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Pulsed UV light activated gas sensing in tungsten oxide nanowires

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Abstract

The present work shows a new way to analyze transient responses of MOX sensors under Pulsed-UV light, that can improve response dynamics and mitigate drift. In particular, we focus on the gas response analysis of tungsten oxide (WO_{3-x}) nanoneedles when exposed to NO_2.
It is known that temperature modulation is useful for extracting more information about the pollutant gases, so we have modulated UV source (325 nm) in order to study the transients of oxidation (when UV is Off for 30 s) and transients of surface reduction or cleaning (UV On for 30 s). Using pulsed UV light activated sensing allows us to obtain responses, even at room temperature, and significantly reduce power consumption.

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Keywords: WO3 nanoneedles; Pulsed UV activation; NO2 sensor

1. Introduction

We have reported previously that tungsten oxide nanoneedles are a suitable sensing layer for detecting gases such as NO_2 , H_2 , H_2S, but in a range of operating temperatures that lie from 200 ºC up to 400 ºC [1,2]. Recently, there have been reports of gas sensors utilizing ultra-violet (UV) activated MOX semiconductors [3,4,5,6], and irradiation of these sensors is an important alternative to activate chemical reactions at metal oxide surface, instead of the more common use of energy-demanding heating. However, the UV light has often been used only for cleaning the gas

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sensing layer, rather than to modify its gas sensing properties. There are other studies using UV irradiation combined with heating to stimulate the gas sensor and improve its sensitivity and selectivity in measurements using the FES method [7]. In this work, we fixed a constant temperature and we switched on and off the UV LED. These processes create a ripple in the output signal (resistance) as we can see at Figure 1. We have found that this ripple has different amplitude and growing/decreasing rates as a function of NO_2 concentration. So, if we calculate the first derivative for the periods when the UV light is switched OFF (i.e., when NO_2 oxidizes the active layer), we obtain the change rate of the material resistance, expressed in ohms/s. This information is to be used for determining NO_2 concentration.

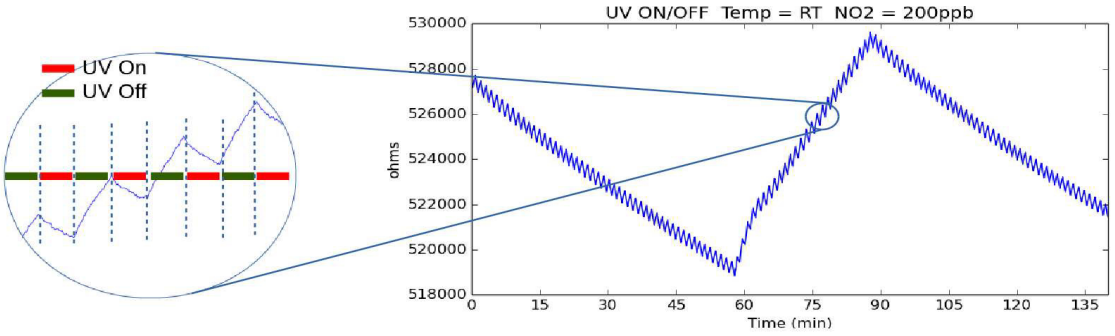

Fig. 1. Response of WO_3 nano-needles at RT we can see the ripple caused from UV switching. The response is coming from a large exposition of O_2 and the sensor is recovering. From each period (UV On and UV Off) we can obtain value data in order to determine the NO_2 concentration

2. Experimental

Tungsten oxide (WO_{3-x}) nano-needles were directly grown on ceramic substrates at 500 ºC via a hot wall aerosol assisted CVD method employing tungsten hexacarbonyl (W(CO) 6, 50 mg) dissolved in acetone (15 ml) and methanol (5 ml). A piezoelectric ultrasonic atomizer was used to generate an aerosol of the solute, while N_2 was used as carrier gas. Those ceramic substrates had printed Pt electrodes on one side and a Pt heater on the other side.

A sensor test chamber was designed and constructed in Teflon. Its inner volume was 24 cm^3 . The chamber contains sockets to which up to six sensors can be plugged in to be tested. The cover lid houses two UV LEDs, so sensors can be operated in 'temperature mode' when a constant current is driven through their heating element while the UV diodes are OFF; in 'UV activation mode ', when heaters are not used and the UV LEDs are ON; and in 'mixed mode', when both heating elements and UV LEDs are used simultaneously. The LED to sensing film distance was set to 12 mm, which considering the radiation aperture of the LED used (120º), ensured achieving a homogeneous UV irradiation of the sensors. The UV LEDs employed were manufactured by SETI, Sensor Electronic Technology I nc., Columbia, SC, US A [8] (model UVTOP320TO39FW) and their maximal emitting optical power was 400 μW at 325 nm. A picture of the sensor chamber and of a gas sensor is shown in Figure 2.

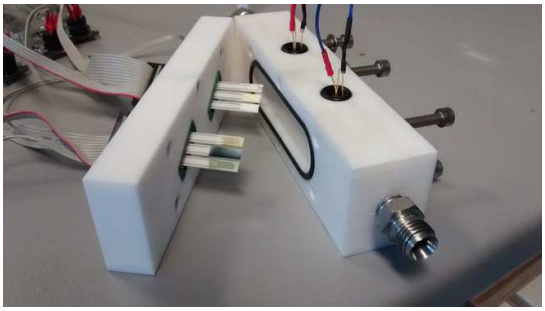

Fig. 2. Teflon Chamber with 6 sensors pluged in and UV LEDs

3. Results and discussion

Figure 3 plots this change rate when the sensor has been exposed to increasing and decreasing steps of NO_2 concentration. It can be derived that gas concentration can be determined in a much faster way than when the sensor is operated at a fixed working temperature.

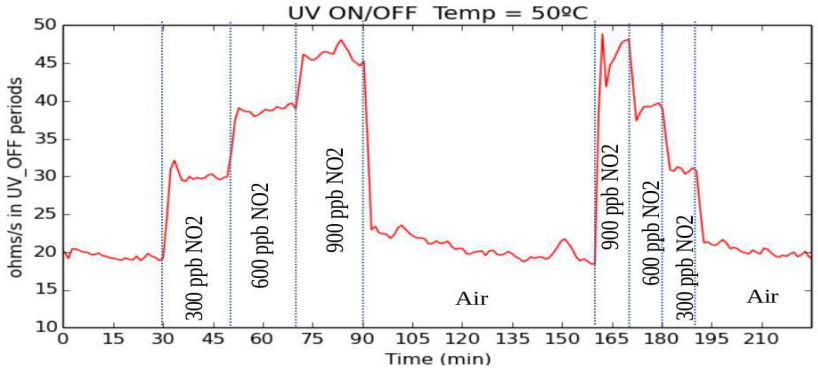

Fig. 3. The sensor has exposed to this 300, 600 and 900 ppb of NO_2, analyzing the ripple and plotting only the first derivative when UV is off we can determine NO_2 concentration, We obtain the same speed values going up in concentration and in reverse mode. For first steps the concentration time is 20 min and for the second ones only for 10 min.

When using pulsed UV light, sensor response can be analyzed employing three different methods. The first consists of analyzing response rates when UV is off (like in Fig. 3). Alternatively, we can check the cleaning or reduction rate when the UV is on. Finally the third method consist of computing the addition of these two rates and taking as important information the maximum that occurs at the beginning of the exposure to NO_2. The maximum of the addition of these two rates as a function of gas concentration is shown in Figure 4. Sensor response was measured as the intensity of the maximum of the addition curve (i.e. ,the sum of rates of reduction and oxidation) as a function of nitrogen dioxide concentration.

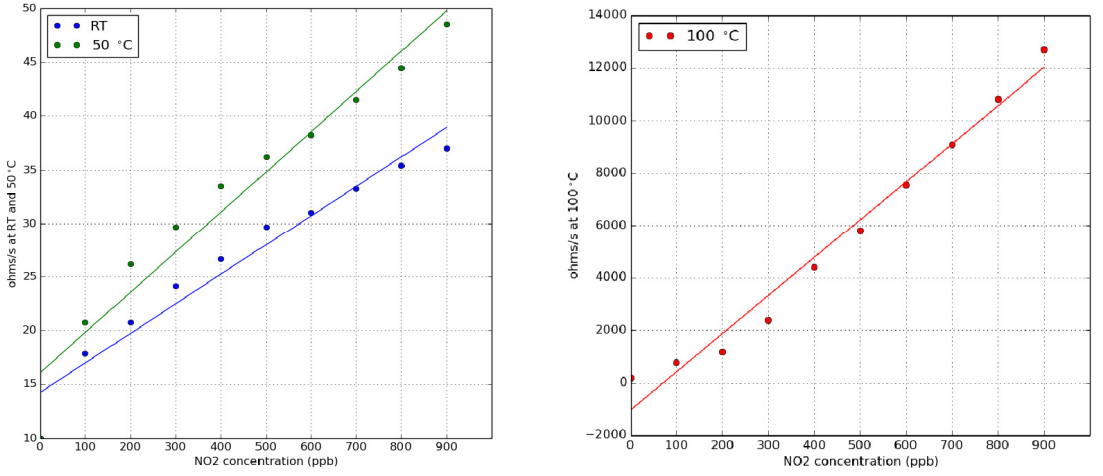

Fig. 4. Response in ohms/s when UV is Off at RT, 50ºC (a) and 100ºC (b), the speed of oxidation have different kinetics depending of temperature

Furthermore, the influence of working temperature on the change rate has been studied. We have tested the sensors using pulsed-UV light at room temperature (RT), 50 ºC and 100 ºC for a range from 100 ppb up to 900 ppb

of NO_2. As we can see in Figure 4, the change rate indeed depends on temperature, obtaining higher values at higher operating temperatures. Figure 4 shows the calibration curves obtained for sensor response. These curves show that there is a quite linear behavior of the response for the range of nitrogen dioxide concentrations measured and also that the sensitivity (i.e. slope of these calibration curves) increases with the operating temperature. A comparison of sensitivity to nitrogen dioxide and power consumption is shown in table 1. Power consumption includes the power supplied to the heating element and the power supplied to the UV diode.

Table 1. Comparative sensitivity

Activation Type	Sensitivity (ppb^{-1})	Power consumption (mW)
UV Pulsed at RT	0.027	41
UV Pulsed at 50 ºC	0.037	151
UV Pulsed at 100ºC	14.50	560

4. 4 Conclusions

5. The effects of combining mild heating with pulsed UV light irradiation of the sensor surface result in a clear enhancement in sensitivity combined to the possibility of making significant saving s in power consumption. This is achieved by exploiting the dynamics of sensor response under pulsed UV light, which convey important information for the quantitative analysis of nitrogen dioxide. Further work is underway to optimize the combined heating and UV pulsing operating mode of metal oxide gas sensors

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References

[1] F.E. Annanouch et al. (2015): Aerosol-Assisted CVD-Grown WO3 Nanoneedles Decorated with Copper Oxide Nanoparticles for the Selective and Humidity-Resilient Detection of H2S. ACS Appl. Mater. Interfaces, 7 (12), 6842.

[2] F.E. Annanouch et al. (2016): Aerosol-assisted CVD-grown PdO nanoparticle-decorated tungsten oxide nanoneedles extremely sensitive and selective to hydrogen. ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.6b00773.

[3] Y. Gui, S. Li, J. Xu, and C. Li, "Study on TiO 2 -doped ZnO thick film gassensors enhanced by UV light at room temperature," Microelectron. J., vol. 39, no. 9, pp. 1120–1125, 2008.

[4] L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, and C. Xie, "Visible-lightactivate mesoporous WO 3 sensors with enhanced formaldehyde-sensing property at room temperature," Sens. Actuators B, Chem., vol. 163, no. 1,
pp. 260–266, 2012.

[5] Q. Geng, Z. He, X. Chen, W. Dai, and X. Wang, "Gas sensing property of ZnO under visible light irradiation at room temperature," Sens. Actuators B, Chem., vol. 188, pp. 293–297, Nov. 2013.

[6] M.-H. Chen, C.-S. Lu, and R.-J. Wu, "Novel Pt/TiO 2 –WO 3 materials irradiated by visible light used in a photoreductive ozone sensor," J. Taiwan Inst. Chem. Eng., vol. 45, no. 3, pp. 1043–1048, 2014.

[7] M. P. Trawka , J. M. Smulko, L. Z. Hasse, C. -G. Granqvist , R. Ionescu, E. Llobet , F. E. Annanouch, and L. B. Kish, " UV-light-induced fluctuation enhanced sensing by WO3-based gas sensors" , IEEE S ensors Journal , Vol. 16, no. 13, July 1, 2016, 5152-5159 .

[8] SETI I nc. , UV diodes datas h eets , 2016, h tt p:// www.s - et.com / s p ec -s h eets /320 nm. p d f (accessed 28 . 06 . 2016)