Correlation between the NO$_2$ gas sensing properties and surface area of ZnO nanofibers, hyerarchical and thin films structures

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Abstract

Aim of this work is to assess relationships between sub-ppm NO$_2$ gas relative response (RR= Rg/Ra) and absolute surface area evolution of: ZnO nanofibers (ZnO-NF), nanofiber-nanowire brush like ZnO (ZnO-NB) and ZnO thin film (ZnO-TN). In a first step ZnO-NFs mats with two different amounts of fibers (LD-ZnO, HD-ZnO, i.e. low and high fiber density), have been initially characterized both as respect to their absolute surface area and to NO2 gas response (20ppb – 1ppm). In a second step, the same previously prepared LD-ZnO and HD-ZnO fibers, have been subjected to hydrothermal growth of side branches ZnO nanorods to yield brush like hierarchical structures (ZnO-NB) with enhanced surface area. ZnO-TN were prepared by sol-gel spin coating. A linear relationship between RRs and absolute surface area of all the prepared samples was found. The bigger the absolute surface area the higher the RRs, the lower the detection limit (down to 20 ppb) respectively. Traditional porous structures like thin films show better RRs as respect to 1D hierarachical structures but slower response times

Key words: ZnO, nanofibers, absolute surface area, NO$_2$, sensing

Electrospinning and near field electrospinning technique [1] has been widely investigated as a simple and robust technique to produce metal oxides nanofibers for gas sensing applications. 1D nanofibers (NF) with attached 1D branched nanowires (NW) (Nanofiber-Nanowire Junctions) comprising both NF-NW homojunctions and NF-NW heterojunctions [2] have been developed to enhance gas response. More recently mixed oxides nanocomposite nanofibers of various chemical compositions have been also proposed [3]. It was demonstrated that gas response depends on many contributions like grain size, surface area, surface defects concentration and eventually the occurrence of *p-n* junctions.

ZnO nanofibers mats with two different amounts of fibers (LD-ZnO, HD-ZnO, i.e. low and high fiber density), have been prepared by increasing the electrospinning deposition time, utilizing a solution of PEO (Polyethylene oxide), CH$_3$CN, Zinc Acetate and DMF.

Figure 1a and 1b show the SEM picture of LD-ZnO-NF, HD-ZnO-NF respectively after annealing at 500 °C for 1 hour. NO$_2$ gas responses of the LD-ZnO and HD-ZnO were recorded and the results shown in Figure 2. The same LD-ZnO and HD-ZnO sensors, after morphological and electrical characterization, were subjected to hydrothermal treatment (at 60 °C for 6–18 h) to enable the formation of side branches ZnO nanorods to yield brush like hierarchical structures namely LD-ZnO-NB and HD-ZnO-NB as shown in Figure 1c. Electrical tests were thus repeated and the results compared in Figure. 2. Finally, spin-coated sol-gel ZnO Thin Films (ZnO-TF) were also prepared and characterized in terms of their microstructural and electrical features. As shown in Figure 2, the gas relative response (RR) increases by increasing the amounts of deposited fibers (i.e. from LD-ZnO-NB to HD-ZnO-NB), improves further in branched ZnO-NB, and yields the highest RRs in traditional thin ZnO films respectively.
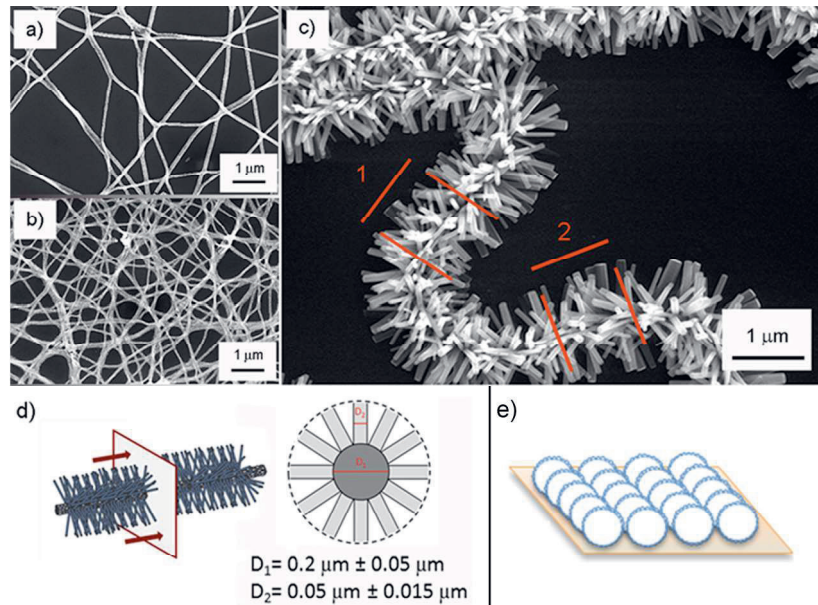
Fig.1. SEM images of low and high density ZnO NF (a,b) after calcining at 500°C for 1h; (c) nanofibers-nanowire brush-like after 18-h hydrothermal process; (d) the nanofibers-nanowire brush like structure; (e) the loosely sintered monolayer of ZnO-TN nanospheres

With the aim to find a relationship between the absolute surface area of the prepared samples and their gas response, by means of SEM observations, the absolute surface area of all the prepared samples was therefore computed.
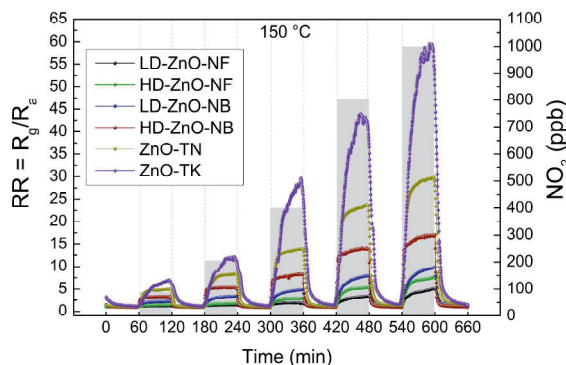

Fig. 2. Comparison of the NO2 RR at 150°C in the range 100 ppb-1 ppm for all the prepared samples

A linear relationship between gas RR and absolute surface of all the investigated structures is shown in Figure 3. The figure highlights that for a given NO_2 gas concentration, the RR increase with increasing the absolute surface and that the linearity is maintained despite different preparation techniques. Considering that the grain size dimensions, concentration of surface defects and chemical composition of all the prepared are designed to be the same, given the same annealing conditions, it turns out the key role played by the absolute surface area. Notwithstanding porous thin films yield the highest RRs, 1D nanofibers-nanowire structures do actually maintain their excellent

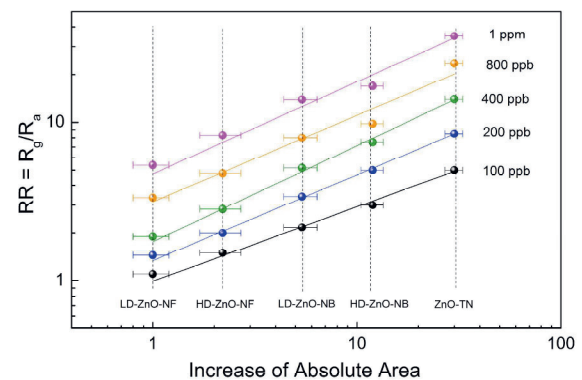sensing properties in terms of surface to volume ratio and faster response.

Fig. 3. NO_2 responses at 150°C as a function of the normalized absolute area (normalized as respect the absolute surface of LD ZnO-NF).

References

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