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Advanced mechanical and electrical characterization of piezoelectric ZnO nanowires for electro-mechanical modeling of enhanced performance sensors

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ABSTRACT

Nano-scale devices based on zinc oxide (ZnO) are expected to be widely used as building-blocks of future innovative sensors due to outstanding properties of this semiconductive material including presence of a direct bandgap, piezoelectricity, pyroelectricity, biocompatibility. Zinc oxide nanostructures can be also conceived as ultra-high efficiency nanogenerators to harvest electrical energy from the strain vibrational energy in order to drive an array of nanosensors. In fact most applications are based on the cooperative and average response of a large number of ZnO elongated micro/nanostructures, such as wires, rods and pillars. In order to assess the quality of the materials and their performance it is fundamental to characterize and then accurately model the specific electrical and piezoelectric properties of single ZnO structures, in an integrated manner. In this paper, we report on the brittle-to-ductile transition that occurs when reducing the size down to the nanoscale, which has been rarely documented. Then we report on focused ion beam machined of high aspect ratio nanowires and pillars and their mechanical and electrical (by means of conductive atomic force microscopy) characterization. Finally, we present new simulation results concerning ZnO nanowires under lateral bending obtained through the classical approach and the finite element method. Here we use a new power-law design concepts to accurately model the relevant electrical and mechanical size-effects whose existence has been emphasized in recent reviews.

1. Introduction

Among the wurtzite semiconductive materials, ZnO has received increasing consideration with respect to other materials of the same family with same crystal structures, such as GaN, InN, and CdS, because it is an attractive low-cost material with outstanding functional properties, such as piezoelectricity, pyroelectricity, presence of a direct bandgap, and biocompatibility [1,2]. The interest is increased by the excellent properties of ZnO at such smaller scales [3–8] a key element to exploit its features for nanotechnologies. Several studies confirmed the presence of giant size effects [9–11] at nanoscale where ZnO structures exhibit better mechanical properties than conventional bulk samples, which present an extreme brittleness. Based on this evidence, bulk ZnO and nanoscale ZnO can be considered as two different materials by electrical and mechanical engineering perspectives. These observations enabled breakthroughs in the development of novel one-dimensional nanostructures [12–17] that overcome the limitations of the bulk material. One dimensional ZnO nanostructures, namely nanowires (NWs) and nanorods, can be realized by precipitation in wet chemistry solutions [18] or can be grown on a variety of substrates using different techniques including CVD growth and hydrothermal growth [19,20] by means of specific catalyst or seed layers.

NWs, with their piezoelectric [21] and piezotronic effects [22], represent the building block of various types of nanosensors [23–27] e.g., strain sensors [28–30], photodetectors [31], biosensors [32], gas sensors [15], humidity sensors [33]. In addition, ZnO NWs can be used as ultra-high efficiency ZnO nanogenerators for driving nanosensors: in these applications one seeks to combine

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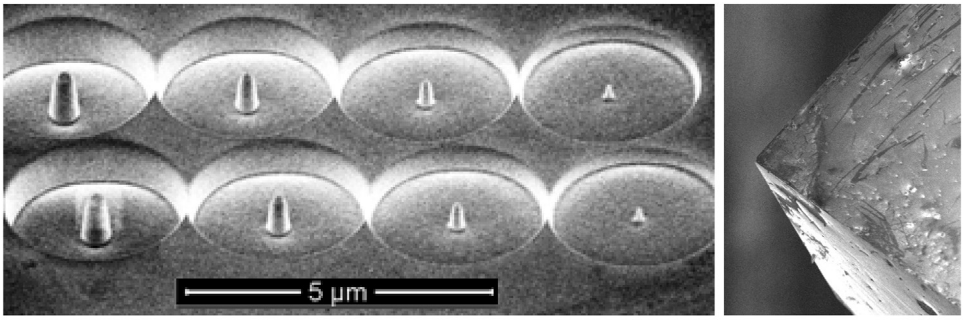

(*a*) (*b*)

Fig. 1. (*a*) SEM micrographs of sub-micrometric ZnO pillars fabricated by FIB machining in closely spaced arrays for ease and repeatability of testing under the nanoindenter in air; (*b*) SEM micrographs of the flat-ended diamond tip used to perform the nanomechanical testing on the ZnO pillars. The flat punch was FIB machined.

piezoelectric and semiconductive properties of ZnO to harvest electrical energy from the strain energy induced in the ZnO by "waste" mechanical stimuli such as vibrations present in the environment [34,35].

Most of the aforementioned devices are based on axial strain (or tensile strain) applied to NWs due to constructive reasons and because simulations [36–39] and measurements [40] have shown that vertical compression is better than lateral bending from both the points of view of high output voltages and mechanical-to-electrical energy transduction capabilities [21]. Moreover, the sensing of transverse forces and deformations is difficult because in the classical axial configuration a transversal sliding of the bottom and top contacts results in opposite strains on the two sides of NWs, compressive and tensile strain, respectively. These conditions dramatically reduce the piezotronic effect and the sensitivity (transducer gain) of the sensor. To overcome this problem, recent theoretical [37] and experimental studies [29] have demonstrated that NWs can be effectively used under lateral bending to effectively transduce a shear/bending force into a piezopotential or a current change through the NW due to the piezotronic effect. The high sensitivity of these ZnO NWs shows their potential to act as the main building blocks for force sensor arrays and high spatial resolution artificial skin.

In this framework, the correct mechanical and electrical characterization of NWs becomes of paramount importance to ensure the construction of high performance and reliable devices. Furthermore, the correct modelling of the behavior of NW and the development of accurate approaches aimed at fully understanding the coupling effects among mechanical, electrical, and piezoelectric properties is fundamental. Physically based simulations offer insights into the device behavior allowing the observation of phenomena that cannot be measured yet on real devices and giving some guidance in the design of actual sensors.

The paper offers a broad multidisciplinary discussion that is structured as follows.

- At first, we focus on the brittle-to-ductile transition that occurs when reducing the size down to the nanoscale, which has been rarely documented. We present preliminary microcompression tests that reveal the presence of plastic deformation in some of the smallest ZnO pillars ever tested by this method [41–43].
- Then, we highlight a strategy for a reliable electrical characterization of individual ZnO nanostructures by means of conductive-atomic force microscopy (C-AFM). The technique is benchmarked on ZnO pillars fabricated by focused ion beam (FIB) machining [40] starting from bulk ZnO with proper metallic layer deposited on top.

Table 1
Young's modulus (*E*) and hardness (*H*) of the substrate.

Statistics	Mechanical Properties	
	E (GPa)	H (GPa)
Mean	131.2	6.6
Std Dev	2.6	0.1

- Finally, we discuss an accurate numerical modelling of NWs under lateral bending, based on the classical approach and the Finite Element Method (FEM), that we have applied successfully to several configurations [45–47].

Our results can provide guidelines for designing high performance piezo-nano-devices for sensors in multiple areas, e.g., electrical, mechanical and chemical processes, paving the way for new design strategies.

2. Mechanical characterization

Submicrometric pillars of different diameters (from 100 nm to 700 nm) were machined out of a ZnO single crystal (0001) by FIB (Crossbeam Nova 2, Fei) in a closely spaced array, such that they could eventually be found under an optical microscope at 500x and could allow performing repeated tests for statistical purposes. The diameter to height ratio was kept below 1:3 to avoid buckling. Fig. 1a shows the arrangement of these pillars as captured by the scanning electron microscopy (SEM). This batch was fabricated using 5 kV of accelerating voltage and 100 pA of beam current in the ion column.

Pillars were individually tested in a nanoindenter (XP, Agilent) outfitted with a flat diamond punch of about 700 nm diameter, as shown in Fig. 1b. The flat end was also fabricated by ion milling in the FIB. Pillars geometry was characterized before and after test by SEM. Nanoindentations at 1 μm depth with a standard Berkovich tip were preliminary conducted to calibrate the set-up (vs. fused silica standard) and to assess the mechanical properties of the ZnO single crystal substrate in terms of Young's modulus and hardness [48], which were estimated by Continuum Stiffness Measurement (CSM). CSM is a well-known method that relies on displacement oscillation of about 2–3 nm in amplitude to measure elastic properties [49,50].

The properties of the substrate were measured first, as reported in Table 1, along with a check in Fig. 2 performed on reference sample of fused silica to insure the reliability of the test. In fact the stability of the measurement system during the ZnO indentation needs to be checked against possible thermal/electronic drifts by making sure that the Young's modulus value of 70 GPa is obtained