Zinc vacancies and interstitials in ZnO nanorods

N. Boukos *, C. Chandrinou, A. Travlos

Institute of Materials Science, National Centre of Scientific Research "Demokritos", Agia Paraskevi, Athens 15310, Greece

ARTICLE INFO

ABSTRACT

Nominally undoped ZnO nanorods, grown by a chemical method, have been post-treated to intentionally incorporate high concentrations of zinc vacancies and zinc interstitials and were studied with electron microscopy and low temperature photoluminescence spectroscopy. The Zn_i are related to the 3.405 eV peak at 4.2 K, verifying that Zn_i is a shallow donor lying 30 meV below the conduction band minimum, while the acceptors V_{Zn} are related to the 3.308 eV peak at 4.2 K and have an activation energy of 123 meV.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

ZnO is a wide band gap (3.3 eV) semiconductor, which has been the subject of intense interest in recent years [1–5]. The attractive features of ZnO for optoelectronic applications, in addition to its wide band gap – similar to that of GaN – are its high exciton binding energy (60 meV) and the availability of bulk ZnO single crystals [4]. Additional advantages of ZnO are that it can be easily processed by wet chemical etching and that it has excellent stability under high-energy radiation [2]. Furthermore, it can be grown in a variety of nanostructured morphologies, and by low cost, low temperature methods [1]. Still a major problem for the fabrication of optoelectronic devices is efficient p-type doping of ZnO. Even though a lot of research effort has been devoted to p-type doping, there is no generally accepted methodology for the production of stable and reproducible p-type ZnO. Furthermore there is disagreement regarding the origin of the above problem. Some researchers have attributed it to unintentional impurity doping such as H forming shallow donor states, while others to self-compensation by intrinsic point defects [3,6–10]. The intrinsic point defects are considered to play a profound role in the electrical behavior of ZnO. Zinc interstitial, Zn_i, is generally considered to act as a donor. However, its position in the energy gap of ZnO and its optical signature are debatable. Electrical measurements by Look et al. [11] identify zinc interstitials as donors, 30 meV below the conduction band minimum; Sann et al. [12] place it $37+/-5$ meV below the conduction band minimum while Hutson [13] finds a binding energy of 51 meV. Also, even if most theoretical calculations predict that Zn_i is a shallow donor, there are controversial reports on its role in the residual n-type character of ZnO [6–10]. Regarding zinc vacancy, V_{Zn}, it is generally considered to act as an acceptor. Once more there is disagreement about its position

in the energy gap of ZnO and its optical signature. Park et al. [14] correlate V_{Zn} with the 3.31 eV line in the photoluminescence spectrum of ZnO estimating its energy level 90 meV above the valence band maximum. Lin et al. [15] estimate its position 300 meV and Zubiaga et al. [16] 90–125 meV above the valence band, while Zhao et al. [17] propose that it is correlated with the green band of ZnO at around 2.5 eV.

The purpose of the present study is to study the optical signatures of Zn vacancies and interstitials utilizing low temperature photoluminescence (PL) measurements in ZnO nanorods, contributing to the understanding of the defect physics of ZnO which is quite complex and to a large extent unknown. Since the method of creating and annihilating V_{Zn} and Zn_i is the controlled in and out-diffusion of Zn atoms from the surface of ZnO, the form of thin nanorods has been chosen, as opposed to bulk single crystal or polycrystalline thin film, in order to minimize the required diffusion lengths while maintaining single-crystalline samples.

2. Experimental details

The ZnO nanorods were grown on seeded oxidized silicon substrates by a wet chemical method described in detail elsewhere [18,19]. The Zn foil used was ultrasonically rinsed in acetone and IPA prior to use. The seeded substrates were prepared by electron gun evaporation of a 200 nm Ti and subsequent 50 nm ZnO thin film in a high vacuum chamber at room temperature.

The growth of the ZnO nanorods was accomplished in a Teflon cell. A 2×2 cm seeded glass substrate and a Zn foil were immersed in the cell. The Ti thin film and the Zn foil were, externally, short-circuited by a wire. The cell was filled with a solution of analytical grade formamide and distilled water and placed in a hot bath. The temperature of the hot bath was kept constant within 1 °C at 65 °C. After a 60 h growth period the samples were thoroughly rinsed in ethanol and dried in air for characterization.

---

* Corresponding author.
E-mail address: nboukos@ims.demokritos.gr (N. Boukos).

The basic reaction underlying the adopted growth method is the accelerated oxidation of Zn in an aqueous solution with the aid of formamide. The natural oxidation of Zn metal by naturally dissolved oxygen in water is very slow due to the formation of a thin passive ZnO layer. When formamide is added in the solution, the following half-cell chemical reaction takes place in the Zn anode region, resulting in the formation of Zn–formamide complexes:

$$Zn + nHCONH_2 \rightarrow [Zn(HCONH_2)_n]^{2+} + 2e^-$$
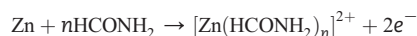
In the vicinity of the substrate, the Zn–formamide complexes decompose, releasing zinc ions that react with the atmospheric oxygen that is dissolved in the solution to form ZnO as shown in the following half-cell reaction:

$$[Zn(HCONH_2)_n]^{2+} + 1/2O_2 + 2e^- \rightarrow ZnO + nHCONH_2$$
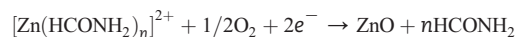
The electrons required are provided through the external short circuit between the Zn metal and the Ti thin film on the silicon substrate. By adding the above partial chemical reactions the net result is the formation of ZnO from zinc metal and oxygen dissolved in the solution, while charge neutrality is preserved by the short circuit between the two electrodes.

After initial growth the following experimental procedure, consisting of consecutive treatments, was adopted in order to produce ZnO nanorods with different concentrations of intrinsic defects. Treatment 1, minimization of initial intrinsic defects: annealing of as grown sample in air at 550 °C for 30 min. As described in an earlier publication [19], any deviation of the Zn/O stoichiometry, during growth, is expected to introduce intrinsic defects in the resulting nanorods. In order to minimize the concentration of these defects in the as grown samples, the above annealing was performed. Treatment 2, introduction of Zn atoms: subsequent e-gun evaporation of Zn metal on the ZnO nanorods in a high vacuum chamber and in situ annealing at 150 °C for 10 min. Since Zn_i are known to be very mobile in ZnO [20], it is expected that the deposited Zn will diffuse into the nanorods forming interstitials and interacting with other already existing intrinsic defects. The amount of Zn deposited was equivalent to a thin film of 5 nm. Treatment 3, partial reduction of excess Zn atoms: subsequent annealing in air at 150 °C for 20 min. The high mobility of Zn_i is expected to result in their partial annihilation. Treatment 4, major reduction of excess Zn atoms: final annealing in air at 550 °C for 60 min. This high temperature anneal is expected to drive out most of the Zn_i and even produce V_{Zn} in the nanorods. Low temperature PL measurements were undertaken after each treatment using a Janis STVP 100 liquid helium flow cryostat fitted on a Horiba Jobin-Yvon iHR320 Spectrometer with a He–Cd laser (325 nm) as the excitation source. The spectrometer was calibrated with an accuracy of 0.06 nm using the 365.015 nm Hg line. The morphology of the resulting samples was determined by scanning electron microscopy, SEM (FEI Inspect microscope, operating voltage 25 kV), while crystal structure was examined by transmission electron microscopy, TEM, (FEI CM20 microscope, operating voltage 200 kV).

3. Results and discussion

Fig. 1a shows a SEM inclined-view image of the as-grown ZnO nanorods. Their mean length and diameter are about 2 μm and 120 nm respectively. The nanorods obtain a hexagonal cross-section and a flat tip. A typical TEM bright field micrograph of one ZnO nanorod is presented in Fig. 1b, exhibiting no extended crystalline defects. The selected area electron diffraction (SAED) pattern of the nanorod, shown in upper inset, verifies that the nanorod is single crystalline. The SAED pattern corresponds to the $\left[2\overline{1}\overline{1}0\right]$ zone axis of wurtzite hexagonal structure ZnO (JCPDS 36-1451). Furthermore, the SAED pattern indicates that the nanorod grows along the c-axis. It should be noticed that subsequent annealing and processing of the samples did not produce any change in their morphology or crystallinity.

The low temperature photoluminescence UV part of the spectrum of the ZnO nanorods after the different consecutive treatments is depicted in Fig. 2. Spectra are shifted on the vertical axis for clarity. The energy position and assignment of the peaks is shown in Table 1. There are two main regions in the spectra. The high energy part comprising of peaks at 3.405, 3.375, 3.364, 3.359, 3.331 and 3.308 eV and the low energy part with less prominent peaks which correspond to phonon replicas of the former, given that LO phonon is 72 meV [21]. The 3.375 eV, B, peak is the well known free exciton of ZnO [21] which is of low intensity due to the existing competitive bound excitons. The 3.364 eV, C, peak is indentified as a donor bound exciton, DBX, [12]. In a previous publication [19], the growth of ZnO nanorods under Zn-lean conditions resulted in the increase of intensity of the 3.359 eV, D, peak and 3.308 eV, F, peak. We had attributed these peaks to an acceptor bound exciton and the associated free electron to acceptor transition, identifying the acceptor as V_{Zn}. Adjustment of Zn/O ratio during growth and the resulting scaling of the 3.359 eV, D, peak led to the conclusion that this peak and the 3.308 eV, F, peak to the associated free electron to acceptor transition, while we have identified the acceptor as the zinc vacancy. It is evident from Fig. 2 that the excitonic peak D scales with peak F and with the amount of Zn diffusing out of the nanorods during successive anneals confirming this former conclusion. This is further strengthened by the temperature dependence of the peaks as discussed below.
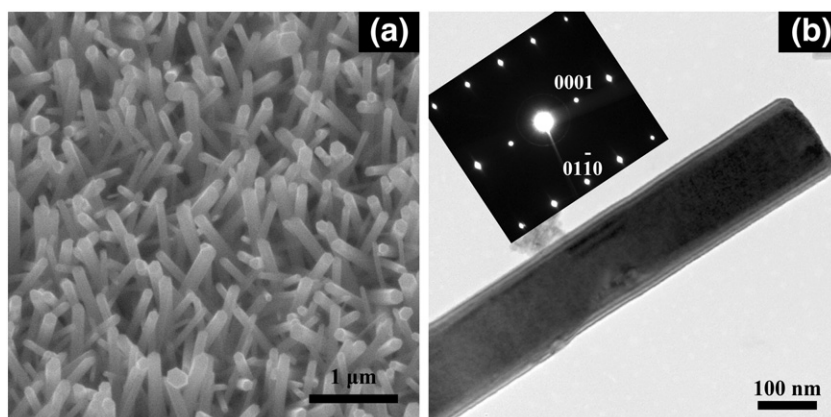

Fig. 1. (a) SEM inclined view of as-grown ZnO nanorods. (b) Typical TEM bright field image and corresponding SAED pattern shown in the inset of an as-grown ZnO nanorod.