Chapter 5

Enhanced Field Emission Properties of ZnO Nanostructures

This chapter primarily deals with the field emission characteristics of novel multipod, marigold, microbelt and tetrahedra nanostructures of ZnO. The studies have been carried out both in the close proximity (C-P) configuration and the conventional field emission microscope (FEM) especially because the use of FEM configuration overcomes the drawback of arc formation at high field values. Interestingly, a current of 1 nA with an ultralow onset voltage of 40 V (for 1 nA) and the current density of $2.8 \times 10^4$ A/cm$^2$ achieved with a field of $1.26 \times 10^5$ V/µm are observed for the single multipod as well as for the arm. The nonlinearity observed in the F-N plots for all the morphologies have been interpreted on the basis of the theory of electron emission from semiconductors. A scheme explaining the field emission behavior in both the high and the low field regions owing to the very high geometrical factor has been picturized in this chapter. The current stability exhibited by these structures is also promising for sustained emission behavior facilitating their application in next generation field emission devices.

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† The field emission was carried out in the Department of Physics, University of Pune.
5.1. Introduction

Application of a sufficiently high electric field ($10^6$-$10^7$ V/cm) normal to the surface of a metal or a semiconductor leads to the emission of electrons by quantum mechanical tunneling through the surface barrier\(^1\). It has diverse technological applications in flat panel displays, microwave-generation devices and vacuum micro/nano-electronic devices.\(^{1,2}\) With the advent of various anisotropic nanostructured materials like CNTs\(^3\), AlN\(^4\), GaN\(^5\), SiC\(^6\), TiO\(_2\)\(^7\), SnO\(_2\)\(^8\) and ZnO\(^6\)\(^{12}\), there has been an upsurge in the interest considering their promising potential as efficient field emission cathodes. This is mainly because it is easier to generate nearly monoenergetic electron beams by accurately controlling the density and the geometry of the emitter. Consequently, field emission from novel nanostructures of ZnO supported on various substrates has been investigated owing to the excellent mechanical, chemical and thermal properties. Besides this, ZnO nanostructures have negative electron affinity and the ease with which the morphology (sharp nanotips) can be controlled makes them an appropriate alternative to carbon nanotubes and other solid-state devices for field-emission microelectronic devices. The effects of geometrical factors, areal density and morphological features have been reported for arrays of multiple needle-like ZnO nanostructures, primarily with the objective of attaining higher values of emission current density and lower onset voltage, compared to various other materials. The minimum emission current density of 1 mA/cm\(^2\) is required to produce the luminance of 300 cd/m\(^2\) from video graphics array-field emissive displays (VGA-FED) with typical high-voltage phosphor screen efficacy of 9 lm/W.\(^13\) Among the reported field emission results of ZnO nanowires, Lin et al. reported the lowest electric field of 4.5 V/\(\mu\)m.

The field emission studies of these nanostructures have been carried out in the close proximity (C-P) configuration wherein the field emitter arrays in the form of thin film are mounted in proximity with an anode screen separated by an insulating spacer (~50 \(\mu\)m to a few mm) as shown in figure 5.1. Electron tunneling in this configuration is generally referred to as ‘thin-film tunneling’. However, such a configuration poses a serious limitation on the strength of the applied electric field as relatively high field may lead to the arc formation. The emission properties can be analyzed by the classic
Fowler–Nordheim (F–N) law,\textsuperscript{14} discussed in detail in chapter 1 (section 1.10.5), which was derived on the basis of the electron-emission properties from a semi-infinite flat metallic surface, used to describe the relationship between the current density (J) and the local field nearby the emitter $E_{\text{local}}$, which is usually related to the average applied field $E$ as follows:

$$E_{\text{local}} = \beta E = \beta \frac{V}{d}$$  \hspace{2cm} -(1)

where $d$ is the interelectrode spacing, $V$ is the applied voltage and $\beta$ quantifies the ability of the emitter to amplify the $E$ and is defined as the field enhancement factor. Considering the screening effect between adjacent emitters, $E_{\text{local}}$ can be expressed by Filip model\textsuperscript{15},

$$E_{\text{local}} = s \frac{V}{r} + (1-s) \frac{V}{d}$$  \hspace{2cm} -(2)

where, $r$, is the radius of the emitter and $s$ is a parameter describing the degree of the screening effect, which ranges from 0 for densely arranged emitters to 1 for a single one. Combining equation (1) and (2) gives the field enhancement factor i.e. the ability of the emitter to amplify the applied field, from the emitter array

$$\beta = 1+s(d/r-1) \cong 1+ \frac{sd}{r}$$  \hspace{2cm} -(3)

Figure 5.1. (a) Schematic of the emitter tip assembly in close-proximity (C-P) configuration; (b) actual Instrument used for studying field emission of nanostructures deposited/coated on Si-wafer in C-P configuration. (Courtesy: Prof. D. S. Joag, Department of Physics, University of Pune)
In order to understand the physics of field emission from such a novel nanostructured ZnO, it is an essential prerequisite to study the field emission characteristics in a conventional field emission microscope (FEM) configuration, along with the C-P configuration. In the conventional FEM configuration, the emitter (cathode), in the form of a fine needle with a tip radius of about $10^{-4}$ cm or less, is placed inside an evacuated chamber, in front of an anode screen, typically 5 to 7 cm apart. (Figure 5.2) In such a configuration, it is possible to enhance the range of applied electric field overcoming the drawback of arc formation observed in C-P configuration.

Figure 5.2. (a) Schematic of the conventional FEM configuration, the emitter (cathode), in the form of a fine needle with a tip radius of about $10^{-4}$ cm or less, is placed inside an evacuated chamber, in front of an anode screen, typically 5 to 7 cm apart; (b) Photograph of field emission instrument used in the present study. (Courtesy: Prof. D. S. Joag, Department of Physics, University of Pune)

In this chapter we demonstrate the field emission studies carried out in both the configurations for various novel ZnO nanostructures namely multipod, marigold, microbelt and tetrahedra synthesized by a modified vapor phase deposition as explained in chapter 4. For a single arm of a multipod structure an ultra-low onset voltage of 40 V
to extract a current of 1 nA has been observed. The F-N theory of electron emission from the metal has already been discussed in detail in chapter 1, section 1.10.5.\textsuperscript{14} The emergence of ultra-low onset voltage has been explained on the basis of theory of electron emission from semiconductors. Further, our results emphasize that the electrons from both the valence and the conduction bands contribute to the field emission current. Interestingly, all the structures exhibit an improved stability implying them to be some of the promising materials for next generation field emission devices.

5.2. Experimental Aspects

5.2.1. Specimen preparation

The experimental details regarding the synthesis of ZnO structures have already been described in chapter 4, section 4.3. In brief, Zn-metal as a starting material was heated at 950°C for 2 h with Ar and O\textsubscript{2} flow rates of 100 sccm and 20 sccm (20% v/v), respectively. The multipod structures were collected at the substrate kept downstream where the temperature was between 300 and 500 °C. The ZnO microbelts and marigold structures were grown on the Si - (100) substrates kept adjacent to the source material where the temperature is 800 °C.

5.2.2. Morphological and structural characterization

The morphology and the structure were characterized using techniques such as XRD, SEM, TEM, XPS in a way similar to that described in chapter 2, section 2.3.

5.2.3. Field Emission studies

5.2.3.1. Construction of conventional FEM tube

The delicate nature of the components and the stringent conditions required for FEM experiments makes its construction intricate and a schematic of an all-glass FEM tube is shown in Figure 3. Basically it comprises of four parts, viz. (a) an emitter tip assembly, (b) an optically transparent conducting coating from inside to serve as an anode, (c) a phosphor screen on top of the conducting coating to display the field emission pattern, and (d) a getter bulb to serve as an appendage pump to improve vacuum conditions in
the sealed-off tube. A getter bulb contains a heating filament of a getter material (0.267 mm diameter titanium wire closely over wound on a tungsten wire of 0.25 mm diameter) that can be evaporated onto a surface at room temperature or below. Chemically active gases are pumped at the evaporated film by chemisorption forming stable chemical compounds with low vapor pressure.

5.2.3.2. Specimen mounting: the emitter tip assembly

5.2.3.2.1. ZnO microbelts and needles grown on Si-wafer

Field emission measurements for ZnO microbelts and marigold structures grown on Si-wafer were carried out in a close proximity configuration in a vacuum chamber with a pressure less than $1 \times 10^{-9}$ mbar at room temperature. The sample was mounted on a stainless-steel stub ($\phi = 6$ mm) using Ag paste as conducting glue, which is known to give a proper ohmic contact. A phosphor screen, used as an anode, was mounted on a linear motion drive parallel to the cathode and held at a distance of 1 mm.

5.2.3.2.2. Multipod structure

The multipods were mounted skillfully, with several attempts, on a tungsten (W)-needle using silver paste (vacuum compatible) under an optical microscope. As seen from the SEM, the silver paste does not have any sharp protrusions that may be expected to contribute to the field emission, which is a surface sensitive technique. Further, the scanning electron microscopy was carried out to confirm proper mounting of a single multipod and a single arm on the tungsten-needles. Two such needles containing a single multipod and a single isolated arm of a multipod were selected for the field emission measurements, carried out in all glass conventional field emission microscope (FEM) tube assembly consisting of an emitter cathode and a transparent anode with $\text{SnO}_2$ and phosphor coating. The emission sites could be seen directly on the anode screen, kept at a distance of 5 cm from the needle.

Also, a nickel tube (1 mm in diameter and 5 mm in length) was crimped at one end keeping the other end filled with silver paste. The multipod structures were inserted into the paste end and dried at ambient temperature. In order to study the effect of areal
density, the loading of the multipods was carried out carefully to yield different densities: higher density sample is referred to as multipod-1 and the lower density sample is referred to as multipod-2.

5.2.3.2.3. Tetrahedral structures on W-tip

The tetrahedral structures were grown directly on the tungsten-needle for field emission studies. The field emission measurements were carried out in all glass conventional field emission microscope tube assembly consisting of an emitter cathode (tetrahedral on tungsten needle) and a transparent anode with conducting screen.

5.2.3.3. Vacuum processing and Instrumentation

The emitter-tip assembly either of C-P configuration or conventional FEM configuration were then mounted on an all-metal ultrahigh vacuum system equipped with a diffusion pump and a liquid nitrogen cooled chevron trap, a sputter ion pump, and a titanium sublimation pump. After baking the tube at 250 °C for 8 h, pressure of 1×10⁻⁹ mbar was obtained. The measurements of the current–voltage (I–V) characteristic and the current-stability (I-t) were carried out at this pressure using a Keithley 485 picoammeter and a Spellman high voltage DC power supply with a proper grounding. Before starting the I-V measurement, the picoammeter was stabilized (as per the instructions in operating manual) for 30 min and zero reading on display was ensured. Also, a special care was taken to avoid any leakage current by using shielded cables with proper grounding. The emission current measurements were carried out at the base pressure ~1 x 10⁻⁹ mbar.

5.3. Results and discussion

5.3.1. Field emission studies of isolated multipods on W-tips

Among various structures of ZnO, the isolated multipod and one of the pods were tested for field emission properties. Interestingly, a current of 1 nA with an ultra-low onset voltage of 40 V is observed repeatedly for the single multipod as well as for the arm (pod) as depicted in figure 5.4, which is highlighted in the inset. The corresponding onset current density and applied field generated at the emitter tip apex are 2.76 x 10⁷ μA/cm² and 3700 V/μm, respectively. For ZnO nanostructures, the lowest ‘threshold field’ in
parallel plate geometry corresponding to the current density of 0.1 \( \mu \text{A/cm}^2 \) is 0.8 \( \text{V/\mu m} \). Further, de Jonge et al. have extracted a current in the range of 0.4 – 80 nA by applying the voltage in the range of 300 – 420 V from a single carbon nanotube attached to a tungsten wire in a geometry similar to that used in the present one. An explicit comparison of our results with the reported ones will be more useful, if done for similar current density. The onset current density in our case is very high (2.76 \( \times \) \( 10^7 \) \( \mu \text{A/cm}^2 \)) and none of the previous researchers have achieved such a high value for ZnO. Therefore, the unique observation of 40 V to draw a current of 1 nA is considered to be ultralow. Remarkably, this voltage is unaffected even after operating the emitter at much higher voltages (10 kV and above) for recording the current-voltage (I-V) characteristics and a total emission current of 1 \( \mu \text{A} \) at 10 kV is observed in all the cases.

Figure 5.5 shows the F-N plot, \( \ln(I/V^2) \) versus \( 10^4 V \) plot derived from the above I-V characteristics of these multipod structures. A very interesting nonlinear behavior is observed in the F-N plot which could be clearly understood for two distinct ranges of applied fields as depicted in figure 6 (a) and (b). In these two ranges, the F-N plots are fairly linear with distinct slopes. For semiconductors, in low current approximation, the F-N plot should be a straight line for electrons emitted from conduction band as well as from valence band. Moreover, we believe that the F-N plot is not sensitive to contributions from surface states and band bending.

![F-N plot](image)

Figure 5.4 (a) Current-voltage (I-V) characteristics of isolated multipod and an individual arm with the inset highlighting the low onset voltage for these samples.
Figure 5.5. An F-N plots of isolated multipod and an individual arm over the large potential range of 40 V to 10 kV.

Figure 5.6. The F-N plot of isolated multipod and an individual arm in the two linear ranges (a) a higher region from 5 kV to 10 kV and (b) a lower region between 40 V and 5 kV.

The field enhancement factor $\beta$ is related to the slope of the F–N plot, $m$, by the following equation$^{17}$

$$\beta = \frac{-6.83 \times 10^3 \phi^{3/2}}{m}$$

- (4)
where, $\phi$ is the work function of the emitter material in eV. In the present case, the work function of ZnO ($\phi$) is assumed to be 5.3 eV and is reported to be independent of the size and aspect ratio of the nanostructure\textsuperscript{18}. In the low field region, the field enhancement factor ($\beta$) is calculated to be $9.25 \times 10^5$ cm\textsuperscript{-1}, which is identified to be directly dependent on the aspect ratio (ratio of length to tip radius) of the nanostructure\textsuperscript{19}.

In the context of F-N theory, for conventional FEM configuration used in the present case, the applied field is defined as $F = \beta V$, where, $V$ is the applied voltage (V) and $\beta$ is the field enhancement factor (cm\textsuperscript{-1}). Further $\beta = 1/kr$, where $k$ is a constant known as the geometrical factor and has the value 5 for hemispherical emitter, and $r$ is the tip radius\textsuperscript{20}. If the same factor $\beta$ is assumed in the two regions, the low field region corresponds to emission from the conduction band of ZnO and the high field region corresponds to an additional emission from the valence band, 3.37 eV below the conduction band. The value of $\phi$ calculated from the slope of the F-N plot in the high field region is 11.24 eV and is in general agreement with the proposed scheme-5.1, wherein the effective work function is assumed to be 8.67 eV ($\phi_e = \phi + E_g$). This difference may be attributed to the contributions from the field penetration-induced band bending. It was demonstrated by Zheng et al.\textsuperscript{21} that for metallic CNT the field penetration at the tip lowers the potential barrier leading to a deep potential well in the region where a large number of excess electrons reside. Moreover, the lowering of barrier height is a non-linear function of the applied field, which is system independent. Indeed, the theory of field emission from semiconductors is not so simple as in the case of metallic emitters\textsuperscript{22,23}. Moreover, the F-N theory cannot resolve the fine structure in the energy distribution of electrons although it describes fairly well, the relationship between the emitted current and the applied field. However, the non-linearity in the F-N plot (Figure 5.5) can be understood upon considering the theory of electron emission from semiconductors as represented in scheme-I, which explains the behavior in both the high and the low field regions owing to a high field enhancement factor and contributions from the valence band states. It is likely that the modification of tip may lead to a drastic alteration of emission current or threshold voltage.
Scheme 5.1. The schematic of the band diagram of bulk ZnO based on the calculation using field emission energy distribution\(^{27}\); VB is the valence band, CB is the conduction band, \(E_g\) is the energy gap of ZnO (3.37 eV) and \(\phi\) is the work function (5.3 eV). In the absence of the electric field there exists a semi-infinite barrier to the emission of electrons present near the Fermi level. However, after the application of the field, this barrier reduces to a triangular barrier as shown. While at the lower fields, electrons in the conduction band are responsible for the emission current, at the higher fields, electrons in the conduction band and those from the valence band with the effective work function of \(\phi_e = \phi + E_g = 5.3 + 3.37 = 8.67\) eV, tunnel to generate the emission current.

Further, assuming hemispherical geometry of the emitter surface, the current density \((J)\) generated at the emitter tip is calculated using

\[
J = \frac{l}{2\pi r^2}
\]

where, \(l\) is the total current and \(r\) is the radius of the emitter tip as estimated from the scanning electron micrograph. The current density from a single multipod and a single arm are 1.48 \(\times\) 10\(^{10}\) \(\mu\)A/cm\(^2\) and 2.76 \(\times\) 10\(^{10}\) \(\mu\)A/cm\(^2\) respectively, measured at an applied field of 1.26 \(\times\) 10\(^5\) V/\(\mu\)m and 1.64 \(\times\) 10\(^5\) V/\(\mu\)m.
5.3.1.2. Tip radius determination using Iterative Approach

If the work function $\phi$ is assumed to be known and uniform, the radius of the tip, correct to within 20%, can be determined from the slope of F-N plot given by equation 1.34. An accurate method of evaluating $r$ is as follows: (a) evaluate $d(\ln(I/V^2))/d(10^4/V)$ for clean tip, (b) assume $S(y) = 1$, $\phi$ is known and assumed to be uniform, (c) from $\beta$ the slope, (d) find $r$ knowing $\alpha$ for the standard tip geometry from $\beta$, (e) then evaluate $y = 3.79 \times 10^{-4} F^{1/2}$ by substituting $F = \beta V$, (f) from tables, find $S(y)$, (g) using this $S(y)$, iterate to no further change in $r$.

The emitter tip radius of the field emitter is calculated using this method wherein the work function of ZnO is assumed to be 5.3 eV. The final value of the radius obtained is 17.4 nm, which is in good agreement with the SEM results (24 nm). A post operation SEM study indicates no significant change in the geometry of the emitter, emphasizing that ZnO is highly resistant to ion bombardment and has excellent structural stability against high electric fields (12 kV and above).\textsuperscript{20} This is especially important for fabricating field emission devices with stable, high current density field emission, as these multipods have remarkable functional stability for repeated performance without any obvious signs of degradation.

In order to harness the advantages of lower threshold voltage and high current density offered by these individual arms of ZnO multipod, a precise control over the spacing is desired. For practical applications of field emission electron sources, along with the emission capability, the current stability is also crucial. Accordingly, figure 5.7 shows the current-time (l-t) plot for the two structures measured with a base pressure of $1 \times 10^{-9}$ mbar. For the single multipod and a single arm, the stability at current levels of 400 nA and 200 nA respectively, is appreciable, as the fluctuations in the field emission current lie within 10% of the average value of the current, which however decays to ~50% of the initial value. Perhaps, the current fluctuations might have been resulted from the dangling bonds on the surface or from the diffusion of adsorbates, on the surface of the multipods\textsuperscript{24}. Moreover, the self-diffusion process of the atoms at the tip of the multipod in the presence of high electric field is also expected to contribute.
Figure 5.7. Current-time transients for both the samples suggesting reasonable stability.

Figure 5.8 shows the field emission micrographs of single multipod and a single arm of a multipod recorded at an applied potential of 10 kV. For single multipod four bright spots on the screen attributed to the emission from the four arms are observed while for a single arm of a multipod only a single bright spot in the middle of the screen is observed.

Figure 5.8. (a) Field emission micrographs of single multipod showing four bright spots on the screen attributed to the emission from the four arms and (b) a single arm of a multipod showing a single bright spot in the middle of the screen. Both the micrographs are recorded at an applied potential of 10 kV. The bar indicates the scale on the screen.

5.3.2. Field emission studies of microbelts and marigold structures deposited on Si wafer, and multipods crimped in Ni tube: A comparison

5.3.2.1. Morphological and structural characterization
Figure 5.9 (a) shows the SEM image of marigold structure deposited on a Si wafer. It consists of a number of nanotips randomly oriented and mostly protruding outwards. The nanotips are conical in shape with shank ~ 1μm in width and the tip apex <100 nm in diameter. The oxides with the belt-like morphology cover cations with different valence states and materials with different crystallographic structures, and it is a common structural characteristic for the family of semiconducting oxides. Figure 5.9(b) shows the SEM image of the microbelts deposited on the Si wafer. These have width between 500 and 5000 nm, and a length of 50 -150 μm. The inset of figure 5.9 (b) shows the SAED pattern, which clearly reveals the hexagonal type ZnO. Figure 5.9(c) and (d) shows the SEM images of the multipod-1 and multipod-2 structures. It is obvious from these images that the number of arms of the multipods is between 4 and 16 and all have a common origin with varying length from 10 to 80 μm. Most of the arms have uniform width, whereas some of them end like a cone (tip apex of ~ 24 nm). In a few other arms, the width suddenly narrows down in the middle to a sharp protrusion.

Figure 5.9. SEM images of ZnO structures mounted for field emission studies (a) marigold, (b) microbelts, which are collected on a Si substrate kept adjacent to the substrate containing the starting material where temperature is 800°C, (c) multipod-1 and (d) multipod-2, mounted with different density on W-tip and are collected downstream where the temperature is between 300 and 500°C.

5.3.2.2. Field emission studies
In case of C-P configuration the applied field is usually calculated as \( E = \frac{V}{d} \), where \( V \) is the applied voltage and \( d \) is the separation. This gives an average electric field and not the field at the apex of an individual emitter tip, due to the complexity posed by large number of emitters on the cathode substrate. On the other hand, in the conventional FEM configuration, the corresponding field generated at the emitter apex is calculated using \( F = \beta V \), and the theoretical field enhancement factor \( \beta = \frac{1}{kr} \), where \( k \) is a constant called as the geometrical factor and has the value 5 for hemispherical emitter, and \( r \) is the tip radius. This field is referred to as local field at the emitter. As a result, comparison of field emitters is pertinent only if the field emission measurements have been performed under the same experimental configurations. I–V characteristics for all the ZnO morphologies are shown in figure 5.10. The overall field emission characteristics exhibited by ZnO structures are observed to obey the F-N theory, except multipod-2 sample. In case of multipod-2, the current seems to be linearly dependent on applied voltage, which may be attributed to the randomness in number of pods, their lengths, sizes and distributions. The onset voltage, required to draw a current of 1nA, for marigold and microbelts is observed to be 3.3 kV and 2 kV, respectively. In case of marigold structures, when the applied voltage is increased beyond 4 kV an arc formation is observed in the C-P configuration. Hence the emission characteristics for these structures could not be investigated at high electric fields. On the other hand for microbelts, no arc formation is observed, suggesting them to be one of the robust materials that can withstand sufficiently high voltages. This could be attributed to the random distribution of microbelts lying parallel to the Si-wafer substrate. Above 2 kV the microbelts exhibit an increase in the current upto 80 μA.

In the case of multipod-1 and multipod-2 structures, the onset voltage is observed to be 5.1 kV and 0.32 kV, respectively. The difference in the onset voltages for the two multipod structures may be due to the variation in areal density. As seen in the SEM images, the areal density of multipod-2 is lower than that of multipod-1. It is expected that the field screening effect will be less in multipod-2 and consequently it exhibits lower onset voltage. This clearly signifies the importance of tuning the density of nanostructures, in order to exploit the advantage of low onset voltage offered by an individual nanostructure.
Figure 5.10. I-V characteristics for different ZnO structures; the onset voltage required to draw a current of 1nA, for marigold and microbelts is observed to be 3.3 kV and 2 kV, respectively while in the case of multipod-1 and multipod-2 structure; the onset voltage is 5.1 kV and 0.32 kV, respectively.

The F-N plot for all the ZnO structures investigated is shown in figure 5.11. Interestingly, all the F-N plots are seen to be nonlinear reflecting the semiconducting nature of ZnO. It is surprising to note that such nonlinear characteristic has not been highlighted for ZnO nanostructures investigated by various researchers. However, a careful observation of reported F-N plots clearly shows a signature of nonlinearity towards relatively high field region. Most of these studies have been carried out in C-P configuration wherein, the emission behavior in high field region could not be carried out. However, in the present case, the conventional configuration mentioned earlier offers the advantage of application of high electric fields. In order to compare the observed F-N plots with the reported ones, we have analyzed the F-N plot in the two electric field regions, namely normal operating region (2 - 4 x 10^4/V) and the high field region (<2 x 10^4/V) respectively. The analyzed F-N plots show two distinct linear natures in the two field regions. It is interesting to note that all the F-N plots show a sudden change in the linearity at a specific knee field value, corresponding to 2 x 10^4 V^-1 in the F-N plot, irrespective of different morphologies. This implies that the knee field is the characteristics of the emitter material. The F-N plot suggests that the field emission is a barrier tunneling process and in the two field regions obeys the equation 1. In these two regions, the F-N plots are fairly linear with distinct slopes.
Although the F–N theory and the formulae used in the field emission microscopy are strictly valid for hemispherical emitter tips which assume a free electron model, a rough estimate of the field enhancement factor $\beta$ could be obtained from the F–N plot [15]. For semiconductors, in low current approximation, the F-N plot is a straight line for electrons emitted from both the conduction and the valence bands. Moreover, we believe that the F-N plot is not sensitive to contributions from surface states and band bending. Further, the deviation from the linearity could also be attributed to the strong dependence of Fermi energy on the applied field.

Taking the work function of ZnO ($\phi$) to be 5.3 eV (as reported to be independent of the size and aspect ratio of the nanostructure)\textsuperscript{17}, the field enhancement factor is calculated for different structures as shown in Table 5.1 along with the onset voltage. If the same $\beta$ is assumed in the two regions, the normal operating range could be attributed to the electron emission from the conduction band. However, when the applied field is further increased, additional emission from the valence band i.e., 3.37 eV below the conduction band also starts contributing to the emission current along with the emission from the conduction band. This phenomenon is reflected as a linear behavior of F-N plot in the high field region. The $\beta$ values, thus calculated using the increased
work function of 8.67 eV \((\phi_0 = \phi + E_g)\) agrees well with the low field region values. However, the difference may be attributed to the contributions from the field penetration-induced band bending. Moreover, the field penetration at the tip lowers the potential barrier leading to a deep potential well in the region where a large number of excess electrons reside\(^\text{19}\). This lowering of barrier height is a nonlinear function of the applied field and is system independent. A post operation SEM study indicates no significant change in the geometry of the emitter, emphasizing that ZnO is highly resistant to ion bombardment and has excellent structural stability against high electric fields.\(^\text{21}\) It also supports our assumption of the same \(\beta\) in the two field ranges. This is especially important for fabricating field emission devices with stable, high current density field emission, as these structures have remarkable functional stability for repeated performance without obvious signs of any degradation.

Table 5.1. The onset voltage and the field enhancement factor \((\beta)\) calculated for different structures of ZnO. In low field region, \(\beta\) is calculated by taking the work function \((\phi)\) of ZnO to be 5.3 eV while at high field region, \(\beta\) is calculated with effective work function to be \((\phi_0 = \phi + E_g = 3.37 + 5.3 = 8.67 \text{ eV})\) where \(E_g\) is the band gap of ZnO.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Field Enhancement Factor (\beta \times 10^5 \text{ cm}^{-1})</th>
<th>Onset Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low field (1-2 kV) ((\phi = 5.3 \text{ eV}))</td>
<td>High field (2-5 kV) ((\phi = 8.67 \text{ eV}))</td>
</tr>
<tr>
<td>Marigold</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>Microbelt</td>
<td>14.5</td>
<td>6.72</td>
</tr>
<tr>
<td>Multipod-1</td>
<td>5.59</td>
<td>2.76</td>
</tr>
<tr>
<td>Multipod-2</td>
<td>30.06</td>
<td>26.24</td>
</tr>
</tbody>
</table>

The emission stability over a definite period of time for these structures is shown in figure 5.12. Marigold structures exhibit a reasonably good stability as compared to that for the microbelts. However, the emission current is found to fluctuate within 20% of the average value in both the cases, which could be attributed to the poor contact between the ZnO structures and the Si-substrate. However, in case of multipods, good stability with current fluctuations within about 15% of the average value is observed. The current fluctuations may also result from the dangling bonds on the surface and/or from the
diffusion of adsorbates, on the surface of the emitters. Moreover, the self-diffusion process of the atoms at the tip of the structures in the presence of high electric field is also expected to contribute to the fluctuations.

Figure 5.12. Variation of the emission current stability over time for different ZnO structures; marigold structure exhibits a better stability in comparison with both the microbelt and the multipod structures.

The field emission images are found to display a number of spots and lobes, which flickers in intensity in accordance with the emission current fluctuations. Figure 5.13 shows field emission micrographs for all the ZnO structures. The microbelts (figure 5.13a) exhibit a stable lobe pattern, while marigold structures exhibit a pattern with large number of uniform dots. This can be attributed to the larger density of the needle like emitter on the marigold structures as can be seen in the SEM images. Further, the emission from these structures depends on size of individual sharp structures. The FE micrograph for multipod-1 shows two lobes that are due to the two long pods in proximity with each other. At low field a large number of dots are seen on the screen, which can be attributed to the large number of smaller pods. However, with increase in the field bright lobe pattern is observed due to the two larger pods (as seen in SEM images). In case of multipod-2, a spot pattern as expected is observed and is attributed to the larger pods. While recording the current stability, (at the set current values) the ZnO structures have not shown any noticeable temporal changes in the emission micrographs. This indicates that the emission sites for all the ZnO structures are sustained without the generation of newer sites. The overall features of the emission micrographs remain in
variant with time; however, the slight variation in the brightness of the emission pattern could be attributed to the reasons mentioned above.

![Field emission micrographs for (a) marigold, (b) microbelts, (c) multipod-1 and (d) multipod-2; each pod of the multipod and the number of sharp tips present on the surface act as active sites from where emission occurs. The bar indicates the scale on the screen.](image)

Figure 5.13. The field emission micrographs for (a) marigold, (b) microbelts, (c) multipod-1 and (d) multipod-2; each pod of the multipod and the number of sharp tips present on the surface act as active sites from where emission occurs. The bar indicates the scale on the screen.

**5.3.3. Field emission from tetrahedral structures**

The tetrahedral structures were grown directly on the W-tips for field emission measurements. Accordingly, Figure 5.14 shows the SEM images of the tetrahedral structures during the very early stages of growth. The size of each individual ZnO particle is approximately 1-1.5 μm with well-developed facets/edges as can be seen in figure 5.14 (b). Figure 5.15 shows the I-V characteristics for a typical tetrahedral structure. Interestingly, an onset voltage of 120 V has been observed corresponding to a current of 1nA and the value seems to be stable even during the operation at higher voltages (>10 kV). The corresponding F-N plot [\(\ln \left( I/V^2 \right) \) vs \(1/V \times 10^4 \)] in figure 5.16 over a wide range of applied voltage, is seen to be nonlinear and could be attributed to the semiconducting nature of the emitter. This nonlinearity of F-N plot observed stands distinct from the behavior reported in literature\(^{12,19}\). This is mainly due to the extended range of voltage applied in the present experiments. Although the F–N theory and the formulae used in the field emission microscopy are strictly valid for hemispherical emitter
tips based on the free electron model, a rough estimate of the field enhancement factor $\beta$ could be obtained from equation (1).

![SEM of tetrahedral structure grown on tungsten-needle with an inset showing the enlarged image.](image)

Figure 5.14. SEM of tetrahedral structure grown on tungsten-needle with an inset showing the enlarged image.

![I-V characteristics of tetrahedral structure of ZnO; an onset voltage of 120 V corresponding to a current of 1nA seems to be stable even during the operation at higher voltages (>10 kV).](image)

Figure 5.15. I-V characteristics of tetrahedral structure of ZnO; an onset voltage of 120 V corresponding to a current of 1nA seems to be stable even during the operation at higher voltages (>10 kV).

The observed plots are found to obey the F-N equation (2) in two distinct ranges of applied voltage. In these two ranges, the F-N plot is linear with distinct slopes. Taking the work function of ZnO ($\phi$) to be 5.3 eV, the field enhancement factor is calculated to
be $5.1 \times 10^5$ cm$^{-1}$. The low field region could be attributed to emission from the conduction band of ZnO and the high field region to the emission from the valence band, i.e., 3.37 eV below the conduction band, as well as the conduction band. Moreover, the un-oxidized Zn species present are also expected to contribute by creating the surface states in the mid gap region of ZnO.

The emission stability recorded over a certain period of time for these structures is shown in figure 5.17. A good current stability with fluctuations within about 15% of the average value is observed over a period of 3 h. The current fluctuations could be attributed to the dangling bonds on the surface or from the diffusion of adsorbates on the surface of the emitters. Moreover, the self-diffusion process of the atoms at the tip in the presence of high electric field is also expected to contribute to the fluctuations. Indeed, the field emission micrograph shows a slightly deformed spherical patterns corresponding to the individual ZnO particle on the tip as depicted in figure 5.17. Each individual particle serves as an emitter supported on the tungsten tip.

![Figure 5.16. The F-N plot of tetrahedral structure showing a nonlinear behavior a characteristic of semiconductor.](image-url)
A unique feature of non-linearity in the F-N plot, a characteristic of the semiconductor, is observed for all multi-pods, marigold, microbelts and tetrahedra ZnO structures. Further, the onset voltage is observed to be dependent on the sharpness of the emitter tip. Moreover, the density and the distribution of the individual emitter tip on the surface govern the field emission properties. The results show that electrons are more easily emitted from ZnO nanostructures with sharp tips, or surface perturbations than from microbelts with uniform diameter implying a strong dependence on the morphology. Therefore, improvement of the emission efficiency further requires continued shrinkage of the tip size.

5.4. Four-probe conductivity measurements

Figure 5.18 shows the temperature dependent I-V measurements of pellet of tetrahedral structure (a), marigold (b) and microbelt (c) grown on Si-wafer. The measurements were carried out in the presence of Ar. Interestingly, tetrahedra structures show ohmic relation attributed to the metallic Zn species present due to incomplete oxidation, while both marigold and microbelt forms exhibit a rectifying feature attributed to the semiconducting nature of the ZnO.
Figure 5.18. Temperature dependent I-V measurements carried out in the presence of Ar for pellet of tetrahedral structure (a), marigold (b) and microbelt (c) grown on Si-wafer.

Table 5.2 depicts the dependence of resistivity of all these structures as a function of temperature and morphology. From the Table 5.2, it is clear that there is no systematic trend in resistivity with temperature. Interestingly, tetrahedra exhibit a metallic behavior; resistivity increases with temperature. However, marigolds exhibit an overall semiconductor feature; resistivity decreases with temperature being the dominant phenomena. It also show a maximum at 200 K, attributed to the presence of zinc suboxides, which governs the resistivity at temperatures between 125 and 200 K, as per Matthiessen’s rule. Matthiessen's rule is an empirical rule which states that the total resistivity of a crystalline metallic specimen is the sum of the resistivity due to thermal agitation of the metal ions of the lattice and the resistivity due to the presence of imperfections in the crystal. Further, the electrical resistivity at room temperature (300 K) for metals is dominated by collisions of the conduction electrons with lattice phonons and at low temperature, by collisions with impurity atoms and mechanical imperfections in the solid\textsuperscript{25}. In tetrahedral structures, the suboxides are assumed to be present as an
impurity in metallic zinc, while in marigold and microbelt reverse is the case. Thus, a similar feature for microbelt is observed, although, impurities in the form of metallic Zn species dominate between 80 and 200 K.

Table 5.2. Resistivity values calculated for different morphologies of ZnO as a function of temperature. In case of tetrahedra the resistivity shows a metallic behavior and for marigold and microbelts a semiconducting behavior is observed.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temp (K)</th>
<th>Tetrahedra</th>
<th>P (Ω-cm)</th>
<th>Marigold</th>
<th>Microbelt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>3.33</td>
<td>97.83</td>
<td>8019.56</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>125</td>
<td>3.57</td>
<td>58.84</td>
<td>8622.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>5.47</td>
<td>60.60</td>
<td>10770.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>273</td>
<td>5.83</td>
<td>52.44</td>
<td>7944.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>7.33</td>
<td>49.84</td>
<td>3026.96</td>
<td></td>
</tr>
</tbody>
</table>

These results along with the field emission results indicate the possibility of controlling the electrical properties of ZnO by virtue of its morphology. Moreover, temperature plays a crucial role in deciding the material performance.

5.5. Limitations of ZnO nanostructures

Although these ZnO nanostructures exhibit encouraging properties, they however suffer from various limitations. The physical processes that take place at the very tip of an emitter play a critical role in the electron emission from the surface. There are various emitter parameters (defects) that influence field emission and more often than not, individual parameter contributions are difficult to identify and characterize. The field screening effect is a commonly observed phenomenon and can be alleviated by synthesizing/assembling vertically aligned nanostructures (having uniform emission) with ideal separation in device configuration on large-area substrates. Accurate current measurements from these structures and the correlation of findings with material properties are vital for making the appropriate links and for the future development of 'designed electronic properties'.
5.5. Conclusions

This chapter summarizes, the unique field emission behavior of the isolated multipod and a single arm of a multipod ZnO structures, exhibiting an ultra-low turn-on voltage of 40 V (for 1nA) and the current density of $2.8 \times 10^4$ A/cm$^2$ achieved with a field of $1.26 \times 10^5$ V/µm. The F-N plots have been interpreted on the basis of the theory of electron emission from semiconductors and a scheme, explaining the field emission behavior in both high and low field regions. Moreover, the formation of sharp tips with nanometer-scale radius of curvature and high mechanical stiffness offers unprecedented advantages, thus providing robust materials for electron sources. In addition, our results also emphasize that tuning of the spacing between the individual field emitters in an array could yield better devices with low threshold voltage and high current density. Further, we believe that the ease with which these multipod nanostructures can be picked up and mounted to facilitate smaller size of emitting area, higher beam current and importantly, longer lifetime promise several new opportunities for making compact and more efficient field emission devices in the near future.

Further, the field emission behavior of different morphologies of ZnO has been studied in both C-P and conventional FEM configuration. F-N plots for these morphologies are found to be nonlinear and linear in the two distinct field regions respectively. Based on the theory of field emission from semiconductors, the low field region corresponds to the emission from conduction band, while the high field region corresponds to the emission from conduction and valence bands of ZnO respectively. The current stability exhibited by the multipod, marigold, and tetrahedral structures is promising for sustained emission behavior facilitating their applications as electron sources. Thus, in order to get excellent field emission, both the small emitter radius and appropriate growth coverage are necessary.
5.6. References