Ozone and nitrogen dioxide gas sensor based on a nanostructured SrTiO.85Fe0.15O3 thin film

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A B S T R A C T
In this manuscript, we report an investigation into the sensitivity of two oxidizing gases (ozone and nitrogen dioxide) for nanocrystalline SrTiO.85Fe0.15O3 thin films deposited by the electron beam physical vapor deposition technique. Annealing treatment at 500 °C enhanced the crystallization and surface roughness of the thin film. Electrical measurements revealed that the thin film was sensitive to oxidizing gases, especially to low ozone gas levels, exhibiting a fast response time, a short recovery time as well as good reproducibility and reversibility. These findings demonstrate the great potential of the SrTiO.85Fe0.15O3 compound to be applied as a selective ozone gas sensor.

1. Introduction
Since the development of first gas detection device based on semiconducting metal oxides, much effort has been devoted to enhancing gas sensor performance [1–5]. Nanostructured materials have drawn the interest of many researchers due to the possibility of improving the sensitivity, selectivity, response and recovery time, as well as reducing the operating sensor temperature [2–4, 6, 7]. These sensors have been widely employed in industry, agriculture and in environment control to detect reducing and oxidizing gases, such as hydrocarbons, oxygen, hydrogen (H2), nitrogen oxides (NO2 and NOx), ammonia (NH3), sulfur dioxide (SO2), carbon monoxide (CO) and ozone (O3) [3, 8–12]. Ozone (O3) is an oxidizing gas used in important fields such as the food industry, drinking water treatment, medicine and agriculture [13–16]. Despite these important applications, ozone levels above 120 ppb become dangerous to human health, and could cause serious health problems [13, 17]. Therefore, the continuous monitoring of ozone levels present in the atmosphere is indispensable. Typical ozone gas sensors are based on SnO2, ZnO, WO3 and In2O3 compounds [7, 9, 11, 12, 18–22]. Despite the progress made, numerous studies have focused on enhancing gas sensing properties, especially selectivity [23–26].

Strontium titanate ferrite (SrTi1−xFexO3, abbreviated STFO) solid solutions are p-type semiconductors which exhibit a cubic perovskite-like structure [12, 27, 28]. The replacement of Ti4+ by Fe3+ creates negatively charged defects (Fe0 Ti3+) [27–31], which due to the electroneutrality conditions, are compensated by the formation of oxygen vacancies (Vo) [28, 32]. The replacement of Ti4+ by Fe3+ creates negatively charged defects (Fe3+ Vo) [27–31], which due to the electroneutrality conditions, are compensated by the formation of oxygen vacancies (Vo) [28, 32]. These solid solutions have been applied as resistive gas sensors, mainly for oxygen and hydrocarbons [1, 10, 12, 31, 33–37]. As shown in Table 1, different methodologies have been employed to prepare STFO thick and/or thin films. In recent years, our group has dedicated efforts toward investigating STFO (0.0 ≤ x ≤ 1.0) solid solutions prepared by using different synthesis routes [7, 38–40]. In an earlier study, the long- and short-range order structure and electronic properties of nanostructured STFO powders were studied [7]. Additionally, for the first
time, the ozone gas sensing properties of nanostructured STFO thin films deposited by electron-beam physical vapor deposition (EB-PVD) were also studied, looking at the influence of the Fe content on ozone gas sensing films [39]. Despite continued progress, the gas sensing properties, particularly the sensitivity of STFO toward ozone and other analyte gases, requires further investigation. In this study, we present a detailed investigation of O3 and NO2 sensing properties of nanostructured SrTi0.85Fe0.15O3 (abbreviated as STFO15) thin films deposited by the electron beam physical vapor deposition (EB-PVD) method. The structural and microstructural properties of STFO15 samples were characterized by X-ray absorption spectroscopy (XAS) and atomic force microscopy analysis, respectively. Gas sensing properties of STFO15 thin film samples toward O3, NO2, NH3, and CO gases were evaluated, mainly concerning its selectivity. Therefore, the focus of this research was to provide a better understanding about the gas sensing properties of the nanostructured SrTi1−xFe2O3 compound.

2. Experimental section

2.1. Deposition of SrTi1−xFe2O3 thin film and characterization techniques

The electron beam deposition technique was used for STFO15 thin film deposition. A target was produced from a nanocrystalline SrTi0.85Fe0.15O3 powder sample synthesized using the polymeric precursor method [40]. The STFO15 thin film, the thickness of which was monitored by a quartz balance, was deposited in a Balzers BAK600 evaporator on Si(100) and SiO2/Si substrates containing 120 nm-thick Pt electrodes. After deposition, the thin films were annealed in an electric furnace under an air atmosphere for 4 h at 500 °C with a heating rate of 5 °C min−1 [39]. Additional details regarding the synthesis procedure of the target as well as the thin film deposition can be found in Refs. 27, 40.

The thin film surface microstructural characteristics were investigated using an atomic force microscope (NT-MDT SolverPro AFM) in tapping mode. The sample thickness was verified by using a field emission scanning electron microscope (FE-SEM, Zeiss Supra35) operating at 5 kV. The microanalysis by energy-dispersive X-ray (EDX) spectroscopy was performed in a spectrometer EDAX-AMETEC (model APOLLO X).

X-ray absorption spectroscopy (XAS) experiments were carried out at the Brazilian Synchrotron Light Laboratory (LNLS), using the XAFS2 beamline. This characterization technique was applied to probe the medium- and short-range order structure of STFO15 thin films deposited onto Si(100) before and after thermal treatment. Ti K-edge XANES (X-ray absorption near-edge spectroscopy) spectra were collected in fluorescence mode, at room temperature, using a 15-element Ge solid state detector (Ge-15). These spectra were recorded between 4960 and 5060 eV using an energy step of 0.3 eV around the edge. For comparison purposes, all spectra were background removed and normalized 5060 eV using a linear step of 0.3 eV around the edge. The Ti K-edge XANES spectra of the STFO15 thin film before and after thermal treatment at 500 °C for 4 h are shown in Fig. 2. The gas response or sensitivity (S) was defined as S = Rgas/Rair, where Rair and Rgas are the electric resistances of the sensor device exposed to dry air and oxidizing gases (O3 or NO2), respectively.

3. Results and discussion

3.1. Structural and microstructural characterizations

Fig. 2 displays the Ti-K edge XANES spectra of the STFO15 thin film before and after thermal treatment at 500 °C for 4 h. Three transitions labeled as P1, P2, and P3 are denoted on the pre-edge region of XANES spectra. Peak P1 is related to the 1s(Ti) → 3d(t2g) transition, whereas P2 peak is due to the 1s(Ti) → 4p(Ti) transition, including some degree of the
1s(Ti) → 3d(eg)(Ti) quadrupole contribution [7,28]. The P3 peak is assigned to a dipole excitation of 1s electrons to t2g and eg orbitals of the neighboring TiO6 [28,41].

Previous results have shown that P2 intensity is directly related to Ti symmetry, exhibiting the lowest intensity for the crystalline cubic structure, whereas in non-crystalline structures it becomes more intense [41]. In amorphous titanate compounds, the intense P2 peak was attributed to the presence of (TiO6) and (TiO5) units [42–45].

Fig. 2 inset shows a lower intensity of the P2 peak after annealing treatment, which can be attributed to an increase in (TiO6) units. Additionally, the P3 peak was visible in the spectrum of annealed sample, revealing an increase in TiO6 octahedra linkage. Likewise, the oscillations in the post-edge region (4980–5020 eV) were more pronounced after annealing. These three effects caused by annealing can be interpreted as an increase in the short and medium range-order around titanium atoms, allowing for the conclusion that the degree of crystallization of the STFO15 sample increased after annealing.

Fig. 3 shows the AFM images of the STFO15 thin film before and after annealing at 500 °C. Before annealing, the sample exhibited a flat surface with an R_{rms} (root-mean-square) roughness around 0.748 nm. After annealing, the sample presented a microstructure characteristic of nanocrystalline thin films exhibiting grain sizes between 30 and 150 nm and an R_{rms} around 4.0 nm.

Fig. 4 shows the EDX spectra of the STFO15 ceramic pellet (used as target) and STFO15 thin film after annealing treatment. The EDX spectra detected the presence of Sr, Ti, Fe, and O elements in both samples, whereas the Si peak was observed only for the thin film. Additionally, the (Sr + Ti)/Fe ratio was approximately 1.2 (ceramic pellet) and 1.4 (thin film), suggesting that the stoichiometry of the STFO15 thin film was preserved during the deposition process (see Fig. 4).

3.2. Gas sensing properties

First, the electrical resistance of the STFO15 thin film before annealing exhibited a higher resistivity, due the presence of several porous (see Fig. 3), resulting in a low densification of the sample. The electrical resistance of the STFO15 thin film annealed at 500 °C presented typical values of metal oxide semiconductor sensors and was then monitored when exposed to 0.8 ppm of O3 (Fig. 5a) and 40 ppm of NO2 (Fig. 5b) for various periods of time at an operating temperature of 260 °C for O3 and 220 °C for NO2. As can be seen, the gas sensor response of the STFO15 thin film was characteristic of a p-type semiconductor [4]. In addition, the STFO15 thin film showed good sensitivity, even for short periods of time, total reversibility and good stability of the baseline toward O3 and NO2 gases. For NO2 gas, it was observed that the sample reached a saturation level at times longer than 30 s.

It is well-established that the detection of oxidizing gases on a p-type sensor material is based on the surface adsorption of the gas
molecules, leading to the formation of a hole-accumulation layer which causes an increase in the current density [4,46,47]. The gas sensor response of the STFO15 thin film for these two oxidizing gases (O$_3$ and NO$_2$) can be explained by the follow reactions [18,46]:

$$\text{O}_3(g) + \text{e}^- \rightarrow \text{O}_2(\text{des}) + \text{O}^-_{\text{ads}} \quad (1)$$

$$\text{NO}_2(g) + \text{e}^- \rightarrow \text{NO}_2(\text{ads}) \quad (2)$$

$$\text{NO}_2(\text{ads}) + \text{O}^-_{\text{ads}} + 2\text{e}^- \rightarrow \text{NO}(\text{ads}) + \text{O}_2(\text{ads}) \quad (3)$$

To determine the optimum operating temperature ($T_{\text{opt}}$), the annealed STFO15 thin film was exposed for 30 s–0.8 ppm of O$_3$ and afterward to 40 ppm of NO$_2$. The results presented in Fig. 6 show a maximum sensitivity value at 260°C for both target gases, which is close to that of traditional metal oxide gas sensors such as WO$_3$, In$_2$O$_3$, and SnO$_2$ [9,11,12,19,20,46,48]. Chow and co-workers synthesized STFO thin films via a sol–gel spin-coating method and applied them as oxygen gas sensors, with an operating temperature ranging around of 350°C for an iron content of $x = 0.2$ [49]. On the other hand, STFO thick films obtained via solid-state reaction method exhibited good gas sensing performance toward oxygen at temperatures above 600°C [33,34,36,50].

Based on the above results, the STFO15 thin film was kept at 260°C and then exposed for 30 s to different O$_3$ levels (0.1–0.8 ppm). As can be seen in Fig. 7, it is noteworthy that the film displayed good sensitivity even at lower O$_3$ levels, total reversibility, as well as good reproducibility. In addition, the response time varied from 26 s (0.1 ppm) to 28 s (0.8 ppm), while the recovery time varied from 72 s (0.1 ppm) to 161 s (0.8 ppm). Although the response time ($t_{\text{res}}$) for STFO15 thin film was greater than for WO$_3$ compound ($t_{\text{res}} \sim 1$ s), the recovery time ($t_{\text{rec}}$) was relatively shorter ($t_{\text{rec}} < 60$ s) [11].
In a similar procedure, the annealed STFO15 thin film was also kept at 260°C and exposed to NO₂ gas. As depicted in Fig. 8, even at 5 ppm NO₂, the material showed a noticeable response as well as good reproducibility and reversibility.

Gas sensing experiments were also performed using the carbon monoxide (CO) and ammonia (NH₃) gases. The STFO15 thin film did not exhibit any sensitivity to these gases in the range of 5 to 40 ppm when measured at different operating temperatures (220–300°C).

Fig. 6. Gas sensor response of the STFO15 thin film exposed to 0.8 ppm O₃ and 40 ppm NO₂ at different operating temperatures.

Fig. 7. Ozone gas sensing response for the STFO15 thin film as a function of the gas level at an operating temperature of 260°C.

Fig. 8. NO₂ gas sensing responses for STFO15 thin film at 260°C for various NO₂ levels (5–40 ppm).

Fig. 9. Sensitivity versus gas concentration in the range (a) 0.1–0.8 ppm O₃ and (b) 5–40 ppm NO₂.

Fig. 10. Gas sensor response of the STFO15 thin film to oxidizing (O₃ and NO₂) and reducing (CO and NH₃) gases at an operating temperature of 260°C.
devices [2,4,51]. Fig. 10 displays the comparison of the sensitivity values of the annealed STFO15 thin film when exposed to oxidizing (O$_2$ and NO$_2$) and reducing (CO and NH$_3$) gases at 260 °C. In order to further exploit the selectivity of the film, we chose similar gas concentrations, i.e., 0.8 ppm O$_2$ and 5 ppm NO$_2$, to compare the gas sensing performance. As can be seen, the annealed STFO15 thin film showed the highest sensitivity to O$_2$ (19.8) when compared to NO$_2$ (4.3) and non-detectable sensitivity to CO and NH$_3$ gases. Based on these findings, we can state that the STFO15 thin film can be considered as a promising material for an ozone gas sensor.

4. Conclusions

We have successfully obtained nanocrystalline SrTi$_{0.85}$Fe$_{0.15}$O$_3$ thin films via the electron beam deposition technique. X-ray absorption spectroscopy measurements showed that the annealing treatment was effective in increasing the degree of crystallization of the STFO15 thin film, which led to an increase in surface roughness, according to AFM analysis. Electrical resistance measurements pointed out the good sensitivity, fast response and short recovery time of the annealed STFO15 thin film when exposed to O$_2$ and NO$_2$ oxidizing gases. Due to the good sensing properties to ozone gas, this material can be considered as a promising material for ozone gas sensors.

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