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RARE EARTH PEROVSKITE-TYPE OXIDES AS GAS SENSORS

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Nanosized $SmFeO_3$ powders, prepared by the thermal decomposition at 700°C of $Sm[Fe/CN)_6]4H_2O$, were used for the fabrication of thick films on alumina substrates with comb-type Au electrodes. The films were fired at different temperatures in the 800-1000°C range. The content of α-terpineol, a component of the organic vehicle, was varied in the range 0.0046-4 wt%. The NO_2 sensing properties of the films were investigated as a function of the materials characteristics. The content of α-terpineol strongly influenced the electrical conductivity and its activation energy. The smaller the amount of α-terpineol, the lower the NO_2 response of the films and the larger their conductivity. Such increase in conductivity is attributed to a different oxygen surface layer on the $SmFeO_3$ surface, which is induced by the decomposition reaction of α-terpineol during sintering. The activation energy is correlated with the NO_2 sensitivity and the materials characteristics (influenced by the preparation parameters). The materials processing parameters are thus of primary concern for the NO_2 sensing properties of the $SmFeO_3$ thick films.

Key words: $SmFeO_3$ powder, terpineol content, NO_2 sensitivity, electrical conductivity, activation energy

Nanozirani prahovi $SmFeO_3$, izdelani s termičnim razpadom $Sm[Fe(CN)_6].4H_2O$ pri 700°C, so bili uporabljeni za pripravo debelih plasti na podlagi iz glinice z comb-tipom Au elektrod. Plasti so bile žgane pri različnih temperaturah med 800 in 1000°C. Vsebnost α-terpineola, sestavina organskega nosilca se je spreminjala v razponu 0.0046 do 4 ut.%. Občutljivost za NO_2 je bila raziskana v odvisnosti od karakteristik materiala. Vsebnost α-terpineola je močno vplivala na električno prevodnost in njeno aktivacijsko energijo. Čim manjša je bila vsebnost α-terpineola, manjši je bil NO_2 odgovor plasti in večja je bila njihova prevodnost. Večanje prevodnosti se pripisuje različnemu sloju kisika na površini $SmFeO_3$, ki ga inducira reakcija razpada terpineola med sintranjem. Aktivacijska energija je korelirana z občutljivostjo za NO_2 in karakteristikami materiala (te so odvisne od parametrov priprave). Zato so parametri procesiranja materiala primarno pomembni za NO_2 senzorske lastnosti debelih plasti $SmFeO_3$.

Ključne besede: $SmFeO_3$ prahovi, vsebnost terpineola, občutljivost za NO_2, elektro prevodnost, aktivacijska energija

1 INTRODUCTION

Recently, the development of reliable and selective solid-state NO_x sensors is strongly needed for environmental monitoring and automotive applications[1,2]. The methods of monitoring NO_x currently approved by the existing environmental standards are based on analytical techniques[3], such as chemiluminescence and IR spectroscopies. The associated equipment is very costly and bulky, and is not easily transportable. Solid-state sensors are inexpensive, small, and can be easy to integrate with electronic circuitry. Their use would be dramatically cheaper than the use of analytical techniques, and would lead to the possibility of a wider distribution of environmental monitoring locations than those existing present[4].

Semiconducting oxides have been studied for the control of air quality inside cars for passengers' comfort[5] and for the possible use in air quality monitoring, in the case of WO_3[6]. Promising candidates for gas sensors are $LnTO_3$ perovskite-type oxides, with Ln = rare earth and T = transition metal, which usually are p-type semiconducting oxides[7]. In particular, thick[8] and thin films[9] of $LaFeO_3$ have shown the capability of NO_2 sensing at concentration levels 1-10 ppm.

Miniaturized robust sensors in form of thick film can be fabricated by screen-printing technology, which allows low-cost mass production with a good reproducibility[10]. However, the use of high quality, controlled oxide powders is needed for the preparation of reliable devices. The conventional method of mixed oxide preparation (solid-state reaction) does not allow a precise control of the powder quality.

The synthesis of ultrafine, homogeneous and chemically pure rare earth perovskite-type oxide powders has been recently performed by the thermal decomposition of the corresponding heteronuclear hexacyano-complexes[11-14], as it has been firstly proposed by Gallagher in 1968[15]. This method allows the preparation of nanosized powders, free of intragranular pores, which are excellent for the fabrication of thick films by screen-printing technology[16].

In the present work, we report results about the NO_2 sensitive electrical response of $SmFeO_3$ thick films, prepared using oxide powders from the thermal decomposition of the heteronuclear complex, $Sm[Fe(CN)_6]4H_2O$, for environmental monitoring application. The main purpose of this study is to correlate the results of the electrical measurements with the materials processing parameters. In fact, the influence of the materials processing pa-

rameters on the sensor properties is an aspect which underwent limited investigation in the relevant literature.

2 EXPERIMENTAL PROCEDURE

The hexacyanocomplex, $Sm[Fe(CN)_6]\cdot 4H_2O$, was synthesized by mixing aqueous solutions of equimolar amounts of $Sm(NO_3)_3 6H_2O$ and $K_3Fe(CN)_6$ under continuous stirring[12]. The resulting precipitate was washed with water, ethanol and diethyl ether, before drying in air at 50°C. The $SmFeO_3$ oxide powder was prepared by the thermal decomposition of the complex at 700°C for 1 hour. The temperature was choosen from thermogravimetric analysis, as the lowest temperature at which the complex is completely decomposed[12].

The pastes for the preparation of the thick films were prepared by mixing in a ball mill for 5 hours this $SmFeO_3$ powder and an organic vehicle, containing α-terpineol, ethyl-cellulose, and buthyl-carbitol acetate. The thick films were deposited from the paste on alumina substrates with comb-type Au electrodes. Films with different microstructures were prepared by firing in air at different temperatures (800, 900, and 1000°C for 1 hour). The content of α-terpineol was also varied with weight steps of one order of magnitude, corresponding to 0.0046, 0.046, 0.46, and 4 wt% over the total content of the paste.

The powders and the thick films were analyzed by scanning electron microscopy (SEM, Model Stereoscan 360, Leica Cambridge), energy-dispersive spectroscopy (EDS, Model eXL II, Link), and X-ray diffraction (XRD, Model PW 1729, Philips, using a Cu Kα radiation with $\lambda = 0.154$ nm).

The electrical d.c. conductivity was measured varying the temperature in different gas atmospheres (air, N_2, and 9 ppm NO_2 in air). The choice of the NO_2 concentration has been made because the value of 9 ppm is at the border between the ranges for environmental monitoring and for combustion control. The gas sensitive electrical properties of the thick films were tested in a measurement chamber where their d.c. conductivity was measured at various temperatures (in the range from room temperature up to 450°C), cycling the gas flow from air to nitrogen, or from air to 9 ppm NO_2 in air.

3 RESULTS AND DISCUSSION

As already reported for $LaFeO_3$ powders prepared by the decomposition of s similar complex[17,18] SEM observations showed that the morphology of $SmFeO_3$ powders prepared by the thermal decomposition of the hexacyanocomplex consisted of large agglomerates (in the size range of micrometers) made of nanosized particles[19]. $SmFeO_3$ powders prepared at 700°C were made of agglomerates of about 0.5 - 1 μm in diameter, each one consisting of nanometric particles of about 50 - 80 nm. The orthorhombic crystalline structure of the $SmFeO_3$ (JCPDS file No. 39-1490) perovskite-type oxide was confirmed by XRD analysis.

XRD analysis confirmed also for all the thick films the sole presence of the peaks of $SmFeO_3$. EDS analysis of the films showed the presence of Sm and Fe. SEM observations showed that the films were highly porous. The morphology of the thick films heated at the lowest temperature, 800°C, was very similar to the morphology of the powders, but with a reduction in the number of the large agglomerates. Sintering of the nanosized particles was very limited, and the presence of necks was rarely observed. The adhesion of the films to the substrates was rather good, as tested with scotch-tape.

With increasing the firing temperature, a growth of the oxide grains was observed. The sintering proceeded with increasing temperature, together with an increase in the number of necks between particles. The average size of the grains was 200 nm at 900°C, while at 1000°C, the grain size increased up to 400 nm. These values are given for the films containing the largest amount of α-terpineol. The decrease in the α-terpineol content caused a progressive decrease in the grain size. This effect was more evident at higher temperature. The $SmFeO_3$ films prepared with the lowest amount of α-terpineol showed an average grain size of about 150 and 250 nm when fired at 900°C and 1000°C, respectively. Sintering was therefore enhanced by the addition of α-terpineol. This can be explained in terms of a reduced number of adsorbate species which may adversely affect sintering of $SmFeO_3$.

In fact, recent results performed on $SmFeO_3$ powders by X-ray photoelectron spectroscopy (XPS)[20] confirmed that the improvement in the sinterability of $SmFeO_3$ powders with the addition of α-terpineol can be ascribed to an easier reaction of the adsorbed oxygen with the product of the α-terpineol decomposition during firing. The strongly chemisorbed oxygen on the surface of pure $SmFeO_3$ hindered the interdiffusion phenomena which occur during sintering, and the grain size remained smaller.

Considering the electrical measurements, increases in conductivity were measured for the $SmFeO_3$ thick films upon addition of NO_2, which means that $SmFeO_3$ behaved as a p-type semiconducting oxide, given that NO_2 is an oxidizing gas. A larger NO_2 response, expressed as the ratio between the conductivities in NO_2 (σ_{gas}) and in air (σ_{air}), was observed at lower temperatures for the $SmFeO_3$ films, while the response time (at 90% of the maximum value) was larger. The NO_2 desorption was slower than its adsorption. At higher temperature, the stability of the response improved and the response became faster. **Figure 1** shows, as an example, the conductivity response at various temperatures (300, 350, and 400°C) of a $SmFeO_3$ thick film sintered at 1000°C with 4 wt% of α-terpineol, when gas flow was changed between air and 9 ppm NO_2 in air. The NO_2 response ($\sigma_{gas}/\sigma_{air}$) was evaluated to be 8.2 at 300°C, 5.4 at 350°C,

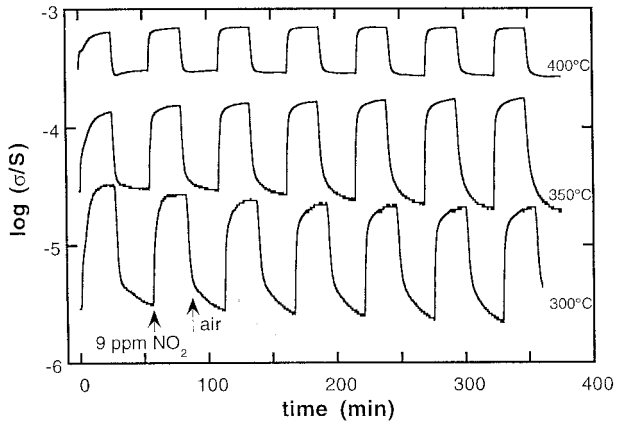

Figure 1: Electrical response at various temperatures of the $SmFeO_3$ thick films fired at 1000°C, with 4 wt% of α-terpineol. Gas flow was changed from air to 9 ppm NO_2 in air

Slika 1: Električni odgovor pri različnih temperaturah za debele plasti $SmFeO_3$ žgane pri 1000°C s 4 ut.% α-terpineola. Tok plina je bil menjan od zraka do 9 ppm NO_2 v zraku

and 2.3 at 400°C, while the response time at the same temperatures was in the order of 7, 5, and 2 minutes, respectively. The smaller response can be ascribed to a reduction of the Debye length with increasing temperature, which results in a decrease in the accumulation layer thickness.

Figure 2 shows the response of the conductivity, measured at 350°C, of different $SmFeO_3$ thick films sintered at 900°C and 1000°C, with 0.46 wt% and 4 wt% of α-terpineol, when the gas flow was changed between air and 9 ppm NO_2 in air. The NO_2 sensitive response of the $SmFeO_3$ samples was hugely affected by the thick-film processing parameters. The content of α-terpineol had a predominant influence on the gas response, while the sintering temperature, and thus the films' microstructure, played a minor role. The content of α-terpineol strongly influenced the conductivity in air of the films. The NO_2 responses of the films prepared with the lowest contents of α-terpineol (sintered at 800°C, 900°C, and 1000°C), which are not showing in **Figure 2**, was in the same range of the response of the films prepared with 0.46 wt% of α-terpineol. The films prepared with the 4 wt% of α-terpineol showed a lower conductivity in air and a larger response. Other films showed conductivities in the 10^{-3} S range, about 2 orders of magnitude higher, and a limited sensitivity.

The films annealed at 1000°C, having thus a larger grain size and a larger resistivity in air, surprisingly showed larger NO_2 responses (the largest response was observed for the film with the largest grain size). These results are opposite to what was expected from the observed films' microstructures. However, these results are consistent with the measured XPS surface compositions[20].

In order to better discuss this behaviour, we performed measurements of the temperature dependence of the conductivity on the thick films. **Figures 3** and **4** show the Arhenius plots in environments with different gases (N_2, air, and 9 ppm NO_2 in air), for the $SmFeO_3$ films sintered at 1000°C with 4 wt% of α-terpineol, and sintered at 900°C with 0.46 wt% of α-terpineol, respectively. The measurements were performed after an exposure to gases long enough to reach stable conditions. For all the samples tested, the conductivity increased in the order NO_2 > air > N_2, confirming the behaviour as a p-type semiconductor of $SmFeO_3$, although at temperatures around 400°C the conductivities in air and in NO_2 became almost the same for the films with the lower contents of α-terpineol.

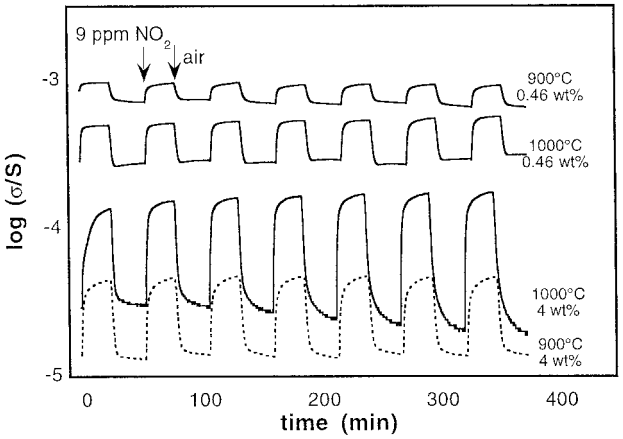

Figure 2: Electrical response at 350°C of $SmFeO_3$ thick films prepared with different organic vehicles (0.46 and 4 wt% of α-terpineol), fired at 900°C and 1000°C. Gas flow was changed from air to 9 ppm NO_2 in air

Slika 2: Električni odgovor pri 350°C debelih plasti $SmFeO_3$, ki so bile izdelane z različnimi organskimi nosilci (0.46 in 4 ut.% α-terpineola), žgane pri 900 in 1000°C. Tok plina se je menjal od zraka do zraka z 9 ppm NO_2

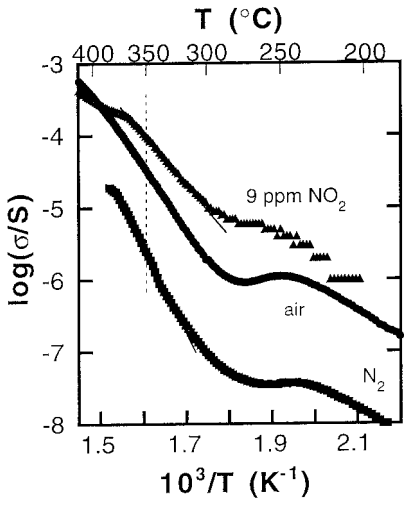

Figure 3: Temperature dependence of the conductivity for the $SmFeO_3$ thick films fired at 1000°C with 4 wt% of α-terpineol, in different gaseous atmospheres

Slika 3: Temperaturna odvisnost prevodnosti za debele plasti $SmFeO_3$ žgane pri 1000°C s 4 ut.% α-terpineola v različnih atmosferah

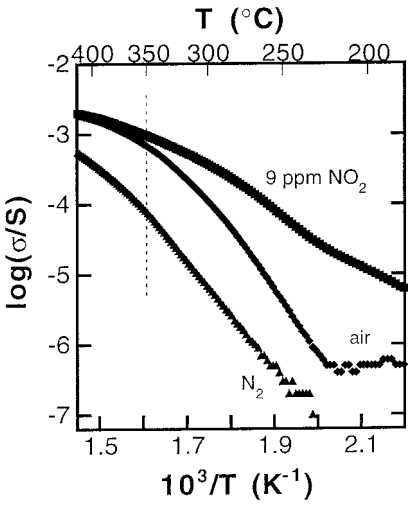

Figure 4: Temperature dependence of the conductivity for the $SmFeO_3$ thick films fired at 900°C with 0.46 wt% of α-terpineol, in different gaseous atmospheres

Slika 4: Temperaturna odvisnost prevodnosti za debele plasti $SmFeO_3$ žgane pri 900°C s 0.46 ut.% α-terpineola v različnih atmosferah

The conductivity of the film sintered at 1000°C with 4 wt% of α-terpineol showed different regions of temperature dependence **(Figure 3)**. In the high and low temperature regions, the conductivity increased with increasing temperature, but with different activation energies, while a transition region was observed at intermediate temperatures. This trend was not observed for the samples with lower content of α-terpineol, which showed only the linear trend at high temperatures, as shown in **figure 4**.

The activation energy (E_a) was calculated for the various samples, considering the temperature dependence of the electrical conductivity of the semiconductors, through the equation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1)$$

where σ is the conductivity, T is the temperature, k is the Boltzmann constant, and σ_0 is the so-called pre-exponential factor[21]. When a semiconductor is prepared under different conditions, its activation energy varies, but in these conditions, σ_0 depends exponentially on E_a, which is known as the Meyer-Neldel rule[22], and may be considered as follows:

$$\sigma_0 = \sigma^* \exp(-E_a/kT^*) \quad (2)$$

where σ* and T* are constant within a class of related semiconductors. This rule is an empirical relation which has been observed for many different conducting materials, either semiconductors or ionic conductors[23-26].

Figure 5 shows the correlation between the activation energy and the logarithm of the pre-exponential factor for various $SmFeO_3$ films tested (samples prepared with four contents of α-terpineol and sintered at 800°C, 900°C, and 1000°C). The relationship between the E_a and the log σ_0, which represent the slope and the intercept of the Arrhenius plots, respectivelly[25], is linear, which means that the Meyer-Neldel rule is respected. For a given sample, the largest activation energy was observed in N_2 and the smallest in NO_2. The films prepared with 4 wt% of α-terpineol showed the largest activation energies. Moreover, the films prepared with the smaller contents of α-terpineol showed activation energies decreasing with increasing the firing temperature, resulting in better NO_2 responses.

Figure 6 shows the correlation between the activation energies in air and in NO_2 for the $SmFeO_3$ films tested. The activation energies in both atmospheres showed very close values when E_a in air was lower than 1 eV. On the other hand, when E_a in air was larger (about

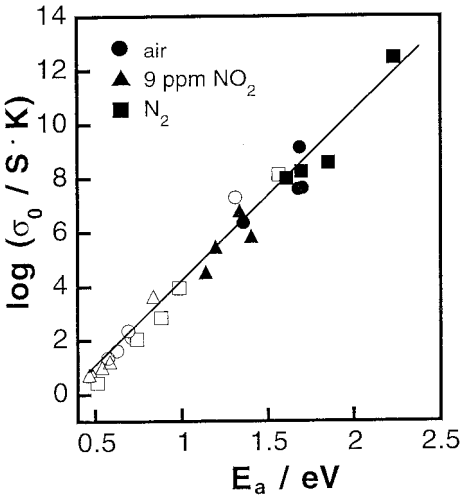

Figure 5: Correlation between E_a at 350°C and log σ_0 for the $SmFeO_3$ films tested (close and open symbols refer to films with 4 wt% of α-terpineol or less, respectively)

Slika 5: Korelacija med E_a pri 350°C in log σ_0 za preizkušene $SmFeO_3$ plasti (prazni in polni znaki se nanašajo na plasti s 4 ut.% α-terpineola ali manj)

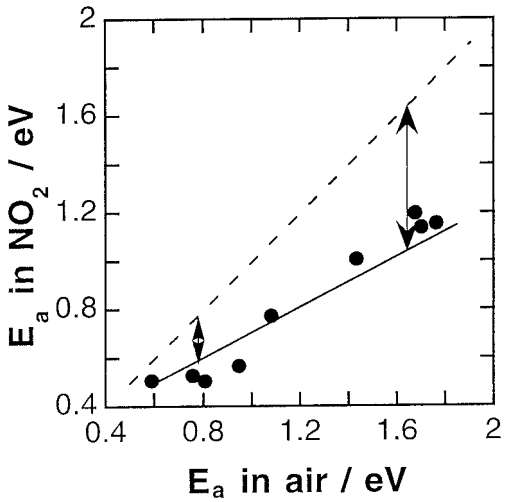

Figure 6: Correlation between the activation energies in air and 9 ppm NO_2, measured at 350°C, for the $SmFeO_3$ films tested

Slika 6: Korelacija med aktivacijsko energijo na zraku in v 9 ppm NO_2 merjena pri 350°C za preizkušene $SmFeO_3$ plasti

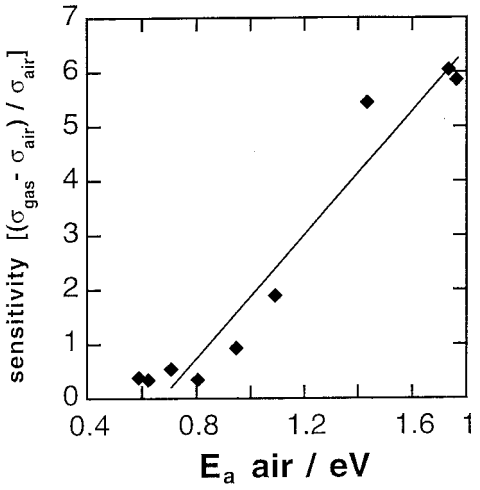

Figure 7: Correlation between E_a in air and the sensitivity to 9 ppm NO_2, both measured at 350°C, for the $SmFeO_3$ films tested
Slika 7: Korelacija med E_a na zraku in občutljivostjo za 9 ppm NO_2 merjena pri 350°C za preizkušene $SmFeO_3$ plasti

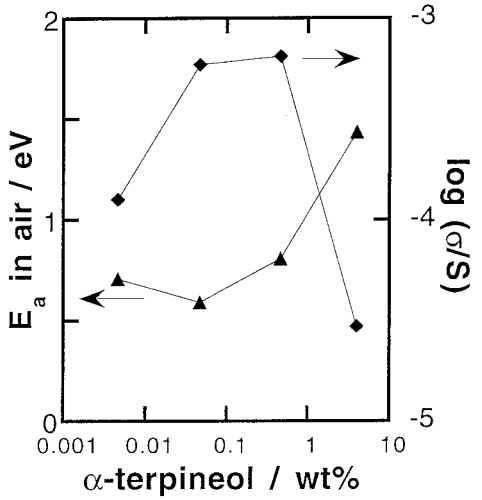

Figure 8: Correlation between the electrical properties (E_a and conductivity) measured at 350°C in air, and the content of α-terpineol for the $SmFeO_3$ films fired at 900°C
Slika 8: Korelacija med električnimi lastnostmi (E_a in prevodnost) merjena pri 350°C na zraku in vsebnost α-terpineola za plasti $SmFeO_3$ žgane pri 900°C

1.8 eV), the contact with NO_2 dramatically reduced E_a. Given the temperature dependence of the conductivity for the various samples (**Figures 3** and **4**) and the XPS results[20], the presence of different surface conditions can explain these results; for the samples which showed a low E_a in air, the surface can be highly conductive and the adsorption of NO_2, a strong oxidizing gas, can only slightly change the number of surface charge carries. On the other hand, for the samples which showed a high E_a in air, the surface conductivtiy is low and the adsorption of NP_2 induces a large increase in the number of holes and, thus, of conductivity.

It is thus clear that the $SmFeO_3$ films having high E_a in air should possess large NO_2 responses. In fact, **Figure 7** shows the correlation between E_a in air and the response to 9 ppm NO_2 (expressed as $[(\sigma_{gas} - \sigma_{air})/\sigma_{air}]$), both measured at 350°C, for the $SmFeO_3$ films. The correlation between the activation energy and the gas sensitivity of the films was linear.

As already reported above, the NO_2 response of the films was largely influenced by the composition of the organic vehicle used. **Figure 8** shows the relationship between the E_a and σ in air, measured at 350°C, and the content of α-terpineol for the films sintered at 900°C. The conductivity increased and E_a decreased with increasing the α-terpineol content up to 0.46 wt%, while a sharp decrease in conductivity with an increase in E_a was observed for the α-terpineol content of 4 wt%. This can be explained by the fact that an increase in α-terpineol content at low levels can improve the films' sinterability, thus enhancing the conductivity, while larger amounts of α-terpineol affect the surface states of $SmFeO_3$ films, causing a reduction in the number of charge carries.

All the reported results can be explained in terms of different surface states for the $SmFeO_3$ films. The presence of surface states (oxygen or hydroxyl adsorbates) causes an increase in the number of acceptor levels for the p-type $SmFeO_3$, and thus an increase in the number of holes, the charge carries. XPS results showed that the presence of a higher content of α-terpineol decreased the bonding strength of the surface states (chemisorbed oxygen)[20]. The decomposition of α-terpineol during firing occurs at relatively high temperatures (boiling point of about 220°C), and may lead to carbon formation, which may react with the oxide surface states. At lower temperatures, in the absence of α-terpineol, surface states may form bridging oxygen at the surface which hinder the sintering. The result is that the larger the α-terpineol content, the more advanced the sintering. In turn, this is accompanied by a large surface reaction, which results in an increase in the activation energy and a decrease in conductivity of the films, and in an increase in their gas response.

The surface states, i.e., the organic vehicle composition, affected the NO_2 sensitive response of the films more than the microstructural changes. In particular, the films prepared with the smaller contents of α-terpineol showed low resistivity and negligible NO_2 response at any firing temperature, for films having small or large grains. This is because the films fired at lower temperatures have a low sintering degree, but a larger amount of surface oxygen, and thus showed lower E_a and NO_2 responses.

4 CONCLUSIONS

The control of all the parameters of the $SmFeO_3$ thick films processing is extremely important to obtain their good NO_2 response. The content of α-terpineol, which is

added in the paste for the fabrication of thick films by screen-printing technology, greatly affected the gas response of the samples. A significant reduction of the NO_2 response and an increase in conductivity were observed for the containing smaller amounts of α-terpineol, independently from the film sintering temperature. The increase in conductivity, which is not correlated with changes in microstructure, is attributed to the surface states adsorbed on the $SmFeO_3$ surface. A different oxygen layer on the $SmFeO_3$ surface, induced by the decomposition reaction of α-terpineol during firing, results in an increase in the oxide conductivity. The correlations existing between activation energy, sensitiviy, and materials characteristics (influenced by the preparation parameters) offer the possibility to tailor the materials in order to obtain given sensing properties.

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