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Hydrothermal-Electrochemical Formation of BaTiO, Films: Electrochemical Characterization of the Early Stages of Growth

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The formation mechanism of BaTiO, films produced by a hydrothermal-electrochemical method was characterized using electrochemical techniques. Experiments were conducted in a three-electrode electrochemical cell, with titanium foil as the working electrode and Ag/AgCl as the reference electrode, in a $0.25M$ Ba(OH)$_2$ solution at 150°C. Hvdrothermal-electrochemical BaTiO, film formation is initially controlled bv charge transfer related to the rate of electrochemical oxidation of titanium. The process later becomes mass transfer controlled, presumably related to the diffusion of Ba^{2+} ions across the built-up $BaTiO_3$ film. A relation between the mechanism of formation of BaTiO, films under both the hydrothermal-electrochemical and the pure hydrothermal methods was established.

I. Introduction

BARIUM TITANATE films are desired in the electronics industry because of their device applications.[1],[2] They are prepared by several techniques, like rf sputtering,[3] vacuum evaporation,[4] laser ablation,[5] chemical vapor deposition,[6] metalorganic decomposition,[7] and sol–gel.[8] All of these procedures require at some stage during the process a high-temperature deposition or h-eatment after deposition that can cause cracking, due to the different thermal expansion coefficients of the substrate and the film, or undesired film/substrate reactions due to enhanced diffusion at those temperatures.

The hydrothermal–electrochemical procedure is an alternative low-temperature route which enable\ the synthesis of crystalline BaTiO, films *in situ* in the 55–200°C range. using simple equipment.[9]–[13] In this method BaTiO, films are produced on a titanium electrode which is anodired in the presence of an electrolyte containing Ba(OH)$_2$ under pressurized conditions. Recent results indicate that polycrystalline BaTiO, films can be prepared at temperatures as low as 55°C using electrochemical activation in a barium acetate electrolyte in an oxygen atmosphere.[9] This technique is very versatile and it has been used to prepare perovskite films of several materials, such as SrTiO,[11]–[14] CaTiO,[15] BaFeO,[11] LiNbO,[11] BaNbO,[15] and Ba$_2$Nb$_5$O,[15]

A closely related technique for film formation is the hydrothermal deposition method in which perovskite films are produced in similar conditions but without electrochemical activation. With this technique BaTiO,[10,16,17] SrTiO,[16] (Ba.Sr)-TiO,[17] and BaZrO,[17,18] films have been obtained.

The hydrothermal–electrochemical film formation technique is not yet well established and there is not much information on the electrochemical mechanism involved in the formation ol these films. Moreover. there is still not a clear understanding of the relationships between the film formation mechanisms for the hydrothermal method and those for the hydrothermal–electrochemical method. Most of the previous work on BaTiO, hydrothermal-electrochemical formation has been performed in two-electrode cells. titanium anode and platinum cathode. In such a system it is not possible to obtain accurate specific information on the electrochemical phenomena occurring at the titanium anode as the measured voltage drop on the cell is the result ol processes at the anode. cathode and in the electrolyte.

In the present study the experimental work was conducted in a conventional three-clcctrode cell. a system which includes ;ı reference electrode for monitoring specific phenomena related to the working electrode. Since such configuration allows the determination of both the cathodic and anodic potentials. this experimental setup enables the study of the mechanism of BaTiO, film formation under hydrothermal-electrochemical conditions, using electrochemical techniques. The emphasis of the present investigation is the determination of the growth mechanisms involved at the early stages of growth.

II. Experimental Procedure

Hydrothermal electrodeposition studies were carried out in the three-electrode hi&pressure clcctrochemical cell represented in Fig. 1(Cortest Inc.). The working electrode was a 1.3 cm² titanium flag made from a 0.025-mm-thick, 99.7%, titanium foil (Johnson Matthey. main impurities C. N. and 0). The counterelectrodr was a 4 cm² platinum foil.

The reference electrode was saturated Ag/AgCl. at 25°C. placed externally to the cell and electrically connected through a pressure-balanced bridge tilled with the electrolyte. Pressure balance was maintained by continuously pumping a small flow of electrolyte into the cell. at 4.72 mL/h, using a high-pressure micropump (ELDEX A-30-S-2). With this design the reference electrode was maintained at ambient temperature. but at system pressure. The Ag/AgCl electrode function5 in this manner in an acceptable way: the electrochemical potential of the Ag/AgCl electrode is constant for a given temperature and independent of pressure and oyxgen in solution. The electrochemical potential of the working electrode is fixed by the potentiostat with respect to the external Ag/AgCl reference clcctrode. This potential E. expressed as V vs Ag/AgCl(25°C), include3 in fact a junction potential arising from the difference in temperature and pressure between the electrolyte in the hydrothermal vessel and the electrolyte in the reference chamber. However. this junction potential is constant for a given working temperature and the experimental setup enables one to subject the titanium working electrode to constant or linearly sweeping potentials.
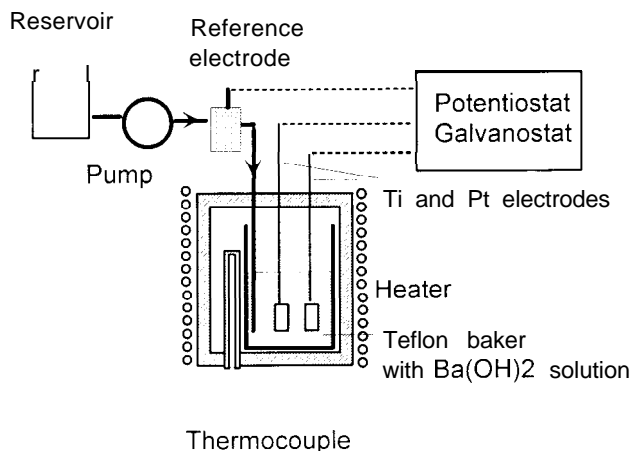
Fig. 1. Schematics of the experimental setup. including the electrochemical cell and key ancillary equipment.

The electrolyte was a nominal $0.25M$ $Ba(OH)_2$ solution at pH 1 I. prepared by dissolving $Ba(OH)_2 \cdot 8H_2O$ (Fluka 98%, main impurity Sr) in deionized water, and it was contained in a Teflon beaker. The water was boiled before the experiment to eliminate dissolved CO_2. Before each experiment the titanium electrode was ultrasonically cleaned with acetone and dried in air. The electrodes were connected to a potentiostat/galvanostat (EG&G Model 173) driven by a universal pro&rammer (EG&G). All experiments were conducted at 150°C. The pressure during the experiments was mainly fixed by the water vapor pressure at 150°C. approximately 5 bar. We believe that the driving force for the hydrothermal process is the temperature and not the pressure, but to our best knowledge no systematic test of this hypothesis has been performed.

The BaTiO, film formation process was characterized by using cyclic voltammetry and chronoamperometry. Several BaTiO, films were produced under potentiostatic conditions and their structure was examined by scanning electron microscopy (SEM). The barium incorporation into the Ti matrix, as well as the film contamination, was examined by X-ray photoelectron spectroscopy (XPS). using a hemispherical analyzer (Perkin-Elmer Model 1257). The samples were excited with unfiltered $Al K\alpha$ radiation.

III. Results and Discussion

(1) Cyclic Voltammetry

The electrochemical formation of BaTiO, under hydrothermal conditions was initially characterized by cycling titanium in the 0 to -190 mV vs Ag/AgCl (satd) voltage range, starting from the initial open circuit potential in the anodic direction. Open circuit potentials established on titanium electrodes in the

$0.25M$ $Ba(OH)_2$ solution at 150°C ranged from -100 to -140 mV vs Ag/AgCl (satd). Potentials (E) in all cyclic voltammograms reported below are given with respect to the Ag/AgCl (satd) reference electrode.

A typical cyclic voltammogram for titanium in the $0.25M$ solution, obtained at 100 mV/s sweep rate, is shown in Fig. 2. The anodic current obtained in the initial anodic sweep from the rest potential up to 0 mV vs Ag/AgCl (satd) is related to the initial stages of formation of the film. After a rapid initial increase in the anodic current there is a peak and a subsequent decay in the current which can be related to the onset of a continuous oxide resistive film. with the subsequent reduction of the reactivity of the initial titanium electrode. After this initial film is formed. the anodic current rises steadily with the increase in the anodic polarization (Fig. 2, $-118 \rightarrow 0$ mV range).

The area enclosed under the anodic peak amounts to a charge of about 3×10^{15} electrons/cm'. which corresponds approximately to the surface atomic density. This means that the peak can be associated with the formation of the first monolayer.

When sweeping back from 0 V in the cathodic direction. the anodic current decreases following a pattern coinciding with the ascending branch in the 0 V $\rightarrow -100$ mV range. When sweeping cathodic. the anodic currents persist now in potential ranges anodic to the initial rest potential (-118 to -190 mV), which indicates that a stable surface film was formed during the former anodic cycle.

When cycling from -190 mV in the onodic direction there is a large cathodic current peak at -163 mV with an associated charge which is much larger than the anodic charge accumulated during the anodic part of the cycle. This shows that the cathodic processes involved are not simply the result of the dissolution of the BaTiO, film. but there are reactions with the electrolyte.

Further characterization of the cathodic phenomena was obtained from cycling voltammograms at lower sweep rates, as the ones shown in Fig. 3. These voltammograms show that the cathodic process consists in fact of two main events: There is first a sharp switch of the current from anodic to cathodic which indicates the moment at which dissolution or breakdown of the anodically formed film takes place. The potential at which the breakdown of the BaTiO, film occurs is more cathodic as the limit of the anodic cycle increases, i.e., when a large charge is passed during the anodic deposition process. The film breakdown is followed by a sharp increase in the cathodic current which indicates the onset of a fast cathodic reaction between the exposed surface and the electrolyte.

(2) Mechanism of Anodic Film Formation

The process of film growth was further characterized by analyzing in more detail the shape and evolution of anodic current waves successively obtained on titanium after the initial nucleation stage. Figure 4 shows cyclic voltammograms for successive cycles conducted in the range of -80 to 0 mV on titanium electrodes. Two main features are apparent from those curves: at higher anodic polarization the current approaches an
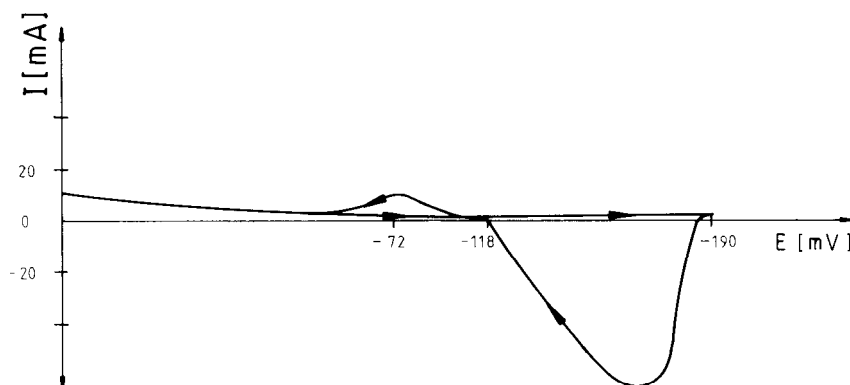

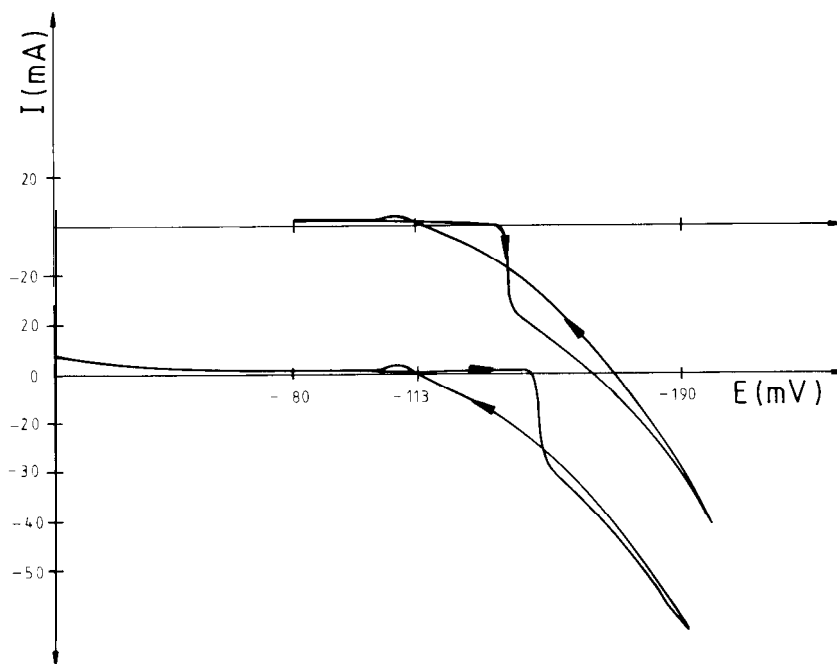Fig. 2. Cyclic voltammogram for titanium electrode at 100 mV/s

Fig. 3. Cyclic voltammograms for titanium electrode at *20* mV/s: (top) anodic limit −80 mV; (bottom) anodic limit 0 mV

exponential increase, indicating a Tafel behavior related to a mechanism controlled by charge transference. On the other hand, successive anodic cycles result in a continuous decay of the anodic current waves. indicating the continuous increase of the resistance related to the continuous buildup of the BaTiO, film.

Strong evidence of the evolution of this process was obtained from current transient measurements obtained at constant anodic potentials. where the current showed a continuous decay with time. Figure 5 corresponds to a potentiostatic current transient obtained by BaTiO, formation at 0 V which shows that linearity of current with $t^{1/2}$ is reached for longer times t. This indicates that during film growth there is a transition from the

formation of the initial BaTiO, layers. when the growth process is controlled by charge transfer. to a stage where the process is controlled by some type of transport processes in the film.

The following reaction pattern has been proposed for the BaTiO, formation under hydrothermal-electrochemical conditions:"

$$Ti \rightarrow Ti" + 4e \tag{1}$$

$$Ti^4 + 6OH \rightarrow Ti(OH)_6^2 \tag{2}$$

$$Ba^2 + Ti(OH)_6^2 \rightarrow BaTiO, + H_2O \tag{3}$$
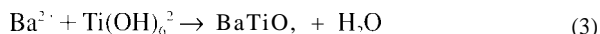
According to the former results, during the initial stages of deposition the process is controlled by the charge transfer step in the anodic dissolution of titanium (reaction (1)). For longer deposition times the process becomes controlled by mass transfer as evidenced by the I–$t^{1/2}$ linear dependence obtained (see Fig. 5), which is typical of diffusion-controlled electrochemical reactions conducted under potentiostatic conditions (Cotrell equation).'" In the present case this mechanism presumably corresponds to the transport of Ba^{2+} ions across the forming layer of BaTiO,.'"

'The process temperature in Ref. 9 was above 100°C. with results shown for 150°C. The current density was 13 mA/cm². approximately 3 times the largest used in the present work.
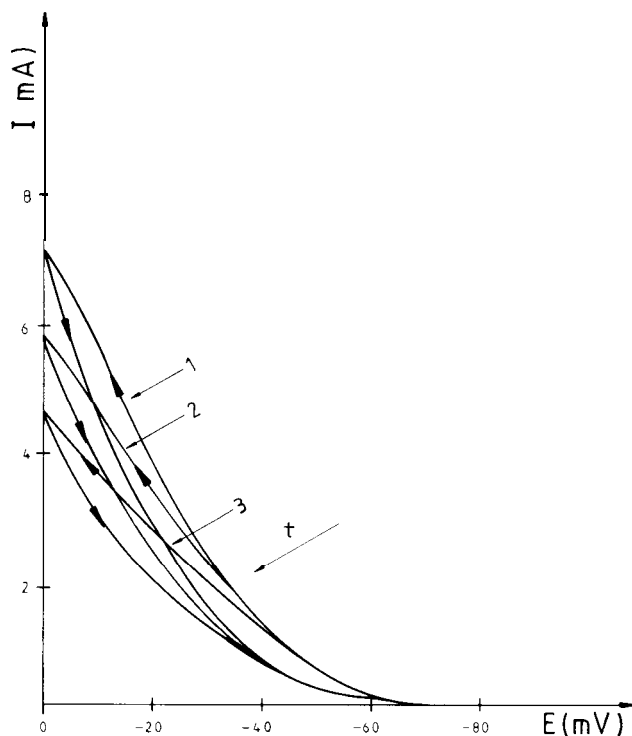

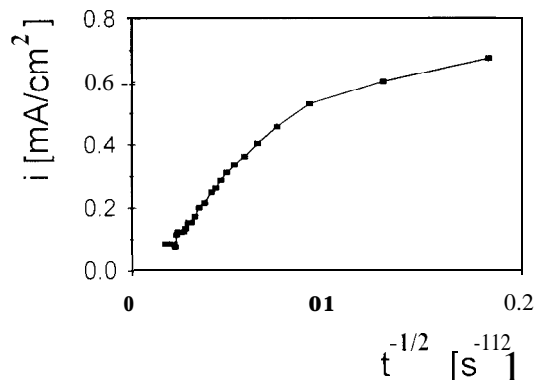**Fig. 4.** Successive anodic cycles for titanium electrode at *2* mV/s.

Fig. 5. I vs $t^{1/2}$ plot of current transient for potentiostatic film formation at E = -38 mV.
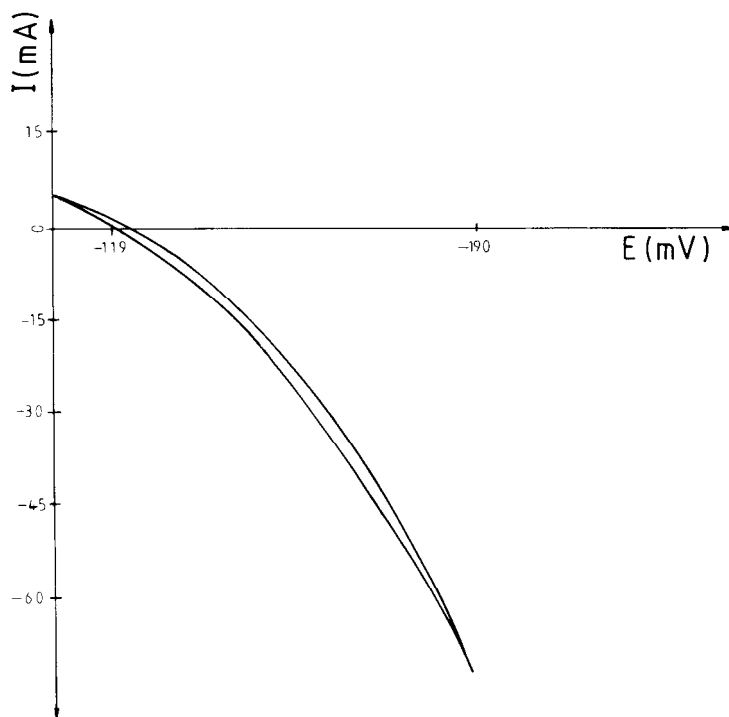
Fig. 6. Cathodic cycle for titanium electrode at 10 mV/s

The phase through which Ba^{2+} ions diffuse is not necessarily a phase completely crystallized. but presumably a highly hydrated structure. In fact XPS analysis of hydrothermal films usually reveals the presence of important concentrations of OH on the surface." In addition. preliminary thermal stimulated desorption experiments also exhibited water evolution from the films during, heating under vacuum.[22]

It is important to indicate that the current flow through the BaTiO, film is not interrupted by the formation of a dielectric layer of BaTiO,. Bacsa *et al.*, working under galvanostatic conditions. suggested that after the first layer of BaTiO, is formed. the growth continues because there could be dissolution of the BaTiO, during the process, thus exposing the bare Ti surface to the solution." This instability has been observed by other workers in anodic titanium oxide layers." [26] It has been observed that the permeability of the oxide layer is due to the formation of weak spots on it. mainly in the form of cracks.[25]

(3) Relation between Hydrothermal-Electrochemical and Pure Hydrothermal Film Formation

Cyclic voltammograms shown above (Figs. 2 and 3) indicated that under cathodic conditions there is a fast cathodic reaction involving the electrolyte. Under the used experimental conditions the large cathodic currents obtained should corre-

Fig. 7. $\log I$ vs E plots for both cathodic and anodic current branches: (a) from first cycle in Fig. 4; (b) from curve in Fig. 5.

spond to the cathodic decomposition of water on titanium according to the reaction

$$H_2O + e \rightarrow \tfrac{1}{2}H_2 + OH- \qquad (4)$$

Experiments in which the titanium electrode was cycled only on the cathodic range of potentials. so that the formation of BaTiO, was avoided. were conducted to further characterize the kinetics of water decomposition in this system. Cyclic voltammograms produced according to this procedure are shown in Fig. 6. The I–E curve obtained shows that the current has an exponential dependence on potential. which indicates that the cathodic process is charge transfer controlled.

Figure 7 shows the I–E relations for both the anodic current (first cycle in Fig. 4) and the cathodic current (from Fig. 6). plotted in $\log (I)$–E coordinates (Evans diagram of corrosion). The data in Fig. 7 allow one to propose a coherent relation between the growth mechanism of BaTiO, films under both pure and hydrothermal–electrochemical conditions. In the case of the hydrothermal-electrochemical route the anodic current which defines the film growth rate is directly applied by an external electrical source. Under potentiostatic conditions the anodic current will be that obtained from curve (a) in Fig. 7. for the specific anodic potential established in the electrode.

In the case of film growth under purely hydrothermal conditions, which occurs when titanium is in open circuit. the charge of the electrons released by the titanium oxidation reaction according to reaction (2) has to be matched by the charge electrons received by the protons according to reaction (1). Therefore. in this case. the rate of formation of the BaTiO, film is given by the anodic current obtained at the mixed potential determined where both Tafel plots intercept each other. This anodic current continuously decays with time as a result of the building up of the BaTiO, film which eventually results in mass transfer control. This process is evidenced in the evolution of the potential of a titanium electrode left in open circuit in the hydrothermal bath (see Fig. 8). This explains the fact that the rate of film growth under pure hydrothermal conditions is slower than under hydrothermal-electrochemical conditions.

In the case of the pure hydrothermal method. the film growth is self-regulated and there is no buildup of layers of intermediate compounds such as anatase.[19] However, when the process is electrolytic. the kinetics of Ti oxidation is specifically enhanced with respect to the other chemical steps. and buildup of interme-
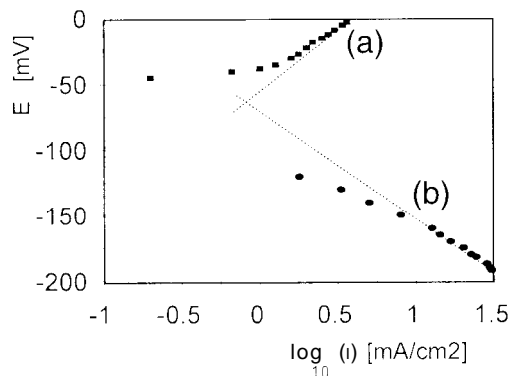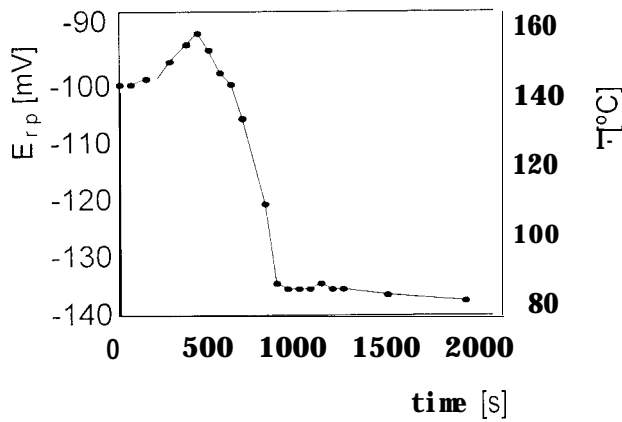
Fig. 8. Time and temperature evolution of the rest potential

diate titanium oxide layers can occur. This in fact is consistent with the finding of Ishizawa, who detected a TiO_2 layer beneath the $BaTiO_3$ film in samples prepared using hydrothermal–electrochemical conditions, but not when using pure hydrothermal conditions.'''

(4) Film Characterization

(A) Surface Analysis. Photoelectron spectra of the surface of the films produced by the hydrothermal-electrochemical method are similar to those reported for films produced under pure hydrothermal conditions.'- This is true despite the different growth conditions, indicating that these differences did not affect the film stoichiometry.

Figure 9 shows a surface scan recorded at a nominal energy resolution of 0.75 eV. Curve (a) represents the surface as received in the analysis chamber. Curve (b) is the same surface after eliminating the surface carbon by sputtering with 4 keV Ar ions (sputtering dose of 1×10^{16} ions/cm'). Trace\ of calcium were detected, but it cannot be resolved in the scale of the graph. Some strontium contamination is indicated. We believe that both calcium and strontium are present in the starting $Ba(OH)_2$ material. It is important to notice that the Ba:Sr ratio, evaluated using the available sensitivity factors,''; amounts to $\approx 5:1$. This is 1 order of magnitude larger than the strontium content in the starting $Ba(OH)_2$, with impurities
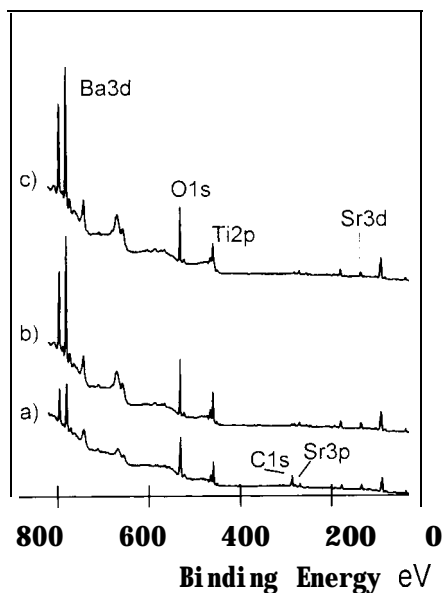
below 2%. The (Ba + Sr):Ti:O ratio, estimated in the same way, was 1:0.8:3, i.e., $(Ba,Sr)TiO_3$, within the experimental error. Finally, curve (c) was recorded deeper in the sample, after a total erosion dose of 11×10^{16} ions/cm'. At this level the estimated atomic ratios were (Ba + Sr):Ti:O $\approx 1:1.1:2.9$ and Ba:Sr $\approx 7:1$.

Hi&resolution spectra are shown in Fig. 10. The broad O1s peak at the surface (a), with a shoulder at higher binding energies, suggests that there is adsorbed water or OH groups. This is frequently observed on the surface of oxides and it is consistent with the preparation method. After the surface layer (curve (b)) is removed, the peak is sharp, indicating a single chemical state. This situation persists deep in the sample (c).

The evolution of the Sr $3d$ peak in depth is indicated below the O1s box. The splitting of the $3d$ photoelectron peak confirmed that the element is strontium. The last box shows the Ti $2p$ peak. The position of the Ti $2p_{3/2}$ peak at 459 eV is characteristic of Ti(IV).²⁷ The shoulder at lower binding energy in the spectrum indicates that some titanium is in a lower oxidation state. It has been observed that the Ar' ion beam partially reduces Ti(IV) leading to this situation even in sintered ceramic $BaTiO_3$ samples. If the sputtering of the film is continued, the peak deforms to a superposition of the Ti(IV) and the Ti peaks, and finally to pure metal
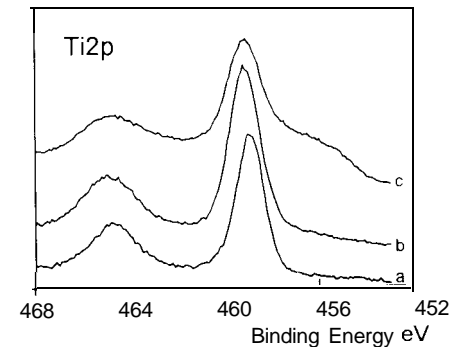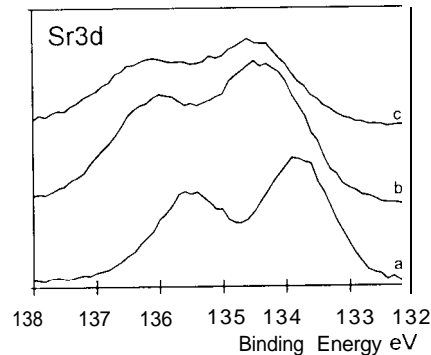

Fig. 9. XPS spectrum of a hydrothermal–electrochemical $BaTiO_3$ film: (a) surface as received: (b) after 4 keV **Ar ion** erosion (1×10^{16} ions/cm'):(c) **after** 11×10^{16} **ions/cm'.**
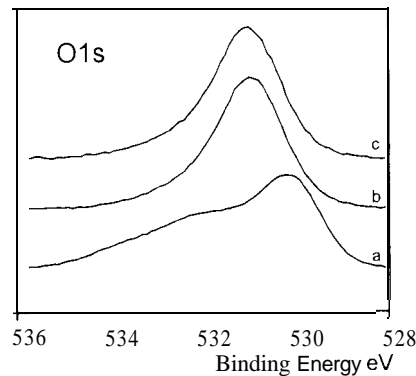

Fig. IO. XPS high-resolution spectra of the O1s, Sr $3d$, **and Ti** $2p$ **peaks: (a)** surface as received;(b) after 4 keV Ar⁻ ion erosion **(I X** 10^{11}ions/cm'):(c) **after** 11×10" ions/cm'.

It appears that the strontium content in the films is always higher than in the starting solution. This was first reported in Ref. 28 for pure hydrothermal films, and has been independently confirmed in Refs. 29 and 30.

(B) X-ray Diffraction: Two kinds of samples were identified. The first group exhibited only the reflections attributable to the substrate. We believe that the film was too thin to provide detectable reflections.

In all other samples, of blue color, the (100), (110), (200), (210), and (211) reflections of BaTiO₃ dominated. Typical XRD data are displayed in Fig. 11, indicating these reflections. The large truncated peaks are reflections from the titanium substrate. The (111) reflection from BaTiO₃ is covered by one of the strong Ti reflections.

The insert is a high-resolution spectrum between 31.0° and 32.0° and reveals no splitting between (110) and (011) reflections, showing that the structure is not tetragonal but cubic, in agreement with the reports from other researchers.

The microstructure of the films reported in this work does not differ from that observed by other researchers.[9,28] However, it has been recently reported that the application of potential steps during the initial stages of growth does influence the grain size.[31]

IV. Conclusions

The mechanism of formation of BaTiO₃ films by the hydrothermal–electrochemical method was characterized.

The study was conducted in a three-electrode electrochemical cell, which enabled the application of electrochemical techniques for the characterization of the film growth process and the formation of BaTiO₃ films under potentiostatic conditions.

Cyclic voltammetric and chronoamperometric studies showed that the hydrothermal–electrochemical BaTiO₃ formation is initially controlled by charge transfer processes related to the rate of anodic oxidation of titanium. The process becomes eventually mass transfer controlled, presumably related to the diffusion of Ba²⁺ ions across the buildup BaTiO₃ film. The derived diffusion coefficient ($D \sim 10^{-8}$ cm²/s) is between the expected values for aqueous solutions and solid state, suggesting that the film through which barium diffuses is not a completely crystallized phase.

The mechanisms of formation under both the hydrothermal–electrochemical and the pure hydrothermal methods are related. In the electrochemical case the rate of film formation is controlled by the anodic current applied by an external electrical source. In the pure hydrothermal case the growth rate of the film is controlled by the anodic current determined by the mixed potential resulting from the anodic oxidation of titanium and the cathodic decomposition of water.
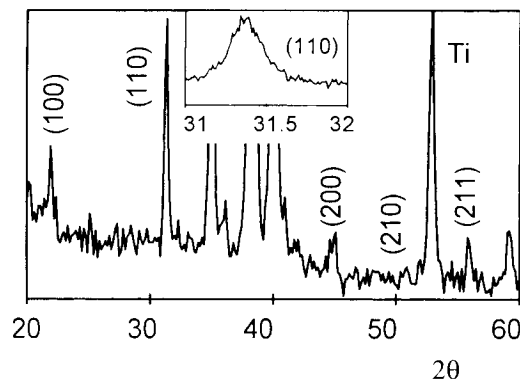
Fig. 11. XRD spectrum of a BaTiO₃ thin film on Ti showing the major BaTiO₃ peaks as well as the Ti substrate peaks. Insert: high-resolution spectrum of the (110) reflection.

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