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The thermal decomposition of metal-organic precursors for epitaxial growth of $SrZrO_3$ thin films

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ABSTRACT

In this paper the thermal decomposition of strontium zirconate metal-organic precursor is investigated by thermal analyses coupled with quadrupole mass spectrometry, Fourier transform infrared spectroscopy and X-ray diffraction measurements. Based on these analyses the decomposition sequence of both individual, and final precursors has been proposed. Starting from this precursor, $SrZrO_3$ (SZO) epitaxial thin films have been deposited on (100)$SrTiO_3$ (STO) single crystalline substrates at a temperature as low as 700 °C, by chemical solution deposition (CSD). The SZO films have a (0 1 0)SZO/(1 0 0)STO out-of-plane epitaxial relationship, and a good surface morphology with a root-mean-square roughness of about 0.8 nm. The structural and morphological properties of the deposited films demonstrate that these precursors are suitable for the deposition by CSD of high quality SZO epitaxial films for applications, e.g. buffer layer for $YBa_2Cu_3O_{7-x}$ -based coated conductors fabrication.

Introduction

The perovskite zirconates have attracted considerable attention due to their good chemical and mechanical stability, high protonic conductivity merging into microelectronic device applications, such as: ferroelectric memories, IR piezoelectric sensors, micro-electromechanical systems, insulators [1]. Both barium, and strontium zirconates are well known for their use as thermal barrier [2]. Furthermore, $BaZrO_3$, as well as $SrZrO_3$ (SZO), can be successfully used as buffer layer in $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting architectures due to their structural and chemical compatibility with YBCO, and similar thermal expansion coefficients [3]. Generally, the buffer layer plays a crucial role in the superconducting architecture, by transferring the texture from the metallic substrate to the superconducting layer through epitaxy and by preventing the chemical reaction between the substrate and the YBCO layer. The most important characteristics of an optimum buffer layer are: a smooth surface morphology, good texture properties and a good crystalline compatibility with YBCO. SZO presents an orthorhombic structure with the *a* and *c* axes very similar, the difference being of only 0.4%. The lattice mismatch between SZO and YBCO is about 7%.

It is generally agreed that the chemical solution deposition (CSD) technique represents a successful tool for thin film processing. The CSD method is very promising since it fulfils the requirements for the fabrication of functional oxide thin films even at industrial level (versatility, low vacuum, inexpensiveness, high deposition rate, easy control of the stoichiometry etc.) [1,4]. Metal-organic deposition (MOD), as an alternative of the CSD method, uses metal alkoxides, carboxylates (acetates, trifluoroacetates, propionates, and naphthenates) and acetylacetonates as precursors [1,5–12]. The use of polar solvents with free hydroxyl group (e.g. propionic acid) improves the wetting properties of the coating solution, avoiding the use of toxic solvents, and reduces the annealing temperatures [13]. The thermal decomposition of the carboxylic acids yields symmetrical ketones with simultaneous release of CO_2 and H_2O [14]. An important step towards good quality films obtained by CSD consists in the understanding of the decomposition processes of the film precursors. The thermal analyses techniques are widely used to study the decomposition and crystallization processes. Recent studies have shown that thin films behave significantly different from powders [15]. Although the substrate obviously plays a crucial role in the thermal decomposition, and the structural evolution of the thin film material, most of the studies have focused on the precursor powders, and not on the deposited films as a consequence of the extremely low film/substrate mass ratio and, therefore, a low signal [16–18].

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In this paper we report on the synthesis, characterization, and thermal decomposition of the metal-organic precursors for the epitaxial SZO thin films growth. To the best of our knowledge, the thermal decomposition of the precursor powder, as well as the epitaxial growth of the SZO thin films using acetates and acetylacetonates as starting reagents, have not been reported. Thermogravimetry analyses coupled with mass spectrometry were used in order to monitor the decomposition process accompanied by the evolvement of fragments formed during annealing. The individual precursor and the final precursor powder, as well as the intermediate products were analysed using X-ray diffraction, and FTIR spectroscopy analyses. The thermal decomposition of the strontium and strontium zirconate precursors has been studied. In order to demonstrate the potential of these precursors, epitaxial SZO thin films have been grown on (100)$SrTiO_3$ single crystalline substrates. The as-deposited films exhibit good structural and morphological properties demonstrating that the precursors are suitable for the deposition by CSD of high quality SZO epitaxial films for applications.

2. Experimental

The SZO coating solution was prepared starting from strontium acetate and zirconium acetylacetonate (Alfa Aesar, 99.99%) reagents. The zirconium acetylacetonate was simply dissolved in an excess of propionic acid, while the strontium acetate was separately dispersed in methanol, an excess of propionic acid was added and further treated with ammonia until the solution became clear. The two solutions were mixed together in stoichiometric ratio under stirring and concentrated by distillation under vacuum (42 mbar, bath temperature 75 °C) for the removal of solvent excess. The precursor powders have been obtained by drying the precursor solutions on a hot plate at 80 °C. The $SrZrO_3$ SZO coating solution with a total metal concentration of 0.2 M was spun on (001)$SrTiO_3$ substrates at a spinning rate of 2500 rpm for 60 s. The dried films were heat treated in air at 700 °C for two hours.

To study the solution chemistry and the phase evolution, thermal analyses coupled with quadrupole mass spectrometry and Fourier transform infrared spectroscopy (FTIR) correlated with X-ray diffraction on powders, were used. The thermal analyses were performed from ambient temperature up to 1000 °C, at a heating rate of 10 °C/min, under air atmosphere using an upgraded computer controlled equipment. The TG-DTA has been hyphenated with a quadrupole mass spectrometer QMS 200 atmospheric sampling system (Residual Gas Analyzer RGA-Stanford Research System) with a ionization potential of 70 eV and a detection mass region of $m/z = 10–90$. The structural properties of the SZO thin films were investigated by X-ray Diffraction (XRD) analyses using a Bruker D8 Discover diffractometer with the Cu Kα1 radiation. Atomic Force Microscopy (AFM) using a Veeco D3100 atomic force microscope was used for the investigation of the film morphology.

3. Results and discussion

3.1. Individual precursor characterization

The individual zirconium and strontium precursors have been studied in order to elucidate the thermal decomposition behavior of the final SZO precursor powder for the epitaxial thin films growth. The overall thermal decomposition of the zirconium precursor, which was studied in our work [19], takes place in three main stages. During the thermal treatment, the evolvement of the fragments with $m/z = 18$, 44 and 57 characteristic for H_2O, CO_2 and 3-pentanone $CH_3CH_2COCH_2CH_3$ were observed. By correlating the TG-MS with the X-ray diffraction measurements on the zirconium precursor powder heat treated at different temperatures [19], the thermal decomposition sequence was established. The precursor formula, $Zr_6O_4(OH)_4(CH_3CH_2COO)_{12}\cdot 11H_2O$, calculated from the thermogravimetrical curve, is in good agreement with the molecular structure, as determined from the X-ray diffraction analysis performed on the single crystal [19].

The evolution of the zirconium oxo-hydroxypropionate complex with temperature was studied by XRD analysis by quenching the powder at different temperatures. It was observed that at 400 °C the precursor powder is in amorphous state. Increasing the temperature up to 700 °C, the XRD diffraction pattern indicates the presence of $ZrOCO_3$ tetragonal phase. The temperature range 300–700 °C corresponds to the thermal decomposition of the zirconium oxo-hydroxypropionate precursor into the $ZrOCO_3$ phase. The decomposition of the $ZrOCO_3$ into ZrO_2 is confirmed by the XRD pattern of the sample heated up to 1000 °C.

Similar to the zirconium precursor, the thermal decomposition of the strontium precursor (Fig. 1a) occurs in three main stages. In the first stage, up to a temperature of 200 °C, the dehydration of the precursor powder takes place, and is accompanied by a weight loss of 11%. The second stage, from 200 to 600 °C, covering two partially overlapping decomposition stages, corresponds to the thermal decomposition of the strontium acetate-propionate precursor into the $SrCO_3$ phase. In the FTIR spectra of the strontium precursor annealed at different temperatures (Fig. 1b) the presence of $SrCO_3$ is evidenced by the existence of the $CO_3{}^{2-}$ group at temperature as high as 750 °C. The FTIR spectrum of the precursor powder (23 °C) indicates the presence of strontium-oxygen bonds at 595 cm^{-1}.

The MS analysis (Fig. 1a) has revealed that the evolved gases correspond to fragments with $m/z = 57$, 43 characteristic for 2-pentanone ($CH_3COCH_2CH_2CH_3$), $m/z = 58$ for acetone (CH_3COCH_3), and $m/z = 44$ for CO_2. The last stage corresponds to the transformation of the $SrCO_3$ into SrO and is accompanied by the evolvement of CO_2, confirmed by the MS analysis at temperatures higher than 850 °C. The total conversion of the strontium acetate-propionate into $SrCO_3$ (23–850 °C) corresponds to a weight loss of 40% and fits the theoretical value taking into account the following precursor formula: $Sr(CH_3COO)(CH_3CH_2COO)\cdot 1.5H_2O$. This precursor formula, as calculated from the thermogravimetric curve, is in good agreement with the TG-MS analyses. It is to be mentioned that the same precursor-type was observed in the case of the thermal decomposition of the barium precursor where the same salts and solvents were used [8].

By correlating the TG-MS analyses with the FTIR spectra the thermal decomposition of the strontium precursor takes place as follows:

$$3Sr(CH_3COO)(CH_3CH_2COO)\cdot 1.5H_2O \rightarrow 3Sr(CH_3COO)(CH_3CH_2COO) + 4.5H_2O \quad (1)$$

$$3Sr(CH_3COO)(CH_3CH_2COO) + 5.5O_2 \rightarrow 3SrCO_3 + CH_3COCH_3 + CH_3COCH_2CH_2CH_3 + 4CO_2 + 4H_2O \quad (2)$$

$$3SrCO_3 \rightarrow 3SrO + 3CO_2 (> 850\,^{\circ}C) \quad (3)$$

The overall decomposition reaction can be written as:

$$Sr(CH_3COO)(CH_3CH_2COO)\cdot 1.5H_2O + 5.5O_2 \rightarrow SrO + 5CO_2 + 5.5H_2O \quad (4)$$