FLEXIBLE AMMONIA GAS SENSOR BASED ON POLYANILINE

Alexandr POŠTA, Josef NÁHLÍK, Alexandr LAPOSA, Jan VOVES

CTU FEE- Czech Technical University in Prague Faculty of Electrical Engineering, Prague, Czech Republic, EU, postaale@fel.cvut.cz

Abstract

In this paper we prepared flexible ammonia (NH_3) gas sensor based on polyaniline (PAni) as an active sensing thin film layer. The sensors function was based on chemiresistive principle with thin film deposited on top of interdigitated electrodes. We measured the change in resistance of the thin film under gas exposure. The PET based foil has been used as the sensors substrate. The Interdigitated electrodes (IDE) has been printed with Fujifilm Dimatix DMP 2831 inkjet printer by nanocoloid silver ink. The active thin film has been prepared by drop casting method from polyaniline nanoparticle dispersion. The morphology of thin films surface was characterized by atomic force microscopy (AFM). The sensors response was investigated in a gas chamber, and the gas flow was controlled by mass flow meters. The sensitivity towards various gases under different concentration in synthetic air has been tested. The tested gases were NH_3, NO_2, CO_2 and CO. The measurement of the sensors response to the different levels of humidity was also conducted. All the measurements were performed at room temperature, which is important feature for the sensor to be able to operate in hazardous environment and it facilitates low-power operation of the sensor as well. We also observed the long-term stability of the sensors response, as well as the effect of bending of the sensing platform on the sensors response and stability.

Keywords: Ammonia, polyaniline, chemiresistive gas sensing, inkjet printing

1. INTRODUCTION

During the last decades, there has been growing interest in a gas sensing technology from many areas including industrial, environmental, domestic, military and many other industries. The ability to detect or monitor different gases became critical during some manufacture processes and in environmental issues, to avoid harmful effects caused by toxic gases. This demand accelerated research in gas sensor industry, and different gas sensing techniques were proposed. In this paper, we present a flexible chemiresistive ammonia gas sensor based on polyaniline as the sensing layer.

Ammonia is natural as well as manufactured compound on our planet. It can be found in our atmosphere, water, soil and is typically found in our body. Although ammonia can be found all around us, the exposure to the high concentration of ammonia gas causes chemical burns of the respiratory tract, skin, and eyes. The ammonia gas can be detected by the human nose since it has a strong, unpleasant and irritating smell [1]. The detection limit of the human nose towards the ammonia gas is around 50 ppm. However, even lower concentrations can be irritating for the humans. The maximal allowed workspace concentration of ammonia is set to be 20 ppm. Today, most of the ammonia in our atmosphere is emitted direct or indirect by human activity [2]. There are so far four major industry areas with a need for ammonia gas sensing application. It is environmental, automotive, chemical industry and medical diagnostics. The detection of ammonia gas in the environment is especially critical near farming areas, where the concentration of the gas can exceed allowed exposure limits. Ammonia from decomposing animal excreta probably accounts for the most significant proportion of the ammonia produced, with the decay of organic materials from plants, dead animals, etc. The presence of ammonia can cause unhealthy conditions for both farmers and the animals especially indoors. The usage of ammonia detection in the automotive industry can be divided into three categories. The first is monitoring of the pollution caused by vehicles exhaust system, the second is control of indoor air condition,

while the third reason is the reduction of NOx in diesel engines. In the chemical industry, the vast majority of ammonia is produced for manufacturing of fertilizers. There are other processes using ammonia such as plastics, synthetic fibers, resins, explosives, and other uses. The detection of NH_3 in very low concentrations is very interesting for medical diagnostics. Ammonia is produced by the human body, and the amount of produced NH_3 can be used for diagnostics of certain diseases using breath analyzers. The detection limit in those systems needs to be in orders of tens to hundreds of ppb. Detection of such concentrations is so far possible by large and expensive optical sensors. The flexible sensor prepared in this paper belongs between solid state chemiresistive group of the gas sensors. As a sensing layer acted a thin film of polyaniline (PAni) and we observed the influence of light irradiation of the sensing layer on the response of the sensor as well as the influence of the sensors bending.

2. AMMONIA GAS SENSING MECHANISM IN POLYANILINE

The first report on chemiresistive properties of polyaniline towards ammonia gas was by Hirata et al. in 1994 [3]. In recent years the attention of the scientific community was dedicated to exploring different nanostructures, composites and flexible sensors based on polyaniline. [4], [5], [6], [7]. The polyaniline belongs to the group of conjugated polymers, although the molecular structure is a little bit different since its absence of strictly alternating single and double bonds. The PAni has unique ability since its doped state can be controlled by the acid/base reaction. The ability of PAni to undergo doping/dedoping under acidic/basic media suggested that this material could be applied as a chemiresistive sensor for the detection of a wide range of compounds. When exposed in ammonia gas, PAni undergoes dedoping by deprotonation [8], [9]. The illustration of the chemical process mentioned above can be seen in **Figure 1** The protons on -NH- groups, were transferred to NH_3 molecules to form ammonium ions while PAni itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed the ammonium ion can be decomposed to ammonia gas and proton [8]

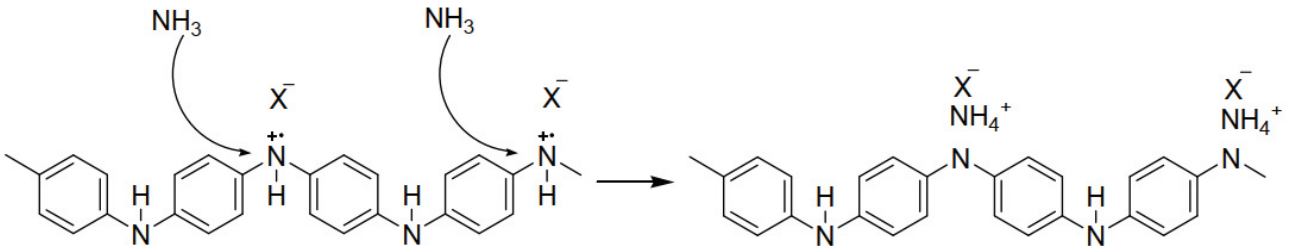

Figure 1 Schematic illustration of the dedoping process in polyaniline during exposure to ammonia gas [8]

3. GAS SENSOR PREPARATION AND CHARACTERIZATION

The gas sensors were prepared by an inkjet printer (IJP) on NoveleTM IJ-220 foil from Novacentrix. It is a PET-based printed electronics substrate for low-cost and low-temperature applications. The sensing array dimension was 16 x 7.7 mm and was connected to PCB by 8 PIN FPC connector. The sensing array consisted of four sensing IDE areas with dimensions approximately 2 x 2 mm each. The electrode width and spacing were designed to be 100 µm. The IDE was printed with Dimatix DMP 2831 drop on demand (DoD) IJP by silver nanoparticle ink Silver jet DGP-40LT-15C from Advanced Nano Products Co.Ltd. The masking layer was printed with ink of SU-8 photoresist XP PriElex® SU-8 1.0 from MicroChem. The active sensing layer was prepared from doped polyaniline (PAni) powder in the form of emeraldine salt obtained from Sigma Aldrich. The PANI was dispersed in laboratory grade p-Xylene from Sigma Aldrich. The dispersion of 2wt% of PAni in p-Xylene was stirred at room temperature and sonicated at 60 °C for 120 min. The thin film of PAni was deposited by simple drop casting method by laboratory pipette The photo of the sensor array with AFM picture of the surface of the sensor in the inset, and the schematic illustration of the sensor can be seen in **Figure 2**

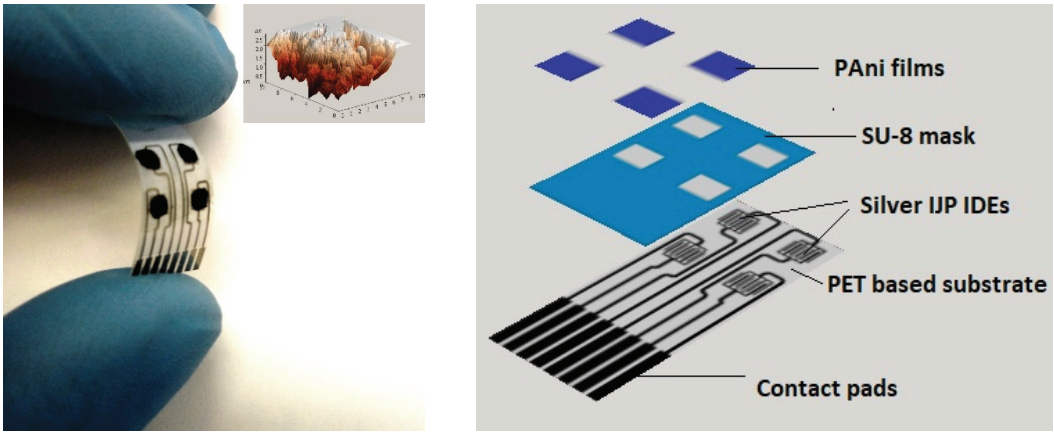

Figure 2 On the left photo of actual sensor (inset AFM picture of the PAni surface) and the schematic illustration of each layer of the fabricated sensors on the right

In **Figure 3** can be seen the experimental setup for measuring the responses and the picture of the test chamber with the attached sensor and LED used for irradiation. It consists of gas bottles with target analytes, reduction valves, mass flow meters, valve switch, source meters, and the test chamber. The data were acquired by the LabVIEW program through the PC. The detection and cleaning stage of the measurements were cycled using two-way our inputs/output valve driven by VICI universal valve actuator controlled by the same LabVIEW program via the serial port. The measurement setup was identical to the one used by Davydova et al. reporting the gas sensing behavior of ZnO/diamond nanostructures. [10]

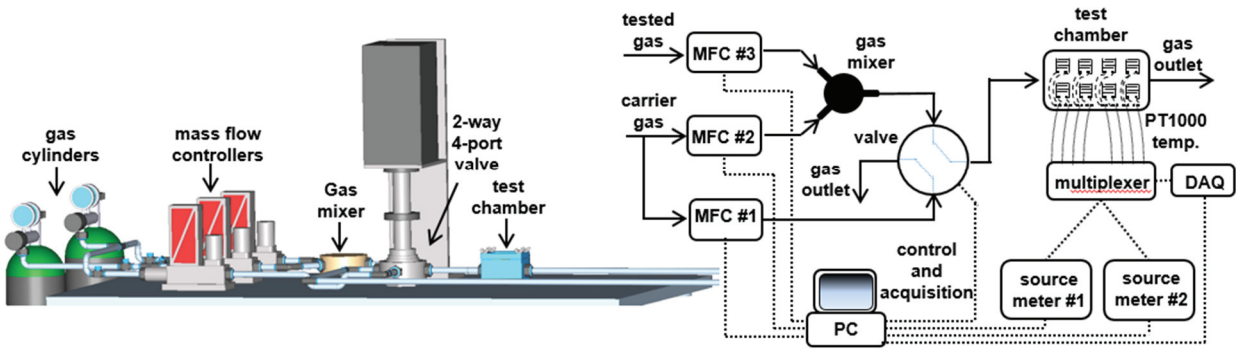

Figure 3 Schematic illustration of measurement setup

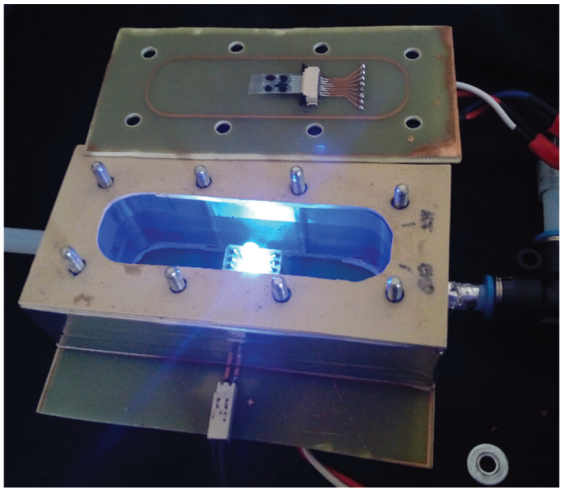

Figure 4 Photo of the test chamber with blue LED light source and the sensor array

The LEDs used for irradiation were powered by Keithley 2230G DC power supply. The LEDs used in experiment were blue, yellow and IR, with wavelength 470, 590 and 940 nm respectively. The picture of the test chamber with light irradiation setup is in **Figure 4**.

4. RESULTS

We measured the response of the sensor to different analytes in synthetic air (SA) (80 % N_2, 20 % O_2). The gas flow was set to 100 ml/min by mass flow meters. The measurement consisted of cleaning cycles (pure SA) and the testing cycles of target analyte mixed with SA. The tested gases were NH_3, CO, CO_2 and NO_2. The response to the 50 ppm of NH_3 analyte can be seen in **Figure 5**. The response to the step function of the NH_3 analyte concentration can be seen in **Figure 6**. In presence of humidity (50 % RH), the response of the sensor to the NH_3 was inhibited. The sensor exhibited negligible additive response towards CO_2 and NO_2 analytes. During exposure to the CO analyte we observed decrease in resistance. When exposed to the different levels of humidity, the resistance of the sensor decreases dramatically and after exposure to 25 % RH there was not any significant drop in the resistance upon exposure to higher RH levels. The bending of the sensor did not show any noticeable effect on the performance of the sensor. One of the goal of this paper was to research the influence of sensors surface by vis-IR light on the sensors response. The response did not show any significant changes upon the exposure to the light irradiation

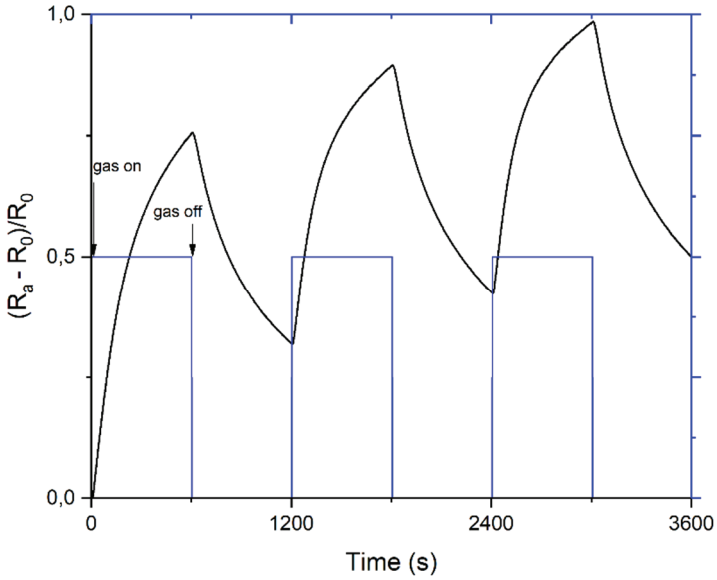

Figure 5 Response of the sensor to the 50 ppm of NH_3 at room temperature

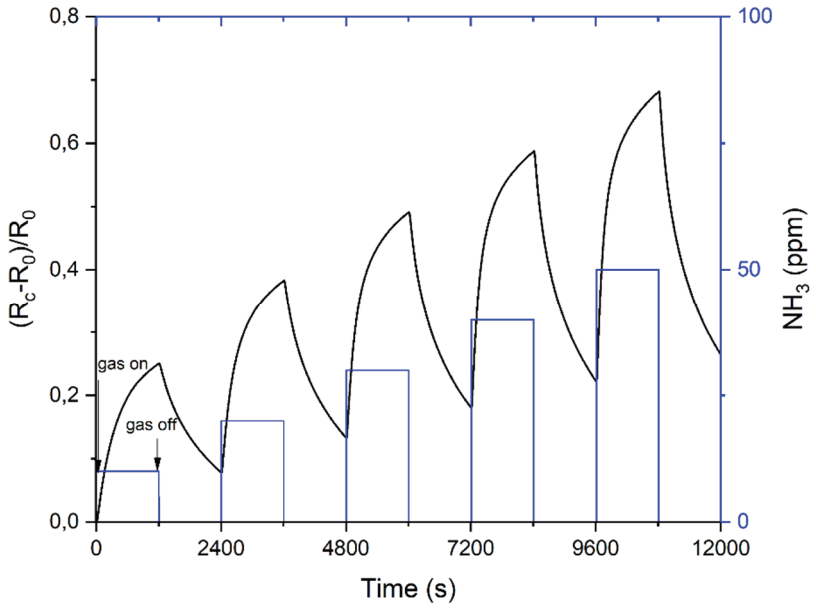

Figure 6 Response of the sensor to the step function of NH_3 concentration at room temperature

5. CONCLUSION

The sensor array was successfully printed by silver ink and then the platform masked by SU-8 photoresist ink utilizing inkjet printing. The drop casting method used for deposition of an active layer showed its limitation especially concerning the film uniformity. This lead to different baseline resistance of fabricated sensing films. The response of sensors array was tested towards different gases in synthetic air at room temperature. The sensors showed good sensitivity towards the NH_3 analyte. At room temperature, the sensor array did not fully recover during the cleaning cycles. The sensor had negligible response towards NO_2 and CO_2 analytes. When exposed to the CO analyte, the resistance of the sensor decreased possibly due to the reducing effect of the analyte and its reaction with adsorbed oxygen on the surface of the sensing layer. The response of the array was also measured under irradiation by vis-IR light. As light sources were used blue (470 nm) yellow (590 nm) and IR (940 nm) LEDs. There was not any noticeable influence caused by light irradiation on adsorption/desorption properties of the sensor. The possible interaction will also be investigated for other wavelengths. Repeated bending of the approximately by 45° did not show any significant decrease in performance.

ACKNOWLEDGEMENTS

This paper was supportedby the CTU student grant No. SGS17/096/OHK3/1T/13 and the project CAV CAAS CZ.02.1.01/0.0/0.0/16_019/0000737

REFERENCES

[1] U.S. Department of Health and Human Services - Agency for Toxic Substances and Disease Registry, “Toxicological Profile For Ammonia,” 2004.

[2] W. OLTHUIS AND A. VAN DEN BERG, “Ammonia sensors and their applications - a review,” vol. 107, pp. 666-677, 2005.

[3] M. HIRATA and L. SUN, “Characteristics of an organic semiconductor polyaniline film as a sensor for NH3 gas,” *Sensors Actuators A. Phys.*, vol. 40, no. 2, pp. 159-163, 1994.

[4] L. ZHIHUA *et al.*, “Sensors and Actuators B : Chemical Fast response ammonia sensor based on porous thin film of polyaniline / sulfonated nickel phthalocyanine composites,” *Sensors Actuators B. Chem.*, vol. 226, pp. 553-562, 2016.

[5] S. SRIVASTAVA, S. S. SHARMA, S. AGRAWAL, S. KUMAR, M. SINGH, and Y. K. VIJAY, “Study of chemiresistor type CNT doped polyaniline gas sensor,” *Synth. Met.*, vol. 160, no. 5-6, pp. 529-534, 2010.

[6] L. KUMAR, I. RAWAL, A. KAUR, and S. ANNAPOORNI, “Flexible room temperature ammonia sensor based on polyaniline,” *Sensors Actuators, B Chem.*, vol. 240, pp. 408-416, 2017.

[7] Z. F. LI, F. D. BLUM, M. F. BERTINO, and C. S. KIM, “Understanding the response of nanostructured polyaniline gas sensors,” *Sensors Actuators, B Chem.*, vol. 183, pp. 419-427, 2013.

[8] H. BAI and G. SHI, “Gas Sensors Based on Conducting Polymers,” *Sensors*, vol. 7, pp. 267-307, 2007.

[9] N. R. TANGUY, M. THOMPSON, and N. YAN, “Sensors and Actuators B : Chemical A review on advances in application of polyaniline for ammonia detection,” *Sensors Actuators B. Chem.*, vol. 257, pp. 1044-1064, 2018.

[10] M. DAVYDOVA *et al.*, “Gas-sensing behaviour of ZnO/diamond nanostructures,” *Beilstein J. Nanotechnol.*, vol. 9, no. 1, pp. 22-29, 2018.