Indium-doped ZnO nanopencils: structural and field emission properties

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Abstract. This paper reports on the direct growth of In-doped ZnO nanopencils on Si substrate by facile thermal evaporation process using metallic zinc and In powders in the presence of oxygen. The as-grown nanostructures were examined in detail in terms of their morphological, structure and field emission properties. The morphological studies, carried out by FESEM, exhibited that the grown structures possess homogeneous morphologies with pointed tips similar to pencils. The typical tip diameters of as-synthesized nanopencils are in the range of ~13 ± 3 nm which reflects that these nanopencils could be a promising candidate for field emission applications. The detailed structural properties revealed that the prepared nanopencils are well-crystalline and possessing wurtzite hexagonal phase. For application viewpoint, the field emission properties of as-grown In-doped ZnO nanopencils were examined which exhibited a very low turn-on voltage of 1.3 kV.

1. Introduction
Recently, the fabrication, characterization and utilization of 1D nanomaterials are receiving great interest due to their peculiar, fascinating physical, chemical and mechanical properties which are different from their bulk counterparts. Among the various possible applications, the utilization of 1D nanomaterials for field emission (FE) devices is one of the most active research areas because of its practical applications in FE displays, x-ray sources and microwave devices, etc [1-4]. Therefore, many studies have been carried out in this area in the past decades. In this direction, the carbon nanotubes (CNTs) were extensively studied for their potential as field emitters and particularly their very high aspect ratio. However, CNTs as field emitters were found to be sensitive to the working environment (especially, H2O and O2 adsorbates) which leads to high instability in the field emission performance [5, 6]. To overcome these problems, researchers have recently tried to use metal oxide nanomaterials for the fabrication of field emission devices [7]. Amongst the various metal oxide materials, the II-VI semiconductor zinc oxide (ZnO) possesses a special place as a “smart material” due to its own properties and wide applications [7]. The attractive properties of ZnO include its wide band gap (3.37
eV), high exciton binding energy (60 meV) at room-temperature, low electron affinity, high mechanical strength and chemical and thermal stability. Hitherto, a variety of ZnO nano- and microstructures have been synthesized using various fabrication techniques and their optical and FE properties have been checked and demonstrated in the literature [7]. Moreover, to enhance the field emission properties of ZnO nanomaterials, various metal doping have also been performed and reported in the literature [7]. By detailed studies, it was found that the shape and size of the doped and undoped ZnO nanomaterials have strong influence on the field emission properties of the material. To examine this fact, in the previous study the, various morphologies of undoped ZnO, such as nanosheets networks and nanorods and Ga-doped ZnO nanoneedles have been investigated for field emission device applications. In this paper, the growth, characterizations and field emission applications of In-doped ZnO nanopencils is presented.

2. Experimental details
In-doped ZnO nanopencils were grown on a silicon substrate by facile thermal evaporation process by using metallic indium and zinc powders in the presence of oxygen. Silicon wafers (1 x 1.5 cm) were used as substrates for the deposition which were ultrasonically cleaned with DI water and isopropyl alcohol and finally rinsed with acetone. In a typical reaction process, high-purity metallic Indium and zinc powders were thoroughly mixed in 1:10 ratio and transferred into a quartz boat and placed at the centre of the quartz tube furnace. Consequently, the cleaned substrates were placed adjacent to the source material. After this arrangement and prior to starting the heating, the quartz tube furnace was evacuated to 10⁻¹~ 10⁻³ mbar and kept under vacuum throughout the synthesis process. After evacuation of the quartz tube, the furnace was heated up to 800 °C using a halogen lamp heating system in the presence of high purity nitrogen and oxygen gases. Once the temperature of the furnace reached over 500 °C, indium and zinc vapors were generated (as the melting point of Indium and zinc powders are less than 500 °C) which were transferred to the substrate by nitrogen carrier gas. The oxygen gas was reacted with the generated zinc and indium vapors and finally the growth was carried out. The reaction was completed in 1 hr. After completing the reaction, the furnace was very slowly cooled down (15 °C/min) to room-temperature and the deposition of a grayish white colored product was observed onto the whole substrate surface. The deposited material was characterized in terms of its morphological, structural and field emission characteristics by using various analytical tools.

3. Results and discussion
3.1 Morphological, compositional and structural properties of as-prepared In-doped ZnO nanopencils
The general morphologies of as-prepared material was examined by field emission scanning electron microscopy (FESEM) and presented in figure 1 (a) which confirm that the prepared material possess pencil-shaped morphologies and that these nanopencils are grown in very high density as. It is also interesting to see that the nanopencils are made of two parts; i.e. a hexagonal nanorod and a nanoneedle which are connected in such a manner that the base of the nanoneedle is attached to the head of hexagonal nanorod. The typical diameters of the base hexagonal nanorods in the nanopencils are ~80 ± 10 nm while the lengths are in the range of ~3 ± 0.5 µm. The diameters for the tips of the nanopencils are ~13 ± 3 nm. The hexagonal morphology of the synthesized nanopencils reveals that the synthesized products possess wurtzite hexagonal phase. It is worth mentioning that such nanostructured morphologies are very promising for the fabrication of field emission devices.

Figure 1 (b) exhibits the typical EDS spectrum of as-prepared In-doped ZnO nanopencils which confirmed that the nanopencils are made of zinc, indium and oxygen as spectrum exhibits peaks only related with these elements. No other peak related with any other element is seen in the EDS spectrum further reveals that the nanopencils are In-doped ZnO without any significant impurity, up to the detection limit of EDS method.

The crystallinity and crystal phases of the as-prepared ZnO nanopencils were examined by x-ray diffraction (XRD) pattern and shown in figure 2. Several well defined diffraction reflections are seen in the observed XRD pattern which are mostly related with the wurtzite hexagonal phase of ZnO.
small diffraction reflection originated at 54.5° is related with In and can be assigned as In (112). In addition to zinc and In reflections in the diffraction pattern, a small reflection appeared at 32.9° which is due to the silicon substrate and can be attributed as Si(002). Finally, due to the presence of a small In peak with other wurtzite ZnO reflections in the pattern reveals that the In atoms are efficiently incorporated into the lattices of grown nanopencils. Moreover, no characteristic diffraction reflection related with any impurity was detected in the pattern within the detection limit of the x-ray diffractometer, which confirms that the synthesized nanopencils are well-crystalline and are pure In-doped ZnO.

![Figure 1](image1.png)

**Figure 1.** (a) FESEM image and (b) EDS spectrum of as-grown In-doped ZnO nanopencils on silicon substrate prepared by thermal evaporation process

![Figure 2](image2.png)

**Figure 2.** XRD pattern of as-grown In-doped ZnO nanopencils on silicon substrate.

### 3.2 Field emission (FE) properties of as-prepared ZnO nanorods on Ti Substrate

The determination of FE property of In-doped ZnO nanopencils was carried out in a vacuum chamber with pressure of 3x10^{-8} mbar. The field emission curve was obtained by increasing the applied voltage from 0 to 3kV with steps of 0.1 kV. The I-V characteristics curve and FE pattern of the In doped ZnO nanopencils along with the corresponding FN plot are shown in figure 3 (a) and (b) respectively.

The turn on and threshold voltages were found to be ~1.3 kV with emission current of 80 nA and 3kV with emission current of 17.15 µA, respectively. It is well known that the distribution of the field around an emitter depends on its shape, therefore, the low turn on voltage of the In-doped ZnO nanopencils can be related to their distinctive geometrical configuration [8]. The In-doped ZnO nanopencils are excellent candidates for FE due to these reasons: i) the ultra-fine part of the tip intensify and strengthen the electric field around the apex of the emitter giving rise to huge enchantment of the local electric field leading to electrons being emitted at low electric field [9]. ii) The two step configuration localizes the electric field on the ultra-fine part of the emitter and therefore avoids emission from unwanted sites specially the thick base of the emitters [9]. The impact of the
doping is equally important to the geometry effect and cannot be ignored. Doping of indium into the ZnO leads to improvement in the electrical properties (i.e. conductivity and carrier concentration) and therefore lowering the work function which gives rise to enhancement of the field emission performance of these emitters [10].

**Figure 3.** FE measurements of ZnO nanopencils; (a) current-voltage curve and the typical FE pattern image (inset of (a)) and (b) corresponding F–N plot.

### 4. Conclusion

In summary, In-doped ZnO nanopencils were grown on silicon substrate by facile thermal evaporation process using metallic In and zinc powders in the presence of oxygen. The detailed morphological and structural properties revealed that the prepared nanomaterials are nanopencils, grown in high density and possessing wurtzite hexagonal phase. The field emission properties of the as-prepared nanopencils grown on silicon substrate were also investigated which exhibited a very low turn-on voltage of 1.3 kV. The field emission results show that the In doped ZnO nanopencils emitters can be very efficient candidate in applications such as flat panel displays and high brightness electron sources.

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