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UV-Light Induced Fluctuation Enhanced Sensing of WO_3-based Gas Sensors

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***Abstract*—To improve efficiency of gas detection by WO_3-based gas sensors, UV irradiation combined with different working temperatures was used to stimulate a gas sensing layer to reach better sensitivity and selectivity of gas detection. Resistance fluctuations of WO_3 layer were studied as additional to DC resistance source of information for improving gas detection. The measurements were carried out in ambient atmosphere of synthetic air (SA), ethanol (C_2H_5OH), nitrogen dioxide (NO_2) or their mixtures. We conclude that UV irradiation can be easily applied to enhance gas sensing properties of WO_3 layer.**

***Index Terms*—sensors, gas detectors, nanotechnology, noise measurements, detection algorithms.**

I. Introduction

THE resistive semiconducting metal-oxide (MOX) gas sensors are currently one of the most investigated groups of gas sensors. They are attractive due to their facility in production and simplicity of their use in practice. The needs for quantitative detection of different gases are fundamental to industrial and environmental safety. The MOX gas sensors are promising for use in detection of low concentrations of different gases due to their low costs, compatibility with microfabrication technologies, and a variety of metal oxides with different gas sensing characteristics [1-4]. Unfortunately, their sensitivity and selectivity are still limited and this is the main force of looking for their improvements. Therefore reliable gas sensor systems having better sensitivity and selectivity are required. Among new and selective methods for the detection of different gases a noise spectroscopy (fluctuation enhanced sensing – FES) has been repeatedly proved as an efficient method in gas sensing area [5-8]. DC resistance of MOX sensor changes in ambient atmosphere of various gases according to their concentration because a sensing layer is reduced or oxidized by the introduced gas according to the alteration of charge carriers' mobility or/and concentration. Likewise, an exposure to different gases can also modify a power spectral density (PSD) of gas sensor's resistance fluctuations what can improve sensitivity and provide a more efficient (selective) gas detection [9, 10].

Recently, there have been reports of gas sensors based on ultra-violet (UV) activated MOX semiconductors [11-14]. Irradiating these sensors is a feasible alternative to activate chemical reactions at metal oxide surface instead of usually more energy consuming heating. Unfortunately, the UV light is used often only for cleansing the gas sensing layer instead of modifying gas sensing properties. In our experimental studies we apply UV irradiation combined with heating to stimulate the gas sensor and improve its sensitivity and selectivity by applying the FES method as well.

It is known that the spectrum of resistance noise is sensitive to gas sensor ambient atmosphere [5-8, 15]. The FES method exploits noise spectroscopy that characterizes resistance fluctuations resulting from interactions between porous gas sensing layer and gas molecules due to adsorption-desorption processes and in that way can improve sensitivity and selectivity of gas detection. The estimated PSD of resistance noise at low frequency range, having $1/f$-like spectrum, forms a spectral "signatures" originating from the chemical environment [5-8, 15-22]. It was proved that the FES has a great potential for improving gas detection and gas mixtures analysis, especially for nanoparticle sensors [7]. Thus, it would be interesting to consider how the FES method would improve gas sensing in the MOX sensors when activated by UV light. The preliminary results confirmed feasibility of the proposed method [23].

A. UV-light irradiation

The UV light can affect gas sensors through the following ways [24-26]:

- change dissociation rate of the adsorbed gases,
- generate charge carriers by increasing electron–hole pairs.

These effects should depend on intensity and wavelength of the applied UV light. The gas sensing layer scatters and absorbs the UV light and therefore determines penetration depth and intensity of the sensing layer conductivity changes. We can suppose that these phenomena should influence gas sensing even at room temperature and therefore should help to decrease sensor's energy consumption.

B. Noise Spectroscopy

In MOX gas sensors, the 1/*f*-like noise depends on ambient gas atmosphere and can be utilized for better gas detection. That noise type in metal oxides depends strongly on oxygen related quantities and replacement of oxygen atoms by other gas molecules [16]. Thus, low frequency noise spectra result from adsorption-desorption processes on the gas sensing layer and their further diffusion inside the sensing layer, as described by Wolkenstein's theory [17].

Generally, the gas sensing process is induced by two phenomena: physisorption and chemisorption [16]. Physisorption is a weak adsorption process, usually related to polarization and van der Waals forces between adsorbate and adsorbent, with the interaction energy smaller than 1 eV. Chemisorption is formed by stronger covalent forces involving partial electron transfer between adsorbent and adsorbate with the greater interaction energy (in the range of 1–10 eV).

According to the Wolkenstein's theory of adsorption, in the MOX gas sensors due to gas adsorption the fluctuations of free charge density give a Lorentzian component in the spectrum having parameters (corner frequency and flat level amplitude at low frequencies) that depend on the absorbed gas. It has been proved that adsorption–desorption noise in MOX gas sensors produces a Lorentzian contribution to the observed noise spectrum [17]. The final 1/*f*-like spectra of the MOX gas sensors in the low frequency range can be treated as a superposition of a large number of Lorentzians as in 1/*f*-like noise models for semiconductor materials. Thus, the sensor working temperature and UV light intensity should influence any disturbances from 1/*f* noise spectrum (crossover frequencies in low frequency range) which can be used to improve gas detection sensitivity and selectivity.

II. Experimental

A. WO_3-based gas sensing layer

Tungsten oxide (WO_3) is n-type semiconducting material with a band gap of about 2.6–2.8 eV. Gas sensors based on WO_3 nanostructures have attracted extensive attention because of their excellent sensitivity and selectivity in detecting a wide range of gases [26]. This is due to their large surface area and ability of improving their sensing properties by additives of rare metals, such as Pt or Au [27, 28]. Many techniques can be used to grow WO_3 nanowires doped with metal nanoparticles. A deposition method based on aerosol-assisted chemical vapor deposition (AACVD) was applied in our case [29-33]. That technique is versatile and relatively inexpensive to reach remarkable gas sensing properties. The synthesis of nanostructures, as well as the decoration with metal nanoparticles (NPs) and the integration in the structure of a device, can be realized in a single processing step. AuNP-decorated WO_3-nanowires (NWs) films were grown at 350ºC by AACVD directly on the electrode area of alumina gas sensor substrates using tungsten hexacarbonyl and hydrogen tetrachloroaurate as precursors [34]. Such nanosensors were used during a study of influence temperature and UV light on noise sensor properties increasing its sensitivity. Figure 1 depicts the AuNP-decorated WO_3-NWs gas sensor together with the UV LED diode employed for its irradiation. The average size of the AuNPs was 10 nm, while the WO_3-NWs were ~5 μm in length and 60–120 nm in width.

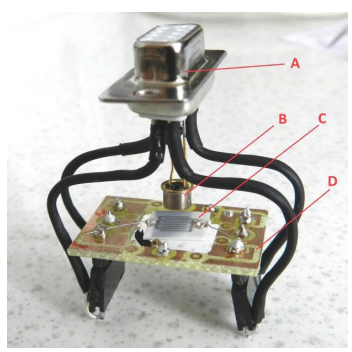

Fig. 1. AuNP-decorated WO_3-NWs gas sensor and a T5F UV LED diode; A – DSUB-9 junction (for connection with a low-noise preamplifier), B – UV LED diode, C – sensor (top side) with the heater (on bottom side), D – a mounting PCB plate.

B. Measurement System

Noise measurements at different temperatures and light intensities were performed using the system presented in Fig. 2. The low-frequency noise measurement setup comprised a low-noise preamplifier MAX4478 with the sensor in its feedback loop and driven by a constant current *I*. The sensor was placed into a gas chamber with a controlled gas flow. The data acquisition board and the bias unit was controlled by computer and the software prepared in LabVIEW environment. The frequency range of the measurement setup was from 0.1 Hz to a few kHz. The carefully shielded input circuit and preamplifier used a self-contained battery powered power supply as in other experiments recording noise time series [35-37]. Voltage fluctuations across the sensor were recorded by 24-bites A/D converters at sampling frequency 4 kHz. About 10^6 noise samples were recorded and further processed by the Matlab scripts to estimate the PSD function at limited level of random error [38].

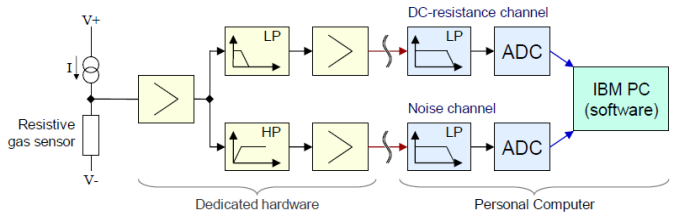

Fig. 2. Block diagram of the measurement system.

The gas chamber (Fig. 3) enabled to establish gas sensor ambient atmosphere comprising of two different calibrating gases diluted in synthetic air. The applied UV LED diode, type T5F36 (Fig. 4), and the heater were controlled by the dedicated software to determine physical conditions of the investigated gas sensing layer (operating temperature, UV-light intensity controlled by the diode current I_d). The diode was fixed to assure the same distance during all measurements (Fig. 2). After some probations we have established that the observed changes in gas sensing layer (DC resistance, noise intensity) induced by UV irradiation have saturated when the diode current exceeded a few mA. Therefore we have limited majority of the presented data to two currents only: $I_d = 0$ mA or $I_d = 6$ mA.

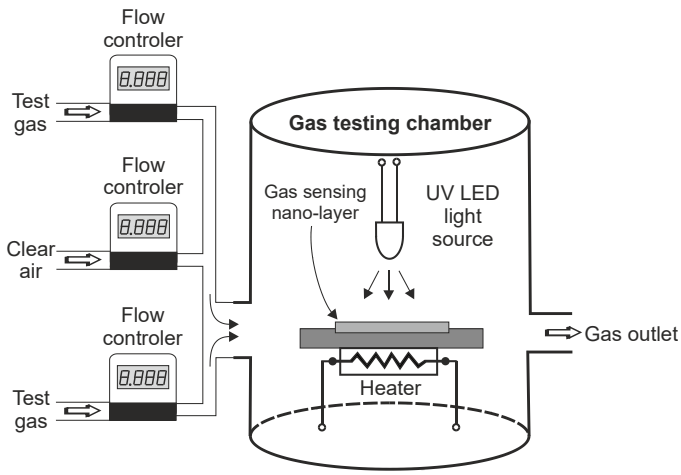

Fig. 3. Schematic diagram of the gas distribution system applied in the experimental measurement setup.

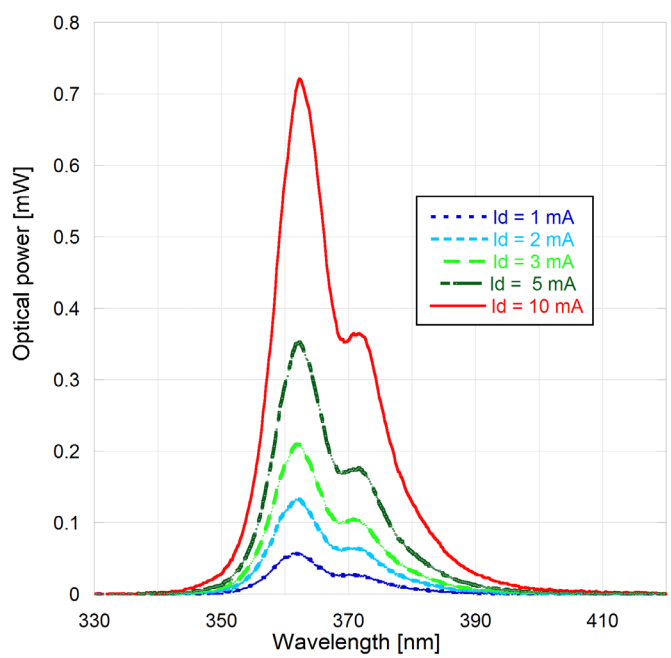

Fig. 4. Optical power spectrum emitted by the applied UV LED diode, type T5F36, when placed at the same distance to power meter as to the investigated gas sensing layer.

III. Results and Discussion

A detailed experimental studies were performed to determine influence of UV-light and working temperature changes on properties of WO_3-NWs gas sensing layer by considering DC resistance or low frequency noise intensity. The mixtures of two different and arbitrary selected gases were applied: ethanol (C_2H_5OH) and nitrogen dioxide (NO_2). The investigated gas sensor was sensitive to each of the considered gases but at various sensitivities. Thus, examining influence of additional factors on gas sensing should lead to potentially interesting results.

Changes of the sensor DC resistance R_S versus UV LED diode current I_d were measured at ambient atmosphere of the selected gases mixtures (Fig. 5). We can conclude that the effect of UV irradiation on DC resistance has saturated for the diode currents I_d above 5–6 mA. The relative change of DC resistance depended on the sensor ambient atmosphere but did not exceed 40% for the considered diode currents and gas mixtures. The more intense changes were observed at presence of NO_2 gas than for C_2H_5OH.

The observed saturation effect can be explained by absorption of the UV light limited to superficial part of gas sensing layer only. Stronger UV light is still limited to thin part of the irradiated layer and does not influence adsorption-desorption processes occurring in their deeper sections. The saturation effect confirms as well that the applied UV irradiation does not change significantly a temperature of the considered sensor. Otherwise we would expect continuous change of DC resistance at more intense UV light because its energy, and eventual heating of the gas sensing layer, should increase continuously by rising the current I_d.

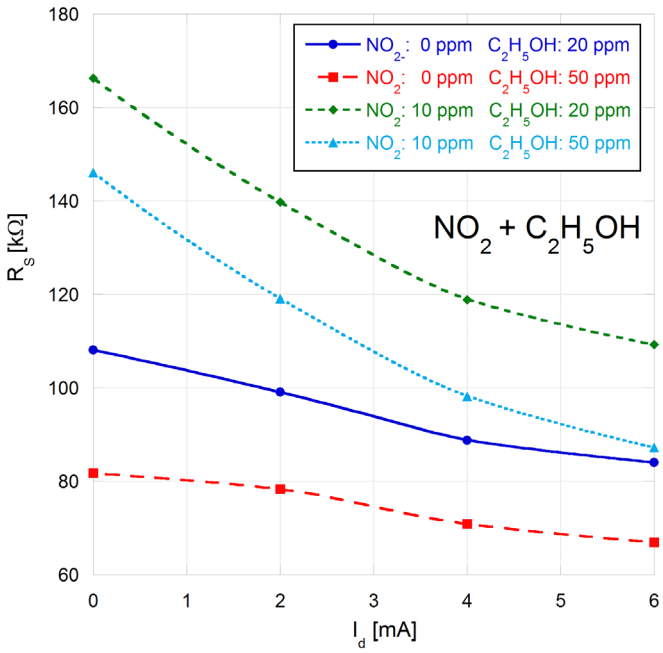

Fig. 5. DC resistance R_S of AuNP-decorated WO_3-NWs gas sensing film versus UV LED-diode DC current I_d at two different concentrations of NO_2 and C_2H_5OH mixtures at operating temperature $T = 200°C$.

The main part of the presented experimental studies focuses on the FES method which could be potentially more efficient for gas sensing than DC resistance only. Thus, voltage fluctuations across the sensor polarized by a constant current I (Fig. 2) were recorded as in other experiments exploring $1/f$ noise as source of information about the investigated objects [39, 40]. Voltage fluctuations are proportional to resistance fluctuations of the sensor and depend on its ambient atmosphere. Therefore, the power spectral density of voltage fluctuations $S_u(f)$ normalized to the squared DC voltage bias $U^2 = (R_S \cdot I)^2$ was estimated to present the quantity independent from the measurement setup. The product $S_u(f)/U^2$ was multiplied by frequency f to expose any deviations from $1/f$ noise spectrum.

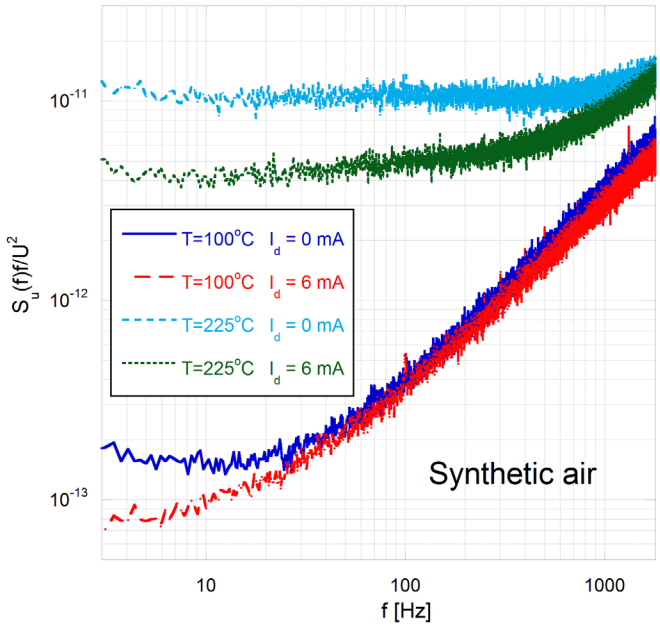

Fig. 6. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across WO_3-NWs sensor biased by the DC voltage $U = I \cdot R_S$ versus frequency f; noise samples were recorded with the UV LED diode at its DC currents I_d equal to 0 mA or 6 mA at the operating temperature of 100°C or 225°C with the sensor placed in dark gas chamber at ambient atmosphere of synthetic air.

The exemplary noise data confirm that operating temperature and UV light influences noise level (Fig. 6) but at different intensities. The 1/f-like noise component decreases by a factor of a few times when the UV-light was switched on. More visible difference in noise intensity, exceeding a factor of ten, can be obtained by changing its operating temperature, at least between the arbitrary selected values of 100°C and 225°C. The presented data can lead to a conclusion that both factors (UV light, temperature) induce changes in the observed low frequency noise and can be utilized to improve gas detection. The white noise predominates down to about 500 Hz when the sensor was heated to 100°C in ambient atmosphere of synthetic air. At higher temperatures 1/f noise can be observed at much lower frequencies only (e.g. at temperature $T = 225$°C the 1/f noise is visible below 10 Hz). Thus, it looks reasonable to apply UV light to modulate gas sensing properties when the sensor operating temperature is between these two mentioned temperatures to observe 1/f-like noise level varied by UV light.

More informative shape of power spectral densities was observed after introducing NO_2 gas and using sensor's operating temperature 200°C (Fig. 7). Following the spectrum shape from the upper limit of the measured frequency band the white noise predominates down to about 400 Hz at dark and even to almost 100 Hz when irradiated by UV light. Next, we can see a region of 1/f-like noise having various slopes.

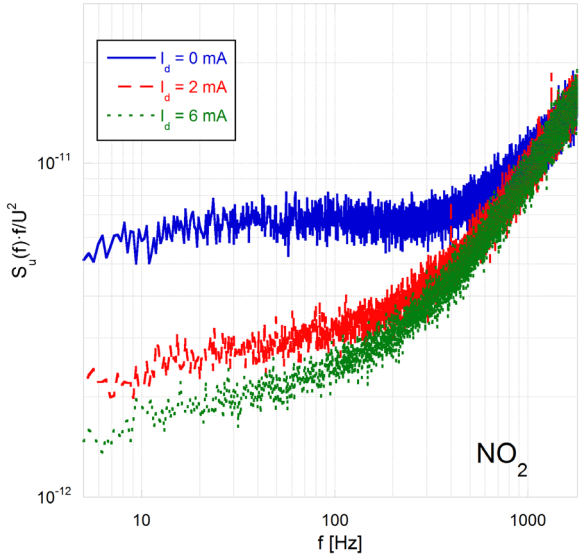

Fig. 7. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across WO_3-NWs sensor biased by the DC voltage $U = I \cdot R_S$ versus frequency f; noise was recorded at the sensor's operating temperature 200°C in an ambient atmosphere of 20 ppm NO_2; UV light irradiation was accomplished by a UV LED diode biased by DC currents I_d equal to 0 mA, 2 mA and 6 mA.

In Figure 8 some selected noise power spectral densities at temperature 175ºC and at UV LED diode irradiation of various intensities have been shown when the gas sensor was in ambient atmosphere of ethanol (C_2H_5OH). When the gas concentration has increased the observed noise level did not change so significantly as in the previously reported case of NO_2 gas (Fig. 7). Moreover, the 1/*f*-like noise preserved its slope in the frequency band when exceeded white noise component. When the UV light was turned on the slope of the observed 1/*f*-like noise has increased and additionally its level changed more intensively when the gas concentration increased. It means that presence of ethanol should be detected by analyzing noise and easily distinguished from presence of some other gases (e.g. NO_2).

To compare the changes of noise spectra in different gas concentrations, the relative changes of power spectral densities at selected low frequency ($f = 30$ Hz) were analyzed (Fig. 9). A drop of noise level at higher ethanol concentrations was more intense when the UV light was applied. It means that UV light could be used to increase sensitivity of ethanol detection at its low concentrations. At the same time noise level saturates at concentrations over 70 ppm when the UV light is applied. That saturation effect is shifted into higher ethanol concentrations when the UV light was turned off (Fig. 9). Thus we can claim that the FES method when applied with UV light should increase sensitivity of gas sensor and its potential applications for detecting wider range of gas concentrations.

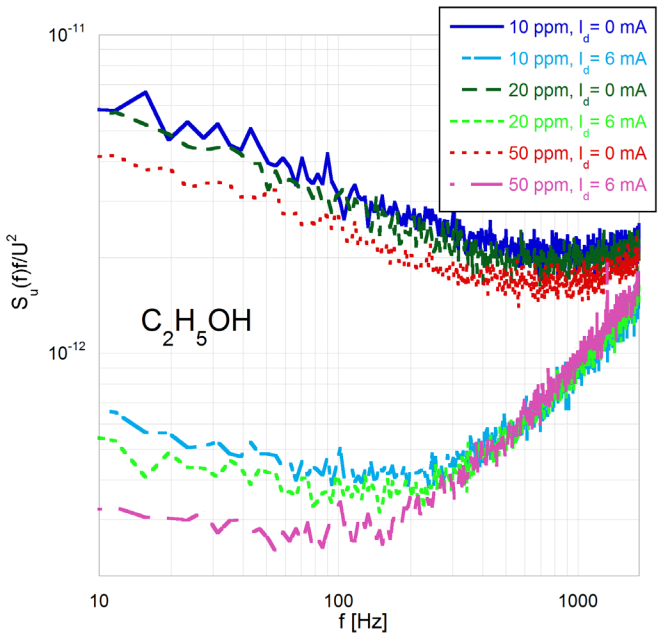

Fig. 8. Normalized product of frequency *f* and power spectral density $S_u(f)$ of voltage fluctuations across WO_3-NWs sensor biased by the DC voltage $U = I \cdot R_S$ versus frequency *f*; noise was recorded at the sensor's operating temperature 175°C in an ambient atmosphere of ethanol (C_2H_5OH) at its selected concentrations (10 ppm, 20 ppm, 50 ppm); the UV LED diode was biased by DC currents $I_d = 0$ mA or $I_d = 6$ mA.

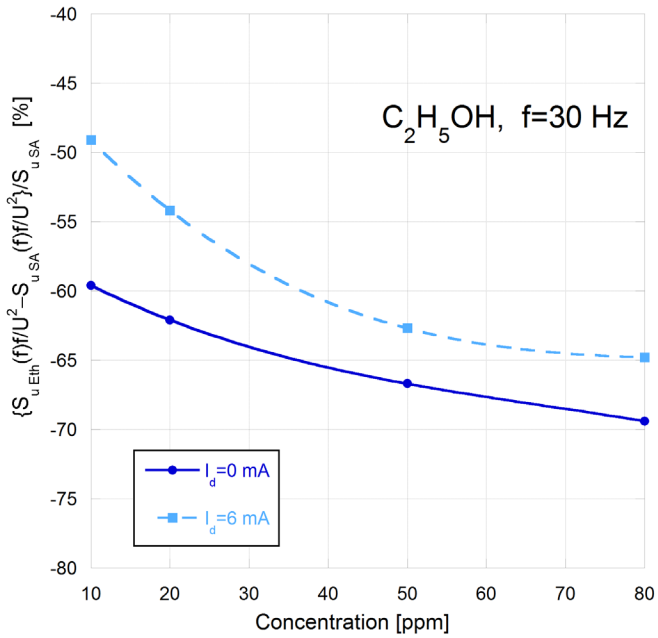

Fig. 9. Relative (referred to the noise spectrum $S_{u\,SA}(f)$ at ambient atmosphere of SA) changes of power spectral density product $S_{u\,Eth}(f)\cdot f/U^2$ at frequency $f = 30$ Hz at ambient atmosphere of ethanol (C_2H_5OH) at different concentrations; the gas sensor operating temperature was 175ºC, the UV LED diode was biased by the DC currents $I_d = 0$ mA or $I_d = 6$ mA.

When we compare relative changes of noise power spectral densities (Fig. 9) with the sensor DC resistance changes (Fig. 10) at the same conditions we can conclude that UV light irradiation effects noise and DC resistance in different ways. At higher concentrations of ethanol the change of DC resistance induced by UV light only is stronger than noise intensity which is more affected by UV light at lower ethanol concentrations. These results suggest that a combination of both quantities would increase gas sensing properties of the investigated WO_3-NWs at various gas concentrations and for different gases. Thus, we can claim that UV light should be used not only for gas sensors cleansing but for improving their gas detection sensitivity and selectivity.

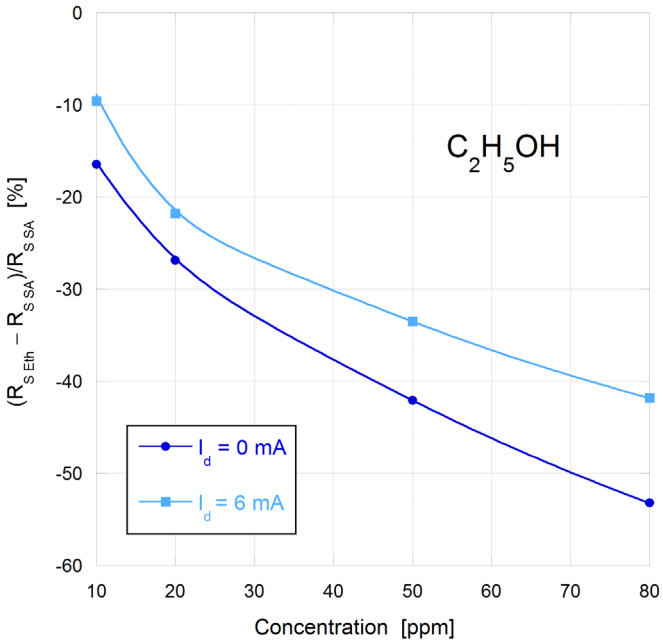

Fig. 10. Relative change of the gas sensor DC resistance observed in ambient atmosphere of ethanol $R_{S\,Eth}$ at its different concentrations and in synthetic air only ($R_{S\,SA}$); the gas sensor operating temperature was 175ºC; the UV LED diode was biased by DC currents $I_d = 0$ mA or $I_d = 6$ mA.

IV. Conclusion

It was found that the WO_3-NWs gas sensor response to selected gases is directly related to the photochemical reaction rate on its surface. The sensor DC resistance is reduced when the UV light irradiates the investigated gas sensing layer. We have also observed a decrease of 1/*f*-like noise intensity induced by the UV light. These effects are more intense when the operating temperature is reduced below 225°C. It means that the proposed modulation can decrease energy required for gas detection. Moreover, the different response of DC resistance and 1/*f*-like noise intensity and its slope should improve accuracy of gas concentration estimation at much wider range.

We can expect that application of non-linear detection algorithms should help to determine composition of gas mixtures using a single gas sensor modulated by UV light and temperature [41, 42]. We suppose that photons having different energy can further advance results of modulation effects by UV light. Illuminating the MOX gas sensor with the radiation comparable with the band gap of the metal oxide can permit lowering of the normally high operating temperature even to room temperature. This permits its use in areas where it would not be possible to work at higher temperatures, thereby significantly enhancing its applicability for different environmental and biological applications.

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References

1. R. Lalauze, *Physico-chemistry of solid-gas interfaces: concepts and methodology for gas sensor development*, Wiley, 2008.
2. G. Korotcenkov, "Gas response control through structural and chemical modifications of metal oxide films: State of the art and approaches," *Sensors and Actuators B*, vol. 107, no. 1, 2005, pp. 209–232.
3. J. Smulko, J. Ederth, L. Yingfeng, L.B. Kish, M. Kennedy, F. Krus, "Gas-sensing by thermoelectric voltage fluctuations in SnO_2 nanoparticle films," *Sensors and Actuators B*, vol. 106, no. 2, 2005, pp. 708–712.
4. P. Heszler, R. Ionescu, E. Llobet, L. F. Reyes, J. Smulko, et al., "On the selectivity of nanostructured semiconductor gas sensors," *Physica Status Solidi B*, vol. 244, no. 11, 2007, pp. 4331–4335.
5. L.B. Kish, R. Vajtai, C.G. Granqvist, "Extracting information from noise spectra of chemical sensors: single sensor electronic noses and tongues," *Sensors and Actuators B*, vol. 71, no. 1, 2000, pp. 55–59.
6. L.B. Kish, H. Chang, M.D. King, C. Kwan, J.O. Jensen, G. Schmera, J. Smulko, Z. Gingl, C. Granqvist, "Fluctuation-enhanced sensing for biological agent detection and identification," *IEEE Trans. Nanotechnology*, vol. 10, no. 10, 2011, pp. 1238–1242.
7. J. Ederth, J. Smulko, L. Kish, P. Heszler, C. Granqvist, "Comparison of classical and fluctuation-enhanced gas sensing with Pd_xWO_3 nanoparticle films," *Sensors and Actuators B*, vol. 113, no. 1, 2005, pp. 310–315.
8. M. Kotarski, J. Smulko, A. Czyżewski, S. Melkonyan, "Fluctuation-enhanced scent sensing using a single gas sensor," *Sensors and Actuators B*, vol. 157, no. 1, 2011, pp. 85–91.
9. L.B. Kish, R. Vajtai, C.G. Granqvist, "Extracting information from noise spectra of chemical sensors: single sensor electronic noses and tongues," *Sensors and Actuators B*, vol. 71, no. 1, 2000, pp. 55–59.
10. L. Hasse, M. Kotarski, J. Smulko, J. Majzner, V. Sedlakova, P. Sedlak, J. Sikula, "Comparison of effectiveness of gas sensing by low frequency fluctuations in resistance and microbalance quartz gas sensors," in *Proc. 21st Int. Conf. ICNF*, Toronto, Canada, 2011.
11. Y. Gui, S. Li, J. Xu, C. Li, "Study on TiO_2-doped ZnO thick film gas sensors enhanced by UV light at room temperature," *Microelectronics Journal*, vol. 39, no. 9, 2008, pp. 1120–1125.
12. L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, C. Xie, "Visible-light activate mesoporous WO_3 sensors with enhanced formaldehyde-sensing property at room temperature," *Sensors and Actuators B*, vol. 163, no. 1, 2012, pp. 260– 266.
13. Q. Geng, Z. He, X. Chen, W. Dai, X. Wang, "Gas sensing property of ZnO under visible light irradiation at room temperature," *Sensors and Actuators B*, vol. 188, 2013, pp. 293–297.
14. M.H. Chen, C.S. Lu, R.J. Wu, "Novel Pt/TiO_2–WO_3 materials irradiated by visible light used in a photoreductive ozone sensor," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 3, 2014, pp. 1043–1048.
15. M. Kotarski, J. Smulko, "Hazardous gases detection by fluctuation-enhanced gas sensing," *Fluctuations and Noise Letters*, vol. 9 no. 4, 2010, pp. 359–371.
16. S. Gomri, J.L. Seguin, J. Guein, K. Aguir, "A mobility and free carriers density fluctuations based model of adsorption–desorption noise in gas sensor," *J. Phys. D: Appl. Phys.*, vol. 41 no. 6, 2008, pp. 065501–065512.
17. T. Contraret, T. Florido, J.L. Seguin, K. Aguir, "A physics-based noise model for metallic oxide gas sensors characterization," *Procedia Engineering*, vol. 25, 2011, pp. 375–378.
18. J. Smulko, M. Kotarski, Z. Topalian, G.A. Niklasson, C.G. Granqvist, L.B. Kish, "Fluctuation-enhanced gas sensing in practice," in *Proc. 21st Int. Conf. ICNF*, Toronto, Canada, 2011.
19. H. Chang, L.B. Kish, M.D. King, C. Kwan, "Binary fingerprints at fluctuation-enhanced sensing," *Sensors*, vol. 10, no. 1, 2010, pp. 361–373.
20. Ł. Lentka, J. Smulko, R. Ionescu, C.G. Granqvist, L.B. Kish, determination of gas mixture components using fluctuation enhanced sensing and the LS-SVM regression algorithm, *Metrol. Meas. Syst.*, vol. 22, no. 3, 2015, pp. 341–350.
21. R. Macku, J., Smulko, P. Koktavy, M. Trawka, P. Sedlak, „Analytical fluctuation enhanced sensing by resistive gas sensors," Sensors and Actuators

B, vol. 213, 2015, pp. 390–396.
22. J. Smulko, M. Trawka, "Gas selectivity enhancement by sampling-and-hold method in resistive gas sensors," *Sensors and Actuators B*, vol. 219, 2015, pp. 17–21.
23. Z. Topalian, J. Smulko, G. Niklasson, C. Granqvist, "Resistance noise in TiO_2-based thin film gas sensors under ultraviolet irradiation," *Journal of Physics: Conf. Series*, vol. 76, 2007, pp. 1–5.
24. S. Mishra, C. Ghanshyam, N. Ram, R. P. Bajpai, R. K. Bedi, "Detection mechanism of metal oxide gas sensor under UV radiation," Sensors and Actuators B, vol. 97, no. 2, 2004, pp. 387–390.
25. H.U. Lee, S.C. Lee, S. Choi, B. Son, H. Kim, S.M. Lee, H.J. Kim, J. Lee, "Influence of visible-light irradiation on physicochemical and photocatalytic properties of nitrogen-doped three-dimensional (3D) titanium dioxide," *Journal of Hazardous Materials*, vol. 258, 2013, pp. 10–18.
26. Y.D. Wang, Z.X. Chen, Y.F. Li, X.H. Wu, "Electrical and gas sensing properties of WO_3 semiconductor material," *Solid-State Electronics*, vol. 45, no. 5, 2001, pp. 639–644.
27. J. Zeng, M. Hu, W. Wang, H. Chen, Y. Qin, "NO_2-sensing properties of porous WO_3 gas sensor based on anodized sputtered tungsten thin film," *Sensors and Actuators B*, vol. 161, no. 1, 2012, pp. 447– 452.
28. Z. Hua, M. Yuasa, T. Kida, N. Yamazoe, K. Shimanoe, "High sensitive gas sensor based on Pd-loaded WO_3 nanolamellae," *Thin Solid Films*, vol. 548, 2013, pp. 677–682.
29. F. Annanouch, S. Vallejos, C. Blackman, X. Correig, E. Llobet, "CO and H_2 sensing with CVD-grown tungsten oxide nanoneedles decorated with Au, Pt or Cu nanoparticles," *Procedia Engineering*, vol. 47, 2012, pp. 904–907.
30. R. Ionescu, A. Hoel, C.G. Granqvist, E. Llobet, P. Heszler, "Low-level detection of ethanol and H_2S with temperature-modulated WO_3 nanoparticle gas sensors," *Sensors and Actuators B*, vol. 104, no. 1, 2005, pp. 132–139.
31. S. Vallejos, P. Umek, T. Stoycheva, F. Annanouch, E. Llobet, X. Correig, P. De Marco, C. Bittencourt, C. Blackman, "Single-step deposition of Au- and Pt-nanoparticle-functionalized tungsten oxide nanoneedles synthesized via aerosol-assisted CVD, and used for fabrication of selective gas microsensor arrays," *Advanced Functional Materials*, vol. 23, no. 10, 2013, pp. 1313–1322.
32. W. Zeng, C. Dong, B. Miao, H. Zhang, S. Xu, X. Ding, S. Hussain, "Preparation, characterization and gas sensing properties of sub-micron porous WO_3 spheres," *Materials Letters*, vol. 117, 2014, pp. 41–44.
33. A. Hoel, L. K. J. Vandamme, L. B. Kish, E. Olsson, "Current and voltage noise in WO_3 nanoparticle films," *J. Applied Physics*, vol. 91, no. 8, 2002, pp. 5221–5226.
34. M. Trawka, J. Smulko, L. Hasse, C.G. Granqvist, R. Ionescu, F.E. Annanouch, E. Llobet, L.B. Kish, "Fluctuation enhanced gas sensing using UV irradiated Au-nanoparticle-decorated WO_3-nanowire films," in *Proc. 8th Intern. Conf. on Sensing Technology*, Sep. 2-4, 2014, Liverpool, UK, pp. 282–286.
35. M. Kotarski, J. Smulko, "Noise measurement setups for fluctuations enhanced sensing," *Metrol. Meas. Syst.*, vol. 16 no. 3, 2009, pp. 457–464.
36. J. Smulko, K. Darowicki, P. Wysocki, „Digital measurement system for electrochemical noise," *Polish Journal of Chemistry*, vol. 72, no. 7, 1998, pp. 1237–1241.
37. J. Smulko, "Methods of electrochemical noise analysis for investigation of corrosion processes," *Fluctuation and Noise Letters*, vol. 6, no. 2, 2006, pp. R1–R9.
38. J.S. Bendat, A.G. Piersol, *Random data: analysis and measurement procedures*, Wiley, 2011.
39. C.G. Granqvist, S. Green, E.K. Jonson, R. Marsal, G.A. Niklasson, A. Roos and L.B. Kish, "Electrochromic foil-based devices: Optical transmittance and modulation range, effect of ultraviolet irradiation, and quality assessment by 1/f current noise," *Thin Solid Films*, vol. 516, no. 17, 2008, pp. 5921–5926.
40. M. Kiwilszo, J. Smulko, „Pitting corrosion characterization by electrochemical noise measurements on asymmetric electrodes," *Journal of Solid State Electrochemistry*, vol. 13, no. 11, 2009, pp. 1681–1686.
41. K. Dunst, G. Jasinski, P. Jasinski, "Potentiometric oxygen sensor with solid state reference electrode," *Metrol. Meas. Syst.*, vol. 21, no. 2, 2014, pp. 205–216.
42. O. Gualdrón, J. Brezmes, E. Llobet, A. Amari, X. Vilanova, B. Bouchikhi, X. Correig, "Variable selection for support vector machine based multisensor systems," *Sensors and Actuators B*, vol. 122, no. 2, 2007, pp. 259–268.