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Drift correction in a porphyrin-coated ZnO nanorods gas sensor

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Abstract

Photoconductivity and gas sensitivity cooperate in porphyrins coated ZnO nanostructures. However, in organic coated semiconductors the former is regulated by a number of mechanisms, involving the charge transfer in the organic layer. Since organic layers are poor conductors these processes are quite slow and the sensor may exhibits a long time drift before to be operative as gas sensor. In this paper we show that under light modulation, the carrier frequency component of the signal is free of drift and it can readily indicate the interaction with volatile compounds.

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Keywords: Porphyrin-ZnO hybird, VOC sensor, Light modulation;

1. Introduction

It has been recently demonstrated that porphyrins coated ZnO nanorods can sense volatile compounds at room temperature and that the sensors behavior, in terms of sensitivity and selectivity, is largely modulated by the visible light absorbed by the porphyrin layer [1]. However due to the limited mobility of organic layers, the photoconductive response of these hybrid materials is slow. Then, when the sensor is illuminated by a continuos light source, the electric resistance shows a long term drift that in some case can totally hinder the response to changes of the gas concentration. A slow drift of the sensor baseline, even if at smaller time scales, is frequently observed in temperature activated metal-oxide semiconductors. To this regards, a number of studies evidences that

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baseline drift and even sensors unreproducibilities are substantially mitigated if the sensor temperature is modulated around baseline value [2]. This parallel between temperature in metal-oxide semiconductors and light in organic-inorganic hybrids prompted us to study the effects of light modulation in porphyrins-ZnO hybrid materials.

2. Experimental

Chemoresistors based on porphyrin coated ZnO nanorods were fabricated onto glass substrates. The couple of electrodes and the seed layer precursor of the hydrothermal growth of ZnO nanorods have been patterned by a Microdrop equipment (nozzle diameter: 70 μm). The electrodes were deposited from a silver solution in a polar solvent with 30.7 % of metal content (ANP Silverjet DGP-40LT-15C from Advanced Nano Products Ltd, South Korea). The seed layer for the ZnO growth was a solution of zinc acetate in ethylene glycol.
ZnO nanorods were grown with a standard hydrothermal growth applied to the seed layer [3]. The method provided a forest of vertical c-axis oriented ZnO nanorods. The nanorods were then functionalized by a Zn tetraphenylporphyrin bearing a peripheral carboxylic group. Fig. 1 shows the fabrication steps. The final aspect of the sensor is shown in Fig. 2. Noteworthy, the vertical nanorods help to homogenize the porphyrin spot avoiding the "coffee rings" occurring in drop casting [4].
The sensor has been biased by a current source and the voltage was measured. The sensor was illuminated by a white LED light, whose spectrum fits with the assumption that the photoconductive effects are due to light absorbance in the porphyrin layer. The light modulation was achieved by a mechanical chopper. The measurement setup is illustrated in fig. 2.

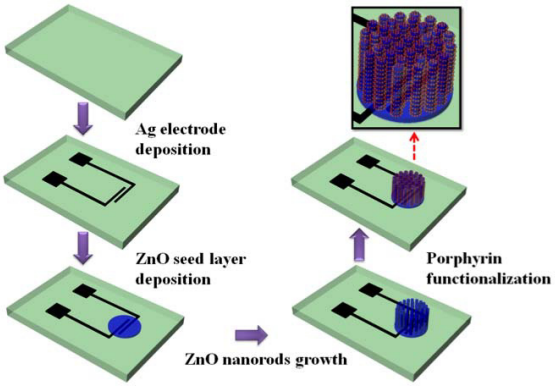

Fig. 1. Construction scheme of the porphyrin coated ZnO nanorods sensor.

3. Results and discussion

Figure 3 shows the voltage spectrum. Due to the square wave modulation, the fundamental (20 Hz) and third harmonic (60 Hz) are visible. The spectrum also shows the d.c. component of the signal given by the time average of the light intensity. Figure 4 shows the magnitude of the d.c. and the modulated components. For the sake of clarity, these quantities, occurring at different amplitudes, are normalized by the first measured value. The sensor was exposed to a repeated pulses of ethanol vapors (with partial pressure of 1.2 kPa) in nitrogen gas carrier. The d.c component is slowly drifting under the effect of the d.c. illumination component and the photoconductivity drift hides the sensitivity to ethanol. On the other hand, the modulated component at the fundamental frequency illustrates the adsorption and desorption of ethanol, with a complete removal of drift. These results suggest the existence of at least two mechanisms in photoconduction, one at very low frequency, probably due to the very slow mobility of charges in the porphyrin layer. The modulation of light is then a viable method for an efficient design and operation of

organic coated metal-oxide semiconductor gas sensors.

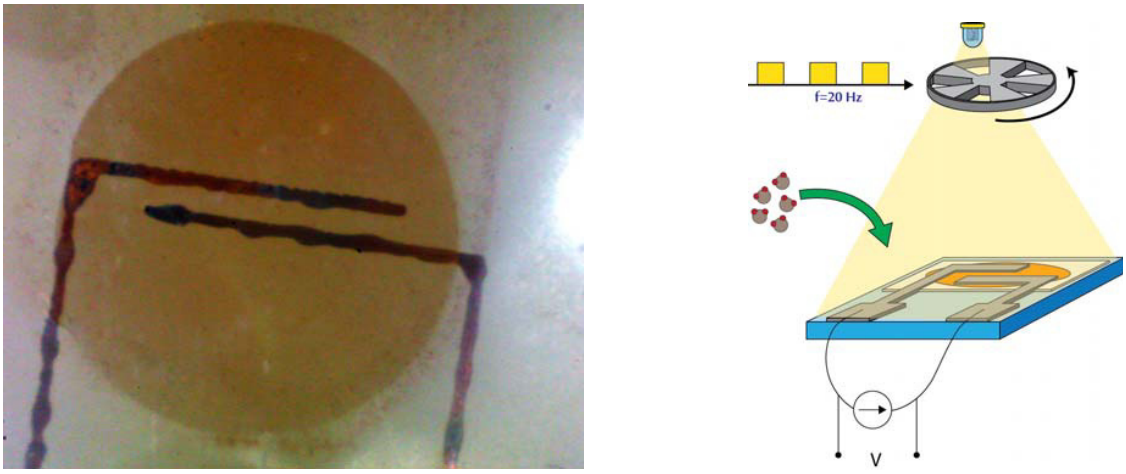

Fig. 2: Left: picture of the sensor active region. The distance between the electrodes is about 300 µm and the lenght of the electrodes is approximately 3 mm. Right: Sketch of the experimental setup The light of a white LED is modulated by a mechanic chop providing a 20 Hz square wave modulation of the light. The sensor is contamporaneously exposed to vapors of volatile organic compounds.

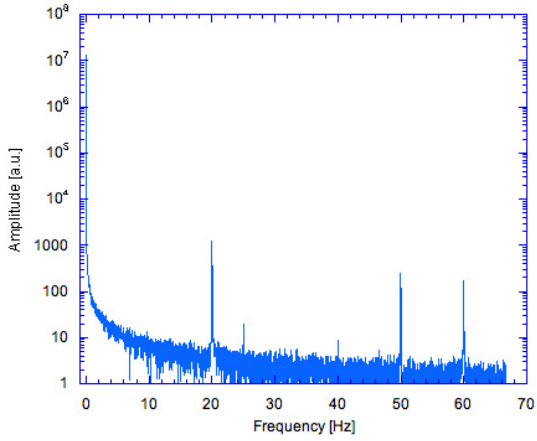

Fig. 3. Spectrum of the voltage drop across the sensor biased with a constant current. In figure, besides the d.c. component, the fundamental (20 Hz) and the third harmonic (60 Hz) are visible. The component at 50 Hz is the usual power network disturbance.

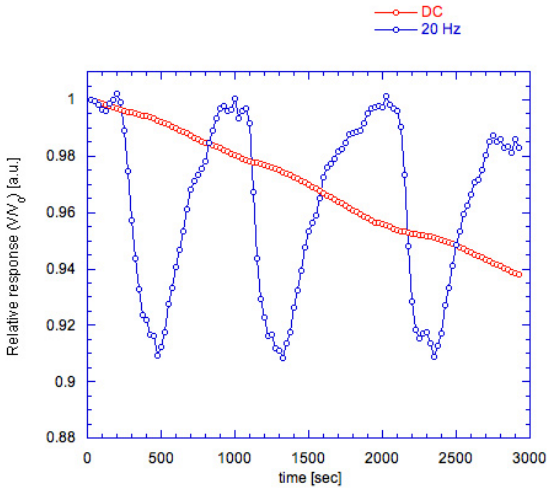

Fig. 4. Comparison of the signal components at d.c. and 20 Hz. As a consequence of repeated pulses of ethanol in nitrogen gas carrier.

4. Conclusions

Light modulation makes possibile to avoid the long-term drift due to the slow stationary processes of charge migrations from the surface of nanostructures to the electrodes.

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