



Semiconducting BaTiO₃-CuO mixed oxide thin films for CO₂ detection

J. Herrán^{*}, G. G^a Mandayo, E. Castaño

CEIT and Tecnun (University of Navarra), 20018 San Sebastián, Spain

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ABSTRACT

A full study of the BaTiO₃-CuO thin-film technology properties as carbon dioxide sensing material is presented. The coatings are deposited by RF-Sputtering and the CO₂ concentration is monitored by impedance measurements. Theoretical foundations are correlated to the experimental results and the principal fabrication and operation parameters are clarified: working temperature and frequency, thickness influence and the introduction of silver as an additive. The BaTiO₃-CuO layer shows higher sensitivity than the actual low-cost commercial CO₂ sensors in the range of the principal applications.

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1. Introduction

Carbon dioxide detection is currently necessary in several key fields such as indoor air quality monitoring. The first parameters to take into account as a measurement of human comfort are temperature and humidity, but carbon dioxide (CO₂) concentration, as a product of human respiration, has traditionally been considered the most critical among indoor air pollutants. CO₂ has been utilized to control the ventilation rate in occupied spaces. Most of the currently available carbon dioxide sensor devices are based on optical principles but they still show integration problems and high prices as major disadvantages.

Several research groups are looking for an efficient and cheap sensor for CO₂ monitoring. In this context, semiconducting materials are always a competitive low-cost choice compared to electrochemical cells. Concretely for carbon dioxide detection, BaTiO₃-CuO semiconductor thick films have been proposed by several research groups [1–7], but the novelty the authors suggest is the use of this material as a thin film in an impedance sensing device. Thin films show advantages when compared to thick films: higher repeatability in fabrication process, greater control on fabrication parameters and better conditions in mass production, which allows lower costs than thick film techniques. In this work, RF sputtered BaTiO₃-CuO semiconductor thin films are used as sensitive material. To the best of the authors' knowledge, this is the first reported CO₂ gas sensor based on BaTiO₃-CuO thin-films with optimum results [8–12].

2. Experimental

2.1. Fabrication

In order to test the electrical response of the samples under carbon dioxide atmospheres two kinds of samples were fabricated: BaTiO₃-

CuO thin layers and the same thin film with silver as an additive. The fabrication process is as follows: Platinum interdigitated electrodes were deposited on an alumina substrate by DC-sputtering. A Cr interlayer was used to improve the Pt adherence to the alumina substrate. In the next step, the BaTiO₃-CuO layers (2 × 2 mm) sensing film was deposited by RF magnetron sputtering from a BaTiO₃-CuO equimolar target. For the samples doped with Ag, a multilayer configuration was used by the growth of four BaTiO₃-CuO layers separated by three Ag additive layers. The Ag additive was deposited during a few seconds by DC-sputtering with the target partially shut to get a small rate of deposition. Changing the deposition times four different atomic silver concentrations were tested: 0, 1.5, 2.26 and 4.52 at%. Finally the samples were annealed in O₂ for 3 h at 700 °C, in order to obtain a stable film at the working temperature.

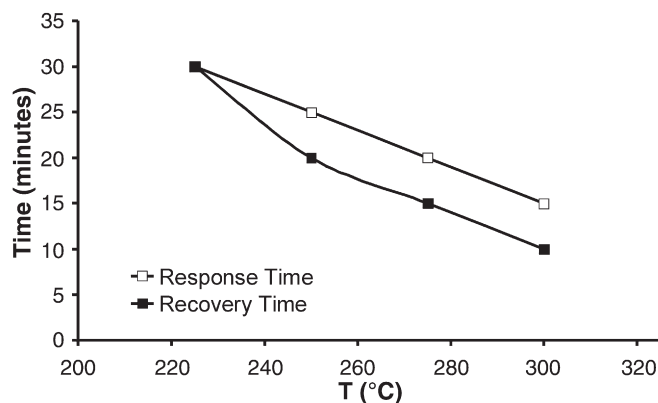


Fig. 1. Response and recovery times of the samples of 275 nm at different working temperatures.

^{*} Corresponding author. Tel.: +34 943 212 800x2925; fax: +34 943 213 076.
E-mail address: jherran@ceit.es (J. Herrán).

Table 1
Response and recovery times for the different BaTiO₃–CuO thicknesses.

Thickness (nm)	Response time (min)	Recovery time (min)
125	2	3
200	5	12
275	10	15
400	20	30

2.2. Characterization techniques

Electrical characterization is performed inside a sealed stainless steel chamber with a PID (Proportional–Integrate–Derivative) controlled self-heating system and external connections. Measurements are performed by a Lock-In amplifier (Model 7265, Signal Recovery). The atmosphere inside the chamber is controlled by a MFC (Mass-Flow-Controller)-based gas mixing system. Previous to impedance measurements the samples are heated and stabilized at the maximum test temperature for 15 h in air with 40% RH. Both stabilization and CO₂–air tests are performed under a fixed flux of 400 sccm.

TOF–SIMS analyses were carried out using an ION–TOF TOF–SIMS IV. Samples were analyzed by the dual beam depth profiling using an oxygen sputter gun with an energy of 1 keV (intensity of 300 nA). Analysis scan was performed with a Bi gun in high resolution mass mode (bunched mode) at an energy of 25 keV (0.98 pA), analysing the spectra of positive ions. Sputtering area was 300 × 300 μm and the analysis area was 50 × 50 μm. After each analysis, the hole formed by sputtering was measured with a profilometer in order to convert the sputtering time into a depth profile.

DRIFT characterization was carried out on the powders of the BaTiO₃–CuO sputtering target, using a Bomem DA3 spectrometer equipped with a Spectra-Tech collector chamber with CaF₂ windows at a spectral resolution of 1 cm^{−1}. The cup was filled with a sufficient

amount of BaTiO₃ powder and DRIFT spectra were acquired at room temperature and atmospheric conditions in the 500–4000 cm^{−1} range. Spectra backgrounds were corrected using a spectrally flat mirror.

3. Results and discussion

3.1. Temperature effects

A BaTiO₃–CuO thin film has been tested in order to measure changes of resistance and capacitance at several working temperatures (200–300 °C) [10]. The highest sensitivity has been observed at working temperatures of 225 and 250 °C for capacity changes and at 250 °C for resistance changes. At the highest working temperature (300 °C) the response and recovery times are the fastest.

In order to choose the most convenient working temperature, a compromise between the sensitivity and the response time must be reached. So, the working temperature is fixed at 300 °C because the system responds with an enough percentage of relative change at the fastest time (Fig. 1).

At higher temperatures an inhibition of the sensor occurs at 400 °C and the thin-film is poisoned (the base line is not recovered when CO₂ is removed of the testing chamber). This behaviour is related to the dehydration of the material [8].

3.2. Thickness influence study

Samples with four different thicknesses have been fabricated in order to determine the influence of this parameter in the response of BaTiO₃–CuO to different carbon dioxide atmospheres.

While for all the different layer thicknesses the sensor response reaches the same value in the stationary state (about 10% of change in

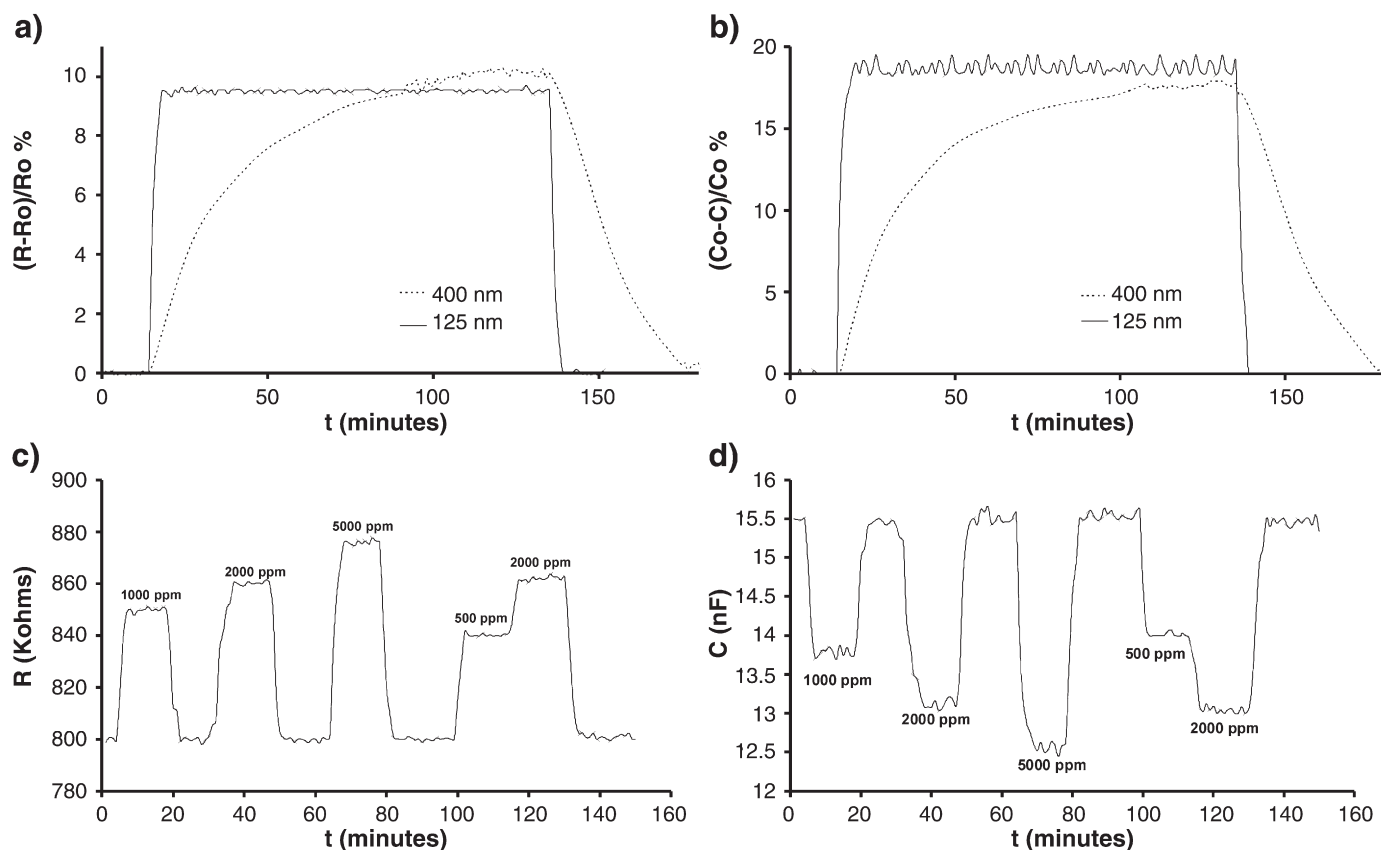


Fig. 2. a) Response in R under 5000 ppm of CO₂, 40% RH and 300 °C. b) Response in C under 5000 ppm of CO₂, 40% RH and 300 °C. c) R variation at various concentrations of CO₂ at $T = 300$ °C. d) C variation at various concentrations of CO₂ at $T = 300$ °C.

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