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AC Response to Humidity and Propane of Sprayed Fe-Zn Oxide Films

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Abstract. Iron-zinc oxide films with different Zn contents were ultrasonically sprayed on glass substrates and inter-digital gold electrodes were evaporated upon them. Films were deposited from solutions containing 2, 10 and 30 at. % Zn. Hematite, amorphous and Franklinite structures turned out, respectively. They were assessed as humidity and propane detectors under alternating-current conditions for frequencies from 1 to 10^5 Hz and temperatures 30 and 250 ^{o}C. Their impedances in dry air, humid air and humid air plus propane were determined from voltage measurements with a Lock-In amplifier. Sensitivities to humidity (53 % RH.) and 189, 500 and 786 ppm of propane from the response of the resistance, reactance and also the total impedance were determined as functions of frequency. The maximum sensitivity to humidity ranges from 24 % up to 308 %. For propane, the maximum sensitivity ranges from 45 % up to 711 %. The largest sensitivity values correspond in all cases to reactance. From the dynamical response, the response and recovery times are determined, along with the concentration-dependence of the sensitivity. The sensing mechanisms are commented. *Copyright © 2009 IFSA.*

Keywords: Iron-zinc oxide films, Ultrasonic spray pyrolysis, AC measurements, Humidity and propane sensors

1. Introduction

Some materials for gas sensors have been widely studied. For instance gas sensors based on SnO_2 [1, 2,], ZnO [3, 4], WO_3 [5, 6] or Cr_2O_3 [7, 8] have been described. In particular, iron oxide has also become an important material for this application [9, 10]. In most of these works, the DC response is reported and only a few workers have provided results based on ac-measurements [11]. In this work, mixed iron-zinc oxide films with distinct zinc content are assessed as humidity and propane detectors. As a consequence of their different composition, these films also bear different structures. Furthermore, not only the resistive response, but also the reactive one is determined. The corresponding ac measurements are carried out for variable frequency and two different temperatures. As a consequence of having the frequency as an extra variable for the electrical response, the possibility of enhancing sensitivity is stressed. Such sensitivity is defined in terms of the response of the real and the imaginary parts of the impedance (Z' and Z'' respectively) and also the total impedance (Z), providing more alternatives for improvement. A comparison of sensitivity, response time, recovery time of Z' (real part), Z'' (imaginary part) and Z (total impedance) among the different sample types is given in this work.

2. Experimental Details

The films were prepared by using the ultrasonic spray pyrolisis method starting with an aqueous (0.05M) solution of iron nitrate nanohidrate, added with an appropriate amount of zinc acetate dihydrate reagent to achieve the desired Zn/Fe ratio. The case of the 2, 10 and 30 Zn at. % solutions is discussed in this work. Depositions were performed during 5 minutes on glass substrates placed upon a stainless steel plate heated at 450 ^{o}C. The carrier gas (nitrogen) flow was 5.9 liters/min and the substrate laid about 1 cm below the nozzle. X-ray diffraction measurements were done to define the composition and structure of each type of film. The a-c measurements for the electrical characterization were made with an SR830 Lock-In amplifier in a simple series circuit. The samples were placed within a controlled-temperature chamber where the atmosphere can also be changed by opening and closing the appropriate valves to control different gas flows. The equivalent circuit is depicted in Fig. 1.

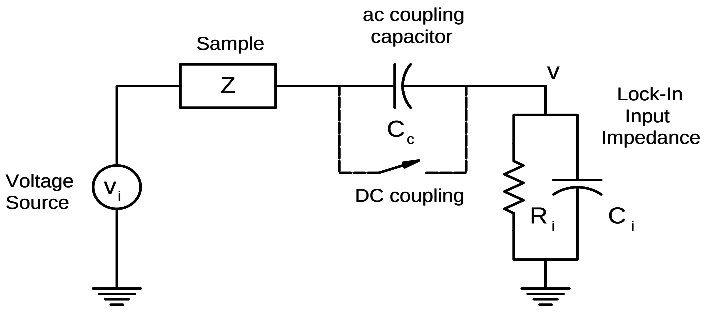

Fig. 1. Equivalent circuit of the ac measurement system. v_i is a sinusoidal voltage. C_c, R_i and C_i belong to the input circuit of the Lock-In amplifier. The dotted line denotes bypassing of the input coupling capacitor when DC coupling is used.

The voltage v_i is a sinusoidal signal whose frequency and amplitude can be controlled. The alternating signal is internally provided by one of the Lock-In amplifier circuits. Z stands for the sample impedance, C_c is an input coupling capacitance of known value that can be bypassed if DC coupling is desired. Finally, R_i and C_i are the resistance and capacitance at the input of the measuring circuit of the

Lock-In amplifier. These last values can be determined experimentally. In our case, after connecting a known test resistance within the above mentioned chamber, C_c, R_i and C_i turned out to be 0.1157 μF, 9.423×10^6 Ω and 150.8 pF, respectively. Hence, by knowing v_i and all the values of elements at the Lock-In input, the Z value can be calculated by measuring the complex voltage v. The data acquisition is computer-controlled at different temperatures and frequencies. With this experimental system, either time, temperature or frequency scans can be performed.

As mentioned above, films from solutions containing 2, 10, and 30 atomic % Zn were prepared. Formerly, they have seen to bear hematite (2 %), amorphous-like (10 %) and franklinite (30 %) structure [12, 13] as it is shown in Fig. 2. Hence, films with different structures were assessed as humidity and propane sensors. Gold evaporated inter-digital contacts on the surface of the films were used for the electrical measurements.

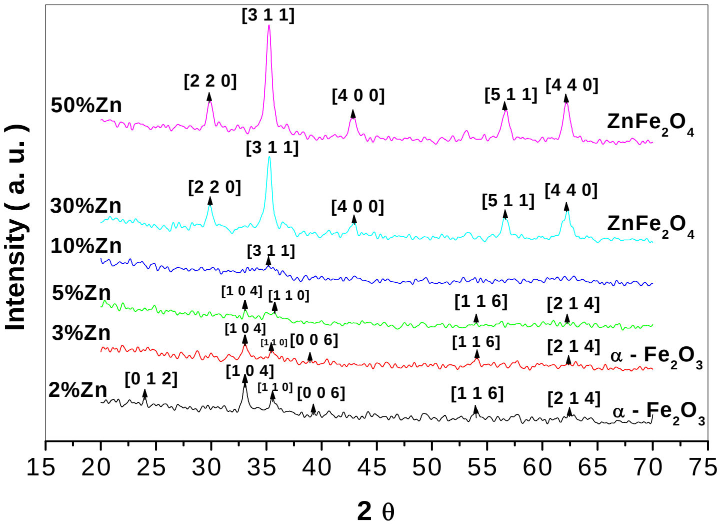

Fig. 2. X-ray diffraction spectra of films deposited from solutions with different Zn content as indicated. It is clear that hematite (α-Fe_2O_3) dominates the film structure for Zn percentages below 5 %, but it is highly disordered for this last value. On the other hand, for 10 % the structure is also highly disordered, but starts to be mainly of Franklinite type ($ZnFe_2O_4$), which dominates for higher Zn percentages.

Frequency scans between 1 and 10^5 Hz with 15 points per frequency decade at two different temperatures, 30 and 250 ºC and under controlled atmospheres were performed. Three different atmospheres were used to interact with the surface of the samples. The first is synthetic dry air (D) consisting of 80 % nitrogen and 20 % oxygen. The second consists of the former dry air that is led through a bubbler to produce air with ~ 53 % relative humidity (H). The third one is humid air added with an appropriate flow of 1000 ppm propane in air to get the desired gas ratio (HP). A total flow about 225 ml/min is used to conduct all the above mixtures into the test chamber. This was kept at near atmospheric pressure along all the measurements.

3. Results

3.1. Frequency Scans

As a result of frequency measurements, several plots can be built for each sample at a given temperature and atmosphere. This is illustrated in Fig. 3 in a similar way to that suggested by

Macdonald et al [14]. In this figure, the results corresponding to the sample with 2 % Zn in dry air (D), humid air (H) and humid air plus 500 ppm propane (HP) at 30 ºC are shown. The projections of the three-dimensional path (not shown for clearness) defined by Z'' as a function of both frequency and Z' are depicted on the coordinate planes. Two of these projections describe the frequency dependence of the real and imaginary parts of the impedance Z. The third one is the so called impedance plot describing the dependence of the imaginary part as a function of the real part of the impedance. In this way, a complete description is provided for any sample. Similar plots for all the samples (2, 10 and 30 % Zn) under three atmospheres (D, H and HP) and two temperatures (30 and 250 ºC) can be obtained, but for the sake of simplicity they are not all shown. In this figure a strong effect of humidity can be observed upon Z' and Z''. It consists of an appreciable decrease of both components for all the frequencies. On the other hand propane tends to reverse back such a decrease, although no totally.

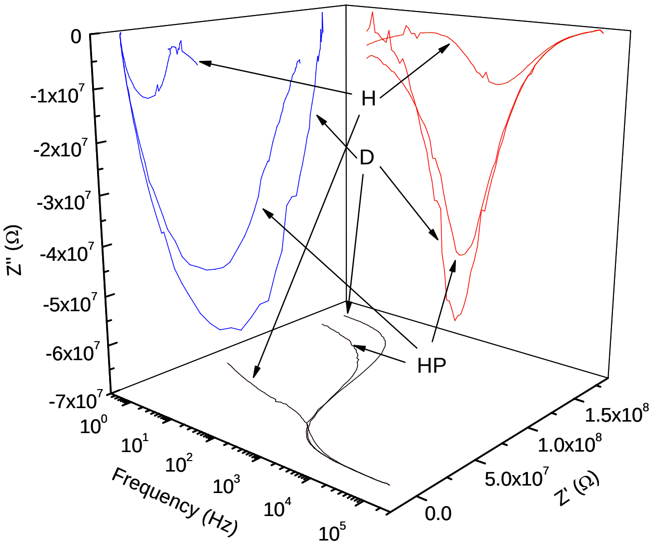

Figure 3. Projections of the three-dimensional paths defined by Z'' vs. both, Z' and the measurement frequency, according to Macdonald et al. In this case, results for the sample with 2% Zn at 30 ºC are shown. In each coordinate plane, three projections are plotted: one for the dry air response (D), the second for the humid air atmosphere (H) and the third one for the humid air plus propane (HP) response. As projections on the coordinate planes, the real and imaginary parts of the impedance are shown as a function of frequency in the horizontal and right-side vertical planes. Besides, the imaginary vs. the real part is also plotted in the left-side vertical plane.

An equivalent circuit can be ascribed to the sample, depending on the frequency behavior of the impedance. Even without explicitly finding the magnitude of the elements in the equivalent circuit, their approximate size can be noticed. For instance, by observing the real part axis in figure 3, a rough idea of the resistive elements can be obtained. In the range of low frequencies, a large decrease of resistive elements, from about 1.5×10^8 Ω down to less than 5×10^7 Ω is seen in Fig. 3 after exposing to humidity the sample. Then, after exposing the same sample to propane, an increase of such resistance up to ~1.3×10^8 Ω is seen. These changes reflect an important effect of both, humidity and propane upon the film properties. In the same way, the imaginary part is also importantly affected under the same circumstances.

3.2. Sensitivity

In order to give a quantitative measurement of the effect of both, humidity and propane upon our samples, the following expression is used here to define the sensitivities (in percentage):

$$S_{H,P}(X) = \left| \frac{X_{H,HP}}{X_{D,H}} - 1 \right| * 100 \qquad (1)$$

In this expression X can be either Z', Z'' or |Z|. From equation (1), the frequency dependence of any of the above mentioned sensitivities can be obtained. The subscript D in the denominator is used with H in the numerator to calculate the sensitivity to humidity, and H in the denominator with HP in the numerator allows to determine the sensitivity to propane within the humid atmosphere.

In Fig. 4 the sensitivities to 53 % R.H. and 500 ppm of propane, calculated with formula (1) are shown in the case of the hematite film (2 % Zn). The amplitude of the measurement signal was 15 mV RMS. Such plots were calculated on the basis of the real part response (squared symbols), imaginary part response (circles) and total impedance response (triangles).

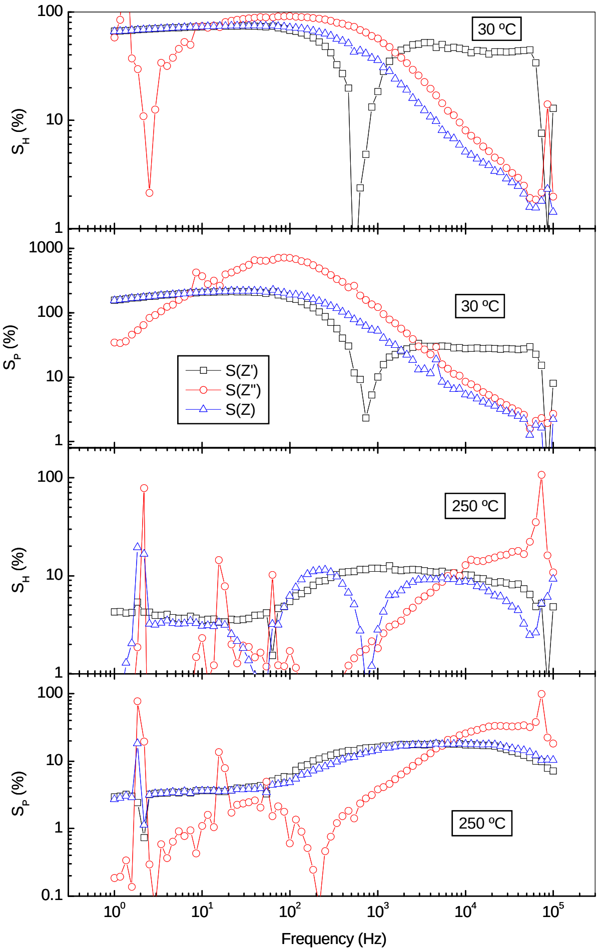

Fig. 4. Sensitivities of the real (squared symbols), imaginary (circles) parts of and total impedance (triangles) as functions of the frequency. Results of the sample with 2% Zn at 30 °C and 250 °C are shown.

Both sensitivities, to humidity S_H and to propane S_P are plotted against frequency. Different behaviors with frequency and magnitudes of sensitivity can be observed in these plots. It is seen that sensitivities at 30 ºC reach larger values than those occurring at 250 ºC. It can also be noticed that the maximum values of reactive responses are larger than resistive ones. For instance, regarding humidity in Fig. 4a $S_H(Z')$ reaches a maximum value of 74 % at 34 Hz while $S_H(Z'')$ is 91 % at 100 Hz. Regarding the case of propane in Fig 4b, $S_P(Z')$ is 219 % at 34 Hz while $S_P(Z'')$ becomes 711 % at 100 Hz. These results correspond to 30 ºC. It is noticeable that lower sensitivities about 10 % are obtained for both humidity and propane at 250 ºC. The exceptions are near frequencies where $S_{H,P}(Z'')$ becomes peaked near 100 %. Near these frequencies, more detailed measurements are needed. However, in the range from approximately 10 kHz to 50 kHz, both $S_H(Z'')$ and $S_P(Z'')$ become around 20 %.

As noted above, some of our results present curves peaked upwards. This normally happens in the imaginary part response. These peaks occur at the frequencies where the curve of the denominator in equation (1) becomes closer to zero. It is clear that frequency regions around such peaks allow getting large sensitivities. In this figure (Fig. 4c) a frequency range where oscillatory imaginary sensitivities are in the order of 1 % or less can be seen. The oscillation is the result of noise effects. Fortunately, this oscillation in our results appears mostly for sensitivities lower than 10 %, then becoming of less practical importance.

The largest sensitivities obtained with the different samples at the two temperatures studied are included in Table 1, confirming that all of them correspond to the response of the imaginary part of the impedance (Z''). From this table turns out that the best film to sense humidity is that with the Franklinite structure (30 % Zn). The corresponding conditions of the measurement are 30 ºC and a frequency range from 1 to 10 Hz. On the other hand, 500 ppm of propane is best detected at 30 ºC and frequency of 100 Hz by the film with the hematite structure (2 % Zn). However, all sensitivities in Table 1 are reasonable, providing several possibilities to detect either humidity or propane. Hence, an important feature of the ac-measurement method, so stressing its relevance, is that maxima under different conditions are obtained at different frequencies.

3.3. Dynamical Behavior

In order to illustrate the time-dependent response of Z', Z'' and |Z| to humidity and propane, this last in different concentrations, we show the hematite (2 % Zn) results in Fig. 5. They were obtained at 30 ºC and 100 Hz with a small signal of 30 mV amplitude. As indicated in the upper graph, a constant relative humidity of 53 % was applied to the sample along time intervals of 10 minutes, allowing for recovery also during 10 minutes each time. Two cycles of this type are shown. In the lower graph three concentrations of propane are applied during 10 minutes to the sample immersed in humid air: 189, 500 and 786 ppm and also 10 minutes intervals are allowed for recovery. The three response types here considered are plotted in both graphs. Once again the Z'' response is clearly larger than the others. We considered the maximum change after applying either humidity or propane to calculate the associated sensitivity. The time needed to reach 90 % of the total change along the corresponding interval is calculated to determine both, the response and the recovery times.

An analysis of curves in Fig. 5 and the graphs corresponding to the other samples (that with 10% Zn was measured under 15 mV at 2 Hz and that with 30 % Zn under 15 mV at 1 kHz) yielded the values related to humidity response shown in Fig. 6. In the upper graph the highest sensitivities to humidity once more belong to the imaginary part of the impedance, being the largest (~ 200 %) that corresponding to the amorphous-like sample (10 % Zn). In the middle graph the response times are the longest for the amorphous-like sample, between 7 and 8 minutes, but for the other samples it is less than 5 minutes, being the shortest that for the hematite sample (2 % Zn), near 2 minutes. In the lower graph the longest recovery times belong to the hematite sample, between 5 and 8 minutes, and the shortest to the franklinite sample, about 3 minutes or lower.

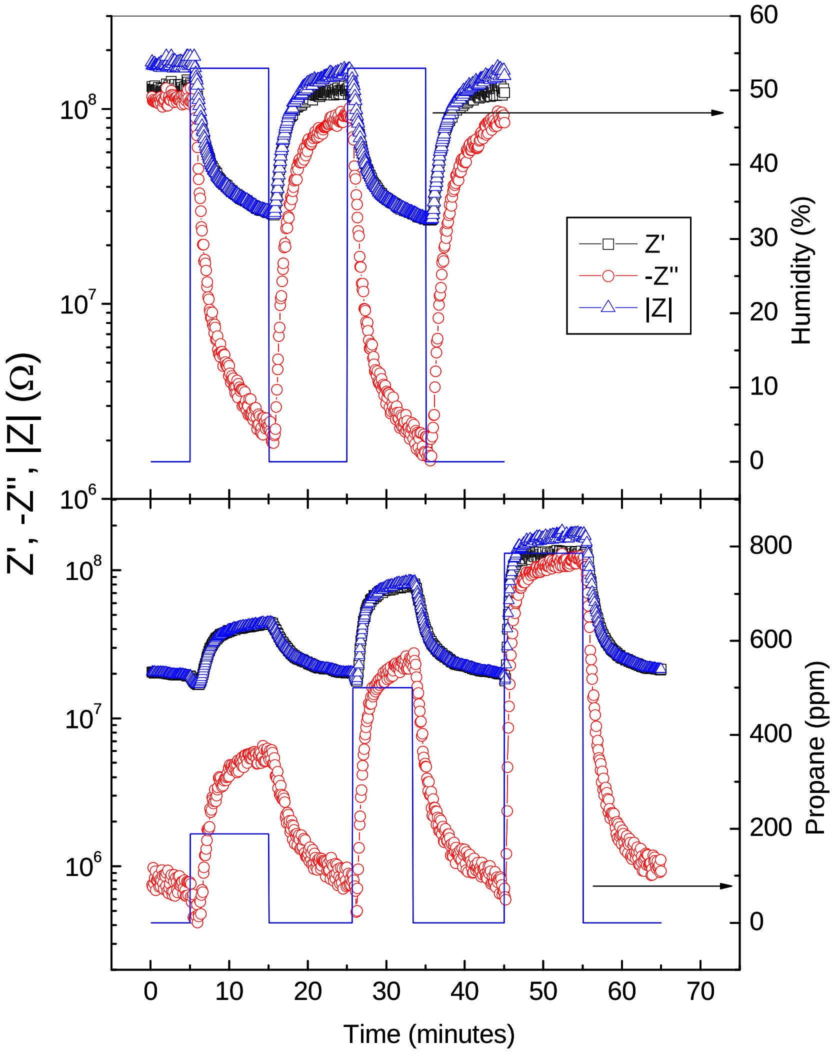

Fig. 5. Dynamical responses of the hematite film (2% Zn) at 30 ºC measured with a 100 Hz, 30 mV sinusoidal voltage. In the upper graph the response of the total impedance and its real and negative imaginary parts are depicted, along with the humidity profile applied. The lower graph depicts the similar responses to different concentrations of propane as indicated by the continuous line, added to humid air.

In Fig. 7 the sensitivity to propane of the three types of response are plotted for the different samples at 30 °C as function of the propane concentration. In the upper graph the responses of the hematite sample are seen to behave exponentially in the range of concentration managed. Instead, the responses of the disordered and franklinite samples are seen to vary linearly with concentration. The corresponding behaviors at 250 °C are found to be reversed with respect to those above mentioned. The largest sensitivities to propane belong mostly to the hematite sample, being similar only that of Z'' of the franklinite sample. The lowest are those of the disordered sample. The response of the imaginary part Z'' turns out to be the highest in all cases. Since Z'' sensitivity is of capacitive behavior, it is related to fixed-charge exchange processes between the film and the test gas. In our samples this effect turns out to be more important than those which change the population of mobile charges that contribute to the conductivity process.

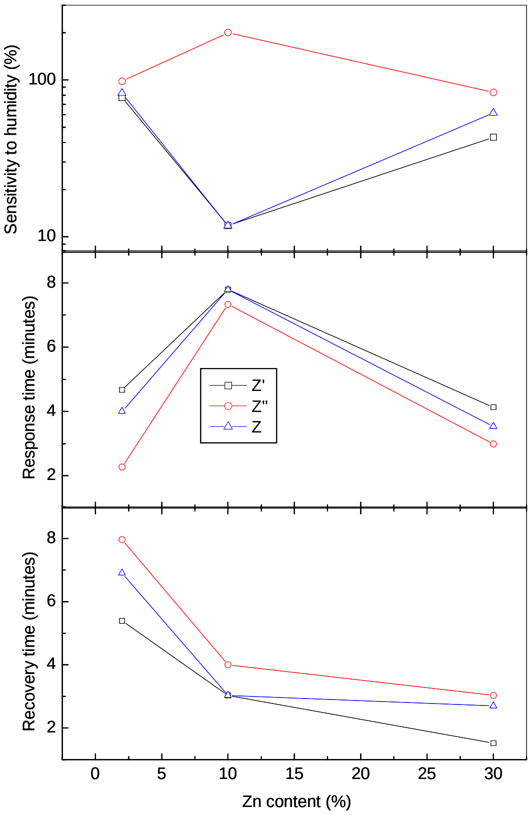

Fig. 6. Results obtained for Z’, Z’’ and |Z| from the analysis of the dynamical response to humidity, as functions of the Zn content. The upper graph illustrates the dependence of the sensitivity on the Zn content. The middle one contains the response time and the lowest the recovery time.

Times associated to the response and recovery processes of the films are plotted in Fig. 8 as functions of the propane concentration. The empty symbols correspond to the response times and the full symbols to the recovery times. It is observed that most of the behaviors are decreasing. Furthermore, most of them are nearly linearly decreasing. The only exceptional case corresponds to the recovery time of the disordered sample and has a global increasing trend with propane concentration. This means that the recovery time of both, Z’ and Z’’ becomes the longest for 786 ppm of propane. Also, the response time of the same sample is the shortest for both Z’ and Z’’. It seems that disorder in the film structure produces fast adsorption and slow desorption processes at 786 ppm. The shortest response times of the real part Z’ are due to the disordered and franklinite samples, decreasing from about 5.3 minutes down to 1.5 minutes. The disordered sample exhibits the shortest Z’’ response times in the range from ~5.5 minutes to ~1.5 minutes. The shortest recovery times belong to the hematite sample for both Z’ and Z’’, being better those for Z’’.

Our experimental results at 30 ºC after exposing to humidity films with the three types of structure mentioned in this work yield a decrease of resistance. At this low temperature it is generally assumed that proton drift is the mechanism which produces these changes on the different materials here studied [10]. As propane is added, its reaction with OH^- radicals leads to intermediate $C_3H_7O^-$ species which in turn trap H^+ to form propanol. Then the ionic conductivity is decreased. This process explains the increase of resistance observed at low frequencies during the measurements for the three types of samples.

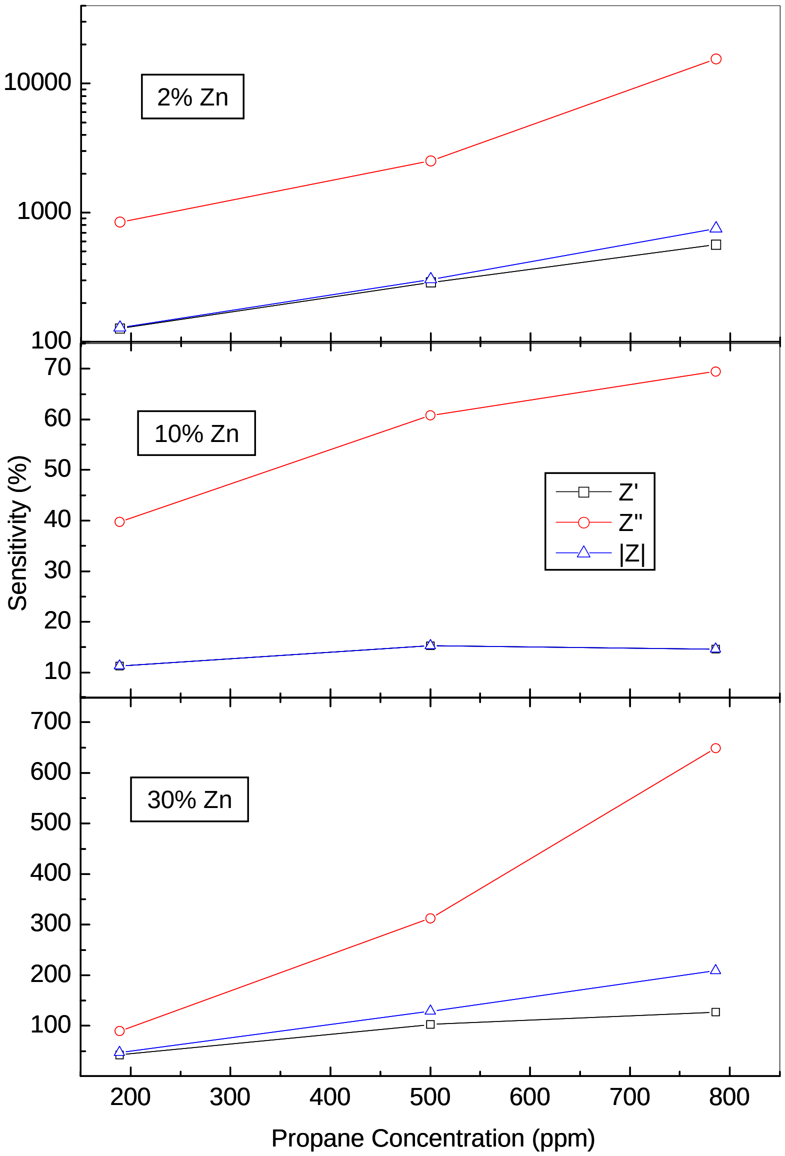

Fig. 7. Sensitivity dependence of Z', Z'' and |Z| on the propane concentration. In the upper graph, an exponential variation can be noticed for the case of the hematite sample. In the middle and lower graphs, the dependence is closely linear for the amorphous and the franklinite samples.

At higher temperatures (250 ºC in our case), humidity is able to alter the status of oxygen on the surface, including both molecular and ionic species [15]. However, we observed a decrease of resistance in the cases of all the three types of samples: hematite (2 % Zn), amorphous-like (10 % Zn) and franklinite (30 % Zn). This would not be so if electronic processes dominate the conductivity, since the hematite sample is expected to be a p-type semiconductor, while franklinite is n-type [16, 17, 18]. Hence, we assume that proton drift still dominates the conductivity. This is consistent with the increase of resistance produced by adding propane.

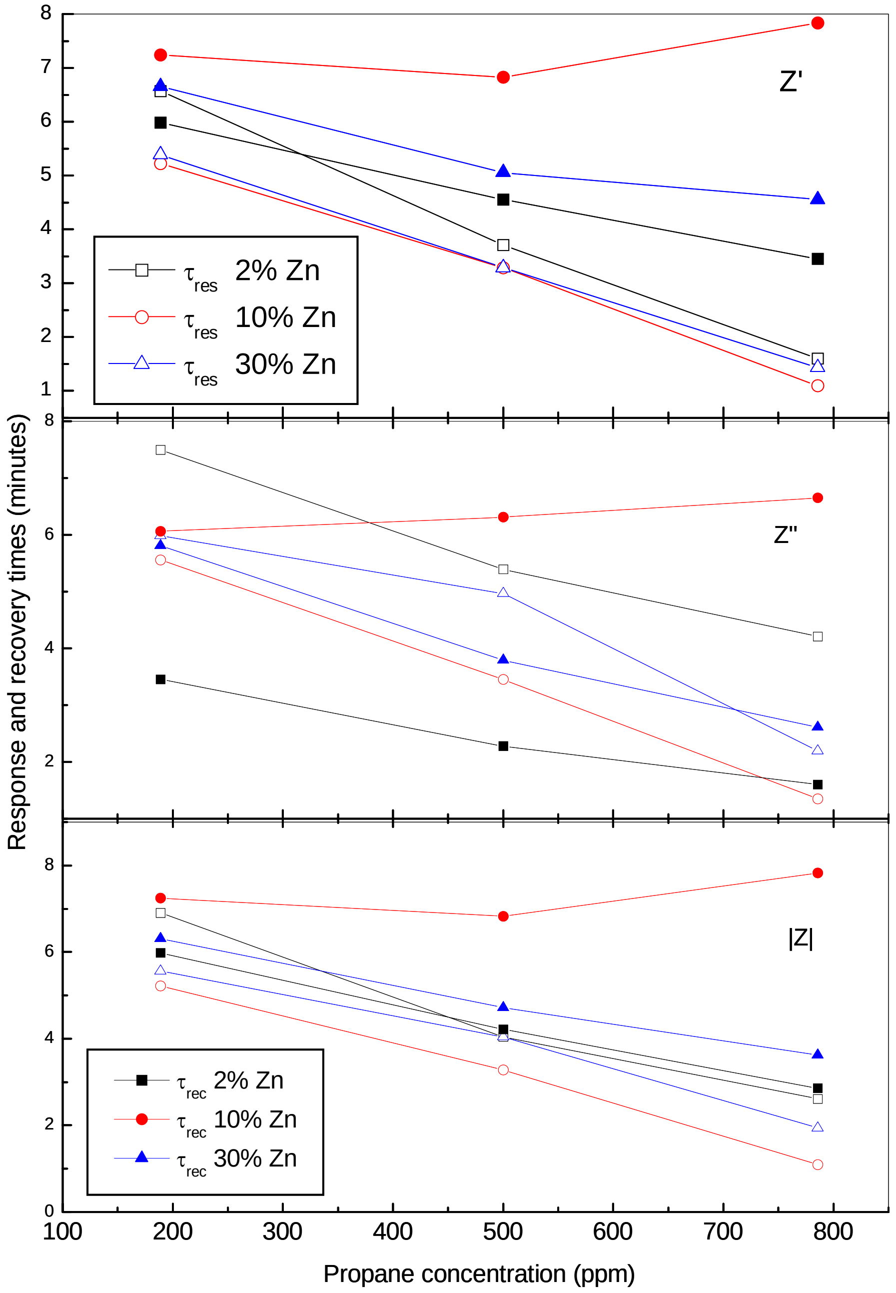

Fig. 8. Behavior of the response and recovery times plotted as functions of the propane concentration. The variations of such times associated to Z’, Z’’ and |Z| of the different samples are described in the upper, middle and lower graphs, respectively. The squares correspond to the hematite sample, the circles to the amorphous one and the triangles to the franklinite sample. Empty symbols describe the response times and the full symbols the recovery times.

4. Conclusion

Iron-zinc oxide films with 2, 10 and 30 at. % Zn possessing different structure (hematite, amorphous and Franklinite respectively) were prepared on glass substrates at 450 ºC by ultrasonic spray pyrolisis from aqueous solution. They were assessed as humidity (53 % R. H.) and propane (189, 500 and 786 ppm) sensors at 30 and 250 ºC. Their response to a sinusoidal alternating voltage signal was measured as a function of the frequency. Sensitivity values on the response of the real and imaginary parts of the impedance and also of the total impedance were determined. The largest sensitivities for both, humidity and propane, were achieved from the response of the imaginary part of the impedance. Sensitivities to humidity and propane as large as ~308 % and ~711 % respectively are obtained from these cases. These figures correspond to the Franklinite-type (30 % Zn) sample at low temperature (30 ºC) and to the hematite sample (2 % Zn) at 30 ºC respectively. At 250 °C, the best sensitivity to propane (242 %) is provided by the amorphous-like (10 % Zn) sample. In general, good maximum sensitivities at both temperatures are achieved by all the samples studied. In the case of our samples, the sensitivity of the total impedance response is not as relevant as that of the imaginary part for most cases. In our view, it is possible to adequately choose a type of sample and temperature according to a desired work frequency. Regarding humidity, Z'' of the disordered sample provides the highest sensitivity; Z'' of the hematite film yields the fastest response; Z' of the franklinite film is the fastest to desorb water. With respect to propane, the highest sensitivity turns out from the response of Z'' of the hematite film. Z' of the three samples behaves linearly with the propane concentration, but Z'' behaves exponentially. The sensing mechanism of water at both temperatures of this work is involved with its decomposition on the surface to produce and adsorb H^+ and OH^- radicals. Then, protons contribute to the ionic conductivity of the films. Under the presence of propane, such proton population is decreased, then increasing the resistance of the films.

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