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Process optimization and characterization of thin films of SrFeO_{3-x} by the pechini method

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Abstract Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique physical-chemical properties. Highly sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings, making them attractive for various industrial applications. In this report we describe our efforts at developing methodology for the fabrication of SrFeO_{3-x} based thin films using a modified Pechini method. Thin films of SrFeO_{3-x} were fabricated using spin coating and a drop coating method developed in-house on Al_2O_3 and Si- substrates. The films annealed at 600°C for one hour show a perovskite phase. The grain size increases with increase in annealing temperature. The influence of various variables such as metal to chelant ratio, drying control reagents, calcination conditions, substrate type and mode of film formation were studied using XRD, optical microscopy, SEM and AFM.

Keywords Perovskite · SrFeO_{3-x} · Thin films, Pechini method · XRD · SEM · AFM

1. Introduction

The discovery that the adsorption of gas on the semiconductor surface causes a significant change in the

electrical resistance of the material [1] initiated the development of commercial gas sensors based on semiconductors whose surface properties are very sensitive to changes in the gas atmosphere. Gas sensors based on thick-film semi-conducting metal oxide materials deposited on ceramic heater substrates are commercially available [2–4]. However, the disadvantage of thick-film devices is their high level of heating power consumption. Thin film technology has the potential to reduce this power consumption to acceptable levels as well as to improve upon sensor sensitivity and selectivity.

SrFeO_x [5–8] and other perovskites based on the $\text{SrFe}_y\text{Co}_{1-y}\text{O}_x$ ($0 \leq y \leq 1.0$; $2.5 \leq x \leq 3.0$) system [9, 10] are mixed ionic electronic conductors in which the reversible oxygen non-stoichiometry may be exploited for gas sensor applications. These materials undergo reversible phase transitions from the conductive cubic perovskite structure to the much less conductive brownmillerite structure. The phase transitions are very sensitive to temperature and gas composition [9, 10], thus providing the basis for a highly sensitive sensor material. It is important to tailor the micro and nano structure of metal oxide gas sensor materials in order to fully optimize their sensitivity, selectivity and response speed [11–14]. Specifically, nanocrystalline metal oxide thick films have been shown to exhibit enhanced sensitivity and selectivity for detection of such gases as CO , H_2 and others. Our previous investigations [7–10] on the sensor applications of perovskite materials involved fabrication of thin films of these materials by pulsed laser deposition (PLD) method using materials synthesized by the solid-state reaction at high temperatures of the corresponding binary metal oxides or carbonates. Low-cost solution methods permit the lowering of the preparation temperature and to improve homogeneity and reproducibility of the material, with the synthesis of porous, ultrafine and chemically pure materials of mixed

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metal oxides at low temperatures. An added advantage of solution methods is the capability of direct fabrication of thin films on various substrates using precursor solutions. Among the different chemical routes, the sol-gel method based on the Pechini-type reaction has received considerable attention because of its relatively simple synthesis scheme.

Although the Pechini process has been used in many studies to synthesize high surface area powders [15, 16], there are only a few studies using the Pechini process to deposit thin films [17]. The Pechini process offers several advantages over other techniques for processing of ceramic thin films, including low cost, good compositional homogeneity, high purity, and relatively low processing temperatures [18, 19]. In this study, a modified Pechini process is developed to prepare a thin, dense, conductive SrFeO_{3-x} based film on alumina and silicon substrates. Several important processing parameters, such as the ratio of citric acid to metal ions, drying and calcination temperatures, drying control reagents and film depositions methods are examined to optimize the quality of ceramic thin films derived from solutions. The film surface and surface morphology were characterized by XRD, optical microscopy, SEM and AFM.

2. Experimental methods

2.1. Materials

All reagents were obtained from Aldrich and used as-received. The purity of the iron (III) nitrate and strontium nitrate starting materials were greater than 99.9% (metals basis). Iron and strontium salts were stored and handled in an inert dry box under argon. Silicon with a 1 μm thick thermally grown SiO_2 layer and alumina were used as substrates for this investigation. The silicon substrate was obtained as 4 inch (111) oriented single side polished Si wafer from University Wafers, USA (www.universitywafers.com). Alumina substrate was obtained from CeramTec AG, Germany, [RUBALIT® 710 (99.6% Al_2O_3); median grain size, $d_{50} = 2 \mu\text{m}$; surface roughness, $R_a = 0.1$]. The wafers were cut into small pieces (1 cm $\times$ 1 cm). Before applying thin films, the substrate wafers were sonicated in CCl_4 for 15 min and rinsed with 2-propanol and water. They were then sonicated in a hot piranha solution of conc. H_2SO_4 and 30% H_2O_2 (3:1) for 30 min to remove any organic matter, rinsed with copious amount of water and dried at 150°C.

2.2. Preparation of SrFeO_{3-x}

A modified Pechini method [20, 21] was used to prepare SrFeO_{3-x} . Analytically pure (99.9%) metal nitrates,

$\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were precisely weighed at the stoichiometric ratio of iron to strontium of 1:1 under argon in a dry box and then dissolved in distilled water with stirring. After the complete dissolution of the added salts, citric acid was added and dissolved by stirring so that a specific molar ratio of citric acid (CA) to total metal ions ($\text{Fe} + \text{Sr}$) was achieved. This ratio (R_a) is defined as $R_a = \text{CA}/(\text{Fe} + \text{Sr})$. The pH of the resultant metal citrate solution was adjusted to a desired range by adding dilute ammonia solution drop-wise. The solution was heated in a water bath while stirring with a magnetic stirrer to obtain a viscous solution. At this stage, ethylene glycol was added in a molar ratio of ethylene glycol (EG) to citric acid of $\text{EG}/\text{CA} = 1.2$. Heating and stirring was continued until the desired viscosity was obtained for thin film applications (Concentration: $\sim 20 \text{ mg metals/mL}$ of coating solution). Concentrated solutions were diluted with ethylene glycol monomethyl ether ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) to achieve the appropriate concentration and viscosity for deposition of smooth films. A few drops of formamide were added to this solution in order to control cracking during annealing of the thin film coatings on the substrates [22].

2.3. Film deposition

The deposition of films on the substrate was attempted by spin-coating, dip-coating and a drop coating technique developed in house. Dip coating was found to result in the poorest adhesion and was therefore not pursued further. Instead, the process was modified slightly by applying 2 drops of starting solution to the substrate pre-heated at 110°C. The solvent was evaporated at 110°C, leaving behind a thin light brown coating. It was fired at 500°C for 30 min followed by calcination at 600°C for 1 h in air. This is referred to as the drop coating technique. Spin coating was carried out at 500 rpm and 1000 rpm for 15 sec followed by at 5000 rpm for 60 sec in air. After each coating, the film was dried at 110°C for 30 min in air and pre-fired at 500°C for 30 min in air. The process was repeated 3 times to prepare a thicker layer. The films studied were typically $\sim 2 \mu\text{m}$ thick, which was confirmed by weight gain and by observation of the fracture cross section of the films using scanning electron microscopy (SEM). Final annealing was carried out in air at 600°C for 1 h. Greater than three applications normally resulted in the cracking of the resulting films because repeated thermal cycles during processing resulted in thermal stresses.

2.4. Measurements

X-ray powder diffraction data were collected between $20^\circ \leq 2\theta \leq 80^\circ$ with a scan rate of $2^\circ/\text{min}$ at room temperature on a Scintag XDS 2000 with a theta-theta geometry

and a copper X-ray tube. The diffractometer had a pyrolytic graphite monochromator in front of the detector. The samples were mounted on a zero background sample holder made of an oriented silicon wafer.

The surface morphology of the thin films was investigated using atomic force microscopy, AFM (Digital Instruments Nanoscope III AFM operating in air in the contact mode) and scanning electron microscopy, SEM (JEOL model JSM-5300).

3. Results and discussion

Solution based thin film technologies offer several advantages such as low cost of production, higher reliability and introduction of catalysts or doping levels to enhance the sensitivity or selectivity. SrFeO_{3-x} based films were successfully prepared on Al_2O_3 and Si wafers by a previously optimized Pechini method [21] using spin coating or a drop coating technique developed in-house. The conditions for achieving smooth surface and minimum porosity included: preheating of the substrate, use of formamide as a drying control reagent and optimal solution viscosity. The film thickness is known to have a great influence on the sensor detection sensitivity of metal oxides [23]. The control of film thickness using spin coating was easier on alumina substrate compared with Si-substrate. For Si-substrates a drop coating technique developed in-house was found to give better results compared with spin coating. With spin coating, most of the solution applied to the substrate was swept away requiring several applications to achieve the desired film thickness. The successive application of coatings on the substrate followed by annealing led to cracking. The dropwise application of the precursor solution on the preheated Si-substrate lead to a slower spread and a thicker film thus requiring fewer applications compared with spin coating.

The adhesion of the heated films to the Al_2O_3 substrates was much better compared to the Si substrates. Unfired films were easily scratched and could be removed from the substrates by scraping. Films heated to a temperature of $T > 300^\circ\text{C}$ were not removed or damaged by limited physical abrasion.

3.1. Structure (XRD)

The XRD pattern for the SrFeO_{3-x} film on Si (100) substrate is shown in Fig. 1(a). The diffraction pattern of the SrFeO_{3-x} powder prepared by the solid state method at 1100°C is shown in Fig. 1(b) for comparison. All the main diffraction peaks belonging to SrFeO_{3-x} are observed in the 2θ scanning range from 20 – 80 , implying that the SrFeO_{3-x} film is single phase with cubic structure.

Fig. 1 XRD patterns for SrFeO_{3-x} : (a) a thin film on a Si substrate; (b) Powder prepared by solid state method at 1100°C

3.2. Microstructural Characterization (SEM, AFM)

Figure 2 shows SEM micrographs of SrFeO_{3-x} thin films deposited on Si and Al_2O_3 substrates and annealed at 600°C . The EDS analyses of the films suggested that the chemical composition was close to that of the desired phase (SrFeO_{3-x}). The molar ratio of citric acid to total metal cations (R_a) affected the adhesion of the heated film to the substrates. With R_a values lower than 3 the adhesion was extremely poor and consequently the films cracked. This is demonstrated by the micrograph shown in Fig. 2(a) representing sample with a R_a value of 1. The optimum value of R_a was found to be between 3 and 4. Subsequent tests were carried out using R_a value of ~ 4 . Because of the adhesion problems on Si substrates associated with spin coating technique, a drop coating technique was developed in-house. Compared with spin coating method drop coating method resulted in much denser films as seen from a comparison of Figs 2(b) (drop coating) and 2c (spin coating). Thicker films as shown in Fig. 2(d) were non-homogeneous with some cracks. The micrograph shown in Fig. 2(e) represent a film prepared using a solution of well characterized powder sample of SrFeO_{3-x} dissolved in an aqueous solution of citric acid. This appears to be clusters of small platelets with some porosity. Figure 2(f) is a typical micrograph for a thin film (film thickness: $\sim 1\ \mu\text{m}$) of SrFeO_{3-x} deposited on an alumina substrate. The microstructure indicates a mono-phase constitution with packed grains in the size range of 50 – $150\ \text{nm}$.

3.3. AFM

Figure 3(a) and (b) are the images of AFM, which show the surface morphology of SrFeO_{3-x} films grown on silicon and alumina substrates respectively. The film morphology on both substrates appears to be similar. The grains are small and have a rather uniform size distribution (~ 30 – $50\ \text{nm}$).

Fig. 2 SEM micrographs of SrFeO_{3-x} films on Si- (a–e) and Al_2O_3 (f) substrates: (a) Spin coating; Ra value in the precursor solution: 1 (film thickness $\sim 2.8 \mu\text{m}$) (b) Drop coating; Ra: 4 (film thickness $\sim 500 \text{ nm}$) (c) Spin coating; Ra: 4 (film thickness $\sim 500 \text{ nm}$) (d) Drop

coating; Ra: 4 (film thickness: $\sim 2 \mu\text{m}$) (e) Precursor solution prepared by dissolving SrFeO_{3-x} powder in citric acid, drop coating; Ra: 4 (film thickness $\sim 1 \mu\text{m}$). (f) Al_2O_3 substrate, spin coating; Ra: 4 (film thickness $\sim 1 \mu\text{m}$)

The thin films exhibit a granular structure indicating their crystalline structure. The morphologies suggest that films are mostly crack free within the viewing area and the grains are dense and homogeneously distributed.

4. Conclusions

SrFeO_{3-x} perovskite thin films were fabricated by a modified Pechini process using spin coating and drop coating

Fig. 3 AFM images of films on: (a) silicon and (b) alumina substrates

methods developed in-house on Al_2O_3 and Si-substrates. The films annealed at 600°C for one hour show a perovskite phase and dense microstructure with a smooth surface. The conditions for achieving a continuous smooth surface with minimum porosity included: preheating of the substrate, use of formamide as a drying control reagent, Ra value of >3 and optimal solution viscosity. The control of film thickness using spin coating was easier on an alumina substrate compared with a Si substrate.

A single application of the optimal viscosity solution yielded better results than successive coating applications on the substrate which resulted in cracking. Repeated thermal cycles during processing for successive coatings generated thermal stresses responsible for cracking in the film.

The adhesion of the heated films to the Al_2O_3 substrates was much better than to the Si-substrates. Unfired films were easily scratched and could be removed from the substrates by mechanical scraping. Films heated to a temperature of $>300^\circ\text{C}$ were not removed or damaged by limited physical abrasion.

The molar ratio of citric acid to total metal cations (Ra) affected the adhesion of the heated film to the substrates. With Ra values lower than 3 the adhesion was extremely poor and resulted in crack formation.

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