DESIGNING NANOARCHITECTURES FOR HYDROGEN GAS SENSOR APPLICATIONS AND DEVICE NANOFABRICATION

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INTRODUCTION

A benign method is developed which enables growth of ZnO and Cu_2O nanoarchitectures based on a solution process with a chemical deposition method and a new concept has been developed for new generation of smart materials. ZnO nanoarchitectures grown from ammonia solution of zinc sulphate permits to be easily transferred to other substrates. This flexibility of substrate choice opens the possibility of using FIB/SEM for handling. The main advantage of the procedure is possibility to fabricate sensitive hydrogen sensor uses single zinc oxide nanorod. Gas sensing characteristics were studied for the structures of ZnO and Cu_2O nanowires, micro/nanoporous and nanostructured films.

1. DESINING ZnO AND Cu_2O NANOARCHITECTURES

Nanoarchitectured materials have attracted recently an increasing interest, due to of their properties and as potential building blocks in fabricating nanodevices. Designing nano-architectures by the control of the sizes, shapes and orientated growth on different types of substrates by various technological regimes, represents a novel research direction of multifunctional nanomaterials. The final aim is to produce hierarchical nanostructures capable of performing sophisticated functions.

Zinc Oxide (ZnO) is an *n*-type semiconductor oxide with a wurtzite structure and with a direct band gap, which is between 3.2 and 3.4 eV at room temperature [1]. Due to of its central symmetry in wurtzite, combined with a large electrochemical coupling, ZnO exhibits strong piezoelectric and pyroelectric properties and a suitable ideally for sensors applications. Pure and doped ZnO are transparent to visible light and conductivity can be increased by doping, therefore are used in a versatile of electronics, nanoelectronics and high-tech applications such as smart windows, chemical, gas and biosensors, solar cells and surface acoustic wave devices [2-3].

Modern trend is in synthesis of nanoscale building blocks - ZnO and Cu_2O - with controlled size, composition and properties, and assemble them into functional nanoarchitectures. That's why in applications of nano-materials-based devices, fabrication process represents the most important step in their realization. In this order of ideas, is necessary to be mentioned, that have been developed many new methods, techniques for synthesis of nanostructures and nanomaterials. The most developed techniques and detailed described in scientific literature are mechanochemistry, lithography, self-assembly [1-4]. On the other hand, production of cheap and reliable nanomaterials (nanotube, nanowires, ultrathin films) and their necessity for new and future electronic and photonic devices require development of new techniques attractive with ability to control the growth, nucleation and thermodynamics of synthesis step.

In the present paper are presented solution process with a chemical deposition method and a new concept has been developed for new generation of smart materials - ZnO and Cu_2O nanoarchitectures uses in nanodevices. Surface morphology and thickness of ZnO and Cu_2O nanowires and micro/nanorods are able to tune and optimize by varying concentrations in chemical bath, deposition times and temperature regimes. Gas nanosensor with H_2 sensitivity and fast response time were fabricated on the base of obtained nanoarchitectures.

2. EXPERIMENTAL DETAILS

Zinc sulfate ($ZnSO_4 \cdot H_2O$) with 99.5% purity, ammonia NH_{3aq} (25%), zinc chloride ($ZnCl_2 \cdot H_2O$) and silver nitrate ($AgNO_3$) with 99.5% purity were used as row materials without further purification. Solutions for ZnO nanoarchitectures growth was prepared based on a chemical deposition method, by dissolving $ZnSO_4 \cdot H_2O$ or $ZnCl_2 \cdot H_2O$ in ammonia NH_{3aq} at room temperature. The strategy utilized for the horizontal growth of ZnO nanorods begins with the used regimes. The zinc concentration in the solutions was 0.05-0.075 mol for 0.5 dm^3. The concentrations of silver as impurity was in the range 0.1 – 1 at.% for obtaining of composition Zn_xAg_{1-}

$_x$O. The glass substrates were cleaned, before deposition, by chloric acid followed by rinsing deionised water (DI, resistivity ~$10^{14}\Omega$·cm) and ethanol:acetone (1:1) mixture, and dried. Solutions were mixed until complete dissolution. The cleaned substrates were immersed in an aqueous solution bath for a time in order to fabricate the nanoarchitectures. All system was mounted on pre-heated laboratory oven and kept at 90 °C for 10 min. Then the substrates were washed with DI water and finally, the product was dried in air at 150 °C for 10 min.

Cuprous oxide nanowires have been deposited at room temperature by reduction route for preparing in the presence of a surfactant, polyethylene glycol-PEG. Hydrazine hydrate was used as the reducing agent. This method requires no complex set-up or techniques.

The as-prepared ZnO nanorod arrays, nano/microrods and Cu_2O nanowires were characterized by X-ray diffraction (XRD) using a Rigaku 'D/B max' X-ray diffractometer (CuK_α radiation source, λ=1.54178 Å). Data acquisition was made with the software Data Scan 3.1 and analyzed with Jade 3.1. The composition and morphologies of ZnO and Cu_2O were characterized by Rutherford backscattering spectroscopy (RBS) General IONEX 1.7 MV Tandetron, Energy dispersive X-ray spectroscopy (EDX), in combination with scanning electron microscopy (SEM) using a JEOL and a Hitachi S800. Transmission electron microscopy (TEM) images were performed with a FEI Tecnai F30 TEM. All in-situ investigations were performed in a modular UHV system (SPECS GmbH) specially designed for the preparation and characterization of nanoscaled materials. The Si/SiO_2 wafers were used as intermediate substrate for ZnO rods transferring and distribution in order to avoid charging problems in the focused ion beam (FIB) system. For the nanosensor preparation, the glass substrate was used and Al electrodes were deposited as template with external electrodes/connections.

3. RESULTS AND DISCUTIONS

Figure 1(a) shows the XRD pattern recorded in the range of 30-90° with a scanning step of 0.02° of ZnO nanoarchitectures. It can be seen that all diffraction peaks are caused by crystalline ZnO with the hexagonal wurtzite structure (space group: $P6_3mc$(186); a = 0.3249 nm, c = 0.5206 nm). The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451). No characteristic peaks of impurity phases such as Zn, S or $Zn(OH)_2$ are observed, and no diffraction peaks except ZnO were found, which indicates that only single-phase hexagonal ZnO is present. The ZnO nanocrystallites are oriented along the *c*-axis in the [002] direction (fig. 1a). The sharp diffraction peaks demonstrate that the ZnO nanorods have high crystallinity.

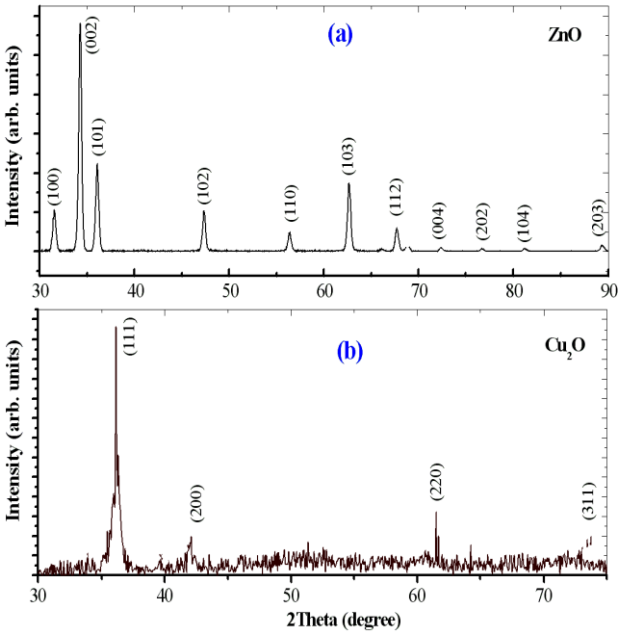

Figure 1. (a) XRD pattern of the ZnO nanowires by the chemical method. (b) Cu_2O nanowires prepared by reduction route in the presence of PEG at 25°C.

Figure 1(b) shows the XRD spectrum of the cuprous oxide nanowires containing peaks that are indexed to crystalline Cu_2O, in peak position and in relative intensity. The peak positions are in good agreement with those for Cu_2O powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS) [Joint Committee on Powder Diffraction Standards, Diffraction Data File, No. 5-666, ICDD International Center for Diffraction Data (formerly JCPDS), Pennsylvania, USA 1991.].

New one-, two-, and three-dimensional ZnO transferable branched nano/microrods are presented in figure 2 (a) on the top of the nanorods arrays. Typical SEM images of the ZnO nanorod arrays-background and individual nano/microrods (on top) are shown in Figure 2 (a), which indicates the obtained product consists of nanorods with an average diameter of 50 nm and 300 nm, respectively.

SEM images of the Cu_2O nanowires are shown in Figure 2 (b), with an average diameter of less than 20 nm.

According to the TEM analysis can be mentioned that the entire as-grown ZnO

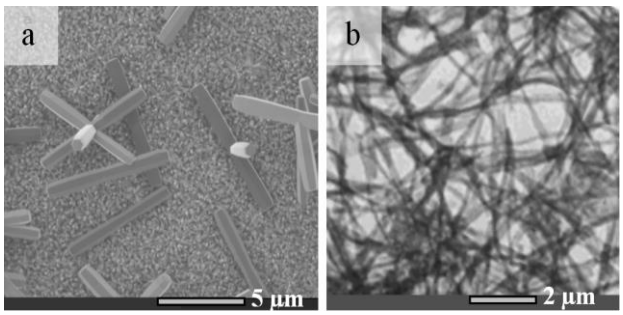

Figure 2. SEM images of: (a) ZnO nanorod arrays and nano/microrods; (b) Cu_2O nanowires prepared by reduction route in the presence of PEG at 25°C.

nanorod is single-crystalline ZnO with a wurtzite structure grown along the [001] direction, which is consistent with the XRD results. The HRTEM lattice fringes and SAED patterns shown in Figure 3 reveal that the nanorods possess a single crystal hexagonal structure without dislocations and stacking faults.

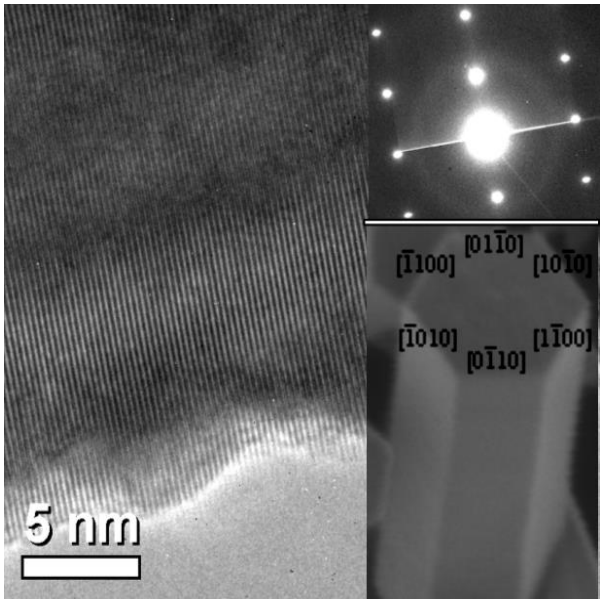

Figure 3. The high-resolution TEM images and the upper inset with the select area diffraction patterns-SAED of the single-crystalline ZnO nanorods. The lower insets display single ZnO rods with hexagonal basis.

Using EDX and RBS, the formation of the ZnO and Cu_2O was confirmed. The Zn:O ratios in our nanostructures were analyzed by RBS and EDX measurement and were found to be 1:1 atomic ratio in all samples. The quality of the grown ZnO rods is demonstrated by the stoichiometric composition deduced from the RBS and EDX analysis as well as by the XRD crystallographic data. Also, by the EDX results prove the Cu_2O sample composition.

The reason behind this preferred crystallization can be understood by considering that ZnO wurtzite crystals have different growth rates for different planes: $V_{(0001)} > V_{(10\bar{1}1)} > V_{(10\bar{1}0)}$ Because of these different growth rates, the controlled synthesis of preferred nanoarchitecture for specific applications can be realized. The crystal synthesis on a specific surface in the aqueous solution is based on heterogeneous nucleation and subsequent growth. Due to the fact that the heterogeneous nucleation takes place at a low level of supersaturation of the complex solution, we can grow different ZnO nanoarchitectures (figure 2) by controlling the reactant concentration, process temperature, and pH value.

According to our experimental observation the growth of ZnO nanorods in aqueous solution can be explained as follows: As the temperature increases the following reactions occur.

$$Zn(OH)_4^{2-} \rightarrow Zn^{2+} + 4(OH)^- \quad \text{dissolution} \quad (1)$$

$$Zn^{2+} + 2(OH)^- \rightarrow ZnO + H_2O \quad \text{nucleation} \quad (2)$$

$$Zn(OH)_4^{2-} + 2H^+ \rightarrow ZnO + 3H_2O \quad \text{deposition.} \quad (3)$$

When the concentration of Zn^{2+} and OH^- exceed supersaturation, ZnO nuclei are formed on the substrate surface. With increasing temperature these complexes become dehydrated and heterogeneous nucleation of ZnO crystals takes place at the interface between substrate and solution. After that, the crystals will grow into nanorods. The $Zn(OH)_4^{2-}$ ions decompose to produce ZnO molecular species [5] which form seeds and grow to form hexagonal nucleus and finally individual nanorods and branched nanorod and three-dimensional nanoarchitectures.

4. NANOFABRICATION OF NANOSENSORS BY IN-SITU LIFT-OUT TECHNIQUE

In the following section the in-situ lift-out technique is described [6]. Usually a microscope and a micromanipulator for the ex-situ lift-out technique has been used to separate individual ZnO nanorods in order to be easily attached- picked -up to the in-situ FIB needle. A micromanipulator mounted beside the stage used in our work permits movements in the nanometre regions along the *x*, *y* and *z* directions. Sample on the stage can be independently rotated, tilted perpendicular to either beam which enable easy arrangement of single ZnO

nanorod on the nanosensor template with Al external electrodes. The needles used for the lift-out step were electro-polished tungsten wire. Figure 4 demonstrates the scanning electron micrograph showing the ZnO nanorod-based hydrogen (H_2) nanosensor fabricated by the in-situ lift-out fabrication route in the FIB/SEM system to the sensor template support and fixed to four electrode/external connections as final nanosensor. In the central part is placed ZnO nanorod with four metallic wires to the external Al connections.

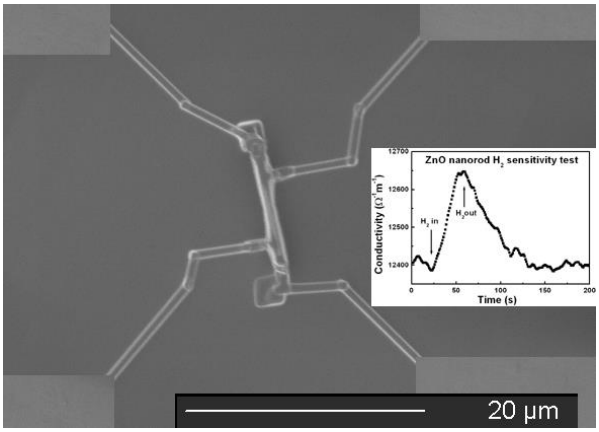

Figure 4. The scanning electron micrograph showing the ZnO nanorod-based hydrogen nanosensor fabricated by the in-situ lift-out fabrication route in the FIB/SEM system to the sensor template support and fixed to four electrode/external connections as final nanosensor. The insets display the H_2 sensitivity characteristics.

The room temperature sensitivity to 150 ppm H_2 of the ZnO nanorod-based nanorsensor is shown in insets of Figure 4. The conductivity changes after 50-80 sec H_2 exposure becomes stable, on the other hand, were restored to the 90% of the original level within 1 min suggesting a resonable recovery time. We repeat the sensor experiment for gas sensitivity to several common gases O_2, CH_4, CO, CO_2 and LPG under the same conditions and found that $|\Delta R/R|$ is less than 0.02% for these gases. We establish that our ZnO nanosensor has certain degree of selectivity.

3. CONCLUSION

In summary, ZnO nanorods arrays, single nanorods and branched nano/microrods were synthesized through a novel low-temperature aqueous solution route. Its have high crystal quality with *c*-axis orientation and each individual ZnO rod showed a hexagonal basis and its dimensions was found to depend on synthesis parameters.

An easy transfer of ZnO nanoarchitectures to any substrate and pick-up by using in-situ lift-out FIB/SEM, opening the possibility of fabrication and studying novel nanosensor and nanodevices. An in-situ lift-out technique has been presented to fabricate first single ZnO nanorod H_2 sensor.

Further work. Further investigations optimization of pure and doped ZnO nanorod growth for electronic and optoelectronic device applications are in progress. It is anticipated that the ZnO rods will find many applications in nanodevices and *p-n* junctions.

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