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Highly sensitive and rapid NO_2 gas sensors based on ZnO nanostructures and the morphology effect on their sensing performances

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Abstract

ZnO nanostructures with different morphologies (nanoparticles, nanorods) have been synthesized using different methods including chemical vapor deposition (CVD) and Sol-Gel. The obtained ZnO nanostructures have been characterized with TEM, SEM, XRD and XPS. Thick films based on the prepared ZnO nanostructures were coated on alumina substrates fitted with gold electrodes and a platinum heater. The responses to NO_2 (≤ 1 ppm) of the different types of ZnO sensors have been studied at working temperatures ranging from 200 to 320°C at 50% of relative humidity. The effects of the synthesis method and the morphology of the ZnO particles on the electrical properties and sensing performances (responses, response and recovery times) of the sensors were demonstrated.

Key words: ZnO, chemical vapor deposition (CVD), sol-gel, screen-printing, NO_2 gas sensors, metal oxides.

Introductions

Zinc oxide is reported to be one of the most interesting semiconducting metal oxides used as a base material in different fields especially in gas sensors [1,2]. ZnO can be obtained with different morphologies depending on the synthesis routes. It was obtained under several forms such as, nanowires, nanorods, and nanoparticles [3,4]. In gas sensors field, the morphology plays an important role on the sensing performance (sensitivity, response and recovery times). In this work, ZnO nanostructures with different morphologies have been synthesized and characterized, highly sensitive and rapid NO_2 gas sensors based on the synthesized nanomaterials were prepared. The effects of the morphology and the synthesis routes on the sensing performances to NO_2 (from 100 ppb to 1 ppm) were studied.

Experimental

By Sol-Gel process, zinc oxide nanoparticles were prepared by adding 0.2 M of zinc acetate $Zn(CH_3COO)_2.2H_2O$ (Merck) to methanol (Merck) at room temperature under magnetic stirring until formation of a clear solution (pH= 5). The pH was adjusted to 11.5 by adding NaOH 1 M (Merck), the maturation time of the precipitate at pH 11.5 was varied from 48 hours (sample ***a***) to 7 days (sample ***c***). After maturation, the samples were washed by demineralized water several times, dried and annealed at 400°C in air. ZnO nanorods synthetized by hydrometallurgical process (sample ***d***) was used as received from REMINEX (Moroccan Company), while the sample (***b***) was obtained by CVD method as following: zinc metallic (Merck) was evaporated at 600 °C into tube furnace. The nitrogen and oxygen were used as carrier and reactant with flow rates of 100 and 50 sccm respectively. To prepare ZnO coatings, the samples were dispersed in terpineol using sonication [1], screen-printed on alumina substrate fitted with gold electrodes and then annealed in air at 400°C for 4 hours. The crystal structures of the samples were defined by X-ray diffraction at room temperature (Siemens D5000, and Germany) using CuK_α radiation. The morphologies were observed by TEM (Philips CM200 120 kV) and SEM (Philips XL20, 20 kV).

Results and discussion

The morphologies and the grain size of the obtained samples were controlled by using different synthesis methods under different conditions. The precipitation of zinc acetate in methanol at room temperature by adjusting the pH to 11.5 (the maturation time was 7 days) gave nanoparticles with a grain size in the range of 20-25nm nm. Alias et al. [4] have reported that the pH of the based-sol and the maturation time play important roles on the grain size of ZnO.

The sample (prepared by Sol-Gel) dried after 48 hours of maturation (sample ***a***) was a mixture of nanoparticles and nanorods with predominant presence of nanoparticles (Fig. 1(a)). While the sample dried after 7 days of maturation (sample ***c***) was homogeneous with a monodisperse population, the average particle size is about 25 nm (Fig. 1 (c)). The CVD is reported to be one of the methods allowing the synthesis of low dimensions ZnO nanostructures with different morphologies such as nanorods, nanowires, nanotetrapods, nanoeedles, and nanomultilegs [5-6]. In this work, following the parameters mentioned in the experimental part (evaporated of metallic zinc at 600 °C with flow rates of nitrogen and oxygen at 100 sccm and 50 sccm respectively, and under atmospheric pressure), the obtained ZnO nanoparticles were different to those reported by D. Barreca et al. [5], the nanoparticles have a spherical morphology with grain size of 20 nm.

The morphology of commercial sample (ZnO nanorods) was characterized by TEM as presented in Fig. 1 (image d). The diameter of the nanorods is about 30 nm.

The morphologies of the samples are summarized in Tables 1 and 2. The TEM images carried out on the samples after annealing in air at 400°C are shown on Fig. 1. As observed, the nanoparticles of all samples have an average particle size (or diameter size) in the range of 30 nm. Although the morphologies of the samples are modified, the XRD analysis confirms that the crystal phases are the same and attributed to wurtzite structure of zinc oxide (JCPDS 36-1451).

Gas sensing characterization

The electrical response of the sensors to NO_2 was measured in the sub-ppm level (≤ 1ppm) at 50% relative humidity; the sensors were heated in air for 24 hours before the test measurements. The data are shown on Fig. 2, the sensors with ZnO nanorods (***d***) and nanoparticles prepared by CVD (***b***) present high responses at the temperature range of 200-320°C compared to those prepared by Sol-Gel. The maximum responses (~10 and ~ 20) to 0.5 ppm NO_2 were observed at working temperature of 280 and 200°C for the sensors (***b***) and (***d***) respectively. Whereas for the sensors prepared by Sol-Gel ((**a**) and (**c**)), the working temperature has an insignificant effect on their responses (0.5 ppm; $R_g/R_a \leq 4$ for all temperature ranges). In term of response and recovery times, the sensors with ZnO prepared by sol-gel were shortest. These observations are shown on Fig. 2. (3). The sensors were exposed to 200-500 ppb NO_2 for repetition tests (5 minutes of each cycle); the data showed that the response and recovery times of the sensors based on ZnO prepared by CVD and hydrometallurgical are two times longer than those prepared by sol-gel. Even if the prepared ZnO nanostructures have similar dimensions (~30 nm), the performances of the sensors strongly depend on the synthesis method and the morphology. More experimental results and explanations will be presented and discussed.

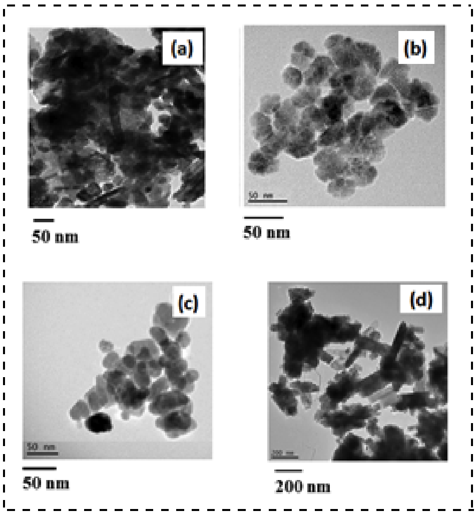

Fig. 1. TEM images of the samples synthesized via different methods summarized in the Tab. 2 (the dimension characteristics of the samples are summarized in the Tab. 1).

Tab. 1: Summary of the dimension characteristics of the sensors; (*) l: length of the nanorods; (**) d: diameter of the nanorods.

T / °C	Morphology	Particle size
(a)	nanoparticles/ nanorods	30 nm d = 30 nm* l = 100 nm**
(b)	nanoparticles	20 nm
(c)	nanoparticles	25 nm
(d)	nanorods	d = 50 nm l = 100 nm

Tab.2: Summary of the synthesis and characterization techniques.

T / °C	Synthesis method	Characterization
(a)	Sol-Gel	XRD/TEM
(b)	CVD	XRD/TEM
(c)	Sol-Gel	XRD/TEM
(d)	Hydrometallurgical	XRD/TEM

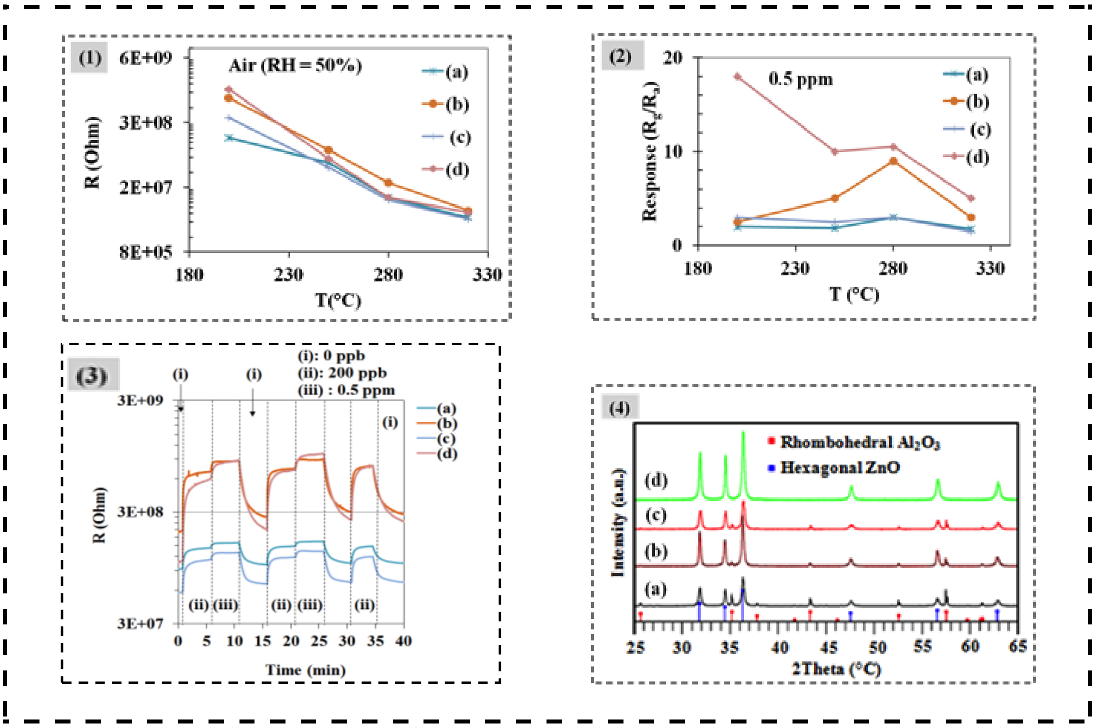

Fig. 2. (1) Evolution of the base line resistances of the sensors vs. working temperature in contact with air (RH=50%); (2): Response of the sensors vs. working temperature to 0.5 ppm NO_2 at 50% relative humidity; (3): Resistance variation of ZnO sensors in contact with different concentrations of NO_2 for repetition tests at 245°C (RH= 50%); (4) XRD patterns of the sensors summarized in the Tables 1 and 2.

Conclusions

In this work, ZnO nanostructures with different morphologies were synthesized and characterized. Their morphologies and crystal structures were determined by TEM and XRD respectively. Highly sensitive and rapid NO_2 gas sensors based on the synthesized ZnO nanomaterials were prepared. The response of the prepared nanomaterials to NO_2 (≤ 1 ppm) were measured at working temperatures ranging from 200 to 320°C at 50% of relative humidity. The effects of the morphology and the synthesis techniques on the sensing performances (selectivity and response time) were demonstrated.

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