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Control of the Morphology of CSD-prepared $(Ba,Sr)TiO_3$ Thin Films

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Abstract

The influence of precursor chemistry and deposition process conditions on the morphology of CSD-prepared $(Ba,Sr)TiO_3$ thin films was investigated. By controlling the film formation process, the morphology of $(Ba,Sr)TiO_3$ films grown on platinum coated silicon substrates at temperatures around 750°C was tailored in order to achieve columnar grain structures. We extend the thermodynamic model for the nucleation process in $Pb(Zr,Ti)O_3$ thin films to the explanation of the crystallization behavior of $(Ba,Sr)TiO_3$ thin films. The influence of the thin film microstructure on the dielectric properties is discussed with respect to the Curie–Weiss behavior of different $BaTiO_3$ films. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

High-permittivity perovskite ceramic thin films based on alkaline earth titanates exhibit an increasing interest due to their potential use in MMICs and DRAMs. With respect to these applications a control of the thin film morphology is of crucial importance for tailoring the electrical properties. Chemical solution deposition (CSD) is capable for the preparation of integrated decoupling and filter capacitors with structures in the micron size scale. Unfortunately, CSD prepared $(Ba,Sr)TiO_3$ films typically exhibit a less controllable randomly oriented polycrystalline microstructure,[1] in contrast to the columnar structured $Pb(Zr,Ti)O_3$ films.[2–6] We investigated the influence of the precursor chemistry[7] and deposition parameters[8] in order to tailor the morphology of CSD prepared $(Ba,Sr)TiO_3$ thin films grown on platinum coated Si substrates. The dependence of the dielectric properties on the morphology of the $BaTiO_3$ films was studied with respect to the temperature dependence of the permittivity.

2 Experiment

The $(Ba,Sr)TiO_3$ thin films were prepared from different alkaline earth carboxylate/titanium alkoxide precursor solutions deposited by spin-coating on platinum coated silicon substrates, i.e. (100) Si-wafer/400 nm SiO_2/20 nm ZrO_2/100 nm Pt. The as-deposited layers were pyrolyzed in a diffusion furnace under oxidizing atmospheres. In a final step the whole film consisting of typically 5 to 20 layers was annealed in oxygen for about 15 min.

In order to differentiate between the influence of the precursor chemistry and the processing conditions on the film formation process, we applied different carboxylate routes, varied the concentration of the CSD solutions in the range of 0·1 to 0·3 M (with respect to the A-site compound), and performed different pyrolysis and annealing temperatures between 250°C and 800°C. In all routes the titanium precursor was Ti-tetra-*n*-butoxide stabilized with acetylacetone in a two molar ratio $[Ti(OBu)_2(acac)_2]$. For the Ba and Sr precursors we studied carboxylates with different length of the alkyl chain, i.e. acetates, propionates, and 2-ethylhexanoates.[7] For the CSD solutions the carboxylates were dissolved in the corresponding carboxylic acid, mixed with the stoichiometric amount of the Ti compound and diluted with the parent alcohol; i.e. 2-methoxyethanol in case of the acetate solution, 1-butanol for the propionate solution, and hexanol for the 2-ethylhexanoate solution.

Based on the above described parameters we analyzed the CSD process for the deposition of

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(Ba,Sr)TiO_3 thin films on Pt/Si substrates with respect to:

1. the decomposition behavior of the precursors;
2. the influence of the solution precursors on the phase formation in the thin films;
3. the influence of the precursors, the solution concentration and the heat treatment on the film morphology and orientation.

3 Results

3.1 Decomposition behavior of the precursors

The decomposition behavior of the alkaline earth carboxylates and the titanium precursor was studied by DTA/TG analysis. With respect to the decomposition of the stabilized Ti-alkoxide to TiO_2 which is complete at approx. 450 °C, the Ba and Sr carboxylates could be divided into two classes. The 'low-temperature' decomposing carboxylates, i.e. the long-chain compounds of barium and strontium and Sr-propionate, form oxides at temperatures below 450 °C. Whereas the 'high-temperature' decomposing carboxylates, i.e. the short-chain compounds like Ba- and Sr-acetate and Ba-propionate, exhibit a two-step decomposition process which results in the formation of oxides at temperatures above 450 °C.[7]

3.2 Phase formation in the thin films

The phase formation process was studied on $BaTiO_3$ and $SrTiO_3$ thin films which were prepared from different precursor solutions and pyrolyzed at temperatures between 250 °C and 700 °C. For this study the annealing temperature was chosen equal to the pyrolysis temperature. All films were analyzed by glancing incidence X-ray diffraction and reflectance FTIR spectroscopy. Figure 1 shows for example the diffraction patterns of $SrTiO_3$ films prepared from Sr-propionate- and Sr-acetate based precursors.

The results of the precursor/temperature study can be summarized as follows:

1. Films which were prepared from CSD-solutions based on the 'low-temperature' decomposing carboxylates crystallize into the perovskite phase at temperatures of about 450 °C ($SrTiO_3$, see Sr-propionate data in Fig. 1) to 550 °C ($BaTiO_3$).[7] The crystallization follows directly after the pyrolysis of the precursors which was confirmed by the IR-spectroscopic data.[7] Thus for those systems the pyrolysis temperature determines the film's crystallization temperature.
2. Films which were prepared from 'high-temperature' decomposing precursors, exhibit crystallization temperatures of approximately 650 °C for both $BaTiO_3$ and $SrTiO_3$ (see Sr-acetate data in Fig. 1). The crystallization into the perovskite phase takes place via the formation of an intermediate phase, which is stable in the temperature range between 550 °C and 650 °C. The intermediate phase is characterized by a high carbonate content, which was shown by the IR-data.[7] Additionally, small XRD peaks appear which correspond to an alkaline-earth-oxo-carbonate phase which was investigated for the Ba–Ti-system by Gopalakrishna Murthy[9] and Hennings,[10] who suggested the composition $Ba_2Ti_2O_5CO_3$. The corresponding Sr-Ti-oxo-carbonate phase ($Sr_2Ti_2O_5CO_3$) which we observed in the films (see Fig. 1) was also discussed by Braunstein *et al.*[11]

3.3 Influence of the CSD parameters on the film morphology and orientation

The morphology and structure of the crystallized pervoskite thin films were investigated by SEM, TEM and HRTEM analyses, and glancing incidence X-ray diffraction (see also Ref.8). The results of the morphology/structure-studies are summarized in the following:

1. Films which were prepared from CSD solutions based on the 'low-temperature' decomposing carboxylates exhibit a random oriented grainy morphology.
2. Films which were prepared from 'high-temperature' decomposing precursor solutions exhibit morphologies and grain orientations which depend on the film deposition conditions, i.e. heat treatment and solution concentration.

The different heating procedures include:

(a) A two-step heat treatment (low pyrolysis temperature around 400–500 °C for each layer and annealing of the whole film at 750 °C) which provides polycrystalline films with grainy morphologies.
(b) A single step heat treatment (crystallization of every deposited layer) which results in film morphologies and grain orientations which depend on the solution concentration.

With lowering the solution concentration from 0·3 to 0·1 M a change in the morphology of the $BaTiO_3$, $SrTiO_3$, and of the $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ films from a grainy structure to columnar grained morphology was observed (see Figs 2 and 3). This change in morphology is accompanied by a

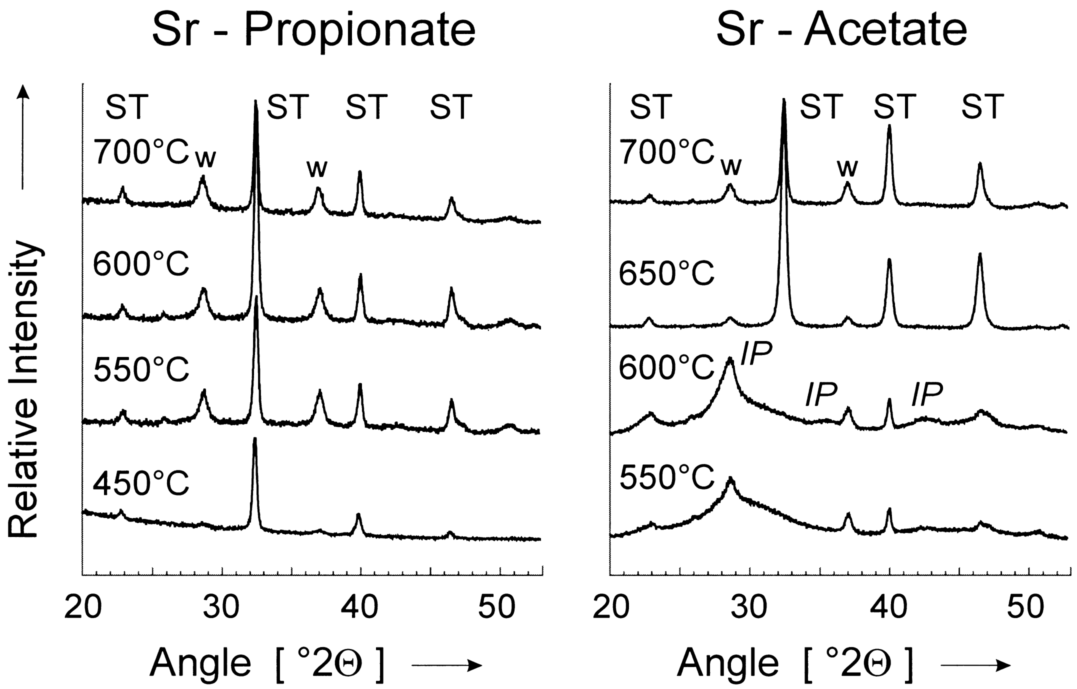

Fig. 1. XRD diagrams showing the phase evolution in SrTiO$_3$ thin films prepared from Sr-propionate and Sr-acetate based precursor solutions. ST: SrTiO$_3$, IP: intermediate Sr–Ti-oxo-carbonate phase (Sr$_2$Ti$_2$O$_5$CO$_3$); w: substrate.

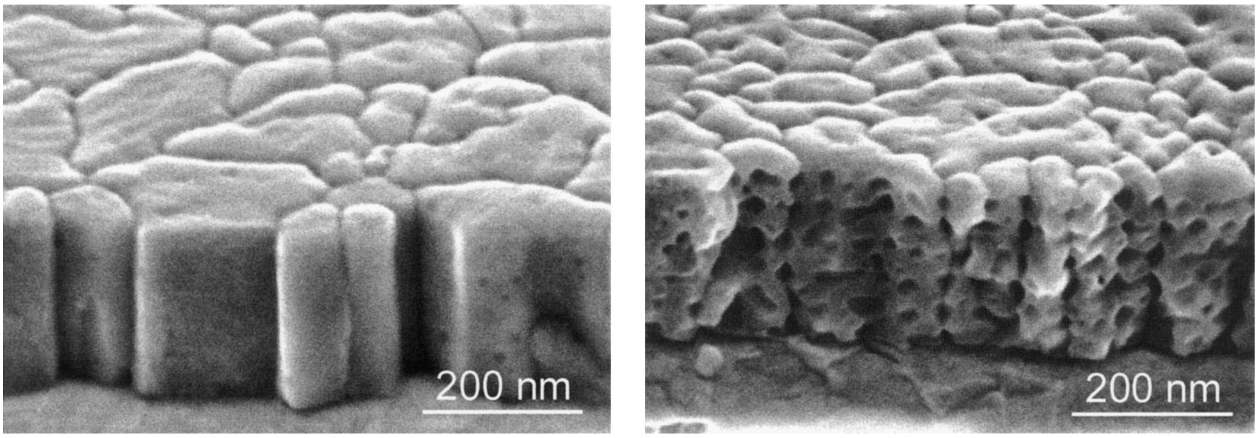

Fig. 2. SEM micrographs of the cross section and surface of two SrTiO$_3$ thin films prepared from acetate precursors; left film: 22 layers, 0·1 M solution; right film: six layers, 0·3 M solution.

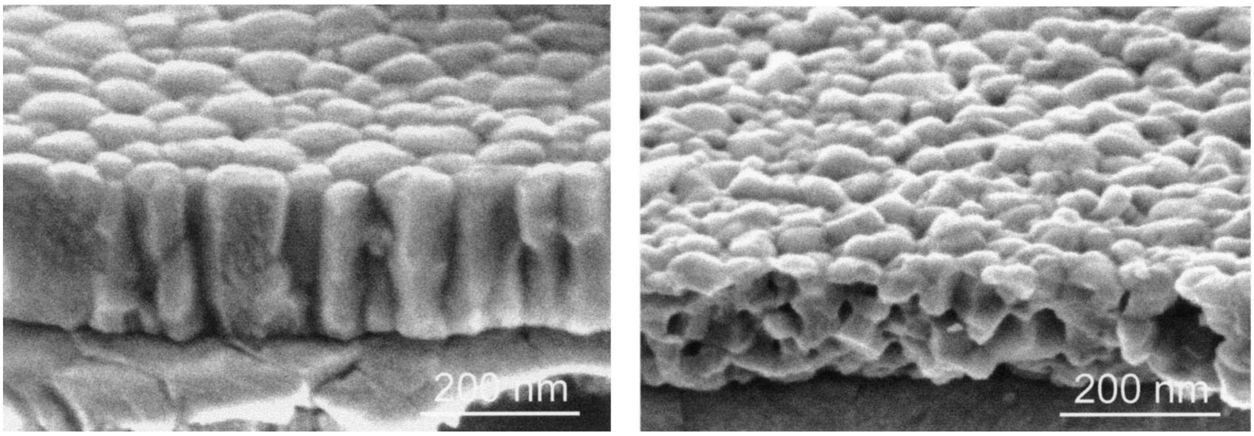

Fig. 3. SEM micrographs of the cross section and surface of two BaTiO$_3$ thin films prepared from propionate precursors; left film: 22 layers, 0·1 M solution; right film: six layers, 0·3 M solution.

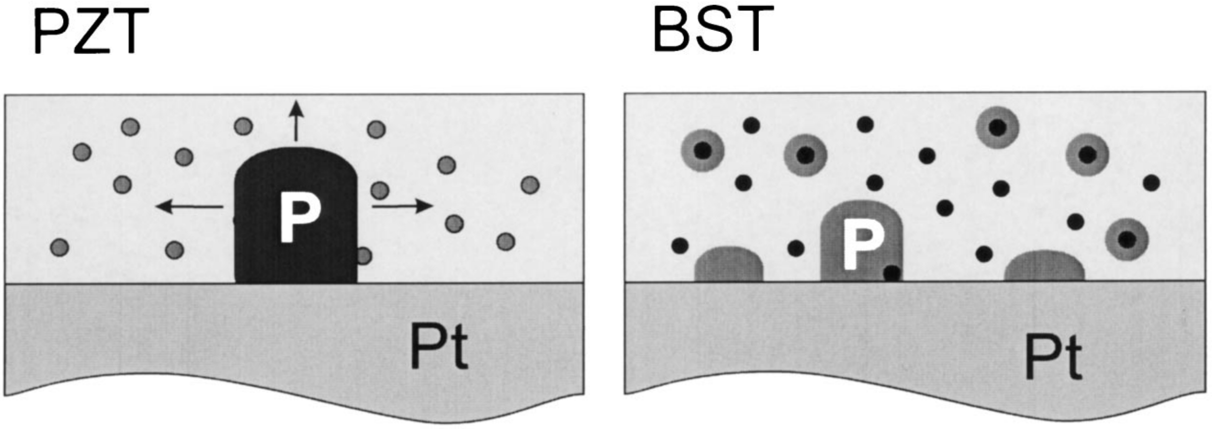

Fig. 4. Schematic pictures which illustrate the beginning of the crystallization in $(Ba,Sr)TiO_3$ compared to $Pb(Zr,Ti)O_3$ thin films.[4] The illustrations show an amorphous matrix with small grains of the intermediate phase inside. In the PZT film, the perovskite phase (P) nucleates at the substrate interface while in the BST film heterogeneous nucleation of the perovskite phase starts at the substrate and at the intermediate phase crystallites.

decrease in porosity. The XRD analyses showed that the columnar morphology induces a higher degree of oriented grains.[8] The columnar grown $SrTiO_3$ thin films exhibit a preferred (111) orientation which follows the (111) orientation of the Pt substrate. The heteroepitaxy of the $SrTiO_3$ grains on the Pt grains was confirmed by HR–TEM micrographs.[8] In contrast, the columnar structured $BaTiO_3$ grains exhibit a preferred (100) orientation. The columns were formed by island growth. At the $BaTiO_3$/Pt interface small grains were observed which were later overgrown by larger grains forming columns by in-grain epitaxy of the different $BaTiO_3$ layers.[8]

4 Mechanisms of the Crystallization Process in $(Ba,Sr)TiO_3$ Films

Following the idea which was introduced by Seifert *et al.*,[2] Lange,[3] Lefevre *et al.*,[4] and Schwartz,[5] the crystallization process in CSD derived thin films can be described by means of the glass crystallization theory. In general the crystallization is characterized by a competition between different crystallization events (i.e. the homogeneous nucleation within the amorphous matrix, and the heterogeneous nucleation at interfaces or at nucleation seeds inside the matrix), each with specific nucleation and growth rates.

Columnar grain growth in the thin films can only be achieved if the possibility for a single nucleation event at the substrate interface is favored over the other nucleation events. Regarding to the theory of glass crystallization heterogeneous nucleation can be favored over homogeneous nucleation by a lowering of the driving force for crystallization which can be achieved by increasing the crystallization temperature or by the influence of an intermediate phase.

In our $(Ba,Sr)TiO_3$ thin films columnar grains were obtained only for precursor solutions which transform to the perovskite phase via the intermediate alkaline earth-titanium-oxo-carbonate phase. Due to the delayed crystallization the driving force is lowered which results in a favoring of heterogeneous nucleation events. In contrast to the intensively investigated PZT thin films which crystallize via the intermediate fluorite phase and easily form columnar grains,[2–6] the BST films only exhibit a columnar grain growth for a small thickness (approx. 10 nm) of the crystallized layers.

According to our investigations[8] and the TEM studies of Gust[1] in comparison to the investigations performed on PZT films[2–6] we attribute the difference in the crystallization mechanism of the two systems to the different effects of the

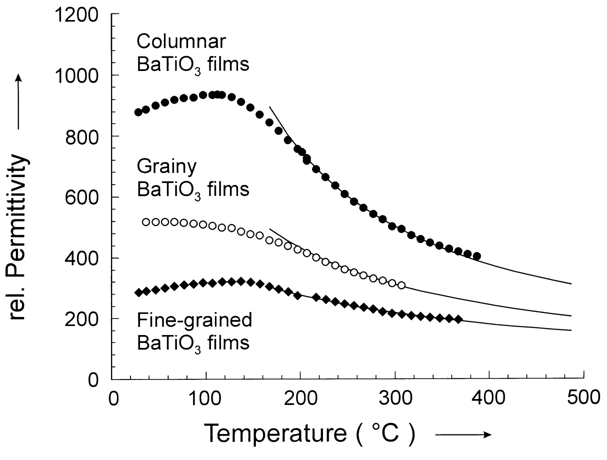

Fig. 5. Temperature dependence of the permittivity of CSD-prepared $BaTiO_3$ thin films (thickness approx. 200 nm) as a function of the film morphology. The measurements were performed on $Pt/BaTiO_3/Pt$ structures at 10 kHz with a 0·1 V signal.

intermediate phases on the nucleation of the perovskite grains (see Fig. 4). The fluorite grains do not act as nuclei for the PZT-perovskite grains[2,4] and therefore the favored nucleation event is the heterogeneous nucleation at the substrate interface. In contrast to this, the oxo-carbonate grains can act as nucleation seeds for the BST-perovskite grains[1] which results in a competition of heterogeneous nucleation events at the seed grains or at the substrate interface. Thus, kinetic aspects which are based on the nucleation and growth rates of the two different events control the film formation process in the BST system. The experimental results show that a tailoring of the BST film morphology can be achieved by influencing the kinetic factors via the deposition conditions, i.e. the control of solution concentration and heat-treatment.

5 Influence of the Thin Film Morphology on the Dielectric Properties

The dielectric measurements which are shown in Fig. 5 were performed on BaTiO$_3$ thin films with different morphologies grown on Pt-coated Si-substrates at temperatures of 750 °C.[12] The increase in the room temperature permittivity from 500 to 900 which is induced by the change in the morphology from grainy to columnar (compare Fig. 3) clearly emphasizes the necessity to control the film formation process.

6 Conclusions

SrTiO$_3$ and BaTiO$_3$ thin films with columnar morphologies were prepared on platinum coated Si substrates at temperatures of about 750 °C. The control of the morphology was performed by a dedicated tailoring of the precursor chemistry and the CSD deposition conditions. On the basis of the experimental results and the extension of the crystallization model for Pb(Zr,Ti)O$_3$ films[2–5] we were able to point out the relevant steps in the crystallization process of CSD-derived (Ba,Sr)TiO$_3$ thin films. Changing the morphology in BaTiO$_3$ thin films from grainy to columnar increases the permittivity at room temperature from about 500 to 900.

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