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Promising Performance of Lead-Free Functional thin films and ceramics

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Abstract. Lead-free functional oxides can be dedicated to numerous applications. Here a part of a complete study on ST and SCT ceramics dedicated to high-Q capacitors is presented, as well as some results on W and WO_3 thin films dedicated to semiconductor gas sensors.

1. Introduction

During the last decades, functional oxides have been intensively studied by the scientific community. They present a wide range of interesting functionalities, such as high dielectric permittivity, piezoelectricity, pyroelectricity and ferroelectricity which have been largely developed in applications such as ceramic capacitors, tunable devices, actuators and sonars, I-R sensors and ferroelectric memories, respectively. More recently, the community attention has been attracted by other properties and materials such as high temperature superconductivity, colossal magneto-resistance, multiferroics, gas sensing, half-metallic behaviour, thermoelectrics and oxides for fuel cells. The extended spectrum of involved material physics has triggered extensive studies to understand the fundamental nature of existing systems, and then to modify and control novel materials for applications. All oxides exhibit various crystalline structures. Among them, one of the best-known family is the perovskite-type crystal structure (ABO_3). In these crystalline structures, the grain boundaries, impurities and structural defects strongly influence the dynamics of ferroelectric or ferroic domains (if the material is not in a paraelectric state). And when other phenomena occur like the catalytic activity, often relies on atomic scale defects such as oxygen vacancies, new defects can be generated. So in the same time the dynamics of defects are strongly influenced by local electric fields, domain boundaries, surfaces

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chemical potentials which are themselves influenced by ferroelectric or ferroic properties and catalytic action. Ferroelectrics display a hysteresis of the electrical polarization, characterized by a remnant polarization at zero electrical field and the possibility to continuously pole the material between positive and negative extrema. Ferroelectrics offer not only possibilities for data storage, their applications cover a wide range, such as magnetic field detection, microwave devices, actuators and sensors, automotive devices, electronic components [1]. In microwave devices, some components have to be tuned to adjust oscillators or filter bandwidths. In this case, ferroelectric thin films are of great interest due to their wide frequency range which can be extended up to 60 GHz [2].
Nowadays, gas detection on the industrial market mainly uses optical sensors, electro-chemical sensors often containing lead, and catalytic sensors based on platinum. Industrial firms producing these lead-based sensors can consume more than a ton of lead per year. This is a concern because lead is one of the most hazardous and polluting raw materials; it affects the central nervous system and has the potential to induce infertility and cancer. In 2008, the modified European Restriction of Hazardous Substances (RoHS) directive appeared, prohibiting the use of hazardous substances like lead, cadmium and mercury. As such, there is an urgent need for lead-free components in Europe, and industry is now trying to produce electronic components and devices which comply with RoHS standards. In this frame, developing innovating gas sensors containing lead-free oxides and dedicated to the detection of hazardous substances is highly encouraged by authorities. Among the different technologies that can be used for the detection of dangerous toxic and flammable gases in industrial sites, as well as for monitoring indoor air quality in houses and public buildings, oxides have been implemented to realize gas sensors, and especially semi conductive gas sensors [3, 4].
In this paper we present our investigations in two different domains of application. In a first part, a study of doped strontium titanate ceramics is presented. In view to develop high-Q capacitors we have studied the effect of the exchange on the site A of the perovskite cell. In the second part, a study of cost-effective semiconductor gas sensors based on tungsten and tungsten oxide thin films is approached.

2. Experimental Methods

2.1. Preparation of SCT ceramics

Ceramic pellets with a diameter of 3 mm and thickness of 3 mm were prepared by solid-state reaction method.[25] $Sr_{1-x}Ca_xTiO_3$ having x= 0, 0.4 show a paraelectric behavior at room temperature. Details on the preparation of samples were given previously [1]. The pellets were sintered at 1400° C for 5 hours in air.

2.2. Preparation of W and WO3 thin films and fabrication of gas sensors

Tungsten double spiral heaters were elaborated by using an optical lithography technique. Tungsten films were deposited by DC sputtering from a tungsten target onto SiO_2 (1µm)/Si (100) N-type substrates. The purity of the target was 99.95 %. The argon pressure was 0.1 Pa. Experimental details of sputtered tungsten films dedicated to gas sensors heaters are presented in a previous study [5]. The substrate dimensions are 4 mm x 2 mm. The choice of a double spiral pattern is due to the lower power consumption when compared to other studied structures [5]. Measurements of the heater temperature as a function of the power supply were made by using a PT 100 sensor stuck on the back of the substrate of the heating element. The results were used to monitor the electric power to be supplied to the heater for keeping the sensor at the desired operating temperature. The heater was then stuck to the sensing element by using silver ink. The basic structure of the gas sensor is presented in Fig. 1. Physical and electrical characteristics of the heater are summarized in Table 1. Tungsten trioxide thin films were deposited onto SiO_2/Si substrates by non-reactive RF sputtering from a WO_3 target (99.99 % pure). Pure argon (99.99 %) was used as the sputtering gas. During the deposition process, the chamber pressure was maintained at 1 Pa, the RF power at 100 W and the substrate was not heated. Subsequently, the WO_3 films were annealed for 6 hours in air at two different

temperatures, 400 °C and 500 °C, in order to study the influence of the annealing temperature on the sensor response. Tungsten interdigitated electrodes were deposited on the top of the active layer by using an optical lithography technique and DC magnetron sputtering. Physical and electrical characteristics of the active layer and electrodes are presented in Table 1. The sensor made with the WO_3 film annealed at 400 °C is noted sensor-400. The sensor made with the WO_3 film annealed at 500 °C is noted sensor-500.

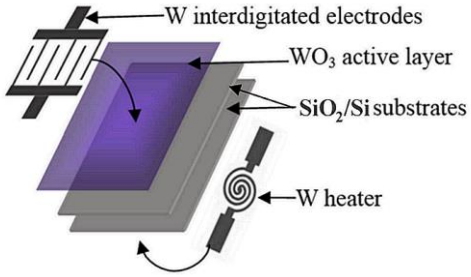


Figure 1. Structure of the gas sensor.

Table 1 Physical and electrical characteristics of the complete sensor: heater and sensing element.

Substrates dimensions	4 mm x 2 mm
W film thickness of the heater	565 nm ± 35
Heater electrical resistance at 20 °C	50 Ω ± 10
W film thickness of the electrodes	300 nm ± 10
Thickness of WO_3 films annealed at 400 and 500 °C	120 nm ± 10
Electrical resistance at room temperature of WO_3 films annealed at 400 and 500 °C	5 MΩ ± 1

3. Results and Discussion

Physical and electrical characterizations

- *SCT ceramics*

X-ray diffraction (XRD) analysis was performed at room temperature in the powder form, on a Philips X'PERT system, with a Kα radiation (λ=1.54056 Å) at 40 kV and 30 mA, with a step of 0.05° per second. Microstructures were examined by Scanning Electronic Microscopy (SEM). Silver paint electrodes were deposited on the samples for electrical measurements. Temperature and frequency dependence of the dielectric properties of ceramics were investigated from 25 °C to 250 °C and from 100 Hz to 1 MHz using a Hewlett Packard HP4284A LCR meter and at room temperature from 1 MHz to 1.8 GHz using a HP4291A impedance analyzer.

- *Tungsten and tungsten trioxide films*

The thicknesses of the films were determined by observing the cross-section of samples by FESEM (Field Emission Scanning Election Microscope JEOL JSM-7100F). The surface morphology and grain size of WO_3 thin films were determined by using an atomic force microscope (AFM) (Multimode AFM, Veeco Instruments). The crystalline structure was studied by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with a monochromatized Cu $K_{\alpha 1}$ wavelength (λ = 1.54056 Å) in θ-2θ Bragg-Brentano geometry. The sensing and heating elements were embedded in commercial cases. The sensors were then placed into a DG-TT7 Solid-State Gas Detector, which is a commercial product of SIMTRONICS SAS. The DG-TT7 detection system communicates with a computer by infrared wireless. Data are operated by a software developed by the firm. The sensors were tested under different conditions and gas concentrations at SIMTRONICS SAS. The sensitivity, response and recovery times and sensor stability were deduced from these experimental measurements.

3.1. Results and discussion on ceramics

XRD patterns of the ST and SCT0.4 powders were given previously [1]. ST material shows a cubic symmetry [6]. For SCT0.4 solid solution, the observed peaks are characteristics of an orthorhombic structure [7]. All peaks shifts to higher angles 2θ with increasing the calcium rate in $SrTiO_3$ material, because the ionic radius of Ca^{2+} (0.99 Å) is smaller of Sr^{2+} (1.44 Å) [8]. The SEM photographs of the ST and SCT0.4 ceramics were given previously [1]. The grain size increases with the substitution of calcium in the $SrTiO_3$ material. The average grain size is estimated using the MagniSci software is about 630 nm for ST and 2 μm for SCT0.4 ceramics. Figure 2a shows the frequency dependence of the dielectric permittivity ε' of ST and SCT0.4 ceramics from 100 Hz to 1 GHz at room temperature. Strontium substitution offered by calcium decreases the dielectric permittivity. The SCT0.4 dielectric permittivity shows a good stability all over the frequency range whereas the $SrTiO_3$ presents dispersion in low frequencies. This is an advantage for high frequency components. SCT0.4 ceramic exhibits a constant dielectric permittivity value (ε'=200) which is lower than the $SrTiO_3$ one, but definitely more stable all over the complete frequency range. Figure 2b presents the frequency dependence of loss tangent tgδ of ST and SCT0.4 ceramics from 100 Hz to 1 GHz at room temperature. SCT could display dielectric losses lower than 3.10^{-4} (value at 1 MHz and 10 MHz) from 1 MHz to 12 MHz, but it was impossible to collect accurate data because the pellet resistance was too high and definitely out of the measurement range for the HP4291A. SCT tgδ value does not exceed 6.10^{-2} at 1 GHz, while $SrTiO_3$ gives a minimum value tgδ = 0.05 from 500 kHz to 3 MHz. Generally for industrial applications, high-Q ceramic capacitors must exhibit Q values higher than 1000 for frequencies up to 100 MHz, or higher than 200 for frequencies ranging from 100 MHz to 1 GHz [9]. For our samples, SCT0.4 gives Q values, where Q = 1/tgδ, higher than 2500 from 1 to 12 MHz, and 300 at 100 MHz. The quality factor Q goes down to 20 at 1 GHz.

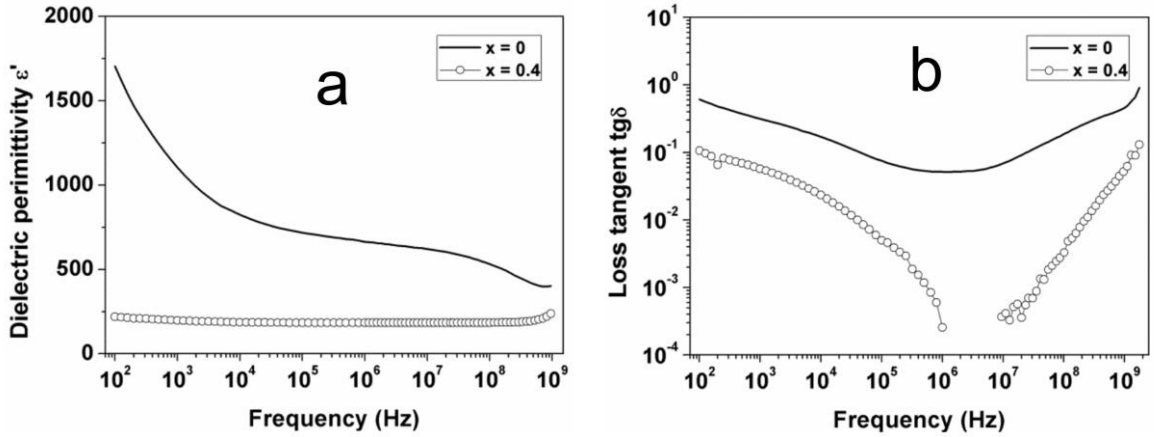


Figure 2. Frequency dependence of the dielectric permittivity (a) and loss tangent (b) of $Sr_{1-x}Ca_xTiO_3$ ceramics (x=0 and 0.4).

3.2. Results and discussion on tungsten and tungsten oxide thin films. Measurements under H_2S

The crystalline structure of thin films was investigated previously [5]. For gas sensors, the sensitivity, defined by the ratio G/G_0, where G_0 and G the sensor conductance in air and under gas respectively, must be higher or equal to unity. Fig. 3a shows the sensitivity evolution of sensor-400 and sensor-500 to 100 ppm of H_2S at various temperatures. The sensor-400 shows a higher sensitivity to H_2S than the sensor-500. The maximum sensitivity value of the sensor-400 is 6.6 whereas it is of 2.4 for the sensor-500. This high-value of the sensitivity, i.e. of 6.6, definitively indicates that WO_3 sputtered thin films annealed at 400 °C can be used to fabricate high-sensitive gas sensors. The higher sensitivity value of the sensor-400 may be explained by the presence of very small grains at the surface of the film. The dynamic response of the sensors under H_2S pulses at concentrations ranging from 20 to 100 ppm for the sensor-400 are shown in Fig. 3b. The response and recovery times of the sensor-400 are of about 20 s and 4 min respectively and remain almost unchanged for H_2S concentrations varying from 20 to

100 ppm. For the sensor-500, the response time is of about 20 s, similar to the sensor-400, but the recovery time is of 2 min. This value of the recovery time is two times lower than that of the sensor-400. Indeed when the sensitivity variation is higher, the variation of the sensor resistance is higher as well. In this case, the sensor needs more time to recover after the exposition to the gas.

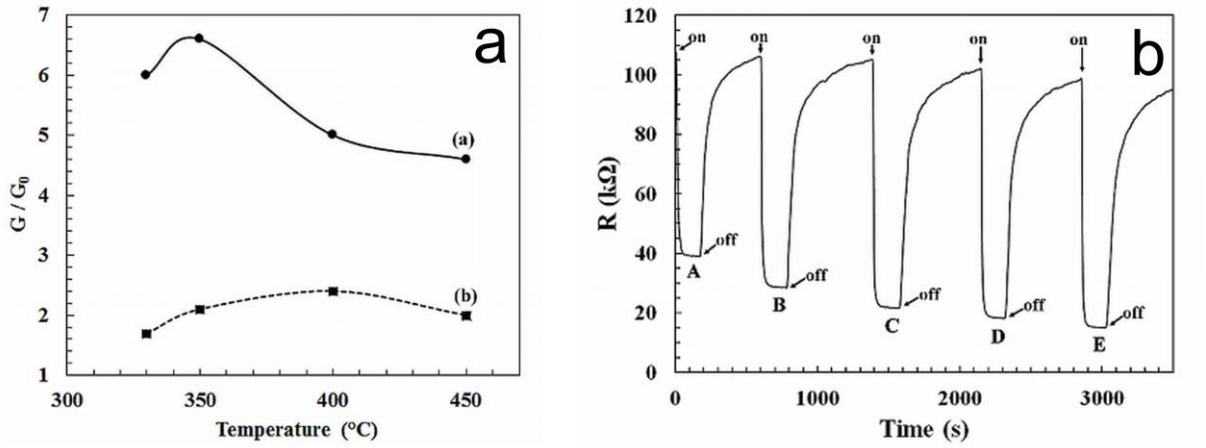


Figure 3. Sensitivity (fig. a) of the sensor-400 (plot a) and the sensor-500 (plot b) under 100 ppm of H_2S in dry air as a function of the temperature. Dynamic response (fig. b) of the sensor-400 under A: 20 ppm, B: 40 ppm, C: 60 ppm, D: 80 ppm, E: 100 ppm of H_2S at 350 °C. ON: H_2S injected, OFF: air injected.

4. Conclusion

In a first part, a study of doped strontium titanate ceramics is presented. The frequency dependence of the dielectric permittivity ε' of ST and SCT0.4 ceramics is studied from 100 Hz to 1 GHz at room temperature. Strontium substitution offered by calcium decreases the dielectric permittivity. The stability of SCT0.4 dielectric permittivity all over the frequency range is an advantage for high frequency components. Moreover SCT0.4 has given very high-Q values.

In the second part, a study of cost-effective semiconductor gas sensors based on tungsten and tungsten oxide thin films is approached. A sensitivity as high as 6.6 has been reached at T=350°C, which is a very good value. The dynamic response has shown a very fast response whatever the H_2S concentration.

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