Using Piezoresponse Force Microscopy for semiconductor ZnO nanowires

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Nowadays, Piezoresponse Force Microscopy (PFM) has become a standard for imaging ferroelectric domain patterns or for studying the piezoelectricity of certain materials [1]. PFM is an extension of contact mode AFM technique and it is based on the converse piezoelectric effect of the material under test. A conductive AFM probe tip is used to simultaneously measure the mechanical response when an electrical voltage is being applied to the sample surface. In response to the electrical stimulus, the sample then locally expands or contracts according to the material piezoelectric coefficient. Usually an AC voltage (V_{bias}) is used to excite the sample, because it allows the use of a lock-in amplifier to read-out the tiny motion generated by piezoelectric effect.

Most of the materials that exhibit piezoelectricity are insulators, it makes the measurement of this property easier because the applied voltage between AFM probe tip and sample substrate is fix and known. However, piezoelectricity can be found in semiconductor crystal with non-central symmetry, especially those who have a wurtzite structure such as ZnO. Piezoelectric and semiconductor materials are very interesting due to its wide range of new applications (e.g. energy harvesting, nanosensing, photonics, etc.), Due to the dual semiconductor-piezoelectric behavior, ZnO nanostructures show the recently discovered nanopiezotronic effect [2].

In this work, we have characterized the topology of ZnO nanowires (NWs) by AFM, different AFM probes have been used to improve the resulting image. SEM was used to observe the samples of ZnO NWs used in our experiments (Fig. 1). They were growth by hydrothermal method [3] over a silicon substrate covered by a Cr/Au bilayer of 20 nm and 50 nm respectively. As observed in Fig. 2, the topology of a single nanowire has been measured, showing the convolution between NW surface and AFM probe tip. Due to electrostatic attraction, NWs are eventually transferred to the AFM probe tip as observed in Fig. 3, making more challenging the imaging procedure.

On the other hand, we have measured the piezoresponse of ZnO nanowires (NWs) which depending on the AFM probe tip material can create a Schottky barrier between NW and the proper tip. Therefore, with this kind of semiconductor samples, for a voltage higher than the diode voltage, current can flow through the NW reducing the overall electric field generated along the NW. Performing an I-V curve before a piezoresponse measurement is crucial to understand the resulting data. When the contact between tip and NW exhibits a rectifying barrier (at V_d) as shown in Fig. 3A, piezoresponse measurement will be reduced for V_{bias} higher than V_d. The higher value of V_{bias}, the larger the piezoelectric motion amplitude, therefore there is a trade-off between V_{bias} and V_d that can ultimately make impossible to extract the real value of the piezoelectric coefficient. To overcome this difficulty, conduction through the NW should be avoided. For instance, a thin layer of an insulator can be deposited by ALD over the sample or a different tip with appropriate working function or passivation coating can be used. Piezoelectric coefficients can be extracted from the forces curves generated when by sweeping the amplitude of V_{bias} at a certain AC frequency and the first and second harmonic of the deflection are measured (Fig.3B).

Finally, piezoelectric coefficient d_{33} of 8.6 pm/V has been measured and the presence of a Schottky barrier has been observed for certain AFM probe tips, suggesting the presence of the nanopiezotronic effect.

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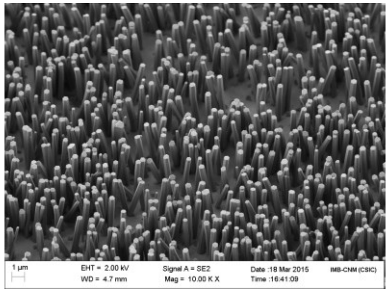

Figure 1. SEM image of ZnO nanowires.

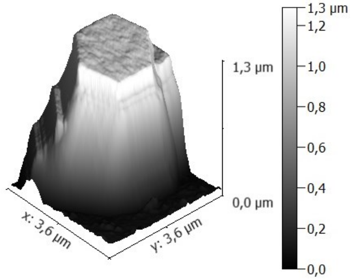

Figure 2. AFM image of ZnO nanowire.

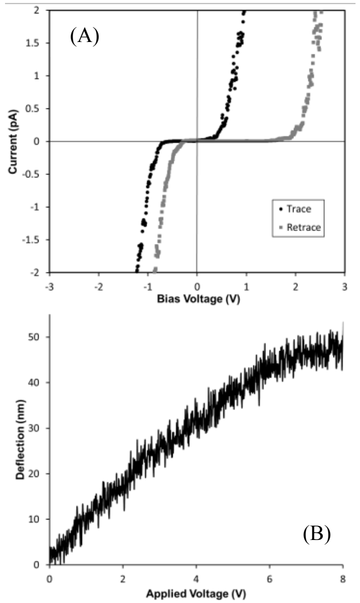

Figure 3. (A) I-V curve of ZnO nanowire with AFM probe tip with Pt/Ir coating and (B) piezoresponse graph (first harmonic).

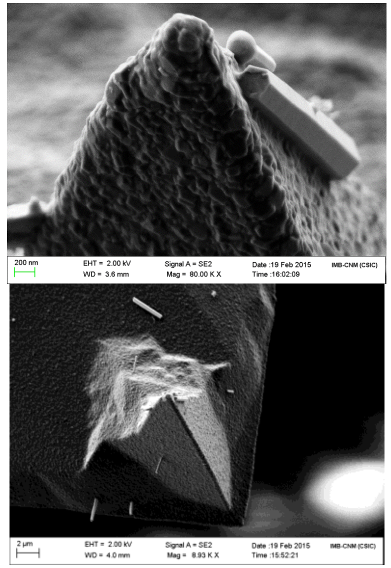

Figure 4. SEM images of AFM probe tip with attached ZnO nanowires after performing measurements