Light irradiation effect on the gas response of pure and noble-metal-doped ZnO sensors

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Abstract. Highly porous pure and noble metal (Ag, PdAg and Pd) doped ZnO nanostructures were fabricated by pulsed laser deposition (PLD) in air at atmospheric pressure (in open air). This technology leads to the formation of nanostructures composed of nanoparticles or nanoaggregates. The as-deposited nanostructures possess a large surface-to-volume ratio, which makes them suitable for gas-sensor applications. In this work, we demonstrated the response of pure ZnO and of Ag-ZnO, Pd-ZnO and PdAg-ZnO sensor elements to NH\textsubscript{3}, CO, ethanol, and acetone exposure under UV light irradiation. The effect was studied of simultaneous UV and red or green light irradiation on the sensor element’s response, selectivity, and response and recovery time. It was found that irradiation by UV and red light has the effect of improving the Ag-ZnO sensor’s response to CO exposure and suppressing its response to NH\textsubscript{3}, ethanol and acetone. The same behavior was exhibited by the pure ZnO sensor element irradiated simultaneously by UV and green light.

1. Introduction

Zinc oxide (ZnO), being a semiconducting metal oxide, is considered as a promising gas sensing material [1]. However, the relatively high operating temperature of the ZnO-based sensors restricts their extensive applications in real-time gas monitoring, especially in flammable and explosive gas atmospheres. Thus, the research efforts have been mainly directed to reducing the operating temperature and enhancing the gas-sensing properties. The effective strategies for improving the gas sensor performance include surface modification, doping and light irradiation [2-4]. In recent years, the attention of researchers has been focused on metal-oxide-based nanostructures, such as ZnO nanostructures. This is due to its large surface-to-volume ratio and, consequently, fast diffusion of gas molecules leading to faster response-recovery time [5, 6]. Different noble metals, (Au [7], Ag [8, 9], Pd [10-12] and Pt [13, 14]), have been used as dopands to further sensitize the ZnO material. These nanocomposites significantly improve the gas-sensing characteristics at room temperature. In [9, 15], the authors reported that light activation is a promising strategy of realizing room-temperature gas sensors on the basis of ZnO nanostructures. It was already demonstrated that UV and visible-light irradiation improves the room-temperature gas sensing properties of ZnO sensors [16, 17]. However, fabricating a
sensor element operating at room temperature with high response and selectivity, fast response and recovery time is still a challenge.

In this work, we report on the fabrication of highly porous nanostructures based on ZnO by means of PLD in open air. We studied the effect of introducing Ag, PdAg and Pd NPs in ZnO on the structures’ morphology and sensing properties. We also followed the response of pure ZnO and of Ag-ZnO, Pd-ZnO and PdAg-ZnO sensor elements to NH₃, CO, ethanol, and acetone exposure upon UV light irradiation. Further, we discussed the effect of simultaneous UV and red or green light irradiation on the sensor elements’ response, selectivity, and response and recovery time. We found that irradiation by UV and red light has the effect of improving the Ag-ZnO sensor’s response to CO exposure, while inhibiting its response to NH₃, ethanol and acetone.

2. Experimental
The gas sensor elements were prepared by PLD carried out in air at atmospheric pressure in a standard on-axis configuration. A ZnO target was ablated by a pulsed nanosecond Nd:YAG laser (Lotis LS-2147) using the fundamental laser wavelength (λ = 1064 nm) at a fluence of 10 J/cm². The ablated material was deposited on a glass substrate kept at room temperature and covered by thermally evaporated gold electrodes. The target-substrate distance was fixed at 8 mm. A set of depositions were performed in order to prepare nanocomposite sensor elements by ablating a mosaic target formed by a ZnO target partly covered by a Ag, a PdAg or a Pd slice (covering ratio 1/3 Ag, PdAg and Pd: 2/3 ZnO). The Pd-to-Ag ratio in the PdAg alloy slice was 75:25.

The surface morphology of the samples was studied by scanning electron microscopy (SEM, Lyra IXU Tescan). The gas sensor measurements were performed in a home-made test chamber at room temperature. The samples were irradiated by a UV LED (λ = 396 nm, intensity 43 mW/cm²) installed at a distance of 1 cm in front of the sample surface. Additionally, a red (λ = 633 nm, intensity 18 mW/cm²) or a green (λ = 470 nm, intensity 18 mW/cm²) LED were placed to irradiate the sensor surface simultaneously with the UV radiation. High-purity N₂ was used as a reference gas at a flow rate of 55 sccs (standard cubic centimeters per second). The test gasses – ammonia (NH₃), carbon monoxide (CO), ethanol (C₂H₅O) and acetone ((CH₃)₂CO) – were injected by a microsyringe into the chamber for one second to reach a concentration of 40 ppm. The gas response was estimated by calculating the ratio $\Delta R/R_0$ (%), where $R_0$ is the sample resistance in the reference gas, $\Delta R = (R_g - R_0)$, $R_g$ being the sample resistance in the test gas. The response time is defined as the time needed to reach 90 % of the maximum gas response after the gas is turned on; and the recovery time is the time needed for the response to fall down to 10 % of its maximum once the gas is turned off.

3. Results
SEM images of the samples produced in open air are presented in figure 1. The deposition process leads to the formation of complex highly porous nanostructures, as we reported earlier [18-20]. Figure 1(a) shows a SEM image of the sample produced by ablating a pure ZnO target. The structure formed is
Figure 1. SEM image of (a) ZnO, (b) Ag-ZnO, (c) PdAg-ZnO and (d) Pd-ZnO composite nanostructures.

highly porous and consists of aggregated nanoparticles. Figure 1(b, c and d) presents SEM images of the samples deposited from a mosaic target formed by a ZnO target partly covered by Ag, PdAg or Pd slices, respectively. As seen, the morphology of the samples does not change substantially when a small amount of the noble metal is added and a nanocomposite is formed.

Since the structures are made of a highly porous semiconducting material, they behave as dielectrics ($R_0 > 2 \text{ G}\Omega$). In this light, using such a structure as a sensor element is practically impossible. However, irradiating the sensor surface with UV light dramatically decreases its resistance. The incident light is absorbed when its photon energy is higher than the band gap of the irradiated material. Once absorbed, a photon creates a hole-electron pair in the semiconductor. The photo-generated electrons enhance the conductivity by going to the conducting band, i.e. the sample’s resistance decreases. We initiated each of our gas-sensing measurements when the respective sensor’s resistance relaxed to a constant value. The response of the pure and Ag-, PdAg- and Pd-ZnO-sensor elements to NH$_3$, CO, ethanol and acetone exposure at 40 ppm under UV light irradiation is demonstrated in figure 2(a). As seen, the highest response to CO, ethanol and acetone exposure is manifested by the PdAg-ZnO sensor element. The Ag-ZnO sensor has the highest response to NH$_3$ compared to the response of the other doped ZnO sensors. In the latter case, the response and recovery time for all gases are estimated to be in the range of 33 – 36 s and 155 – 196 s, respectively. When the sensor elements are irradiated simultaneously with UV and red light, the response of the sensor elements changes (figure 2(b)). The additional irradiation with red light increases the response of pure and Ag- and PdAg-doped ZnO to all gases, while not affecting the Pd-ZnO sensor’s response. The ZnO sensor under red irradiation demonstrated the highest response to NH$_3$ compared to the response of doped ZnO. The PdAg-ZnO sensor exhibits the highest response to CO, ethanol and acetone. As also seen, the red light irradiation enhances the Ag-ZnO sensor’s response to CO exposure and suppresses the sensor response to NH$_3$, ethanol and acetone.

The Ag-ZnO sensor’s response time to the tested gases is between 40 – 60 s, with the recovery time being in the range of ~ 500 – 650 s; i.e., the presence of Ag NPs increases the times for response and recovery of the sensor element. The presence of PdAg and Pd NPs in ZnO does not change the response time, but substantially increases the time for recovery of the sensors. The gas response of the sensor elements irradiated simultaneously with UV and green light is presented in figure 2(c). The response of Pd-ZnO sensor to all gases slightly decreases compared to the response of the sensor irradiated with UV and red light. In this case, the response time is comparable with that of the Pd-ZnO sensor additionally irradiated with red light. However, the time for recovery of the sensor to all tested gases significantly decreases under UV and green light irradiation (~ 325 – 610 s). The green irradiation decreases the response of the Ag-ZnO sensor to all gases compared to the response of pure...
ZnO and worsens the selectivity obtained when the sensor surface is irradiated additionally with red light. Also, the highest response to NH$_3$ exposure is registered when the PdAg-ZnO sensor’s surface is irradiated with UV and green light. In the latter case, the sensor response and recovery time are estimated to be 52 s and 1078 s, respectively. When the pure ZnO sensor is simultaneously irradiated with UV and green light, its response to CO substantially increases compared to response of the sensor irradiated with UV or UV and red light. At the same time, the response of the green-light irradiated ZnO sensor to NH$_3$, ethanol and acetone decreases compared to its response in the case of red-light irradiation. It should be further noted that irradiation with red or green light only did not bring the sensor to an operating regime, i.e. did not change the initial sensor resistance $R_0$. The response of the

![Figure 2. Comparison of the response of the ZnO, Ag-ZnO, PdAg-ZnO and Pd-ZnO sensors to different gases at the fixed concentration of 40 ppm under (a) UV light irradiation; under UV light irradiation performed simultaneously with (b) red and (c) green light.](image1)

![Figure 3. Responses of the ZnO sensor to different gases at 40 ppm under (a) UV light irradiation, (b) under UV light irradiation performed simultaneously with red light and (c) UV light irradiation performed simultaneously with green light.](image2)
ZnO sensor element to different gases under UV, UV and red light, and UV and green light irradiation is shown in detail in figure 3. The ZnO sensor’s response under UV irradiation is slightly higher to NH₃ and acetone compared to its response to CO and ethanol, as shown in figure 3(a). The response and recovery time for all gases are estimated to be in the range of 33 – 36 s and 155 – 196 s, respectively.

A well-defined reaction of the ZnO sensor under UV and red light irradiation is registered under exposure to each of the gases (figure 3(b)). Also, the sensor’s response to all tested gases increases, with the lowest enhancement obtained upon CO exposure. The red light irradiation of the ZnO surface leads to a slight increase of the time of sensor’s response to all tested gases (~ 1.2 – 1.3 times), while the increase of its recovery time is in the range of 3 – 3.5 times. A significant increase of the sensor’s response to CO is observed when the ZnO sensor surface is irradiated with green light (figure 3(c)). The sensor’s response to all other gases – NH₃, ethanol, and acetone – was suppressed. We associate the improvement of the sensor selectivity with a local heating effect. Additional light irradiation enhances the adsorption/desorption rate of the particular gas molecules on the sensor surface. It could be concluded that the response and selectivity of the sensor element could be modified either by using suitable dopands, or by suitable light irradiation of the sensor’s surface.

4. Conclusions
In this work, we present results on the gas sensing properties of pure and composite nanostructure based on ZnO and noble metal nanoparticles. Highly porous structures were obtained by PLD in open air, a technology that is easily transferable to industrial production. The gas detection regime was achieved after UV light irradiation. It was found that the selectivity of the sensor elements could be modified by using a suitable dopand or by suitable light irradiation of the sensor surface. The presence of Ag in the ZnO nanostructure substantially improved the sensor element’s response to all tested gases; the highest enhancement of the sensor’s reaction was obtained under CO exposure. Additional irradiation of the Ag-ZnO sensor with red light improved the response to CO, while for other tested gases – NH₃, ethanol, and acetone – the response was suppressed. When the pure ZnO sensor was simultaneously irradiated with UV and green light, a significant increase of the sensor’s response to CO exposure was observed, while the response to all other tested gases was suppressed. The presence of dopands, as a whole, increased the time for response and recovery of the sensor elements.

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