

# Peculiarities of electron field emission from ZnO nanocrystals and nanostructured films

A.A. Evtukh<sup>a</sup>, V.G. Litovchenko<sup>a</sup>, M.O. Semenenko<sup>a</sup>, V.A. Karpyna<sup>b</sup>,  
G.V. Lashkarev<sup>b,\*</sup>, V.I. Lazorenko<sup>b</sup>, V.D. Khranovskyy<sup>b</sup>, L.I. Kopylova<sup>b</sup>,  
I.Yu. Okun<sup>b</sup>, Yu.P. Piryatinsky<sup>c</sup>

<sup>a</sup> Lashkarev Institute of Semiconductor Physics, NASU 41 Prospekt Nauki, Kyiv, 03028, Ukraine

<sup>b</sup> Institute for Problems of Material Science, NASU, 3 Krzhizhanovskogo, Kyiv, 03680, Ukraine

<sup>c</sup> Institute of Physics, NASU, 46 Prospekt Nauki, Kyiv, 03650, Ukraine

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## Abstract

ZnO microcrystals and nanocrystals were grown on silicon substrates by condensation from vapour phase. Nanostructured ZnO films were deposited by plasma enhanced metal organic chemical vapour deposition (PEMOCVD). The parameters of field emission, namely form-factor  $\beta$  and work function  $\phi$ , were calculated for ZnO structures by the help of the Fowler–Nordheim equation. The work functions from ZnO nanostructured films were evaluated by a comparison method. The density of emission current from ZnO nanostructures reaches  $0.6 \text{ mA/cm}^2$  at electric force  $F = 2.1 \cdot 10^5 \text{ V/cm}$ . During repeatable measurements  $\beta$  changes from  $5.8 \cdot 10^4$  to  $2.3 \cdot 10^6 \text{ cm}^{-1}$ , indicating improvement of field emission. Obtained values of work functions were  $3.7 \pm 0.37 \text{ eV}$  and  $2.9\text{--}3.2 \text{ eV}$  for ZnO nanostructures and ZnO films respectively.

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## 1. Introduction

Microsized and nanosized ZnO crystals are of great interest and show prospects for developing new optoelectronic display systems, sources of UV radiation, LEDs based on heterostructures,

\* Corresponding author.

E-mail address: [gvl35@ipms.kiev.ua](mailto:gvl35@ipms.kiev.ua) (G.V. Lashkarev).

etc. First of all, ZnO is able to generate UV excitonic luminescence and so-called deep-level luminescence in the green and yellow ranges of optical spectra. Due to the high binding energy of excitons ( $E_b = 60$  meV, that exceeds essentially the thermal energy at room temperature (RT),  $kT = 26$  meV) it is possible to observe effective UV photoluminescence and even lasing at RT and higher temperatures in polycrystalline ZnO films, which was demonstrated in papers [1–3].

Moreover, ZnO is a prospective material for developing electron field emitters for application in various vacuum devices as cold cathodes. First, ZnO, as other wide band gap semiconductors (GaN, AlN), has low electron affinity, high mechanical firmness and chemical stability. Second, ZnO can be deposited in form of microstructures and nanostructures. Nanostructured materials with high aspect ratio such as nanotubes and nanorods are considered as prominent materials for application in devices of vacuum microelectronics and nanoelectronics as electron field emitters. One-dimensional (1D) ZnO structures are used as alternative materials to carbon nanotubes for field emission devices [4,5]. However, electron field emission (EFE) from semiconducting nanostructures based on ZnO has not been studied much. Thus, it is necessary to investigate the basic parameters of EFE from micro-sized and nano-sized ZnO objects. In this paper the investigations of EFE peculiarities from ZnO microstructures and nanostructures deposited on silicon substrates by different technologies are presented. Morphology as well as crystal structure were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Photoluminescence spectra from the obtained ZnO structures are also presented. Moreover, we have also investigated EFE from nanocrystalline ZnO films deposited on Si tips by the plasma enhanced metal organic chemical vapour deposition (PEMOCVD) technique. We assume that Si tips coated by ZnO films display more efficient electron field emission due to the lowering of the work function in this structure.

## 2. Experimental data

### 2.1. Growth of crystalline semiconducting ZnO structures

Crystal structures of ZnO with various shape and size were grown by condensation from the vapour phase. The deposition process was carried out in a thin quartz tube. As an initial material highly purified ZnO powder mixed in equal molar ratio with carbon powder was used. The mixture was loaded in an alumina boat which was placed at the centre of the tube, inserted in a horizontal furnace, and heated up to 1100 °C. A temperature gradient of about 50 °C/cm occurred along the tube. The boat with the initial material was placed in the high-temperature region while the monocrystalline silicon substrates were placed in colder regions, at temperatures 500–800 °C.

The ZnO films were deposited by the PEMOCVD technique [6,7]. The system consists of a horizontal quartz chamber with electrodes supplied by 13.56 MHz voltage. First the chamber was evacuated to a pressure of 10 Pa. Then, an argon–oxygen gas mixture was introduced into the chamber at a pressure 50 Pa. The setup was equipped with an additional device for thermal decomposition of the solid metal organic precursor, zinc acetylacetonate (Zn(AA)). Its vapour was transported into the chamber by the argon gas carrier. The Zn(AA) vapour excited by plasma discharge in the argon–oxygen atmosphere totally decomposes and generates zinc ions which react with active oxygen forming ZnO molecules which deposit on the substrate. The substrate temperature was maintained in the range 250–300 °C. Thicknesses of deposited films were in the range 150–300 nm.

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