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Article

A Novel Type Room Temperature Surface Photovoltage Gas Sensor Device

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Abstract: In this paper a novel type of a highly sensitive gas sensor device based on the surface photovoltage effect is described. The developed surface photovoltage gas sensor is based on a reverse Kelvin probe approach. As the active gas sensing electrode the porous ZnO nanostructured thin films are used deposited by the direct current (DC) reactive magnetron sputtering method exhibiting the nanocoral surface morphology combined with an evident surface nonstoichiometry related to the unintentional surface carbon and water vapor contaminations. Among others, the demonstrated SPV gas sensor device exhibits a high sensitivity of 1 ppm to NO_2 with a signal to noise ratio of about 50 and a fast response time of several seconds under the room temperature conditions.

Keywords: room temperature gas sensor, surface photovoltage effect, porous ZnO nanostructured thin films

1. Introduction

Despite more than 50 years of development, the resistive type gas sensors systems based on metal oxide (MOX) materials still exhibit some critical, fundamental limitations [1-4], which can be divided into two groups.

The first one concerns the analytically useful characteristics limited to good sensitivity (usually at the level of single ppm, strongly depending on the gas) with a rather poor selectivity (strongly dependent on humidity, that can be improved by noble catalytic metals), as well as poor dynamic parameters such as a long response time (tens of seconds) combined with a rather very long recovery time (single minutes). The latter is especially relevant when compared to the responsiveness of animal and human olfaction [5,6].

The second group concerns mainly the high temperature working conditions, usually in the range of 200÷400°C causing high power consumption in the devices, combined with their limited reversibility (stability), adversely affecting their costs of fabrication and possible commercialization [7,8].

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In the recent years some innovative ideas appeared in the literature how to overcome these limitations including the unsolved technical and technological problems.

One such concerns applying various dimensionalities of the gas sensing materials. Nanoscale MOX materials and fabrication technologies have allowed the fabrication of novel type sensing architectures, what additionally helped to broaden the fundamental understanding of their sensing mechanism [8-13]. However, despite more than one decade of studies the useful MOX characteristics including sensitivity (only about 1 order better with respect to 3D thin films or even 2D nanolayers) and selectivity combined with the dynamic parameters such as response/recovery times (only slightly shorter with respect to 3D thin films/ 2D nanolayers) are still below the common expectations [12,13].

A second way concerns the application of selected metal oxides for specific gases based on their better specific response in terms of the above mentioned analytical characteristics. It should be underlined that up to now tin dioxide, SnO_2, is the most popular gas sensor material (~ 40% of papers, 60% of commercial gas sensors). However, in the last few years zinc oxide, ZnO, appeared as second common gas sensor material (~20% papers). This is due to the fact that its electron mobility is at the level of ~10^2 [$cm^2/V{\cdot}s$] similar to SnO_2, while the electron conductivity is at the level of 10^3 [$1/\Omega{\cdot}cm$], what is one order higher than SnO_2 [12-15].

A third way concerns using of novel type sensing transduction principles or innovative transducers using flexible sensors with smart textiles, as well as new sensing architectures including Schottky-contact nanosensor, FET chemical sensors, surface ionization sensors and magnetic gas sensors as recently reviewed by Comini [16].

However, within these ideas the influence of the work function variation and related effects on gas sensing have been ignored. Perhaps it was related to the fact that these effects are based essentially on the variation of contact potential difference (CPD) using mainly Kelvin vibrating capacitor, what was already commonly used as the gas sensors transduction since many years [17,18]. Moreover, it is also well known, that this method exhibits a rather poor sensitivity because of a low signal to noise (S/N) ratio, and that this method was mainly applied for studies of porous semiconductor materials [19-21]. This is probably the reason why up to now only an incomprehensibly weak attention was given to the use in gas sensors of the effect of work function variation of gas sensing materials (including MOX) after external optical excitation in the so called surface photovoltage effect [22].

In general, the surface photovoltage (SPV) is defined as a change of the surface potential barrier upon illumination, which is related to a photon induced charge generation and redistribution within the Space Charge Region (SCR) of the semiconductor. The surface potential variations may be measured with the commonly known Kelvin probe technique after external illumination. What is crucial, the SPV effect mainly depends on the incident photon energy with respect to the band-gap of the semiconductor under investigation and the light intensity [22].

Even sub-band gap photons can modify the charge at the semiconductor surfaces by exciting the trapped carriers at a well defined energy, i.e. when using the photons of energy $h\nu = E_C - E_A$ *or* $h\nu = E_A - E_V$, where E_C and E_V are the energy of bottom of conductive band and the top of valence band at the surface, respectively, whereas the E_A is the energy level of traps induced by adsorbed gas species, the specific electron transitions from a surface state to the conduction band (or from the valence band to the surface states) can be observed. In both cases the variation of band bending at

the semiconductor surfaces is observed, corresponding to the variation of surface potential, what can finally be measured as the variation of work function.

These two specific effects are the base of the so-called Surface Photovoltage Spectroscopy (SPS) method [22] commonly used for many years to detect electronic states in the band gap originating from semiconductor surfaces commonly used for control of quality of semiconductor surfaces in aspect for their potential application in solid state microelectronics [23]. What is crucial, when using the photons of energy $h\nu$ higher than band gap E_{bg} ($h\nu > E_{bg}$) this effect of variation of band bending (surface potential and subsequent work function) at the semiconductor surfaces is evidently stronger [22].

It should be pointed out that, according to the available literature, recently there were only limited attempts of using the photovoltaic effects in gas detection. However, in these studies performed mainly by the group of Yamada [24-26], mistakenly called as surface photovoltage effect, only the photocurrent was measured across the MIS structures based on mesoporous silica films exposed to limited toxic gases like NO and NO_2. Moreover, what is also puzzling, there has been only limited interest of using the true SPV effect even in the basic studies of gas interaction with MOX materials [27,28], without any reference to use this effect potentially for the toxic gas detection. This is why in our group, having significant experience in the use of very high sensitivity SPV effect for the control of quality of semiconductor surfaces in contact with different atmospheres [23], the systematic studies focusing on the application of SPV for the control of interaction of toxic gases with selected MOX gas sensor materials have been lately carrying out. As the result of these studies, a novel type of a room temperature gas sensor device utilizing a sensing mechanism based on the measurements of the SPV effect on porous nanostructures ZnO electrodes was developed.

In this paper the details of above mentioned SPV gas sensor system based on porous ZnO nanostructured thin films are described. However, at the beginning, the fundamental physicochemical properties of porous ZnO nanostructured thin films were analyzed with a special emphasis on the local surface chemistry and morphology, absolutely indispensable for the interpretation of basic analytical sensing parameters of the elaborated novel type SPV gas sensor system.

2. Materials and Methods

As was mentioned above, in the constructed gas sensor device porous ZnO nanostructured thin films were used as the sensor material. They were deposited onto Si (100) substrates by direct current (DC) reactive magnetron sputtering of a 99.95%-pure Zn target in an 6N argon–oxygen sputtering mixture at oxygen concentration of 33% under total working pressures of 1.5 mTorr, using the Surrey NanoSystems 1000C reactor. After deposition, the ZnO films were annealed *ex situ* in a 6N-pure oxygen flow at 800 °C using a Mattson SHS-100 rapid thermal processing (RTP) furnace. Other technological details combined with the results of fundamental characterization of their bulk chemistry and morphology by chosen experimental methods performed at the Institute of Electron Technology, Warsaw, Poland, have been already described elsewhere [29,30].

Having in mind our recent experiences in studies of tin dioxide SnO_2 thin films nanostructures as the commonly used oxide gas sensor material [31], the local surface chemistry of these porous ZnO nanostructured thin films was controlled by X-ray Photoelectron Spectroscopy (XPS) method at the Institute of Electronics, Silesian University of Technology, Gliwice, Poland. The experimental details of XPS studies have recently been described in our recent paper [32].

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The elaborated surface photovoltage (SPV) gas sensor system contains of 3 main parts, as shown **in Figure 1**.

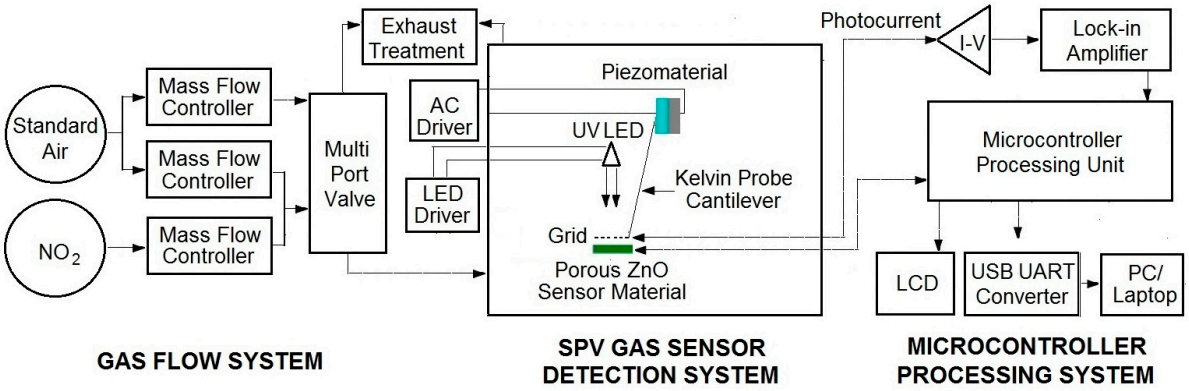

Figure 1. Simplified block-scheme of elaborated surface photovoltage (SPV) gas sensor system (device).

Apart from the typical gas flow system containing selected gases, mass flow controllers with multiport valve, it contains the SPV gas sensor detection system combined with microcontroller processing system for data processing and acquisition.

The elaborated SPV gas detection system is based on the reverse Kelvin probe flat type vibrating capacitor system. The capacitor subsystem consists of the porous ZnO nanostructured thin films as a flat gas sensor material playing the role of the active electrode, combined with the reference flat Cu metallic grid-type electrode on specific vibrating cantilever after piezoelectric driving using AC voltage generator.

The alternating SPV signal is measured as the variation of work function of the gas sensor material (with respect to the vibrating reference Cu electrode) as the result of its surface band bending variation after UV illumination by a UV5-400-30 type LED diode (Bivar Company). It should be pointed out that the alternating SPV signal can also be measured using the static reference Cu electrode combined with UV LED light modulated by respective driver. However, the latest approach does not allow the phenomena recognition that is responsible for the surface potential change. In other words, at the complex gas sensor system, the potential barrier is a sum of a fixed charge potential that may arise from the adsorbed species, strict surface region gas molecule reorganization, and carrier generation and redistribution in the SCR region.

For the measuring and acquisition of the SPV signal response in selected gases the microcontroller processing system is used containing the data processing control unit working with, among others, the I/V photocurrent converter (amplifier), the respective DAC and ADC converters, and finally the zero self-compensating lock-in amplifier for the reverse Kelvin probe flat vibrating capacitor system. Moreover, microcontroller processing system is equipped with USB to UART converter for laptop connection, enabling the use of our SPV gas sensor system as a mobile device.

In our test experiments of the elaborated SPV gas sensor system (device) a mixture of pure nitrogen dioxide NO_2 in standard synthetic air was used at different concentrations.

3. Results and Discussion

As was mentioned above in our SPV gas sensor system the porous ZnO nanostructured thin films deposited onto Si (100) substrate was used as the gas sensing material for which the bulk

chemistry and morphology have been characterized by chosen experimental techniques [29], as shortly summarized below.

Using the Rutherford Backscattering Spectroscopy (RBS) it was shown that the obtained ZnO layers were almost stoichiometric with the oxygen to zinc atomic ratio close to 1. In turn, using the Scanning Electron Microscopy (SEM) it was observed from the cross-sectional images, that the obtained ZnO layers exhibit nanocoral morphologies as shown in [29] Their polycrystalline character was also confirmed by X-ray Diffraction (XRD) showing powder diffraction patterns, also described in [29]. However, since from our experience with SnO_2 nanostructures we know that they contain a significant surface nonstoichiometry related to undesired strong surface carbon and water vapor contaminations, the additional XPS studies of the local surface chemistry our porous ZnO nanostructured thin films have additionally been performed. Such information is absolutely indispensable when trying to understand the gas sensing mechanism since the sensor effect appears just on the surface of the gas sensing materials at the depth related to Debye length [12,13], which is quite similar to the information depth of XPS method. The obtained XPS results are shortly described and interpreted below.

3.1. Local surface chemistry of the porous ZnO nanostructured thin films

At the beginning the XPS survey spectrum for the porous ZnO nanostructured thin films used in our SPV gas sensor device has been recorded shown in **Figure 2** in two various binding energy ranges.

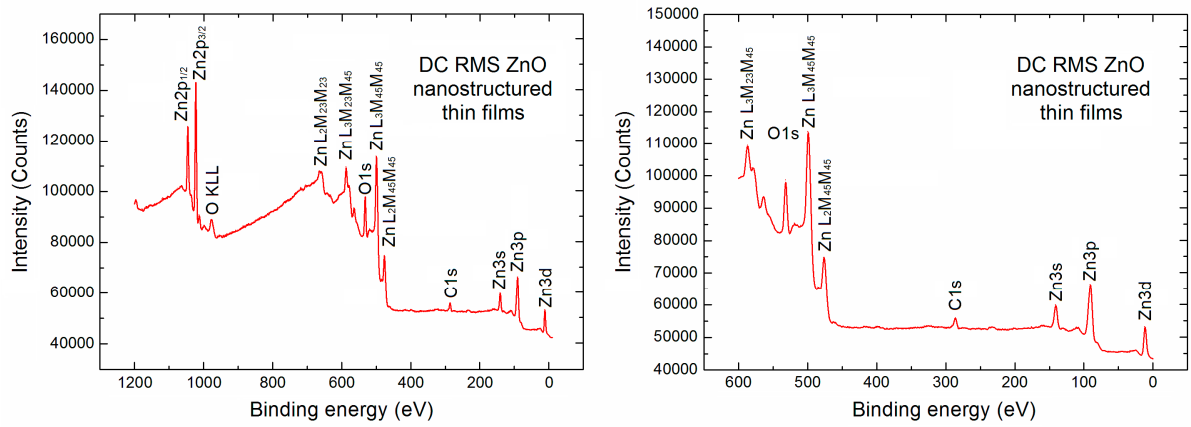

Figure 2. XPS survey spectra (full and in limited 600 eV BE range) of the ZnO nanostructured thin films used in our SPV gas sensor.

On the left side a typical full XPS survey spectrum in the binding energy (BE) range (1200 eV) is visible, what confirms that apart from the Auger electron lines (can be usually skipped) the contribution from the basic elements of ZnO derived from the respected XPS core level Zn2p, O1s, Zn3s, Zn3p and Zn3d lines is observed. Moreover, what is crucial in our studies, an evident undesired contribution of the C1s XPS lines at BE ~ 286.0 eV is observed, what confirms that the strong undesired C contamination exists at the surface of porous ZnO nanostructured thin films used in our SPV gas sensor device.

Commonly, basing on the relative intensity (height) of Zn2p, O1s and C1s core level lines and the well known analytical formula [33-35] and the respective atomic sensitivity factors related to the height of the above mentioned Zn2p, O1s and C1s peaks, the relative concentration of the selected elements can be calculated. However, because of the undesired high background in our observed XPS full survey spectrum of 1200 eV binding energy (BE) range with the additional useless Auger electron emission lines, the relative concentration of main elements at the surface of porous ZnO nanostructured thin films has also been estimated on the base of survey spectra in the limited binding energy range (600 eV) (right side in Fig.2).

Our calculation showed that our porous ZnO nanostructured thin films were rather far from the surface stoichiometry. The relative [O]/[Zn] and [C]/[Zn] concentration reached the values 0.63 and 0.31, respectively. It means that this is in an evident contrary to the information obtained by using the RBS method, where the oxygen to zinc atomic ratio was close to 1. This is probably related to the different information depth of both methods because for the RBS method it is at the level of hundreds of nm, whereas for XPS it corresponds only to the subsurface region of depth at the level of ~ 3 nm [33-35].

The different information depth was probably a reason that an evident C contamination was observed by XPS in our studies for our porous ZnO nanostructured thin films (with relative C]/[Zn] concentration of ~ 0.31), what was impossible by using the RBS method.

This is why at the next step of our analysis we have focused on the local surface chemistry of our porous ZnO nanostructured thin films, with a special emphasis on the specific surface bondings.

Our analysis was based on the deconvolution procedure of O1s and C1s spectral lines using the Casa XPS SPECS software. The obtained results are described below.

Figure 3 presents the XPS O1s and C1s lines after deconvolution using Gauss fitting ((left and right column, respectively) for the porous ZnO nanostructured thin films.

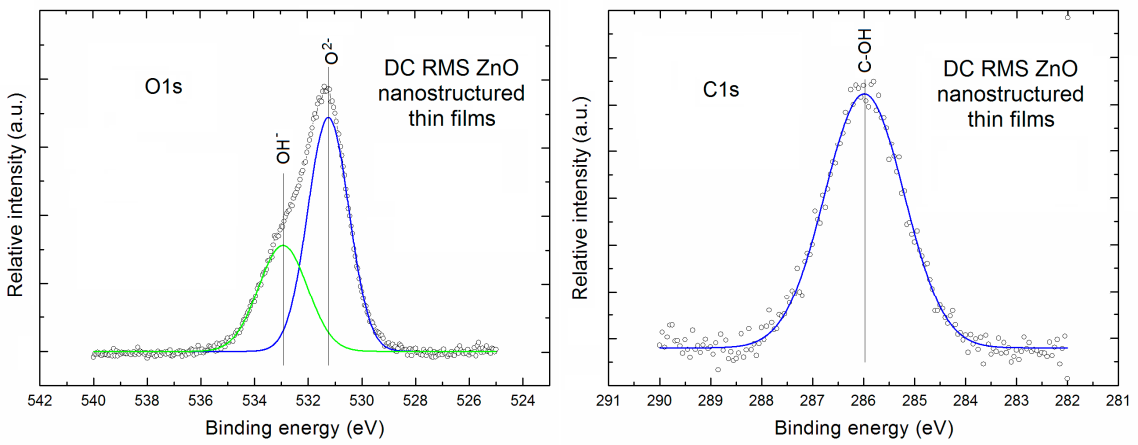

Figure 3. The XPS O1s and C1s lines after deconvolution using Gauss fitting procedure for the porous ZnO nanostructured thin films.

It is clearly visible, that the XPS O1s line of our porous ZnO nanostructured thin films is evidently asymmetric. After Gauss deconvolution (with very high line fitting (RMS ~ 0.998)) it consists of two evident components. A first one is located at the binding energy of ~ 531.2 eV and can be attributed to the O^{2-} ions in ZnO lattice of our porous ZnO nanostructured thin films, whereas a second one at binding energy ~ 532.9 eV can be attributed to the oxygen atoms in OH^- groups at the

surface of our porous ZnO nanostructured thin films. The similar two above mentioned components of the O1s XPS line was recently observed, among other, by Gazia et [36] for the spongelike nanostructured ZnO films deposited from the sputtered nanostructured zinc films. In addition, on the base of deconvoluted XPS O1s line the relative area of specific components in to O^{2-} ions with respect to the surface OH^{-} groups was determined as equal to 1.85, what means that even at the surface there is domination of O^{2-} ions related to ZnO crystalline lattice.

In turn, the XPS C1s line of our porous ZnO nanostructured thin films is practically symmetric. After its Gauss deconvolution (with high line fitting (RMS ~ 0.98)) it contains only one component always being observed at the binding energy of ~ 286 eV, what can be attributed to the C-OH surface bondings, commonly observed at the surface of various metal oxides, what is easy available in the NIST X-ray Photoelectron Spectroscopy Database [37].

Taking all above into account, what is crucial, it should be underlined, that in our experiments the existence of undesired water vapor combined with carbon contaminations at the surface of our porous ZnO nanostructured thin films having the nanocrystalline, columnar structures of cross section in the range of several nm [29], cannot be ignored when their sensing properties are analyzed. This is crucial because this information, probably well undesired and commonly ignored in the available literature, will be additionally commented in the next chapter, where the gas sensor characteristics of our novel type gas sensor system (device) will be analyzed.

3.2. Gas sensing characteristics in NO_2 atmosphere

As was mentioned above the porous ZnO nanostructured thin films were used as the static electrode in the gas sensor system (device) using the surface photovoltage effect. As was mentioned above, the gas detection effect is based on the variation of ZnO surface charge and subsequent surface potential due to the interaction of toxic NO_2 gas with our gas sensor material.

Already the primary experiments proved our expectations that our novel type SPV gas sensor system is working at room temperature. However, to reach the constant primary surface potential and subsequent constant starting value of SPV signal allowing the repeatable working conditions of our system the standard dry synthetic air was flowing via the system for several hours. It was related to the fact that only in such conditions there is a real chance for the removing of undesired water vapor molecules physically adsorbed at the surface of our gas sensor materials being previously in the natural air (usually wet) atmosphere.

Only after that we have focused on the registration of variation of SPV signal with variation of the concentration of active gas NO_2 in the standard dry synthetic air. In this experiments we have focused on two aspects.

On the base of registration of the relative variation of SPV signal as a function of NO_2 concentration the detection threshold of our SPV gas sensor system (related to its sensitivity) was determined, combined with the analysis of their dynamic characteristics like response time and respected recovery time at specific NO_2 concentrations.

Our experiments showed that the elaborated novel type SPV gas sensor system allows the detection of NO_2 gas up to 1 ppm, at the signal to noise (S/N) ratio at the level ~ 50. The obtained data for the lowest, selected NO_2 gas concentration in the main range of 1÷5 ppm were taken down in the form of diagram shown in **Figure 4**.

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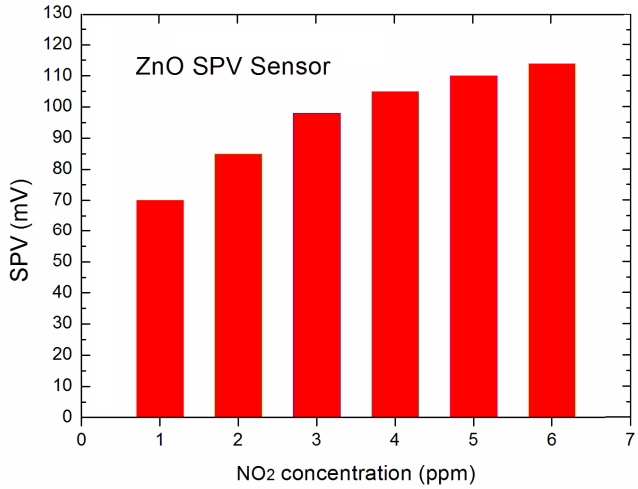

Figure 4. The variation of SPV signal as a function of NO_2 concentration.

At this point it should be underlined that perhaps our system is able to detect the NO_2 gas detection below 1 ppm, since the signal to noise (S/N) ratio was at the level ~ 50, but our gas flow system (shown in Fig.1) was only able to work in repeatable and reliable measuring condition only up to 1 ppm. Nevertheless, the obtained results look very promising having in mind that our strong SPV signal even at 1 ppm of NO_2 was reached already at room temperature working conditions. This is not possible by using the common resistive type gas sensor based on various forms of ZnO as gas sensor material [12,13]. Moreover, it should be also underlined that the respective, relative sensitivity is even at room temperature of about 1 order better with respect to commonly used various forms of ZnO thin films working at evidently higher temperature in the range of 200-350° C [12,13]. This is extremely important advantage of our SPV gas sensor system having in mind that the high concentration of undesired H_2O vapor and C surface contaminations at the surface of our gas sensing material can play a role of evident barrier for the more effective gas sensing effect.

As was mentioned above, at the next step of our experiments we have focused on the determination of dynamic characteristics of our SPV gas sensor system including response time and respected recovery time at specific NO_2 concentrations. The obtained results look promising.

Figure 5 shows the time dependent variation of SPV signal related to the dynamic parameters for the middle value of NO_2 concentration (3 ppm) within the recently mentioned its main range used in our experiments.

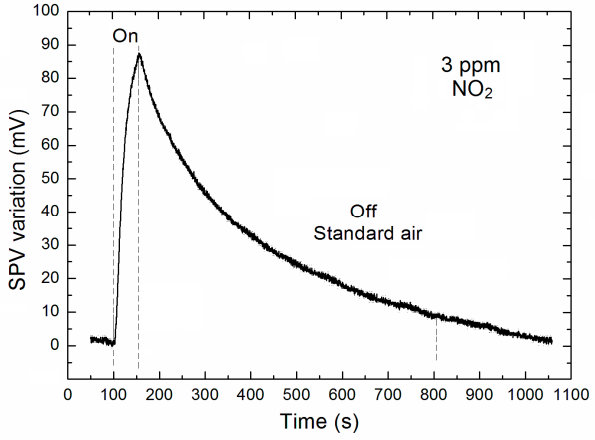

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Fig.5. The variation of SPV signal as a function of time for the 3 ppm NO_2 concentration.

As it is commonly accepted in literature, the respective gas sensor dynamic characteristics (response and recovery times, respectively) are defined as the respective time at which the signal reaches 90% value of its full relative variation. Taking it into account it is clearly visible that for 3 ppm NO_2 concentration the response time is at the level of about 50 s. Its estimated values for all other NO_2 concentration used in our experiments are summarized in Table I. What is important, as mentioned above, the response time varies in the range of 52 ÷ 24 s for the variation of NO_2 concentration the our main range of 1÷5 ppm, respectively.

Of course, these values are not spectacular with respect to the commonly used the resistive type gas sensor based on various forms of ZnO as gas sensor material. However, it looks very promising since was obtained already at the room temperature working conditions.

What concern the second dynamic parameter - recovery time, it look not so promising because for the 3 ppm NO_2 concentration it is at the level of about 680 s (~11 mins). Its estimated values for all other NO_2 concentration used in our experiments are also summarized in **Table I.**

Table I.

Response time and respective recovery time of SPV signal of our SPV gas sensor device for the main range of NO_2 concentration used in our experiments.

SPV gas sensor dynamic parameters	NO_2 concentration [ppm]				
	1	2	3	4	5
Response time [s]	52	42	38	30	24
Recovery time [s]	~1500	900	680	580	500

However, what should be also underlined the recovery time triply decreases for the variation of NO_2 concentration the range of 1÷5 ppm, respectively. Of course, it looks rather poor as considerably long. However, it has already been reached when leaving the porous ZnO nanostructured thin films in the standard synthetic air at room temperature, without any additional regeneration effects. This observation can be treated as the direct proof that the target gas was only physically adsorbed onto the inner surfaces of the porous ZnO nanostructured thin films having the columnar type morphology. As a consequence, because the adsorption/desorption process of the NO_2 gas at the surface of our gas sensor material is rather slow, it causes that the better dynamic characteristics cannot be expected. However, it should be pointed out that probably even very slow regeneration effect of gas sensor material in the dry standard synthetic air was additionally enhanced by the continuous irradiation of our porous ZnO nanostructured thin films by the UV-LED source used in our SPV experiment, what can lead to the small drift of gas sensor material temperature. This is why our SPV gas sensor system exhibits natural tendency to even slow auto-regeneration.

The regeneration effect can be additionally improved by using the additional IR-LED source. Our primary experiments are very promising in this aspect since the recovery time can be reduced by factor 5. Nevertheless, it needs additional experiments for the determination of precise conditions of the precisely controlled thermal regeneration (self-heating) of our porous ZnO nanostructured thin films after exposure to the target gases. Perhaps this self-heating effect can improve the sensitivity of our SPV gas sensor system, what was additionally observed at higher NO_2 concentration. However, this last approach slightly decreases the main advantage of our SPV gas

sensor system, i.e. room temperature working conditions during both the exposure of gas sensor material to target gas and its subsequent regeneration, without any additional external device like power supply. Nevertheless, it can be consider as an option in aspect for their potential future commercialization. Nowadays, the electronic progress allow for further miniaturization by applying the ready on chips IC's that increase importance of studying novel examination techniques like a reverse Kelvin probe approach.

5. Conclusions

In our studies a novel type room temperature surface photovoltage (SPV) gas sensor system based on the reverse Kelvin probe with vibrating grid type electrode and porous ZnO nanostructured thin films system has been successfully developed.

The initial XPS experiments showed that for our porous nanostructured ZnO thin films an evident surface nonstoichiometry is observed combined with the high undesired H_2O vapor and C surface contaminations.

In turn, our gas sensing experiments showed, among others, that the elaborated surface photovoltage gas sensor system exhibits a relatively high sensitivity in NO_2 atmosphere (up to 1 ppm at signal to noise ratio ~50) and relatively fast response time (~ several seconds). Having identified undesired H_2O vapor and C surface contaminations, we can see a potential for performance improvement, when the contaminants are removed. The presented device is significantly advantageous over the commonly used resistance type MOX gas sensor not only by using the nondestructive SPV effect measurements, but most importantly by operation at room temperature.

In currently ongoing works we aim at improving the sensor system performance, in particular by increasing the sensitivity and shortening the response and recovery times. We plan to test heat-cleaning of the electrode by additional IR-LED source and to study other ZnO/MOX nanostructures with extended internal surfaces for the more effective adsorption/desorption effects of target gasses during the gas sensor working conditions.

Author Contributions: Conceptualization, M.K. and J.S.; Methodology, P.T.; Software, P.T.; Investigation, M.K. and M.A.B.; Writing-Original Draft Preparation, M.K., M.A.B.; Writing-Review & Editing, J.S.; Supervision, M.K., J.S.; Project Administration, M.K, J.S., A.P.; Funding Acquisition, M.K and A.P.

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Conflicts of Interest: The authors declare no conflict of interest.

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