Crystallization Study of SrTiO₃ Thin Films

Prepared by Dip Coating

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In this study, the crystallization process of SrTiO₃ thin films, prepared by a chemical method, was characterized by Fourier Transformed Infra Red (FT-IR), Grazing Incident X-ray Diffraction (GIXRD), Thermal Analysis (TG) and X-ray Absorption Near Edge Structure (XANES). The results showed that an amorphous inorganic phase is formed, consisting of clusters of oxygen five-coordinate titanium. The amorphous phase begins crystallizing at temperatures above 450 °C. No intermediate crystalline phase and no preferential orientation was observed for films deposited on MgO (100). FT-IR results suggest the presence of the carbonate group. However, the low thermal stability of this group and the low crystallization temperature of the observed SrTiO₃ phase indicate that this carbonate is adsorbed.

1. Introduction

Ferroelectric thin films have been intensively studied due to the intense technological and scientific interest in their potential applications. Among the several thin film processing techniques, chemical methods such as sol-gel and Metalorganic Decomposition (MOD) have received special attention due to the possibility of strict stoichiometric control, the low deposition costs involved (simple deposition methods such as dip and spin coating can be used) and the large substrate area that can be covered. There are, essentially, three different types of sol-gel: colloidal sol-gel, inorganic polymeric gel derived from organometallic compounds and gel routes involving the formation of organic polymeric glass (polymeric precursor method). The polymeric precursor method, based on the Pechini process[1], has been successfully used to obtain ceramic powders[2-4] and ceramic thin films[5-7].

During the crystallization process of thin films chemically prepared by the polymeric precursor method, an intermediate inorganic amorphous phase is observed after the pyrolysis step[5-7]. As a consequence, the thin film crystallization process resembles the inorganic glass crystallization process. Recently, Schwartz *et al.*[8], using a standard glass nucleation approach, proposed a model in which the degree of orientation and microstructure of thin films prepared by MOD are correlated with the thermodynamic barrier to nucleation. They showed that a change in the crystallization driving force results in a microstructural modification due to the variation that occurs in the barrier heights for interface (film/substrate) and surface nucleation. In another recent paper, Gust *et al.*[9] showed that BaTiO₃ thin films prepared by sol-gel present an intermediate phase, presumably BaTiO₂.CO₃, that is subsequently transformed into BaTiO₃. Random nucleation in the film was observed for different substrates.

G. Braunstein *et al.*[10] studied the crystallization of SrTiO₃ thin films prepared by MOD[10]. They observed an intermediate crystalline carbonate phase and suggested that this phase delays crystallization and promotes a random nucleation process.

The objective of this work was to study the crystallization of SrTiO₃ thin films prepared by the polymeric precursor method. Preliminary studies[7] have shown that the SrTiO₃ phase crystallizes from an inorganic amorphous phase, with no crystalline intermediate phase, as observed during the powder synthesis[3]. Thus, this perovskite oxide might be a suitable material to investigate the crystal-

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lization of thin films prepared by chemical methods. This study may contribute to a better understanding of the crystallization of thin films prepared by sol-gel.

2. Experimental Procedure

2.1. Synthesis and deposition

The precursor solution was prepared by the dissolution of strontium carbonate in a aqueous titanium citrate solution, prepared from titanium isopropoxide. The molar ratio between titanium and strontium was 1.00 and the citric acid/metal ratio was set at 1.28 (molar ratio). Ethylene glycol was added to the citrate solution to promote polymerization between the titanium citrate and strontium citrate. The citric acid/ethylene glycol ratio was fixed at 40/60 (mass ratio). Figure 1 presents a flow chart for thin film preparation using the polymeric precursor method.

A polymeric solution with a viscosity of 7 mPa s was used for dip coating deposition. Prior to coating, the MgO (100) substrate was cleaned by immersion in a sulfochromic solution, followed by rinsing several times in deionized water. The dip coating was conducted by immersion of the cleaned MgO (100) substrate (1 cm x 1 cm) in the polymeric solution, followed by controlled withdrawal at a speed of 0.7 cm/min. After deposition, substrates were dried on a hot plate (~150 °C) and heat-treated at 325 °C for 8 h in an oxygen flow (pyrolysis step). After pyrolysis, the films were heat treated at different temperatures for 2 h (crystallization step).

2.2. Characterization

Phase evolution was characterized by GIXRD, using Cu Kα radiation with a grazing incident angle of $\alpha = 2°$ and LiF (100) as monochromator, and FT-IR in the transmission mode. The weight loss and pyrolysis behaviors of the gel-derived powders were studied by TG. The microstructure was characterized by transmission electron microscopy (TEM).

Ti K-edge XANES spectra were collected at the LNLS (Laboratório Nacional de Luz Sincrotron, Campinas, Brazil) facility using the EXAFS (Extended X-Ray Absorption Fine Structure) beam station. The LNLS storage ring was operated at 1.36 GeV and 60 - 100 mA. Data were collected at the Ti K-edge (4966 eV) in the total electron yield mode for thin film samples, and in the transmission mode for powder samples. The beam was monochromatized using a Si (111) channel-cut monochromator and the energy step was equal to 0.5 eV. The energy calibration of the monochromator was checked after each spectrum using a Ti metal foil to provide good energy reproducibility.

Crystalline powder samples were used as structural references: r-TiO_2 (rutile, a commercial powder standard). Solid state reaction was used for β-Ba_2TiO_4: $BaCO_3$ and TiO_2 were mixed in the stoichiometric amount required for
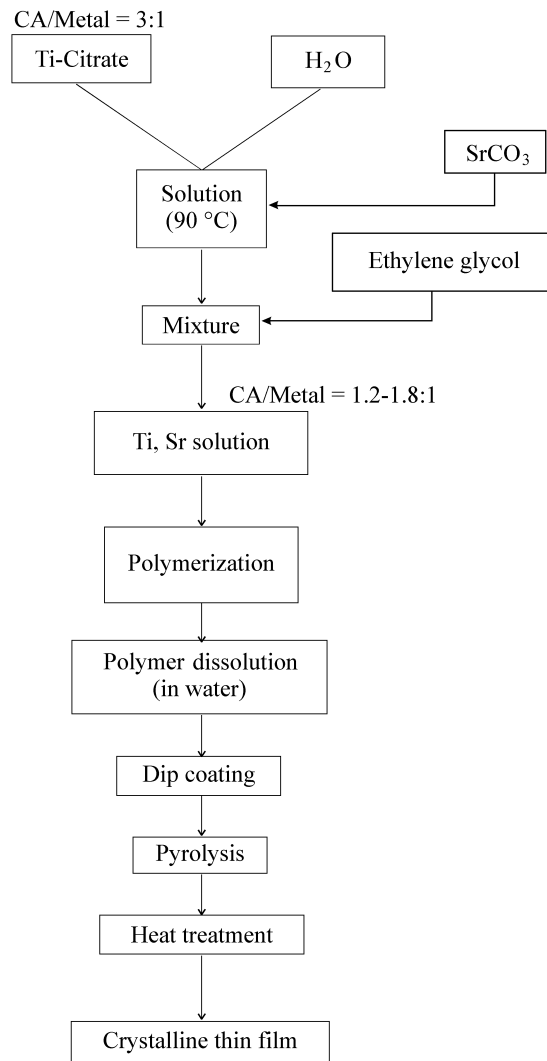
Figure 1. Flow chart for the preparation of $SrTiO_3$ thin film using the polymeric precursor method.

the desired phase and heat-treated at 1100 °C for 4h. $Ba_2TiSi_2O_8$ (fresnoite) was obtained from a glassy sample. $SrTiO_3$ were prepared by the polymeric precursor process.

The Ti atoms present coordination 6 in r-TiO_2 and coordination 4 in β-Ba_2TiO_4, while they are coordinated by 5 oxygen atoms in $Ba_2TiSi_2O_8$. The XANES experimental data were analyzed using the (XAS) programs of Michalowicz[11]. The XANES spectra were normalized to an edge jump of unity, after removal of the background absorption, by subtraction of a linear function extrapolated from the pre-edge.
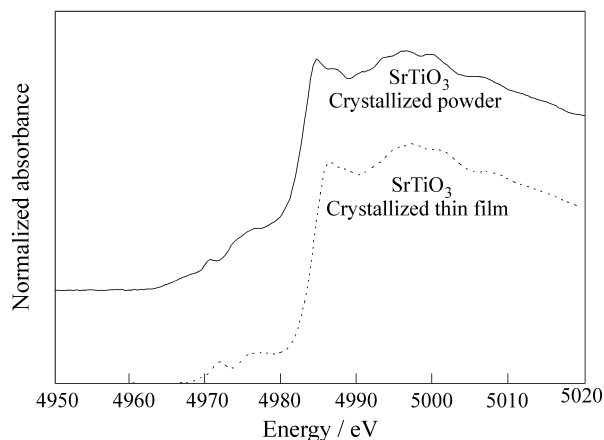
3. Results and Discussion

3.1. XANES results

Figure 2 presents the Ti K-edge XANES spectra of $SrTiO_3$ crystallized thin films compared to $SrTiO_3$ crystallized phase spectra, while Fig. 3 shows the Ti K-edge

XANES spectra of $SrTiO_3$ crystallized thin films compared to $SrTiO_3$ amorphous thin films. The pre-edge feature of a Ti K-edge XANES spectra located at approximately 4970 eV are usually attributed to energy level transitions from Ti 1s to the Ti3d/O2p molecular orbital[12-14]. Dipole selection rules forbid 1s → 3d transition (Laporte) but allow this when p-d orbital mixing occurs, as is the case when Ti is located in a TiO_4 tetrahedron or in a $(^{[5]}TiO)O_4$ site (*i.e.*, without a center of symmetry)[14]. The height and position of the pre-edge feature are direct functions of the degree of p-d mixing, site distortion and oxidation state[12-14].
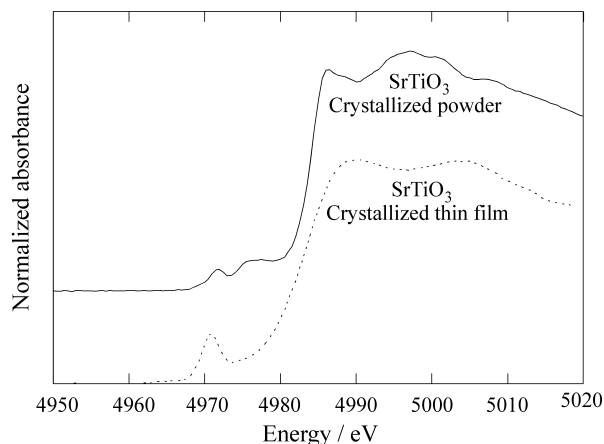
Qualitative information can be obtained from XANES spectra using model compounds. Farges[14] made an experimental study of the 1s → 3d transition as a function of Ti coordination ($^{[4]}$Ti, $^{[5]}$Ti and $^{[6]}$Ti). Based in the 1s → 3d energy position and normalized height, Farges obtained structural information of Ti atoms in crystalline and glassy fresnoites[14]. Using the information obtained by Farges and comparing the XANES spectra of $SrTiO_3$ compounds presented in Figs. 2 and 3, we were able to obtain qualitative information about Ti atoms in our samples.

The 1s → 3d energy position and Ti coordination number for model compounds are presented in Table 1. As can be observed, the position and height of the 1s → 3d transition depends on the Ti coordination number.

We then compared the 1s → 3d energy position of $SrTiO_3$ crystallized and amorphous powder samples and the 1s → 3d energy position of crystallized and amorphous thin films. The position of the 1s → 3d transition and the Ti coordination number for these four samples are also presented in Table 1. As can be observed, the crystallized thin film presents a similar Ti coordination when compared to the $SrTiO_3$ crystallized powder phase. A mixture of Ti atoms with coordination five and six was observed for these two samples. However, comparison of the crystallized thin film with the amorphous one showed a significant change
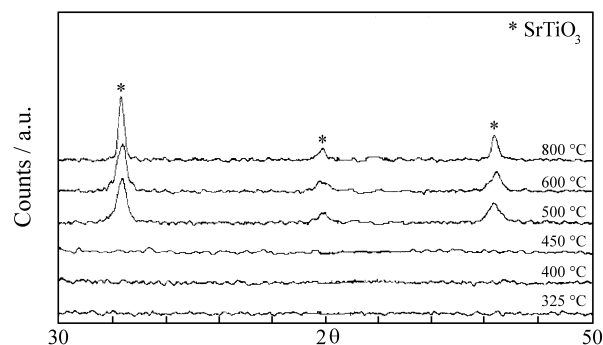
Figure 3. Ti K-edge XANES spectra of $SrTiO_3$ crystallized thin film compared to the $SrTiO_3$ amorphous thin films.

in Ti coordination. In the amorphous thin films most of the Ti atoms presented coordination five, with a small number of Ti atoms in coordination four and six. These primary results indicate that the coordination of the Ti atoms in the $SrTiO_3$ thin films depends on their physical state, *i.e.*, whether they are crystalline or amorphous.

3.2. Phase evolution and microstructure

Figure 4 presents GIXRD patterns of $SrTiO_3$ thin films on MgO (100) substrate heat treated at different temperatures for 2 h. At 325 °C a diffuse XRD pattern, related to an amorphous phase, is observed. The film remained in the amorphous state up to 450 °C. TG analysis up to 450 °C of the polymeric precursor, heat-treated at 325 °C for 8 h in an O_2 flow, showed no weight loss. This result suggests that the amorphous film, characterized by XANES and GIXRD, consists of an inorganic amorphous phase. At 500 °C we observed an XRD pattern of crystalline $SrTiO_3$ single phase. No preferential orientation is reported between 500 °C and 800 °C, which characterizes a polycrystalline thin film. Fig. 5 presents a TEM micrograph of the film heat treated at 600 °C. Well defined grain structure and crack free microstructure are observed. It is worth noting that no

Figure 2. Ti K-edge XANES spectra of $SrTiO_3$ crystallized thin film compared to the $SrTiO_3$ crystallized powder sample.

Figure 4. GIXRD patterns of $SrTiO_3$ thin film on MgO (100) heat treated at different temperatures.

Table 1. 1s → 3d transition position and Ti coordination number for the reference compounds (*) and for the SrTiO₃ samples.

Samples	1s → 3d Position (eV)	[4]Ti	[5]Ti	[6]Ti
*Ba₂TiO₄	4969.2	100	-	-
*Ba₂TiSi₂O₈	4970.5	-	100	-
*r-TiO₂	4971.3	-	-	100
SrTiO₃ crystallized powder	4970.8	0	< 40	> 60
SrTiO₃ amorphous powder	4970.1	≈ 30	≈ 40	≈ 30
SrTiO₃ crystallized thin films	4971.0	0	< 30	> 60
SrTiO₃ amorphous thin films	4970.5	< 10	> 90	< 10

intermediate crystalline phase, such as a carbonate phase, was detected by the GIXRD analysis. A carbonate intermediate phase was characterized by XRD during the SrTiO₃ powder synthesis using the polymeric precursor method[3].

Figure 6 presents the FT-IR spectrum of the film heat-treated at different temperatures. At 325 °C, only vibrations related to the carboxyl group (COO⁻) at 1620, 1402 and 1320 cm⁻¹ are observed. At 400 and 450 °C, the vibration at 1620 cm⁻¹ was not observed and the peak intensity at 1402 cm⁻¹ appeared to decrease. A weak broad peak at 1460 cm⁻¹ is observed at these temperatures. The peak at 1460 cm⁻¹ might be related to a carbonate phase (CO₃⁻² group). However, the carbonate phase identified by FT-IR during the SrTiO₃ powder synthesis, using the same method, showed a highly accentuated peak at 1450 cm⁻¹ [3]. Using FT-IR, Braunstein *et al.*[10] observed a carbonate peak at 1425 cm⁻¹ for SrTiO₃ thin film prepared by MOD, for samples heat treated at temperatures ranging from 500 to 600 °C. They observed the crystallization of the SrTiO₃ phase at temperatures above 700 °C. In our work, the peak at 1460 cm⁻¹ is not observed at temperatures above 450 °C. Hence, the broad peak observed in the amorphous thin film, associated with low thermal stability, is likely related to a non-structural CO₃⁻² group, *i.e.*, an adsorbed carbonate group.

3.3. General discussion

The experimental results showed that, during the crystallization process of SrTiO₃ thin films prepared by the polymeric precursor method, an intermediate inorganic amorphous phase was formed after the pyrolysis process. The XANES results showed that the amorphous phase is basically composed of small clusters formed by oxygen five-coordinated Ti (([5]TiO)O₄). Thus, during the transition from amorphous to crystalline, a significant transformation occurs in the Ti-O clusters, as indicated in reaction (1):

([5]TiO)O₄ {Amorphous}T > 450 °C →
                                   [6] TiO₆ {Crystal}   (1)
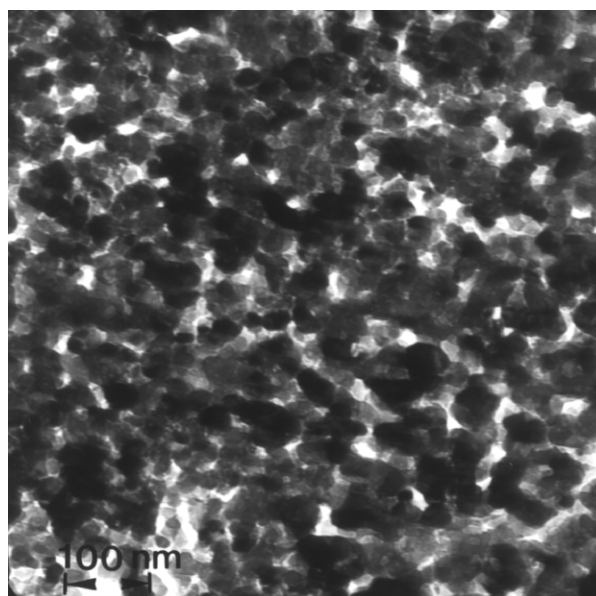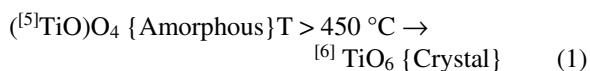
Figure 5. TEM micrograph of the SrTiO₃ thin film heat treated at 600 °C, 2 h.
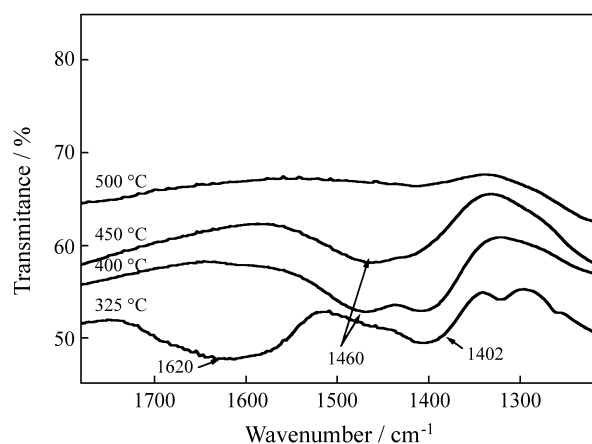
Figure 6. FT-IR spectra of a thin film heat treated at different temperatures.

As described in Eq. 1, the oxygen five-coordinated Ti in the amorphous state will transform into oxygen six-coordinated Ti (Ti in octahedral position) in the crystalline

state. Crystallization around 500 °C is close to the crystallization temperature of SrTiO$_3$ thin films amorphized by ion implantation[10] or prepared by physical vapor deposition (PVD)[16]. This low temperature crystallization is a strong indication that crystallization occurs directly from the amorphous state, with no intermediate phase involved.

The film remained in the amorphous phase up to 450 °C. The formation of a polycrystalline thin film, for films heat-treated at temperatures above 450 °C, suggests a nucleation process controlled by surface nucleation. This nucleation process will promote crystallization from the surface/film interface towards the film/substrate interface. Thus, no epitaxial growth is observed in the SrTiO$_3$/MgO(100) system.

4. Conclusion

These experimental results lead to the following conclusions: after the pyrolysis step, an inorganic amorphous phase is formed consisting of small clusters of oxygen five-coordinated Ti (([5]TiO)O$_4$); the amorphous phase begins to crystallize at temperatures above 450 °C, with no preferential orientation and with no intermediate crystalline phase; FT-IR results suggest the presence of what is probably an adsorbed carbonate group.

Acknowledgments

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