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Recent developments in soft, solution processing: one step fabrication of functional double oxide films by hydrothermal–electrochemical methods†

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Based upon thermodynamic considerations, we propose ‘soft, solution processing’, as a means to fabrication of shaped, sized, and controlled advanced materials from aqueous solutions without excess heat, energy consumption, expensive equipment, and precursor(s) as one of the most economical and environmentally friendly preparation techniques for advanced materials. We have succeeded in the fabrication of double oxide thin films such as $BaTiO_3$, $SrTiO_3$, their solid solutions, and $LiNiO_2$ at fixed temperatures between 60 and 150 °C by hydrothermal–electrochemical methods. Nucleation and growth of the films takes place at the interface between the alkaline (earth) component in the solutions and anodically treated metal plates. The structures and properties of these films are described. A novel method to fabricate $BaTiO_3/SrTiO_3$ layered thin films by changing the solution compositions in flow-cell equipment is presented.

Introduction

Modern society needs advanced ceramic materials with sophisticated functions and high performances. A number of substances with particular compositions, crystal structures and specified properties have been investigated for this purpose. [In our considerations ‘substance’ is characterized by (1) a particular chemical composition, (2) a particular physical state including structure, and (3) particular properties based upon its composition and structure. Since ‘material’ should be defined as a substance mostly in the solid state which is used or to be used for certain application(s), we must add the following features to define ‘material’: (4) a particular shape, (5) a certain size, (6) location, and (7) orientation.[1]] Unfortunately, it is difficult to give desired shapes, forms and sizes to inorganic materials, owing to their high brittleness. Organic materials such as polymers and plastics or metallic materials can be generally deformed when local stresses (above their yield stresses) are applied to them, but inorganic materials, particularly ceramics, tend to break due to brittle fracture.[2–4] Therefore, ceramics are fabricated by rather special ‘ceramic processing’ which consist of two steps: (1) synthesis of powders, and (2) shape-forming by firing/sintering of the powders or melting (in the case of glasses).[5] Both steps usually require high temperatures and thus consume a lot of energy. Novel processing using a gaseous phase, like CVD, MOCVD, *etc.*, or vacuum systems such as sputtering, MBE *etc.*, require even higher energy than standard high temperature processing.[6] All these techniques have resulted in environmental problems because the consumed energies are emitted as exhaust gas(es) or exhaust heat (entropy) except for the part involved in the product. In particular, vacuum systems seem to be worse because they need continuous pumping to maintain vacuum and their exhaust gas(es) cannot be cycled due to their diluted large volumes.

Fortunately, we can fabricate shaped, sized, reacted and/or oriented ceramic materials, without firing/sintering or melting, without vacuum and expensive equipment, *in situ*, by soft, solution processing (denoted hereafter as SSP).[1,7] SSP is defined as ‘environmentally friendly processing using (aqueous) solutions’. In this paper a thermodynamic and environmental background to SSP is given. In addition, recent important developments in the field of SSP, such as fabrication of double oxide thin films including multilayered materials and applications of a new solution flow system, are presented.

Thermodynamic and environmental features of soft, solution processing

Generally speaking, SSP gives similar results to any other processing using fluids (such as vapor, gas, plasma) and/or beam/vacuum processing. However, the total energy consumption of all these processing routes should be the lowest in aqueous systems, because a much larger excess of energy is necessary to create melts, vapor, gas or plasma than to form an aqueous solution at the same temperature.[1] This idea can be easily demonstrated using the simple example of $BaTiO_3$. The energy diagram for the formation of $BaTiO_3$ from various precursors is shown in Fig. 1. The driving forces (ΔG) for representative synthesis reactions of (1), (2), (3), (4), and (5) are 38, 727, 3685, 17, and -14 kcal mol^{-1}, respectively at room temperature.[8,9]

$$\mathrm{BaO\ (crystal) + TiO_2\ (crystal) = BaTiO_3\ (crystal)} \quad (1)$$

$$\mathrm{Ba\ (vapor) + Ti\ (vapor) + 3/2O_2\ (gas) = BaTiO_3\ (crystal)} \quad (2)$$

$$\mathrm{Ba^{2+}\ (gas) + Ti^{4+}\ (gas) + 3O^{2-}\ (gas) = BaTiO_3\ (crystal)} \quad (3)$$

$$\mathrm{TiO_2\ (crystal) + Ba^{2+}\ (aq) + 2OH^-\ (aq) - H_2O\ (aq) = BaTiO_3\ (crystal)} \quad (4)$$

$$\mathrm{Ba^{2+}\ (aq) + Ti(OH)_4\ (aq) - H_2O\ (aq) - 2H^+\ (aq) = BaTiO_3\ (crystal)} \quad (5)$$

This means that any processing using gaseous ions requires a huge activation energy of 727–3685 kcal mol^{-1} to make solid $BaTiO_3$ and this energy must be discarded into the environment, because the raw materials of Ba and Ti must be solid oxide(s) or carbonate(s) ore. On the other hand, since the lattice energy of BaO and TiO_2 is almost equal to the hydration (solvation) energy of Ba^{2+} and Ti^{4+} ions, solution processing consumes very little energy (ΔG, driving force) if only the synthesis activation energy (ΔG^*) can be overcome. Fig. 1

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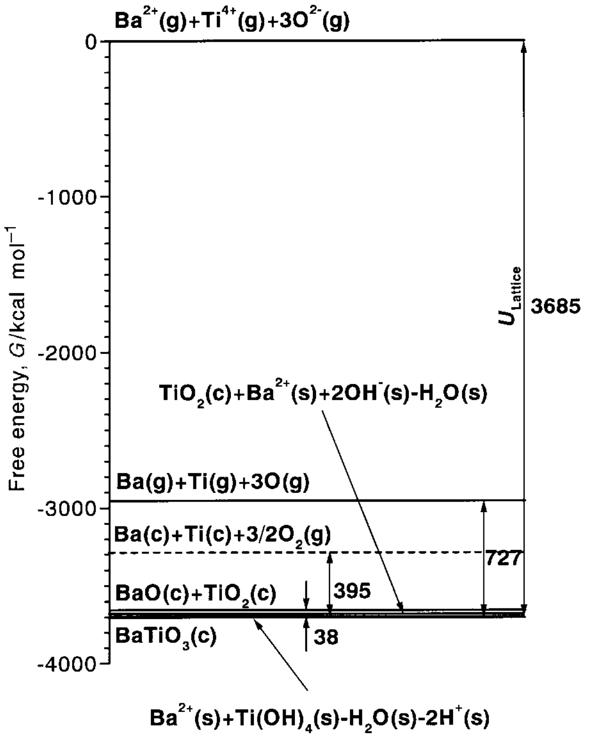

Fig. 1 Energy diagram for the formation of $BaTiO_3$ using solid and/or gas precursors (g, s and c correspond to the gaseous state solution state and the crystalline state, respectively). Compiled from ref. 8 and 9.

gives the fundamental thermodynamic background for the environmental problems related to materials processing.

A temperature–pressure map for various kinds of materials processing is shown in Fig. 2. Solution processing is located in the *p–T* range characteristic of conditions of living on earth. All other processing routes are associated with increasing temperature and/or increasing (or decreasing) pressure, therefore they are environmentally stressed. From the environmental point of view, solution processing should be the most environmentally friendly. Nevertheless, previous studies on ceramic films by solution processing have been limited except for the 'sol–gel' or 'pyrolysis' methods,[10,11] which are regarded as solid rather than solution methods because solvents must be driven out of the system before formation of the crystalline material.

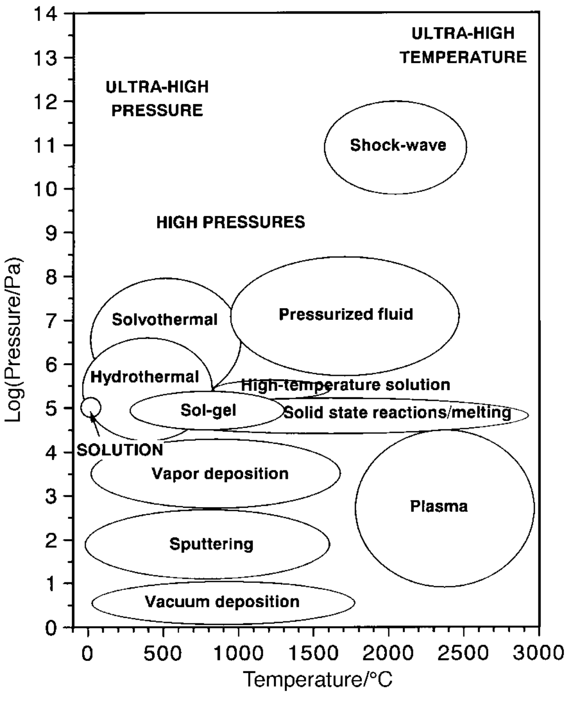

Fig. 2 Schematic *p–T* diagram for preparative techniques for advanced ceramic materials.

In spite of the environmental and energetic advantages of SSP, film formation of multicomponent inorganic materials is quite difficult from solution systems. In contrast, film formation is rather easy from gas or plasma systems. The gaseous species are always in high energy states (see also Fig. 1), thus the ΔG and the ΔG^* are sufficiently provided for reaction to yield crystalline compounds with desired shape/size *via* several steps such as diffusion, adsorption, reaction, nucleation, and growth.[6] Generally speaking, $\Delta G^* \propto (\Delta G)^{-n}$, where $n=2$ for the nucleation process. On the other hand, species in aqueous solutions are hydrated (or chelated by some complexing agents), thus they have only a small ΔG for the reaction, thus rather high ΔG^* values are necessary for the reaction to occur by overcoming the hydration (chelation) energies of ions. Electro- or electroless-plating of metals is achieved by reducing of metal ion(s) electrochemically or chemically.[12] However, in the case of ceramic materials, particularly multicomponent ones, special activation of all the components is needed, anions must be oxidized at the same time as reduction of cations. Since this simultaneous multiactivation is quite difficult, ceramics could scarcely be fabricated directly from solutions previously. However, we have demonstrated that direct fabrication of ceramic films can be achieved using interfacial reactions between reactive substrates of metal, alloy, or oxide and species in aqueous solution activated thermally (hydrothermal) electrochemically, or by a combination (hydrothermal–electrochemical).[7] Other activation methods like photo-, sono-, electro-, mechano-, complexo-, or even bio-activation are possible to accelerate the interfacial reactions.[1,13]

Applications of soft, solution processing for thin film fabrication: hydrothermal–electrochemical technique

Preparation techniques of thin films can be divided into two categories: (1) dry methods, such as vacuum deposition, sputtering, ion plating, CVD *etc.*,[6] and (2) wet methods such as dip, spray coating of organic/inorganic precursors, sol–gel,[10,11] electrodeposition,[14] *etc.* All these methods usually require high temperatures (above 500 °C) to crystallize as-deposited amorphous films or to decompose the precursor to yield an appropriate compound. Such heat treatments often result in cracking and/or peeling of the deposited layers, formation of undesired compositions by evaporation, dissociation, and/or reaction of the film with the substrate, moreover they are energy consuming. In particular, it is difficult to form dense films by organometallic and metallorganic processing, because decomposition of the precursors may result in porous ceramic layers.

Therefore, low temperature, *in situ* fabrication of crystalline, thin films is essential to improve their quality, lower costs and make the whole process environmentally friendly. This was accomplished, by introducing the hydrothermal and/or electrochemical methods of film preparation.[15] These techniques allow various double oxide films to be prepared on such substrates as metal, alloy or oxide.[7] The substrate works as an electrode which reacts chemically and/or electrochemically (by passing electrical current) with the cation components of the surrounding solution. This processing route may involve the following reactions:[16] (1) hydrothermal reaction between anodically oxidized film and solution components; (2) electrochemical reaction with solution component(s); (3) electrolytic oxidation of dissolved species and hydrothermal reaction; (4) hydrothermal reaction between anodically dissolved species and solution components; (5) electro-discharge reaction between anodic oxidized film with solution component(s); (6) electro-deposition of charged oxide particles.

Advantages of the hydrothermal/electrochemical techniques are: (1) one step (direct) formation of shaped/sized/deposited/oriented ceramics; (2) low fabrication temperatures (minimized consumption of energy); (3) any shape, any size; (4) possibility of using a closed flow system, allowing easy charging, separation, cycling and recycling; (5) relatively high growth rate of the films (up to several µm per hour); (6) versatility. In addition, SSP gives products with much higher homogeneity than solid state processing and with higher density than gas or vacuum processing (faster growth rate). There is a wide variety of combinations of solvent/solute systems. Liquids may be beneficial for charging, transportation, mixing and/or separation of products. They are completely adaptable for cycling/recycling of material processing in closed systems. Moreover, liquids give the possibility for acceleration of diffusion, adsorption, reaction rate and crystallization (nucleation and growth), especially under hydrothermal conditions.

For these reasons, various thin films have been successfully prepared by the hydrothermal and/or electrochemical method. Examples include polycrystalline PZT,[17,18] ZnO,[19] TiO_2,[20] ferrites,[21–23] PbS,[24] CdSe,[24] $BaTiO_3$,[15,25–31] $SrTiO_3$,[32–36] $Ba_xSr_{1-x}TiO_3$,[37] $CaTiO_3$,[38] $BaFeO_4$ ($BaFeO_{3-x}$),[16] $LiNbO_3$,[16] $PbTiO_3$,[39] ABO_4 oxides (A = Ca, Ba, Sr; B = W, Mo)[40,41] and complete series of their solid solutions.[42] The microstructures and chemical compositions of these materials can be controlled in a wide range at temperatures in most cases not exceeding 200 °C, sometimes even at room temperature.[40–42] The fabrication of epitaxial thin films,[26,43] monomolecular layers,[24] and even superlattices[44,45] have also been reported.

In the following two sections, new developments in the field of SSP are described. In both sections the experimental procedure and advantages of the applied techniques over previously used ones for the particular material are also briefly mentioned.

Hydrothermal–electrochemical synthesis of $LiNiO_2$ films

All-solid-state lithium rocking chair secondary microbatteries have been considered as the most suitable power source for microelectronics.[46–51] However, the synthetic approach in previous works required highly sophisticated multistep procedures such as chemical vapor deposition, sol–gel methods, and sputtering.[46–53] Such fabrication routes require high energy and materials consumption, expensive precursors, and complicated instrumentation.

In the course of trying to develop an alternative, economic, and low-temperature process that can produce the desired lithiated cathode films on chips, we have succeeded in the electrochemical preparation of active $LiNiO_2$ films by electrochemical–hydrothermal treatment on nickel plates.[54–56] This fabrication can be interpreted in terms of the electrochemical oxidation of nickel metal electrodes in a concentrated LiOH solution at fixed temperatures between 60 and 200 °C. The electrochemical process, *i.e.* electrochemical oxidation of nickel plates, was realized galvanostatically with a fixed current density between 0.1 and 10 mA cm^{-2} in a three-electrode arrangement using nickel working and auxiliary electrodes and a temperature controlled Ag/AgCl reference electrode.[57] The reaction time depends on the applied current density and fabrication temperature. Although detailed experimental procedures have been described previously,[54–56] note that the prepared $LiNiO_2$ films were not subjected to any post-synthesis heat treatment. The used LiOH solution containing dissolved nickel species, nickelite ions $HNiO_2^-$ in practice, can be recycled by filtering it and replenishing the LiOH, which is environmentally and economically beneficial.

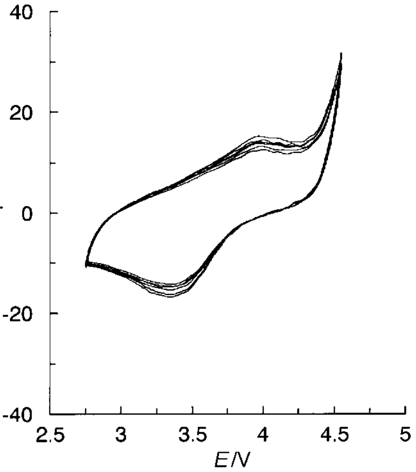

Fig. 3 Cyclic voltammograms of the $LiNiO_2$ film prepared at 125 °C with a current density of 1.0 mA cm^{-2} taken in 0.1 M $LiClO_4$ propylene carbonate (potential is referred to Li/Li^+ electrode) with a scan rate of 5.0 mV s^{-1}.

The electrochemical–hydrothermal treatment of polished nickel plates led to the formation of a visually detectable cobalt-blue film. The structural purity and chemical composition of the films were confirmed by X-ray diffraction and X-ray photoelectron spectroscopy, respectively.[54–56] According to X-ray diffraction, scanning electron microscopy (SEM) cross-section views, and atomic force microscopy (AFM) surface images, the films show good crystallinity despite the low fabrication temperature without any post-synthesis annealing.[54–56] Further evidence for the formation of $LiNiO_2$ films was obtained from their cyclic voltammograms (Fig. 3) since the peak potentials characterizing oxidation and reduction are similar to those for a $LiNiO_2$ powder electrode.[55] Films prepared between 125 and 175 °C can also be reversibly oxidized and reduced in lithium perchlorate ($LiClO_4$) propylene carbonate solutions for >5 electrochemical cycles, and therefore are possible cathodes for lithium rechargeable microbatteries.

The films prepared under different conditions show different electrochemical activity, surface morphology, and film thickness.[55,56] The apparent effect of the fabrication temperature on the surface morphology, for instance, is demonstrated by comparing the AFM surface images of the nickel substrate and the films prepared at different temperatures (Fig. 4).

While purely hydrothermal treatment of nickel substrates leads to the formation of $Ni(OH)_2$ films, by use of the electrochemical–hydrothermal approach under supplementary galvanostatic charge with the same hydrothermal conditions, $LiNiO_2$ films can only effectively be prepared in a single synthetic step from nickel substrates.[54–56] In addition, the electrochemical oxidation of nickel plates in alkaline solution at room temperature leads to the formation of NiOOH films. Therefore, the electrochemical anodic process is necessary to obtain trivalent nickel and the hydrothermal process is necessary for the cationic exchange reaction between Li^+ and H^+.

Multilayered thin films in the $BaTiO_3$–$SrTiO_3$ system: integration issues of soft, solution processing

It has been shown in the previous sections that a variety of technologically important thin films can be prepared by hydrothermal and/or electrochemical techniques. It seems therefore that we should start to think seriously about how to integrate the hydrothermal/electrochemical methods with functional

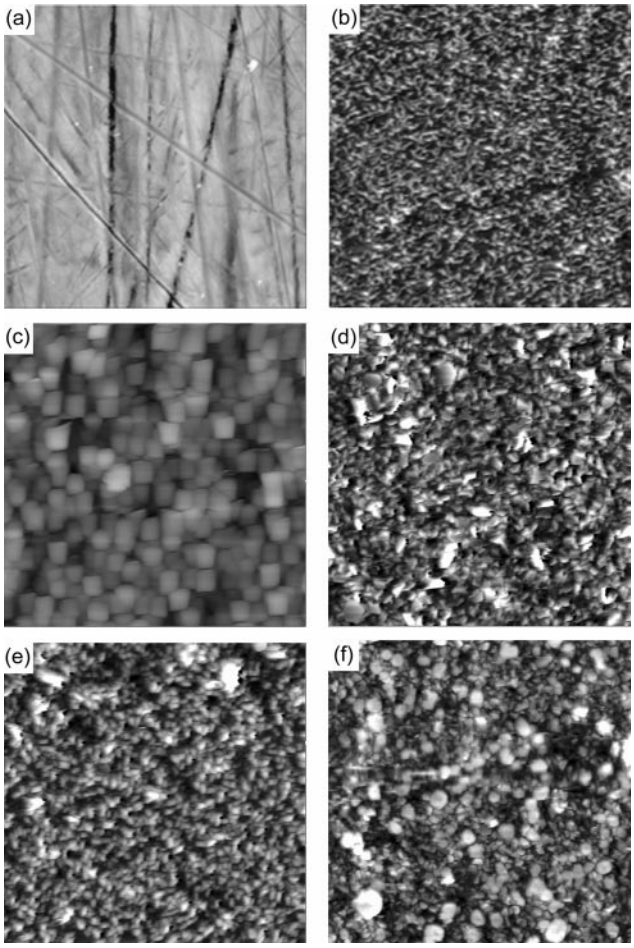

Fig. 4 Atomic force microscope (AFM) images of (a) the Ni substrate polished with 1.0 μm diamond paste, and (b)–(f) the $LiNiO_2$ films prepared at different temperatures with a current density of 1.0 mA cm^{-2}: (b) 100 °C, (c) 125 °C, (d) 150 °C, (e) 175 °C and (f) 200 °C. Image size is 7.5 μm × 7.5 μm in each case.

device technology which has been dominated by physical vapor deposition[6] and chemical vapor deposition.[6] In addition to PVD and CVD, some processing routes aimed at fabrication of integrated circuits use chemical solution processing (etching, sol–gel).[58] In some cases, the (electro)chemical routes are considered as alternatives for the presently used vapor techniques (*e.g.* copper deposition).[59]

From this point of view, fabrication of ceramic thin films in the solution flow below 200 °C (this is the maximum temperature for wide industrial applications of the hydrothermal technique) is very important and may find multiple applications. The best suited equipment for this purpose seems to be a solution flow system for hydrothermal–electrochemical synthesis. Such equipment is similar to flow cells used in geological studies[60] or in materials engineering (ferrite plating),[21,22] and allows fabrication of multilayered thin films by simply changing the flowing solution and/or adjusting the processing conditions. Moreover the flow can be closed, enabling easy recycling of the solutions.

We have selected the $BaTiO_3$–$SrTiO_3$ system to demonstrate the fabrication of multilayered ceramic films under solution flow. Recently, attention has focused on multilayered films in this system,[61–66] as they may find applications as DRAM capacitors with high relative permittivity and reduced leakage current,[62–64] tunable multilayer capacitors, waveguide phase shifters, filters, *etc.*[66] The previous preparation routes to $BaTiO_3$–$SrTiO_3$ multilayered structures, such as tape-casting,[66] dip-coating,[65] and magnetron sputtering[62–64] had several disadvantages such as high vacuum and/or temperatures in the range of 500–700 °C.

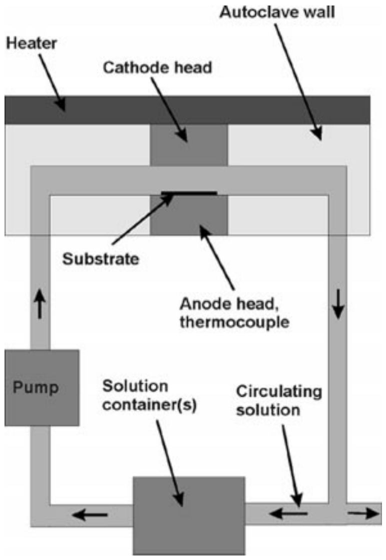

Fig. 5 General schematic diagram of the flow cell for hydrothermal–electrochemical synthesis.

All the experiments were accomplished in our flow cell for hydrothermal–electrochemical synthesis. A general schematic diagram of the equipment is shown in Fig. 5. Single-phase, single layer and multilayered thin films in the $BaTiO_3$–$SrTiO_3$ system have been fabricated using titanium substrate and Ba and Sr acetates. A detailed description of the fabrication procedure has been published elsewhere.[67–69]

Results of syntheses carried out in open and closed flow were almost the same. Single phase $BaTiO_3$, $SrTiO_3$ or $Ba_xSr_{1-x}TiO_3$ have been prepared at 120–200 °C, when the current density did not exceed 1 mA cm^{-2}. Effects of flow rate on grain size are shown in Fig. 6. The grain size increases almost linearly with increasing flow rate, reaching a plateau at approximately 20 cm^3 min^{-1}. Effects of the flow rate in our experiments are in fact similar to the effects of stirring applied in growth of crystals from solutions or melts. Usually, they lead to an increase in the probability of spontaneous nucleation, reduction of supersaturation inhomogeneities, and increase of the growth rate.[70] The growth rate of crystals increases with increasing solution flow rate until a limiting rate is reached when the growth rate becomes controlled by

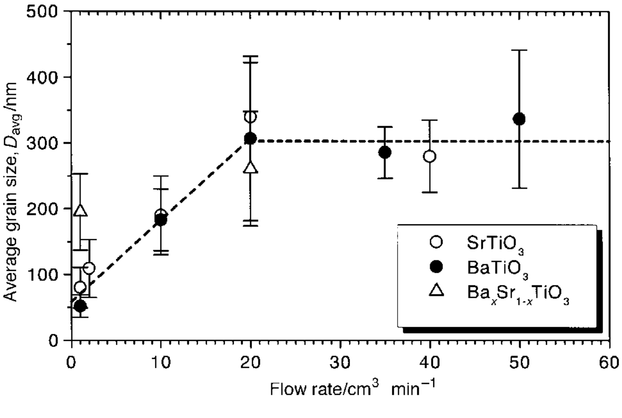

Fig. 6 Average grain size of the $BaTiO_3$, $SrTiO_3$, and $Ba_xSr_{1-x}TiO_3$ single-phase thin films prepared in the flow cell by the hydrothermal–electrochemical method at 150 °C (1 h, 1 mA cm^{-2}) as a function of the solution flow rate. Error bars denote standard deviations for the average values. Solution flow rates were in the range of 1–50 cm^3 min^{-1} which corresponds to the Reynolds numbers of about 46–2300, within a region of laminar flow.[67]

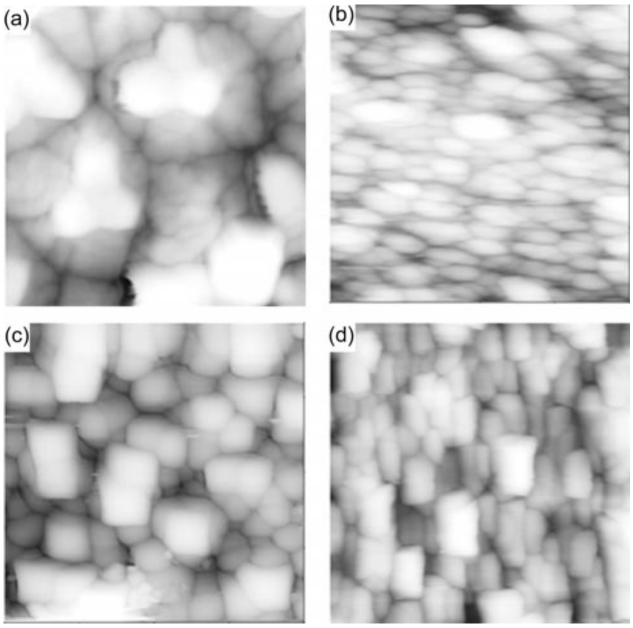

Fig. 7 Atomic force microscopy images of the $SrTiO_3/BaTiO_3/Ti$ multilayer (a) after step 1, *i.e.* the $BaTiO_3$ surface, (b) after step 2, *i.e.* the $SrTiO_3$ surface; and the $BaTiO_3/SrTiO_3/Ti$ multilayer (c) after step 1, *i.e.* the $SrTiO_3$ surface, (d) after step 2, *i.e.* the $BaTiO_3$ surface. Image size is 1.0×1.0 μm in each case.[67]

the interfacial kinetic processes.[70] Our results suggest that the microstructure of the films at various flow rates is controlled by the growth rate, which initially increases, and then remains unchanged for flow rates >20 cm^3 min^{-1}.

$SrTiO_3/BaTiO_3/Ti$ and $BaTiO_3/SrTiO_3/Ti$ layered thin films have been fabricated at 150 °C (step 1: deposition of the first layer + step 2: deposition of the second layer), by changing the flowing solution. XRD patterns of the double layers showed distinct peaks derived from single-phase $SrTiO_3$ and $BaTiO_3$ layers.[67] The presence of $Ba_xSr_{1-x}TiO_3$ solid solutions has not been detected by XRD, but we cannot preclude dissolution of small quantities of Ba in the $SrTiO_3$ layers or *vice versa*. Results of AFM measurements are shown in Fig. 7. They clearly show different microstructures of the surface of the single layers and the double layers. These data demonstrate that initially formed $BaTiO_3$ and $SrTiO_3$ layers have been covered by layers of $SrTiO_3$ and $BaTiO_3$, respectively. XPS data confirmed presence of the Sr- or Ba-rich layer on the surface and the Ba- or Sr-rich layer, respectively, below.[67,71] The formation mechanism of the multilayered thin films in the $BaTiO_3$–$SrTiO_3$ system by the hydrothermal–electrochemical technique will be discussed in detail elsewhere.[72]

The processing described may be applied generally for various single and/or multilayered thin films. The possibility of solution recycling during hydrothermal–electrochemical synthesis of the thin films in the $BaTiO_3$–$SrTiO_3$ system is important because it minimizes the environmental impact of the process.[1] The technique using the solution flow under hydrothermal–electrochemical conditions is an important step in integration of the solution processing with functional device technology and may find applications as an inexpensive and environmentally friendly way to fabricate various single and/or multilayered thin films and functionally graded materials.

Summary

A thermodynamic concept for energetic and environmental problems related to materials synthesis has been proposed. It concludes that soft, solution processing, *i.e.* solution processing using (aqueous) solutions, should be the most economical and environmentally friendly. Several advanced ceramic materials have been successfully fabricated using this technique.

Well crystallized, electrochemically active $LiNiO_2$ films for lithium rechargeable microbatteries were fabricated in a single step by the electrochemical–hydrothermal treatment of nickel plates in a concentrated LiOH solution at fixed temperatures between 60 and 200 °C without any post-synthesis annealing. The film properties show the obtained $LiNiO_2$ films to be as suitable cathode films.

Layered thin films in the $BaTiO_3$–$SrTiO_3$ system have been prepared in a solution flow system by the hydrothermal–electrochemical method in a single step by simply changing the flowing solution which is its main advantage over closed autoclaves. Changing the flow rate allows additional control of film morphology by enhancing the growth rate. This processing route may serve as an inexpensive and environmentally friendly way to fabricate functionally graded thin films and seems to be an important step in the application of the hydrothermal/electrochemical techniques to fabrication of integrated electronic devices.

SSP allows fabrication in aqueous solution of shaped/sized/oriented ceramics in one step, without firing/sintering or melting. This technique requires simple equipment and low temperatures. The morphology and chemical composition of the resulting ceramics can be easily controlled by adjusting the processing conditions. SSP provides an inexpensive and environmentally friendly route to advanced ceramic materials, and therefore is one of the most promising technologies for the 21st century.

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