Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 25 (2011) 896 – 899

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXV, September 4-7, 2011, Athens, Greece

Novel printed nanostructured gas sensors

J. Kukkola[a], E. Jansson[b], A. Popov[c], J. Lappalainen[a,*], J. Mäklin[a], N. Halonen[a], G. Tóth[a], A. Shchukarev[d], J.-P. Mikkola[d,e], H. Jantunen[a], K. Kordás[a], J. Hast[b], T. Hassinen[b], A. Sunnari[b], K. Jokinen[c], H. Haverinen[c], R. Sliz[c], G. Jabbour[c], T. Fabritius[c], R. Myllylä[c], A. Vasiliev[f], N. Zaretskiy[f],

[a]*Microelectronics and Materials Physics Laboratories, University of Oulu, P.O. Box 4500, FI-90014 Oulu, Finland*
[b]*VTT, Technical Research Center of Finland, Finland*
[c]*Optoelectronics and Measurement Techniques Laboratory, University of Oulu, Oulu, Finland*
[d]*Technical Chemistry, Department of Chemistry, Umeå University, Sweden*
[e]*Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Åbo-Turku, Finland*
[f]*Institute of Applied Chemical Physics, RRC Kurchatov Institute, Moscow, Russia*

Abstract

There is a need for low-cost mass-production circuits on various substrates, possibly performing some simple functions as switches, antennas, displays, and sensors. Also in the field of gas sensors widely used in several applications there is a need for such novel fabrication technologies and materials. In this paper, we present three gas sensor structures fabricated using novel printing techniques. Inkjet and gravure printing techniques were used for fabrication of resistive WO_3 nanoparticle gas sensors for detection of NO, and inkjet printing was utilized for fabrication of solid electrolyte (mixture of $H_3PW_{12}O_{40}$ and PVC) in a nanostructured Metal-Electrolyte-Insulator-Semiconductor (MEIS) transistor for detection of H_2. The sensor structures were found to be sensitive for detection of NO below 10 ppm, and H_2 below 100 ppm concentrations in synthetic air, respectively.

Keywords: Gas sensor; Semiconductor; Inkjet; Gravure; Printing; Capacitance; Resistance

1. Introduction

Currently available gas sensors are often rather expensive to fabricate, have high energy consumption and low selectivity. Thus, using novel fabrication techniques and nanomaterials, such as inkjet and gravure printing, new approaches and functionality of the gas sensors can be achieved. In the following,

* Corresponding author. Tel.: +358-8- 5532720; fax: +358-8-5532728.
E-mail address: jyla@ee.oulu.fi.

1877-7058 © 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
doi:10.1016/j.proeng.2011.12.220

there are three examples of gas sensor structures fabricated using nanoscale materials and printing techniques. Gas sensors based on tungsten oxide (WO_3) particles have been researched fo more than 20 years, mainly due to material sensitivity towards nitric oxides, but inkjet printing is almost uncovered in the literature [1].

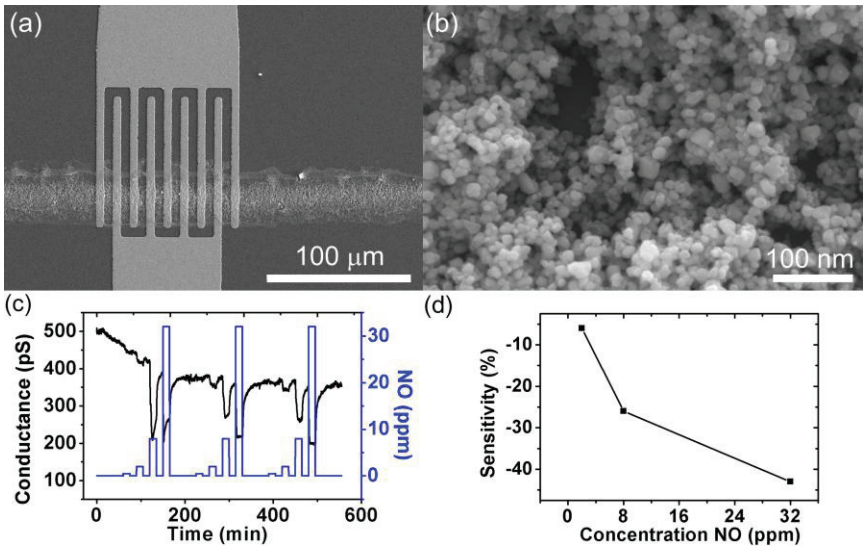


Fig. 1. (a) and (b) FESEM images of inkjet-printed WO_3 nanoparticles on Si/SiO_2 substrate with Pt-electrodes. (c) Response of the resistive WO_3 gas sensor to NO analyte gas in air buffer at 220 °C. (d) Sensitivity of the sensor towards different levels of NO at 25 V bias at 220 °C.

2. Inkjet-printed resistive WO_3 nanoparticle gas sensor

One type of resistive gas sensors was fabricated by ink-jet printing. For the ink fabrication, 20 mg of WO_3 nanoparticles (Sigma-Aldrich) were dispersed in 100 ml of deionized water by ultrasonic agitation for 3 hours. The obtained dispersion was left to sediment for 1 day. Gray opaque supernatant dispersion on top was collected and used for inkjet printing. 100 layers using 10 droplets with 20-µm spacing were printed on Si/SiO_2 substrates with interdigital Pt-electrodes. Relative dense and uniform layer of WO_3 nanoparticles was obtained, as shown in Fig. 1(a,b). The manufactured structures were used as resistive gas sensors at 220 °C for NO gas. The response of the sensor was visible even at 2 ppm of NO, as shown in Fig. 1(c). In this measurement, the sensor signal drifts initially. This could be avoided by keeping the sensor at 220 °C for extended period before the measurements. Sensitivity of the sensor was defined as a value $[G_{NO}\text{-}G_{air}]/G_{air}$, G_{NO} and G_{air} are the conductance of the sensor in NO-air mixture and in air, respectively. The sensor was observed to have nonlinear sensitivity, as shown in Fig. 1(d), with the highest relative sensitivity at lower concentrations.

3. Gravure-printed resistive WO_3 nanoparticle gas sensor

Another type of resistive gas sensor was manufactured by gravure-printing WO_3 nanoparticles onto metal electrodes on a flexible polyimide Kapton HN foil, as shown in Fig. 2(a). The nanoparticles were dispersed in solvent together with binders and surfactants to obtain printable inks with 30-40 wt% WO_3 concentration. The printed layer was dried in an oven at 250 °C for 2 h. The sensitivity to NO gas was

determined by measuring the printed layer conductance at different gas concentrations and temperatures, as shown in Fig. 2.(a). The printed sensor gave a clear response to NO even at 5 ppm. The response improved with increasing gas concentration and chamber temperature. In addition, the increase in the nanoparticle content of the ink, ink layer thickness, and layer coverage improved the sensor performance.

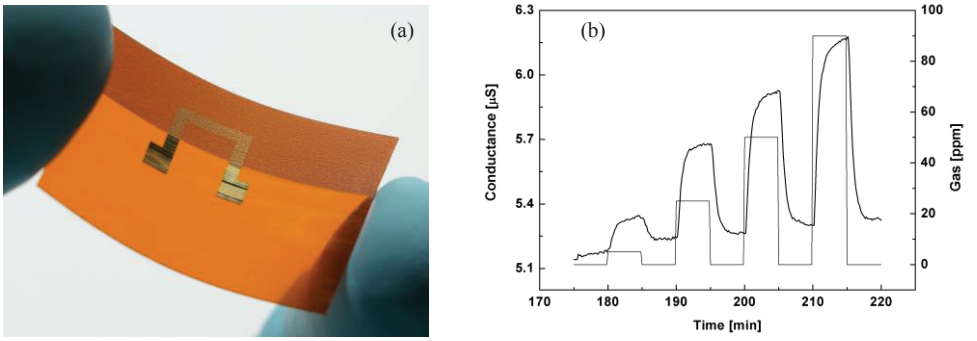


Fig. 2. (a) Gravure-printed resistive gas sensor on a flexible plastic foil with interdigital metal electrodes and (b) its response to NO gas of different concentrations in air buffer gas at 200 °C.

4. Inkjet-printed capacitive gas sensor based on solid electrolyte

In addition to resistive gas sensors, also capacitive gas sensors were fabricated. Their main advantage is ability to function without heating (at room temperature). In this case, the sensor represented a capacitor formed by a proton-conducting layer of solid electrolyte deposited on an oxidized (SiO_2) surface (200-nm-thick) of a silicon substrate. Prior to deposition, the electrolyte (mixture of $H_3PW_{12}O_{40}$ and PVC) was diluted in distilled water and filtered through a 0.2-um filter. The whole structure was sandwiched between 15-nm-thick platinum top and 150-nm-thick aluminum bottom electrodes. Tests were performed in hydrogen with concentration of 100-2100 ppm in synthetic air as carrier gas at 20-25 °C. The change in capacitance was measured at frequencies 1-100 kHz. Typically, clear response was observed already for 100 ppm concentration of H_2, which was the only gas that sensor was sensitive to, as is shown in Fig. 3.

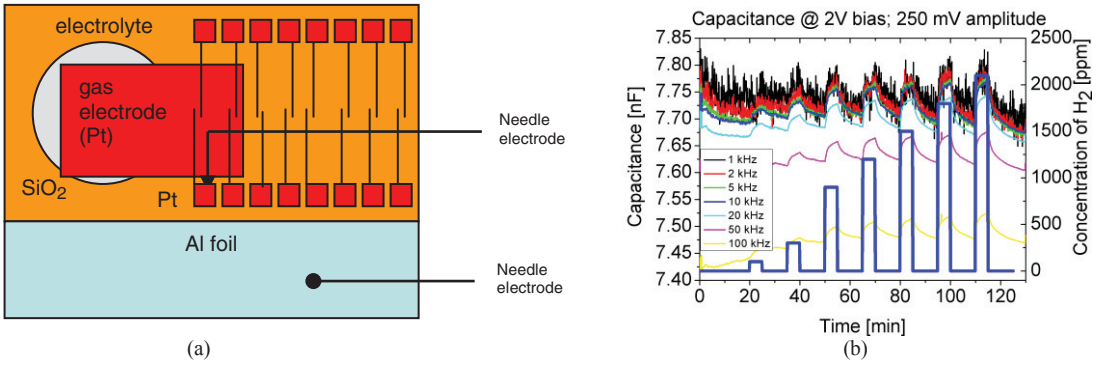
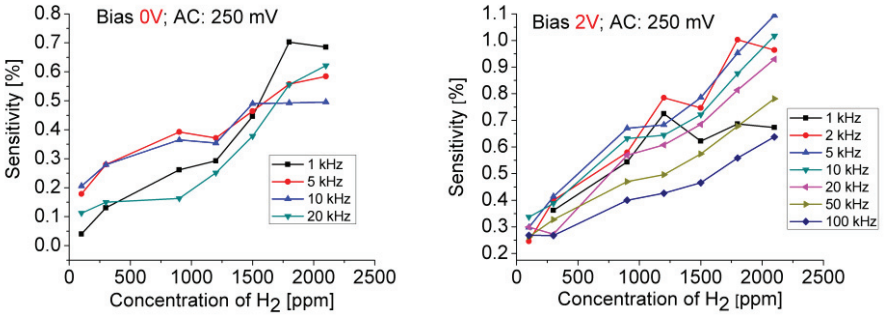


Fig. 3. (a) Outline of the capacitive sensor and (b) sensor response to the H_2 at 2 V constant bias and 250 mV amplitude (frequencies applied: 1-100 kHz).

It was found that the signal, i.e. change of capacitance, is small and noisy at lower frequencies of 1-2 kHz but increases at higher frequencies of 50-100 kHz. In order to reveal sensitivity of the sensor on the H_2 concentration, a value $[C_{max}-C_{min}]/C_{min}$ was calculated; C_{max} is the maximum value of capacitance in presence of hydrogen, C_{min} is the minimum value of capacitance in the absence of hydrogen, for one measurement cycle of H_2 injection and successive purging with synthetic air. As it is shown in Fig. 4, the sensitivity depends not only on the H_2 concentration and frequency but also on the bias applied. Higher bias voltage and gas concentration within the tested limits led to higher sensitivity. Optimal frequencies were found to be 5-20 kHz.

Comparing manufactured electrolyte-based capacitive sensors with nanoparticle-based resistive gas sensors, it was concluded that the capacitive sensors had much lower sensitivity (1% or lower) and higher sensing limit (100 ppm) than the resistive ones (hundreds % and units ppm, respectively). Nevertheless, they can be designed to be more selective, like in our case to H_2, and are able to work at room temperature. Possible ways to overcome the mentioned weaknesses are to decrease the thickness of the deposited electrolyte layer.



(a) (b)

Fig. 4. Sensitivity of the capacitive sensor towards different levels of H_2 at bias (a) 0 V and (b) 2 V for varied frequencies.

5. Conclusions

Three different types of printed gas sensors were successfully demonstrated. Printing is concluded to be cost-effective method for gas sensor preparation. It has environmental benefits, since very little waste of sensing material is produced. The process temperatures during printing are at the scale of room temperature, while most of the other gas sensor preparation methods demand elevated temperatures. Printing is a promising fabrication method for large-scale production of gas sensors.

Acknowledgements

Financial support of TEKES (Segase projects) and Academy of Finland (RoCaNaMe) is acknowledged. J.K. acknowledges Graduate School of Infotech Oulu (Finland), the Riitta and Jorma J. Takanen foundation and the Emil Aaltonen Foundation. N.H. acknowledges NGS-Nano graduate school (Finland). G.T. acknowledges the academy researcher post received from the Academy of Finland.

References

[1] Akiyama M, Tamaki J, Yamazoe N. Tungsten oxide-based semiconductor sensor highly sensitive to NO and NO_2. *Chem Lett* 1991;**20:**1611-4.