Point field emitters based on rod-like ZnO nanocrystals

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Abstract. New semiconducting anisotropic materials for field emitters, such as ZnO, are of interest from practical and scientific standpoints. Usually, rod-like nanocrystals have a length of few hundred microns and a radius of curvature less than hundred nm. In the present work, rod-like nanocrystals ZnO with high aspect ratio are investigated. They are obtained by high-temperature pyrolysis of Zn compounds. FIB Quanta 200 3D is used for preparation, structure characterization and field emission experiments. With the help of a Kleindiek micromanipulator, the most suitable crystal rods are transferred to the tungsten needle tip and fixed using tungsten gaseous injection system (GIS). As a result, ZnO point emitters are formed with a tip radius of curvature less than 50 nm. Emission characteristics revealed a field amplification coefficient ($\beta$) of about 1500 for an anode-cathode distance of 50 $\mu$m.

1. Introduction

Rod-like ZnO crystals with high aspect ratio are promising as semiconducting, high melting temperature materials for field emission. There are few investigations dedicated to the field emission of ZnO individual crystals. Current-voltage ultra low threshold field emission characteristics were obtained from a single multipod [1]. Anode-cathode distance dependence of the enhancement coefficient was investigated by transmission electron microscopy in situ [2]. In [3], the correlation between resistance and emission of individual ZnO nanostructures has been measured as an anode with manipulator was brought directly to the ZnO tip.

2. Experimental

Rod-like crystals were obtained by high temperature pyrolysis of organic Zn compounds in presence of Al as a catalyst. Rods that are most suitable for the emission experiments are hundred microns long and from 40 to 100 nm in diameter. The shape of crystals has been characterized by scanning electron microscopy (SEM) with a JEOL JSM- 7401F and the crystal structure has been investigated with an FEI Titan 80-300 (Figure 1,2,3). From lattice imaging (HREM) it is possible to say that the growth direction is [0001] and the surface of the rod-like crystals is clean. Both SEM and HREM revealed narrowing endings and round tips ($r=50$ nm).

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Emission experiments have been performed in situ using a focused ion beam (FIB) Quanta 200 3D with Kleindiek micromanipulator and tungsten gaseous injection system (GIS). The anode was mounted on the end of micromanipulator to enable control of the anode-cathode distance in the range 5-50 µm. The anode itself was prepared by tungsten evaporation on manipulator needle. The anode diameter was about 5 µm (figure 4). The emission measurements have been performed at pressure about 10^{-4} Pa. The field amplification coefficient $\beta$ can be calculated using equation (1) [4]:

$$\beta = \frac{I_{\text{em}}}{I_{\text{th}}}$$
where \( l \) is the length of the rod and \( r \) is its apex radius. So for a 100 \( \mu \)m rod-like emitter with apex radius 50 nm, the amplification coefficient is \( \beta = 1123 \).

The current-voltage characteristics have been recorded with a Keithley 6487 combined unit, which contains the current meter and the controlled source with voltages up to 500V in steps of 5 V. When the anode-cathode distance is 2 \( \mu \)m at 500 V then the ZnO crystal is destroyed (corresponding to an electric field of 250 MV/m).

One can model the emission properties of cold field emitters using Fowler-Nordheim equation:

\[
\ln\left( \frac{J}{E_i^2} \right) = \ln\left( \frac{A}{\varphi} \right) - \frac{B\varphi^{3/2}}{E_i} \quad (2),
\]

where \( J \) is the current density, \( E_i \) the intensity of the local electric field, \( A = 1.56 \times 10^{-10} \text{A}^2 \text{V}^{-2} \text{eV} \), \( B = 6.83 \times 10^{10} \text{eV}^{-3/2} \text{V}^2 \text{m} \) and \( \varphi \) the work function for ZnO. Local electric field is usually calculated using the formula:

\[
E_i = \frac{B}{\beta} \frac{\varphi^{3/2}}{\varphi} \quad (3),
\]

where \( V \) is the applied voltage, and \( d \) is the distance between the anode and cathode. Accordingly, Eq. (2) and \( J = l/2\pi^2 r^2 \) (relationship between current \( I \) and current density \( J \) for the spherical cathode) in our case yield:

\[
\ln\left( \frac{I}{E_i^2} \right) = \ln\left( \frac{2\pi^2 A\beta^2}{\varphi} \right) - \frac{B\varphi^{3/2}}{E_i} \quad (4)
\]

From the slope \( K \) of this dependence it is possible to calculate the coefficient \( \beta \):

\[
\beta = \frac{B\varphi^{3/2}}{K} \quad (5)
\]

Using the micromanipulator some thin and long rods have been picked out and mounted on the end of tungsten needle (obtained by chemical etching) by local tungsten evaporation. As a result, a point

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**Figure 4.** Field emission experiment:

(a) rod-like ZnO mounted on the tungsten needle tip,
(b) anode is moved close to the ZnO tip.
emitter has been formed (Figure 4). Table 1 shows the results of the calculation of the coefficient $\beta$ for four different distances $d$ for the same sample on the basis of the curves in Figure 5, 6.

![Figure 5](image1) ![Figure 6](image2)

**Figure 5.** Field emission current as a function of electric field and anode-cathode distance.  
**Figure 6.** Fowler-Nordheim plot.

| $d$, $\mu$m | $K$, V$^{\mu}$m | $\beta$ | maximal current, $\mu$A |
|-------------|-----------------|--------|----------------------|
| 5           | 7137900         | 116    | 1.3                  |
| 17          | 3100000         | 264    | 1.0                  |
| 38          | 589718          | 1413   | 0.012                |
| 50          | 557191          | 1500   | 0.2                  |

### 3. Conclusion

A technique of preparation of point emitters from rod-like ZnO crystals using the FIB Quanta 200 3D device has been developed. The threshold values of the electric field, at which the emitters break down, is measured as 250 V/$\mu$m. Rod-like ZnO crystals revealed substantial amplification coefficient $\beta$, which strongly depends on $d$. We believe that rod-like ZnO crystals are encouraging candidates for field emission materials. Low emission current stability is associated with deficient vacuum in the SEM chamber. In the future experiments the characteristics will be measured in ultra high vacuum.

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