Electrochimica Acta 137 (2014) 290–297

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Field Effect Transistor with Electrodeposited ZnO Nanowire Channel

Camelia Florica [a], Elena Matei [a], Andreea Costas [a], Maria Eugenia Toimil Molares [b], Ionut Enculescu [a,*]

[a] National Institute of Materials Physics, Magurele, Romania
[b] GSI, Darmstadt, Germany

ARTICLE INFO

Article history:
Received 6 March 2014
Received in revised form 5 May 2014
Accepted 22 May 2014
Available online 2 June 2014

Keywords:
Nanowire transistor
Electrodeposition
ZnO

ABSTRACT

ZnO nanowires were prepared by electrochemical deposition in polycarbonate ion track templates. After the deposition process the polymer templates were dissolved in dichloromethane and the nanowires were harvested by ultrasonication in isopropyl. A droplet of nanowire suspension was placed on a Si/SiO_2 substrate patterned with interdigitated electrodes. By means of electron beam lithography single nanowires were selected and provided with electrical contacts. We found that in order to obtain reliable electrical contacts and typical field effect characteristics the electrode deposition process needs to be adapted to the 3 D shape of the wires and that annealing and passivation treatments are necessary.

1. Introduction

Fabrication of nanostructures with controlled morphology is an attractive field of research due mainly to the high application potential. Practically, precise shape control in the case of nano-objects enables one to further tailor materials functionality and to design devices which make use of consequent specific properties. An approach which enables one to obtain nanostructures with precise shape and dimensions is the so called template method, where the synthesis represents a replication of a chosen object [1,2]. A wide range of templates were employed for this purpose, from nanoporous membranes such as anodic alumina [3,4], polymer ion track membranes [5,6] or titania nanotubes [7] to DNA [8] or proteins [9]. The replication methods are also diverse and a few examples are electrochemical [10,11] or electroless deposition [12], chemical synthesis [13], atomic layer deposition [14].

Zinc oxide is one of the most intense studied material these days and the sought applications range from energy production [15] andphotocathalysis [16] to light emitting devices [17], sensors [18] or logic circuits [19]. A wide band gap (3.3 eV) semiconductor, with an excitonic binding energy of 60 meV, zinc oxide is attractive besides itsintrinsic physical properties to its high occurrence/low cost and non-toxicity. The material is also remarkable from the point of view of polymorphism of its nanostructures, from belts and rods to platelets and flowers, tunable as a function of preparationmethod and specific conditions. Different electronic devices were fabricated using zinc oxide, among them of utmost importance being field effect transistors [20,21].

The group of methods which, at this moment, lead to the fabrication of zinc oxide nanowires with properties considered most appropriate for applications in nanoelectronicsare based onvapour/liquid/solid routes of preparation [22,23]. However, these methods are rather costly, cheaper alternatives being sought.

Electrochemical deposition of semiconductors is a method which was proven as a relatively low budget, easily scalable techniquefor preparing semiconducting materials [24,25]. When employed in conjunction with a template approach, electrochemical deposition allows the fabrication of semiconductor materials with tailored morphology, suited for certain functionality.

Zinc oxide electrodepositionwas extensively studied during the last two decades being a cheap and scalable alternative to more expensive preparation methods. By carefully choosing the deposition conditions one can tailor the properties of the desired material, including here its morphology, structure and its electrical and optical properties [26–28]. From this point of view electrochemical deposition it is one of the most flexible preparation methods.

In the present paper we describe our results regarding the preparation of field effect transistors using nanowires prepared by electrodeposition in ion track templates. Up to this moment such devices were fabricated exclusively using nanowires prepared by VLS approaches, more demanding in terms of infrastructure than electrodeposition. Besides the nanowire growth process, in the transistors fabrication algorithm, electron lithography, and subsequent annealing and surface passivation were employed.Our

* Corresponding author.
E-mail addresses: encu@infim.ro, i.enculescu@gmail.com (I. Enculescu).

http://dx.doi.org/10.1016/j.electacta.2014.05.124
0013-4686/

results show an excellent behaviour of the nanowire based devices, including here typical field effect transistor behaviour, with saturated source–drain characteristics and I_{on} to I_{off} ratios of about 10^4. The transport properties show carrier mobility in excess of 100 cm^2/Vs.

Weproved in this way that electrodeposited nanowires are an interesting alternative to those prepared by other approaches. Moreover, the template method allows a better control of the morphology of the nanostructure, enabling the fabrication of devices with precisely controlled characteristics.

2. Experimental

Polymer foils (30 micrometer thick polycarbonate) were irradiated at GSI's UNILAC with swift heavy ions with a specific energy of 11.4 MeV/nucleon. Each ion passing through the foil leaves a track which, in appropriate conditions, can be selectively removed, leading to the formation of nanopores with the shape and dimensions determined by the etching conditions [6].

Track etching was performed using 5 M NaOH and 10% vol. methanol solutions at 50 °C for 300 s, the etch rate for this experimental conditions being 2 micrometers/hour. Pore diameters of approximately 200 nm were obtained.

On one face of the porous membrane a metallic film is deposited (first a thin gold layer (50 nm) is sputtered and then covered with copper (10 micrometers) by electrochemical deposition)whichis further employed as working electrode for the electrochemical deposition experiments.

The growth of ZnO is performed in a potentiostatic mode, in a double walled glass electrochemical cell, a typical three electrode set–up being employed. The polymer foil is clamped in a PVDF support with the porous face exposed to the growth solution. A 2 cm^2 platinum foil is used as auxiliary electrode and a saturated calomel electrode as reference. The deposition experiments were carried out at about 90 °C, the bath being thermostated using an external bath/water recirculator.

The chemicals,$Zn(NO_3)_2{\cdot}6H_2O$ and polyvinylpirrolidone (PVP) with 10.000 molecular mass, from Sigma Aldrich were employed as received. Milipore 18 MΩ·cm, ultrapure, deionized water was employed for preparing the electrochemical baths.

After the electrodeposition process the polymer template was dissolved in chloroform. The arrays of nanowires were carefully washed in ultrapure chloroform and isopropanol and characterized by means of optical reflection spectroscopy, photoluminescence, scanning electron microscopy and X ray diffraction.

The nanowires were furtherremoved from the substrate and dispersed in ultrapure isopropanol by ultrasonication, different nanowire/isopropanol suspensions being obtained.

In order to prepare the substrates photolithography was employed for fabricating the interdigitated electrode systems on n^{++} Si/SiO_2 wafers. The distance between two neighboring electrodes was 50 micrometers, Ti/Au being deposited by sputtering and evaporation respectively.

A droplet of nanowire suspension was placed on the substrate with deposited electrodes and further electron beam lithography was employed for providing individual nanowires with electric contacts.The sample prepared as described above was introduced in the scanning electron microscope (Hitachi) with ebeam lithography accessory (Raith). An alignment of the sample with the interferometric stage was made and after, the locations of nanowires suitable for contacting were determined and stored. Further the sample was covered with electron resist (PMMA) and rectangles with specific dimensions (5×40 μm), connecting the ends of the nanowires with the interdigitated electrodes were draw by means of the electron beam. A developer was employed for removing the

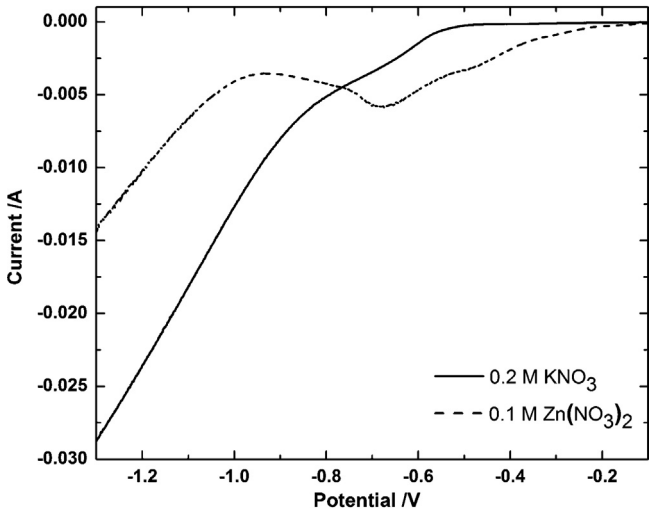

Fig. 1. Electrochemical polarization curves for - solid line: blank solution containing 0.2 M KNO_3 and 1 g/l PVP and–dashed line: ZnO growth bath containing 0.1 M $Zn(NO_3)_2$ and 1 g/l PVP.

irradiated PMMA revealing a rectangular surface which connects the ends of the nanowires with the interdigitated contacts. The metallic electrodes were deposited and lift of was performed, the result of the process being the contacted nanowires.

The sample was finally mounted on a ceramic substrate. Three electrode pads were available for each nanowire on the ceramic substrate namely two corresponding to the source and drain and the third corresponding to the gate. These pads were connected to the deposited source and drain contacts and to the n++ silicon substrate which plays the role of a back gate. A probe station wasused for electrical characterization i.e. for contacting the three previously defined pads.

3. Results and discussions

Zinc oxide electrodeposition is extensively studied since almost two decades. Several deposition routes were discovered, the one we chose for the present work being based on a nitrate bath [29]. In this case the possible electrode reactions are related to:

(a) water reduction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

(b) nitrate ions reduction:

$$2e^- + NO_3^- + H_2O \rightarrow NO_2^- + 2OH^- \quad (3)$$

(c) (c) or zinc ions reduction:

$$Zn^{2+} + 2e^- \rightarrow Zn$$

The global reaction coresponding to zinc oxide formation is:

$$Zn2 + +2OH- \rightarrow Zn(OH)2 \rightarrow ZnO \downarrow + H2O \quad (4)$$

In Fig. 1 the electrochemical polarization curves for depositing zinc oxide when employing a zinc nitrate bath are presented. The polarization curve is also presented for a solution containing only the nitrate ions, i.e. potassium nitrate. The data presented in the two curves enables us to identify the peaks corresponding to nitrate and zinc ions reduction.The curve corresponding to potassium nitrate solution presents a current increase corresponding to cathodic nitrate ion reductionwhile water reduction processes