



Gas sensing and conductivity relationship on nanoporous thin films: A $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ case study



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ABSTRACT

In this work, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) thin films were synthesized with the polymeric precursor method and characterized by structural (X-ray diffraction) and morphological (scanning electron microscopy) techniques. These films were composed of a single CCTO phase and presented high surface porosity. The gas sensing response and conductivity-type relationship were investigated by two different approaches. Gas sensing measurements performed at different temperatures using different atmospheres showed that the CCTO has n-type gas sensing behavior and can detect small amounts of oxidizing gases with high sensitivity and selectivity. The type of intrinsic conductivity was also investigated through thermopower measurements, which indicated intrinsic n-type conductivity in CCTO thin films prepared with the polymeric precursor method and confirmed the direct relationship between the gas sensing behavior and the intrinsic conductivity of CCTO.

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1. Introduction

Chemical gas sensors based on metal oxide semiconductor (MOS gas sensors) have attracted significant attention due to their simplicity, low cost, small size, easy integration into electronic devices and versatility for applications in different areas, such as environmental, health, automotive and security applications [1,2]. In recent years, researchers have focused their attention on finding new and/or nanostructured materials, such as thin films, nanoparticles and nanobelts, for the development of gas sensors with high sensitivity and selectivity combined with low energy consumption [3,4].

In this context, the perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is under intense study for applications in new electronic devices, owing to its excellent dielectric and non-ohmic properties [5–7]. In addition, this material exhibits multifunctional properties, such as photoluminescence, resistive switching and gas sensing behavior, thus making it attractive for a wide range of applications [8–10]. However, in gas sensing, the dual behavior of these films is not fully understood. Kim et al. have reported n-type gas sensing behavior and higher H_2 sensitivity in macroporous CCTO thin films prepared with pulsed laser deposition (PLD) [11]. Using the same deposition technique, Deng et al. have reported p-type conductivity due to the difference in the oxygen partial pressure conditions during the deposition process [12]. However, p-type behavior has also been reported by Joanni et al. in films prepared with rf-sputtering, whereas Parra et al. have shown that mesoporous thin films prepared with the sol–gel method display an n-type gas sensing

response [13,14]. These studies have indicated that gas sensing behavior depends not only on the growth method but also on the intrinsic parameters of the deposition technique. Moreover, the gas sensing behavior and intrinsic conductivity relationship is not well defined in the literature for this material and it is still under discussion.

In light of these predictions, the main goal of this work was to investigate the gas sensing behavior and intrinsic conductivity relationship of nanoporous CCTO thin films prepared with the polymeric precursor method (PPM). The gas sensing behavior was studied at different temperatures and atmospheres using several gas concentrations. In addition, thermopower measurements were performed to confirm the intrinsic charge-type in these films. Our results indicated a direct correlation between the gas sensing behavior and intrinsic conductivity in these CCTO thin films.

2. Experimental details

2.1. Synthesis procedure

CCTO thin films were prepared with the polymeric precursor method (PPM) [15]. This method consists of the preparation of polymeric solutions by dissolving soluble cation sources, such as nitrate and carbonate, into water, followed by the addition of chelating and polymerizing agents, such as citric acid and ethylene glycol, respectively, for the formation of a polymeric solution by a polyesterification reaction at an appropriate temperature [16]. The PPM is useful for the preparation of a wide range of oxides because it allows for mixing of the cations on a molecular level, leading to homogeneous oxide films [17,18].

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The resulting polymer solution from PPM can be coated on a substrate, with techniques such as dip- or spin-coating. Then, using an appropriate heating setup, the polymer film can be pyrolyzed to produce crystalline oxide thin films with dense or porous morphologies. The advantages of this sample preparation route are the fine control of the film thickness, through multiple solution depositions, and the grain size and porosity, through the temperature and time of crystallization annealing [19,20].

In this work, the polymeric solution was prepared at a molar ratio of metal: citric acid: ethylene glycol of 1:3:3. Stoichiometric amounts of calcium carbonate (CaCO_3 , Sigma-Aldrich, 99.999%), copper(II) carbonate basic ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, Sigma-Aldrich, 99.99%) and titanium(IV) isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$, Sigma-Aldrich, 99.999%) were dissolved in an aqueous nitric acid solution (0.1 M) at 50 °C and under constant stirring. After homogenization, citric acid was added to the solution for the formation of metal chelates. Then, the temperature was increased to 90 °C, and ethylene glycol was added to achieve polymerization. The solution viscosity was adjusted to 30 cP by controlling the deionized water content using a Brookfield viscometer (Model-DV III+). CCTO solution layers were deposited on alumina substrates by spin-coating at 4000 rpm for 30 s, followed by heat treatment at 370 °C for 30 min, using a heating rate of 20 °C/min, to remove organic material. This process was repeated 3 times; then, the thin films were annealed at 775 °C for 30 min, using a heating rate of 10 °C/min, in air to obtain the crystalline phase.

2.2. Characterizations

Thin film phase analysis was performed with X-ray diffraction (XRD; Rigaku, Model Rint 2000) at room temperature, and the surface of the annealed films was analyzed using a field emission scanning electron microscope (FEG-SEM; JEOL, Model 7500F). Interdigitated platinum electrodes (100 μm Pt fingers spaced by 200 μm) were sputtered at room temperature on the surface of CCTO films to perform the gas sensing measurements.

Gas sensing tests were performed at 200 °C, 250 °C and 300 °C, and the resistance was monitored using a stabilized high voltage source measuring unit (Keithley, Model 237) at a constant voltage of 10 V with a 1 s delay per point. The gas sensing response of the CCTO thin films was analyzed during cyclic exposure (20 min gas exposure with 60 min recovery) to different concentrations of testing gases. For the oxygen test, clean dry air was used as the oxygen source, with dry N_2 as the baseline gas. For H_2 (between 20 to 1000 ppm) and NO_2 (between 2 to 100 ppm) test gases, the baseline gas was dry air. To achieve

this, certified pre-mixed gas mixtures, containing a trace of the test gases diluted in dry air (H_2 (1000 ppm) and NO_2 (100 ppm) (White Martins) were mixed with clean dry air using mass flow controllers (MKS). The total gas flow rate (test gas plus baseline gas) was kept constant (100 sccm) during all tests.

3. Results and discussion

Fig. 1a shows a typical XRD pattern for a CCTO thin film grown on an alumina substrate at 775 °C for 30 min. CCTO peaks were indexed as the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ cubic body-centered perovskite-related phase with space group $\text{Im}\bar{3}$. The X-ray pattern showed that the CCTO thin film was free of secondary phases, and the relative intensities of the peaks indicated the formation of a polycrystalline sample without a preferential orientation. The additional peaks observed in the XRD pattern were related to the Al_2O_3 phase from the substrate.

Porosity has a strong influence on the gas sensing behavior of semiconductor oxides [21]. Therefore, a quick annealing treatment at 370 °C for 30 min was performed for organic removal, followed by a final annealing treatment at 775 °C for 30 min to induce the phase crystallization, with the goal of increasing the surface porosity. Fig. 1b shows a typical SEM image of the CCTO thin film surface. The SEM characterization indicates that the quick annealing used in this work was an efficient way to improve the surface porosity of the CCTO thin films compared to the literature results for other perovskite thin films prepared with PPM [18,19]. In addition, the film shows a homogeneous grain size distribution, with an average width of approximately 50 nm.

The mechanism of gas detection in metal oxide semiconductors has been described by different models [2]. The most accepted mechanism is related to the transfer of free charge carriers between the absorbed molecules and the semiconductor surface. For instance, in n-type semiconductors with oxygen as the analyte gas, this mechanism, called the ionosorption model [22,23], occurs when neutral oxygen molecules are physisorbed at the semiconductor surface, and chemisorption proceeds by the transfer of electrons from the surface to oxygen molecules, i.e., an electron from the oxide surface is trapped by the absorbed oxygen molecules. This in turn results in a lowering of the Fermi level and the formation of a depletion layer by the band bending. This band bending increases with the concentration of chemisorbed ions at the surface until a steady state is achieved. As a result, there is a decreased electron concentration at the oxide surface, leading to an increase in surface resistance and, consequently, sensor resistance. The opposite occurs for a reducing gas [24].

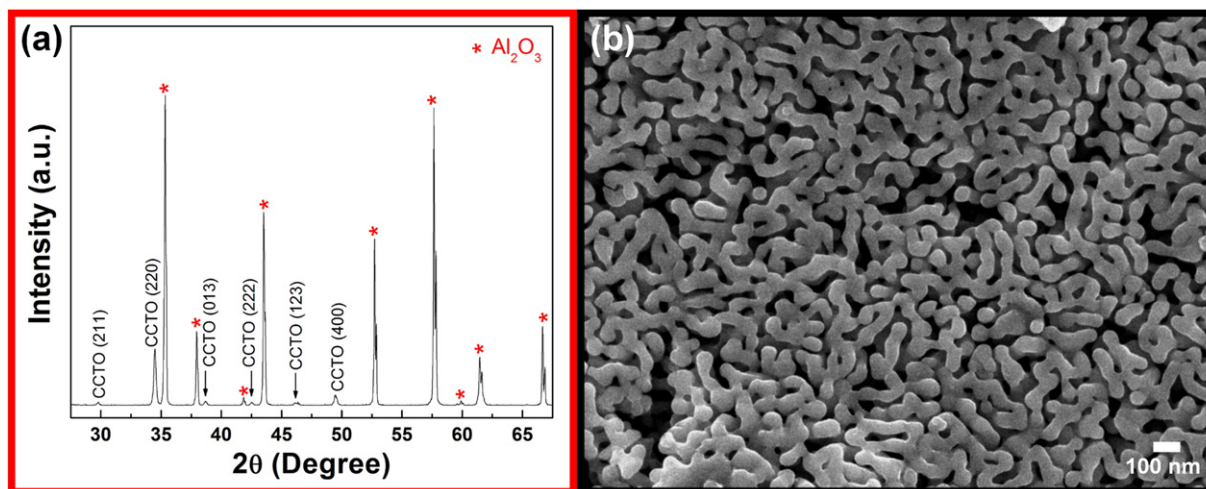


Fig. 1. (a) X-ray pattern of a CCTO thin film. Miller indices (hkl) are related to the CCTO phase (JCPDS 75–2188), and the symbol (*) is related to the Al_2O_3 phase (JCPDS 71–225). (b) Surface SEM image of the CCTO thin film.

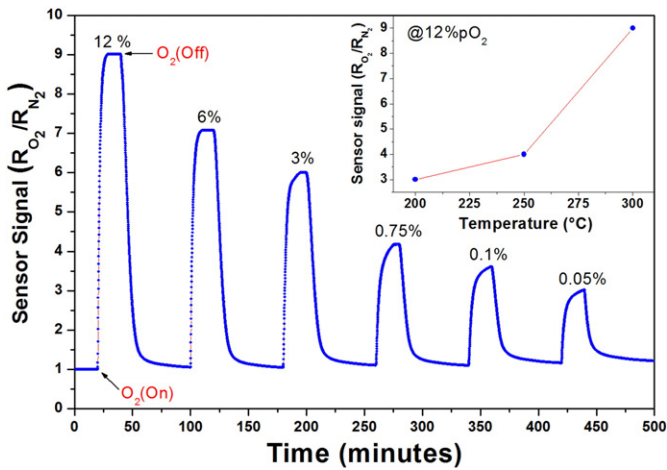


Fig. 2. Gas sensing response plots as a function of the oxygen partial pressure (%pO₂) at 300 °C for the CCTO thin film. Inset: sensor signal as a function of temperature at 12% pO₂.

The reverse behavior is observed for a p-type gas sensor, i.e., oxidizing gases induce an accumulation of holes near the surface, resulting in a decrease in sensor resistance, whereas reducing gases deplete holes near the surface, resulting in an increase in sensor resistance [24]. Moreover, the intrinsic conductivity in semiconductor oxides is also correlated with the effect of changing the oxygen partial pressure (pO₂) in the electrical resistance of the material [23].

So, we can establish a relationship between the gas sensing behavior and intrinsic conductivity in a semiconductor oxide, which will indicate the type of the majority charge carriers. In n-type semiconductor oxide, the changing in material resistance must satisfy three requirements: i) resistance increases when the device is exposed to an oxidizing atmosphere; ii) decreases when exposed to a reducing atmosphere; and iii) increases with increasing in oxygen partial pressure. The opposite behavior is expected for the p-type semiconductor oxide [23,24]. Based on these assumptions, the CCTO thin films were tested to study the gas sensing characteristics and determine the conductivity type.

The gas sensing response of CCTO thin films as a function of the oxygen partial pressure measured at 300 °C using N₂ as the baseline is

shown in Fig. 2. The sensor signal or sensor response was defined as the ratio of the sensor resistance measured when exposed to the target gas (R_{gas}) to the resistance in the baseline gas (R_{air} or R_{N₂}) for oxidizing gas and vice versa for reducing gases, i.e., in this work R_{O₂}/R_{N₂} (Fig. 2) or R_{NO₂}/R_{air} and R_{air}/R_{H₂} (Fig. 3). When oxygen was used as the analyte, the CCTO thin film exhibited an increased sensor response when exposed to an oxygen atmosphere, i.e., the CCTO resistance increased in the presence of oxygen molecules, indicating an n-type gas sensing response. In addition, the n-type gas sensing characteristic was evidenced by the oxygen partial pressure dependence when the sensor signal and, consequently, the resistance increased with increasing oxygen concentration, as seen in Fig. 2.

Additionally, the sensor signal decreased when the temperature decreased, i.e., the sensor signal was temperature-dependent, with higher response at higher temperature (see inset in Fig. 2). Based on this finding and the literature results [11], new tests were performed using NO₂ and H₂ as target gases and dry air as the baseline gas at 300 °C, as shown in Fig. 3. Our results showed that the CCTO thin films were sensitive to both reducing (H₂) and oxidizing (NO₂) gases, displaying reversible sensor response down to the lowest levels of gas exposure. As expected, the CCTO gas sensing response for these thin films was typical of n-type semiconductors, i.e., the resistance increased when exposed to oxidizing gas and decreased for reducing gas and, in both cases, the sensor response increased with increasing gas concentration. Moreover, there was good selectivity for oxidizing gases with the sensor response at 100 ppm, more than 5-fold larger for NO₂ than for H₂. In summary, our results satisfy the three gas sensing characteristics, indicating that CCTO thin films prepared with PPM have predominant n-type (electronic) conductivity. These results also corroborate those obtained by Parra et al. for CCTO films prepared with the sol-gel method, which is similar to our work [9].

The gas sensing and conductivity relationship is true for many semiconductor oxides [23]; however, it is not necessarily a law once that the switching of these mechanisms has been observed for some materials [25,26]. Thus, a double check with another electrical measurement is required to confirm this characteristic in CCTO thin films. The conductivity type can be directly determined by thermopower measurements, in which the movement of charge carriers due to a temperature gradient generates a voltage difference [27]. The charge carriers respond to an electric field in the same direction of the temperature gradient, depending on their charge (positive charges respond in the same direction as

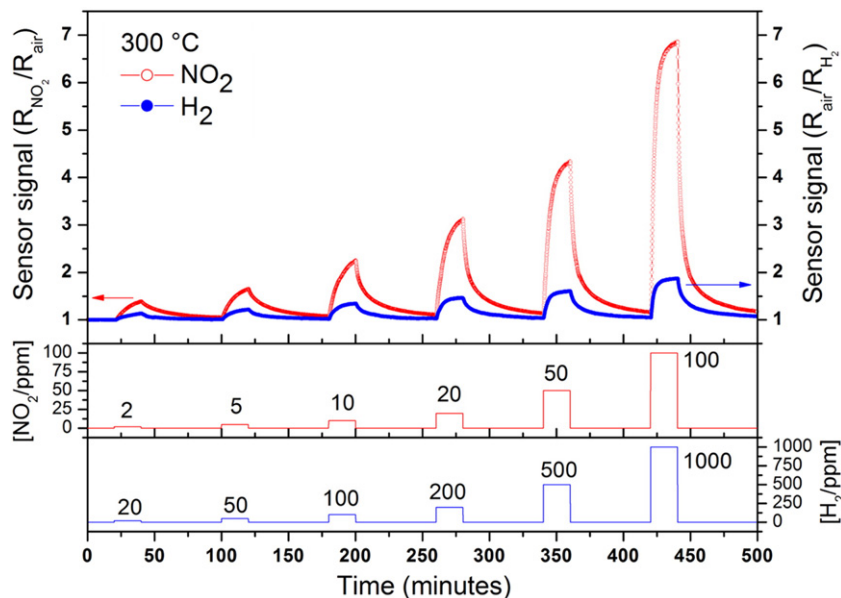


Fig. 3. Gas sensing response plots for different gases as a function of the gas concentration at 300 °C for the CCTO thin film. The NO₂ response (2–100 ppm) is linked to the left axis, and the H₂ response (20–1000 ppm) is linked to the right axis.

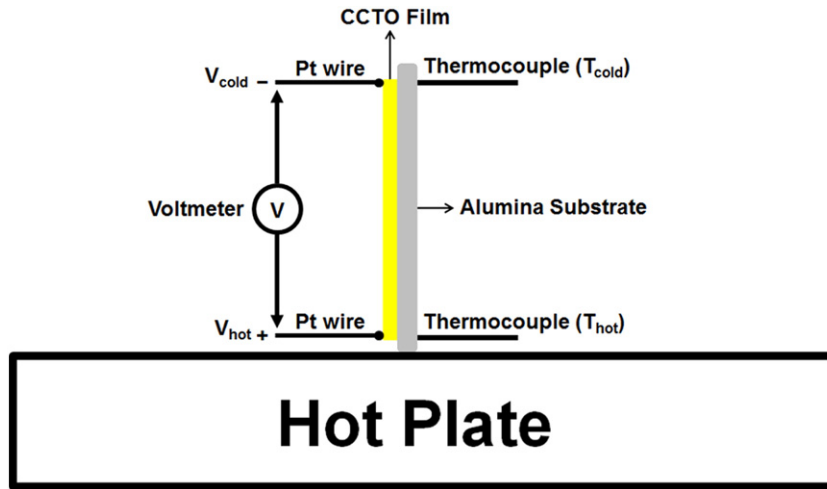


Fig. 4. Schematic illustration of the thermopower measurements.

the electric field, whereas negative charges respond in the opposite direction). This response is characterized by the signal of the ratio between the electric field and the temperature gradient, called the Seebeck coefficient (S), i.e., in n-type semiconductors, which have electrons (negative charges) as the major carriers, the electric field (\vec{E}) between the hot and cold ends and the temperature gradient (∇T) point in the opposite direction, which results in a negative Seebeck coefficient (S). Likewise, for p-type semiconductors, the opposite behavior is observed, with a positive Seebeck coefficient (S). These relationships can be expressed by the following equation:

$$S = \frac{\vec{E}}{\nabla T} \quad (1)$$

or

$$S = - \frac{V_{hot} - V_{cold}}{T_{hot} - T_{cold}} \quad (2)$$

where T_{hot} , T_{cold} , V_{hot} and V_{cold} are the temperatures and voltages at the hot and cold ends, respectively, as shown in Fig. 4. To perform the thermopower measurements, platinum wires were used as the electric contact and pasted (using platinum paste) at the ends of the surface of the CCTO film. A voltmeter was used to measure the voltage difference between the cold and hot ends. Two thermocouples were used to monitor the temperature at both ends of the back side of the alumina substrate, and a hot plate was used as the heating source, as shown in Fig. 4. Our experiments indicate a voltage difference between the hot and cold ends of approximately +45 mV for a temperature variation between the ends of approximately 40 °C, i.e., a negative Seebeck coefficient ($S < 0$). These results corroborate our gas sensing results, confirming that the CCTO thin films prepared with PPM display n-type conductivity and indicating that there is a direct correlation between the gas sensing behavior and the conductivity type in this material.

Recently, a theoretical study has proposed that oxygen vacancy defects can affect the electronic structure of CCTO, depending on the oxygen regime during the synthesis conditions [28]. Furthermore, Rupp et al. and Knauth et al. have reported that ceria and titanium-based thin films are affected by the initial processing route, leading to changes in the near-ordering of oxygen-cation bonds [29,30].

We hypothesize that either the reducing atmosphere, as a consequence of organic decomposition, in wet-chemical processing or gas environments, due to changes in the oxygen partial pressure during the deposition procedure, in physical processing can affect the formation of oxygen-related defects on the crystalline CCTO structure during

thin film processing, leading to a different conductivity type. To confirm whether oxygen-related defects are the determining factor of changes in the conductivity type in CCTO thin film, additional studies, already in progress, must be completed to deconvolute the main mechanism controlling CCTO conductivity.

4. Conclusions

Single-phase CCTO thin films were prepared with the polymeric precursor method on alumina substrates, presenting polycrystalline grains and high surface porosity. The gas sensing response indicated that CCTO film has high sensitivity and selectivity to oxidizing gases and that CCTO films prepared via MPP have n-type conductivity, which was confirmed by thermopower measurements. Explanations for this behavior were proposed, identifying the oxygen-related intrinsic effects during film processing as the main mechanism responsible for controlling the type of gas sensing response and conductivity in CCTO thin films. These results indicate that CCTO thin film is a promising material to be used as active element in gas sensor devices for the detection of oxidizing gases.

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