

STM and STS characterization of ZnO nanorods

M. Herrera-Zaldívar^{a,*}, J. Valenzuela-Benavides^a, U. Pal^b

^a Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apdo. Postal 2681, Ensenada, BC 22800, Mexico

^b Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, Mexico

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Abstract

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) techniques were used for the morphological and electronic characterization of zinc oxide nanorods. Well crystalline ZnO nanorods of about 200 nm mean diameter and up to 5.0 μm in length were synthesized by a modified hydrothermal technique at low temperature, using ethylenediamine as a soft surfactant. By means of STM we could detect the formation of prismatic hexagonal and non-prismatic rounded shape ZnO nanorods. Formation of aligned grain structures induced by strain relaxation in the nanorods were also observed. Using STS we could determine the band gap and deep level states related with the formation of oxygen vacancies in the nanostructures by a strain relaxation process.

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1. Introduction

Synthesis and characterization of one-dimensional (1D) compound semiconductor nanostructures are of great interest due to their strong application potential as building blocks for nanoscale electronic and photonic devices [1,2]. One-dimensional zinc oxide, a direct wide band gap (3.37 eV) semiconductor with large exciton binding energy (60 meV), is one of the most important functional oxide nanostructures, exhibiting near-UV emission [3], piezoelectricity [4], and a promising material for sensing [5], field emission and other optoelectronic applications [6,7]. Several nanometer and micrometer size ZnO structures of various geometries [7–13] have been produced recently using high [14–17] and low temperature techniques [18,19]. While the production of nanostructures with a particular morphology and the desired electronic properties is of great challenge for the materials

scientists, a better understanding using effective characterization tools is essential for a successful technological application of these materials.

In this work we report morphological and electronic characterization of ZnO nanostructures using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) techniques. STM was employed for the high resolution surface characterization of chemically synthesized ZnO nanorods in order to better understand the growth mechanism and surface structure, while STS was used to estimate the surface band gap and investigate the presence of deep level defects in the band structure.

2. Experimental

ZnO nanorod structures were synthesized using a modified hydrothermal technique. In a typical synthesis, zinc acetate dihydrate $[(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}]$ (Baker) was added to a 10% ethylenediamine aqueous solution

* Corresponding author. Fax: +52 646 1744603.

E-mail address: zaldivar@ccmc.unam.mx (M. Herrera-Zaldívar).

under vigorous stirring (initial pH = 13.2) until the pH reached 11.0. Sodium hydroxide (NaOH) (99.9%, Aldrich) pellets were then added to the solution to increase the final pH to a value of 12.0. The final mixture solution was heated above 80 °C and kept between 80 and 100 °C for 4 hrs under constant stirring, after which the mixture was cooled down to room temperature. The white precipitate that formed in the reaction vessel was filtered and washed several times with deionized water and then dried at room temperature.

For SEM and STM observations, a drop of the powder sample previously dispersed in water was deposited on a gold coated glass surface and dried in vacuum. A JEOL JSM5300 SEM and a NanoScope E STM (Digital Instruments) operating in ambient conditions were employed.

All STM images presented in this work were taken in constant current (topographical) mode, using electrochemically etched W wire or mechanically sharpened Pt–Ir wire as tips. With Scanning Tunneling Spectroscopy, the occupied and unoccupied states can be probed by monitoring the tunnel current when the sample is negatively and positively biased, respectively. In our study, I – V data was collected following a common procedure: the feedback loop of the microscope that controls the vertical motion of the tip is interrupted for 0.1 ms and the bias voltage digitally ramped from an initial to a final preselected value, while the corresponding tunnel current is digitally sampled. Data is presented here as the ratio $(dI/dV)/(I/V)$, which gives a rather direct measure of the surface density of states of the sample [20–22]. The spectroscopic results presented in this work have been found to be reproducible between different zones on the nanorods, with no apparent influence from the two different types of tips used.

Monochromatic CuK_α radiation from a Phillips X'Pert diffractometer operating at 30 keV and 30 mA filament current was used for recording the diffraction pattern of the sample.

3. Results and discussion

In Fig. 1 we show a typical SEM micrograph of the ZnO nanorod structures. We can observe the nanorods with diameters between 130 and 300 nm and of 2–6 μm in length. The X-ray diffraction (XRD) spectrum of the as-grown nanostructures (Fig. 2) revealed the formation of a well crystalline ZnO wurtzite phase. The XRD pattern together with high resolution electron micrographs (HREM) (not presented) of the sample give the lattice constant values of $a = 0.32$ nm and $c = 0.54$ nm.

STM images revealed more detailed topographical information of the samples, making it possible to observe two types of nanorods with prismatic and non-prismatic

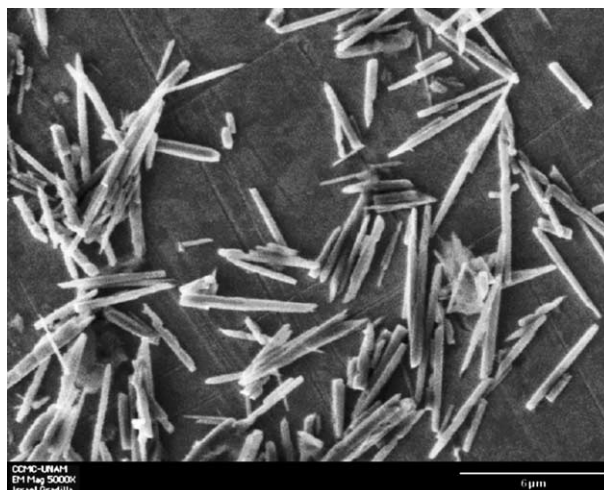


Fig. 1. SEM image of dispersed nanorods on a gold coated glass substrate.

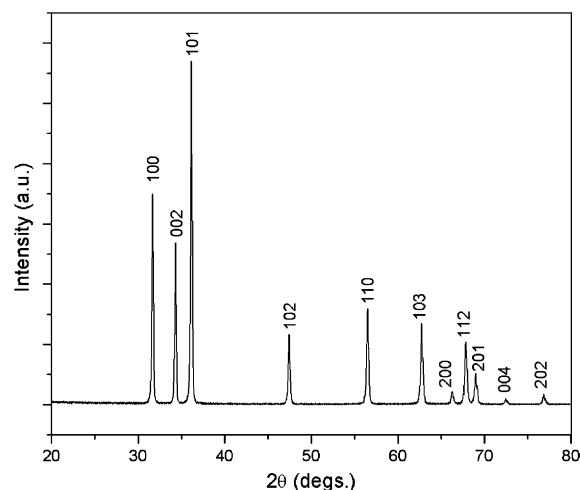


Fig. 2. The XRD pattern of the ZnO nanorods.

shapes. A prismatic shaped nanorod is basically a well ordered crystal with visible $\{10\text{--}10\}$ planes. Fig. 3 shows a section of a prismatic nanorod, where a flat surface or facet is clearly observed. Although a direct measurement of the width of the nanorod from the image gives a value of around 230 nm, this value is overestimated because of the conical shape of the tip and its convolution with the object been scanned, resulting in an apparently wider structure. An STM image of the facet is shown in Fig. 4(a), where equally spaced terraces of around 10 nm wide running perpendicular to the c direction of the nanorod can be seen. Each one of these terraces seems to be covered by an elongated grain structure, as shown in Fig. 4(b).

The observed alignment of terraces is a direct consequence of the preferential growth direction of the nanorod along the c -axis as reported for similar nanostructures [23,24], furthermore, from the measured c lat-

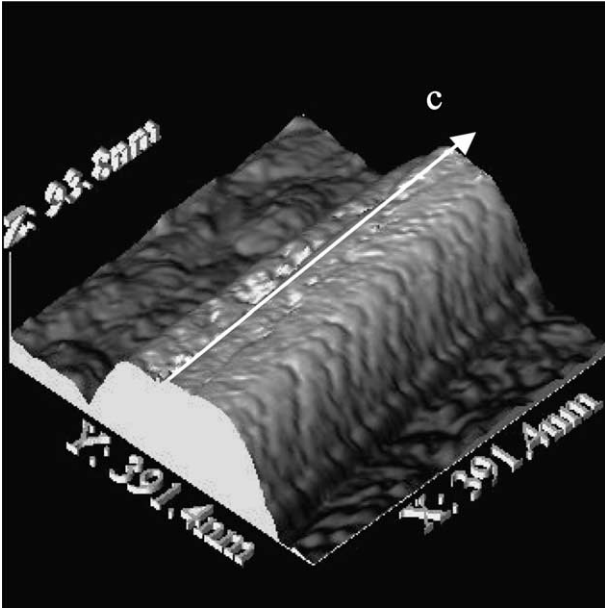


Fig. 3. STM image of a prismatic nanorod acquired with 2.5 V sample bias voltage and 1.2 nA tunnel current.

tice parameter it is reasonable to assume the nanorod structure is under tensile strain. We estimate a value for the tensile strain of $\sigma_{zz} = 40.4 \times 10^{-3}$, which is relatively high (the tensor component along the preferential growth direction is defined as $\sigma_{zz} = \frac{c}{c_0} - 1$, where c_0 and c are the equilibrium and the strain lattice parameters, respectively). Such a high value could produce changes in the band-gap for ZnO nanorods, as pointed out by Lee et al. [16] for nanorods of different diameter. We were not able to detect any difference in the band-gap for our samples with the STS technique used that could be attributed to a variation of nanorod diameters.

The STS spectra of the prismatic nanorods (Fig. 5) reveals a surface band gap value of about 3.5 eV. Since this band gap value is in agreement with other STS measurements reported for the same compound [25], we believe that exposure to ambient conditions has no noticeable effect on our results. The curve also shows the presence of surface deep levels (small bump at the bottom of the curve) about 2.5 eV above of the valence band, attributed to the presence of oxygen vacancies.

The study of the grain structures in the terraces is important since the ZnO grains could contain a higher density of point defects. As pointed out by Jeoung et al. [26], the green emission (2.2 eV) intensity in ZnO films depends on their grain structure, which in turn is originated by oxygen vacancies or Zn interstitials. The presence of surface oxygen vacancies was also reported for nanocrystalline ZnO [27]. The role of oxygen vacancies on the green emission was demonstrated by Zhang et al. [28], where they also reported a deep level at 2.3 eV above the valence band and found this state

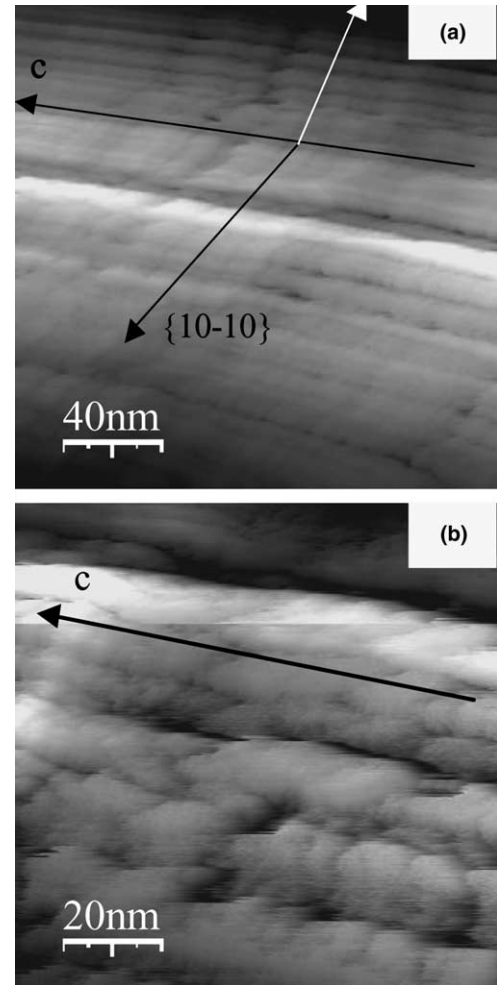


Fig. 4. STM topography image of (a) the terraces and (b) the grain structure of a prismatic nanorod acquired at 2 V sample voltage and 1 nA tunneling current. The arrows indicate the c -direction and the prismatic planes.

to be related to the presence of neutral oxygen vacancies.

STM images of non-prismatic nanorods (Fig. 6) revealed no discernible flat surface or facets. Through a closer inspection we could observe a granular structure covering the surface, as demonstrated in Fig. 7(a) and (b). This observation suggests that, although a rough and granular surface is covering the nanorods, the core could retain a well ordered crystalline structure of a prismatic nanorod.

STS measurements on non-prismatic nanorods revealed the same deep levels observed for prismatic nanorods (arrow in Fig. 8), although a rectification effect (inset in Fig. 8) prevented the determination of the position of the valence band. A further investigation is necessary to explain the rectifying effect in such grain structures.

The grain structure in this type of nanorods would have the same defect structure as that of the prismatic

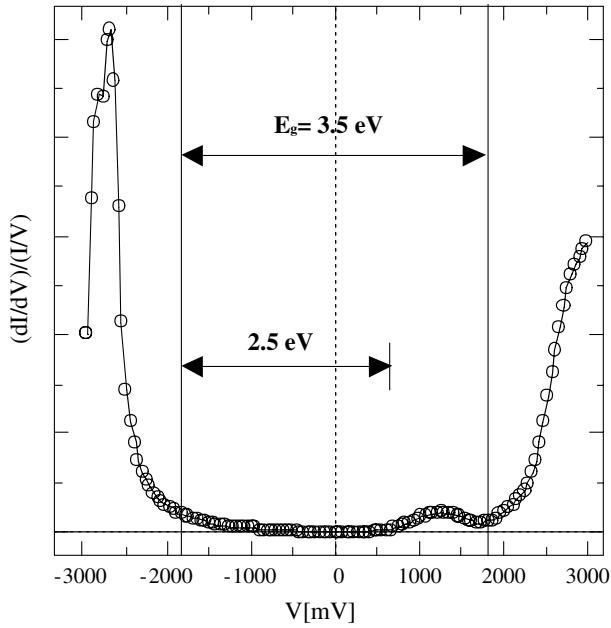


Fig. 5. Normalized differential conductance spectrum from a prismatic nanorod where the flat region of the curve corresponds to the energy gap. The valence and conduction bands are at the left and right respectively.

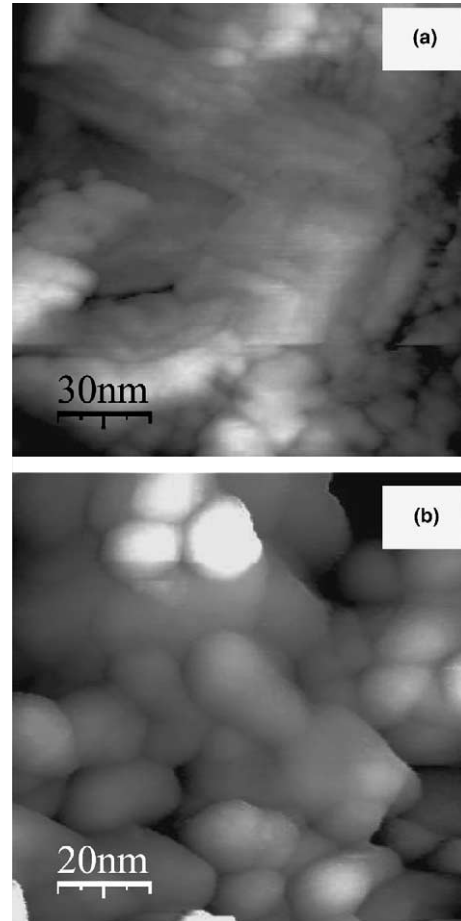


Fig. 7. STM images, acquired at 2.5 V and 1 nA tunneling current, that shows the (a) aligned grain structure and (b) the disordered grain structure of a non-prismatic nanorod.

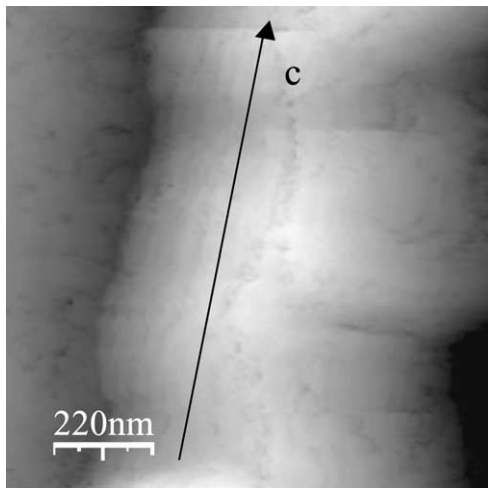


Fig. 6. STM image of a non-prismatic nanorod acquired at 2.5 V sample voltage and 1 nA tunnel current.

nanorods, since they are formed during the same growth process. Oxygen vacancies in the nanorods probably are formed by a strain relaxation process. In relaxed ZnO an increase of the green emission was observed to be associated with an increase of point defects [29]. A relax structure could also explain the difference observed in grain shape between a non-prismatic (round shape) and a prismatic (elonged) nanorods.

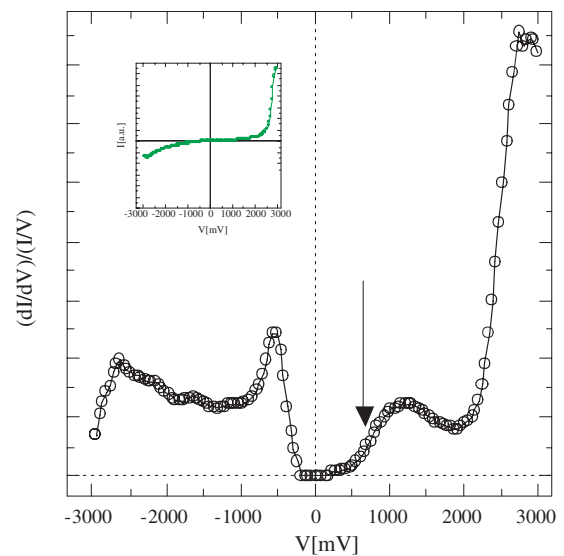


Fig. 8. Normalized differential conductance spectrum from a non-prismatic nanorod. The arrow indicates the deep level position at approximately 600 mV and the inset presents the $I-V$ curve.

4. Conclusions

Uniform, well crystalline ZnO nanorods were synthesized by a modified solvothermal technique. STM and STS techniques were used successfully to evaluate the surface morphology and electronic properties of the nanostructure surfaces. Through STM, we could distinguish ZnO nanorods with different surface morphologies. The surface band gap along with the deep levels related to oxygen vacancies were evaluated. Grain structures on the surfaces of prismatic and non-prismatic nanorods are formed due to strain relaxation at the nanostructure surface.

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