

Systematic study of inorganic functionalization of ZnO nanorods by Sol-Gel method

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Abstract. A systematic study of the inorganic surface functionalization of ZnO nanostructures by sol-gel method is shown. We have emphasized on the evolution of morphology properties of samples as a function of functionalization parameters. In addition, the effects on thermal stability and some optical properties of samples are discussed.

1. Introduction

During many decades gas sensors have been required for many practical applications, such as explosives and drugs detection, control of air quality and food safety. In addition, more recently these devices have attracted a lot of attention in the medical field. This is because gas sensors can be used to make medical diagnosis and monitoring of some clinical treatments by detecting the different organic volatile compounds (OVCs) content in human breath [1,2]. In the last decades a wide diversity of gas sensing technologies has been developed among them, it is worth noting the gas sensors based on the variation of electrical properties of metal oxide semiconductors (MOS). This is due to MOS based gas sensors offer several technological advantages, e.g., direct electronic transducing, high sensitivity, low cost and suitability to portable devices fabrication [3,4].

In the last years, different investigations have been established in order to optimize some essential properties of MOS based gas sensors such as sensitivity, selectivity and work temperature [3,5]. In this regard, several studies have demonstrated that the sensitivity of these devices can be significantly enhanced by using nanostructures instead thin films [6,7]. However the effective gas response of MOS nanostructures depends on their shape and size. Among a variety of OMS nanostructures, quasi-1D nanostructures (nanowires, nanorods and nanobelts) have shown the best gas response because these nanostructures exhibit higher surface-volume ratio which favours absorption and desorption process of gas molecules on the material surface [6,7]. Nevertheless, in spite of these substantial advances, the enhancing of sensitivity and selectivity parameters continues to have key importance in research and development of gas sensors [5,6]. In this context, surface functionalization of sensing materials has proved to be a promising path to improve these gas sensors characteristics. In the case of MOS nanostructures, functionalization process has been usually done by coating the nanostructures surface with noble metals (nanoparticles or thin films) [8,9]. Noble metals are used to coat OMS surfaces because they are high-



effective oxidation catalyst and this characteristic can enhance the reactions on gas sensor surfaces. Although some sensor properties can be improved using this kind of surface modification, e.g., sensitivity [8,9], new functionalization routes are still required in order to enhance additional gas sensor properties as selectivity. Indeed, much effort is doing nowadays with the aim of achieving effective functionalization process with accurate control, reliability, thermal stability and low cost.

In view of the above, in this work we present a systematic study of inorganic surface functionalization of ZnO nanorods. Samples were TiO₂ coated by low-cost method. We have emphasized on the thermal stability and procedure of surface functionalization in order to allow a suitable control on the morphological and physical properties of functionalized nanostructures. ZnO and TiO₂ were selected due to their interesting properties related to gas sensing (thermodynamic stability, surface chemistry, humidity sensitive, suitable electronic configuration and special catalytic activity) which can be enhanced in combination [10]. Moreover ZnO exhibits additional interesting properties such as piezoelectricity, biocompatibility and non-toxicity, making the ZnO nanostructures attractive candidates for biomedical and biosensor applications [11].

2. Experimental

Vertically aligned ZnO nanorods were grown by metal organic chemical vapour deposition system without catalyst on c-sapphire substrates according to the procedure described in our previous work [12]. TiO₂ functionalization was done by wet chemical method using titanium, acetic acid and propylene glycol precursors. In this experiment, a 0.1M aqueous ethanol solution of titanium was kept under constant stirring using a magnetic stirrer for 2 hours at 100°C. Simultaneously aqueous ethanol solution of acetic acid, polyvinyl alcohol and distilled water was also prepared in the same way by stirring during 10 minutes. Both solutions were carefully mixed using magnetic stirrer for 5 minutes at room temperature and subsequently deposited on ZnO nanorods by spin coating. The thickness of TiO₂ layers was obtained by making several coatings on nanorods (e.g., 2, 4 and 6). After each coating, samples were dried at 200°C during 10 minutes. Coated samples were finally annealed between 500-600°C during 2 hours to reach the required TiO₂ structural phase.

In accordance with the samples characterization, morphologies of samples were examined by scanning electron microscopy (SEM-Jeol JSM 5600). Thermogravimetric analysis was performed using a TA Instruments 2050. For these measurements, the samples were heated at rate of 10°C/min and pure Ni gas (99.999%) with a 60mL/min flux was used for all experiments. Crystalline structure was analysed by powder X-ray diffraction (Bruker, D8-Advance) while optical properties were evaluated by UV-visible spectrophotometer Shimadzu UV-2600 equipped with an integrating sphere and 300-800nm wavelength range.

3. Results and discussion

The influence of spin-coating parameters on morphology and optical properties of functionalized ZnO nanorods have been evaluated. This was done by means of systematic studies by varying coating parameters such as spin frequency, number of coatings (i.e., film thickness) and annealing temperature of the deposited TiO₂ layers (see Table 1).

Typical 2 θ X-ray diffraction (XRD) scans belong to pristine ZnO nanorods and TiO₂ layers are shown in Figures 1(a) and 1(b), respectively. For pristine ZnO nanorods samples, the diffraction peaks at 34.5 and 71 were indexed to (0002) and (0004) crystal planes of the wurtzite hexagonal structure of ZnO (lattice constants of $a=0.324982\text{nm}$ and $c=0.520661\text{nm}$). This diffractogram evidences clearly the preferential c-orientation of nanorods as it is usually reported in literature. Otherwise, exhibited peaks in XRD of TiO₂ layers were ascribed to anatase structure, which is known as the more suitable phase of TiO₂ for gas sensor applications [13]. Figure 2 exhibits the thermogravimetric (TG) measurements of samples

before and after functionalization process. For pristine and functionalized samples TG analysis reveals insignificant mass-loss ($\sim 0.1\%$) between room temperature and 400°C . These results show that our samples present only minor desorption of the surface-adsorbed water and the chemical residual species, which can remained after the TiO_2 layers growth. In addition, because chemical reactions between ZnO and TiO_2 are no evidenced in TG scans, TiO_2 functionalization can be seen as thermodynamically stable into the studied temperature range, which is included in the work temperature range of the most gas sensors based on OMS materials [6,7].

Table 1. Deposition parameters used for functionalized samples.

| Sample | Spin Frequency (rpm) | Annealing Temperature ($^\circ\text{C}$) | Number of Coatings |
|----------|----------------------|--|--------------------|
| FZnO1-2C | 2000 | 600 | 2 |
| FZnO2-4C | 2000 | 600 | 4 |
| FZnO3-6C | 2000 | 600 | 6 |
| FZnO4-2C | 1000 | 500 | 2 |
| ZnO5A | ---- | 600 | 0 |

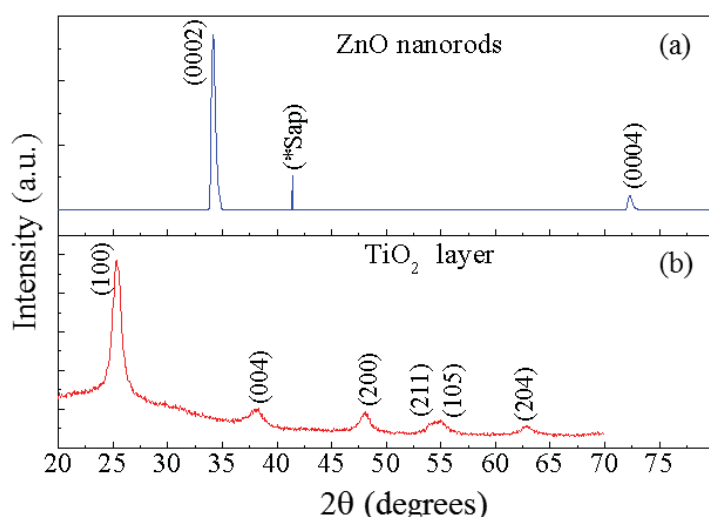


Figure 1. Typical 2θ X-ray diffraction scans belong to (a) ZnO nanorods and (b) TiO_2 layers. The diffraction peak labelled with a star comes to c-sapphire substrate of ZnO nanorods samples.

Morphology properties of samples were examined by scanning electron microscopy (SEM). Figure 3 illustrates the typical SEM images of pristine ZnO nanorods (left column) and functionalized ZnO nanorods (right column). For pristine samples, SEM images show vertically aligned ZnO nanorods with hexagonal facets. Nanorods exhibit diameters between 150nm and 850nm and lengths between $7\mu\text{m}$ and $15\mu\text{m}$. In the case of functionalized samples, samples have been analyzed taking in account the thickness of deposited TiO_2 layers, namely, sample with 2 coatings (FZnO1-C2, Figures 3(g)-(h)); sample with 4 coatings (FZnO2-C4, Figures 3(i)-(j)) and sample with 6 coatings (FZnO3-C6, Figures 3(k)-(l)). TiO_2 layers with smoothed but cracked surface can be observed in the top-view SEM images of all functionalized samples. However, vertically aligned ZnO nanorods are not present in samples with major number of coatings (4 and 6 times), see cross-view SEM images. Indeed, the analysis of results has allowed to determine that ZnO nanorods tend to be detached from the sample surface because spin-coating process and hence the fallen nanorods are agglomerated with TiO_2 layers (insets Figure 4(i) and Figure

4(j)). Moreover, the detaching of ZnO nanorods from surface sample, when TiO₂ films are spin-coated, can be the principal origin of layer cracking observed in our functionalized samples.

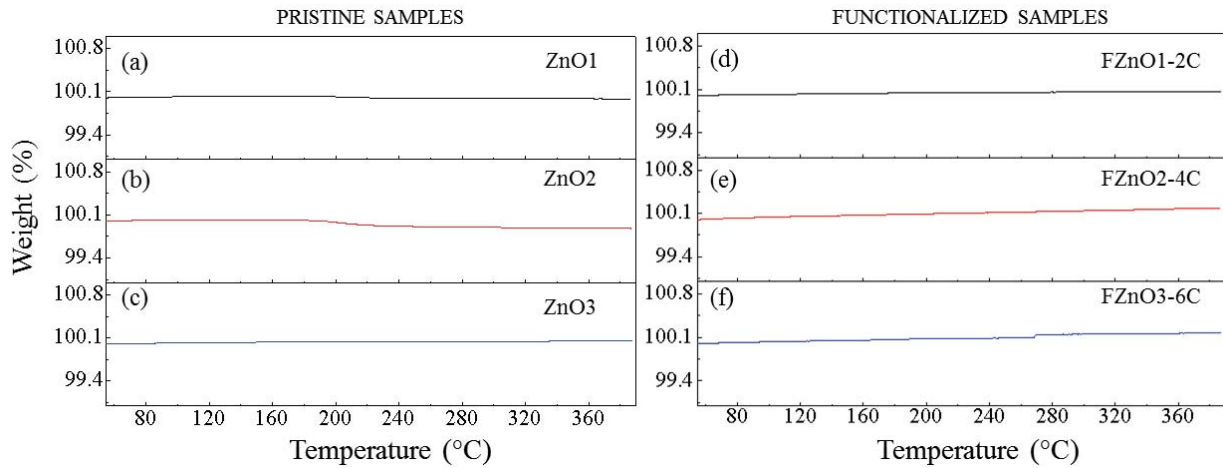


Figure 2. Thermogravimetry measurements of (a)-(c) pristine ZnO nanorods and TiO₂-coated ZnO nanorods (d) 2; (g) 4 and (f) 6 times.

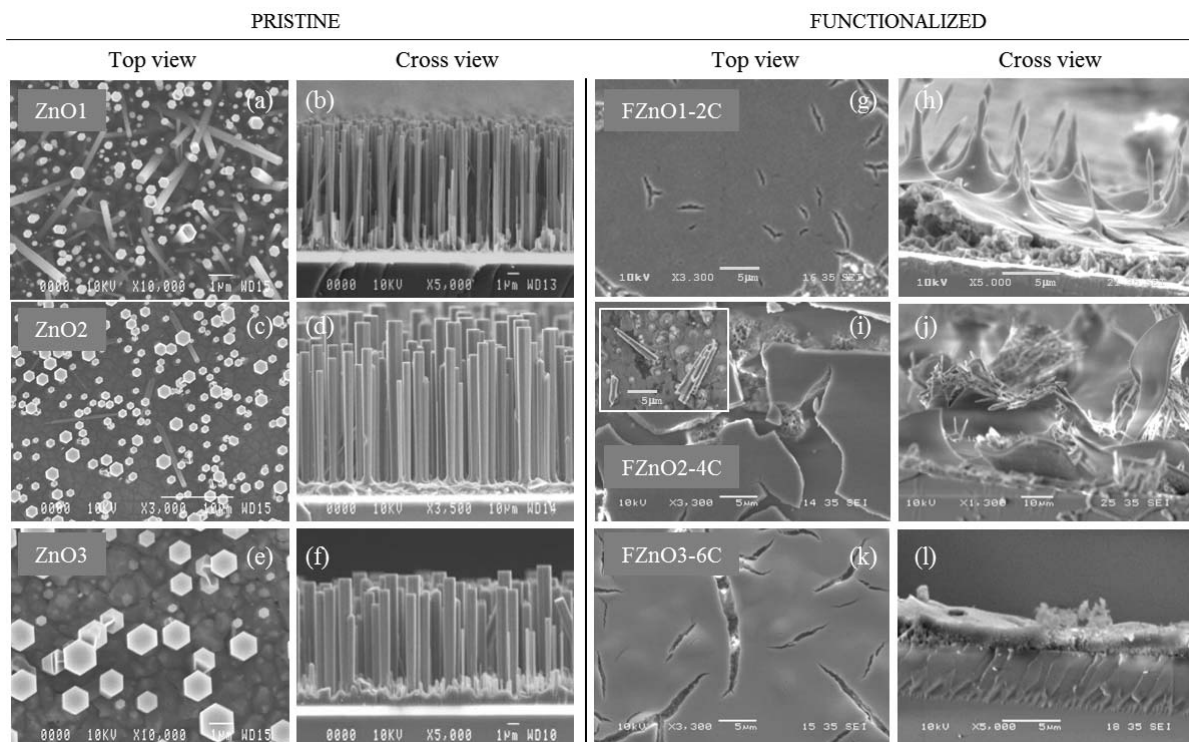


Figure 3. SEM images of (a)-(f) pristine ZnO nanorods and TiO₂-coated ZnO nanorods (g)-(h) 2; (i)-(j) 4 and (k)-(l) 6 times.

In this regard, our systematic study also has enabled to establish that this latter issue can be lessened by varying the spin process during layer deposition. SEM images of surface functionalized samples with minor number of coatings (2 times), i.e., sample with minor full rotation time, evidence that vertically aligned ZnO nanorods can remain on sample after Ti₂O coating, Figure 3(h). Similarly, Figures 4(a) and 4(b) shows that TiO₂ layer can be deposited on the top of nanorods arrays, without losing the vertical alignment of nanostructures, by halving the spin frequency parameter. The annealing process done to TiO₂ layers for its part has revealed to induce undesirable coalescence effects in ZnO nanorods. The analysis of pristine ZnO nanorods annealed between 500°C and 600°C, has shown this thermal procedure tends to favour the lateral growth of nanorods giving rise to a loss of self-assembly ZnO nanorods arrays and the characteristic high surface-volume ratio of nanorods, Figures 4(b) and 4(d).

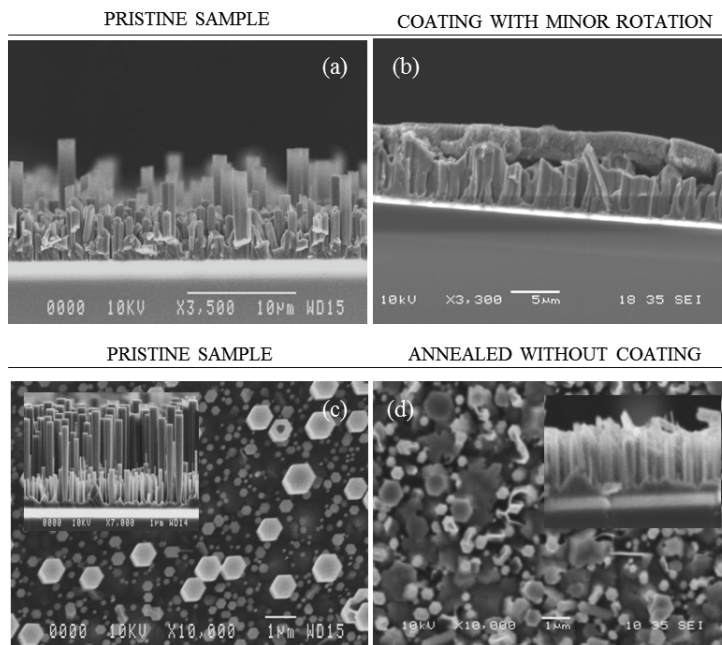


Figure 4. SEM images of pristine ZnO nanorods (a) and (c); TiO₂-coated ZnO nanorods with spin frequency at 1000 rpm (b) and ZnO nanorods annealed at 600°C.

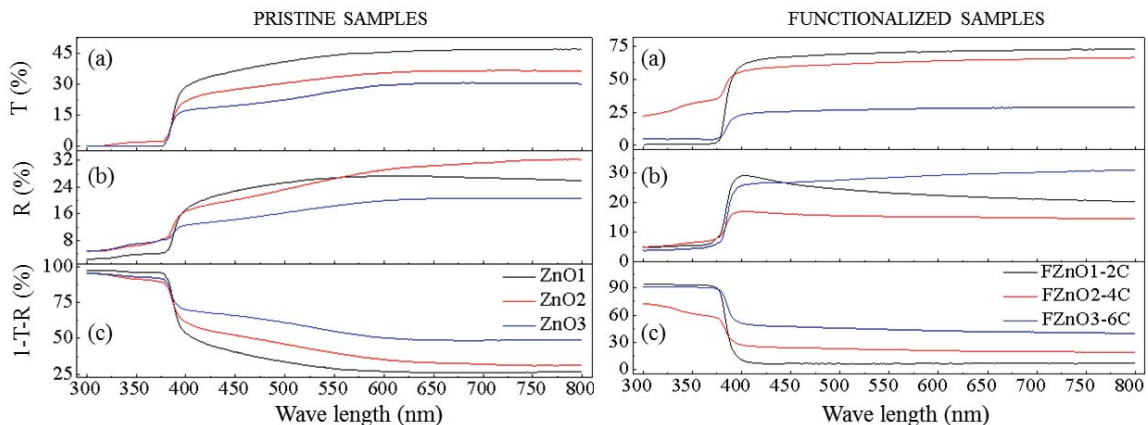


Figure 5. Spectra of transmittance (T), reflectance (R) and absorbance with included effect of scattering centers (1-T-R) for: (a)-(c) pristine ZnO nanorods; (d)-(f) TiO₂-coated ZnO nanorods.

Optical properties of pristine and functionalized ZnO nanorods have been also investigated. Transmittance and reflectance spectra of samples were acquired at room temperature using UV-vis spectrophotometer. Absorbance spectra were calculated from the transmittance data taken in consideration scattering centres due to ZnO nanorod arrays observed in our samples [14]. The transmittance, reflectance spectra in Figures 5(a)-(b) and calculated absorbance in Figure 5(c) for the different pristine samples, reveal a similar behaviour when the energy of excitation photons exceeds the ZnO band gap ($\lambda < 380\text{nm}$). The major variations of light transmittance, reflectance and absorbance from these pristine samples occur within visible light region ($400 < \lambda < 800\text{nm}$). This can be primarily attributed to the morphology differences between samples, that is, diameter, length, density (#nanorods/area) and vertical alignment of ZnO nanorods (Figures 3 (a)-(f)). In the other hand the transmittance spectra, for functionalized ZnO nanorods, displays major variations and a decrease in visible range. This behaviour is observed to be enhanced for the sample coated with the thickest TiO₂ layer (FZnO1-C6), Figure 5(d). We are certain of this transmittance decrease is caused because reduction of scattering centres in our functionalized samples according with the undergone detaching of ZnO nanorods. That is why the optical spectra of these samples seem to be principally governed by TiO₂ material.

4. Summary and conclusions

Vertically aligned ZnO nanorods were surface functionalized with TiO₂ layers by using optimized spin-coating parameters. Thermogravimetry measurements have allowed showing that TiO₂ functionalization is thermodynamically stable in a wide temperature range, 25-400 °C. The analysis of the functionalization process has enabled to conclude that coating conditions such as spin and annealing process have key importance in development of MOS nanostructures surface-functionalization by spin-coating method. Both parameters have shown to affect significantly some morphology properties of functionalized ZnO nanorods samples (vertical alignment and the aspect ratio (diameter/volume) associated directly with absorption and desorption process of gas molecules on MOS nanostructures surface.

References

- [1] Di Natale C, Paolesse R, Martinelli E, Capuano R 2014 *Anal. Chim. Acta* **824** 1
- [2] Righettoni M, Amann A, Pratsinis S 2015 *Materials Today* **18** 163
- [3] Chengxiang W, Longwei Y, Luyuan Z, Dong X, Rui G 2010 *Sensors* **10** 2088
- [4] Korotcenkov G 2007 *Mater. Sci. Eng. B* **139** 1
- [5] Liu X, Cheng S, Liu H, Hu S, Zhang D, Ning H 2012 *Sensors* **12** 9635
- [6] Barth S, Hernandez-Ramirez F, Holmes J D, Romano-Rodriguez A 2010 *Prog. Mater. Sci.* **55** 563
- [7] Arafat M M, Dinan B, Akbar S A, Haseeb A S M A 2012 *Sensors* **12** 7207
- [8] Wang D, Ma Z, Dai S, Liu J, Nie Z, Engelhard M H, Huo Q, Wang C, Kou R 2008 *J. Phys. Chem. C* **112** 13499
- [9] Ruiz A M, Cornet A, Shimanoe K, Morante J R, Yamazoe N 2005 *Sens. Actuat. B* **108** 34
- [10] Kalyamwar V S, Raghuwanshi F C 2013 *Adv. Mat. Lett.* **4** 895
- [11] Mahbubur Rahman Md, ASaleh Ahammad A J, Jin J-H, Jung Ahn S, Lee J-J 2010 *Sensors* **10** 4855
- [12] Montenegro D N, Souissi A, Martínez-Tomás C, Muñoz-Sanjosé V, Sallet V 2012 *J. Cryst. Growth* **359** 122
- [13] Tang H, Prasad K, Sanjines R, Levy F 1995 *Sens. Actuat. B* **26** 71
- [14] Fekete M, Ludwig W, Gledhill S, Chen J, Patti A, Spiccia L 2014 *Eur. J. Inorg. Chem.* **1** 75