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Novel gas sensor with dual response under CO(g) exposure: Optical and electrical stimuli

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ABSTRACT

In this work, a lanthanum (La) doped ceria (CeO_2) film, which depicted a dual gas sensing response (electric and optical) for $CO_{(g)}$ detection, was obtained by the microwave-assisted hydrothermal (HAM) synthesis and deposited by the screen-printing technique, in order to prevent deaths by intoxication with this life-threatening gas. An electric response under $CO_{(g)}$ exposure was obtained, along with an extremely fast optical response for a temperature of 380 °C, associated with Ce^{+4} reduction and vacancy generation. A direct optical gap was found to be around 2.31 eV from UV–Vis results, which corresponds to a transition from valence band to 4f states. Due to the anomalous electron configuration of cerium atoms with 4f electrons in its reduced state, they are likely to present an electric conduction based on the small polaron theory with a hopping mechanism responsible for its dual sensing response with a complete reversible behaviour.

1. Introduction

Ceria (CeO_2) has been considered an important nanomaterial for applications in catalysis [1,2], fuel cells [3], ultraviolet absorbers [4], hydrogen storage materials [5], oxygen sensors [6], optical devices [7], polishing materials [8], and for which the use of nanocrystalline powders is an important factor [9]. Several methods have been developed to prepare ultra-fine CeO_2 powder, including hydrothermal [10], precipitation (for oxalate [11], carbonate [12,13], peroxide [9], hydroxide [14], polymeric precursor [15,16], complexion with citric acid [15], the flow method [17], organometallic decomposition [18] and microwave-assisted heating technique [19–21]. Among the various methods, the hydrothermal crystallization is an interesting process to directly prepare pure fine oxide powders with reduced contamination and low synthesis temperature. The conventional hydrothermal method requires longer soaking times at a low temperature (below 200 °C) to obtain the ceria powders. For this reason, the introduction of microwave heating to the conventional hydrothermal method is advantageous for the synthesis of various ceramic powders because the microwave heating permits a reduction of processing time and energy cost. Particles with desired size and shape can be produced if parameters such as solution pH, reaction temperature, reaction time, solute concentration and the type of solvent are carefully monitored [22]. A modification of the hydrothermal method developed by Komarneni et al. [23–25] involves the introduction of microwaves during the hydrothermal synthesis to increase the kinetics of crystallization by one to two orders of magnitude compared to the conventional hydrothermal. The microwave-assisted hydrothermal (MAH) method shows advantages such as rapidity, convenience, and cost-effectiveness. Ceria systems with nanosized particles were successfully synthesized by the MAH method utilizing a relatively low temperature and short reaction time [26]. In this present work, the authors describe the conditions of formation of the ceria via MAH, introduce the advantages of microwave irradiation method and also report in details the method used. In previous work, our group worked on the preparation of CeO_2 films coming from nanostructures obtained by the microwave-hydrothermal methods and its gas sensing measurements have been carried out to rationalize the type and number of surface adsorbed groups and overall nanostructure. Variations of electrical conductance, as a consequence of gases adsorption onto semiconductor oxide film surfaces, were observed [27]. In polycrystalline materials, it is widely accepted that barriers formed between particles or grains have a Schottky-type nature and that they govern the electrical behaviour. Adsorption of gaseous species at the grain boundaries can induce changes in the barrier heights and in the donor concentrations. Most researchers

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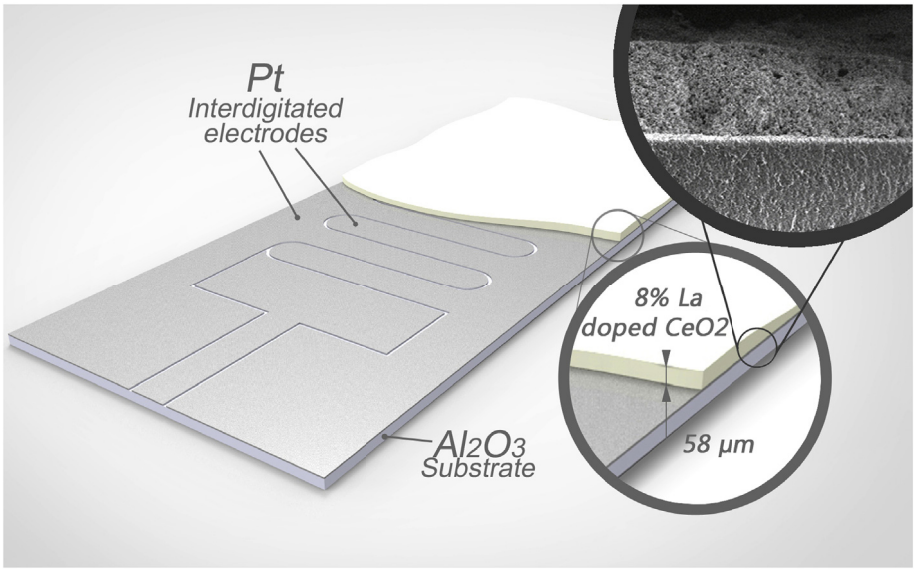

Fig. 1. Substrate with the interdigitated electrodes deposited by a home-built micromachining laser along with the 8% La-doped film deposited.

in the field consider that many oxide semiconductors have a large number of oxygen vacancies, conferring their *n*-character, with cerium oxide being a potential candidate [28,29]. It is known that oxygen is chemisorbed on the surface of the oxide, increasing the barrier height and width of surface barriers. In this fast process, the equilibrium with atmospheric oxygen would be reached rapidly. Subsequently, in a second process, we found for metal oxide semiconductors that oxygen diffuses slowly into the grains (at temperatures above 200 °C), annihilating vacancies and reducing the donor concentration. Besides, as was proposed by Tuller et al. and Wuilloud et al. [30,31], rare-earth oxides with 4f-shells of the lanthanide ions are likely to present narrow bands and then the electrical conduction would involve 4f electrons that migrate by an activated hopping mechanism.

The pure CeO_2 is a poor ionic conductor with a band gap of 6 eV [31] adopting the fluorite structure (space group Fm3m) with singly or doubly ionized oxygen vacancies (V_O.,$V_{\ddot{O}}$) as the predominant ionic defect. Ceria-based electrolytes have been extensively studied and made much progress. In particular, some singly doped-electrolytes can be obtained by doping the ceria host structure with other cations, such as $Ce_{1-x}Gd_xO_{2-\delta}$, Ce_{1-x} $Sm_xO_{2-\delta}$, $Ce_{1-x}Y_xO_{2-\delta}$, showing high oxide ion conductivity at intermediate temperatures (500–700 °C) [32–36]. Various rare-earth doped ceria systems (La, Sm, Pr) have successfully been prepared by hydrothermal treatment, providing low-temperature preparation and morphological control of ultrafine particles of uniform crystallite dimension [37–39]. Replacement of Ce^{4+} with divalent or trivalent ions results in the creation of oxygen vacancies [40], and the choice of the dopant is usually advocated by the ability of the dopant to minimize the internal strain of the lattice [41–43]. Therefore, we show, in the present study the role of lanthanum (La) doping on the structure and chemistry of ceria thin films and the resultant variation in the resistance under $CO_{(g)}$ atmosphere. The main goal of lanthanum addition, with a lower valence state of La^{3+} (r = 0.110 nm) than Ce^{4+} (r = 0.097 nm), was to reduce the conductivity, along with a lattice expansion, resulting in an improvement of the CO sensing properties.

2. Experimental procedure

Lanthanum doped CeO_2 nanopowder was synthesized by the microwave-assisted hydrothermal method. The experimental procedure was based on the dissolution of cerium (III) nitrate hexahydrate [$Ce(NO)_3{\cdot}6H_2O$; 99%-Sigma] in an aqueous medium, under constant magnetic stirring. Separately, lanthanum oxide (La_2O_3) (99% purity - Aldrich) was dissolved in a nitric acid medium and added to the solution. The resulting mixture was heated at 70 °C under stirring and its pH adjusted through the addition of basic aqueous solution 2 mol L^{-1} of KOH (99.5% purity - Synth) until a pH~10. The resulted solution was transferred into a sealed Teflon autoclave and placed in a hydrothermal microwave (2.45 GHz, 800 W). The reaction system was heat-treated at 100 °C for 8 min with a heating rate fixed at 10 °C/min and then allowed to cool naturally. The nanopowders were centrifuged and washed with deionized water and then dried in a laboratory oven at 100 °C for 2 days. The obtained nanostructures were characterized by X-ray powder diffraction (XRD) using a (Rigaku-DMax/2500PC, Japan) with Cu-Kα radiation (λ = 1.5406 E) in the 2θ range from 20 to 80° with 0.2 °/min. The crystallite size d was calculated using Scherrer equation $d = \frac{0.94\lambda}{\beta \cdot \cos\theta}$, where λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) for (1 1 1) reflection, and θ is the diffraction angle of the main peak. The obtained powder was used to prepare a film through the screen-printing technique based on a paste composed of an organic binder (glycerol) using a solid/organic binder ratio of 0.6 g/mL. The used substrates were composed of 96% dense insulating alumina (Al_2O_3), on which electrodes with an interdigitated shape had been delineated by sputtering. An adhesion layer consisting of 25 nm titanium (Ti) was deposited and, without breaking the vacuum, a platinum (Pt) 200 nm film was deposited over the Ti layer. For defining the interdigitated electrodes, the substrates with the metal films were placed in a home-built micromachining laser, producing the substrate seen in Fig. 1. Later, films were thermally treated in dry air atmosphere up to 380 °C and maintained at this temperature for 2 h, using a heating rate of 1 °C/min in order to evaporate the binder. The FT-IR spectra were recorded with a Rayleigh – WQF-510A model spectrometer in transmittance mode. Infrared spectroscopy was used for monitoring some of the structural modifications occurring during the synthesis process with the KBr pellet technique. Ultraviolet–visible (UV–vis) spectroscopy for the optical absorbance spectra was taken using a Cary 5G (Varian, USA) spectrophotometer in diffuse reflection mode. The morphology of film surface was observed using a high-resolution field-emission gun scanning electron microscope (FEG-SEM) Supra 35-VP (Carl Zeiss, Germany). The electrical resistance characterization of films were measured during a temperature variation as well as with time variation in a temperature of 400 °C, to be close to that observed for the optical response (~380 °C) and to the working temperature, achieved at a rate of ~2 °C/min in vacuum, dry air and in CO atmosphere, with a constant pressure of 50 mmHg, during the entire cycling. Worth to mention that the electrical measurements were done in