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Full paper

Nanotransducers on printed circuit boards by rational design of high-density, long, thin and untapered ZnO nanowires

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ABSTRACT

Nanotransducers can offer crucial advantages in comparison with conventional sensors and actuators. However, interfacing and packaging nanostructures into complete electronic systems is very complex. Here we describe a wet chemical method for cointegrating arrays of ZnO nanowires into systems on printed circuit boards (PCBs). First, we deposit on the PCB a MnOOH layer for reproducibly increasing the nanowires density. Afterwards, we numerically demonstrate that the ligand ethylenediamine, at the isoelectric point of the ZnO nanowires tips, can effectively control, at very low concentrations, both zinc speciation and supersaturation in the nutrient solution. Accordingly, we combine potassium chloride and ethylenediamine, produced *in situ* from a safer precursor (ethanolamine), for concurrently thinning the nanowires (top width around 60 nm) and stabilizing their top faces. Our synergic approach enables the solution growth of ZnO nanowires which are untapered and have high densities ($> 8/\mu m^2$) and record length (> 15 μm) and aspect ratio (> 200) for plastic substrates which may not withstand high temperatures. These characteristics permit to simultaneously add the top electrode, package the nanowires, improve their mechanical robustness and connect to the electronic interface by a simple flip chip adhesive bonding procedure. As proofs of concept we describe flexible PCB heaters (electrical to thermal energy conversion) with power densities comparable with state of the art flexible heaters and a wearable piezotronic heartbeat detector comprising both ZnO nanowires (mechanical to electric energy conversion) and electronics on a single flexible PCB. Our results open the way to the cointegration of nanotransducers and electronics on conventional PCBs.

1. Introduction

Nanowires (NWs) offer unique opportunities for electronics, including energy harvesting [1,2], ring oscillators [3], photosensor arrays [4], low threshold lasers [5], mechanical sensors [6], and electronic skins [7]. However, though NWs can be grown in solution on almost any substrate [8,9], the integration of high-quality NWs into complete systems is still elusive. In fact, the co-integration of devices fabricated with different technologies is often an intricate challenge. For instance, only recently a sensor array for the *in situ* sweat analysis could be fully integrated on a Printed Circuit Board (PCB) [10], which is the standard substrate for assembling electronic components. In order to embed NWs-based devices in PCBs, for easy packaging [2], it would be possible to grow vertically aligned arrays of NWs on the PCB copper, deposit a polymer to wrap the nanowires (for improving the mechanical robustness and preventing short circuits [2]) and, finally, add the top electrode and connections. Zinc oxide (ZnO) NWs are likely the easiest quasi-1D nanostructures to be grown in solution and also have remarkable properties, including piezoelectricity, pyroelectricity and semiconductivity [11]. However, plastic substrates such as PCBs may not withstand the high temperature annealing of ZnO seed layers. This is an important issue because, in absence of a pre-deposited ZnO seed layer, conventional wet-chemical procedures for growing ZnO NWs on metals tend to result in low reproducibility [12,13] and in short, sparse and low aspect-ratio NWs. Moreover, though ammonium hydroxide can increase the length and density of ZnO NWs directly grown on metals, the resulting NWs are tapered [14]. All these characteristics are problematic as, for instance, short and sparse NWs increase the risks of short circuits during packaging and tapered ends hinder good electrical contacts.

To the best of our knowledge, the integration of ZnO NWs by a rational approach on complete packaged PCBs with fully functional

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devices has not yet been reported. Here we rationally design a wet-chemical procedure for reproducibly growing high-density, long, thin and untapered ZnO NWs on PCBs and then package and interface the NWs to conventional electronics. First, we obtain both high reproducibility and high NWs densities by pre-functionalizing the PCB copper with a manganese oxohydroxide (MnOOH) layer, similar to an approach previously applied to glass substrates [13]. Afterwards, we select a pH value close to the isoelectric point of the ZnO NWs tips, thus preventing significant electrostatic interactions between the NWs tips and ions in solution. Subsequently, we adopt MEA (monoethanolamine) in order to *in situ* produce the more harmful EDA (ethylenediamine) and, thus, thin the NWs and, at the same time, tune the supersaturation degree. Finally, since chloride ions may not appreciably change the speciation and solubility of zinc in solution, we demonstrate that tiny amounts of potassium chloride are already sufficient to effectively stabilize the NWs tips and, thus, synergistically counter-act the tapering induced by EDA. This strategy minimizes harmful reagents and consistently results in high density (> 8 NWs/μm^2), long (> 15 μm in a 12 h growth) and untapered NWs which have the highest reported aspect-ratio (> 200) for NWs grown without using temperatures which are not compatible with conventional flexible substrates and PCBs. These NWs on a PCB are easy to be packaged and co-integrated with complete electronic systems. As proofs of concept, we demonstrate flexible PCB nanoheaters and a flexible PCB comprising both electronics and an ultra-sensitive ZnO NWs piezotronic sensor for heart-beat detection. Our results open the way to the co-integration of NWs-based devices and electronics on PCBs.

2. Experimental

2.1. ZnO NWs synthesis

We chose conventional, commercially available flexible copper-PCBs (Mega Electronics, Cambridge, UK) as low-cost substrates for all the experiments. These PCBs consist of a 50 μm thick polyester film, single side epoxy-bonded with an electro-deposited high-ductility (EDHD) 35 μm copper film. We cut each PCB into square samples. We performed experiments on control samples and on PCB samples pre-treated with potassium permanganate. In the latter case, we placed the samples in glass beakers filled with potassium permanganate solution (Sigma Aldrich, $KMnO_4$, low in mercury, ACS reagent, ≥ 99.0%), with $KMnO_4$ concentrations of 0.5 mM, 5 mM and 50 mM. The beakers were sealed and placed onto a hot plate at 90 °C for 20 min, then we extensively rinsed the PCB samples in Millipore water and sonicated them for 1 min in Millipore water using an Elma SIOH Elmasonic bath system. We prepared the nutrient solutions for ZnO NWs growth with ultra-pure DI water (Barnstead Easypure II filtration system, resistivity at 25 °C > 18.2 MΩ·cm). We performed all the experiments with a nutrient solution composed by 7.5 mM zinc nitrate hexahydrate (Sigma Aldrich, purum p.a., crystallized, ≥ 99.0% (KT)), 3.75 mM hexamethylenetetramine (Sigma Aldrich, HMTA, ACS reagent, ≥ 99.0%), 0.10 M NH_4OH (Fisher ammonium hydroxide 35% v/v in water), 2 mM polyethylenimine (Sigma Aldrich, PEI, ethylenediamine branched, average Mw ~800, average Mn ~600). In addition to this nutrient solution, we differentiate the experiments by varying the content of potassium chloride (Fluka, KCl, purum p.a. > 99.0%) with 0 – 0.5 – 5 – 50 mM and by adding different amine molecules: monoethanolamine (Sigma Aldrich, MEA, reagent Plus ≥ 99.0%), diethanolamine (Sigma Aldrich, DEA, reagent Plus ≥ 99%), triethanolamine (Sigma Aldrich, TEA, ≥ 99%) at 7.5 mM concentration. Monoethanolamine was used at different concentrations (from a minimum of 0.75 mM to a maximum of 75 mM) in order to investigate its effects on the NWs growth. We soaked the substrates in 250 mL nutrient solutions. The reaction occurred for 12 h at 85 °C in Memmert oven. Speciation plots to evaluate zinc chemical species present in solution were obtained from HySS, 4.0.31, Hyperquad Simulation and Speciation software. The software permits to retrieve the concentrations of the zinc species present in the zinc nutrient solution as a function of the pH and of the concentrations of zinc ligands. Calculations are executed at standard conditions (25 °C) and at 85 °C by estimating conditional equilibrium constants.

2.2. Statistical analyses

The ZnO NW densities are measured from SEM pictures using the ImageJ software. ZnO NWs are counted and their lateral sizes are measured from squared areas of $2 \times 2\ \mu m^2$ selected from comparable regions of top view SEM images. ZnO NWs densities are expressed as average counts per μm^2 – this value derives from the average of ZnO NWs counts from 6 areas each of $2 \times 2\ \mu m^2$ (see Supporting Information 1). The NWs lateral sizes (measured at the center of the NW and at the top of the NW) were measured as average values from 15 NWs selected from a square area of $2 \times 2\ \mu m^2$. The lengths are averaged from 15 NWs selected from side view images. From such values, we could calculate aspect ratios. We compared NWs densities, lengths and diameters by Analysis of Variance (ANOVA), Tukey's post tests.

2.3. ZnO NWs characterisation

We analysed topographical and morphological features of the grown ZnO NWs by acquiring scanning electron microscopy (SEM) images of the samples with an FE-SEM (LEO SUPRA 1250, Oberkochen, Germany). We performed Energy Dispersive X-ray spectroscopy (EDX) with a Quanta INCA system. In order to prevent sample surface charging, we connected a corner of the copper layer of the PCB to the grounded SEM chamber, without covering the nanowires with a thin gold layer. The XPS analysis was carried out by the Kratos AXIS Ultra DLD equipped with an Al Kα source ($h\nu = 1.4866$ keV). Each specimen was analysed at an emission angle of 0° as measured from the surface normal. The elements presented on the samples were identified from their survey spectra. The survey spectra were acquired at a pass energy of 80 eV and a step size of 1.0 eV. To obtain more detailed information, high-resolution spectra were also recorded from individual peaks at 20 eV pass energy with a step size of 0.05 eV. The components for the element peaks due to the different chemical species have a Gaussian/Lorentzian shape and are quantified using nonlinear least-squares regression. The spectra were analysed by the XPS Peak software (4.1 version). Photoluminescence spectra were acquired by the ZLX-PL-I instrument (excited by HeCd laser at 340 nm). XRD data were acquired by Philips XRD spectrometer (X'per pro, Cu Kα). During packaging, the two PCBs layers were held in compression (applied pressure: 3.9 kPa) with an adhesive interlayer for 48 h at room temperature. The square wave generated by the bracelet was acquired by the analog input of the multifunction data-acquisition U2331A Modular Multifunction Data Acquisition instrument (Keysight technologies). The ZnO heaters have been characterized by a FLIR i7 thermal camera (140 × 140 pixel), with emissivity set to 0.95.

3. Results and discussion

3.1. Temperature, pH, container volume, growth time and definition of the reference nutrient solution

A key obstacle to the rational design of wet-chemistry methods for synthesizing NWs is the very high number of critical parameters, including temperature, pH, container volume, growth time, and concentrations of all the reagents. Therefore, we first identified the parameters whose optimal values could be, approximately, predicted. In order to achieve a good length (*e.g.* longer than 10 μm, as required for minimizing the risks of short-circuits during packaging [2]), a 12 h growth and a 80 mL solution volume can be sufficient. Standard PCBs may not withstand, especially for prolonged times, high temperatures (*e.g.* even 95 °C for 12 h can already result in deformations of the plastic