RESEARCH PAPER

2D Porous ZnO Nanosheets: One Pot Synthesis with Low Turn-on Field

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ABSTRACT

Low turn-on field of 2.3 V/μm was found for the emission current density of 10 μA/cm^2 from 2D porous ZnO nanosheets. High current density of 0.76 mA/cm^2 was drawn at an applied field of 4.1 V/μm. The observed low turn-on field of porous ZnO nanosheets has been found to be superior to the other ZnO nanostructures reported in the literature. Also, the emission current stability over a period of 3 hr is found to be better. The field emission current density-applied field (J-E) and current-time (I-t) measurements were carried out in all metal field emission microscope by using 'close proximity' (also termed as 'planar diode'). The porous ZnO nanosheets were synthesized by Chemical Bath Deposition (CBD) method at room temperature followed by annealing at 200 °C. The annealed ZnO nanosheets were subjected to structural and morphological analysis prior to the field emission studies. The XRD spectrum of the as-synthesized product reveals formation of crystalline hexagonal phase of ZnO. Simple synthesis route with superior field emission properties indicate the possible use of porous ZnO nanosheets for micro/nanoelectronic devices.

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INTRODUCTION

Due to the high potential application in micro/nano electronics devices, semiconducting nanostructures such as nanowires [1], nanorods [2], nanotubes [3], nanowires [4], nanobelts [5], nanobeads [6] and nanosheets [7] have gain much attention of researchers toward synthesis. Among them Two-Dimensional (2D) nanosheets possesses various interesting features due to their special geometry and high aspect ratio [8]. Therefore, considerable efforts have been made to synthesized 2D nanosheets. The interesting properties of 2D nanosheets have been explored and used for various applications such as energy storage and conversion, catalysis, electronic devices, sensing, biomedicine and field emission [9]. Nowadays, 2D materials have been widely studied for field emission application due to their high electrical conductivity [10-17].

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Field emission is purely quantum mechanical phenomenon where electrons are emitted from surface of nanomaterials under the action of strong electrostatic field and it is geometry dependent phenomenon. Various 2D nano materials proved themselves as an excellent field emitter [7, 10-17]. A vast literature survey, including recent reports [18-20] indicate that, field emission studies of porous ZnO nanosheets are not found to be explored. Hence, exploration of the field emission studies of the porous ZnO nanosheets is important for the scientific and technological advancement.

A Zinc Oxide (ZnO) is a promising material which exhibit quite superior physical and chemical properties. ZnO is an n-type semiconductor having a wide band gap of 3.37 eV with a large exciton binding energy of 60 meV [21]. ZnO nanostructures have been explored for a wide range of applications such as solar cells, sensors, displays, catalysis, and photocatalysis [22]. Furthermore, ZnO with large surface architecture can be synthesized via various low cost chemical methods [23, 24]. Recently, we have reported the synthesis of 2D cactus like ZnO by using simple solution chemistry route [25].

In the present paper, we report the synthesis of porous ZnO nanosheets by modified Chemical Bath Deposition (CBD) technique. Possible reason behind observation of low-turn on field is discussed in detail.

MATERIALS AND METHODS

Synthesis of porous ZnO nanosheet

All the chemicals were purchased from Sigma-Aldrich, India, and were used as received without further purification. Prior to the deposition, silicon (Si) substrates were cleaned in dilute HCl for 5 sec. Further they were, ultrasonically cleaned with soap solution followed by rinsing with acetone for 15 min and then finally rinsed with double distilled water. The synthesis of porous ZnO nanosheet was done by soft chemical route on pre cleaned Si substrate. The process includes: (i) modification of Si substrate with a thin layer of densely and uniformly coated ZnO nanoparticles by modified CBD technique, followed by (ii) growth of porous 2D ZnO nanosheets in aqueous solution using CBD method [26]. The film preparation was performed at low temperature (< 100 °C) followed by annealing at 200 °C for 1 hr to get pure ZnO phase. The complete reaction mechanism and preparation parameters were similar as reported earlier [27].

In brief; initially for the deposition of dense/compact ZnO layer, 0.05 M zinc acetate dihydrate solution was prepared in DDW with addition of 25% NH_3 till the pH becomes ~11. This resultant solution was used as a source of cations which is kept at room temperature. The DDW maintained at 90 °C is used as a source of anions. Modified CBD technique was used for the deposition of dense/compact ZnO layer over Si substrate. The dipping time in a cationic and anionic precursor was 5 s and 10 s, respectively. The similar process was repeated for 20 immersion cycles to get the appropriate ZnO layer. It is then washed with DDW, dried in air followed by annealing at 200 °C for 1 hr and used for further deposition of porous ZnO.

Porous ZnO nanosheets were chemically deposited using mix solution of zinc acetate dihydrate (0.2 M) and hexamine (hereafter HMTA, 0.02 M) in DDW. In order to maintain the pH ~11, the addition of 25% NH_3 solution as a complexing agent with a constant stirring was done. The pre modified Si substrate (coated with dense ZnO) was introduced in above solution maintained at room temperature for 20 hr. The as deposited film was annealing at 200 °C for 1 hr to remove the hydroxides and improve the crystallinity of the nanosheets.

Characterizations

Phase identification of the porous ZnO nanosheets was made by X-ray Diffraction (XRD) by D8 Advance, Bruker instrument. The FT-IR spectrum was recorded on a JASCO FT-IR 6100 spectrophotometer in a KBr matrix. The morphology of porous ZnO nanosheets was studied by using Field Emission Scanning Electron Microscope (FESEM) (Model Hitachi S-4800) and by Transmission Electron Microscope (TEM) (Tecnai G^2 20 Twin, FEI). Energy dispersive X-ray spectroscopy (EDS) was used to know the elemental composition from the chemically prepared ZnO film. The field emission current density-applied field (J-E) and current-time (I-t) measurements were carried out in all metal field emission microscope by using 'close proximity' (also termed as 'planar diode'). The detail vacuum processing with field emission measurement is explained in our previous report [28].

RESULTS AND DISCUSSION

Structural and optical studies

XRD pattern of the porous ZnO nanosheets is

depicted in Fig. 1(a). The XRD spectra of annealed ZnO nanosheets show set of well diffracted peaks such as 31.8°, 34.4°, 36.3°, 47.6°, 56.6°, 62.8°, 69.1°, 72.7°. All aforesaid peaks are indexed to the hexagonal structure of ZnO with lattice parameter a = 3.249 A°, c = 5.206 A° (JCPDS file No. # 36-1451). Diffraction peaks found at 68° and 75.9° are indexed to Si.

FT-IR analysis

The FT-IR spectra of the ZnO powder sample was measured in the range of 4000-700 cm^{-1} as presented in Fig. 1(b). The IR peaks at 419 cm^{-1}, 518 cm^{-1}, 1095 cm^{-1}, and 1648 cm^{-1} suggesting formation of ZnO. The peaks at 1547 and 1419 cm^{-1} are due to symmetric and asymmetric stretching vibration of C=O group of acetate suggesting presence of acetate anionic moieties at ZnO surface. The broad feature around 3400 cm^{-1} corresponds to the stretching mode of the O-H bond, indicating the presence of hydroxide groups [29, 30]

Morphological and elemental studies

Fig. 2 depicts the FESEM and TEM images of porous ZnO nanosheets with EDS spectra. Fig. 2 (a) indicate large and uniform coverage of porous ZnO nanosheets on entire substrate and on careful observation of Fig. 2 (b) signify that the average thickness of ZnO nanosheets is 30 nm. TEM characterizations were carried out to study the morphology of 2D porous ZnO nanosheets. Fig. 2 (c) shows the bright field images of porous ZnO nanosheet.

The compositional analysis of prepared film was performed with the help of energy dispersive

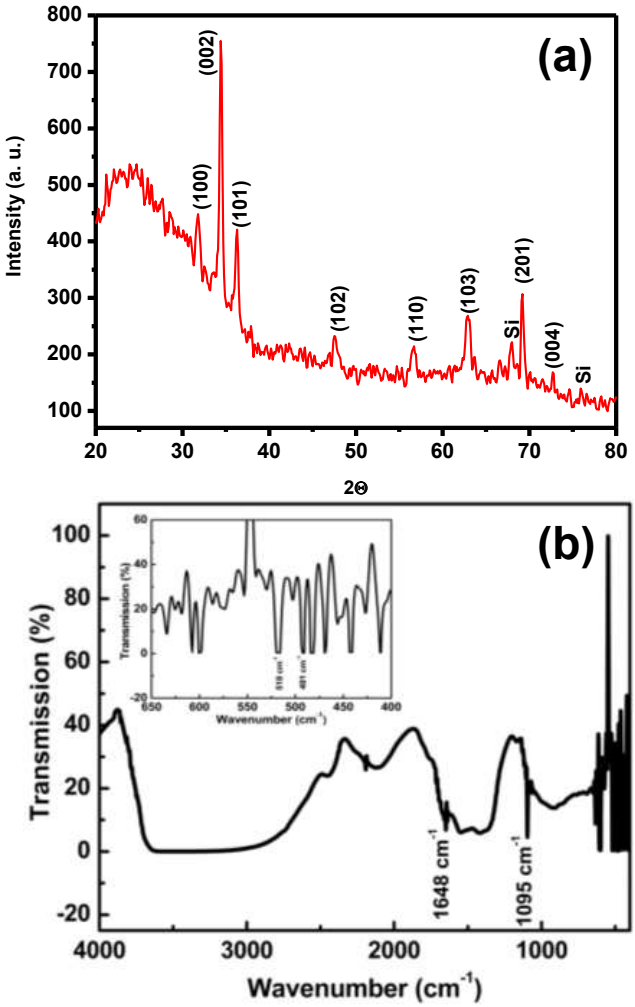

Fig. 1(a). X-ray diffraction pattern of porous ZnO nanosheets. (b). FT-IR spectra of porous ZnO nanosheets.

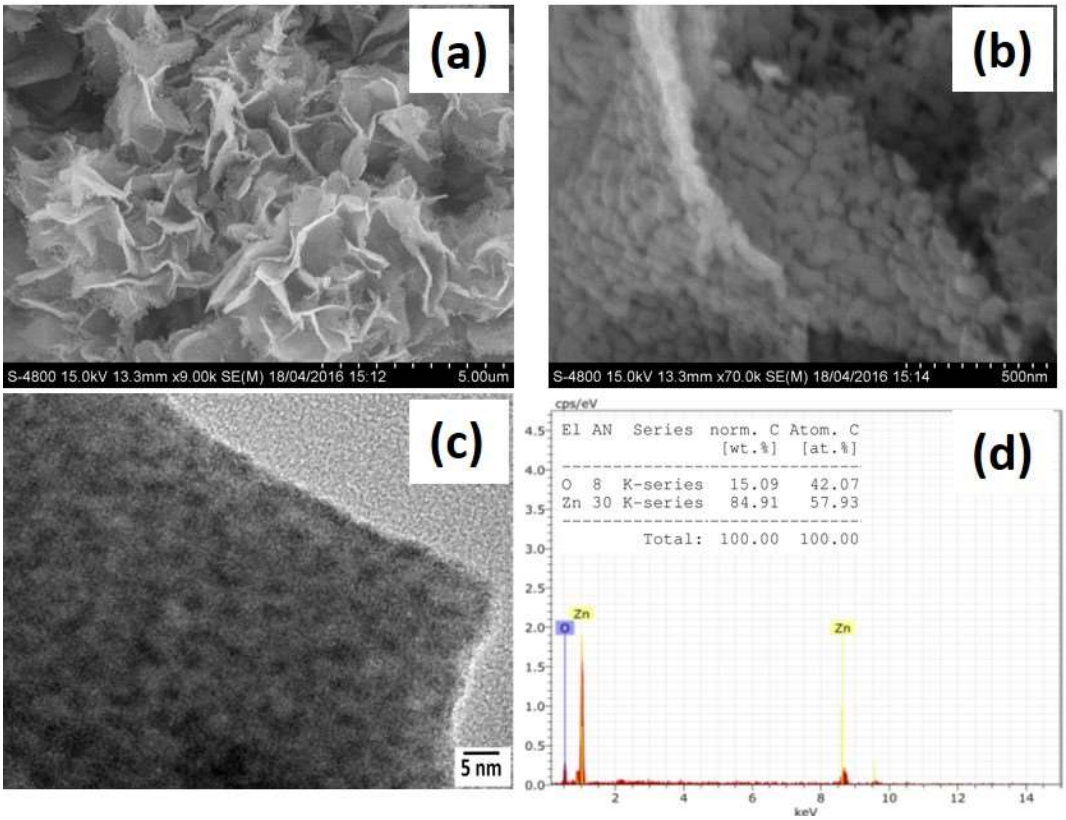

Fig. 2. (a) Low magnification and (b) high magnification FESEM (c) TEM images and (d) EDS of porous ZnO nanosheets.

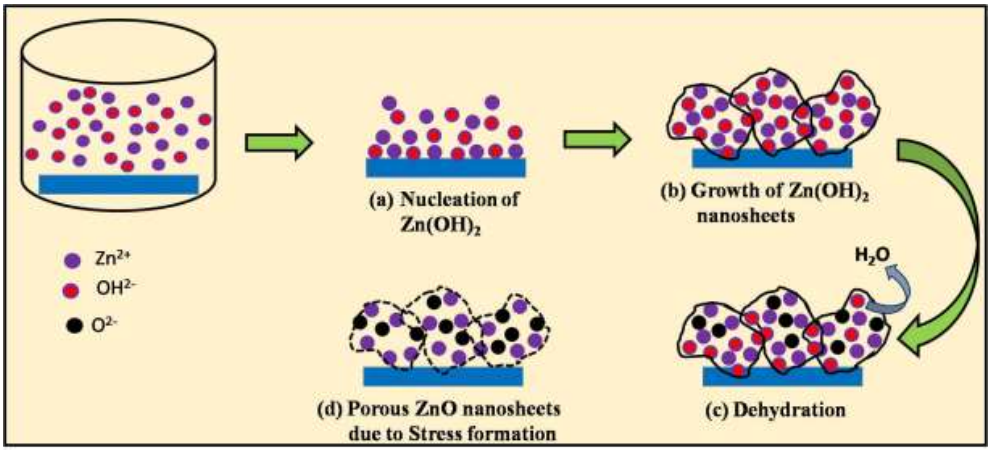

Fig. 3. Growth mechanism of porous ZnO nanosheets.

X-ray spectroscopy (EDS) attached with SEM. The EDS spectrum shown in Fig. 2 (d) demonstrates the occurrence of only Zn and O elements indicating high purity of ZnO material. The average atomic% of Zn:O is in the ratio of 58:42 tabulated as inset.

Growth mechanism for porous ZnO nanosheets

Initially, the formation of $Zn(OH)_2$ nanosheets is takes place at room temperature (27 °C) by nucleation and growth process as illustrated in Fig. 3 (a) and (b). Then the as-deposited $Zn(OH)_2$ film was air annealed at 200 °C for 60 min to form pure ZnO phase. The phase transformation is takes place due to dehydration [7, 31] and is illustrated as Fig. 3 (c) & (d). The release of water vapors from the as-deposited $Zn(OH)_2$ film may result in the

change of chemical bond length from 1.956 Å of $Zn-(OH)_2$ to 1.937 Å of Zn-O which then leads in to contraction of crystal lattice. Hence, tensile stress is formed on the surface which further results in the cracking of crystal lattice. In such way, the successive lattice contraction and rearrangement of atoms give rise to the formation of porous ZnO nanosheets.

Field emission studies

The J-E plot of porous ZnO nanosheets is shown in Fig. 4 (a). It shows that the turn-on field defined as the field required to draw an emission current density of 10 μA/cm^2 has been found to be 2.3 V/μm. The maximum current density of 0.76 mA/cm^2 has been achieved for the applied electric field of 4.1 V/μm. Observed low turn-on field of porous ZnO nanosheets is found to be superior than reported ZnO nanostructures. A comparison is summarized in table 1 [32-37]. Observation of low turn-on field of porous ZnO nanosheets may attribute to porous nanosheets which offer large number of emission sites [38]. Also, sharp edges of the porous nanosheets (thickness = 30 nm) and good crystal quality may responsible for the observation of low turn-on field [14].

The F-N plot, i.e., ln (J/E^2) versus (1/E), derived from the observed J-E characteristic is shown in Fig. 4 (b). The F-N plot indicates overall linear behavior with saturation at high field. The I-t plot

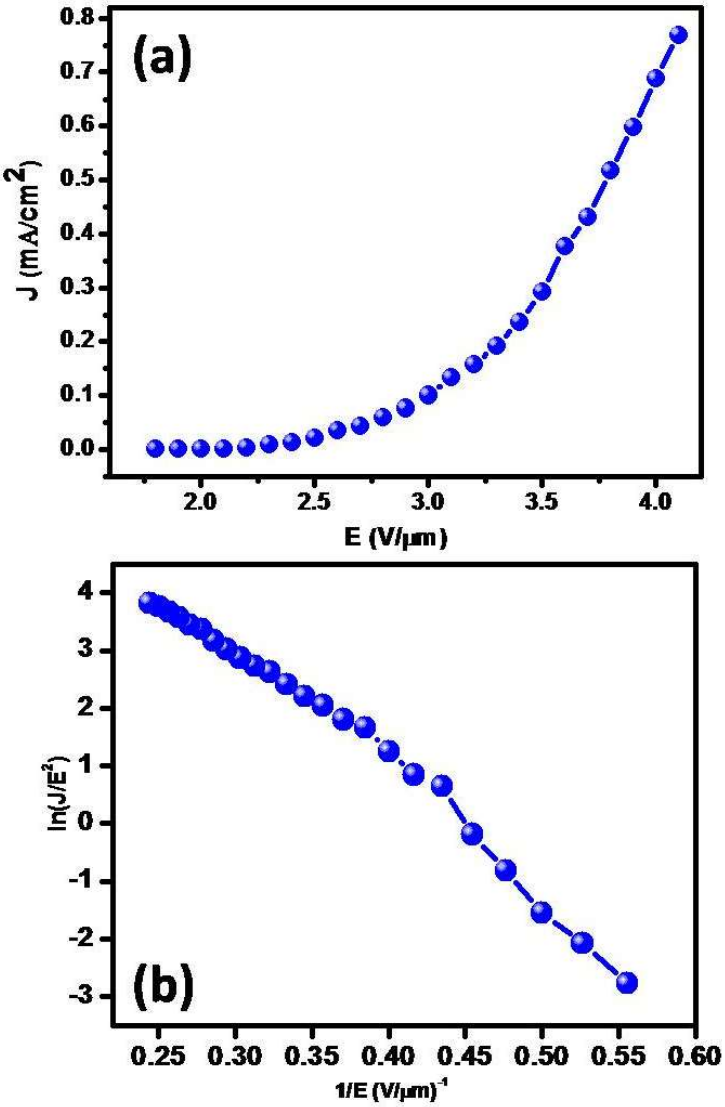

Fig. 4. (a) J–E plot of porous ZnO nanosheets, (b) Corresponding F-N plot.

Table 1. Turn-on field values of the ZnO nanostructures reported in the literature.

ZnO nanostructures	Turn-on field (V/μm) (for J= 10 μA/cm^2)	Reference
Porous Nanosheets	2.3	Present study
Nanowire on Nanoplate	4.8	32
Nanowires	7.8	33
Nanosheets	5.9	34
Nanosheets	5	35
Nanotubes	7 (0.1 μA /cm^2)	36
Nanoneedle	2.4 (0.1 μA /cm^2)	37

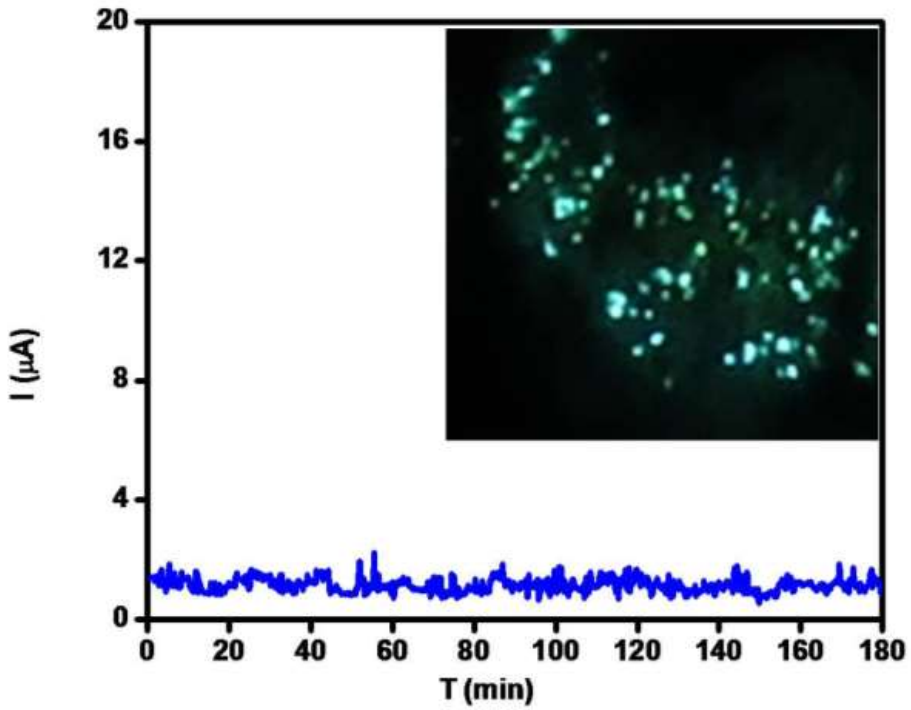

Fig. 5. I-t plot of porous ZnO nanosheets with field emission image as inset.

recorded at the preset of 1 μA emission current for the duration of 3 hr is shown in Fig. 5. The small amounts of ups and downs in emission current are observed and are may be due to various atomic scale processes occurring during field emission [39]. Interestingly, it is observed that the field emission current remains constant for the entire duration of measurement. Field emission image shown as inset of Fig. 5 depicts large number of bright spots.

CONCLUSION

2D porous ZnO nanosheets were synthesized by using low temperature CBD method. Porous ZnO

nanosheets show excellent field emission behavior in terms of low turn-on field, high emission current density and stable emission current. The observed low turn-on field of porous ZnO nanosheets may be due to nanometric feature. The observed turn-on field of porous ZnO nanosheets has been found to be superior than other ZnO nanostructures reported in the literature. Observation of stable emission current with low turn-on field indicates that, 2D porous ZnO nanosheets may used as electron source in electronic devices.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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