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The gas sensing properties of porphyrins-coated laterally grown ZnO nanorods

Y. Sivalingam[a], E. Martinelli[a], L. Businaro[b], A. Gerardino[b], L. Maiolo[b], A. Catini[a], G. Pomarico[c], F. Basoli[c], R. Paolesse[c], C. Di Natale[a,*]

[a]*Department of Electronic Engineering, University of Rome Tor Vergata, Rome, Italy*
[b]*CNR-Institute for Photonics and Nanotechnologies, Rome, Italy*
[c]*Department of Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy*

Abstract

Porphyrins coated ZnO is an interesting material where the exposure to light and gas may cooperate to modulate the respective sensitivities. In this work, the gas sensing properties of porphyrins functionalized laterally grown ZnO nanorods are introduced. The porphyrin layer incompletely coats the semiconductor surface in order to keep both ZnO and porphyrins in contact with analyte. It is known that UV light may prompt the chemical sensitivity of ZnO replacing the high temperature condition. Here we demonstrate that because of the photo-injection of electrons from porphyrin to the ZnO, the same impact could be acquired with visible light.

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Keywords: ZnO nanorods; Lateral growth; Porphyrins; Photoinjection.

1. Introduction

It is known that the conductivity of porphyrins-coated ZnO nanorods is influenced by adsorbed molecules and visible light illumination [1]. Noteworthy, the exposure to visible light greatly modulate the sensitivity and the selectivity of the surface voltage [2,3]. In spite of simplicity, hydrothermal growth requires a seed layer that incase

* Corresponding author. Tel.: +39672597348; fax: +3962020519.
E-mail address: dinatale@uniroma2.it

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of planar electrodes may hinder the real conductivity of the nanorods. This drawback can be avoided patterning the seed layer in the shape of the electrode. The application of the hydrothermal growth achieves a network of nanorods interconnecting the two electrodes.
In this paper, we report on the fabrication of a low cost and room temperature gas sensor device based on a laterally grown ZnO nanorods synthesized by hydrothermal route. The synthesized ZnO nanorods were functionalized using monocarboxy TPP. In this work, the usefulness of monocarboxy TPP functionalized ZnO nanorod photo activated gas sensing behaviour in dark and visible light illumination was investigated.

2. Experimental

2.1. Seed layer patterning

To realize practical porphyrins-functionalized ZnO nanorods based gas sensor arrays, good contacts are required on both ends of the nanorods. 1 µm spaced electrode fingers were obtained by means of electron beam lithography of the patterns on a COP33/PMMA bilayer film followed by sputter deposition of 300nm ZnO and of 100nm Cr as capping layer and liftoff process.

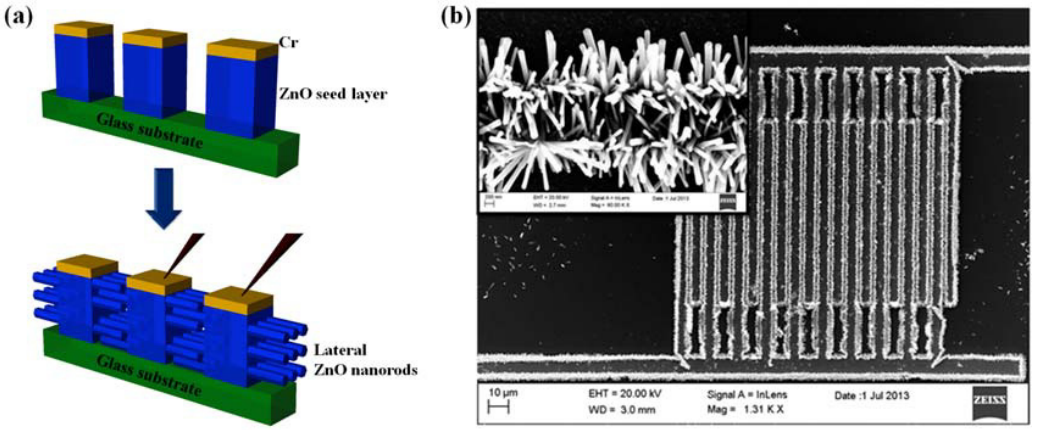

Fig. 1. (a) Scheme of lateral grown ZnO nanorods. (b) FESEM image top-view of the sensor. In the inset the magnified view of the space between the electrodes.

The reason to choose the COP33/PMMA bi-layer dwells in the thick ZnO film deposition which requires the need to achieve inverse "V" shapes in the resist layer for the correct removal of the excess material deposited during the sputtering process (Fig. 1a).

2.2. ZnO nanorods growth and porphyrins-functionalization

Hydrothermal method was applied to grow C-axis laterally grown nanorods. Chromium layer was served as the growth barrier of vertical ZnO nanorods. The final structure is shown in figure 1b. Noteworthy a number of nanorods may grow on the edge of the vertical structure. The ZnO nanorods were functionalized by drop casting deposition of a free base tetraphenylporphyrin terminated with a carboxyl group to promote the adhesion to the ZnO surface.

3. Results and Discussions

Figure 2 shows the I/V curve in dark and under the visible light provided by a white LED. Being the ZnO transparent to the visible light, the photoconductivity is only due to the porphyin absorbance. However, the small

photocurrent indicates a non complete coverage of the ZnO surface.

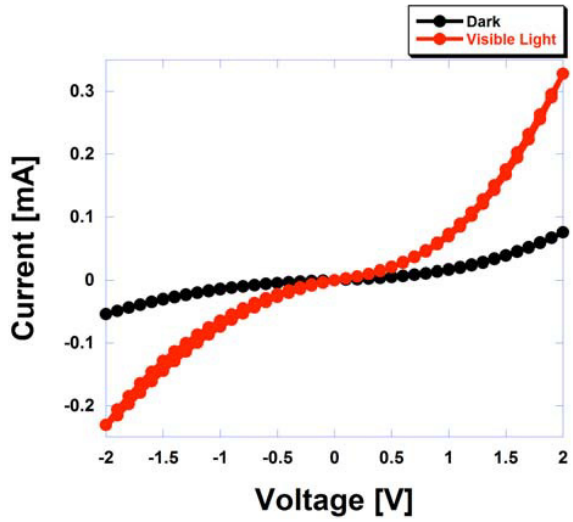

Fig. 2. I-V curves of porphyrin coated ZnO nanorods in dark and under visible light.

Figure 3 shows the conductivity variations, at room temperature, due to the exposure to a sequence of ethanol diluted in nitrogen gas.

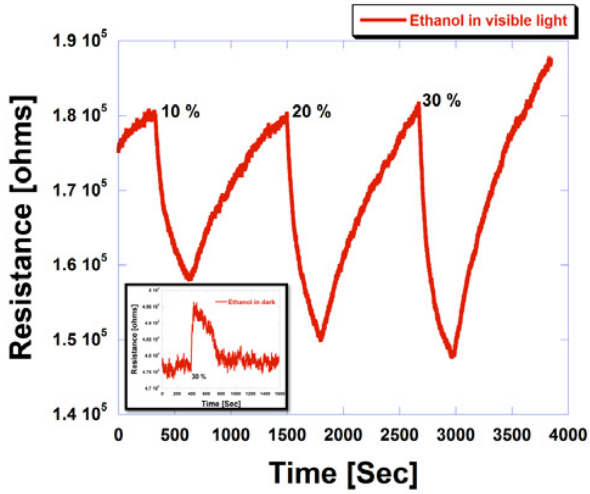

Fig. 3. Sensor resistance in visible light measured at growing concentrations pulse of ethanol at 10%, 20%, and 30% of saturated vapour in N2. In the inset the response to 30% of saturated vapor pressure in dark.

This effect may be explained considering that the ZnO surface is partially covered by the porphyrin film and then the analyte interacts both with the porphyrin and the ZnO. In the dark the sensitivity of the sensor is mainly due to the interaction with the porphyrins. The exposure to light enriches the ZnO of photoinjected electrons and changes the surface reactivity prompting the sensitivity to ethanol. The same effect can be observed under UV light [4].

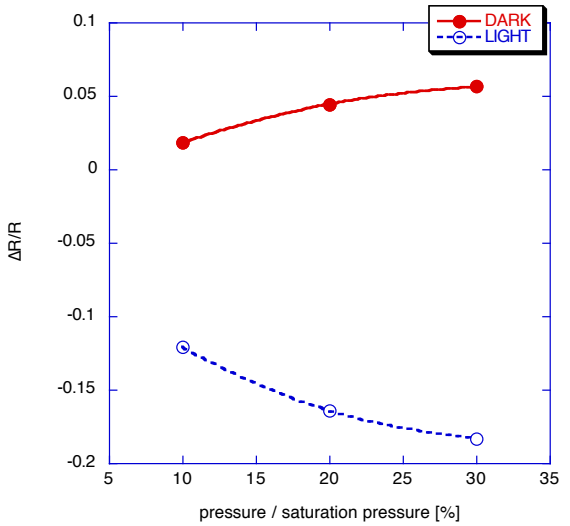

Fig. 4. The response curve plots the relative resistance change as a function of the analyte concentration.

Here, due to the porphyrin photoinjection the ZnO activation is driven by visible light. The effect of the illumination can be appreciated in figure 4 where the sensor response versus ethanol concentration in dark and under white light is plotted.

4. Conclusion

A photo-activated gas sensor based on hydrothermally synthesized and monocarboxy TPP functionalized laterally grown ZnO nanorod device have been developed. The change of the resistance showed when the sensor is exposed to a pulse of ethanol in dark and under visible light illumination. The light enhanced gas sensing behaviour was observed. The relative resistance shift as a function of the concentration showed the nonlinear behaviour of specific adsorption processes, when the number of adsorption sites is limited. It is interesting to observe that in gas and in light the exposure to ethanol results in an opposite change of the resistance, hence photo-activation introduce a further degree of freedom for gas sensor array development.

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