4. Gas sensors based on WO_3 nanocrystalline powders

Introduction

As already mentioned in Chapter 1, most authors have found that gas sensor devices based on tungsten oxide exhibit good properties for the detection of ammonia (NH_3), hydrogen sulphide (H_2S) and nitrogen dioxide (NO_2). Results concerning gas sensors based on WO_3 nanocrystalline powders for the detection of the previously mentioned gases are reported in this chapter. The purpose of this investigation was to evaluate the sensing properties of thick-film gas sensors based on WO_3 obtained from tungstic acid and to determine the effect of different additives (copper, vanadium and chromium) on sensor response. Interference of humidity on the detection of these gases was also evaluated. To the best of our knowledge, this is the first time this chemical route is used in the field of gas sensors and it is also the first time these additives are used in combination with WO_3.

The chapter is divided into five main sections. The first four sections examine the sensing properties of the materials studied: pure WO_3 and copper, vanadium and chromium-catalysed WO_3. Each of these sections contains three subsections corresponding to each target gas. Typically, sensors were evaluated at different working temperatures under one concentration of the target gas in dry air. Once suitable working temperatures were found, sensor responses to different concentrations of that gas, as well as influence of humidity, were evaluated.

The last section of the chapter, *Discussion and conclusions,* will provide a tentative interpretation of the reported results based only on the test data presented herein. As already mentioned, a further discussion of the results will be provided in Chapter 6.

4.0 Experimental procedure

In a typical test session, sensors were firstly operated at 350ºC overnight under a flow of synthetic air (200/ml) in the test chamber. The variation of the sensor resistance to a certain concentration of the target gas in dry air (500 ppm of ammonia, 20 ppm of hydrogen sulphide and 1 ppm of nitrogen dioxide) was recorded at different operating temperatures (between 200ºC and 350ºC). Sensor response was evaluated as R_{AIR}/R_{NH3} for ammonia, R_{AIR}/R_{H2S} for hydrogen sulphide and R_{NO2}/R_{AIR} for nitrogen dioxide, where R_{AIR} was evaluated before target-gas introduction and R_{GAS} was evaluated after 20 minutes of exposure. Lower operating temperatures were not tested in order to avoid high sensor resistance that may mislead the measurements.

After this preliminary test, one or more temperatures were selected for further tests, according to the sensor response and the dynamic behaviour of the sensor. At these temperatures, sensor response to lower concentrations of each gas was examined. Besides, interference of humidity was also examined at these selected temperatures. Wet air was let flow overnight before testing the sensors in order to stabilise sensor signal. While results of all sensors are reported for the first preliminary measurements, only results of selected sensors are shown for the second part. As explained in Chapter 1, more emphasis has been placed on ammonia and hydrogen sulphide test than in nitrogen dioxide test.

Sensors were tested continuously at least for one week for every gas and different sensors based on the same material were used to test sensor response to different gases.

4.1 Gas sensors based on pure WO_3

4.1.1 Ammonia detection

Sensor response to 500 ppm of NH_3 was studied for gas sensors based on 400 and 700ºC-annealed pure WO_3. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{NH3}, where R_{AIR} was evaluated before ammonia introduction. Results are shown in Fig. 1, which shows that sensor response has a minimum for both sensors around 250ºC and 300ºC. Maximum sensor response is found at 200ºC sensor based on 700ºC-annealed WO_3 ($R_{AIR}/R_{NH3}\approx 6$).

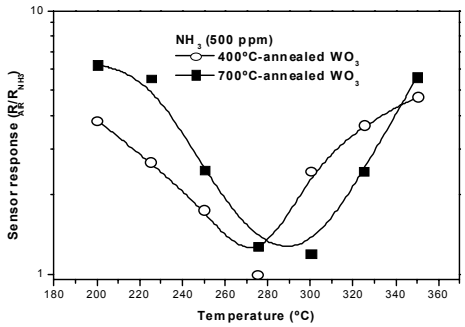

Fig. 1: *Sensor response of 400 and 700ºC annealed WO_3 to 500 ppm of NH_3 in synthetic air at different working temperatures.*

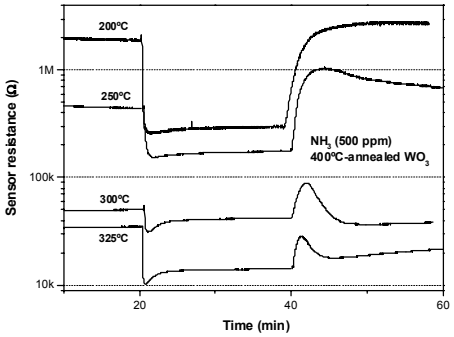

Fig. 2: *Variation of 400ºC-annealed WO_3 sensor resistance to a pulse of ammonia (500 ppm) in synthetic air for different working temperatures*

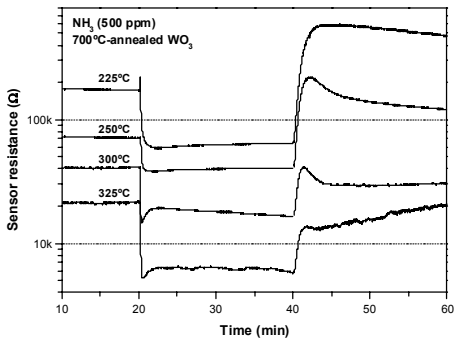

Fig. 3: *Variation of 700ºC-annealed WO_3 sensor resistance to a pulse of ammonia (500 ppm) in synthetic air for different working temperatures*

Dynamic sensor response at different working temperatures is shown in Fig. 2 (400ºC-annealed WO_3) and 3 (700ºC-annealed WO_3). Sensor response of both sensors presented an abnormal behaviour for temperatures over 300ºC: an abrupt decrease of resistance followed by a slow increase when NH_3 was introduced and a reverse behaviour when NH_3 was removed. For lower temperatures, overshooting problems were found on the resistance

value when NH_3 was removed, as the resistance was higher than before NH_3 introduction. Besides, recovery times were too long for the range of temperatures studied.

Finally, in order to check if this abnormal behaviour appeared under lower concentrations of NH_3, sensors were tested at different concentrations of ammonia in synthetic air. Results for sensor based on 700ºC-annealed WO_3 are shown in Fig. 4. It is evident the abnormal behaviour is still present at low NH_3 concentrations. When operated at 275ºC, sensor resistance shows abrupt increases and decreases of resistance when atmosphere is changed. On the other hand, it has overshooting problems when it is operated at 200ºC. At this temperature, it is remarkable that sensor resistance even increases with the introduction of 20 ppm of NH_3.

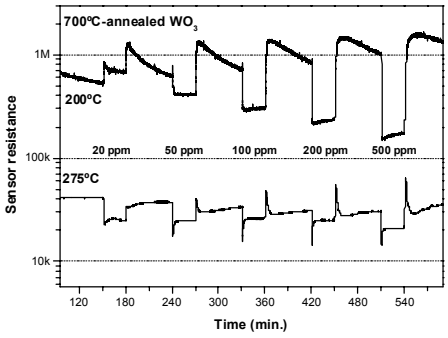

Fig. 4: *Variation of the 700ºC-annealed WO_3-based sensor resistance under pulses of NH_3 (20-500ppm) in synthetic air.*

It is evident from these results that gas sensors based on pure WO_3 obtained by this chemical route are not suitable at all for ammonia detection in the range from 20 ppm to 500 ppm in synthetic air.

4.1.2 Hydrogen sulphide detection

Sensor response to 20 ppm of H_2S in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed pure WO_3. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{H2S}, where R_{AIR} was evaluated before hydrogen sulphide introduction. Results are shown in Fig. 5a. It displays that sensor response increases for both sensors as operating temperature decreases, so maximum sensor response was found at 200ºC. In the case of 700ºC-annealed WO_3, $R_{AIR}/R_{H2S} \approx 90$. Fig. 5b shows the dynamic sensor response of both materials at 200ºC. Both sensors present a fast sensor response and recovery at this temperature. Therefore, they seem suitable to detect this gas concentration.

Since 200ºC was found to be a suitable temperature for H_2S detection, further studies were performed at this temperature. Particularly, sensor response to lower concentrations of hydrogen sulphide and influence of humidity were studied. Results of sensor response to

different concentrations of H_2S (from 1 ppm to 10 ppm) in dry and humid ambiences are reported in Fig. 6a, whereas Fig. 6b shows the dynamic sensor response of 400ºC-annealed WO_3. It is interesting to notice that, although gas sensor based on 700ºC-annealed WO_3 showed a higher sensor response in dry air, the opposite situation occurred under humid conditions. In other words, although both sensors presented a decrease in sensor response when humidity was present, this effect was greater in the case of 700ºC-annealed WO_3. As suggested by Fig. 6b, this reduction in sensor response was mainly due to the rise of sensor resistance in H_2S-ambiance when humidity is present. It is also worthy of consideration that sensor recovery under humid conditions is faster than in dry air, as it is shown in Fig. 6b.

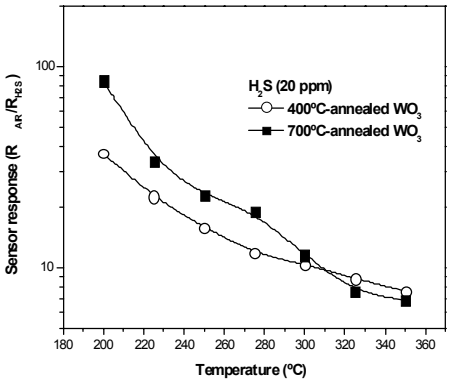

Fig. 5a: *Sensor response of 400 and 700ºC-annealed WO_3 to 20 ppm of H_2S in synthetic air at different working temperatures.*

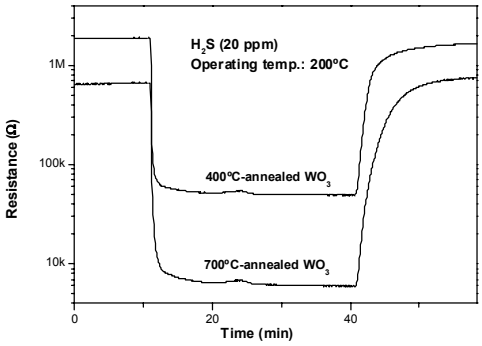

Fig. 5b: *Variation of the 400ºC and 700ºC-annealed WO_3-based sensor resistance under a pulse of H_2S (20 ppm) in synthetic air.*

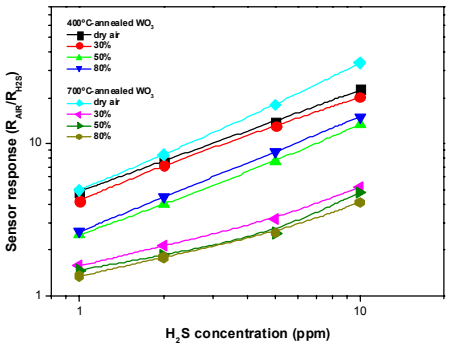

Fig. 6a: *Sensor response of 400 and 700ºC-annealed WO_3 to different concentrations of H_2S in synthetic dry and humid air (relative humidity is indicated).*

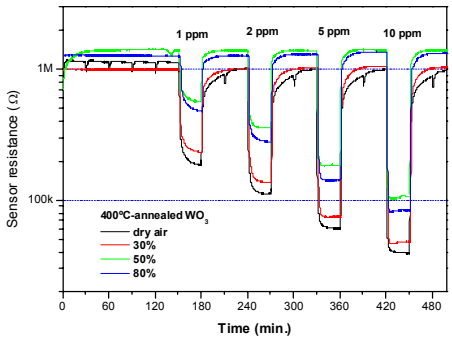

Fig. 6b: *Sensor response of 400ºC-annealed WO_3 to different concentrations of H_2S in synthetic dry and humid air (relative humidity is indicated).*

Finally, after noticing the great influence of humidity on sensor response, a final test was performed. Pulses of humidity (1 hour) were introduced in atmospheres of synthetic air and

H_2S (2 ppm) in synthetic air, keeping the concentration of this gas constant. Fig. 7 shows the results for the gas sensor based on 400ºC-annealed WO_3. This experimental procedure, the study of the dynamical response of metal oxide gas sensors to pulses of humidity in atmospheres containing a target gas, has revealed as a very useful method to investigate the interaction of not only water, but also that of the target gas with the sensing material. When humidified air was introduced in a background of synthetic air, resistance decreased very fast and afterwards increased slowly, reaching a final value very close to the resistance value in dry synthetic air. Nevertheless, this value can not be considered the final value of the resistance in humid air since the stabilisation can take around ten hours. On the other hand, this behaviour is completely different when the background is H_2S in air. In this case, there is not a fast decay of resistance but an important increase when humidity is introduced. When dry air is reintroduced again, previous sensor resistance value is recovered, although response time is slower.

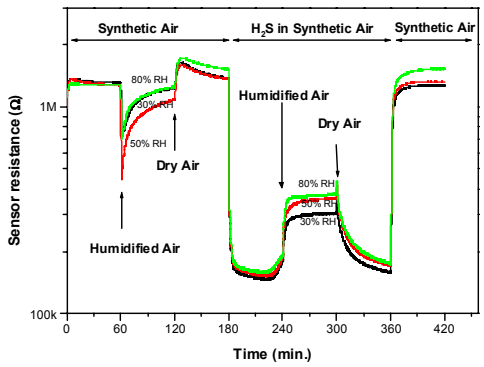

Fig. 7: *Sensor resistance variation (400ºC-annealed WO_3) to pulses of humidity (30, 50 and 80% relative humidity) in a background of synthetic air and H_2S (2ppm) in synthetic air.*

4.1.3 Nitrogen dioxide detection

Sensor response to 1 ppm of NO_2 in synthetic air was studied for gas sensors based on 400ºC and 700ºC-annealed pure WO_3. Sensor response was evaluated as the ratio of resistance R_{NO2}/R_{AIR}, where R_{AIR} was evaluated before nitrogen dioxide introduction. Results are shown in Fig. 8. It can be seen that sensor response increases for both sensors as operating temperature decreases, so maximum sensor response was found at 200ºC. Besides, 700ºC-annealed WO_3 showed a higher sensor response in the range of temperature analysed. In the case of 700ºC-annealed WO_3, $R_{NO2}/R_{AIR} \approx 10$.

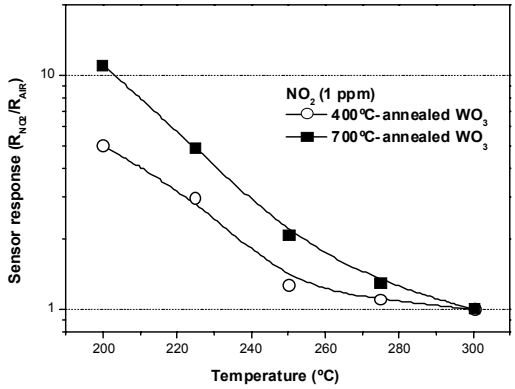

Fig. 8: *Sensor response of 400 and 700ºC-annealed WO_3 to 1 ppm of NO_2 in synthetic air at different working temperatures.*

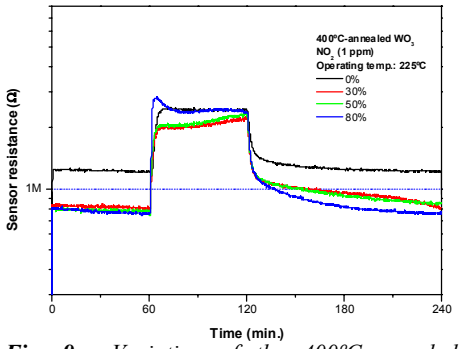

Fig. 9a: *Variation of the 400ºC-annealed WO_3-based sensor resistance under a pulse of NO_2 (1 ppm) in synthetic dry and humid air (relative humidity is indicated).*

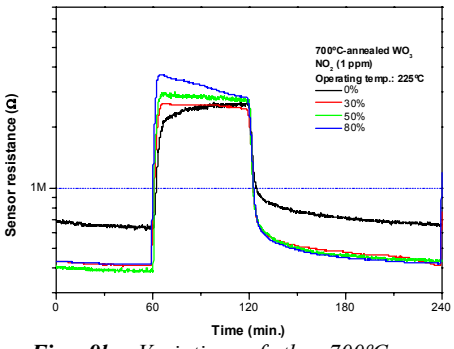

Fig. 9b: *Variation of the 700ºC-annealed WO_3-based sensor resistance under a pulse of NO_2 (1 ppm) in synthetic dry and humid air (relative humidity is indicated).*

Further studies were performed at 225ºC, though, due to large recovery times found at lower temperatures. Results of the response to 1 ppm f NO_2 in dry and humid air for both series of samples are shown in Fig. 9a and 9b. It is shown that sensor recovery can take tenths of minutes, which is already rather long. It is also very interesting to notice that sensor resistance is nearly independent of humidity when NO_2 is present, while it slightly decreases in pure synthetic air.

Finally, sensor response to different concentrations of NO_2 at this temperature was evaluated. Results are displayed in Fig. 10. It reveals that sensor based on 700ºC-annealed WO_3 exhibits a higher sensor response, as well as a low dependence with humidity. This sensor is able to detect at least 0.2 ppm of NO_2 in synthetic air.

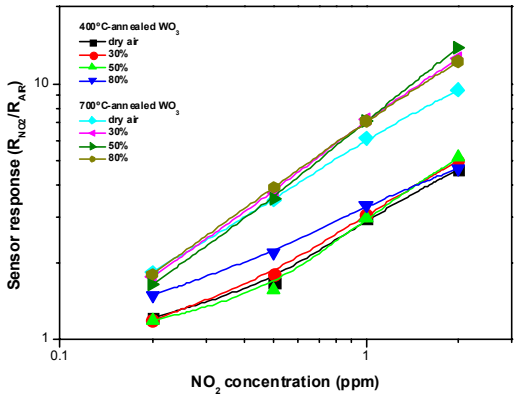

Fig. 10: *Sensor response of 400 and 700ºC-annealed WO_3 to different concentrations of NO_2 in synthetic dry and humid air (relative humidity is indicated).*

4.1.4 Conclusions

The main conclusions that can be drawn from the previously presented results concerning the sensor response of 400ºC and 700ºC-annealed pure WO_3 obtained by this route are:

- Pure WO_3 is not suitable for the detection of ammonia in the range of 20 to 500 ppm of NH_3 in synthetic air due to abnormal sensor resistance behaviour.
- 700ºC-annealed WO_3 shows a higher sensor response to H_2S in dry synthetic air than 400ºC-annealed WO_3. Sensor response raises as operating temperature decreases, so its optimum operating temperature appears to be 200ºC.
- It was found that sensor resistance in H_2S atmosphere augments when humidity is present, leading to a lower sensor response. However, sensor response to hydrogen sulphide of 400ºC-annealed material is less influenced by the presence of humidity.
- 700ºC-annealed WO_3 shows a better sensor response to NO_2 in dry synthetic air than 400ºC-annealed WO_3. Sensor response increases as operating temperature decreases, but its optimum operating temperature appears to be 225ºC after taking into account recovery time.

- 700ºC-annealed also presents a lower dependence with humidity since sensor resistance in synthetic air or NO_2 atmospheres is not highly dependent on humidity.

Finally, selected characteristics of these sensors are presented in Table 1.

Gas	*Material Annealing temperature (ºC)*	*Operating temperature (ºC)*	*Sensor Response* 0%	50%	*n* 0%	50%
H_2S (5ppm)	WO_3 700ºC	200	34	2.6	1.2	-
	WO_3 400ºC	200	19	7.6	0.7	1.1
NO_2 (1ppm)	WO_3 700ºC	225	6.1	7.2	0.7	0.7
	WO_3 400ºC	225	3.0	3.0	0.8	1.0

Table 1: *Selected characteristics of gas sensors based on pure WO_3. Material, operating temperature, sensor response and factor n (in dry air and 50% of relative humidity) are presented (Factor n is calculated after fitting $R_{AIR}/R_{H2S} \propto C^n$ and $R_{NO2}/R_{AIR} \propto C^n$, where C is the gas concentration in ppm).*

4.2 Gas sensors based on copper catalysed WO_3

4.2.1 Ammonia detection

Sensor response to 500 ppm of NH_3 was studied for gas sensors based on 400 and 700ºC-annealed WO_3:Cu. Nominal atomic copper/tungsten concentrations were 0.2, 1, 2 and 5%. After stabilisation at each working temperature, 500 ppm of NH_3 in synthetic air were introduced in the chamber test, followed by purge with synthetic air. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{NH3}, where R_{AIR} was evaluated before ammonia introduction. Operating temperature was varied between 200ºC and 350ºC.

Results are shown in Fig. 11a (400ºC-annealed) and 11b (700ºC-annealed). Sensor response of pure WO_3 has also been added for the sake of comparison. It is evident that sensor response also shows a minimum between 250ºC and 300ºC, depending on the sensor. This behaviour is very similar to that previously reported for those sensors based on pure WO_3. Only sensor based on 700ºC-annealed WO_3:Cu(0.2%) presents a different behaviour. Its sensor response has a low variation in the range of operating temperatures studied and shows a maximum at 250ºC.

As a matter of fact, most of them present their maximum sensor response around 200ºC as in the previous case. Sensor response at this temperature is shown in Fig. 12 as a function of the nominal copper/tungsten concentration. It is interesting to notice that both series of sensors present a maximum of sensor response at WO_3:Cu(2%). Maximum sensor response is showed by sensor based on WO_3:Cu(2%) operated at 200ºC ($R_{AIR}/R_{NH3}\approx26$).

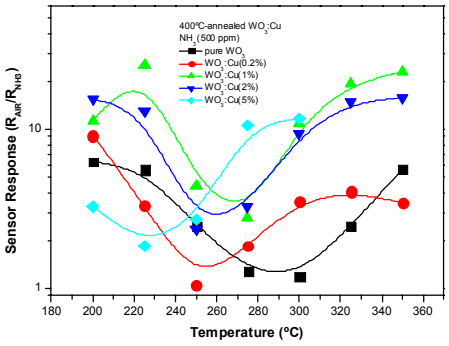

***Fig. 11a**: Sensor response of 400ºC-annealed WO_3:Cu to 500 ppm of NH_3 in synthetic air at different working temperatures.*

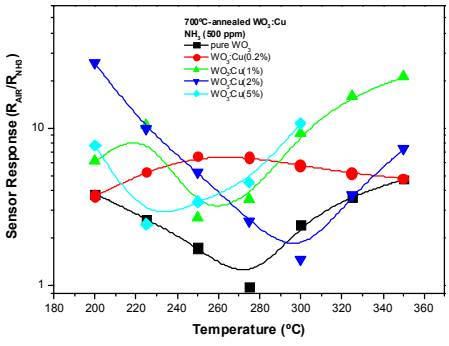

***Fig. 11b:** Sensor response of 700ºC-annealed WO_3:Cu to 500 ppm of NH_3 in synthetic air at different working temperatures.*

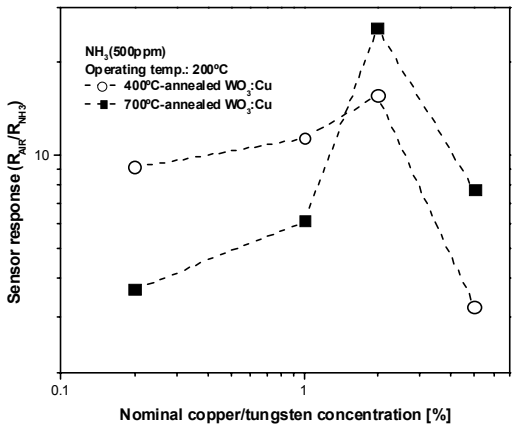

Fig. 12: *Sensor response of WO_3:Cu to NH_3 (500 ppm in synthetic air) as a function of nominal copper/tungsten concentration*

However, most of these sensors still presented the abnormal behaviour previously described in the case of pure WO_3. Only WO_3:Cu(2%) annealed at 700ºC presented a satisfactory dynamic sensor response. On top of this, this material already presented the highest sensor response among WO_3:Cu-based sensors. Fig. 13 shows the variation of sensor resistance to 500 ppm of NH_3 in synthetic dry air at different operating temperature. Sensor response presented an abnormal behaviour for temperatures over 300ºC. However, it showed a good performance when operated at lower temperatures, presenting a maximum sensor response at 200ºC.

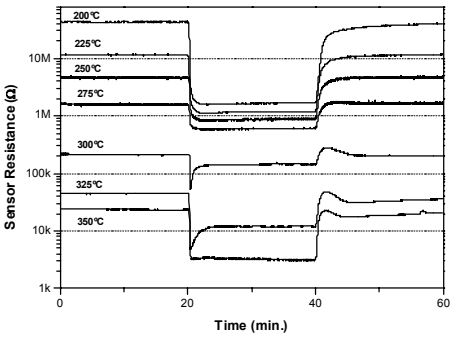

Fig. 13: *Variation of 700ºC-annealed WO_3:Cu(2%) sensor resistance to a pulse of ammonia (500 ppm) in synthetic air for different working temperatures.*

Since 200ºC was found to be a suitable temperature for NH_3 detection, further studies were carried out at this temperature. Particularly, sensor response to lower concentrations of ammonia and influence of humidity were studied. Results of 700ºC-annealed WO_3:Cu(2%) sensor response to different concentrations of NH_3 (from 20 ppm to 500 ppm) in dry and humid ambiences are reported in Fig. 14a, whereas Fig. 14b shows the dynamic sensor response of 400ºC-annealed WO_3. It is interesting to notice that sensor resistance (both in pure or NH_3-containing synthetic air) decreased in the presence of humidity. However, the

ratio of resistances R_{AIR}/R_{NH3} was maintained rather constant in the range of humidity analysed, what makes this material very interesting for ammonia detection with the interference of humidity. On the other hand, sensor response and recovery gets slower in the presence of humidity.

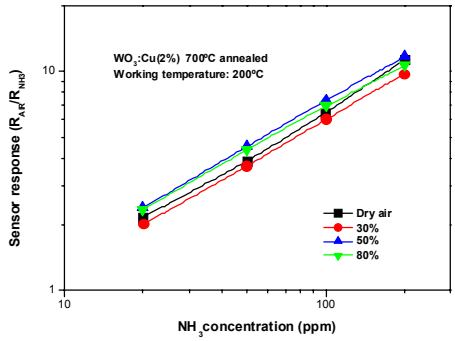

Fig. 14a: *Sensor response of 700ºC-annealed WO_3:Cu(2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

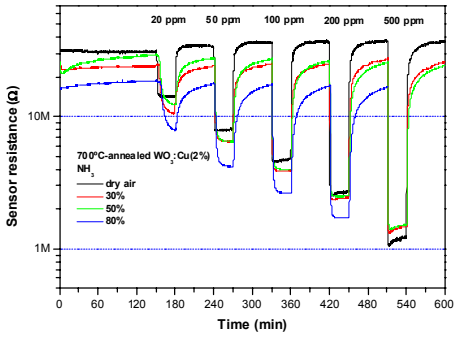

Fig. 14b: *Dynamic sensor response of 700ºC-annealed WO_3:Cu(2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

4.2.2 Hydrogen sulphide detection

Sensor response to 20 ppm of H_2S in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:Cu. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{H2S}, where R_{AIR} was evaluated before hydrogen sulphide introduction. Results are shown in Fig. 15a (400ºC-annealed) and 15b (700ºC-annealed). These figures illustrate that sensor response increases for both series of sensors as operating temperature decreases, so maximum sensor response was found at 200ºC. In the case of 400ºC-annealed WO_3, only 0.2% and 2 % copper catalysed WO_3 were able to improve the sensor response exhibited by pure tungsten oxide. On the other hand, pure 700ºC-annealed WO_3 was still more sensitive than WO_3:Cu annealed at that temperature. Altogether pure 700ºC-annealed WO_3 still presents the best sensor response to 20 ppm of hydrogen sulphide. Fig. 16 shows the sensor response to 20 ppm of H_2S in dry syntehtic air at 200ºC as a function of nominal copper content. It is remarkable that 5% of copper makes the worst sensor response in both cases.

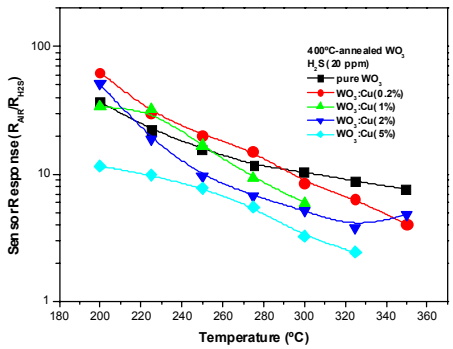

Fig. 15a: *Sensor response of 400ºC-annealed WO_3:Cu to 20 ppm of H_2S in synthetic air at different working temperatures*

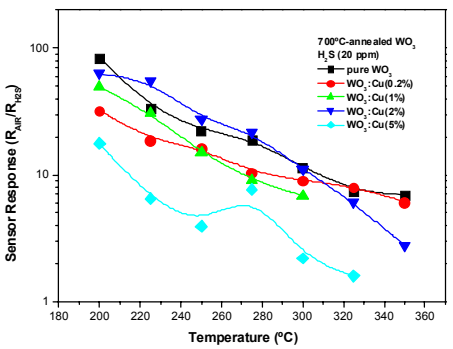

Fig. 15b: *Sensor response of 700ºC-annealed WO_3:Cu to 20 ppm of H_2S in synthetic air at different working temperatures*

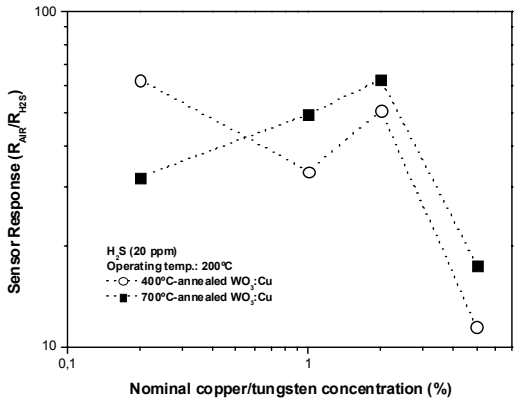

Fig. 16: *Sensor response of WO_3:Cu to H_2S (20 ppm in synthetic air) as a function of nominal copper/tungsten concentration.*

Since 400ºC-annealed WO_3:Cu(0.2%) presented the best sensor response of copper-catalysed WO_3 at 200ºC, further studies were performed with this material at this temperature. Sensor response to lower concentrations of hydrogen sulphide and influence of humidity were analysed. Fig. 17a displays the sensor response to different concentrations of H_2S (from 1 ppm to 10 ppm) in dry and humid ambiences, whereas Fig. 17b shows the dynamic sensor response. As in the case of pure tungsten oxide, humidity makes sensor response decrease. This is again due to the high dependence of the sensor resistance to humidity when hydrogen sulphide is present.

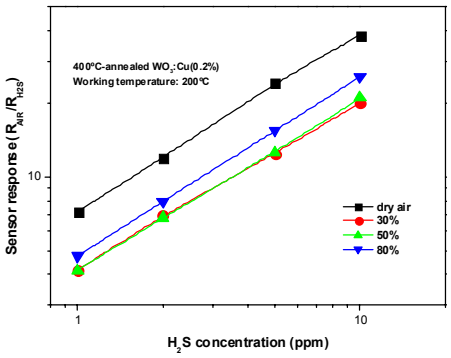

Fig. 17a: Sensor response of 400ºC-annealed WO_3:Cu(0.2%) to different concentrations of H_2S in synthetic dry and humid air (relative humidity is indicated).

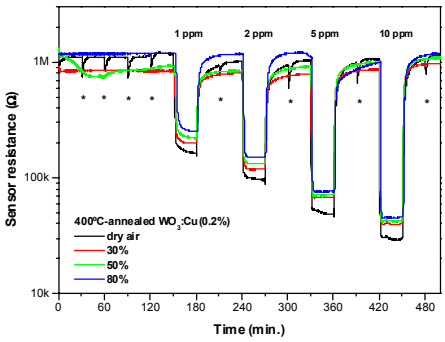

Fig. 17b: Dynamic sensor response of 400ºC-annealed WO_3:Cu(0.2%) to different concentrations of H_2S in synthetic dry and humid air.

4.2.3 Nitrogen dioxide detection

Sensor response to 1 ppm of NO_2 in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:Cu. Sensor response was evaluated as the ratio of resistance R_{NO2}/R_{AIR}, where R_{AIR} was evaluated before nitrogen dioxide introduction. Taking into account previous results, sensor response was only studied at 200ºC, as it was found that sensor response raised when operating temperature decreased in the range 200ºC-350ºC. Results of sensor response as a function of nominal copper concentration are shown in Fig. 18. It is shown that 1% copper catalysed WO_3 presented a very high sensor response. However, dynamic sensor response was not satisfactory at all, even for those sensors with a moderate sensor response. Fig. 19 shows the dynamic sensor response of the WO_3:Cu(1%) (700ºC) and WO_3:Cu(0.2%) (400ºC). Although 700ºC-annealed WO_3:Cu(1%) shows a high sensor response, it can be very low for low concentrations of NO_2. Besides, sensor recovery is also very slow. In the case of 400ºC-annealed, its sensor

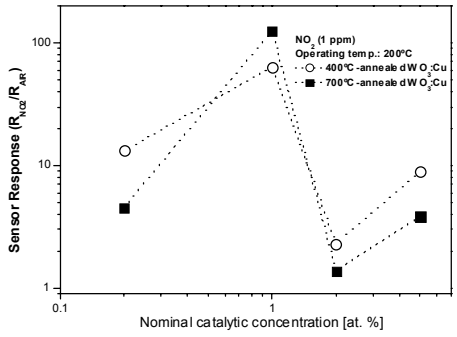

Fig. 18: Sensor response of WO_3:Cu to NO_2 (1 ppm in synthetic air) as a function of nominal copper/tungsten concentration.

recovery was also very slow. Therefore, these sensors seem to be not completely suitable for the detection of NO_2 in the ranges studied.

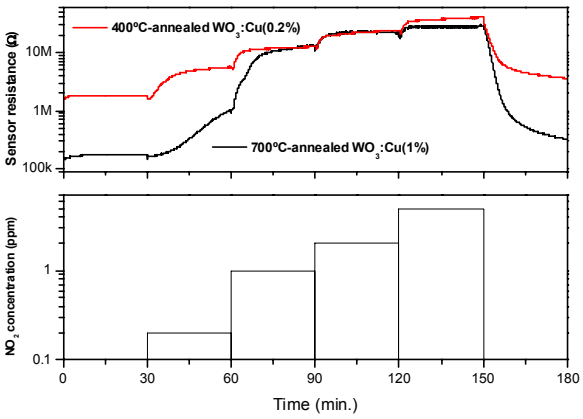

Fig. 19: *Dynamic sensor response of 400ºC-annealed WO_3:Cu(0.2%) and 700ºC-annealed annealed WO_3:Cu(1%) to different concentrations of NO_2 in synthetic dry.*

4.2.4 Conclusions

Previously presented results concerning the sensor response of 400ºC and 700ºC-annealed copper-catalysed WO_3 lead to the following conclusions:

- Most gas sensors based on copper catalysed WO_3 still presented an abnormal sensor response to ammonia, similar to that previously reported for pure WO_3.
- Only 700ºC-annealed WO_3:Cu(2%) presented a suitable dynamic behaviour when operated at 200ºC. On top of that, it presented a good sensor response to NH_3 in the range from 20 to 500 ppm and a low interference from humidity. Therefore, this material is considered as suitable for ammonia detection in the studied ranges.
- Gas sensors based on 400ºC-annealed WO_3:Cu(2%) showed an improved sensor response to hydrogen sulphide with low interference from humidity in the range 30-80% of relative humidity. On the other hand, gas sensors based on 700ºC-annealed copper catalysed WO_3 were not able to improve the sensor response of pure WO_3 annealed at that temperature.
- High sensor response to NO_2 was achieved when copper was introduced in 1% atomic percentage. However, dynamic behaviour was not satisfactory at all in the range of NO_2-concentration analysed.

Finally, selected characteristics of these sensors are presented in Table 2.

Gas	*Material Annealing temperature (ºC)*	*Operating temperature (ºC)*	*Sensor Response* 0%	50%	*n* 0%	50%
NH_3 (100ppm)	WO_3 :Cu(2%) 700ºC	200	6.5	7.4	0.8	0.6
H_2S (1ppm)	WO_3:Cu(0.2%) 400ºC	200	24.4	12.7	0.7	0.8

Table 2: *Selected characteristics of gas sensors based on WO_3:Cu. Material, operating temperature, sensor response and factor n (in dry air and 50% of relative humidity) are presented. (Factor n is calculated after fitting $R_{AIR}/R_{GAS} \propto C^n$, where C is the gas concentration in ppm).*

4.3 Gas sensors based on vanadium-catalysed WO_3

4.3.1 Ammonia detection

Sensor response to 500 ppm of NH_3 was studied for gas sensors based on 400 and 700ºC-annealed vanadium-catalysed WO_3. Nominal atomic vanadium/tungsten concentrations were 0.2, 1, 2 and 5%. After stabilisation at each working temperature, 500 ppm of NH_3 in synthetic air were introduced in the chamber test, followed by purge with synthetic air. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{NH3}, where R_{AIR} was evaluated before ammonia introduction. Operating temperature was varied between 200ºC and 350ºC.

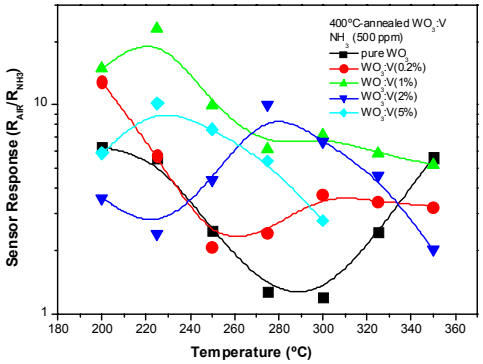

Fig. 20a: *Sensor response of 400ºC-annealed WO_3:V to 500 ppm of NH_3 in synthetic air at different working temperatures.*

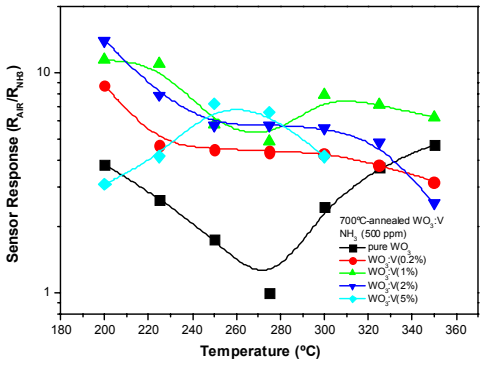

Fig. 20b: *Sensor response of 700ºC-annealed WO_3:V to 500 ppm of NH_3 in synthetic air at different working temperatures.*

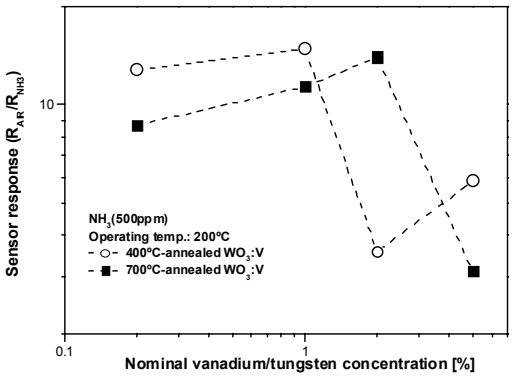

Fig. 21: *Sensor response of WO_3:V to NH_3 (500 ppm in synthetic air) as a function of nominal vanadium/tungsten concentration*

Results are shown in Fig. 20a (400ºC-annealed) and 20b (700ºC). Sensor response of pure WO_3 has also been added for the sake of comparison. It is evident from these figures that vanadium addition is not only affecting the value of sensor response, but also its dependence with operating temperature. The characteristic minimum of sensor response exhibited by pure WO_3 around 250ºC-300ºC is even disappearing in the case of WO_3:V(5%), displaying a maximum of sensor response between 225ºC and 250ºC. Additionally, sensor response is enhanced when vanadium is introduced at 1% and 2% atomic percentages.

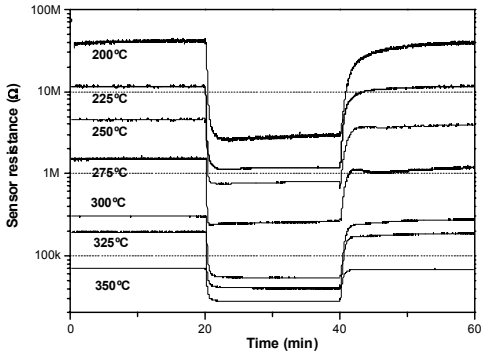

Fig. 22: *Variation of 700ºC-annealed WO_3:V(2%) sensor resistance to a pulse of ammonia (500 ppm) in synthetic air for different operating temperatures*

Fig. 21 compares the sensor response of 400ºC and 700ºC-annealed materials as functions of vanadium content. This figure indicates that higher sensor responses are achieved by gas sensors based on 400ºC-annealed WO_3:V(1%) and 700ºC-annealed WO_3:V(2%).

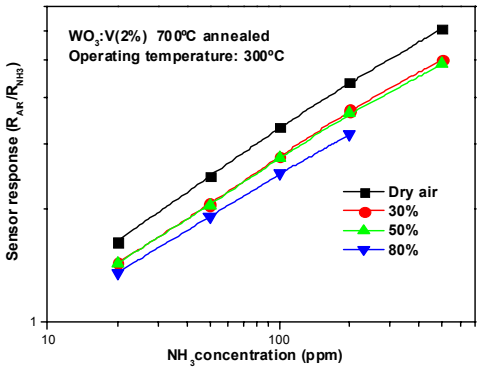

Fig. 23a: *Sensor response of 700ºC-annealed WO_3:V(2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

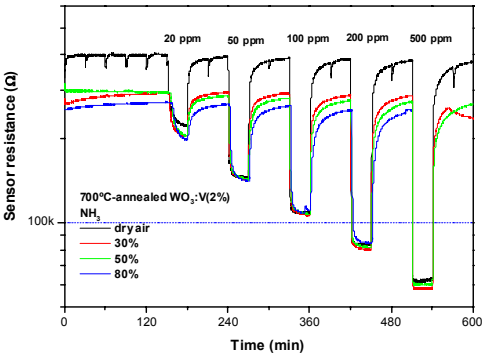

Fig. 23b: *Dynamic sensor response of 700ºC-annealed WO_3:V(2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

However, there was little improvement of the abnormal behaviour previously presented by some of these sensors. Gas sensors based on 700ºC-annealed WO_3:V(2%) presented, however, good dynamic characteristics at most operating temperatures tested, as displayed

by Fig. 22. Although sensor response was clearly higher at lower temperatures, fast sensor recovery was achieved when operated at higher temperatures.

Taking into account these features, 300ºC was found to be a suitable temperature for fast NH_3 detection. Therefore, further studies were carried out at this temperature. Particularly, sensor response to lower concentrations of ammonia and influence of humidity were studied. Results of 700ºC-annealed WO_3:V(2%) sensor response to different concentrations of NH_3 (from 20 ppm to 500 ppm) in dry and humid air are reported in Fig. 23a, whereas Fig. 23b displays the dynamic sensor response. It is interesting to notice that sensor resistance in synthetic air decreases in the presence of humidity but its value is rather independent of the relative humidity. On the other hand, sensor resistance in ammonia ambience is very similar in dry and wet air. As a result, the ratio of resistance R_{AIR}/R_{NH3} decreases in wet ambiences but it is rather independent from the actual relative humidity. This makes this material very interesting for ammonia detection with the interference of humidity.

4.3.2 Hydrogen sulphide detection

Sensor response to 20 ppm of H_2S in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:V. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{H2S}, where R_{AIR} was evaluated before hydrogen sulphide introduction. Results are shown in Fig. 24a (400ºC-annealed) and 24b (700ºC-annealed).

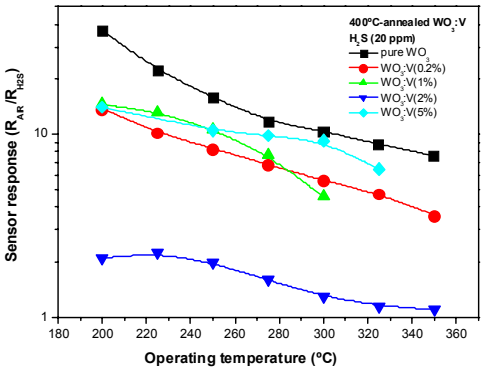

Fig. 24a: *Sensor response of 400ºC-annealed WO_3:V to 20 ppm of H_2S in synthetic air at different working temperatures.*

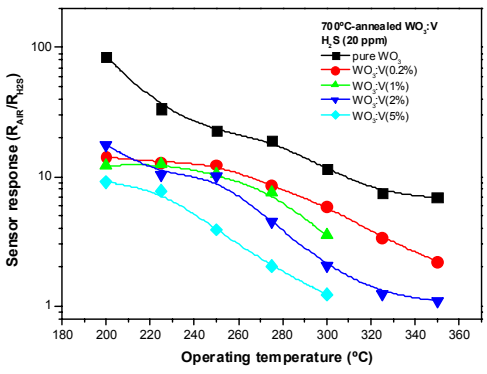

Fig. 24b: *Sensor response of 700ºC-annealed WO_3:V to 20 ppm of H_2S in synthetic air at different working temperatures.*

These figures illustrate that vanadium addition to WO_3 leads to a lower sensor response to hydrogen sulphide. This happened for any combination of vanadium concentration and annealing temperature tested. The dependence of sensor response with operating temperature shows a similar pattern for both pure and vanadium catalysed WO_3.

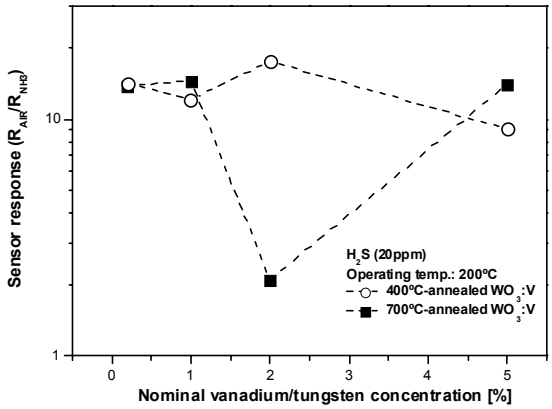

Fig. 25: *Sensor response of WO_3:V to H_2S (20 ppm in synthetic air) as a function of nominal vanadium/tungsten concentration*

Fig. 25 displays the sensor response to 20 ppm of hydrogen sulphide as a function of nominal vanadium content. It reveals that sensor response is very similar for all the materials tested but for 700ºC-annealed WO_3:V(2%).

The outcome of these tests is that sensor response of tungsten oxide to hydrogen sulphide is adversely affected by the addition of vanadium under the specific characteristics reported here. Due to these unsuccessful results, no more data concerning the sensor response of WO_3:V to lower concentrations of hydrogen sulphide or interference of humidity are showed hereafter.

4.3.3 Nitrogen dioxide detection

Sensor response to 1 ppm of NO_2 in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:V. Sensor response was evaluated as the ratio of resistance R_{NO2}/R_{AIR}, where R_{AIR} was evaluated before nitrogen dioxide introduction. Taking into account previous results, sensor response was only studied at 200ºC, as it was found that sensor response increased when operating temperature decreased in the range 200ºC-350ºC. Results of sensor response as a function of nominal vanadium concentration are shown in

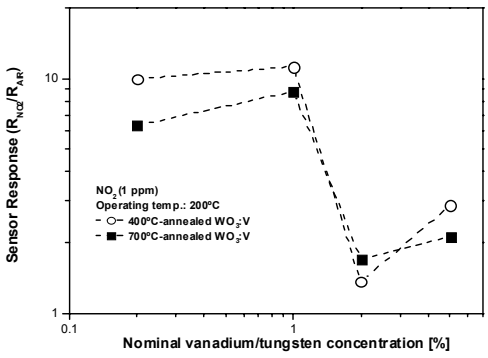

Fig. 26: *Sensor response of WO_3:V to NO_2 (1 ppm in synthetic air) as a function of nominal vanadium/tungsten concentration*

Fig. 26. It is shown that 400ºC-annealed WO_3:V(1%) presented the highest sensor response. However, dynamic sensor response was not satisfactory at all, as it happened in the case of copper-catalysed WO_3. Therefore, vanadium addition was not able to improve the performance exhibited by pure WO_3-based gas sensors in nitrogen dioxide detection.

4.3.4 Conclusions

The main conclusions that can be drawn from the previously presented results concerning the sensor response of 400ºC and 700ºC-annealed vanadium-catalysed WO_3 obtained by this route are:

- Some of the gas sensors based on vanadium catalysed WO_3 still presented an abnormal sensor response to ammonia, similar to that previously reported for pure WO_3.
- 700ºC-annealed WO_3:V(2%) presented a satisfactory dynamic behaviour throughout the range of temperatures tested. Particularly, sensor response to ammonia at 300ºC was interesting due to its fast sensor recovery. At this temperature, interference of humidity was only important between dry air and humid air, in other words, sensor response was not greatly affected by changes in relative humidity, provided it was over 30%.
- Sensor response to hydrogen sulphide decreased as vanadium was introduced, revealing that these sensors are not interesting for H_2S detection.
- Sensor response to nitrogen dioxide was not actually enhanced as vanadium was introduced. What is more, dynamic behaviour was not completely satisfactory, indicating that these sensors are not interesting for NO_2 detection.

Finally, selected characteristics of these sensors are presented in Table 3.

Gas	*Material Annealing temperature (ºC)*	*Operating temperature (ºC)*	*Sensor Response* 0%	50%	*n* 0%	50%
NH_3 (100ppm)	WO_3 :V(2%) 700ºC	300	3.3	2.7	0.4	0.4

Table 3: *Selected characteristics of gas sensors based on WO_3:V. Material, operating temperature, sensor response and factor n (in dry air and 50% of relative humidity) are presented (Factor n is calculated after fitting $R_{AIR}/R_{NH3} \propto C^n$, where C is the gas concentration in ppm).*

4.4 Gas sensors based on chromium catalysed WO_3

4.4.1 Ammonia detection

Sensor response to 500 ppm of NH_3 was studied for gas sensors based on 400 and 700ºC-annealed chromium-catalysed WO_3. Nominal atomic chromium/tungsten concentrations were 0.2, 1, 2 and 5%. After stabilisation at each working temperature, 500 ppm of NH_3 in synthetic air were introduced in the chamber test, followed by purge with synthetic air. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{NH3}, where R_{AIR} was evaluated before ammonia introduction. Operating temperature was varied between 200ºC and 350ºC.

Results are shown in Fig. 27a (400ºC-annealed) and 27b (700ºC). Remarkably, sensor response was very similar for both annealing temperatures. As it has been previously presented for other sensors, sensor response shows a minimum between 250ºC and 300ºC, depending on the sensor. Sensor response of pure WO_3 has been added for a comparison. As these figures display, the maximum sensor response is achieved at 200ºC, with sensor response values between 40-80 for chromium-catalysed WO_3 sensors. Therefore, although the trend of the sensor response with temperature is not apparently affected by chromium addition, its value is clearly enhanced.

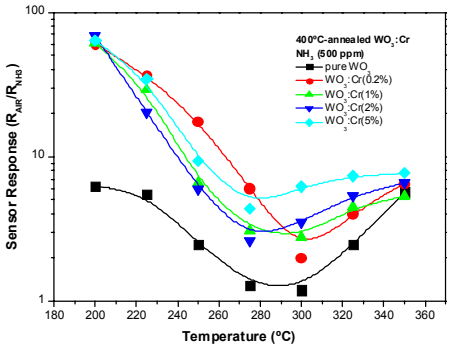

Fig. 27a: *Sensor response of 400ºC-annealed WO_3:Cr to 500 ppm of NH_3 in synthetic air at different working temperatures*

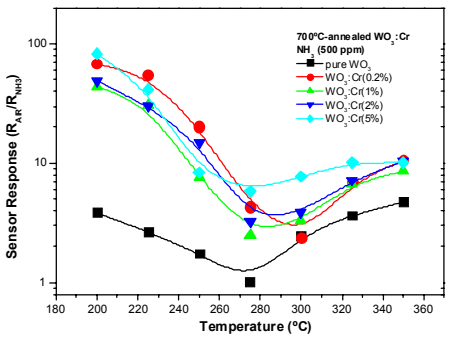

Fig. 27b: *Sensor response of 700ºC-annealed WO_3:Cr to 500 ppm of NH_3 in synthetic air at different working temperatures*

Sensor response at 200ºC temperature is shown in Fig. 28 as a function of the nominal chromium/tungsten concentration. It is interesting to notice that while chromium content in 400ºC-annealed materials is affecting sensor response, it is not in the case of 700ºC-

annealed powders. Maximum sensor response is exhibited by sensor based on WO_3:Cr(1%) (400ºC annealed) operated at 200ºC ($R_{AIR}/R_{NH3}\approx 82$).

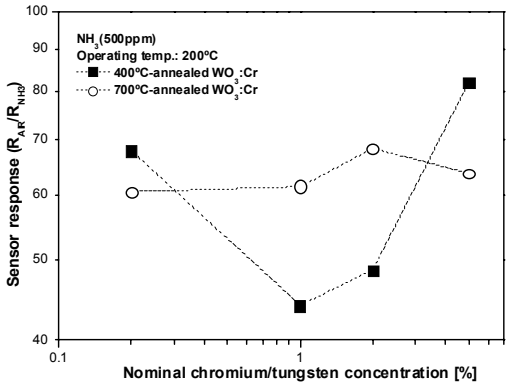

Fig. 28: *Sensor response of WO_3:Cr to NH_3 (500 ppm in synthetic air) as a function of nominal chromium/tungsten concentration*

Unfortunately, some of the sensors presented the abnormal behaviour previously described in the case of pure WO_3 and thus they are not suitable for ammonia detection. WO_3:Cr(0.2%) annealed at 700ºC presented a satisfactory dynamic sensor response, however. On top of this, this material showed a high sensor response to ammonia, what makes it an excellent candidate for NH_3 detection. Fig. 29 displays the variation of sensor resistance to 500 ppm of NH_3 in synthetic dry air at different operating temperature. Sensor response presented an abnormal behaviour for temperatures over 300ºC. On the other hand, it exhibited a good performance when operated at lower temperatures, presenting a maximum sensor response at 200ºC. However, its resistance at this temperature was rather high (over 10 MΩ), so 225ºC was also considered to be an interesting operating temperature. It leads to a lower sensor resistance and faster sensor recovery, although sensor response is slightly lower.

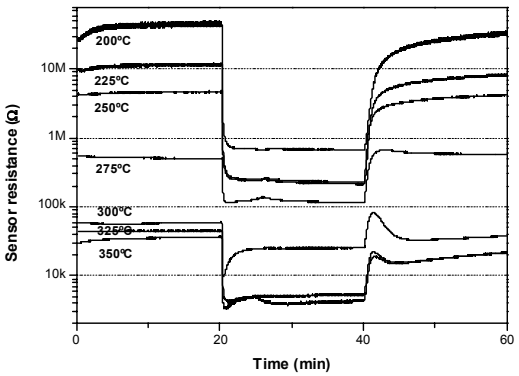

Fig. 29: *Variation of 700ºC-annealed WO_3:Cr(0.2%) sensor resistance to a pulse of ammonia (500 ppm) in synthetic air for different operating temperatures*

Since 225ºC was found to be a suitable temperature for NH_3 detection, further studies were performed at this temperature. Particularly, sensor response to lower concentrations of ammonia and influence of humidity were studied. Results of 700ºC-annealed WO_3:Cr(0.2%) sensor response to different concentrations of NH_3 (from 20 ppm to 500 ppm) in dry and humid ambiences are reported in Fig. 30a, whereas Fig. 30b shows the dynamic sensor response. It is interesting to notice that sensor resistance (both in pure or NH_3-containing synthetic air) decreased in the presence of humidity. The ratio of resistance R_{AIR}/R_{NH3} is also reduced as humidity increases, indicating that humidity has an important interference in the ammonia sensor response.

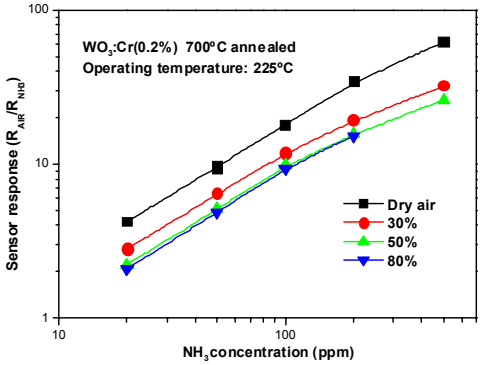

***Fig. 30a**: Sensor response of 700ºC-annealed WO_3:Cr(0.2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

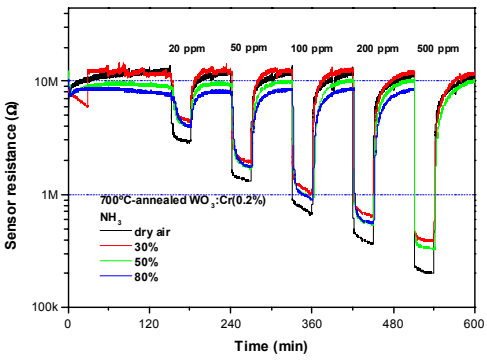

***Fig. 30b:** Dynamic sensor response of 700ºC-annealed WO_3:Cr(0.2%) to different concentrations of NH_3 in synthetic dry and humid air (relative humidity is indicated).*

4.4.2 Hydrogen sulphide detection

Sensor response to 20 ppm of H_2S in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:Cr. Sensor response was evaluated as the ratio of resistance R_{AIR}/R_{H2S}, where R_{AIR} was evaluated before hydrogen sulphide introduction. Results are shown in Fig. 31a (400ºC-annealed) and 32b (700ºC-annealed). It is evident that sensor response increases for both series of sensors as operating temperature decreases, so maximum sensor response was found at 200ºC. The addition of chromium, even at 0.2% atomic concentration, was able to substantially improve the sensor response to hydrogen sulphide. In the case of 400ºC-annealed powders, this sensor response was extremely high, near 1000 at 225ºC for WO_3:Cr(1%).

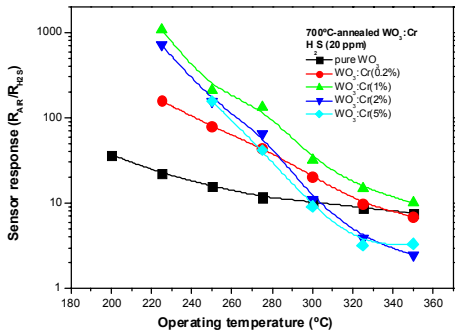

Fig. 31a: *Sensor response of 400ºC-annealed WO_3:Cr to 20 ppm of H_2S in synthetic air at different working temperatures*

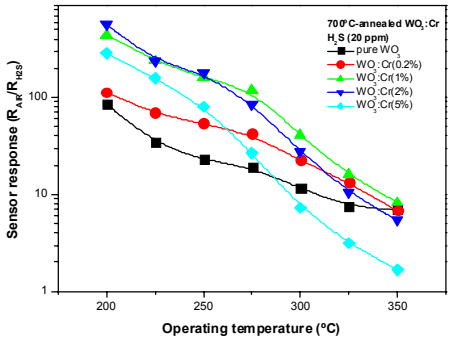

Fig. 31b: *Sensor response of 700ºC-annealed WO_3:Cr to 20 ppm of H_2S in synthetic air at different working temperatures*

Nevertheless, gas sensors based on 400ºC exhibited a high sensor resistance due to chromium addition and an extremely high sensor response at 200ºC. These factors may lead to misleading results in sensor response due to the limitations of the measurement system, so sensor response has been only evaluated between 225ºC and 350ºC for these sensors (250ºC and 350ºC for WO_3:Cr(5%)). What is more, although these sensors presented such a high sensor response, their dynamic behaviour was not satisfactory at all due to a very long sensor recovery. Therefore, 300ºC was considered as a suitable temperature for the detection of hydrogen sulphide. Sensor response at this temperature is displayed in Fig. 32 as a function of the nominal chromium/tungsten concentration. It is interesting to notice that the maximum sensor response is found when chromium was introduced in 1% atomic concentration for both annealing temperatures.

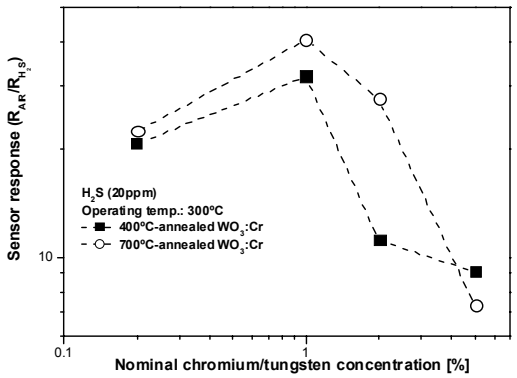

Fig. 32: *Sensor response of WO_3:Cr to H_2S (20 ppm in synthetic air) as a function of nominal chromium/tungsten concentration*

Fig. 33 illustrates de dynamic sensor response of 700ºC WO_3:Cr(2%) at a number of operating temperatures. It becomes evident from this figure that sensor recovery can be very slow when the sensor is operated at temperatures under 300ºC. Sensor response of 700ºC-annealed pure WO_3 operated at 225ºC is also included for a comparison. Further studies were performed with this material at 300ºC. Particularly, sensor response to lower concentrations of hydrogen sulphide and the influence of humidity were studied.

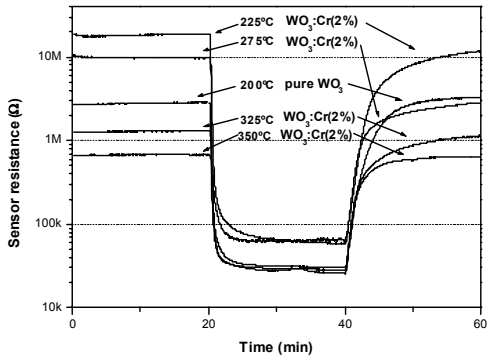

Fig. 33: *Variation of 700ºC-annealed WO_3:Cr(2%) sensor resistance to a pulse of hydrogen sulphide (500 ppm) in synthetic air for different working temperatures.*

Fig. 34a shows the sensor response to different concentrations of H_2S (from 1 ppm to 10 ppm) in dry and humid ambiences, whereas Fig. 34b shows the dynamic sensor response. Humidity makes sensor resistance decrease its value in both pure air and hydrogen sulphide ambiences. These figures illustrate that humidity has a considerable interference in the detection of hydrogen sulphide, as it was revealed in the case of pure tungsten oxide.

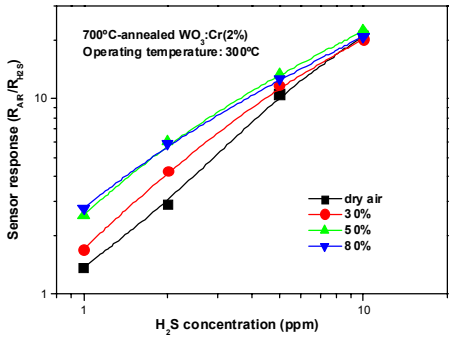

Fig. 34a: *Sensor response of 700ºC-annealed WO_3:Cr(2%) to different concentrations of H_2S in synthetic dry and humid air (relative humidity is indicated).*

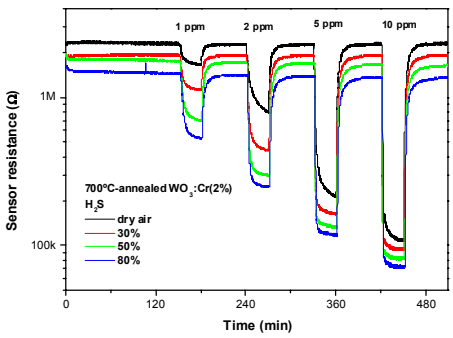

Fig. 34b: *Dynamic sensor response of 700ºC-annealed WO_3:Cr(2%) to different concentrations of H_2S in synthetic dry and humid air (relative humidity is indicated).*

4.4.3 Nitrogen dioxide detection

Sensor response to 1 ppm of NO_2 in synthetic air was studied for gas sensors based on 400 and 700ºC-annealed WO_3:Cr. Sensor response was evaluated as the ratio of resistance R_{NO2}/R_{AIR}, where R_{AIR} was evaluated before nitrogen dioxide introduction. Taking into account previous results and since sensor resistance can have very high values at low temperatures, sensor response was only studied at 250ºC. Results of sensor response as a function of nominal chromium concentration are shown in Fig. 35a. This figure indicates a similar dependence of sensor response with nominal chromium content for both annealing temperatures. Maximum sensor responses are achieved with 0.2% and 2% chromium atomic percentages. However, dynamic sensor response was not completely satisfactory, as revealed by Fig. 35b. This figure shows the dynamic sensor response of 700ºC annealed WO_3:Cr to different concentrations of NO_2 (0.2-2 ppm). It is evident from this figure that sensor recovery can be very slow.

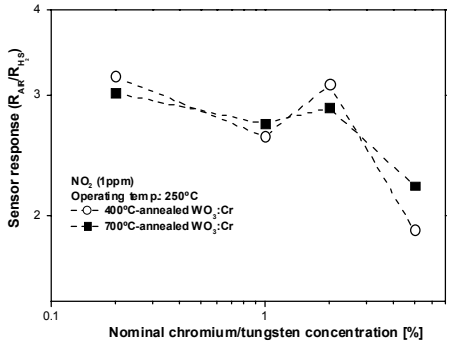

Fig. 35a: *Sensor response of WO_3:Cr to NO_2 (1 ppm in synthetic air) as a function of nominal chromium/tungsten concentration*

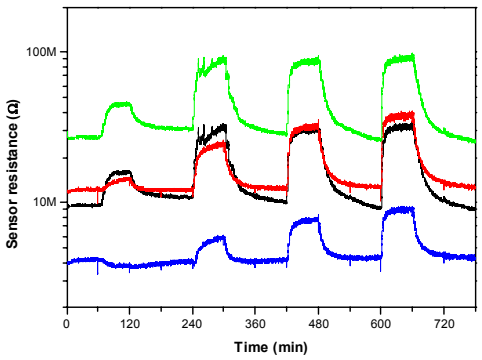

Fig. 35b: *Dynamic sensor response of 700ºC-annealed WO_3:Cr to different concentrations of NO_2 in synthetic dry*

4.4.4 Conclusions

The results presented above concerning the sensor response of 400ºC and 700ºC-annealed chromium-catalysed WO_3 lead to the following conclusions:

- Chromium addition significantly increases the sensor response to ammonia, although the trend of the response, as well as the abnormal behaviour in some sensors, still remains.

- Sensors based on WO_3:Cr(0.2%) exhibited a high sensor response to ammonia combined with a fast sensor recovery. Nevertheless, interference of humidity appeared to be important.
- Chromium addition enhances the sensor response to hydrogen sulphide, especially at low temperatures. The maximum sensor response was achieved when chromium was introduced in 1-2% atomic concentrations and operated at 200ºC
- These sensors presented a very slow recovery when operated at temperatures under 300ºC, what motivated to operate them at that temperature. Sensor based on WO_3:Cr(2%) exhibited a moderate sensor response at 300ºC, as well as a fast sensor recovery. However, the interference of humidity was again important in hydrogen sulphide detection.
- Sensor response to nitrogen dioxide was not completely satisfactory due to high sensor resistance and long recovery times.

Finally, selected characteristics of these sensors are presented in Table 4.

Gas	*Material Annealing temperature (ºC)*	*Operating temperature (ºC)*	*Sensor Response* 0%	50%	*n* 0%	50%
NH_3 (100ppm)	WO_3 :Cr(0.2%) 700ºC	225	18.2	9.8	0.7	0.7
H_2S (5ppm)	WO_3 :Cr(2%) 700ºC	300	10.6	13.41	0.9	0.7

Table 4: *Selected characteristics of gas sensors based on WO_3:Cr. Material, operating temperature, sensor response and factor n (in dry air and 50% of relative humidity) are presented (Factor n is calculated after fitting $R_{AIR}/R_{GAS} \propto C^n$, where C is the gas concentration in ppm).*

4.4 Discussion and conclusions

Sensor resistance in air

Fig. 36 displays the dependence of sensor resistance on operating temperature for the different materials analysed.

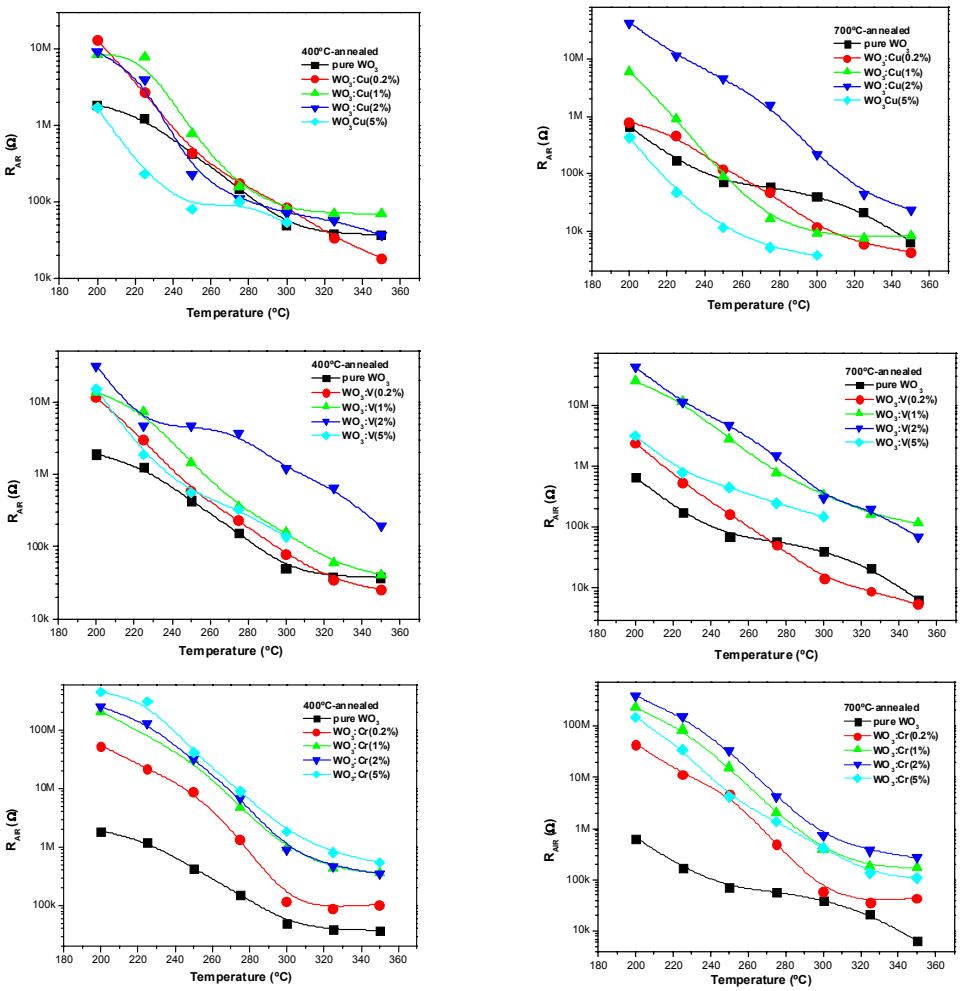

Fig. 36: *Variation of sensor resistance in air with operating temperature for copper, vanadium and chormium-catalysed WO_3-based sensors.*

Firstly, sensor resistance of pure 400ºC-annealed WO_3 is slightly higher than that of 700ºC-annealed. Since there is a clear grain size growth as annealing temperature increases from 400ºC to 700ºC, this could be enough to explain this change of resistance. More grain barriers would appear in thick films based on 400ºC-annealed powders and thus they would present a higher sensor resistance. However, considering this very simple model, the value

of the resistance should be an inverse function of grain size, what is obviously not happening in our case, since sensor resistance of 400ºC-annealed WO_3 is actually only slightly higher. In fact, the value of sensor resistance is dependent on many other factors that make the discussion not so straightforward. Sensor resistance is basically dependent on (1) the barrier height that carriers must overcome to from grain to grain and (2) the concentration of carriers, mainly dependent on bulk vacancies. In practice, it is well known that the main parameter is the barrier height, since small changes in this barrier can modulate greatly the final sensor resistance. These changes in barrier height are mainly dependent on adsorbed oxygen ions on the interface between grains and the adsorption of these oxygen ions is dependent on the surface defects of the grains, mainly oxygen vacancies. On the other hand, variations of orders of magnitude of carrier concentration are needed to produce significant changes in sensor resistance. Therefore, it is not possible to attribute the decrease of resistance with annealing temperature only to grain growth.

In the case of catalysed samples, this discussion is further complicated by the presence of these additives. Therefore, it is extremely difficult to try to establish a general dependence of sensor resistance on grain size. On the other hand, this figure reveals a clear picture of the influence of additive addition to WO_3: sensor resistance at lower temperatures increases as additives are present. This feature clarifies that electrical sensitisation may work in these sensors: additives centres do increase sensor resistance and, provided this increase is due to a raise in intergrain barrier potential and that these centres undergo redox processes, these could explain the increased sensor response presented by many catalysed WO_3 sensors. This will be further clarified after analysing surface reactions in Chapter 5 and drawing final conclusions in Chapter 6.

There are some individual features that are worth noting. Sensor resistance at higher temperatures is not clearly correlated with additives presence in the case of copper. Moreover, WO_3:Cu(5%)-based sensors present a lower sensor resistance than even pure WO_3. Bulk migration of copper ions and creation of donor levels than can alter the carrier concentration should not be ruled out. However, this interpretation is very tentative and further studies should be carried out to decide on the nature of this effect. On the other hand, sensor resistance of vanadium and chromium-catalysed WO_3 were nearly always higher than the values of pure WO_3. It is especially interesting the case of chromium, which make sensor resistance raise more than two orders of magnitude.

Ammonia sensor response

From the previous results, it is evident there is a key point that needs further discussion: the abnormal dynamic behaviour of some sensors under ammonia presence.

Surprisingly, pure tungsten oxide showed an abnormal dynamic behaviour when ammonia was introduced and removed. Some gas sensors based on catalysed WO_3 presented it too. Although a great number of publications have shown nice sensor response to ammonia by gas sensors based on metal oxides (see chapter 1 and references therein), it must be pointed out that some other did not. Overshooting phenomena [1,2], very long recovery time [3,4] or even increase of sensor resistance as ammonia is introduced [5] have been reported without a single explanation when dealing with gas sensors based on WO_3 or other metal oxides. Of course, it is unknown how many research groups have also found these misleading results and have not dare to publish them.

To the best of the author knowledge, only the research group of Prof. Egashira and Prof. Shimizu have tackled these phenomena. The abnormal behaviour showed by pure WO_3 in NH_3 detection has been already described for TiO_2 and In_2O_3 based gas sensors [6,7] and it was attributed to the unselective catalytic oxidation of ammonia to NO. Ammonia oxidation can follow several competitive reactions on the metal oxide surface. At least three main reactions have been proposed for NH_3 oxidation:

$$2NH_3 + 3O_o \rightarrow N_2 + 3H_2O \quad (1)$$

$$2NH_3 + 5O_o \rightarrow 2NO + 3H_2O \quad (2)$$

$$2NH_3 + 4O_o \rightarrow N_2O + 3H_2O \quad (3)$$

where O_o is oxide in regular oxygen site, and it can be substituted by appropriate amounts of chemisorbed O^- or O_2^- or even lattice oxygen. All these reactions are possible and produce a resistance decrease. Although WO_3 has shown a rather low sensor response to NO in an inert atmosphere [8], it is very well known that NO is easily transformed into NO_2 in the presence of oxygen, becoming NO_x. Tungsten oxide is sensitive to sub-ppm concentrations of NO_2, which induces a resistance increase. When NH_3 is introduced,

sensor resistance decreases because oxygen ions are consumed and the intergrain potential barrier diminishes; however, if NO_x is produced by reaction (2), the resistance would increase, since chemisorbed NO_x^- traps electrons. When NH_3 is removed, oxygen is quickly adsorbed on the surface and the sensor resistance increases; however, NO_x^- is hard to desorb [6], what would explain overshooting problems on the resistance after NH_3 removal. Although the oxidation of ammonia to NO is reported to increase with temperature [9], sensor response to NO_x decreases when temperature increases. Both combined effects would contribute to induce a minimum between 250ºC and 300ºC.

In brief, sensor response of pure WO_3 to NH_3 has an abnormal behaviour that may be due to the catalytic transformation of NH_3 into NO_x. However, NH_3 oxidation over sensor platinum electrodes or heater should not be ruled out.

The reason why some of the additives tested here were able to eliminate this abnormal behaviour remains obscure if only these test results are taking into account. In principle, a more selective oxidation of ammonia (ideally through reaction 1) would produce a non-reactive product (e.g. N_2). As to N_2O, it is also reported to not be highly reactive on metal oxide surfaces. Of course, if the material is not very sensitive to NO_x, it would help in avoiding this interference too. However, the real panorama is much more complex than that described by reactions 1-3. These reactions only describe the whole process and many intermediate reactions must be actually considered. After the presentation of DRIFTS and TPD data, a more elaborated discussion will be provided.

From the materials tested, 700ºC-annealed WO_3:Cu(2%) presented a normal dynamic behaviour at 200ºC. Besides, it presented a good sensor response to NH_3 in the range from 20 to 500 ppm and a low interference from humidity. Therefore, this material is considered as suitable for ammonia detection in the studied ranges. As to vanadium catalysed tungsten oxide, 700ºC-annealed WO_3:V(2%) presented a normal dynamic behaviour throughout the range of temperatures tested. Particularly, sensor response to ammonia at 300ºC was interesting due to its fast sensor recovery. At this temperature, interference of humidity was only important between dry air and humid air, so as to say, sensor response was not greatly affected by changes in relative humidity provided it was over 30%. Finally, sensors based on WO_3:Cr(0.2%) exhibited a high sensor response to ammonia combined with a fast sensor recovery. Nevertheless, interference of humidity appeared to be important.

Hydrogen sulphide sensor response

According to literature, the most common H_2S sensing mechanisms of gas sensors based on metal oxides are:

(i) combustion of H_2S or SH with oxygen species (either adsorbed oxygen or lattice oxygen) [10,11]

(ii) replacement of lattice oxygen by sulphur, which may lead to a change in surface conductivity [12,13]

Regarding specifically the detection of hydrogen sulphide by WO_3, Barrett et al. [14] stated that, since WS_2 has a higher conductivity than WO_3, exchange of lattice oxygen by sulphur (sulphurisation) was responsible for the increase of conductivity when the atmosphere was changed from synthetic air to H_2S. However, in a more recent article by Frühberger et al. [15], it was concluded that oxygen vacancies are produced on the surface of WO_3 by the consumption of oxygen species by H_2S and that sulphurisation would need atmospheric pressures of H_2S. In spite of the high number of publications devoted to H_2S detection by WO_3-based sensors, no more papers have seriously wonder about which is the sensing mechanism.

From our test data, it can not be concluded which one of these two routes is actually happening. After presenting the TPD data, a clearer picture of the situation will be provided. Test data indicate that sensor response to hydrogen sulphide increases as operating temperature decreases in the range between 200ºC and 350ºC. A similar situation has been described in some papers [14,16], what reveals that hydrogen sulphide needs a low activation energy to react on the surface of WO_3.

One interesting point is the influence of humidity on sensor resistance when hydrogen sulphide is present (see Fig. 7 in this chapter). It is remarkable that, as water make decrease the sensor resistance in pure air, sensor resistance increases when humidity is introduced in the presence of hydrogen sulphide. The reduction of sensor resistance in pure air when humidity is present, followed by a slow increase, is a common reported effect for different metal oxides, especially SnO_2. The decrease in sensor resistance was attributed to the dissociatively reaction of water with lattice oxygen, which leads to the formation of oxygen vacancies and so to a resistance decrease [17,18]. The following slow resistance increase could be due to the recombination of the OH^- ions with the lattice oxygen vacancies previously formed. Adsorption of hydroxyl groups and hydrogen sulphide molecules will

be discussed in detail in chapter 5, but it can be advanced that both molecules are probably bonded to unsaturated surface tungsten cations. Finally, test revealed that only chromium addition enhances the sensor response to hydrogen sulphide, especially at low temperatures. The maximum sensor response was achieved when chromium was introduced in 1-2% atomic concentrations and operated at 200ºC. However, these sensors presented a very slow recovery when operated at temperatures under 300ºC, what suggested to operate them at that temperature. Sensor based on WO_3:Cr(2%) exhibited a moderate sensor response at 300ºC, as well as a fast sensor recovery. It must be pointed out that the interference of humidity was again important in hydrogen sulphide detection. The reason why sensor response is enhanced by chromium introduction will be clarified with TPD data in chapter 5.

Finally, it is necessary to point out that the addition of copper to WO_3 showed no significant change in sensor response to H_2S. This is quite a remarkable result, especially considering the high number of publications reporting that CuO-SnO_2 sensors exhibit a high sensor response to hydrogen sulphide [12,13,19]. Briefly, these papers claim that copper oxide is transformed into copper sulphide, which has a higher conductivity, and thus sensor responses increases dramatically. In our case, this effect was not found since sensor response of copper catalysed WO_3 was similar or even slightly lower than that of pure WO_3. This suggests that either this sulphurisation is not happening or its electrical effect is not as effective as in the case of tin oxide. The reason could be the different disposition of copper, since it those papers CuO is really forming islands between SnO_2 grains and, as shown in Chapter 3, this is not our case.

Nitrogen dioxide sensor response

According to Gurlo et al. [20], sensor response of metal oxide-based gas sensors to nitrogen dioxide is due to adsorbed species that capture electrons and thus make sensor resistance increase. The different adsorbed species can be NO_2^-, O^- and $2O^-$, depending on the operating temperature. The nature of the specific interacting species might be deduced from the slope of the sensor response-NO_2 concentration graphs [20]. However, it is well know that this factor is highly dependent on the thick film microstructure [21], so this consideration might be misleading.

In any case, these species must adsorb on surface defects-reducing states, such as metal cations in low oxidation states or oxygen vacancies [22]. Accordingly, a possible

interaction mechanism between nitrogen dioxide and WO_3 may be through superficial W^{5+} states:

$$NO_2 + W^{5+} \leftrightarrow (W^{6+} - NO_2^-)$$

An interesting result reported here is that 700ºC-annealed pure WO_3 sensors exhibited a higher sensor response than 400ºC-annealed ones. Although grain growth is well reported to lead to lower sensor response, it has been reported for WO_3 thick-film gas sensors that when crystallite size was between 25 and 60 nm, sensor response to nitrogen dioxide was independent of crystallite size [23]. Besides, test also revealed that sensor resistance in the presence of humidity remained the same as in dry air, what makes this material very interesting for nitrogen dioxide detection with low interference from humidity. This fact may indicate that nitrogen dioxide is able to displace water from the surface and thus avoid its recombination with oxygen species.

Finally, high sensor response to NO_2 was achieved when copper was introduced in 1% atomic percentage. However, the dynamic behaviour was not completely satisfactory in the range of NO_2 concentration analysed, since long recovery times were found. Probably, unsaturated copper cations are present on the surface of tungsten oxide, becoming adsorption centres for NO_2 molecules. However, it is well know that these molecules are strongly adsorbed, so the recovery of the sensor can be extremely long.

4.6 References

[1] E. Llobet, G. Molas, P. Molinàs, J. Calderer, X. Vilanova, J. Brezmes, J.E. Sueiras, X. Correig, *Fabrication of highly selective tungsten oxide ammonia sensors*, J. Electrochem. Soc. 147 (2000) 776-779.

[2] K. Mitzner, J. Sternhagen, D. Galipeau, *Development of a micromachined hazardous gas sensor array*, To be published in Sens. Actuators B.

[3] M. Fleischer, M. Seth, C.Kohl, H. Meixner, *A study of surface modification at semiconducting Ga_2O_3 thin film sensors for enhancement of the sensitivity and selectivity*, Sens. Actuators B 35-36 (1996) 290-296.

[4] M. Aslam, V.A. Chaudhary, I.S. Mulla, S.R. Sainkar, A.B. Mandale, A.A. Belhekar, K. Vijayamohanan, *A highly selective ammonia gas sensor using surface-ruthenated zinc oxide*, Sensors and Actuators B 75 (1999) 162–167.

[5] Alexey A. Tomchenko, Gregory P. Harmer, Brent T. Marquis, John W. Allen, *Semiconducting metal oxide sensor array for the selective detection of combustion gases*, To be published in Sens. Actuators B.

[6] Y. Takao, K. Miyazaki, Y. Shimizu, M. Egashira, *High ammonia sensitive semiconductor gas sensors with double-layer structure and interface electrodes,* J. Electrochem. Soc. 141 (1994) 1028-1034.

[7] Y. Shimizu, T. Okamoto, Y. Takao, M. Egashira, *Desorption behavior of ammonia from TiO_2-based specimens – ammonia sensing mechanisms of double-layer sensors with TiO_2-based catalyst layers*, J. Mol. Catal. A 155 (2000) 183-191.

[8] B. Fruhberger, N. Stirling, F. G. Grillo, S. Ma, D. Ruthven, R. J. Lad and B. G. Frederick, *Detection and quantification of nitric oxide in human breath using a semiconducting oxide based chemiresistive microsensor*, Sens. Actuators B 76 (2001) 226-234.

[9] J. Gallardo, V. Sánchez, G. Ramis, G. Busca, *An FT-IR study of ammonia adsorption and oxidation over annatase-supported metal oxides*, Appl. Catal. B 13 (1997) 45-58.

[10] V. V. Malyshev, A. V. Pislyakov, *SnO2-based thick-film-resistive sensor for H_2S detection in the concentration range of 1-10 mg m-3*, Sens. Actuators B 47 (1998) 181-188.

[11] G. Fang, Z. Liu, C. Liu, K. Yao, *Room temperature H2S sensing properties and mechanism of CeO_2-SnO2 sol-gel thin films*, Sens. Actuators B 66 (2000) 46-48.

[12] J. Tamaki, K. Shimanoe, Y. Yamada, Y. Yamamoto, N. Miura, N. Yamazoe, *Dilute hydrogen sulfide sensing properties of CuO-SnO_2 thin fil prepared by low-pressure evaporation method*, Sens. Actuators B 49 (1998) 121-125.

[13] S. Manorama, G. Devi, V. Rao, *Hydrogen sulfide sensor based on tin oxide deposited by spray pyrolysis and microwave plasma chemical vapor deposition*, Appl. Phys. Lett. 64 (1994) 3163-3165.

[14] E. Barrett, G. Georgiades, P. Sermon. *The mechanism of operation of WO_3-based H_2S sensors*, Sens. Actuators B 1 (1990) 116-120.

[15] B. Frühberger, M. Grunze and D. J. Dwyer, *Surface chemistry of H_2S-sensitive tungsten oxide films*, Sens. Actuators B 31 (1996) 167-174.

[16] J. Solis, S. Saukko. L. Kish, C. Granqvist, V. Lantto, *Semiconductor gas sensors based on nanostructured tungsten oxide*, Thin Solid Films 391 (2001) 255-260.

[17] G. Heiland, D. Kohl, in T. siyama (ed.), *Chemical sensor technology*, Vol. 1 Kodansha, Tokyo, 1-35.

[18] Y. Matsuura, K. Takahata, K. Ihokura, *Mechanism of gas sensitivity change with time of SnO_2 gas sensors*, Sens. Actutators 14 (1988) 223-232.

[19] R.S. Niranjan, K.R. Patil, S.R. Sainkar, I.S. Mulla, *High H2S-sensitive copper-doped tin oxide thin film*, Mat. Chem. Physics 80 (2003) 250–256.

[20] A. Gurlo, N. Barsan. M. Ivanovskaya, U. Weimar. W. Gopel, *In_2O_3 and MoO_3-I In_2O_3 thin film semiconductor sensors: interaction with NO_2 and O_3*, Sens. Actuators B 47 (1998) 92-99.

[21] D.E. Williams, Keith F. E. Pratt, *Microstructure effects on the response of gas-sensitive resistors based on semiconducting oxides*, Sens. Actuators B 70 (2000) 214-221

[22] M. Ivanovskaya, A. Gurlo, P. Bogdanov, *Mechanism of O_3 and NO_2 detection and selectivity of In_2O_3 sensors,* Sens. Actuators B 77 (2001) 264-267.

[23] J. Tamaki, Z. Zhang, K. Fujimori, M. Akiyama, T. Harada, N. Miura and N. Yamazoe, *Grain-size effects in tungsten oxide-based sensor for nitrogen oxides*, J. Electrochem. Soc., 141 (1994) 2207-2210.