

Ozone sensing properties of ZnO nanostructures grown by the aqueous chemical growth technique

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Abstract

ZnO nanostructures were deposited on glass substrates by the aqueous chemical growth technique at mild temperatures (95 °C). In general, flowerlike nanostructures are formed, their morphology and dimensions depending on deposition time. Under ultraviolet irradiation and subsequent exposure to ozone atmosphere, the ZnO samples show electrical current changes of three up to six orders of magnitude at room temperature, depending on surface morphology, substrate coverage and average thickness. Samples deposited for 5 h exhibit the highest ozone sensor response, i.e. 10⁶, due to their high surface-to-volume ratio. It is concluded that the ZnO nanostructured samples grown by aqueous chemical growth at low temperatures are promising candidates for semiconductor room temperature ozone sensors.

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1. Introduction

Gas sensors have a great impact in many areas, such as environmental monitoring, domestic safety, public security, automotive applications, air conditioning in airplanes, spacecrafts and houses, sensor networks, etc. [1,2]. The development of gas sensor devices with optimized stability, selectivity and sensitivity at room temperature (RT) has been gaining prominence in recent years [3]. The gas sensing properties are related to the surface state and morphology of the material. Nanostructured materials present new opportunities for enhancing the properties and performance of gas sensors because of the much higher surface-to-volume ratio than that of coarse micrograined materials [1,3–5].

Semiconductor metal oxides have attracted great attention as gas sensing materials due to their advantageous features, such as high sensitivity under ambient conditions, low cost and simplicity in fabrication [1,6]. Among metal oxides, tin dioxide (SnO₂) [6] is the one that has received by far more attraction. This is probably due to its high reactivity to many gaseous species. However, this characteristic of SnO₂ has also revealed a lack of selectivity, and thus investigation on other metal oxides has been considered necessary [7].

Among others, ZnO-based elements have concerned much attention as gas sensors because of their chemical sensitivity to different adsorbed gases, high chemical stability, amenability to doping, non-toxicity and low cost [5,8,9]. ZnO is an n-type semiconductor of wurtzite structure (lattice parameters *a* and *c* in the ratio of *c/a* = 1.633) with a direct bandgap of ~3.37 eV at RT [10]. The Zn atoms are tetrahedrally coordinated to four O atoms, where the Zn 3d-electrons hybridize with the O 2p-electrons.

Ozone sensing has been studied for ZnO films produced by several physical techniques, such as sputtering [11,12], pulsed laser deposition (PLD) [13] and molecular beam epitaxy (MBE)

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[14], contrary to chemical techniques that have not been extensively reported before.

Aqueous chemical growth (ACG) is a novel and inexpensive technique for depositions at mild temperatures (below 100 °C) [15–17]. It does not require complicated setups or high-pressure containers. Furthermore, it is entirely safe and environment friendly, since water is the only solvent used. In this work, ACG was applied to create ZnO nanostructures and investigate their ozone sensing characteristics. In particular, the ozone sensing properties of flowerlike ZnO nanostructures deposited on glass substrates at low temperatures were studied, in relation with deposition time and nanostructures' morphology.

2. Experimental details

ZnO nanostructures were grown by ACG on glass substrates using an equimolar (0.01 M) aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ as a precursor. The solution and the substrates were placed in Pyrex glass bottles with autoclavable screw caps and heated at 95 °C for 1, 5, 10 and 20 h. After each induction time, the substrates were thoroughly washed with MilliQ water to eliminate residual salts or amino complexes, and dried in air at the same temperature. Before deposition, all substrates were cleaned with spectroscopic grade propanol and acetone, washed with MilliQ water and dried under a N_2 gas flow. The crystal structure of the ZnO nanostructures was determined by X-ray diffraction (XRD) using a Rigaku diffractometer with $\text{Cu K}\alpha$ X-rays, while their surface morphology was observed by a JEOL scanning electron microscope (SEM). Finally, the ozone sensing properties of the ZnO nanostructures were investigated at RT by electrical measurements, which were performed in a special designed glass reactor described elsewhere [12]. Briefly, photoreduction was achieved by exposing the samples directly to the UV light of a mercury pencil lamp in vacuum for 15 min in order to obtain

steady state conditions. For the subsequent oxidation, the chamber was backfilled with ozone at a pressure of 800 mbar (ozone concentration in the chamber was ~ 1 ppm). After exposure of the samples to ozone for 45 min, no further changes of the current could be observed. This behavior was completely reversible through many cycles of photoreduction and oxidation. All current measurements were carried out at a fixed bias of 1 V at RT. Current–voltage (I – V) measurements were always performed before the cycling started in order to ensure the ohmic nature of the contacts. In the present study, the sensor response S of the samples is defined as the ratio of the electrical current I in the photoreduction (I_{ph}) and oxidation (I_0) states, i.e. $S = I_{\text{ph}}/I_0$.

3. Results and discussion

Figs. 1a and b presents typical XRD patterns of ZnO nanostructures grown on glass substrates for 1 and 5 h, respectively. They exhibit sharp diffraction peaks, which correspond to the wurtzite ZnO hexagonal $P6(3)mc$ structure. For 1 h growth, only the first three characteristic peaks of ZnO are clearly present possibly due to the initial stage of the reaction, which results in partial crystallization of the material. For longer growth periods (≥ 5 h), however, all the peaks attributed to the wurtzite ZnO structure are revealed according to JCPDS card file No. 36-1451 (see Fig. 1(b) for 5 h); no impurities or other phases were detected. For 5 h growth, the calculated lattice parameters values are $a = 3.2490 \text{ \AA}$ and $c = 5.2031 \text{ \AA}$. As a result, a ratio of $c/a = 1.601$ is deduced, which is a value very close to that for the ideal hexagonal structure ($c/a = 1.633$ [10]). This indicates the very good crystallinity of the ZnO samples grown by ACG.

The mean crystallite dimensions (d) of the ZnO nanostructured samples were calculated using Scherrer's equation:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2}} \cos \theta \quad (1)$$

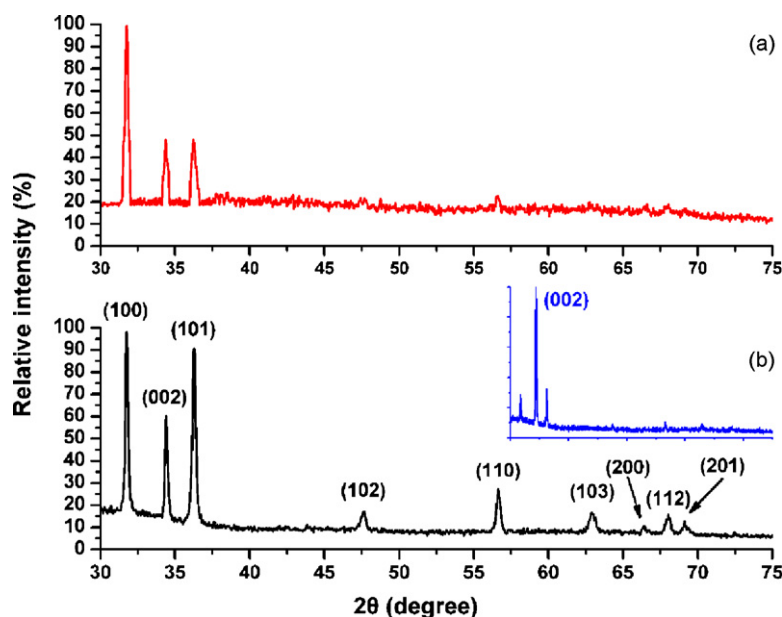


Fig. 1. XRD patterns of ZnO nanostructures synthesized by ACG at 95 °C on glass substrates for (a) 1 h and (b) 5 h. In the inset of (b) the XRD pattern of ZnO grown on glass for 20 h is presented.

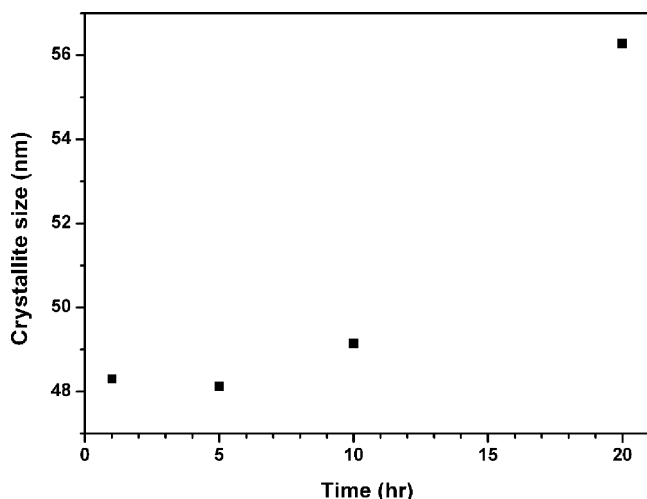


Fig. 2. Crystallite dimensions of ZnO nanostructured samples vs. deposition time.

where β is the measured broadening of a diffraction line peak at an angle of 2θ at half its maximum intensity (FWHM) in radians, β_0 the instrumental broadening, $K = 180/\pi$, λ the X-rays wavelength (0.154056 nm) and θ is the Bragg diffraction angle. By fitting various peaks to Scherrer's equation, crystallite size values between 48 and 56 nm were obtained. The results are presented as a function of deposition time in Fig. 2 for $2\theta = 31.74^\circ$. The crystallite size increases with time, indicating better crystallinity of the samples grown at longer periods. It is also noticeable that at 20 h growth the 34.42° peak becomes dominant, revealing a preferred growth orientation along the c -axis, i.e. the (002) direction, which is perpendicular to the glass substrate (see inset of Fig. 1(b)).

SEM micrographs of the ZnO nanostructures formed on glass substrates at 1, 5 and 20 h are presented in Fig. 3. For 1 h growth, sponge-like nanostructures are formed, out of which uniform shaped nanorods emerge; however, only a partial coverage of the substrate area could be achieved due to the initial stage of

the growth (inset of Fig. 3(a)). For 5 h growth, flowerlike nanostructures consisting of nanorods with diameter ranging from 500 to 800 nm and length of $\sim 7\text{--}8\ \mu\text{m}$ are formed (Fig. 3(a)). However, the size of the flowerlike structures is not uniform and a lot of single rods (diameter $\sim 1\ \mu\text{m}$, length $\sim 10\ \mu\text{m}$) are also present as one can see in Figs. 3a and b. When the growth time increases to 20 h, the flowerlike architectures develop further and become dominant with substrate coverage of about 80% (Fig. 3(c)). They consist of uniform nanorods with a typical diameter of $\sim 800\ \text{nm}$ and length of several microns ($\sim 7\text{--}8\ \mu\text{m}$). The average thickness of the ZnO samples increases with growth time, as it can be approximately deduced from the side views of the SEM images (Figs. 3b and d), in accordance with literature [15]. All nanorods have hexagonal cross-section (for example, see the inset of Fig. 3(c) for 20 h growth), implying the occurrence of the wurtzite ZnO crystal structure as it was also demonstrated by XRD.

The electrical current changes for the ZnO nanostructures on glass under photoreduction and subsequent ozone exposure are presented in Fig. 4(a). As it can be seen, the as-deposited ZnO samples are quite insulating ($\sim 2 \times 10^{-11}$ to 5×10^{-12} A) indicating the low concentration of defects, i.e. oxygen vacancies, in the samples. The current changes are larger in the case of the 5 h ZnO sample (Fig. 4(a)). Photoreduction causes an increase of the current up to ~ 5 orders of magnitude (from 4.6×10^{-11} up to 4.7×10^{-6} A), while subsequent ozone treatment results in a current decrease by six orders of magnitude (down to 3.8×10^{-12} A). Four cycles of photoreduction and oxidation clearly demonstrate the reversibility of the current changes in the ZnO samples (see Fig. 4(b) for the 5 h case). For samples grown at 1, 10 and 20 h, the observed current changes are apparently smaller (Fig. 4(a)). Although I_0 is almost stable for all ZnO samples, ranging from 1.7×10^{-11} to 1.7×10^{-12} A, I_{ph} shows a quite large deviation. It is highest for the 5 h sample, i.e. 4.7×10^{-6} A, and least for the 1 h sample, i.e. 1×10^{-8} A. The enhanced I_{ph} value is thus responsible for the higher sensor response towards ozone that is observed for the 5 h sample (see Fig. 5). We shall next attempt to correlate the sensing behaviour

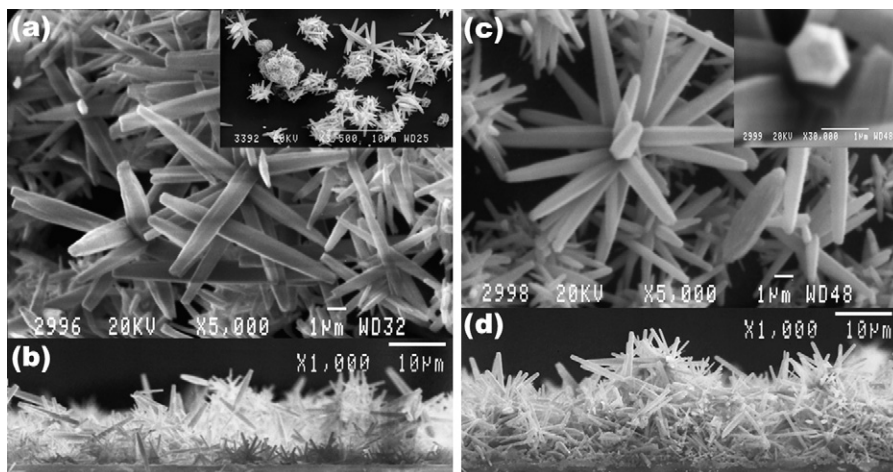


Fig. 3. SEM images of ZnO nanostructures grown by ACG at 95°C on glass for 1 h (inset of (a)), 5 h (top view (a), side view (b)) and 20 h (top view (c), side view (d)). In the inset of (c) the hexagonal shape of the ZnO nanorods is clearly observed.

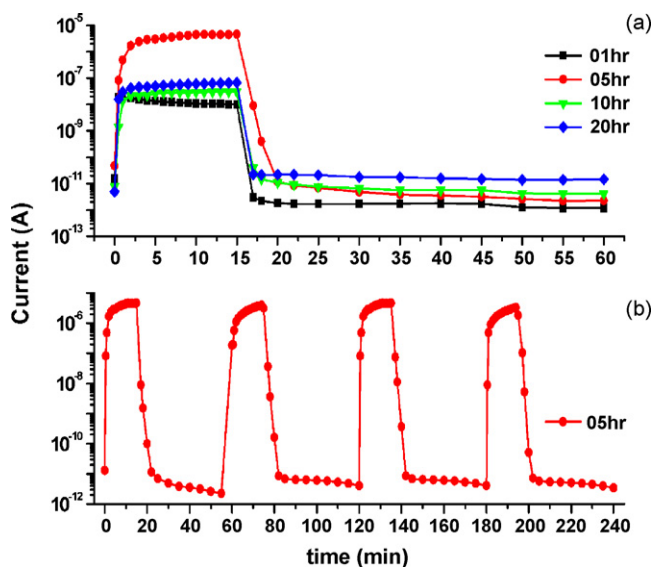


Fig. 4. (a) Current changes measured at 1 V for several deposition periods (1, 5, 10 and 20 h) and (b) photoreduction and oxidation cycles for the 5 h ZnO sample.

of the ZnO nanostructures grown by ACG with their morphological and structural properties.

The electrical current/conductivity changes in ZnO and other n-type semiconductors under photoreduction and subsequent exposure in oxidizing gas atmosphere are in general explained by the formation and annihilation of oxygen vacancies at the metal oxide surface. UV irradiation of the samples with energy larger than the bonding energy between Zn and O leads to the transformation of an oxygen atom from a bound state to the gaseous state and thus the creation of charged oxygen vacancies (single or doubly ionized). Therefore, an increase in the free electron concentration occurs. Subsequent exposure to oxidizing gases, such as O_3 , leads to annihilation of the charged oxygen vacancies at the metal oxide surface and, hence to a drastic decrease of the carrier concentration, which can be directly correlated with the gas concentration [1,3,6].

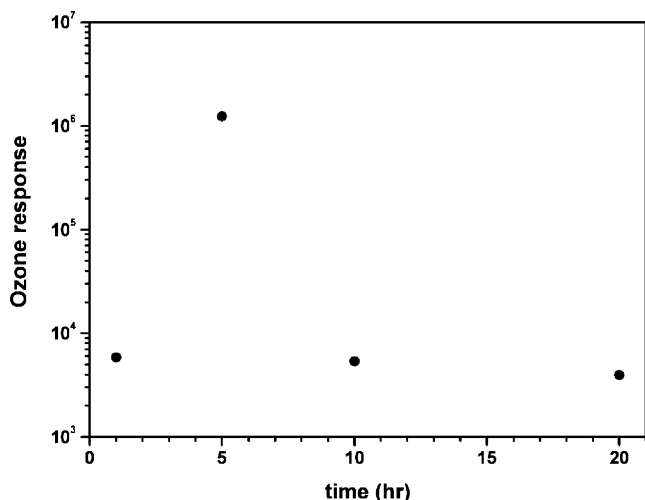


Fig. 5. Ozone sensor response of ZnO samples grown by ACG vs. deposition time.

After 1 h deposition, the ZnO nanostructures are at the initial stage of their growth, consisting mainly of sponge-like structures (inset of Fig. 3(a)), and cover only a small percentage ($\sim 35\%$) of the substrate. It is assumed that the small substrate coverage and the minimal formation of nanostructures lead to the small current changes observed under subsequent photoreduction/oxidation cycles ($I_{ph} = 1 \times 10^{-8}$ A, $I_o = 1.7 \times 10^{-12}$ A). It is, in general, believed that the electrical current changes in semiconductor metal oxide sensors are mainly controlled by the interactions of UV irradiation and oxidizing gas atmosphere with the metal oxide surface [9,11,18,19]. Therefore, the small surface-to-volume ratio of the 1 h ZnO sample leads to the lowest S value observed ($S = 5.9 \times 10^4$) among the investigated sample series. The 5 h sample, on the other hand, consists of flower-like nanostructures and single rods (Figs. 3a and b), reaching a $\sim 80\%$ substrate coverage. The formation of flowerlike nanostructures with nanorods of 500–800 nm diameter results in an increase of the surface-to-volume ratio. This in turn leads to an improvement of S up to six orders of magnitude for the 5 h sample ($S = 1.2 \times 10^6$, see Fig. 5). As the growth time increases further to 10 and 20 h, the ZnO samples get thicker, the flower-like architectures are uniform with nanorods larger in diameter (~ 800 nm) and the crystallite size increases. Thus, the surface-to-volume ratio decreases and consequently the ozone sensor response drops ($S \sim 3.9 \times 10^3$).

4. Conclusions

ZnO nanostructured samples were prepared on glass by ACG at different deposition times of 1, 5, 10 and 20 h. The structural analysis revealed that the ZnO hexagonal wurtzite is the only crystallographic phase detectable. Depending on the growth time, ZnO sponge-like nanostructures (1 h) transform into flowerlike architectures with increasing deposition time (5–20 h). All samples show remarkable electrical current changes at RT under subsequent photoreduction/oxidation cycles in UV and ozone atmosphere (1 ppm). However, the 5 h sample shows the maximum sensor response towards ozone due to its high surface-to-volume ratio. The effect is reproducible after many photoreduction/oxidation cycles. It is concluded that the ZnO nanostructured samples grown by ACG are promising candidates for inexpensive RT ozone detection.

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Biographies

George Kenanakis has graduated from the Chemical Engineering Department of the Polytechnic School of the Aristotle University of Thessaloniki in 2003. He is finishing his master studies in the Chemistry Department of Crete University. Since October 2005, he is enrolled as a PhD student in the University of Crete, Chemistry Department.

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George Kiriakidis received his MSc from UMIST and his PhD from the University of Salford, UK. Since 1981, he is an assistant professor in the Physics Department of the University of Crete, and a senior researcher at FORTH since 1985. He has founded and is the leader of the Photonic and Electronic Materials Laboratory at IESL/FORTH and is currently involved in thin-film technology with emphasis on transparent conducting oxides for gas sensing and food processing applications.

Nikos Katsarakis is a researcher at IESL/FORTH and an assistant professor at the School of Applied Technology of the Technological and Educational Institute of Crete. He obtained his PhD in 1996 at the Institute for Chemical Technology of Inorganic Materials of the Graz University of Technology, Austria.