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Zinc Oxide Dosimeter-type NO_2 Sensor Prepared by Discontinuous Powder Aerosol Deposition

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Summary:
NO_2 dosimeters operated at room temperature provide an opportunity to detect the NO_2 concentration in ambient air and, specifically, directly mean values NO_2. It is evaluated whether the functional material, Al-doped zinc oxide, can also be applied by a room temperature process, the discontinuous powder aerosol deposition. The sensors are subsequently characterized with respect to their NO_2 dosimeter behavior at room temperature. Additionally, the influence of a low temperature annealing step of the DPAD-films on the NO_2-dosimeter characteristics is investigated.

Keywords: dosimeter-type sensor, NO_2 detection, zinc oxide, powder aerosol deposition, room temperature device

Dosimeter-type NO_2-sensor

NO_2 detection in ambient air is still challenging, especially concentrations in the range of ppb. For air quality control the detection of the hourly mean values or the total amount (dose) of NO_2 over a certain time interval are important. The working principle of a dosimeter-type NO_2 sensor operating at room temperature is described in [1] and [2]. The gas dosimeter detects the total dose of NO_2, i.e., the timely integration of the concentration over a certain time span, directly. The impedimetric device is based on sol-gel-synthesized Alumina-doped Zinc oxide (Al:ZnO) as functional material applied in thick-film technology [3]. During the first operation phase, the sorption phase, the NO_2 molecules are sorbed and the measured resistance changes almost linearly with the sorbed NO_2 amount. In absence of NO_2, the resistance remains constant. After reaching a certain loading state, which means that the adsorption sites are occupied, an UV-initiated regeneration phase follows. It releases all sorbed NO_2-species. Afterwards, a new loading cycle starts. The dosimeter allows for the detection of NO_2 at ppb-levels and therefore also the resulting hourly mean values.

Discontinuous Powder Aerosol Deposition

In contrast to the preparation of screen-printed thick films with consequent sintering steps at higher temperatures, the (discontinuous) powder aerosol deposition ((D)PAD) allows to prepare ceramic films at room temperature [4]. The ceramic powders are aerosolized by a carrier gas flow and accelerated into a vacuum chamber by a pressure gradient (Fig. 1). The impact of the particles leads, depending on the kinetic energy of the particles, to the formation of dense ceramic films on the substrates. Powder quantities below 100 mg can be deposited by DPAD. The nanocrystalline structure with many grain boundaries and the distorted lattice of the as deposited film lead to a high resistance of the film. Mild annealing (far below the sintering temperature) allows for restoring the reduced electric conductivity close to bulk values again [4,5].

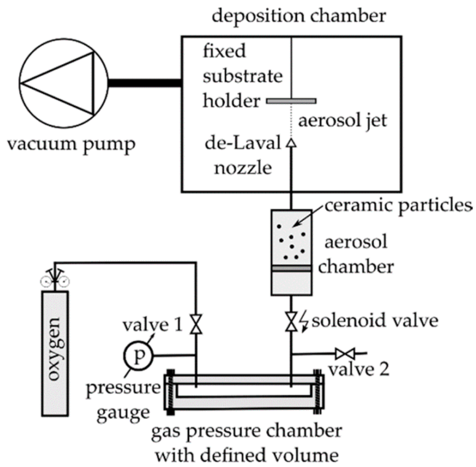

Fig. 1. Scheme of discontinuous powder aerosol deposition DPAD [4]

For a room temperature sensor device like a Al:ZnO-NO_2 dosimeter, a preparation technology working at room temperature would be advantageous. Therefore, sol-gel synthesized Al:ZnO-powders were deposited as sensing layers by DPAD and the dosimeter-type sensing characteristics of the films were investigated.

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Experimental

Al:ZnO powder with 5% Al was synthesized as descried in [3]. The powder is then deposited by DPAD on top of platinum-interdigitated electrodes (IDE). To cover the IDE-area, three circular shaped films of Al:ZnO are applied. The resulting sensor device consists of a platinum heating structure on an alumina substrate and the Pt-IDE covered with the Al:ZnO-film.

The sensor behavior was investigated in dry synthetic air with NO_2 concentrations between 0 and 200 ppb at a constant flow rate. The impedance of the sensors was measured (U_{eff} = 100 mV, f = 1 Hz) and the resistance was calculated assuming an $R||C$ equivalent circuit. Before and after each measurement, the sensor was regenerated by UV-light exposure (385 nm). Additionally, the influence of thermal annealing of the Al:ZnO-films from 100 to 400 °C on the dosimeter signal (measured at RT) was characterized.

Results and Discussion

The relative resistance change $(R-R_0)/R_0$ (R_0: resistance in base gas; R: resistance with NO_2), measured at room temperature, during exposure to four NO_2 pulses are shown in Fig. 3. Indicated are the thermal annealing temperatures that are applied to the films. The sensor signal increases linearly for all annealing temperatures during NO_2 exposure and remains constant during NO_2-pauses. The sensor shows typical dosimeter-type behavior. An influence of the annealing temperature on the dosimeter behavior can be observed.

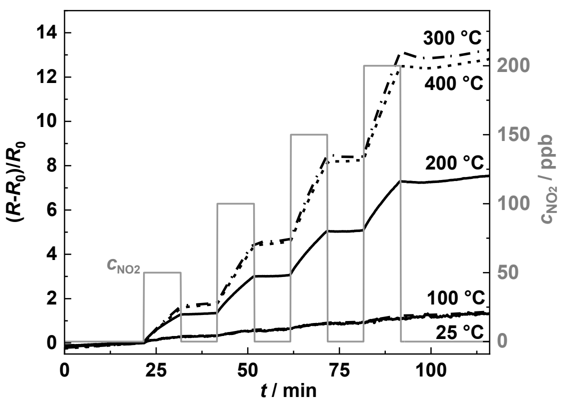

Fig. 3. Dependence of the relative resistance change $(R-R_0)/R_0$ on the NO_2-amount and the annealing temperature measured at room temperature

Fig: 4 shows the characteristic dosimeter curves, $(R-R_0)/R_0$ versus the calculated NO_2-dosis (in ppb s). Compared to screen-printed films, as expected, the DPAD-films show a lower NO_2-sensitivity. A linear relationship is visible, and the sensitivity increases with increasing annealing temperature. It is expected that the observed sensitivity increase is due to occurring oxygen desorption processes and additionally effects due to the thermal annealing of the film (relaxation of stresses, morphology changes). These processes will be investigated more in detail.

Conclusion

The work shows, that DPAD-deposited Al:ZnO films are sensitive to NO_2 at room temperature and provide dosimeter-type behavior. An influence of a thermal annealing on the dosimeter properties is observed which will be investigated in the future. Additionally, the effect of humidity needs to be addressed.

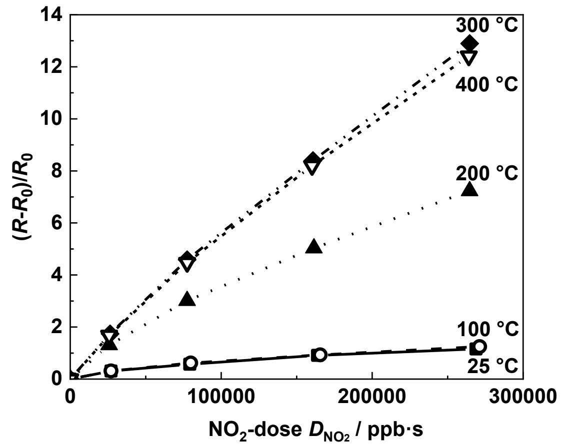

Fig. 4. Relative resistance change $(R-R_0)/R_0$ versus calculated dose of NO_x in dependence of sensor annealing temperature

References

[1] R. Wagner, D. Schönauer-Kamin, R. Moos, Novel Operation Strategy to Obtain a Fast Gas Sensor for Continuous ppb-Level NO_2 Detection at Room Temperature Using ZnO - A Concept Study with Experimental Proof, *Sensors*, 19, 4104 (2019); doi: 10.3390/s19194104

[2] R. Wagner, D. Schönauer-Kamin, R. Moos, Influence of Humidity and Different Gases on a Resistive Room Temperature NO_2 Gas Dosimeter Based on Al-Doped ZnO for ppb-Concentration Detection, *Journal of The Electrochemical Society* 167, 167516 (2020); doi: 10.1149/1945-7111/abcb65

[3] L. Vogel, R. Wagner, R. Moos, D. Schönauer-Kamin, Investigations on the crystal growth mechanism of one-pot-synthesized Al-doped ZnO and its UV-enhanced room temperature NO_2 gas sensing characteristics, *Functional Materials Letters*, 11, 1850087 (2018), doi: 10.1142/S179360471850087X

[4] M. Linz, J. Exner, J. Kita, F. Bühner, M. Seipenbusch, R. Moos, Discontinuous Powder Aerosol Deposition: An Approach to Prepare Films Using Smallest Powder Quantities, *Coatings* 11, 844 (2021); doi: 10.3390/coatings11070844

[5] Exner, T. Nazarenus, D. Hanft, J. Kita, R. Moos: What Happens during Thermal Post-Treatment of Powder Aerosol Deposited Functional Ceramic Films? Explanations Based on an Experiment-Enhanced Literature Survey, *Advanced Materials* 32,1908104 (2020), doi: 10.1002/adma.20190810