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Effect of annealing temperature on the crystallization and oxygen sensing property of strontium titanate ferrite sol–gel thin films

Chee Lap Chow [a,*], Hui Huang [a], Wan Chia Ang [a], Hai Liu [b], Yizhong Huang [b], Man Siu Tse [a], Ooi Kiang Tan [a]

[a] School of Electrical and Electronics Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
[b] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

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ABSTRACT

$SrTi_{0.6}Fe_{0.4}O_{3-\delta}$ (STF40) gas sensors were deposited using a novel modified sol–gel route. The influences of thermal annealing (400–750 °C) on the crystallization and oxygen sensing performance were investigated. As revealed by XRD, TEM and XPS studies, the deposited sol–gel thin films had amorphous structure and the formation of cubic perovskite phase started at 450 °C. The crystallization of the films improved with annealing temperature and completed at around 650 °C. The oxygen sensing characterization of the film sensors were carried out using a custom-designed gas sensing characterization system. Abnormal n-type oxygen sensing response was observed for the sensors annealed at 400 and 450 °C, which was found attributed by the n-type amorphous phases that remained in the sol–gel films. On the other hand, good and repeatable p-type oxygen sensing response was obtained for sensors annealed at 500 °C and above.

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1. Introduction

With the increasing awareness and concerns on the importance of the environmental protection and pollution control, research activities in the area of gas sensors have attracted a lot of attention in recent years. Among all the sensors technologies, semiconductor metal oxide gas sensors are probably the most investigated and commonly applied due to their relatively simple design, low cost, ease of fabrication, resistance to severe condition and high sensitivity [1–3]. Some commonly used semiconductor metal oxides for gas sensing applications are tin oxide, zinc oxide, indium oxide, titanium oxide and iron oxide. These are relatively simple binary metal oxides and are normally n-type semiconductors. Other promising materials for gas sensing application are ternary oxide and complex metal oxides. Among these, perovskite oxides with ABO_3 structure have been reported as gas sensors material due to its attractive properties such as excellent gas sensitivity, mixed ionic-electronic conductivity, excellent doping flexibility, ability to accommodate large amount of dopants and defects, high melting and/or decomposition temperature [4,5].

Strontium titanate ferrite ($SrTi_{1-x}Fe_xO_{3-\delta}$ or STFx in short) is a continuous solid state solution between the two end members, strontium titanate ($SrTiO_3$) and strontium ferrite ($SrFeO_3$). Due to the difference in their preferential oxidation states (+4 for Ti and +3 for Fe), oxygen vacancies are formed to maintain charge balance in the system. This inherent non-stoichiometry makes STFx highly sensitive to oxygen partial pressure (pO_2) and an excellent potential candidate for oxygen sensors [6]. More importantly, the discovery of negligible resistance dependency on temperature between 700 and 900 °C for STF35 ($x = 0.35$) has opened a new chapter for its applications in automotive oxygen sensors [7]. Also, Moos et al. reported that the introduction of doping into STFx can tailor the pO_2 range of negligible temperature dependence of resistance [8]. In the past decade, a lot of great research works were reported on the preparation techniques, electrical properties, gas sensing mechanisms and defect chemistry of STFx materials [9–15].

In this study, STF40 ($x = 0.4$) thin films were deposited using a novel modified sol–gel spin-coating method and the sensing properties to oxygen were studied. Sol–gel process is an attractive alternative to other method for synthesis of ceramic due to its advantages such as simple equipment to be used, thin film formability, easy control of composition and good homogeneity. Moreover, nanosized sensing material could be produced since lower synthesis temperature was expected compared with the conventional high-temperature solid state reaction. The physical properties of the thin films were studied using X-ray diffraction (XRD), field-emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). The effect of thermal annealing temperature on the crystallization and oxygen sensing response was evaluated and discussed.

* Corresponding author. Tel.: +65 6790 6537; fax: +65 6793 3318.
E-mail address: chow0059@e.ntu.edu.sg (C.L. Chow).

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2. Experimental

2.1. Material preparation

Strontium acetate (Nacalai Tesque), titanium butoxide (Aldrich, 97%) and iron nitrate (Merck, 99%) were used as starting materials. Iron nitrate was dissolved in solvent 2-methoxyethanol (Sigma–Aldrich, 99.8%), then heated at 60 °C and stirred with acetylacetone (Merck, 99%) in a molar ratio of 1:6, which acted as a chelating agent. Titanium butoxide was mixed with proper amount of acetylacetone (1:4 molar ratio) and heated separately at 60 °C. Then, Ti and Fe solutions were mixed together and stirred continuously without heating to obtain a well-homogenized Ti + Fe solution. At the same time, strontium acetate was dissolved in glacial acetic acid at around 60 °C. Proper amount of deionized water was added to promote the dissolution process. Too high an amount of deionized water would cause precipitation in the sol–gel. The Sr solution was then mixed with the prepared Ti and Fe solutions to form STF40 sol. Finally, 2-methoxyethanol was added as solvent to adjust the molarity and viscosity of the sol. The as-prepared sol was left overnight for one day to allow for sufficient hydrolysis.

The gold interdigital electrodes (25 μm line/25 μm spacing) were deposited on the Si/SiO_2 wafer using the photolithography metal lift-off process. The STF40 sol was spun on the wafer substrate with gold interdigital electrodes using spin coater (Laurell Technologies) in a fume hood chamber with constant 10% humidity. Each deposited sol layer was then baked at 150 °C followed by 300 °C for 5 min each. Five spin-coated layers STF40 thin films were obtained and fabricated into gas sensing devices. The final devices were annealed at 400–750 °C for 1 h under synthetic air ambient with a flow rate of 1 slm using Lindberg tube furnace. Fig. 1(a) and (b) shows the schematic structure and the optical image of the STF40 film sensor, respectively. The final annealed film thickness was around 90 nm as measured from FESEM cross-sectional images.

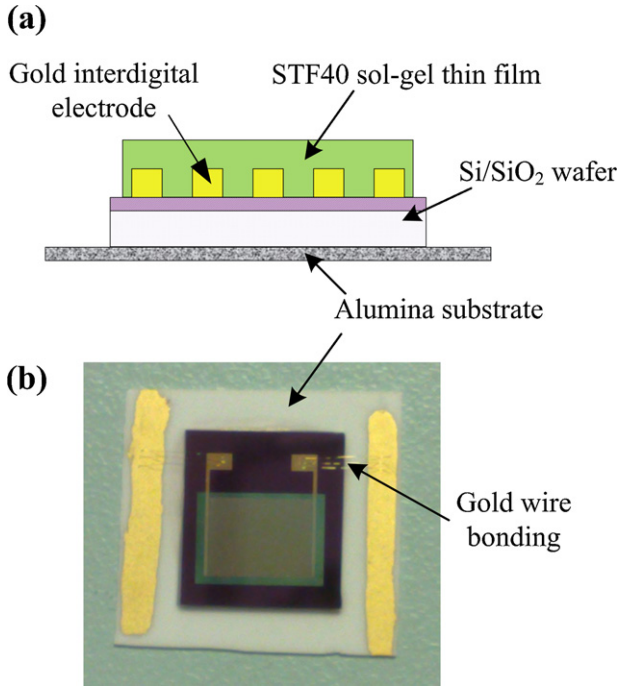

Fig. 1. (a) Schematic structure of STF40 film sensor, (b) optical image of STF40 film sensor.

2.2. Material and device characterization

The crystallography of the STF40 thin films was studied using XRD measurements. The XRD patterns were recorded at room temperature using Siemens D5005 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 40 mA. The surface morphologies of the thin films were observed using FESEM (Jeol-6340F). The thin film TEM samples were prepared using focused ion beam technique (FEI Nova 600i) and the microstructure of the thin films was analyzed using a transmission electron microscope (JEOL 2010) operating at 200 kV. XPS characterization was carried out using a Kratos AXIS spectrometer with monochromatic Al K_α (1486.6 eV) X-ray radiation powered at 150 W. The base pressure in the sample analysis chamber was set to less than 1×10^{-8} mbar. To minimize the charging effects, a low energy electron flood gun was used as charge neutralizer. The survey spectra (pass energy of 160 eV) in the range of 0–1200 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra (pass energy of 40 eV) over different element peaks in 0.1 eV steps.

The oxygen sensing properties of the sensing devices were carried out with the Keithley 236 source measurement unit in a custom-designed gas-sensing characterization system programmed with the National Instruments' LABVIEW version 8.5. The sample mount test gas chamber was designed to strategically position the sensing device, on the heater stage in the gas chamber with electrical feed-through, under the direct influence of the test gas flow. Oxygen sensing response of STF40 sensing devices with different annealing temperatures were characterized at different operating temperatures (150–300 °C) and oxygen concentrations (1–100%).

3. Results and discussion

3.1. Material characterization

A detailed crystallography study was carried out using XRD to investigate the phase formation at different annealing temperatures. Fig. 2 illustrates the XRD patterns for as-deposited STF40 thin film and thin films annealed at different temperatures of 400, 450, 550, 650 and 750 °C for 1 h. No significant phase existed for the as-deposited film and film annealed at 400 °C. For films annealed at 450 °C and above, the main peaks observed coincided with the standard pattern of STFx materials with cubic perovskite structures

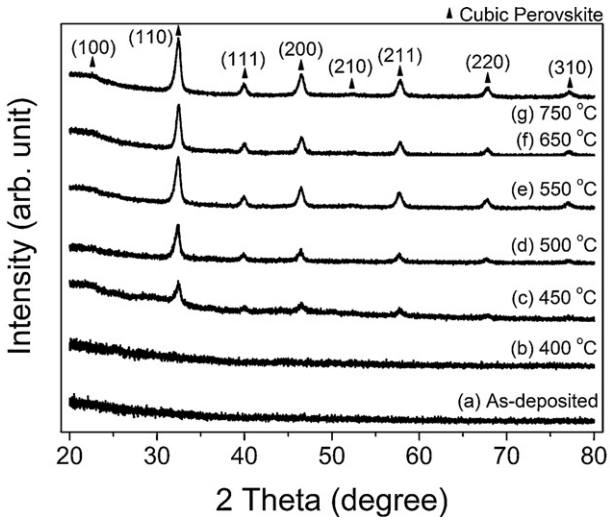

Fig. 2. XRD patterns of the STF40 thin films annealed at different temperatures for 1 h.

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