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Solution growth of ZnO sub-micro rods enhanced by electric field

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Abstract. Recently the one-dimensional ZnO nanostructures have attracted much attention in gas sensor applications owing to their increased role of the surface. The authors have obtained ZnO rods of sub-micron size using the solution growth method with the growth temperature below 100°C. Investigations indicate that the rods have a well-defined hexagonal morphology and a wurtzite structure. The best uniformity and alignment of the sub-micron crystals was however obtained when electrodeposition from aqueous solution was developed. Sizes of these rods depend on the growth parameters. Moreover electrodeposition leads to a faster growth rate of ZnO sub-micron rods (2 hrs) as compared to the growth from solution (8 hrs). After electrodeposition the rods can be easily reoriented in external electric fields by using substrates with electrodes of appropriate geometry and configuration (dielectrophoretic effect). This enables the preparation of samples which can be used in gas sensor technology.

Key words: nanowires, electrodeposition, dielectrophoretic effect, zinc oxide.

1. Introduction

Zinc oxide is a wide band gap n-type semiconductor material with E_g reaching 3.4 eV. ZnO has a large excitonic binding energy of about 60 meV which makes it a very attractive material for room temperature UV lasing application [1]. Its very high piezoelectric coefficient $e_{33} = 1.2$ C/m^2 enables the applications in surface acoustic wave devices [2]. Very good transparency in the visible region of light and the existence of shallow donor states make it attractive as a transparent conductive coating e.g. in solar cell applications [3]. Moreover textured nanocolumns of ZnO can be applied as a light-collecting part of a solar cell [4], which leads to minimization of the optical losses. Thin films of ZnO consisting of nanoparticles of sizes below 100 nm deposited by electrospray method [5] can be used as thermal and corrosion protection layers for metal substrates. Due to chemical sensitivity of zinc oxide to different adsorbed gases, its high thermal stability, amenability to doping, non-toxicity and low cost, it has been also used as a semiconducting material in gas sensing applications [6, 7].

Recently the one-dimensional ZnO nanostructures have attracted much attention in gas sensor applications owing to their increased role of the surface [8]. In particular there has been intense activity to grow ZnO nanorods using a number of techniques like vapor phase transport, thermal decomposition of precursors, hot-wall laser deposition, oxidation of Zn metal, reduction of ZnS powder followed by oxidation at high temperature and inert environment, metallorganic chemical vapour deposition (for a review see [9]). Gas phase techniques involve however the high processing temperatures and expensive equipment, which may limit the applications. For commercial applications it is desirable that the growth temperature is low enough to make it energy efficient. Recently one observes successful attempts to grow ZnO nanorods from solutions [10–14] with the growth temperature below 100°C. With the help of these methods one can also obtain some degree of vertical alignment of deposited nanorods. Better alignment is however obtained using the electrodeposition technique [15]. Additionally the nanorods can be easily reoriented after deposition in external electric fields by using substrates with electrodes of appropriate geometry and configuration (dielectroforetic effect) [13].

2. Deposition of sub-micro rods

2.1. Solution growth method I. In the first experiments the simple one-step solution growth method was applied, similarly to that described in [13]. The glass substrates were dipped in a solution prepared from equimolar (0.01 M) zinc acetate dehydrate $Zn(CH_3COO)_2$ and methenamine $C_6H_{12}N_4$ dissolved in de-ionized water. The structures were grown at a constant temperature of 95°C for 8 hrs. After growth, the samples were washed with deionized water and dried in air at room temperature and then annealed at 500°C for 15 min.

2.2. Solution growth with seeding (method II). The second method was based on the two-step process, where in the first step the seeding of the substrate by ZnO nanoparticles was done (the technology was similar to that in [13]). First a solution was prepared from zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$ dissolved in 100 ml ethanol. The solution was heated at 60°C and stirred for 1 hr, then cooled down and cetyltrimethylammonium hydroxide (CTAOH) was added. The solution was heated again at 60°C for 2 hrs and then cooled down. The cleaned substrates were dipped in the prepared solution and then heated at 250°C for 12 hrs.

In the second step the seeded substrates were dipped in a solution of 0.0068 M zinc nitrate with methenamine and then heated at 90°C for 24 hrs. After growth the samples were rinsed with de-ionized water and dried at room temperature.

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2.3. Solution growth with the help of electric field (method III). Following the procedure described in [15] the solution was prepared by dissolving zinc acetate dehydrate and hexamethylenetetramine in water. The glass substrate with deposited silver film was attached to cathode, the anode was made up of platinum. All electrodes were submerged into the solution and deposition was done potentiostatically with a constant potential of the cathode with respect to the saturated calomel electrode.

The presence of electric field (driving force) may cause the seeding of the cathode surface with ZnO nanoclusters formed in a solution at the growth temperature and these seeds then grow further from solution in the presence of the driving force. Moreover electrodeposition leads to a faster growth rate of ZnO sub-micro rods (2 hrs) as compared to the growth from solution (8 hrs).

3. Morphology and structure

The SEM micrographs of representative samples obtained by described above methods are shown in Figs. 1–3. Perfect hexagonal end planes and well faceted side surfaces of the sub-micro rods are clearly seen. In the case of growth from solutions, Fig. 1 and Fig. 2, one observes

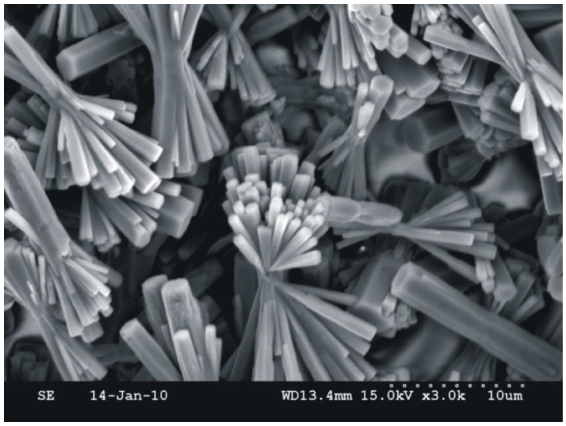

Fig. 1. SEM image of ZnO sub-micro rods obtained with solution growth method I

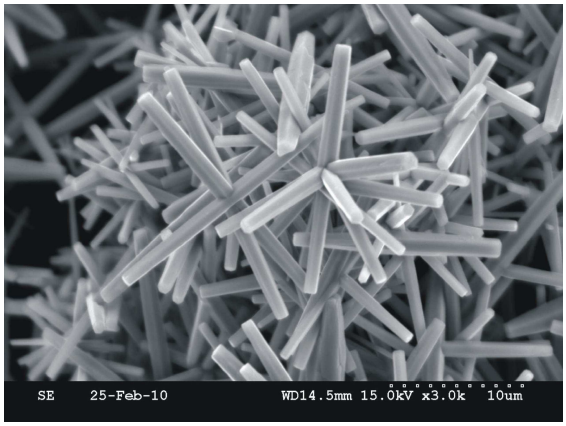

Fig. 2. SEM image of ZnO sub-micro rods obtained with solution growth method II

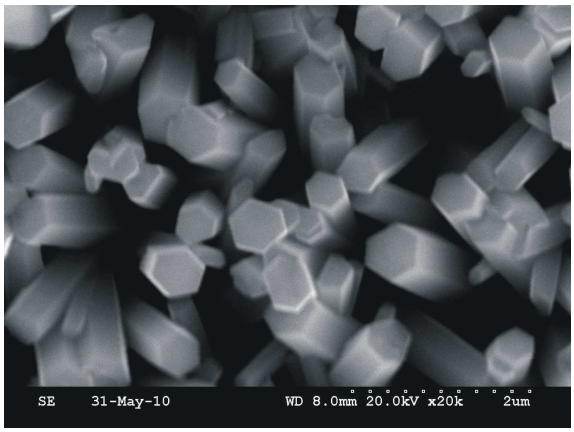

Fig. 3. SEM view of the aligned ZnO sub-micro rods electrodeposited onto glass substrate covered with a silver film (growth method III)

the bunches of sub-micro rods and sometimes single separate sub-micro crystals of higher diameter and length. The most uniform nanocolumns with perpendicular orientation to the substrate one observes for samples obtained by electrodeposition, Fig. 3. In this case the diameters of sub-micro rods vary between 300 and 500 nm with the length reaching 20 μm.

X-ray diffraction studies were performed using X'Pert NPQ Philips diffractometer with Cu Kα radiation in a parallel beam geometry, Figs. 4–6. The XRD patterns in Fig. 4 and Fig. 5 do not differ essentially from the pattern of ZnO powder shown for reference. XRD pattern for the sample obtained by electrodeposition, Fig. 6, indicates a high degree of preferred growth orientation in the <002> direction. The calculated from Fig. 6 texture coefficient $R_{texture}$(hkl), defined as the ratio of intensity of a particular peak with index (hkl) to the sum of intensities of all major peaks, reached about 90% for the (002) peak. This confirms the conclusions drawn from the SEM observations.

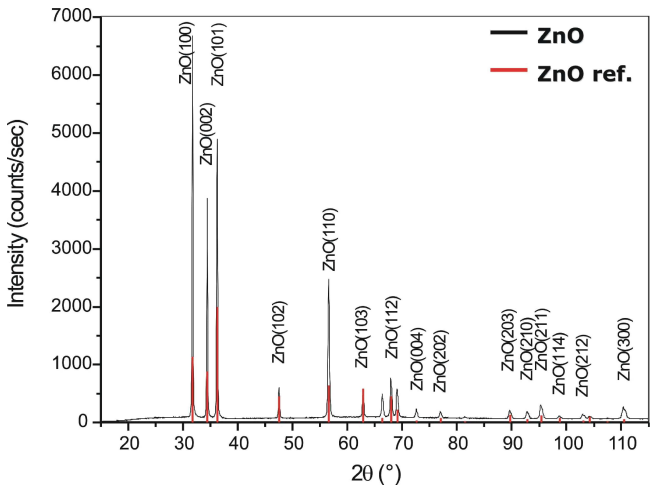

Fig. 4. X-ray diffraction peaks for ZnO sub-micro rods deposited with method I. The positions of diffraction peaks for ZnO powder (in red) are given as a reference. The wurzite hexagonal structure ($a = 0.3250$ nm, $c = 0.5206$ nm) can be seen in agreement with JCPDS data

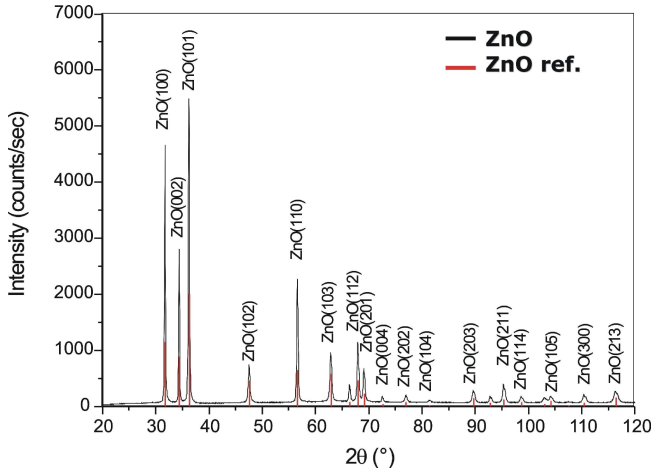

Fig. 5. X-ray diffraction peaks for ZnO sub-micro rods deposited in the two-stage process (method II)

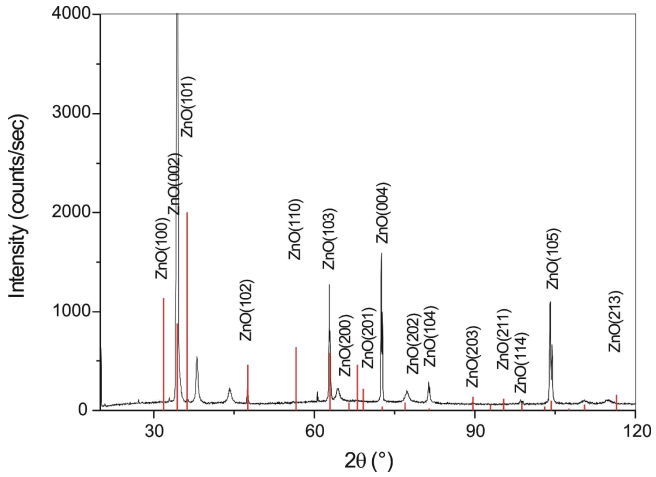

Fig. 6. X-ray diffraction peaks for ZnO sub-micro rods obtained by electrodeposition (method III). The sub-micro rods exhibit hexagonal symmetry and are oriented with their c-axis normal to the substrate (reflections from (002) planes prevail). The peaks which are not labelled at $2\theta = 38.15^\circ$ and 44.32° belong to silver (metallic electrode)

4. Manipulation of ZnO sub-micro rods using dielectrophoretic effect

Dielectrophoresis technique, widely known from applications to bioparticles, provides an effective way to manipulate the particles automatically. The authors used ceramic LTCC gas sensor substrates with interdigitated Au electrodes in order to cover them with ZnO sub-micro rods obtained previously in electrodeposition experiment. The preparation procedure was as follows. ZnO sub-micro rods were first dissolved in the deionized water and then the solution was put in an ultrasonic water bath. Finally, the fixed amount of solution was dropped between the electrodes. AC signal of appropriate amplitude and frequency was applied to the electrode pair and the applied voltage was kept until the solvent totally evaporated.

Partial alignment of the sub-micro rods was obtained in the regions of higher electric field, Fig. 7.

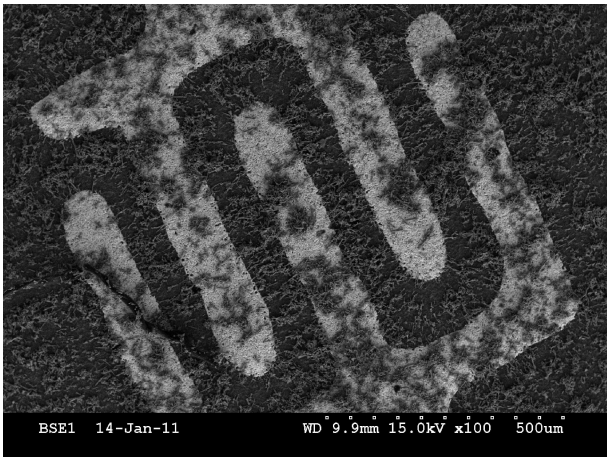

Fig. 7. SEM image of the partially aligned ZnO sub-micro rods between the interdigitated Au electrode array. The applied voltage frequency was 1 MHz and amplitude 10 V, respectively

5. Conclusions

The technology of electrodeposition from water solution can be considered as a source of ZnO sub-micro rods with perfect crystallinity. The growth process proceeds at temperatures below 100°C that makes its energy efficient in commercial applications, e.g. in gas sensor applications. The obtained sub-micro rods can be easily reoriented by external electric fields using electrodes with appropriate configuration and a.c. voltages of adequate magnitude and frequency.

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