The gas sensitivity of Porphyrins coated ZnO nanorods

Yuvaraj Sivalingam[1], Gabriele Magna[1], Eugenio Martinelli[1], Roberto Paolesse[2], Corrado Di Natale[1]
1 Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Roma
2 Department of Chemical Science and Technology, University of Rome Tor Vergata, Via Ricerca Scientifica, 00133 Roma

The prospect of tailoring the physicochemical properties of semiconductors crafts a fascinating scenario to develop ad hoc materials for specific applications. In this regard, the surface coverage of solids with organic/inorganic sensitive layers is a common method to provide new features without undermining the bulk traits [1]. Concerning organic-semiconductor coupling; a large number of metal-oxides have been functionalized with a multitude of carbon-based molecules such as polymers, phthalocyanines, porphyrins and biological elements [2]. In the midst of this crowd, the combination of ZnO nanorods and porphyrins is enticing because of the electron transport properties and the facile immobilization of the molecules onto the semiconductor surface [3]. In fact, the wide use of porphyrins like sensitive layer is due to their variety of possible chemical interactions, the established structure-sensitivity relationship [4] and the match of their photo-absorption properties to the solar spectrum. On the other hand, zinc oxide provides the possibility to fabricate ordered vertical structure with high surface/volume ratio by a simple and low-cost procedure.

Recently we found that the conductivity of porphyrins coated ZnO nanorods is influenced both by adsorbed molecules and visible radiation and that the exposure to white light greatly enhances the gas sensitivity and selectivity [5]. Many factors can be tuned in order to improve the ultimate performance of material such as the porphyrins structure or the crystal plane orientation of semiconductor surface [6]. For example, we recently shown the influence of metal-coordination complex on photovoltage of ZnO nanorods coated with porphyrins under different chemical environments has been evaluated [7]. Obviously, this is only one aspect of the overall functionalization process. In fact, the architecture of porphyrin arrangement plays a crucial role in the diffusion and solubility properties of analytes [8]. In recent years, the development of nanoporous or nanostructured materials aimed at maximize surface/volume ratio has been a hot topic in many fields like photovoltaic application (e.g. Dye-Sensitized Solar Cells) and chemical sensors.

Nevertheless, if the solar or chemical sensitive dye does not completely cover the underlying surface this effort could result vain. In this context, solution coating does not always provide a uniform coverage of the ZnO surface and as a consequence the potentialities of the porphyrin-ZnO material are not fully exploited.. Herewith, a hybrid material growth recipe where porphyrins are added directly to the precursor solution of the hydrothermal method is illustrated. The basic idea of the proposed procedure is to functionalize the material progressively during the nanorod formation.

The comparison of the sensing properties under different illumination and chemical environment of this functionalized materials with respect to solvent coated nanorods has been performed measuring the contact potential difference with the Kelvin probe. The Kelvin probe offers a simple solution to evaluate the surface properties of organic and inorganic materials. It has been used for instance to estimate the band bending at organic/semiconductor interface [9].

The gas sensitivity has been investigated exposing the two materials, hybrid and solution coating nanorods, to different concentrations of six organic compounds (three alcohols and three amines) in dark and under white illumination. The variation of the Contact Potential Difference (CPD) show that in the case of the hybrid material the exposure to visible light enhances the response to reducing agents while in casting coated material the enhancement is observed only for strongest electron donor molecule. Finally, the principal component analysis suggests that the light modulation could improve both the selectivity of a single sensor and the discrimination performance of an array of CPD transducers based on such functionalized materials.

References

[1] M. A. Filler, S. F. Bent, *Progress in Surface Science*, 73 (2003) 1–56
[2] M. A. Neouze and U. Schubert, *Monatsh Chem*, 139 (2008) 183–195
[3] H. Saarenpää et al. *J. Phys. Chem. C*, 116, (2012) 2336–2343
[4] C. Di Natale et al *Sens. Actuators B* 68 (2000) 319–323.
[5] Y. Sivalingam et al. *J. Phys. Chem. C*, 116 (2012) 9151–9157.
[6] R. Gonzalez-Moreno et al. *J. Phys. Chem. C* 115 (2011) 18195–18201
[7] Y. Sivalingam et al. *J. Mater. Chem.* 22 (2012) 20032-20037
[8] C. Di Natale et al. *Materials Today* 13 (2010) 46-52
[9] H. Ishii et al. *Phys. Stat. Sol.* 201(6) (2004) 1075–1094.