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

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The rebuttal answer to the reviewer' comments

The text marked in red color was introduced into the revised manuscript

Reviewer: 1

Recommendation: Publish Unaltered

Answer: We would like to thank you again for your time and efforts during reading and suggesting amendments improving our manuscript.

Reviewer: 2

Recommendation: Publish in Minor, Required Changes (as noted in the Comments section. This rating may not be assigned for Sensors Letters.)

Answer: We would like to thank you again for your detailed reading and efforts to improve the manuscript to much better state.

Comments:

Thank you for making the changes from 1st draft. There are just a few items that need modification

1)page 4 "When the product of power spectral density Su(f) multiplied by frequency f is presented (Fig. 7, Fig. 8) " ##should also include Figure 6 in this list
Answer: Thank you very much for suggesting that change. We have included Figure 6 into the text: (p. 4, left column, l. 4 and l. 5): "(Fig. 6, Fig. 7, Fig. 8)".

2)page 4 "several dozen of Hz" "some hundred" ##please use scientifically appropriate language that is more specific (ie 'near 100 Hz" or 'between 80 and 120 Hz")
Answer: Thank you again for suggesting the more precise sentence. We have change that sentence (p. 4, left column, l. 14) according to your suggestion: "Johnson noise dominates down to near 10 Hz when the sensor was heated to 100 °C in SA."

3)""It was found that the response of WO3 NW gas sensors to selected gases is directly related to the photochemical reaction rate on their surface, as presented in literature [43]." ##It is especially important that the conclusions summarize the findings of the paper. This sentence still states that the paper finds the response is related to the photochemical reaction rate, and the add-on only indicates that the findings are consistent with reference 43. Thus this sentence is still inaccurate. I suggest adding 'estimated' as in "is directly related to an estimated photochemical reaction rate on the surface, based on reference [43]"
Answer: Thank you again for the suggested clarification. We have introduced your suggestion into the first sentence of the section "IV. Conclusions" (p. 5): "It was found that the response of WO_3-NW gas sensors to selected gases is directly related to an estimated photochemical reaction rate on the surface, based on reference [43]."

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

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***Abstract*—WO_3-based gas sensors were investigated under UV-light irradiation and at different working temperatures with the object of achieving superior sensitivity and selectivity. Resistance fluctuations in the WO_3 layer were studied together with DC resistance measurements. The data were taken in synthetic air, ethanol, nitrogen dioxide, and mixtures of these gases. We conclude that UV irradiation can easily be applied to enhance the gas sensing properties of a WO_3 layer.**

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

I. Introduction

Resistive semiconducting metal-oxide (MOX) gas sensors are currently subject to many investigations. These sensors are attractive owing to their facile production and simple use, and they are able to meet the demands for quantitative detection of various gases in industrial settings and for environmental safety. The MOX gas sensors are promising for detection of low concentrations of different gases as a consequence their low cost, compatibility with microfabrication technologies, and the availability of a variety of metal oxides with different gas sensing characteristics [1-4]. Unfortunately, the sensitivity and selectivity of the MOX sensors are still limited, and this is the main driving force for seeking improvements. Among the new and selective methods for gas detection, noise spectroscopy (fluctuation enhanced sensing, FES) has repeatedly proved itself as an efficient method [5-8]. The DC resistance of MOX sensors changes in ambient atmospheres of various gases according to their concentration, because a sensing layer is reduced or oxidized by the gas so that its charge carrier mobility or/and concentration are altered. Likewise, an exposure to different gases can modify a power spectral density (PSD) of the gas sensor's resistance fluctuations, which can improve sensitivity and provide more efficient (selective) gas detection [9, 10].

Recently, there have been reports of gas sensors utilizing ultra-violet (UV) activated MOX semiconductors [11-14], 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 sensing layer, rather than to modify its 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 in measurements using the FES method.

It is known that the spectrum of resistance noise is sensitive to the gas sensor's ambient atmosphere [5-8, 15]. The FES method exploits noise spectroscopy, ensuing from resistance fluctuations due to interactions between a porous gas sensing layer and gas molecules involved in adsorption–desorption processes, and is able to provide high sensitivity and selectivity of gas detection. The PSD of resistance noise recorded at low frequencies has an $1/f$-like spectrum which forms a spectral "signature" characteristic of the chemical environment [5-8, 15-22], and it has been proved that FES has a great potential for gas detection and gas mixtures analysis, especially for nanoparticle sensors [7]. Thus it is interesting to investigate how the FES method is able to improve gas sensing in MOX sensors when activated by UV light. Preliminary results of the present work confirm the feasibility of the proposed method [23].

A. UV-light irradiation

UV light can affect gas sensors by [24-26]

- changing the dissociation rate of the adsorbed gases, and
- generating charge carriers by increasing the number of electron–hole pairs.

These effects depend on the intensity and wavelength of the UV light. The gas sensing layer scatters and absorbs the radiation and therefore determines its penetration depth and consequently the magnitude of the conductivity changes in the gas sensing layer. We can suppose that these phenomena affect gas sensing even at room temperature, and therefore they should be important for decreasing sensor's energy consumption.

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B. *Noise Spectroscopy*

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

Generally, the gas sensing process is caused 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 interaction energy smaller than 1 eV. Chemisorption, on the other hand, is formed by stronger covalent forces involving electron transfer between adsorbent and adsorbate with greater interaction energies, typically in the range of 1–10 eV.

According to Wolkenstein's theory, gas adsorption on the MOX sensor leads to fluctuations of the free-charge density with a Lorentzian spectral component having parameters that depend on the absorbed gas, and it has been shown experimentally that adsorption–desorption noise in MOX gas sensors produces a Lorentzian contribution to the observed noise spectrum [17]. The final low-frequency 1/*f*-like spectra of the MOX gas sensors can be treated as a superposition of a large number of Lorentzians, which is similar to the case of 1/*f*-like noise models for semiconductor materials [16]. Thus the sensor's working temperature *and* the intensity of the UV light irradiation should influence any deviation from a 1/*f* noise spectrum, and these effects can be used to improve gas detection sensitivity and selectivity.

II. Experimental

A. *WO_3-based gas sensing layer*

Tungsten oxide (WO_3) is an *n*-type semiconducting material with a band gap of 2.6–2.8 eV. Gas sensors based on WO_3 nanostructures have attracted extensive attention because of their excellent sensitivity and selectivity for detecting a wide range of gases [26]. These favorable properties are due to the large surface area and the ability of improving the 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, and a deposition method based on aerosol-assisted chemical vapor deposition (AACVD) was applied in our case [29-33]. That technique is versatile, relatively inexpensive and able to reach remarkable gas sensing properties. The synthesis of nanostructures, as well as their decoration with metal nanoparticles (NPs) and device integration, can be realized in a single processing step.

Films of AuNP-decorated WO_3 nanowires (NWs) were grown at 350 ºC by AACVD directly on the electrode area of alumina gas sensor substrates by use of tungsten hexacarbonyl and hydrogen tetrachloroaurate as precursors [34]. Such nanosensors were used to study the influence of temperature and UV light on noise-based sensor properties in order to increase the sensitivity. Figure 1 depicts the AuNP-decorated WO_3-NW 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.

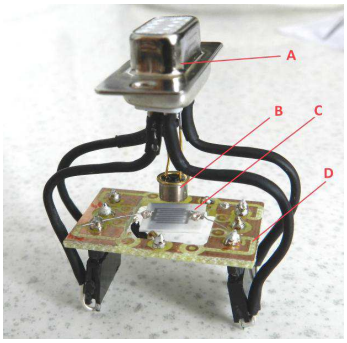

Fig. 1. AuNP-decorated WO_3-NW gas sensor and a UV LED diode: (A) DSUB-9 contact for connection to a low-noise preamplifier, (B) UV LED diode, (C) sensor (top) with heater (bottom), (D) PCB mounting plate.

B. *Measurement System*

Noise measurements at different temperatures and UV light intensities were performed using the system presented in Fig. 2. The low-frequency noise measurement set-up comprised a low-noise preamplifier (MAX4478) with the sensor in its feed-back loop and driven by a constant current I = 12.5 μA. The DC voltage across the sensor for this bias current was no lower than 1.11 V. The sensor was placed in a gas chamber with a controlled gas flow. The data acquisition board and the bias unit were controlled by a computer, and the software was prepared in a LabVIEW environment. The frequency range of the measurement set-up was from 0.1 Hz to a few kHz. The carefully shielded input circuit and preamplifier used a self-contained battery-powered 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 a sampling frequency of 4 kHz. About 10^6 noise samples were recorded and further processed by Matlab scripts to estimate the PSD function at a limited level of random error [38].

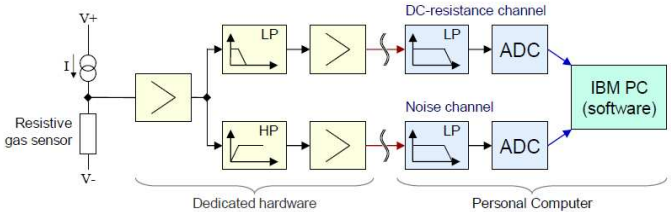

Fig. 2. Block diagram of the measurement system.

The gas chamber (Fig. 3) enabled us to establish a gas sensor ambient atmosphere comprised of two different gases diluted in synthetic air (SA). The UV LED, type T5F36 (Fig. 4), and the heater were controlled by a dedicated software to determine physical conditions of the investigated gas sensing layer (operating temperature and UV-light intensity controlled by a diode current I_d). The diode was fixed

so as to assure the same distance to the sensor during all measurements (Fig. 2). We established that the observed changes in the gas sensing layer (DC resistance and noise intensity) induced by UV irradiation were saturated when the diode current exceeded a few mA, and therefore we limited the majority of the presented data to two currents only: $I_d = 0$ and $I_d = 6$ mA.

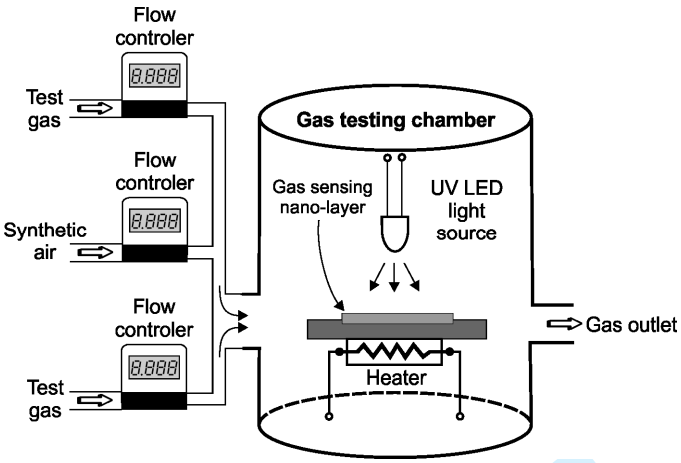

Fig. 3. Schematic diagram of the gas distribution system in the experimental set-up.

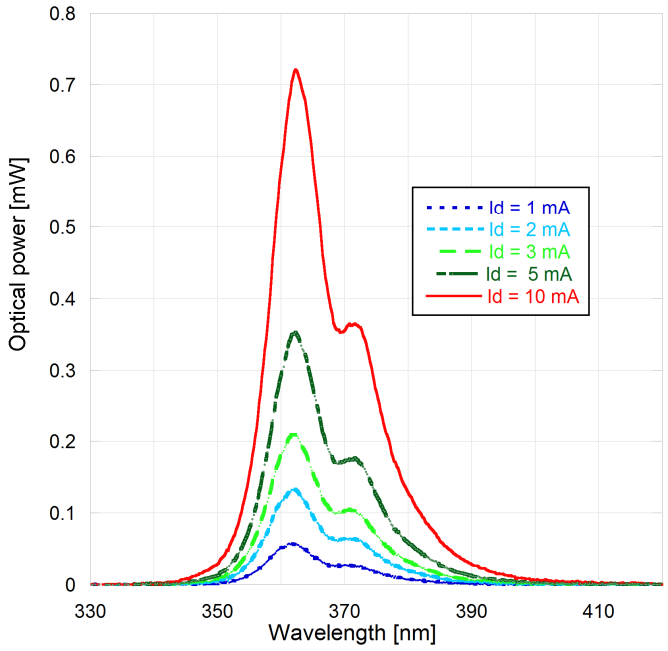

Fig. 4. Optical power spectrum emitted by the UV LED, with the diode current set to the shown values I_d, when placed at the same distance to the power meter as to the gas sensing layer.

III. Results and Discussion

Detailed experimental studies were performed to determine the influence of UV light and working temperature on the properties of the WO_3-NW gas sensing layer, specifically with regard to DC resistance or low-frequency noise intensity. Mixtures of two different and arbitrary selected gases, ethanol (C_2H_5OH) and nitrogen dioxide (NO_2), were used. The gas sensor was sensitive to both of the gases, but with different sensitivities. This difference is advantageous for assessing the influence of additive factors on gas sensing.

Changes of the sensor's DC resistance R_S versus I_d were measured at normal pressure for the selected gas mixtures (Fig. 5). We can conclude that the effect of UV irradiation on R_S has saturated when I_d is above 5–6 mA. The relative change of DC resistance depends on the sensor's ambient atmosphere but does not exceed 40% for the studied diode currents and gas mixtures. The changes were larger for NO_2 gas than for C_2H_5OH.

The observed saturation effect can be explained by absorption of the UV light in the surface part of gas sensing layer only. Stronger UV light is still confined to a thin part of the irradiated layer and does not influence the adsorption–desorption processes occurring deeper into the sensor. The saturation effect also confirms that the UV irradiation does not significantly change the sensor's temperature of the sensor, as monitored during the measurements.

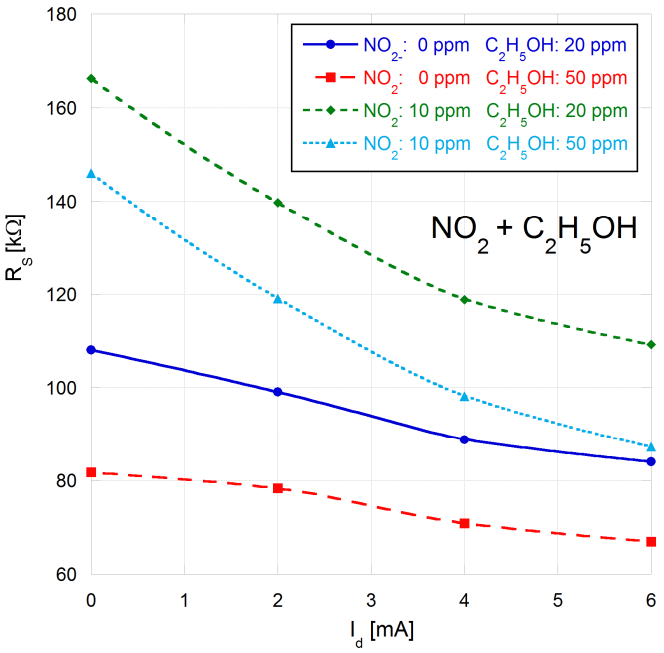

Fig. 5. DC resistance R_S of a AuNP-decorated WO_3-NW gas sensing film versus UV LED-diode DC current I_d at the shows concentrations of NO_2 and C_2H_5OH mixtures at an operating temperature of 200 °C.

Most of the experimental studies were focused on the FES method, which potentially could be more efficient for gas sensing than DC resistance measurements alone. Thus voltage fluctuations across the sensor, polarized by a constant current I (Fig. 2), were recorded as in other experiments of $1/f$ noise as a source for information about the studied sample [39, 40]. Voltage fluctuations are proportional to resistance fluctuations in the sensor and depend on its ambient atmosphere. Therefore the PSD of voltage fluctuations $S_u(f)$ was normalized by the squared DC voltage bias $U^2 = (R_S \cdot I)^2$ in order to present data that are independent of the measurement set-up. The product $S_u(f)/U^2$ was multiplied by frequency f to clearly show deviations from a $1/f$ noise spectrum.

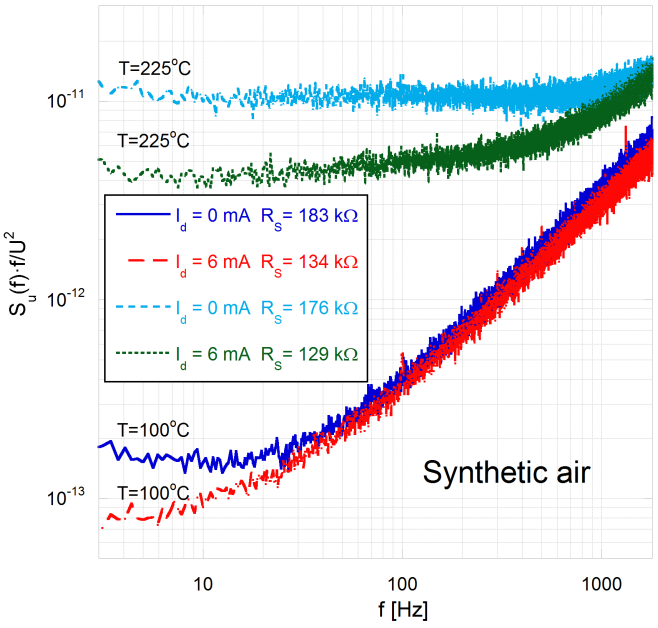

Fig. 6. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across a WO_3-NW sensor, biased by the DC voltage $U = I \cdot R_S$, versus frequency. Noise was recorded with the UV LED at the shown values of DC current I_d and operating temperature T with the sensor placed in a dark gas chamber in an ambient atmosphere of synthetic air.

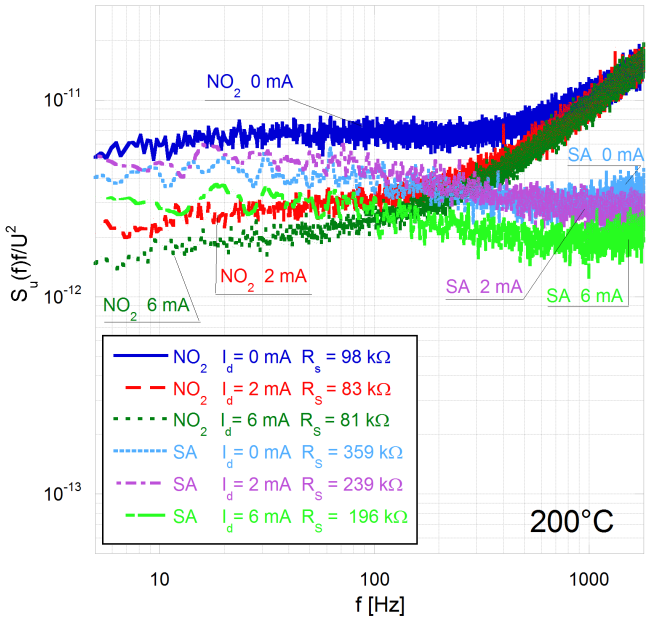

Fig. 7. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across a WO_3-NW sensor, biased by the DC voltage $U = I \cdot R_S$, versus frequency. Noise was recorded at an operating temperature of 200 °C in an ambient atmosphere with 20 ppm of NO_2 and in synthetic air (SA). The UV LED was biased at the shown values of DC current I_d.

Figure 6 reports an example of noise spectra and confirms that operating temperature and UV illumination influences the data to different extents. When the product of power spectral density $S_u(f)$ multiplied by frequency f is presented (Fig. 6, Fig. 7, Fig. 8) the $1/f$ noise appears as a horizontal line and any disturbances from the $1/f$ noise are more visible. The $1/f$-like noise component decreased by a factor of a few times when the UV-light was switched on. An even stronger difference in noise intensity, exceeding a factor of ten, could be obtained by changing the sensor's operating temperature between 100 and 225 °C. The presented data lead to the conclusion that both UV light and operating temperature induce changes in the observed low frequency noise and can be utilized to improve gas detection. Johnson noise dominates down to near 10 Hz when the sensor was heated to 100 °C in SA. The $1/f$-like noise can be observed only at much lower frequencies, specifically below 10 Hz. At higher temperatures, $1/f$-like noise starts to dominate at higher frequencies (for 225 °C the domination starts since some hundred Hz). Thus UV light can be applied to modulate the gas sensing properties and alter the $1/f$-like noise level when the sensor's operating temperature is between 100 and 225 °C.

Even more informative shapes of the PSDs were observed after introducing NO_2 gas and setting the sensor's operating temperature to 200 °C, as shown in Fig. 7. Following the spectrum shape from the upper limit of the measured frequency band, Johnson noise dominates down to about 400 Hz under dark conditions and down to almost 100 Hz when the sensor was irradiated by UV light. At lower frequencies, one can see a region of $1/f$-like noise characterized by different slopes.

Figure 8 shows noise PSDs at a temperature of 175 ºC and for various intensities of UV LED irradiation when the gas sensor was in an ambient atmosphere of C_2H_5OH. An increase of the gas concentration changed the noise level in a similar way as in the previously reported case of NO_2 gas (Fig. 7). Moreover, the $1/f^{\alpha}$ noise preserved its slope α until it was surpassed by the white-noise component. When the UV light was turned on, the slope α of low frequency noise was decreased and its level changed to a larger degree when the gas concentration was increased. Additionally, its slope has changed when intensity of the UV light increased by increasing the UV diode current I_d (Fig. 7). This means that the presence of ethanol could be detected by analyzing noise and easily distinguished from presence of some other gases (*e.g.*, NO_2) using various detection algorithms.

To compare differences in noise spectra for different gas concentrations, relative changes of PSDs were analyzed at a low frequency of 30 Hz (Fig. 9). The drop of the noise level upon increasing ethanol concentration was more pronounced when the UV light was applied, which means that UV light can be used to increase the sensitivity of ethanol detection at low concentrations. Furthermore, the noise level saturates at concentrations above 70 ppm when the UV light is on. This saturation effect shifted towards higher ethanol concentrations when the UV light was turned off. Thus it is evident that the UV light combined with the FES method is able to increase a gas sensor's sensitivity and its potential for detecting a wider range of gas concentrations.

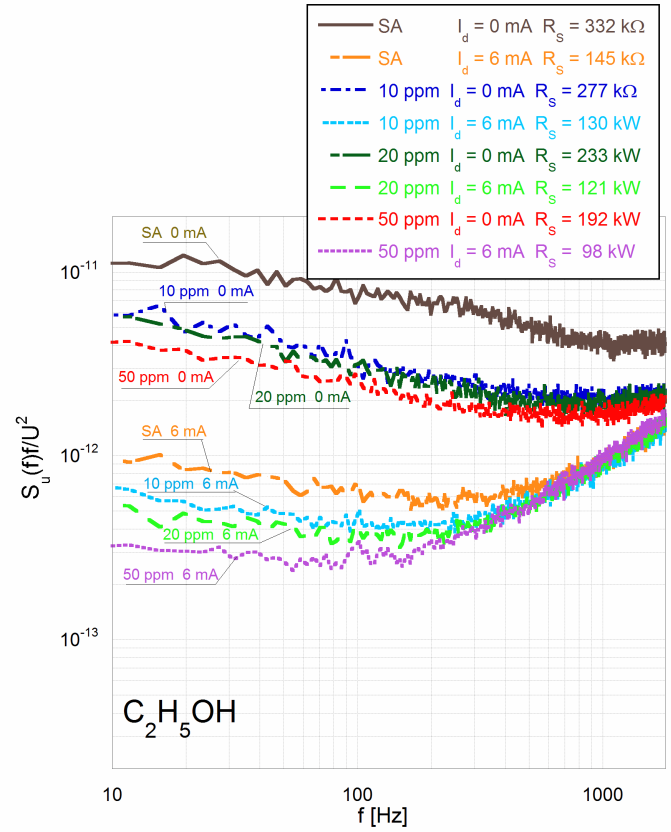

Fig. 8. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across a WO_3-NW sensor, biased by the DC voltage $U = I \cdot R_S$, versus frequency. Noise was recorded at an operating temperature of 175 °C in an ambient atmosphere of ethanol with the shown concentrations or SA only. The UV LED was biased at the shown values of DC current I_d.

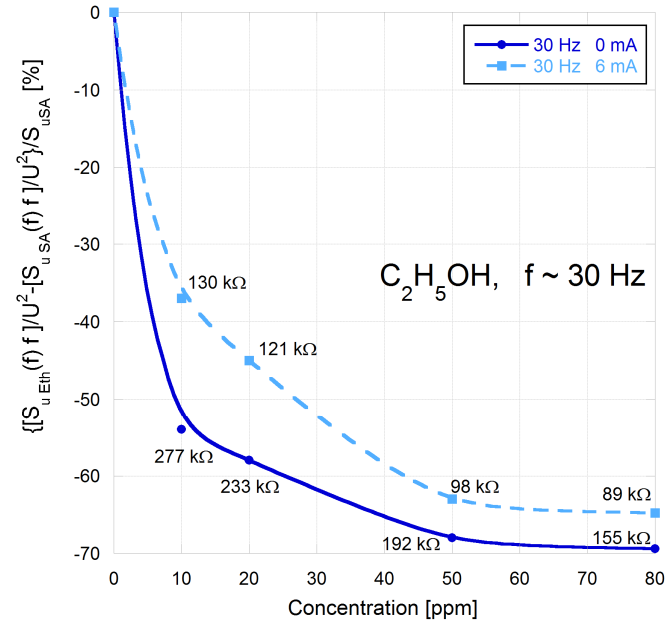

Fig. 9. Power spectral density product $S_{u\,Eth}(f) \cdot f/U^2$ averaged over five frequency bins around the frequency f = 30 Hz for an ambient atmosphere of ethanol (Eth), relative to corresponding data for synthetic air (SA), at different concentrations. The gas sensor operated at 175 ºC, and the UV LED was biased at the shown DC currents I_d.

When comparing the changes of noise PSDs (Fig. 9) with the changes in the sensor's DC resistance (Fig. 10) for the same conditions, we can conclude that UV irradiation influences noise and DC resistance in different ways. Moreover, noise measurements should improve detection level of ethanol when compared with the DC resistance measurements only. We can claim that the limit for fluctuation enhanced gas sensing method should be rather below 1 ppm of ethanol. At high concentrations of ethanol, the change of DC resistance induced by UV light only is stronger than for the noise intensity, which is more affected by UV light at low ethanol concentrations. These results suggest that a combination of data on noise and DC resistance could increase the gas sensing properties of the investigated WO_3-NW samples at various gas concentrations and for different gases. Thus we find that UV light can be used not only for cleaning of gas sensors but for improving their gas detection sensitivity and selectivity.

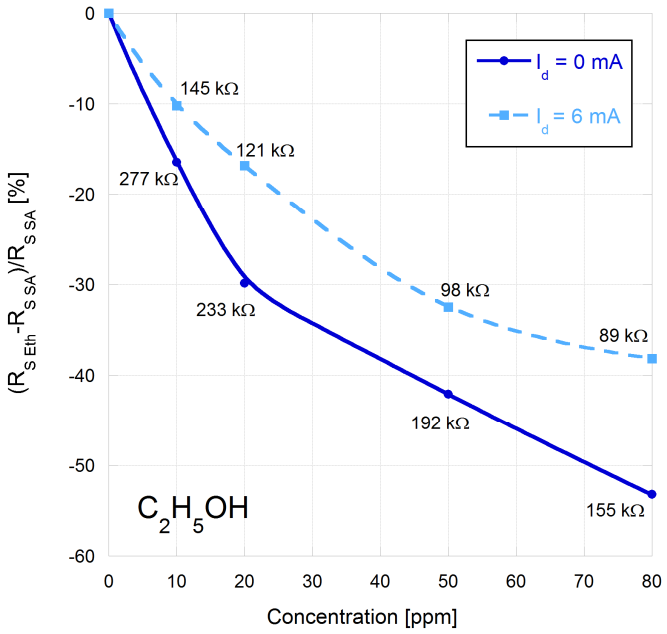

Fig. 10. DC resistance R_S for a gas sensor in an ambient atmosphere of ethanol (Eth), relative to its resistance in synthetic air (SA), at different concentrations. The gas sensor operated at 175 ºC, and the UV LED was biased at the shown DC currents I_d.

IV. Conclusion

It was found that the response of WO_3-NW gas sensors to selected gases is directly related to an estimated photochemical reaction rate on the surface, based on reference [43]. That conclusion was confirmed by the estimated attenuation length of 145 nm for the applied UV light (362 nm) and using the data for WO_3 layer from the reference [44]. The sensor's DC resistance is reduced upon UV irradiation. We also observed a decrease of the 1/*f*-like noise intensity induced by UV light. Additionally, its slope has changed when intensity of the UV light increased by increasing the UV diode current Id (Fig. 7). These effects are more pronounced when the operating temperature is lowered and lies at a value below 225 °C. Hence the proposed sensing technique can decrease the energy required for gas detection. In our experimental

studies, when the prototype and suboptimal heater was applied, a change of the operating temperature between 175°C and 225°C required additional power of about 1.4 W. The applied UV diode required only 27 mW (6 mA x 4.5 V) and resulted in more significant change of noise level when compared with the change induced by the mentioned temperatures. Moreover, the different responses of DC resistance and 1/*f*-like noise intensity to changes in gas concentration can be used to improve the selectivity of investigated gases detection within a wide range of their concentration.

We expect that non-linear detection algorithms can help to determine compositions of gas mixtures by the use of a single gas sensor modulated by UV light and temperature [41, 42], and we suppose that photons with different energies can further advance the possibilities for efficient gas detection in the presence of UV light. Illuminating the MOX gas sensor with radiation comparable with the band gap of the metal oxide can allow a lowering of the normally high operating temperature and permit sensors to be used in areas where high temperatures are not permissible, thereby enhancing their applicability for different environmental and biological applications.

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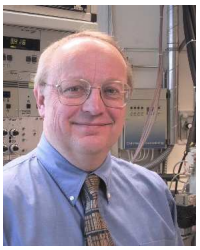

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