

# Photoluminescence of ZnTe nanowires prepared by electrochemical etching of bulk ZnTe

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**Abstract** — We demonstrate the preparation of ZnTe nanowires with the diameter of 50 nm from bulk p-type ZnTe by means of electrochemical treatment in a pulse regime. The nanowires demonstrate photoluminescence characteristics identical to those of the initial bulk material. The luminescence is shown to come from recombination of excitons bound to an acceptor and from recombination of two types of donor-acceptor pairs involving a shallow acceptor and two species of donors, one of which is shallow, and another one is deep. Since the initial crystals are doped with Na, it is suggested that the acceptor involved in all these three transitions is related to Na.

## I. INTRODUCTION

Over the last decade, artificial nanostructuring of semiconductor materials has emerged as an effective tool for controlling their optoelectronic properties. Particularly, efficient optical phonon engineering, induced birefringence, strongly enhanced second harmonic generation and terahertz emission have been demonstrated [1–5].

Apart from these one-component nanostructures, porous semiconductors represent suitable templates for the fabrication of nanocomposites via filling the pores with other inorganic and organic materials including conducting polymers, which considerably extends the possibilities for developing light emitting devices and hybrid solar cells. When the characteristic dimensions of the porous skeleton entities correlate with or are much smaller than the wavelength of the electromagnetic radiation, a strong diffuse scattering of light takes place in the nanocomposite leading to the onset of light localization [6]. Because of the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling inorganic materials on the nanometer scale opens opportunities for the development of future generations of solar cells [7]. Especially important are widebandgap p-type nanostructured semiconductor templates, which can be filled with n-type ZnO and constitute a promising basis for a new type of cost effective solar cells.

The electrochemistry offers an easily accessible and cost-effective approach for tailoring the morphology of semiconductors by introducing porosity on a variable length scale. This approach has been demonstrated [5] in Si and III-V compounds using wet chemical etching. A variety of porous semiconductor architectures have been produced by anodic chemical etching, including periodic pore arrays [8]. While the electrochemical etching is a versatile tool for use in nanostructuring of narrow and

medium bandgap materials such as Si, InP, GaAs, GaP, use of this method for wide bandgap II–VI semiconductors is still a challenge. The related difficulties are linked with controlling the conductivity of the source material, as high carrier concentration is needed to apply anodic etching for nanostructuring.

Among II–VI compounds, the effect of photoetching on the photoluminescence (PL) of n-CdSe was studied many years ago [9], but the authors claimed the formation of etch pits rather than pores. Recently we succeeded in introducing pores into n-type CdSe [10] and we observed gain of luminescence in the porous regions characterized by strong light scattering [11]. Formation of porous network in a p-type II–VI material, namely, in p-CdZnTe, was demonstrated by Erne *et al* [12,13]. Also, Zenia *et al* subjected p-ZnTe crystals to electrochemical etching and observed the formation of needlelike structures exhibiting a blueshift of the excitonic transition energies [14].

In this paper we demonstrate the nanostructuring of bulk ZnTe substrates by means of pulse electrochemical treatment, and investigate the photoluminescence properties of the nanostructured material.

## II. EXPERIMENTAL DETAILS

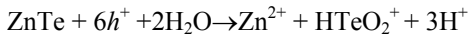
Na doped <110> oriented ZnTe substrates with the free hole concentration of  $3 \times 10^{18} \text{ cm}^{-3}$  were anodized in a double-chamber electrochemical cell as described elsewhere [8]. The temperature of the electrolyte was kept constant with a thermostat. The electrolyte was continuously pumped through both chambers of the double cell with the help of a peristaltic pump. The area of the sample exposed to the electrolyte solution was  $0.25 \text{ cm}^2$ . The anodic etching was carried out in a  $\text{HNO}_3:\text{HCl}:\text{H}_2\text{O}$  electrolyte with the ratio of 5:20:100 at  $25^\circ\text{C}$  with the application of 0.3 sec voltage pulses with frequency of 1 Hz and amplitude of 5 V. After the etching the samples were dipped in a solution of polysulfide to remove oxidation products, and then rinsed in de-ionized water.

The resulting morphology of the etched samples was studied using a TESCAN scanning electron microscope (SEM).

Photoluminescence (PL) was excited by 488 nm line of an Ar<sup>+</sup> laser, and 325 nm line of a He-Cd laser and was analyzed by means of a double spectrometer having a resolution better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryostat.

### III. RESULTS AND DISCUSSIONS

The typical morphologies of anodized samples at two stages of treatment are shown in the SEM images presented in Fig. 1. The etching process starts at surface imperfections, possibly dislocations, and proceeds by the growth of etch pits. The overall dissolution process can be described by the reaction [14]



where  $h^+$  are holes.

The form of the etch pits depends on the symmetry of the surface. A multitude of etch pits are realized on the surface of the sample electrochemically treated during 15 min (upper image in Fig. 1). The rectangular symmetry of an etch pit illustrated in the inset of Fig. 1 is typical for a (110) oriented surface [14]. Lateral growth of the pits proceeds until the peripheries of the pits begin to intersect.

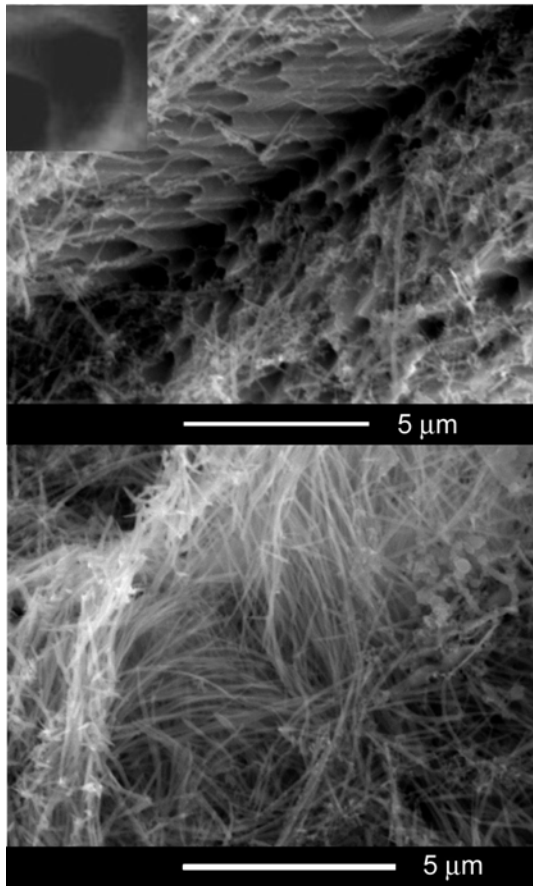


Fig.1. SEM view of a ZnTe sample after 15 min (upper image), and 30 min (lower image) of electrochemical treatment. Inset is the large view of an etch pit.

Further etching leads to the formation of a conglomeration of nanowires with the diameter around 50 nm as shown in the lower image of Fig. 1.

The investigation of photoluminescence demonstrates the high quality of the produced ZnTe nanowires since the emission intensity and the PL spectrum are practically identical to those of the initial bulk material.

Fig. 2 presets the PL spectra of the ZnTe nanowires measured at different temperatures. The sample shows a band-edge emission peak at 2.377 eV followed by two dipper bands at 2.330 eV and 2.304 eV previously attributed to donor-acceptor pair (DAP) recombination and its LO phonon replica [15,16].

Apart from near-band-edge emissions, a broad and structured deep-level-related PL band is observed at lower photon energies. This band corresponds to a zero-phonon line at 2.240 eV with a series of phonon replica at 2.213 eV, 1.187 eV, 2.161 eV, etc. Previously a similar structured band with the zero-phonon line at 2.246 eV has been observed in this spectral range in ZnTe single crystals [17,18,19], and it has been attributed to DAP recombination with Cu as an acceptor.

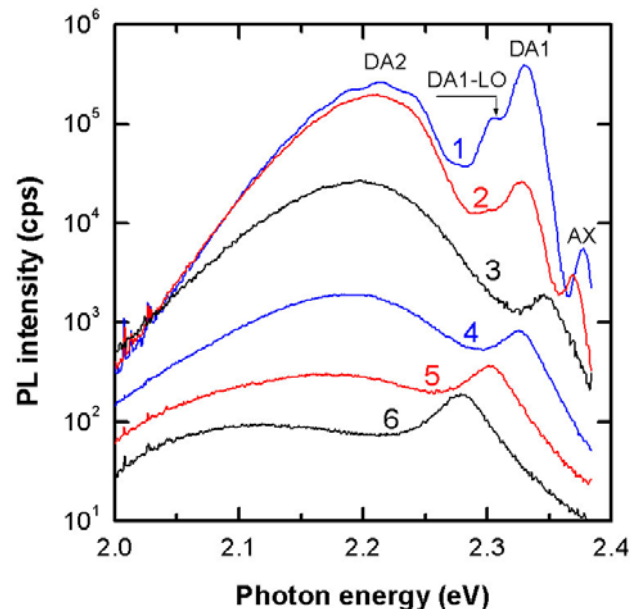


Fig. 2. PL spectra of ZnTe nanowires excited by the 488 nm laser line at the temperature of 10 K (curve 1), 50 K (curve 2), 100 K (curve 3), 150 K (curve 4), 200 K (curve 5), and 250 K (curve 6).

Since our as grown ZnTe samples are doped with Na, we suggest that the two observed DAP emission bands (DA1 and DA2) have this impurity as an acceptor involved in the DAP transition. In the case of the DA1 transition the donor involved is shallower than the Na acceptor. The sharp decrease of the intensity of the DA1 emission band in the temperature interval 10 – 100 K (see Fig. 2) is due to the ionization of the donor impurity with increasing temperature. By the contrary, the donor involved in the DA2 transition is deep enough, and the decrease of the intensity of the DA2 PL band in the temperature interval 100 – 300 K is due to the ionization of the Na acceptor.

As concerns the excitonic emission, previously a PL band at 2.375 eV associated with the recombination of excitons bound to an unidentified acceptor has been observed in MOCVD grown ZnTe layers [15,16], and a PL band at 2.377 eV has been attributed to the recombination of excitons bound to Cu acceptor in bulk ZnTe single crystals [17,18,19]. In spite of a practical coincidence of the position of the AX band observed in our nanowires with the position of the band associated with the excitons bound to Cu acceptor, we believe that the excitons observed in our nanowires are bound to the Na acceptor, since this is a major acceptor impurity in our samples.

Figure 3 compares the PL spectra of the ZnTe nanowires measured under the excitation with two different laser lines, and with different excitation power density.

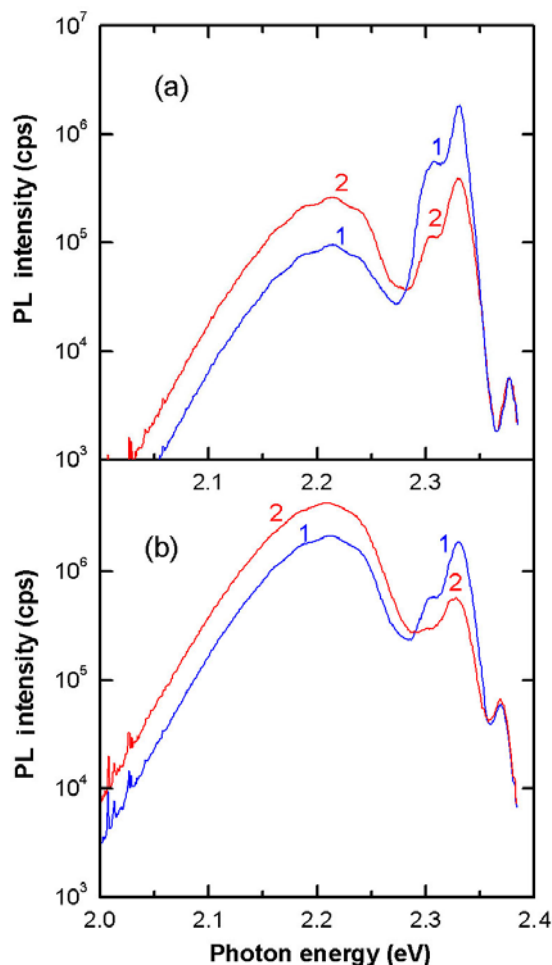


Fig. 3. PL spectra of ZnTe nanowires measured at 10 K under excitation by 325 nm He-Cd laser line (1) and 488 nm Ar<sup>+</sup> laser line (2) with excitation power density of 100 W/cm<sup>2</sup> (a) and 1000 W/cm<sup>2</sup> (b).

One can observe that the increase of the excitation power density by an order of magnitude in both cases leads to the increase on the AX PL band intensity by a factor of 10, i. e. it increases linearly with increasing the excitation power density. This is consistent with the excitonic nature of this PL band. In contrast to this, the intensity of the DA1 PL band practically does not change. This behaviour is explained by a sublinear dependence of the intensity of emission with increasing the excitation power density

usually observed for DAP transitions [10,20], and by the heating of the sample under excitation power densities as high as 1000 W/cm<sup>2</sup>. The heating of the sample is confirmed by the shift of the AX PL band from 2.377 eV to 2.369 eV with the excitation power density increase from 100 W/cm<sup>2</sup> to 1000 W/cm<sup>2</sup>. As one can see from Fig. 2, the temperature increase from 10 K to 50 K leads to a decrease of the DA1 PL band intensity by more than one order of magnitude.

The analysis of Fig. 3 also shows that the intensity of the DA1 PL band is higher under the excitation by the 325 nm laser line, while the intensity of the DA2 band is higher under the 488 nm laser line excitation. Taking into account that the radiation with the wavelength of 325 nm is absorbed in a thinner layer at the surface of the sample as compared to the 488 nm radiation, one can suggest that the concentration of the shallow donor involved in the DAP transition with the Na acceptor is higher on the surface of nanowires, while the concentration of the deep donor is higher in the bulk.

#### IV. CONCLUSION

The results of this study demonstrate the preparation of high optical quality ZnTe nanowires by means of pulse electrochemical treatment. The pulse anodization does not change the crystal quality of the material in spite of the production of nanowires with the diameter of 50 nm, i. e. an enormous increase of the surface to volume ratio. Taking into account the p-type conductivity and the high quality of the produced ZnTe nanostructures, one can assume that the combination with n-type ZnO represents a promising basis for the development of cost effective, high efficiency nanostructured solar cells.

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