

Hydrothermal epitaxial growth of perovskite films

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The hydrothermal growth of heteroepitaxial perovskite films, as reviewed for BaTiO₃, Pb(Zr,Ti)O₃ and K(Nb,Ta)O₃, on single crystal perovskite substrates occurs by the island mode of growth is affected by solution chemistry. Films can be synthesized at temperatures as low as 90°C. Islands, nucleated on the ledges, grow and coalesce. Coalescence of slightly misoriented grains (mosaic blocks) produce threading dislocations at the interface where they meet. As for most epitaxial processes, dislocations are also observed at the interface due the lattice misfit of the substrate and film structures. The aqueous solution chemistry effects interfacial chemistry, *e.g.*, via specific adsorbing ions, confirmed by adsorption measurements, and plays an important role in controlling film faceting. Protons are incorporated during synthesis; cation vacancies occur to charge balance the protons. The point and line defects can be removed by heating; the point defects degrade the dielectric properties.

Key words: Perovskites, epitaxy, hydrothermal.

Introduction

Materials with the perovskite and perovskite type structures, have properties that includes high dielectric constant, ferroelectricity, superconductivity, etc that are important in electronics. Epitaxial thin films required for electronic devices have predominantly been prepared by ultra-high vacuum (UHV) vapor phase methods (*e.g.* pulsed laser deposition, metal-organic chemical vapor deposition, and sputtering) [1]. Economic reasons drive the interest in replacing vapor phase methods with chemical solution routes that include the deposition of precursor molecules that decompose to inorganic materials during heating and the direct solution synthesis routes emphasized here to grow epitaxial thin films at low temperatures [2]. Hydrothermal synthesis has been widely used to synthesize powders. It is a technique that involves the growth of oxides (and several important sulfides) directly from aqueous solutions, generally at temperatures between 50°C and 400°C [3-5]. Hydrothermal epitaxy, under high pressure and temperature, was first used to explore metal oxide ferromagnetic materials intended for bubble memory device applications [5]. Hydrothermal epitaxy was also demonstrated for CdS on InP substrates [6]. This review will only describe recent discoveries concerning the epitaxial growth of BaTiO₃ [7-12], Pb(Zr,Ti)O₃ [13, 14], KNbO₃ [15, 16], and KTaO₃ [17, 18] which are synthesized from reactants at high concentrations of

OH⁻. Specifically, the review will discuss the epitaxy phenomenon, the effect on specifically adsorbing ions, and the incorporation of protons within the synthesized structure.

The Epitaxy Phenomena

The epitaxy of BaTiO₃ on SrTiO₃ single crystal substrates at temperatures as low as 90°C and at ambient pressures [7] have led to the greatest understanding of features controlling epitaxial growth. It is obvious that the material to be synthesized must be the stable phase under the hydrothermal conditions used for epitaxy. For the perovskites listed above, these conditions are generally at high OH⁻ molarity. Phase equilibrium calculations for the Ti-Ba-H₂O system by Osseo-Asare *et al.* [19] indicate that close to room temperature, BaTiO₃ is the thermodynamically favored phase at pH > 12 and high (2 M) concentrations of Ba²⁺. Aqueous solutions of BaOH is (the water is first boiled to reduce the CO₂) is reacted with a titania source with a high surface to volume ratio (*e.g.* anatase powder or a Ti-alkoxide that precipitates an amorphous titania colloid) [7]. Although TiO₂ is nearly insoluble in water, any solubilized species will quickly be removed from the solution when discovered by a Ba⁺⁺ ion that forms a molecule of BaTiO₃. Two soluble Ti species have been proposed. Both are based on the hydrolyzation of Ti, either as [Ti(OH)₆²⁻] [21] or [Ti(OH)₄] [22] and the subsequent reaction with Ba²⁺ ions to precipitate BaTiO₃ either as particles that can grow epitaxially on the TiO₂ particles and as oriented nuclei on a SrTiO₃ substrate. The reaction between BaOH and TiO₂ is generally complete within 24 hr at 150°C.

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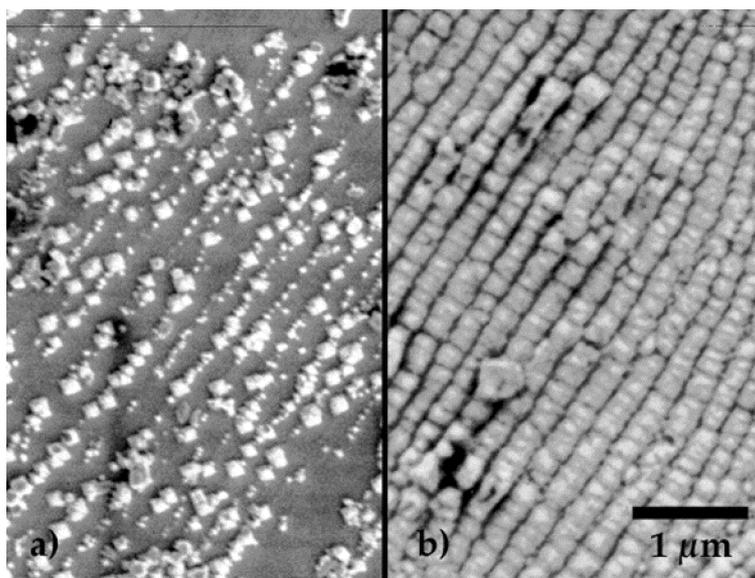


Fig. 1. SEM micrographs [1 h, 1 M Ba(OH)₂] showing (a) {111} faceted BaTiO₃ islands 50 to 100 nm in size forming along surface steps of the SrTiO₃ substrate followed by (b) coalescence to eventually form a film that covers the substrate [10].

Figure 1 illustrates the sequential growth of BaTiO₃ on a SrTiO₃ single crystal substrate. As shown, BaTiO₃ nuclei are first observed to nucleate on step edges on the substrate [10]. The shape of the nuclei depend on specifically adsorbing species. They have an octahedral (111 faces) shape when only BaOH is used as the source of OH⁻ ions. The use of other bases with BaOH (e.g., NaOH, KOH, and NMe₄OH) will produce cubic (100 faces) nuclei. The nuclei grow and eventually cover the substrate to form a 'single crystal' film composed of mosaic blocks, each formed from the initial nuclei, shown in Fig. 2a [8]. Dislocations observed at the interface, shown in Fig. 2b [8], accommodate much of the lattice mismatch between the BaTiO₃ and SrTiO₃. The structure of the BaTiO₃ films are not tetragonal, as expected, but cubic. Heat treatment is required to transform the structure to the tetragonal phase. It is uncertain if the cubic structure is caused by the size of the mosaic blocks, *i.e.*, nanocrystalline BaTiO₃ powder is not tetragonal at room temperature, or if defects, discussed below stabilize the

cubic structure. Studies to control the size of the mosaic blocks though the number of nuclei per unit area have not been carried out. But the synthesis of (Ba,Sr)TiO₃ and (Ba,Pb)TiO₃ solid-solutions have been demonstrated with mixed precursors (BaOH + SrOH); the (Ba,Pb)TiO₃ solid-solutions can have the tetragonal structure.

During the growth of BaTiO₃, it is known that Ba⁺⁺ ions specifically adsorb onto the surface of the SrTiO₃. Zeta potential measurements for SrTiO₃ powder as a function of the Ba⁺⁺ concentration show that the isoelectric point (pH where surface is electrically neutral) shifts to higher and higher values with increasing Ba⁺⁺ concentration, until the isoelectric point can no longer be measured. The reason for this is that B⁺⁺ is attracted to negative surface sites and specifically adsorbs on the surface. Its double, positive charge compensates only one negative site, and thus causes the site to become positive. As more Ba⁺⁺ is adsorbed, the surface charge changed from negative to positive. Thus, during epitaxy, the surface is always covered with a monolayer of Ba⁺⁺

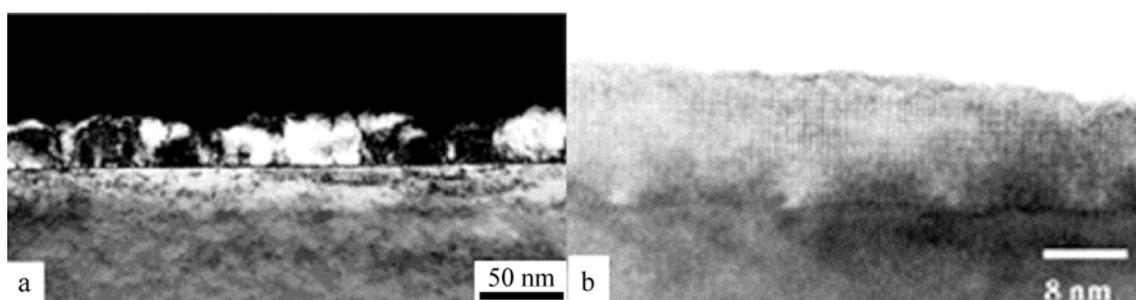


Fig. 2. (a) Microstructure of BaTiO₃ film consists of small mosaic blocks with slightly different orientation relative to one another as shown by this dark field TEM image. Threading dislocations from boundaries between the blocks. (b) Higher resolution of same film showing dislocations at interface to accommodate the differential lattice mismatch between the BaTiO₃ film and the SrTiO₃ substrate [10].

ions. High resolution TEM observations suggest that this layer is present during the initial island formation [8]. The effect of the specific adsorption of Ba^{++} is not understood, except it must be 'pushed' away as the BaTiO_3 is added to cause film growth and particle growth [7].

$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ and PbZrO_3 epitaxial thin films have been produced in an aqueous solution (10 M KOH) at ambient pressure and low temperatures (90–150°C) on (001) SrTiO_3 and LaAlO_3 single crystal substrates with $\text{Pb}(\text{NO}_3)_2$ and ZrOCl precursors in CO_2 free water [13, 14]. Growth of the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ and PbZrO_3 thin films initiates by the formation of {100} faceted islands which grow together to produce thin films with very smooth surfaces. EDS analysis of the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin film shows that the Zr : Ti ratio is nearly identical to the molar ratio of the precursors. NMR studies show that potassium is incorporated into the structure during synthesis.

Epitaxial KNbO_3 thin films [15] were hydrothermally grown on single crystal SrTiO_3 substrates at 125–200 °C in 15 M KOH solutions containing pre-dissolved Nb_2O_5 (0.0015 M). Solution ^{93}Nb NMR spectroscopy studies showed that the Nb_2O_5 precursor powder fully dissolved to form a hexaniobate ion that eventually reacted with the K^+ ion to form the perovskite phase. The orthorhombic KNbO_3 film had two, (110) and (001), out-of-plane orientations. Both orientations have a small mismatch with the substrate and the orthorhombic structure is the stable phase at the growth temperature. Epitaxy imitates with the nucleation of islands. During an initial period, the island grow and coalesce to form a blocky, but relatively flat film. Tower-like structures, each containing a central screw dislocation start to grow to cover the film after the initial period.

Like-wise, epitaxial KTaO_3 thin films [17] were synthesized by the hydrothermal method below 175°C in highly alkaline aqueous KOH solutions. KTaO_3 films formed in 7 M KOH solutions contained a defect pyrochlore phase that had two, (400) and (111), out-of-plane orientations. The (400) oriented pyrochlore phase was epitaxially related to the SrTiO_3 substrate while the (111) oriented pyrochlore phase had four in-plane variants. No intermediate pyrochlore phase was formed for synthesis at 15 M KOH, that is, pyrochlore-free KTaO_3 films could be grown. Pyrochlore-free films were also grown at 7 M KOH by delaying the introduction of the SrTiO_3 substrate into the synthesis solution until the conditions to nucleate the pyrochlore phase had dissipated.

In addition to the direct synthesis routes reviewed above, electrodeposition has been used to epitaxially growth BaTiO_3 thin films on SrTiO_3 single crystal substrates with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) conducting, epitaxial buffer layers [20]. The epitaxial films appear to consist of very small (≤ 10 nm) particles that are attracted to

LSMO surface. The film, composed of nano-meter size particles, completely covered the substrate when the reaction was performed at temperatures between 60 and 90°C with LSMO potential of -0.5 to -1.0 volts against a Pt counter electrode. It appeared that an electrophoretic force, acting on BaTiO_3 nuclei within the solution, facilitated the deposition of the film.

Protons Incorporated During Synthesis

Protons are incorporated during the synthesis of all of the perovskite discussed above. The presence of the proton in the lattice has been clearly established by FTIR and NMR spectroscopy [12]. The protons are interstitial defects incorporated within the electron cloud of an oxygen ion. The size of the OH^- ion within the structure is not too different that the size of the oxygen ion. Cation vacancies are needed to balance the charge introduced by the proton. In reality, the proton and the required vacancies are part of an equilibrium chemical composition, which depends on the OH^- concentration within the aqueous media, the temperature and pressure. As expected, the protons adversely affect the dielectric properties of the perovskites.

The protons are removed from the structure by heating. Mass spectroscopy combined with TGA measurements show that water is the product of heating. Proton removal requires charge compensation within the structure, *i.e.*, an electron has to be removed from the structure for every proton. Although the removal of the electron could be accomplished by the change of the valance of the B ion in the ABO_3 perovskite structure (*e.g.*, the oxidation of Ti^{+3} to Ti^{+4} in the BaTiO_3 material) and cation ion diffusion is not expected at the lower temperatures (>200°C), most investigator believe that an oxygen ion is removed from the structure for every two protons *via* the reaction:



Thus, one oxygen vacancy is created for every two protons and one oxygen removed from the structure in the form of a water molecule.

Although the diffusion of interstitial hydrogen via the hopping from one oxygen to another is expected to be rapid relative to the diffusion of oxygen, the question of how oxygen concurrently diffuses with the protons has been a point of concern. That is, diffusion of oxygen requires oxygen vacancies. Goh *et al.* [16] have recently suggested that the proton and oxygen diffusion initiates at the surface and proceeds inwardly with time. In this manner, oxygen vacancies are first created at and near the surface as water is removed from the structure: the concentration of vacancies moves inwardly with time, analogous to a drying front within a powder compact. No pre-existing oxygen vacancies are required with this hypothesis, namely, the are only

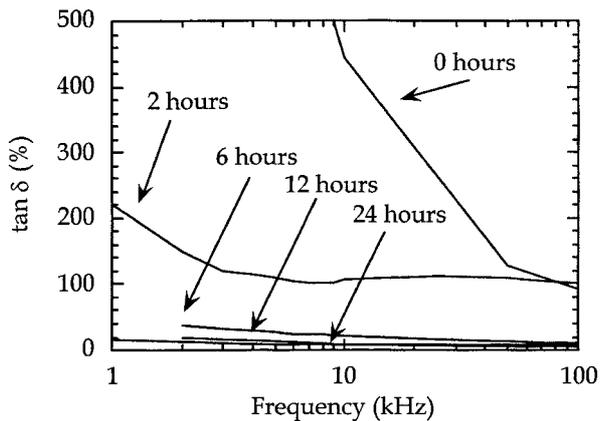


Fig. 3. Loss tangent versus frequency as a function of time heat treated at 300°C for Ag-BaTiO₃-SrRuO₃-SrTiO₃ capacitor, where the BaTiO₃ film was hydrothermally synthesized as an epitaxial layer on the buffered layer, SrRuO₃-SrTiO₃ substrate [11].

created as water is removed from the structure as interstitial protons and the oxygen required to maintain charge balance within the structure.

To understand the effect of the protons on properties, the dielectric constant and loss tangent measurements [12] of an epitaxial BaTiO₃ thin film prepared by the hydrothermal method described above was determined after various heat treatments. For this study, the epitaxial film was synthesized on a special SrTiO₃ containing an epitaxial SrRuO₃ layer that acted as a bottom electrode. A layer of Ag was deposited on top of the epitaxial BaTiO₃ layer so that a Ag-BaTiO₃-SrRuO₃-SrTiO₃ capacitor was fabricated to measure dielectric properties in a frequency range of 1 to 100 kHz at 0.01 V_{RMS}.

The initial as-synthesized BaTiO₃ film displayed a dielectric constant of 450 with very high losses ($\tan \delta \sim 100\%$) at 10 kHz. One hour heat treatments at 200°C initially resulted in a significant decrease in dielectric constant and an increase in dielectric loss followed by a marked decrease in dielectric loss and recovery of dielectric constant at 400–600°C. The initial high dielectric loss, which subsequently decreases with time and temperature, can be attributed to migration losses due to incorporated OH⁻ and H₂O that are removed by heat treatment. As shown in Fig. 3, heat treatment at moderate temperatures (300°C) and for longer times (12–24 h) causes $\tan \delta$ to decrease to ~8% at 10 kHz. Further improvements in loss tangent could not be attained by heat treating for longer periods at 300°C. FTIR analysis showed that water was lost occurred from powders (prepared with the films) during the heat treatments used for property measurements.

TGA experiments performed on BaTiO₃ powders were performed to quantify the extent of weight loss due to ‘surface adsorbed’ H₂O and structural OH⁻ at various heat treatment temperatures and to determine the rate of weight loss. The amount of ‘surface adsorbed’ H₂O was inferred by measuring the weight changes during

both heating and cooling. It was discovered that protons and oxygen were lost *via* the above equation during heating to 800°C, but during cooling, weight was regained. It was assumed that regained weight was due to surface adsorption of water. Calculation, based on only the unrecoverable weight lost, suggested that a proton was associated with approximately 1 of every 4 oxygen ions within the structure, *i.e.*, about one OH⁻ substitutes of every four O²⁻ ions. An equivalent number of cation vacancies would have to exist to charge compensate for the protons [23].

Similar TGA and FTIR experiments were performed on KNbO₃ powders; mass spectroscopy was also performed to confirm that the weight loss was due to the evolution of water per the above equation [16, 18]. After taking the recoverable weight loss into account, the KNbO₃ powders synthesized in 6.7 M KOH had an unrecoverable weight loss of 0.54 wt% while the 15 M KOH powder had an unrecoverable weight loss of 0.94 wt%. For the powders synthesized in 6.7 M KOH, EDS revealed a K/Ta ratio of 0.96, indicating that 8% of the potassium sites and 1% of the niobium sites are vacant to charge compensation the approximately protons associated with approximately 4% of the oxygen ions within the structure. For the 15 M KOH powder, similar data suggested that approximately 6% of the oxygen ions have an adjacent proton in the as-synthesized structure. For this powder EDS measurements resulted in a K/Ta ratio of 0.94; 9% of the potassium sites and 2% of the niobium sites are vacant as the 15 M KOH powder. That is, the 15 M KOH powder had a greater defect density relative to the 6.7 M KOH powder.

Concluding Remarks

Epitaxial films of many important perovskites can be prepared *via* a low temperature hydrothermal method. The films are formed via the nucleation of ‘islands’ and their coalescence during growth. The number of islands, and thus the number of threading dislocations per unit area due to the grain boundaries formed by island impingement, will depend on the number of nuclei formed per unit area. The defects can not be removed unless the films are heated to much higher temperatures. Studies relating nuclei density to hydrothermal conditions are needed.

Although epitaxial films can be prepared at very low temperatures (*e.g.* below the temperature of boiling water) relative to other methods, interstitial protons are naturally incorporated during synthesis. Cation vacancies must also be incorporated during synthesis to charge compensate the protons. The incorporation of both cation vacancies and interstitial protons are unwanted for most electronic applications, other than proton conduction. It can only be concluded that the defect structure is an equilibrium composition at high basic synthesis conditions. Thus, although processing

can be carried out near room temperature, elimination of the protons requires subsequent high temperature processing.

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