Single ZnO nanowire based transistors passivated with gelatin
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Abstract
In this paper, we describe the influence of the protein based gels on the electric properties of a single ZnO nanowire based field effect transistor in order to use such devices in sensing applications. The fabrication of the field effect transistors covered with a biocompatible gel, involved four steps: the synthesis of ZnO nanowires, the field effect transistors fabrication process, the covering of contacts of the nanowire with a poly(methylmethacrylate) thin layer and the coating of the nanowire’s surface with gelatin. The ZnO nanowires were obtained via electrochemical route by using polycarbonate membranes as templates. The photolithography technique was employed for fabricating Ti/Au interdigitated electrodes on SiO2/Si heavily n++ doped substrates. Further, a suspension of nanowires was placed on the patterned substrates and ZnO nanowires were contacted using electron beam lithography. The sensitive element of the field effect transistor, in this case the ZnO nanowire, was covered with gelatin to show how the performance of the device changes. In biosensing applications, no effect or an improvement of the transistors characteristics would be ideal. The described fabrication technique could be used to obtain devices like sensors which can perform in air.

Introduction
The electronic devices field is an important part of the industry of each country which promotes the access to innovation and information. Thus, researchers who are active in this area try to develop new devices with improved properties by using structures with reduced dimensions (Crespilho et. all, 2013). Sensors, in particular biosensors, are very attractive for current research due to the high demand of devices with good selectivity, sensitivity and fast response time (Chien et. all, 2006). A great number of biosensors based on nano-sized particles, wires and films were reported in the literature for being use in aqueous environments (Clark e.t all, 2010). ZnO is an intensive studied material due to its high biocompatibility and non-toxic nature, being easy to synthesize via chemical or electrochemical route and to functionalize with biological species (Choi et. all, 2010; Zhang et. all, 2013). A biosensor is a complex system composed of two main elements: the electronic unit which can be a field effect transistor (FET) that converts the chemical reaction between biological species attached to the sensitive component into an electrically quantifiable signal. There are some described methods for putting in contact the electronic part with the biological elements, such as physical or chemical adsorption, covalent immobilization or by using hydrogel matrices (Putzbach and Ronkainen, 2013). Several studies have been reported on the functionalization of such nano-dimensional
materials with some proteins, enzymes or nucleic acids in order to obtain biosensors with certain specificity (Li _et al._, 2014). However, the biomolecules binding structures can be difficult to achieve, in some cases being almost impossible due to the chemical incompatibility (Ronning _et al._, 2011). The use of hydrogels in this field shows many advantages like inexpensive starting materials, easy of synthesis and deposited on substrates, but the main feature is that they can absorb a large amount of liquid offering a favorable environment for biological species. Gelatin and protein based gels are very used for entrapment of proteins due to the biocompatibility, easy of preparing, stability and they are immediately availability (Tabata and Ikada, 1998).

In this work, the electrical properties of single ZnO nanowire based FET before and after passivation with a layer of gel were investigated. Gelatin from bovine skin was used to cover the sensitive element of the FET (ZnO nanowire surface). The typical electric characteristics of FET were analyzed before and after passivation. The ZnO nanowires and also the FET morphology were analyzed by scanning electron microscopy (SEM). The gelatin was chosen because the gelatin based gels are good candidates to be used as polymer matrices for protein embedding.

**Results and Discussion**

As it was mentioned before, this paper is focused on nanowire based devices which could be used as sensors. For this purpose, in order to observe the influence of surfaces FET passivation with a polymer matrix on the electrical characteristics several steps were made. ZnO nanowires were synthesized using the electrochemical deposition technique. Polycarbonate membranes irradiated with heavy ions (GSI, Darmstadt) were chemical etched in a 5M NaOH and 10% methanol aqueous solution at 50°C to obtain pores with controlled diameters. The growth of nanowires was made using an electrochemical cell with three electrodes: the reference electrode was a commercial calomel electrode, platinum plates were used as counter electrode and the gold coated membranes as the working electrode. The electrochemical bath consisted in a Zn(NO$_3$)$_2$·6H$_2$O and polyvinylpyrrolidone aqueous solution which was maintained at 90°C. After the deposition process, the polymer matrices were dissolved in chloroform and the ZnO nanowires were collected by ultrasonication in ultrapure isopropyl alcohol. In Figure 1 are presented de SEM images of ZnO nanowires prepared at a potential of -1000 mV. The ZnO nanowires have a high aspect ratio with well defined cylindrical shapes, having diameters of 100 nm.

![Figure 1. SEM images (at various magnifications) of ZnO nanowire prepared at -1000 mV.](image)

Further, the photolithography technique was used for fabricating interdigited electrodes on SiO$_2$/Si heavily n++ doped substrates. The distance between two electrodes was 50 μm. A drop of the nanowire suspension was placed onto the interdigited electrodes and further ZnO nanowires were contacted using electron beam lithography (EBL) on different electrodes. Figure 2 shows a ZnO nanowire before (a) and after (b) EBL contacting process. The FET was then coated with a poly(methylmetacrylate) (PMMA) thin layer using spin coating method in
order to protect the contacts, and after that, the samples were another time exposed to the electron beam in order to uncover a part of the nanowire (Figure 2c). The electrical characteristics of resulting FET were measured by applying voltage up to 4V between the source and drain and up to 15V between the gate and source.

In Figure 3 a sketch of the devices before (Figure 3(a)) and after (Figure 3(b)) covering with gelatin can be observed. The I-V characteristics of the ZnO nanowire based FET having the ZnO nanowire surface exposed to air present non-ideal shapes due to the possible interactions between the surface states of the semiconductor and the air, leading to an increase in resistivity and not showing a saturation of the source-drain current even at higher applied voltages. Gelatin was used for passivating the surface of the previously exposed ZnO nanowire. The gelatin gel was synthesized by dissolving 0.25g of gelatin from bovine skin in Millipore water and heating it at 40°C for 10 minutes. The gelatin solution (5% w/v) was spincoated in order to cover the exposed nanowire and after the gelification process the specific electrical measurements were made. The mobility of the charges in the FET channel was calculated considering the capacity of an infinite cylinder (the ZnO nanowire) situated on an infinite plan and it had values up to 76 cm²/Vs. The ratio between of the ON/OFF current states (I_{ON}/I_{OFF}) was up to 10⁴. The values of these parameters of single ZnO nanowire based FET coated with gelatin are similar with those reported for semiconducting channels fabricated using laborious and expensive methods as gas/liquid/solid techniques. The use of a gel in this case can improve the specific electrical properties of the ZnO nanowire based FET (Figure 3d) and also can be a proper environment for the entrapment of proteins to be used in the biosensing field.
Concluding Remarks
In conclusion, the electrical characteristics of a single ZnO nanowire based FET were investigated before and after passivation with a gelatin based gel thin film. By using measuring the I-V curves characteristics, it was possible to determine the specific FET parameters such as mobility and $I_{ON}/I_{OFF}$ ratio. As it could be observed from the electrical measurements, after the passivation with gelatin, the ZnO nanowire based FET has a behavior like theoretical like transistors behavior with having I-V saturating characteristics which have a shape reaching a level of saturation. In a further work, some tests regarding the entrapment of the proteins in a gelatin based gels will be made. These devices with improved characteristics could be used for biosensing applications working in air if biomolecules entrapping inside the gel would be made.

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References


