

# Nucleation and Inhibition Control during the Hydrothermal–Electrochemical Growth of Barium Titanate Films

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The control of the microstructure of  $BaTiO_3$  films grown on titanium by the hydrothermal–electrochemical method was investigated. Experiments were conducted in a three-electrode high-pressure electrochemical cell in a  $0.1M Ba(OH)_2$  electrolyte at 150°C. Results showed that the spontaneous initial nucleation linked to pure hydrothermal  $BaTiO_3$  formation can be inhibited by cathodically protecting the titanium electrode from the moment it is immersed in the electrolyte. The application of initial nucleation pulses of varying cathodic potentials affected the grain size of the deposit. It is suggested that the formation of a titanium oxide layer is a necessary step previous to the nucleation of  $BaTiO_3$ .

# I. Introduction

THE hydrothermal, electrochemical, and hydrothermal-electro-The hydrothermal, electrochemical, and hydrotherma ates,<sup>1,2</sup> zirconates,<sup>3</sup> tungstates,<sup>4</sup> and molybdates<sup>5</sup> is a field of increasing interest because of the comparatively low temperature needed for the synthesis of these polycrystalline films. The hydrothermal and/or electrochemical treatment of a metallic substrate immersed in a strongly alkaline solution (pH >12) of alkaline-earth ions leads to a well-adhered stoichiometric thin film. This low-temperature route was developed by Yoshimura and co-workers at the Tokyo Institute of Technology for the preparation of BaTiO<sub>3</sub> layers, achieved by the immersion of a titanium substrate in a Ba(OH)<sub>2</sub> solution at 100°–200°C, in open circuit or under anodic conditions.<sup>2</sup> This led to the formation of films  $\sim 100$ nm thick in the cubic paraelectric phase, although the stable phase at room temperature is the tetragonal one. Cho et al. reported the hydrothermal preparation of ferroelectric, tetragonal BaTiO<sub>3</sub> films at 220°C using 24 h treatments in 2N Ba(OH)<sub>2</sub>.<sup>6</sup>

Until now most of the work in this area has focused on the synthesis of more complex materials, the improvement of their electrical properties, and their technological applications. Recent developments have been the growth of high-resistivity ( $10^{12}$   $\Omega$ ·cm) BaTiO<sub>3</sub> films on silicon by annealing the wet-synthesized

films in oxygen at 300°C,<sup>7</sup> and the patterning of 10  $\mu$ m microstructures of BaTiO<sub>3</sub> on platinum-coated silicon.

Although a growth mechanism for BaTiO<sub>3</sub> was proposed early on,<sup>1</sup> the detailed growth kinetics have not yet been fully understood. Ishizawa et al. found a multilayer structure in the electrochemical-hydrothermal films, with an anatase layer forming between the metallic titanium substrate and the BaTiO<sub>3</sub> film. They proposed that the titanium oxide acts as a precursor for the BaTiO<sub>3</sub> film formation, a process in which the barium ions would have to diffuse through the oxide against the electric field. In fact, it has also been demonstrated that BaTiO<sub>3</sub> films can grow hydrothermally on TiO<sub>2</sub> single crystals.<sup>8</sup> The use of tracers for the diffusion study showed that the predominating diffusing species is the barium ion along with oxygen.9 However, preliminary results in the Ba(Ti,Zr)O<sub>3</sub> system suggest that the motion of the transitionmetal ions can also be important.<sup>10</sup> Water also incorporates during the BaTiO<sub>3</sub> film formation, as is evidenced from the thermal desorption measurements under vacuum, which indicate vapor desorption between 200° and 400°C.<sup>11</sup> Water removal after the film has been fabricated modifies the electric properties of the BaTiO<sub>3</sub> films, as shown by Kajiyoshi et al., who reported an increase in resistivity after annealing at 300°C.

Electrochemical measurements have indicated that the  $BaTiO_3$  film formation is initially controlled by charge transfer related to the oxidation of titanium, and later on by mass transfer.<sup>12</sup> Electrochemical studies have also indicated that during the hydrothermal formation of  $BaTiO_3$  a potential is induced on the titanium, varying between -100 and -140 mV versus Ag/AgCl (25°C) during the film growth. This potential corresponds to a corrosion potential and is induced by the concurrence of both an anodic reaction, the oxidation of titanium, and a cathodic reaction, the reduction of water. These results suggest that by electrochemically controlling the potential of titanium, it is possible to control the film growth rate if desired and even to inhibit its growth completely. Then, with this approach, it would be possible to control the deposit morphology.

In the present work we report the application of controlled potential techniques to the hydrothermal growth of  $BaTiO_3$  films on titanium. This procedure enabled the inhibition of pure hydrothermal growth as well as the control of nucleation and grain size in films formed under anodic conditions.

### **II. Experimental Procedure**

The experiments were performed in a three-electrode highpressure electrochemical cell of 200 cm<sup>3</sup> (Cortest, Inc.). The working electrode was a  $10 \times 15 \text{ mm}^2$  titanium sheet (99.7%,

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Johnson Matthey) polished with 50 nm alumina powder, and the counterelectrode was a 4 cm<sup>2</sup> platinum foil (99.7%). An external reference electrode of saturated Ag/AgCl at 25°C was connected through a conductivity bridge as described elsewhere.<sup>12</sup> All potentials in the text below are referred to the saturated Ag/AgCl at 25°C. The electrodes were connected to a potentiostat/galvanostat (EG&G PAR 273A). All experiments were performed with 0.1 and 0.2*M* Ba(OH)<sub>2</sub> solutions (Fluka, >98% purity). The solutions were prepared with deionized water previously boiled to eliminate dissolved CO<sub>2</sub>. The working temperature was 150°C in all cases.

Two types of experiments were conducted, one type dealing with cathodic protection and the second type focused on the microstructure control using controlled potential techniques. The films were characterized using X-ray diffraction (XRD, Siemens Model D 5000), X-ray photoelectron spectroscopy (XPS, Physical Electronics System Model 1257), and scanning electron microscopy (SEM, JEOL Model J8M-25-S2).

# III. Results

XRD measurements were possible only on the thickest films, leading to diffractograms similar to those already reported in Ref. 12 and showing that they consisted of cubic  $BaTiO_3$ .

# (1) Inhibition of Hydrothermal Growth by Cathodic Protection

Hydrothermal–electrochemical experiments normally incorporate an initial purely hydrothermal step due to the reactions that occur during the heating period that cannot be avoided. In the present experiments it was possible to avoid this effect by immersing the titanium working electrode in the electrolyte only when the working temperature was reached. In addition, the titanium electrodes were immersed, subjected to a small cathodic protective current, immediately followed by a cathodic potential ranging from -250 to -500 mV versus Ag/AgCl during 30 s.

Figure 1 shows the time evolution of the net cathodic current obtained during the protection step at different potentials for treatments in a 0.1M Ba(OH)<sub>2</sub> solution. The influence of these potentials on the inhibition of BaTiO<sub>3</sub> growth was assessed by the degree of barium incorporation into the titanium substrate, monitored through XPS by recording the dominant Ba 3d5/2, O 1s, and Ti 2p photoelectron signals. Table I shows the relative surface concentrations of barium, oxygen, and titanium, estimated from the XPS peak heights using available sensitivity factors.<sup>13</sup> The values in the table are compared with those of a commercial BaTiO<sub>3</sub> single crystal that was used as a stoichiometric reference.

Figure 2 shows the XPS spectra for the samples protected with -300 and -500 mV. After the surface was cleaned by sputtering the samples with 4 keV Ar ions with doses of 0.25 mC/cm<sup>2</sup>, all of the samples showed some degree of barium incorporation. However, the sample protected with -500 mV showed a Ba content



Fig. 1. Current density during the application of cathodic protection on a Ti metal substrate immersed in 0.1M Ba(OH)<sub>2</sub> at 150°C.

 
 Table I.
 Atomic Concentrations in Samples Protected under Different Conditions

Sample and protection procedure <sup>†</sup>	Concn (at.%)		
	Ba	0	Ti
Ti, -250 mV, 30 s	14	65	21
Ti, -300 mV, 30 s	16	63	21
Ti, -400 mV, 30 s	15	63	22
Ti, -500 mV, 30 s	5	72	23
BaTiO <sub>3</sub> single crystal	16	63	21

 $^{\dagger}\text{All}$  measurements were performed after cleaning the sample with 4 keV argon ions.



**Fig. 2.** XPS spectra recorded after 0.25 mC/cm<sup>2</sup> erosion doses. Sample protected with (a) -300 mV and (b) -500 mV, both for 30 s at  $T = 150^{\circ}\text{C}$  and  $[\text{Ba}^{2+}] = 0.1M$ .

considerably lower than that of the others, with a value far below that observed in stoichiometric  $BaTiO_3$ .

The depth distribution of barium in the electrode was determined by XPS depth profiling. Figure 3 represents the profiles of the -300 and the -500 mV samples. The elemental concentrations are expressed as atomic percent, as calculated from the peak height intensity. Barium exhibited a deep penetration in the -300mV sample and a shallow one in the -500 mV one. In the latter sample, a direct correlation was observed between oxygen and barium, and also an inverse correlation between oxygen and titanium. This is consistent with the results reported by Kajiyoshi *et al.*, where the barium and oxygen were shown to diffuse together.<sup>9</sup>

Cathodic protection also has an effect on the morphology of the hydrothermally grown deposit. The SEM micrograph in Fig. 4(a)



Fig. 3. XPS depth profile showing the elemental depth distribution in samples protected with either -300 or -500 mV.



**Fig. 4.** SEM micrographs of samples grown: (a) in  $0.1M \operatorname{Ba(OH)}_2$  at 150°C without cathodic inhibition (pure hydrothermal growth), (b) under cathodic inhibition of -300 mV for 30 s, showing partial inhibition of growth, and (c) under -500 mV for 30 s, leading to complete inhibition of growth. The bar indicates 1  $\mu$ m.

shows the typical morphology of a BaTiO<sub>3</sub> film hydrothermally formed when the titanium electrode is left in open circuit in the Ba(OH)<sub>2</sub> solution. If the titanium electrode is immersed with a -3 mA × cm<sup>-2</sup> cathodic protective current density for 3 s, and it is then held at a potential of -300 mV versus Ag/AgCl for 30 s at 150°C, the formation of BaTiO<sub>3</sub> nuclei is partially inhibited in some regions of the surface, as shown in Fig. 4(b). A higher degree

# (2) Influence of Nucleation Pulses on the Microstructure

The formation of an electrodeposit starts with the nucleation and growth of isolated nuclei, which then coalesce into a continuous film. The rate of nuclei formation  $J_o$  depends on the overpotential  $\eta$  through:

$$J = J_0 \exp(-K/\eta^2)$$

where  $J_0$  and K are constants.<sup>14</sup> The number of nuclei increases with time until a final saturation density is reached. The final nuclei density also depends on the initial overpotential; the larger the overpotential is, the higher the nuclei density obtained.<sup>15</sup>

In BaTiO<sub>3</sub> hydrothermal film growth, nuclei formation and growth occur at the potential which is spontaneously established on the titanium electrode, which, according to the mixed potential theory, is determined by the kinetics of the cathodic and anodic reactions.<sup>12</sup> This potential evolves during the hydrothermal growth in values ranging between -140 and -130 mV versus Ag/AgCl. See for instance Fig. 5, which shows the evolution of the rest potential of a Ti electrode immersed in 0.2*M* Ba(OH)<sub>2</sub> at 150°C.

It has been shown that an adequate control of the initial nuclei density number with potentiostatic techniques can strongly modify the morphology of an electrodeposit.<sup>16</sup> Therefore, it is appealing in the present case to evaluate the influence of the initial nucleation potential on the morphology of the formed film. The abovereported experiments showed that the application of potentials cathodic to the rest potential can result in the inhibition or severe decrease of the number of formed nuclei. In the experiment reported here we examined the influence of increasing the nuclei number through the application of potentials more anodic than the rest potential. The following procedure was applied:

During the heating period the titanium electrode was maintained outside of the solution. When the working temperature of 150°C was reached, the electrode was immersed and simultaneously protected with a cathodic current density of 2 mA/cm<sup>2</sup>. Afterward two procedures were used:

(a) The sample was left in open circuit for 4 h so that pure hydrothermal growth would occur.

(b) A nucleation pulse of +500 mV was applied for 4 s and then the sample was left in open circuit, so that pure hydrothermal growth occurred during another 4 h.

The influence of the nucleation pulse on the film microstructure was evaluated from the SEM observations. The surface morphologies obtained on the BaTiO<sub>3</sub> films are shown in Fig. 6. These



Fig. 5. Measurement of the rest potential at  $150^{\circ}$ C. The sample was directly immersed in the solution of 0.2M Ba(OH)<sub>2</sub>.



**Fig. 6.** SEM micrographs of films grown at  $T = 150^{\circ}$ C in 0.1*M* Ba<sup>2+</sup>: (a) without initial pulse, hydrothermal for 4 h; (b) under a nucleation pulse of +500 mV for 4 s, and then open circuit for 4 h. The bar indicates 1  $\mu$ m.

results show that the application of an initial overpotential pulse results in films with smaller grains and a more evenly distributed grain size than those obtained in the pure hydrothermal case. This is because the formation of a larger number of initial nuclei provides more growth sites, which results in a more homogeneous grain size distribution of the BaTiO<sub>3</sub> on the titanium electrode surface. This behavior is consistent with results obtained after the application of an initial nucleation pulse in the formation of metal electrodeposits.

### IV. Discussion

Inhibition of BaTiO<sub>3</sub> growth under hydrothermal conditions can be reached when the titanium cathode is protected with potentials below -500 mV. Our results suggest that BaTiO<sub>3</sub> film inhibition is a consequence of the inhibition of the surface oxidation of titanium, which in turn reduces the available titanium oxide film, a necessary precursor for hydrothermal BaTiO<sub>3</sub> film growth. This is an independent confirmation of the mechanism proposed by Ishizawa et al. in which the titanium oxide film precedes the BaTiO<sub>3</sub> formation.<sup>17</sup>

The results regarding the application of nucleation pulses indicate that the initial pulse sharply increased the number of BaTiO<sub>3</sub> nuclei initially formed. This arises from the fact that in this system an increase in the anodic potential is linked to a larger supersaturation of oxygen anions, which in an electrochemical system is proportional to the overpotential  $\eta = E - E_{oc}$ , where E is the applied potential and  $E_{oc}$  the open circuit potential. This supersaturation would induce the formation of a large number of nuclei, which therefore do not reach larger sizes because to grow they must compete for a limited supply of ions from the solution. On the other hand, pure hydrothermal growth, without the initial pulse, can be associated with an initially low nuclei density. In this case the formation of a continuous BaTiO<sub>3</sub> film requires larger lateral growth of the individual initial nuclei, which occurs simultaneously with nucleation of new islands, resulting in a more uneven nuclei size distribution.

### V. Conclusions

The growth of BaTiO<sub>3</sub> films on Ti in Ba(OH)<sub>2</sub> solutions under controlled potentials in hydrothermal conditions enables the modification of the film microstructure. It is possible to inhibit the spontaneous hydrothermal BaTiO<sub>3</sub> formation if the titanium electrode is protected with a suitable cathodic potential. The threshold cathodic potential for inhibition at 150°C in 0.1M Ba(OH)<sub>2</sub> solutions is approximately -500 mV. On the other hand, the application of initial anodic potential pulses triggers the nuclei formation, resulting in the growth of BaTiO<sub>3</sub> films with smaller grain sizes and a more even morphology than in the pure hydrothermal case.

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