 °C, the organic contents of LMM-derived films are reduced and their ferroelectric properties are indeed comparable to that of the LAA-derived films.

The “aging” characteristics of an acetic acid/methanol solvent-based lead zirconate titanate (PZT) precursor solution, prepared by the Inverted Mixing Order (IMO) process, have been studied for an extended period of time by Boyle *et al* [3]. The films generated from the IMO process exhibit an increase in thickness as a function of solution age due to chemical “aging” (esterification) of the precursor solution. This increased thickness results in a decrease in the microstructural uniformity, which affects the electrical and optical properties. Another study of “ageing” effect of the films reported by Kushida *et al*[5] indicated that ageing of the solution is found to promote (100)-orientation of lead titanate films. Characterizing the solution by viscometry indicated that the preferred (100)-orientation might be attributable to the increase of molecular size in the solution. A study on  $\text{Bi}_4\text{Ti}_3\text{TiO}_{12}$  thin films clear showed that the aging of the solution had a strong influence on the texture of the final crystallized film. A linear increase in viscosity suggested an increase in metallo-oligomer size with ageing time of the precursor solution, which result in enhance in c-orientation of the films with the time on four substrates-- Pt electroded Si(100), Si(111), fused  $\text{SiO}_2$ , and Pt electroded Si. Fuierer *et al*[6] believed that crystallization and orientation of the BTT films were apparently controlled not by epitaxy, but rather by the oligomeric structures that condensed in the solution as it aged, and concluded that templating effect of the -Ti-O-Ti-O-Ti-O- oligomers led to c-axis-oriented ceramic films because similarity in bond pattern between oligomer and final crystal structure.

The concentration of solution can affect the individual layer thickness, which in turn strongly affect the structure, ferroelectricity, and dielectric properties of the thin film. A sol-gel derived (Sr,Ba)TiO<sub>3</sub> thin films deposited by Cheng *et al* [7] shown that the films with an individual layer thickness of 60nm deposited with 0.4M solution shown

small equiaxed grain, cubic structure, temperature-independent dielectric constant, and no ferroelectricity. The film with individual layer thickness of 8 nm deposited with 0.01M solution shown columnar grains, tetragonal structure, large dielectric constant, and good ferroelectricity.

## 2.2. Nature of substrate

It has been illustrated that the microstructure and orientation of the perovskite film can be manipulated by the choices of the substrate properties including roughness and lattice matching with the film, which had been reported in many literatures for various kind of ferroelectric films.

Origin of orientation in sol-gel-derived lead titanate films was investigated by Kushida *et al* [5]. It was found that more strongly (100)-oriented film forms on Pt-coated Si than on the fused quartz and a highly (001)-oriented films with azimuthal orientation are grown on a (100)  $\text{SrTiO}_3$  single-crystal dish. These can be attributed to better lattice match between  $\text{PbTiO}_3$  film and  $\text{SrTiO}_3$  substrate and The orientation of the (001)-oriented film is reverse to the substrate. During the coating process, rapid heating at 400°C for the intermediate pyrolysis of each coating can produce (100)-oriented  $\text{PbTiO}_3$  columnar nuclei. Epitaxial overgrowth originating at these columnar nuclei led to formation of the (100)-oriented film. Orientation of sol-gel-deposited  $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  (PST) ferroelectric thin films on two different substrates were similarly researched by Zhai *et al*[8]. Films derived on the  $\text{LaNiO/Pt/Ti/SiO}_2/\text{Si}$  substrates shown a strong (100) preferred orientation and shown a non-uniform rounded grain size distribution and have a larger polarization and lower coercive field  $E_c$ . The perovskite phase for PST thin films deposited on  $\text{Pt/Ti/SiO/Si}$  substrates had a preferred (110) orientation. An annealed LNO-buffered substrate showed a highly preferred (100) orientation. Authors believed that the LNO layer not only served as a useful metal oxide bottom electrode but also formed a template with a preferred (100) orientation to enable growth of high-quality PST films, however the Pt-buffer substrate shown a highly preferred (111) orientation and enabled the growth of a preferred (110) orientation in PST films. Similarly, ferroelectric  $(\text{Pb}_{0.76}\text{Ca}_{0.24})\text{TiO}_3$  (PCT) thin films grown on  $\text{LaNiO}_3$  (LNO) coated Si(1 1 1) and fused quartz substrates by using a sol-gel process shown the highly (1 0 0)-orientation and random orientation, respectively[9]. (100) oriented PCT films have the remanent polarization ( $P_r$ ) and coercive electric field ( $E_c$ ) values were 9.3  $\mu\text{C}/\text{cm}^2$  and 64 kV/cm. However, a sol-gel-deposited  $\text{Pb}_{0.6}\text{Ca}_{0.4}\text{TiO}_3$  (PST) ferroelectric thin films on (111)  $\text{Pt/Ti/SiO/Si}$  substrates prepared by Tang *et al* [10] shown a highly (001) preferred orientation. The (001) oriented PCT films shown a remanent polarization ( $P_r$ ) and coercive electric field ( $E_c$ ) values of 23.6 $\mu\text{C}/\text{cm}^2$  and 225kV/cm, respectively. Authors believed that this is a new type of nucleation and growth, the highly (001)

orientation is considered to represent self-texture growth in accordance with minimum surface-energy condition.

The orientations of a lead zirconat titanate films deposited on different substrates were researched by Hirano *et al* [11] using metallo-organics. The crystal symmetry of sapphire (a-alumina) is hexagonal, MgO has an NaCl type structure, whereas both PZT and SrTiO<sub>3</sub> have perovskite structure. The lattice mismatches between PZT and SrTiO<sub>3</sub> along a-axis and c-axis are 3.4% and 6.2%, respectively. Therefore the degree of orientation of the (100)-oriented PZT films decreases in following order, SrTiO<sub>3</sub>(100)>MgO(100)> sapphire (001). A deposited Pt layer on Si had a (111) preferred orientation, thus (111)-oriented PZT film was formed on the Pt deposited Si substrate because the crystallographic matching of PZT (111) to Pt (111). Similarly, high oriented chemically prepared thin films of Pb(Zr<sub>0.04</sub>Ti<sub>0.96</sub>)O<sub>3</sub> on both (100) MgO single crystals and (100) Pt deposited (100) MgO substrates had been fabricated by Tuttle *et al* [12]. The PZT films with highly (001)-preferential orientation were fabricated on platinumized MgO substrates. Randomly oriented PZT films was formed on (100) Pt deposited (100) MgO substrates. Highly (001) oriented PZT films had higher remanent polarization (61 μC/cm<sup>2</sup> compared to 41 μC/cm<sup>2</sup>) and lower relative dielectric constant (368 compared to 466) than PZT films that were randomly oriented.

Strontium barium niobate Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN) thin films, especially highly c-axis-oriented SBN thin films, are desired for optical applications, such as electrooptic properties, photorefractive, and nonlinear optical applications. The sol-gel-derived SBN thin films on various substrates were investigated by Koo *et al* [13]. SBN films with c-axis preferred orientation were obtained on MgO (100) substrates. SBN films deposited on Si(100) and fused silica had polycrystalline structures. On MgO substrate the oriented crystallization which forms the single tetragonal phase occurred at a lower crystallization temperature than those of polycrystalline films because of better lattice match between the film and the MgO substrate than other substrates. Further properties study shown that all the SBN films were highly transparent in the wavelength range from 0.2 to over 1.4μm, but the absorption edges of the films are dependent on the film composition, and both remanent polarization (Pr) and coercive field (Ec) values of the SBN films increase as Sr content in the film composition increases.

Bismuth-containing layered perovskites have been found to be excellent ferroelectric properties and a very high curie temperature and good fatigue resistance. Larger remanent polarization 2Pr of the films can be achieved when the film has larger degree of orientation at direction of the spontaneous polarization vector. A chemical solution deposited Bi<sub>3.2</sub>Nd<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> ferroelectric thin films were fabricated by preannealing then rapid thermal annealing the films at 400 °C and 700 °C respectively [14]. When the film was deposited on the (111)Si substrate, preferred a-oriented film was obtained at annealing time of 3min,

however the degree of the a-orientation was decreased with increasing the annealing time. But the degree of a-orientation of the film deposited on the (100) Si substrate was increased with annealing time. Similarly, a Bi<sub>3.2</sub>Y<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> film was deposited on the (100) Si substrate with same two-step heating process [15], the degree of a-orientation of the film was also increased with annealing time. Additionally, a Bi<sub>3.2</sub>La<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> film deposited on the (100) Si substrate with same two-step heating process shown very highly a-orientation[16]. Together with SEM and AFM analyses authors concluded that a-orientation and its increases can be attributed to the good matching of lattice parameter a and b of film to the Si substrate and preannealing effect. With increasing the annealing time, the effect of the substrate was enhanced. Thus, the a-orientation degrees were increased with increasing annealing time on (100) p-Si substrate, but decreased with annealing time on (111) p-Si substrates.

To control the orientation of the ferroelectric film, various seeding layers have been utilized to bring about appropriate lattice match between film and substrate except for using different substrates. In a literature on a sol-gel derived Pb(MgNb)O-PbTiO (PMNT) thin films, Gong *et al*[17] reported that a (001) PbO seeding layer introduced to the interface between the PMNT film and Pt(111)/Ti/SiO<sub>2</sub>/Si substrate enhanced the (001) preferential orientation of the PMNT film. Effects of TiO<sub>2</sub> seeding layer on crystalline orientation and ferroelectric properties of Bi<sub>3.15</sub>Nd<sub>0.85</sub>Ti<sub>3</sub>O<sub>3</sub> thin films were investigated by Li *et al* [18]. The BNT thin films deposited directly on the Pt(111)substrate exhibited a highly random orientation, with the (117) peak showing highest intensity. While after adding a thin TiO<sub>2</sub> seeding layer, the (117) peak was no longer the most intense due to a drastic increase in the (200) diffraction peak intensities. They<sup>[18]</sup> believed that the TiO<sub>2</sub> seeding layer decreases the lattice parameter mismatch between the BNT thin film and Pt(111) substrate, which can minimize the nucleation energies of the BNT thin film. The BNT film on TiO<sub>2</sub> seeding layer showed a higher degree of squareness and thus larger remanent polarization. The fatigue test exhibited very strong fatigue endurance up to 10<sup>9</sup> cycles for both films.

The lattice mismatch between (100) BaTiO<sub>3</sub> film and (100) LaAlO<sub>3</sub> substrate is 5.38%, such magnitude of the mismatch may limit the effectiveness of these substrates in promoting heterogeneous nucleation at the surface compared to nucleation within the bulk of the film although structure match between the film and the substrate. Thus, the BaTiO<sub>3</sub> films prepared on the LaAlO<sub>3</sub> were randomly oriented, as reported by Schwartz *et al* [2]. However, when BaTiO<sub>3</sub> or PbTiO<sub>3</sub> seeding layers were deposited on the LaAlO<sub>3</sub> substrate using diluted precursor solutions and higher spinning rates, the BaTiO<sub>3</sub> films were highly (h00) oriented with the (100) and (200) planed parallel to the (100) LaAlO<sub>3</sub> substrate surface. Similar highly (h00) oriented SrTiO<sub>3</sub> films were prepared after deposition of SrTiO<sub>3</sub> seed layer. The effectiveness of the seed layer in promoting texturing was strongly dependent

on the both the seed layer and heat treatment conditions. While seed layers prepared at lower temperatures were similar in their general appearance to those prepared at higher temperatures, heat treatment of the seed layer at higher temperature of 1100 °C was necessary to optimize the orientation of the subsequently deposited films [2].

Some seeding layers which can be formed at low temperature, such as PbO, can be achieved by adding excess starting materials in precursor solutions. The effects of excess lead on orientation in sol-gel-derived BiScO<sub>3</sub>-PbTiO<sub>3</sub> thin films deposited on the Pt(111)/Ti/SiO<sub>2</sub>/Si(111) substrate were studied by Wen *et al* [19]. The results shown that a higher lead excess concentration could enhance the (100) orientation of the BSPT thin films. The formation of the (100) orientation was attributed to the (100)-oriented PbO nanocrystals seeding layer formed during the pyrolysis process, which has lattice matching with the BSPT films. However, an orientation study [20]. of Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> films deposited on the Pt(111)/Ti/SiO<sub>2</sub>/Si(111) substrate indicated a (111)-oriented Pt<sub>5-7</sub>Pb (111) intermediate phase was forming between the substrate and films during the pyrolysis step, and this provided the template for growth of (111)-oriented PZT film. A PZT(100) textured film was observed if (001)-oriented PbO seeding layer first formed on the substrate since there is a reasonable lattice match between (001) PbO and (100) PZT. Note that the Pt<sub>5-7</sub>Pb intermediate phase apparently tends to form in MOD-derived films due to the existence of a localized highly reducing atmosphere. Additionally, in a study on lanthanum-doped PZT (PLZT) thin films derived using a methoxyethanol-based sol-gel process, Tani *et al* [21] suggested that whenever the Ti from the adhesion layer formed PtTi on the surface, a (111) perovskite PLZT texture was obtained. Further, they also concluded that under conditions where the top surface was free from Ti (and therefore free of any intermetallic phase), a (100) PLZT texture was observed, since this texture represented minimum surface energy. In a literature on influence of platinum-based electrodes on the microstructure of sol-gel and MCD prepared lead zirconate titanate thin films, Spierings *et al* [22] also reported that annealing of the as-deposited Ti/Pt electrodes results in the formation of hillocks. These hillocks serve as nucleation sites for perovskite formation and thus determine the microstructure and preferred orientation of the crystallized PZT films.

### 2. 3. Condition of heat treatment

The microstructure of the ferroelectric film can be controlled by change of film-substrate interface (as discussed above), nucleation of film during pyrolysis and heating process, and calcining temperature and calcining time.

In an elegant report on the electron microscopy of sol-gel-derived thin film, Reaney *et al* [23] mentioned that PZT films developed a (111) or (100) texture if the

lower-temperature pyrolysis step was conducted at 350°C or 420°C respectively. In another systematic investigation from the same group, Brooks *et al* [24] suggested that on low-temperature pyrolysis (T=350°C), the X-ray detected amorphous PZT films first fully transformed into a metastable, oxygen-defect pyrochlore phase, nanocrystalline phase then fully and rapidly transformed to perovskite phase of PZT. Based on their experimental data, Brooks *et al* [24] further hypothesized that when the films were pyrolyzed at 420°C, the PZT films transformed into a stable pyrochlore phase, which slowed down the transformation of this phase into perovskite. They suggested the (100) orientation was observed owing to suppression of the (111) orientation and because (100) is an energetically favored growth direction. In another study on the PZT thin film, Liu *et al* [25] reported that (111) texture was observed when the films were pyrolysis at 300 °C and then 400 °C, however (100) texture was observed when films only pyrolysis at 300 °C. They suggested during the 400 °C step a layer of (111) perovskite seed nuclei develop at Pt substrate and film interface, which is not formed when the 400 °C step is excluded. However, Chen *et al* [26] reported that if the film held at 450 °C for 0.5 h, cooled, then rapidly heated to 700 °C and held for 0.5 h, a very strong (100) texture was obtained. After 450 °C pyrolysis only pyrochlore phase is detectable by XRD, thus pyrochlore-perovskite transformation, and the growth of (100) texture are all achieved at 700°C. If the 450 treatment is replaced by pyrolysis at 350 or no pyrolysis, followed by rapidly heating to 700 °C, then a (111) texture is observed. In this case, after pyrolysis at 350°C for 0.5h, the films were still mostly amorphous. They concluded that the (111) texture requires an initial seeding treatment associated with the formation of an intermediate (001) PbO and the (111) texture can be attributed to the formation of Pt<sub>5-7</sub>Pb in the PZT/Pt interface that provides lattice matching between PZT(111) and Pt<sub>5-7</sub>Pb(111). Further study verified that the transformation temperature of pyrochlore to perovskite is 550°C, above this temperature Pt<sub>5-7</sub>Pb directly nucleated (111) texture, and below this temperature Pt<sub>5-7</sub>Pb oxidizes to form (001) PbO which in turn can nucleated (100) PZT film. These reverse results may be attributed to the differences in starting materials of precursors. In the study of Chen *et al*, more complex organo-metallic compounds were utilized as starting materials.

Heating rate from room temperature to calcining temperature can also affects the orientation and

crystal phase of the ferroelectric film. A texture development of lanthanum modified lead titanate thin films obtained by chemical solution deposition on silicon-based substrates was studied by Ricote *et al* [27]. The experiments shown that a fiber type, mixed (100) and (001) preferential orientation, is obtained when high heating rates are used during crystallization. A TiO<sub>2</sub> thin film was prepared using sol-gel process by Ohga *et al* [28], who reported that rapid heating resulted in columnar rutile grains, whereas slow heating—at a rate of 10°–20

°C/min—caused equiaxed anatase grains to form. The effects of heating rate on densification of the TiO<sub>2</sub> film were also studied by Keddar *et al* [29,30]. Additionally, in a study of (Ba<sub>0.99</sub>Bi<sub>0.01</sub>)TiO<sub>3</sub> ferroelectric film deposited on the p-Si(111) substrate, He [31] suggested that the heating rate have obviously influence on microstructure of the thin films, the tetragonality (*c/a*) and *c*-preferred oriented columnar character of the films was increased with increasing heating rate from 15°C/min to 100°C/min. The ferroelectric Bi<sub>3.2</sub>Nd<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> thin films deposited on p-Si(100) substrates using metalorganic solution deposition process have been studied by He *et al* [32]. The BNT films with extremely different orientations were achieved by using different annealing schedules. The *a*-axis and *c*-oriented films can be achieved using preannealing and no preannealing followed by rapid thermal annealing respectively, the orientation degrees can be increased with increasing the annealing time and annealing temperature respectively. Similarly, Bi<sub>3.2</sub>Nd<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> and Bi<sub>3.2</sub>Y<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> thin films deposited on p-Si(100) substrates also studied [15,16]. Two films showed similar annealing effects on the orientations. The changes in orientation degrees with annealing time and annealing temperature were only different with the BNT films. The *c*-axis oriented columnar BNT and BLT films resulted from rapid thermal annealing without preannealing can be explained as follow. During rapid heating, the films were bulk nucleated throughout the film originating at film surface. In this nucleation process, a columnar nuclei perpendicular to substrate surface was formed in the film and became original site of epitaxial overgrowth and resulted in formation of the *c*-oriented columnar film in the process of crystallization. At lower annealing temperature, columnar nuclei and its effect were weak and resulted in less *c*-orientation degree, which increased with annealing temperature. When the films were preannealed at lower temperature 400°C, the nuclei produced in the films were not similar column as formed in rapid heating process, thus resulted in formation of the platelike *a*-preferred orientation films.

The crystallization atmosphere dependences of the crystallization and microstructure of the ferroelectric film also appear in some literatures. Hirano *et al* [11] reported that calcination of precursor films in a H<sub>2</sub>O-O<sub>2</sub> gas mixture was found to be effective not only for low-temperature crystallization of perovskite PZT deposited on different substrates, but also for obtaining the preferred orientation of PZT films. While the film calcined in O<sub>2</sub> gas, they did not shown preferred orientation of PZT films. Authors believed that H<sub>2</sub>O-O<sub>2</sub> gas mixture can effectively remove the carbonate generated during calcination, as reported in the low-temperature synthesis of LiNbO<sub>3</sub> powders [33], water vapor promotes the condensation reaction of the terminated alkoxy group in the precursors, leading to the crystallization of single-phase-oriented perovskite on the MgO and Pt/Ti/SiO<sub>2</sub>/Si substrates. Additionally, a Bi<sub>3.15</sub>Nd<sub>0.85</sub>Ti<sub>3</sub>O<sub>12</sub> ferroelectric films have been deposited on Pt/Ti/SiO<sub>2</sub>/Si substrate by a sol-gel process and

crystallized in nitrogen, air and oxygen environments, respectively, by Hou *et al* [34], who reported that the crystallization environments is important in determining the crystallization and ferroelectric properties of the BNT thin films. The film crystallized in nitrogen at relatively low temperature of 650 °C, and exhibits excellent crystallinity and ferroelectricity. While the films annealed in air and oxygen, they did not show good crystallinity and ferroelectricity until they were annealed at 710 °C and 730°C respectively.

#### 2. 4. Film thickness

Thickness dependence of the microstructure of ferroelectric thin film can also been seen in some literatures. In the literature on TiO<sub>2</sub> thin film prepared using sol-gel process, Ohga *et al* [28] also mentioned that repeated deposition resulted in columnar grains and rutile structure except for the effects of the heating rate. They believed that the tendency of the thicker film to crystallize as rutile during rapid heating was attributed to the rapid grain growth of fine anatase grains. In the literature of Bi<sub>3.2</sub>La<sub>0.8</sub>Ti<sub>3</sub>O<sub>12</sub> ferroelectric thin films prepared on p-Si(100) substrates using metalorganic solution deposition process, authors<sup>[16]</sup> reported that the (200)-orientation degree ( $I_{(200)}/I_{(117)}$ ) of BLT films obtained by preannealing at 400 °C were increased from 5.70 to 35.71 with increasing thickness from 5 layers to 10 layers. When the preannealing is not carried out, the (008) orientation was only achieved in the 10 layers film prepared by rapid thermal annealing, (002)-orientation was obtained in 5 layers film. Further study [35] shown that high content of citric acid in the precursor solution enhanced the evolution of the (200) orientation of the BLT films with same repeated depositions. Authors assumed that the thicker films, produced by repeated deposition or high content of citric acid increasing the viscosity of the solution, can provided more matrix for growth of the *a*-oriented BLT film along the direction perpendicular to the p-Si (100) substrate surface when the preannealing is carried out. In the condition of no preannealing, the crystallization is controlled by substrate and columnar nuclei perpendicular to substrate surface formed by rapid thermal annealing. The columnar nuclei has dominant effect that resulted in the formation of the (008)-oriented BLT film in the thicker film, but the p-Si(100) substrate has dominant effect that resulted in the formation of the (200)-oriented BLT film in the thinner film.

#### 3. Summary

Through manipulation of processing conditions, it was possible to exert a significant influence over the microstructure and orientation of perovskite thin films. It is obvious that comprehensive utilization of the various processing dependences is very essential to fabricate the thin films with a reasonable orientation and excellent

ferroelectric properties. Of course, the processing dependence may exhibit some difference between various kinds of the thin films, some new processing effect would remain to be found out. Thus further detailed investigation is necessary for preparation of any specific perovskite films.

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