NEW FABRICATION APPROACH to ZnO MULTIPLE NANOFIBER SENSORS

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ABSTRACT

In the presented work, ZnO nanofiber sensor structures designed and fabricated using a standard microelectronic device technology were studied. The structures in the configuration of a resistor with chemically active ZnO multiple nanofibers deposited by electrospinning method were prepared. Investigation of inclusion in the process reactively sputtered AlN insulating film to improve the robustness of the nanofibres on the substrate was undertaken. Selective wet chemical etching of AlN film using photoresist developers and a photoresist mask to define the sensor active area was studied. The Ti/Au ohmic contacts were fabricated using the lift-off photolithography process. Topography of the sensor structure details was investigated using AFM. Electrical characterization by means of I-V measurements was made. Sensitivity to the physiologically relevant concentration of Bovine Serum Albumin in water solution was shown.

Key words: ZnO nanofibres, AlN film coating, biosensor

INTRODUCTION

ZnO nanofibres (NFs), as quasi one-dimensional semiconductor nanostructures, due to high surface-to-volume ratio reveal improvement of crucial sensors parameters as sensitivity and response times. ZnO NFs could be of special interest in biomedical applications due to their relatively low biological toxicity [1]. The electrospinning method of ZnO nanofibres fabrication provides relative simplicity of their positioning on a chosen substrate [2, 3]. Additionally, such deposited nanofibers are characterized by a highly developed surface induced by the nanocrystalline structure. On the other hand, a main disadvantage of the electrospinning method is a relatively weak adhesion of the NFs to the substrate after the necessary calcinations process, as well as instability and vulnerability to acid and alkaline solutions. These properties impose limitations on the use of standard electronic device manufacturing techniques such as preparation of substrates, photolithography and the lift-off pro-

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cess for contact metallization and passivation of the device which results in incompatibility of the electrospun ZnO NFs and the Si processing. Although the ZnO based nanostructures have been reported as gas and optical sensors [4, 5], their fragility in water environments requires additional chemical treatment for their commercial biosensors applications. Detection of either biological molecules concentrations and activities in physiological fluids or water containing tissue is of fundamental importance in life sciences and medical diagnostics. This led us to the study of applicability of mass production manufacturing techniques in ZnO nanofiber sensor fabrication, based on large area substrates and pattern definition obtained by photolithographic methods resulting in high yield and low manufacturing cost.

In the present work, design and fabrication of ZnO multiple nanofiber sensor structures using a standard microelectronic device technology were studied. The structures with chemically active electrospun ZnO nanofibers were prepared. Two innovative fabrication steps, were proposed. Firstly, an insulating film of reactively sputtered AlN was applied on the nanofibers surface to protect the NFs against the reactants in further processing. Secondly, selective wet chemical etching of AlN film and ZnO NFs through a photoresist mask to define the active sensor area was performed using photoresist developers. The structures in the configuration of a resistor were prepared with the Ti/Au ohmic contacts fabricated using the lift-off photolithography process. Electrical characterization of fabricated structures by means of I-V measurements was made. Sensitivity to the physiologically relevant concentration of Bovine Serum Albumin (BSA) in aqueous solution was tested. BSA, due to its native adsorption properties, was selected to demonstrate the role of the protein's charged amino acids on the ZnO surface charge and therefore on its conductance.

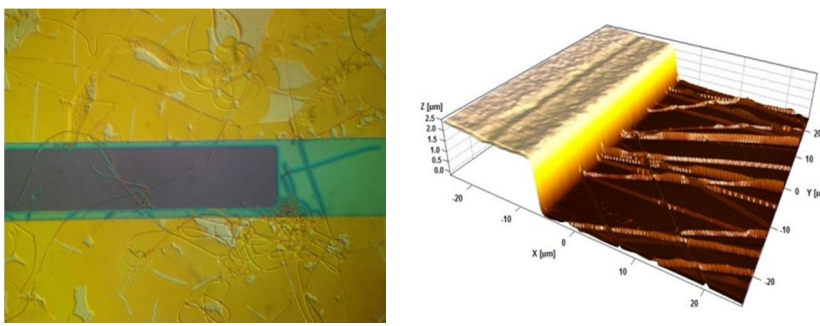
METHODS OF STRUCTURE FABRICATION AND ANALYSIS

ZnO nanofibres were deposited on 10 x 10 mm^2 thermally oxidized Si substrates by electrospinning method. The precursor containing 0.25 g of zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) in 1.25 g solution of 10% polyvinyl alcohol (PVA, MW = 72 000) was placed in a syringe and then a constant flow rate through a syringe pump was established to obtain multiple fiber deposition at high electric potential difference of 10 kV between the syringe tip and the substrate. The fibers were formed in ambient temperature 22°C and humidity of 40%. Finally, the process of calcinations at 700°C for 4h in oxygen ambient was performed. After calcinations, the fibers showed wurtzite structure of nanometer size crystallites with average diameter from 5 nm to 30 nm [6]. The diameter of a single NF averaged at 300nm. Such prepared NFs sensor substrates were coated with a dielectric layer of AlN by pulsed DC reactive magnetron sputtering in Ar/N_2 (6N) gaseous atmosphere using Al target. The processing was done at total pressure of 5×10^{-2} mbar with no substrate heating.

The thickness of the AlN layer was of the order of a typical thickness of a ZnO nanofiber, i.e. in the range from 200 nm to 400 nm. To improve the NFs coating, multiple processing of AlN sputtering could be performed, especially in the case of thicker or cross-linked nanofibres.

Then, a lift-off photolithography technique was used to pattern photoresist (AZ 4110) and define the area for contact electrodes. The next important step, was a precise etching of AlN layer exposed in the photoresist openings. It was done in the solution of Microposit 351 developer diluted in H_2O (1:5). Appropriately controlled photoresist opening step allowed fabrication of the ohmic contacts made of Ti/Au (50/1000 Å) evaporated in a UHV system. To protect the contacts, a layer of a photosensitive polyimide was deposited by a spin-on method and a photolithography process was used to define the active region of the sensor. The active region in between the contacts had a length of 80μm and a width of 5mm. In the final processing step the ZnO nanofibers in the active region were gradually exposed by carefully selected process of etching AlN layer also in a solution of photoresist developer. Control of the process was possible by observing change of the substrate interference colors by means of an optical microscope.

To study structure and morphology of such fabricated NFs samples AFM and optical microscope were used. Details of the active region of the NFs sensor are shown in *Fig. 1*.



a) b)

Fig. 1 - Details of the ZnO NFs sensor active region: a) an opening patterned in the etched AlN (green) showing the SiO_2 substrate (violet) with NFs on it; b) an AFM view of an edge of the active region with a polyimide layer protecting the contacts

The structures were investigated using AFM to evaluate the coating applicability of the AlN film for good coating and covering the ZnO NFs. Standard point probe measurements were performed to check the stability of the ohmic contacts and to find I-V characteristics in different environments. To test sensing properties of the sensor structures commercially available Bovine Se-

rum Albumin (Calbiochem product, 99.0 %, pH: 7.1) was used. The BSA solution was prepared from lyophilized powder of BSA (99%) with concentration of 10 mg/ml in DI water.

RESULTS AND DISCUSSION

Fig. 2 presents AFM images of the ZnO nanofibers after depositon and calcinations at 700ºC on SiO_2/Si substrate. The images were taken before and after covering the NFs with the protective AlN sputtered film. The topography image and phase images are shown with the latter of special importance, since the phase image represents component contrast of the investigated surface.

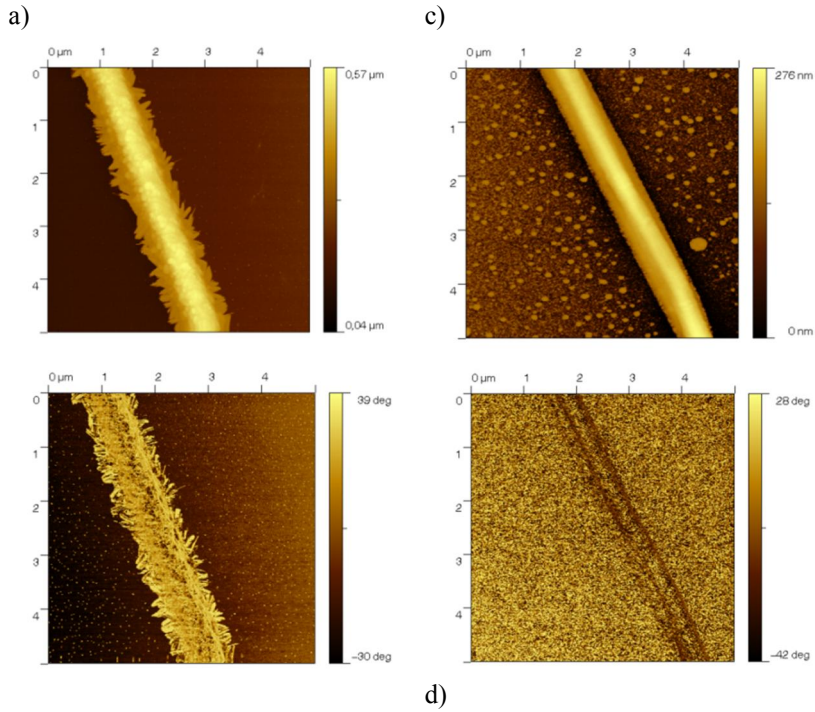


Fig. 2 – Topography (a) and phase (b) AFM images of a ZnO NF on SiO_2 substrate without AlN coating; topography (c) and phase (d) AFM images of a ZnO NF on SiO_2 substrate covered by 200nm sputtered AlN film. Scan area 5µm ^{x} 5µm

It is seen that the ZnO NF after coating with AlN film has much smoother surface (*fig2c*.) in comparison to the state before coating (*fig.2a*). The phase images shown in *fig.2b* and fig.2d give information about changes of the composition of the scanned surface. On this basis we could believe, that after AlN

processing the NF is almost completely covered with AlN, since a very little shadowing was visible.

The I-V measurements have shown stability and linearity of the Ti/Au ohmic contacts to the ZnO NFs. *Fig. 3* demonstrates response of the sensor device to air, pure (10Mohmcm) deionized (DI) water and a BSA water solution. The BSA solution was prepared from lyophilized powder of BSA (99%) with concentration of 10 mg/ml in DI water.

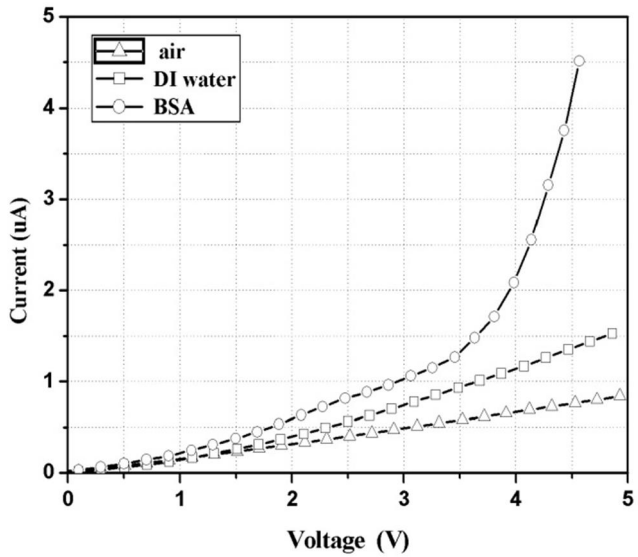


Fig. 3 – The I-V characteristics of the ZnO NFs sensor structure measured in various environments: air ambient, DI water, BSA 10mg/ml DI water solution

Rise of current (conductivity) in the water environment, according to a well known mechanism is attributed to decrease of the NF surface depletion layer due to removal of adsorbed oxygen atoms[7]. In case of impact of BSA molecules on the current rise several factors have been postulated, e.g. adsorption of ionized atoms present on the biomolecule surface may change the conductance of ZnO nanofibers by altering the surface charge [8].

CONCLUSIONS

We developed and tested ZnO multiple nanofiber sensor structures for biological application with a robust design applicable to the standard microelectronic device processing which include reactively sputtered AlN dielectric film, the lift-off photolithography and a polyimide passivation layer. Application of insulated AlN layer resulted in more reliable positioning of ZnO nanofibers on

the substrate. On the other hand, selective etching of the AlN layer did not hamper the sensing capabilities of the ZnO nanofibers. The structures have shown expected I-V characteristics and responsivity to physiologically relevant BSA concentrations in aqueous solution.

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