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1. Introduction

Nanowires of a variety of materials have gained importance in the past decade owing to their potential for reliable integration into electronic devices. In particular, this importance is due to their application in flat panel display technology as well as in the cold cathode technology for electron tube devices such as microwave tubes. This is because the conventional thermionic emission devices are accompanied with high power dissipation due to high cathode temperature. With the emergence of nanomaterials, there has been an upsurge in the research publications reporting on their field emission behaviour. This is because of the advantage of nanometric dimensions, making them suitable for field emission. Several metallic and semiconducting nanomaterials are found to operate delivering high current density at a lower applied potential as compared to the conventional field emitter counterparts. The nanowire form of various materials is suitable for the observed field emission properties. Additionally, the materials to be investigated must possess vacuum compatibility (low vapour pressure), high mechanical strength (should be able to withstand mechanical stress due to high electric field), and resistance to ion bombardment (due to residual gases in the vacuum chamber) and low work function. The emission current density is usually in the range of 10-100 mA/cm$^2$ for the applied field of 1-20 V/µm. It should be possible to deposit the nanomaterials on the flat substrate such as Si, with uniform density and with relative ease, to be used as a field emitter cathode.

The materials of interest from field emission point of view can be classified into the following broad classes: Carbon nanotubes, graphene, carbon fibre; Nanoforms of wide band gap materials such as SiC, GaN, AlN, BN, ZnO; other semiconductors such as Si, CdTe, CdS; and nanostructures and nanowires of established electron emitters such as LaB$_6$.

In this chapter, emphasis will be given on the field emission phenomenon, an account of development in theory of field emission, basic methodology; and a brief review of the field emission work carried out on nanowires.

2. The field emission phenomenon

Field electron emission from metals and semiconductors has attracted the attention of researchers for the past more than sixty years. In the phenomenon called field emission,
electrons tunnel out from metal or semiconductor surface into vacuum under the action of high electrostatic field $\sim 10^6-10^7$ V/cm. A systematic study of field emission under ultrahigh vacuum conditions has led to the development of the technique Field Emission Microscopy (FEM), the detailed treatment of which can be found in the literature (Gomer, 1961). The quantum mechanical tunneling emission current – field strength relation was derived by Fowler and Nordheim in the year 1928 (Fowler & Nordheim, 1928). A refined account of field emission and field emission spectroscopy has also been taken (Modinos, 1984).

The traditional and most useful application of field emission to surface science is in the study of surface diffusion of adsorbates over clean metal surfaces. In this application of the original FEM technique, an emitter is uniformly covered with an adsorbate and the current emanating from a very small region of the surface of the emitter is measured. This technique is called the probe hole technique (Oostrom, 1966), in which various single crystal planes of an emitter can be accessed in a single experiment.

Apart from the usefulness of field emission in surface science, there are technological applications. Field emission sources are routinely used in scanning electron microscopy and e-beam lithography because of their small optical size. In fact, a high density two dimensional array of emitters can be fabricated by a variety of techniques resulting into emitters suitable for flat panel displays and even for electron tube devices (Spindt, 1991). Early work on field emission devices consisted of micro-fabricated metallic tip array (commonly from Mo), but these devices suffer from several factors degrading the operating performance. One of the crucial factors limiting the operational stability and lifetime of these metallic emitters is tip degradation due to Joule heating at high emission currents and ion bombardment causing erosion and blunting of the tips. These Spindt cathodes currently find use in ion sources, mass spectrometers. Huge efforts have been invested in developing displays based on Spindt cathodes with some success (Chalamala, 1998). Obtaining sharp and robust materials capable of delivering high emission current densities at lower operating voltages is an ongoing effort.

2.1 The Fowler-Nordheim equation

The basic formulation of quantum mechanical tunneling of conduction electrons from a plane metal surface into vacuum was conceived by Fowler and Nordheim (Fowler &
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Nordheim, 1928) resulting into the Fowler-Nordheim (F-N) equation. The equation representing tunneling from an exact triangular barrier (Fig. 1) without any correction factors is given by

$$J = 6.2 \times 10^6 \frac{(\mu/\varphi)^{1/2}}{(\mu+\varphi)} E^2 \exp \left[ -6.8 \times 10^7 \frac{\varphi^{1/2}}{E} \right] \text{amp/cm}^2$$

(1)

for all energies expressed in electron volts and the electric field $E$ in volts per centimetre. Here, $\varphi$ is the work function of the metal, $\mu$ is the Fermi energy and $J$ the field emission current density in amps/cm$^2$.

The above derivation is based on the exact triangular surface potential barrier. However, the electronic charge density at the surface does not end abruptly at the terminating metal surface and the barrier, therefore, cannot be expected to be straight up. Also, the image force potential reduces the surface potential barrier by a corresponding image term $V_x$.

$$V_x = -\frac{e^2}{4\pi x}$$

(2)

where $e$ is the electronic charge and $x$ is the distance from the metal surface. With this correction in the potential, the F-N equation acquires the form

$$J = 6.2 \times 10^6 \frac{(\mu/\varphi)^{1/2}}{\alpha^2(\mu+\varphi)} E^2 \exp \left[ -6.8 \times 10^7 \frac{\varphi^{1/2} \alpha}{E} \right],$$

(3)

$\alpha$ is the image correction term

$$\alpha = (1 - y)^{1/2}$$

(4)

and

$$y = 3.8 \times 10^{-4} E^{1/2} / \varphi$$

(5)

In the above, the zero point of the potential energy is taken to be at $\varphi + \mu$ above the bottom of the conduction band. Detailed treatment of the F-N equation for electron tunneling from metal surface can be found in the literature (Gomer, 1961; Fowler & Nordheim, 1928; Modinos, 1984).

In case of the semiconductors, the field electron emission theory is complex. Various aspects such as the contribution of the effective electron mass, field penetration, surface states, doping with n type or p type impurities and band structure have to be taken into account. Field emission from semiconductors has been dealt with by Stratton (Stratton, 1962) who considered the effect of the field penetration and surface states on electron emission. He pointed out that the field emission characteristic dominated by the surface states should be strongly temperature dependent while that dominated by field penetration is not. Baskin et al (Baskin, 1971) have analysed field electron emission behaviour of an n-type semiconductor based on the field emission from conduction band. A detailed account of the theory field emission from semiconductors is available (Modinos, 1984). Recently, there have been attempts to revisit the theory of Fowler-Nordheim tunneling. The standard theory has been reformulated by Forbes and Deane (Forbes & Deane, 2007) leading to an insight into linearity of F-N plot. A revised mathematical form for empirical field emission current –voltage characteristics has also been obtained by Forbes (Forbes, 2008).
2.2 Application of F-N theory to the field emission from nanomaterials

The F-N theory primarily considers tunneling of electrons from flat planar surface of metals. The image potential corrected F-N equation (Eq.3) can be written as

\[
J = a \varphi^{-1} P_f E^2 \exp \left( - \frac{b \varphi^2}{E} \right),
\]

Where \( P_f \) is the prefactor given by

\[
P_f = 4 \varphi^{3/2} (\mu)^{1/2} / (\varphi + \mu),
\]

\( \mu \) is the Fermi energy and \( \varphi \) is the work function. \( P_f \) is of the order of unity and can be set as equal to unity. Thus,

\[
J = a \varphi^{-1} E^2 \exp \left( - \frac{b \varphi^2}{E} \right),
\]

Here, \( a \) and \( b \) are constant (\( a = 1.54 \times 10^{18} \text{ A eV V}^{-2}, \ b = 6.83 \text{ V}^{-3/2} \text{ Vnm}^{-1} \))

The electric field \( E \) is the local electric field (surface field). In case of the nanoparticles deposited on the flat cathode surface in the diode geometry, the electric field (applied or macroscopic field) between the cathode and the anode separated by a distance \( d \) with a potential difference \( V \) is given by,

\[
E = \frac{V}{d}
\]

However, local electric field \( E \) at the surface of a nanoparticle can be much higher than \( E \) by a factor \( \beta \),

\[
E = \beta E
\]

Here, \( \beta \) is the field enhancement factor.
From eq (9) and (10),

\[
E = \beta (V/d) = (\beta / d) V
\]

The factor \((\beta / d)\) is the voltage to local field conversion factor. In terms of the macroscopic field \( E \), the F-N equation (8) becomes,

\[
J = a \varphi^{-1} \beta^2 E^2 \exp \left( - \frac{b \varphi^2}{\beta E} \right),
\]

\( I = S \times J \)

where \( I \) is the emission current (A) and \( S \) the emitting area, \( \beta \) is the field enhancement factor. The factor \( \beta \) is related to the emitter geometry. In certain cases, the field enhancement factor \( \beta \) can be expressed as \( \beta = h/r \) where \( h \) is the height and \( r \) is the radius of curvature of the tip of the emitting structure. The local electric field at the tip surface depends upon actual tip geometry (shape). For the elongated, cylindrical emitters the height to diameter (thickness) ratio is called the ‘aspect ratio’. The emission performance of an emitter can be enhanced by increasing the ‘aspect ratio’. Usually calculation of the factor \( \beta \) is complex. There exist several models for the calculation of \( \beta \). These models are not uniformly applicable and may
vary for different types of materials as well as geometry. The value of $\beta$ can be calculated from the slope of the F-N plot, but the value obtained may be physically unrealistic.

Many of the field emission studies on nanomaterials have been motivated from the electron sources point of view. Therefore, the current stability for a long duration operation, the effect of residual gas pressure, effect of adsorption and desorption causing local work function variations become important parameters. The areal density of emitters on a cathode surface plays an important role in controlling the local electric field at the surface of an emitter. Higher density leads to a screening effect and lower density reduces this screening and causes rise in the local field at each emitter.

2.3 Recent developments in the theory of field electron emission from nanomaterials

As seen from the literature Eq. (12) has been widely used to fit the experimental data and calculate from the slope of the $\ln(J/E^2)$ versus $1/E$ (F-N) Plot, the field enhancement factor $\beta$ (dimensionless) even for multiple emitters. Strictly, the F-N theory is valid for a single, metallic, planar emitter. Even for semiconducting emitters, the same equation is seen to be assumed. For semiconductors, the effect of band structure, surface states and field penetration have to be accounted for, and the theory is not simple to apply to practical emitters. The theory of field electron emission from carbon based emitters has been recently addressed to. An excellent account of early work on carbon based film emitters and other nanostructured heterogeneous materials and also hypotheses about emission mechanism have been reported by Forbes (Forbes, 2001). The F-N equation (Eq.12) has also been used by researchers to describe field emission from carbon nanotubes (CNT’s) against many theoretical difficulties (Forbes, 2010). Recently a detailed analytical treatment of field emission from nanowall emitter has been attempted by Qin et. al. (Qin, 2011). The theory is very complex. The authors have shown that the F-N equation will not describe the electron emission from a nanowall of very small width (less than $\approx 2$nm).

The F-N behaviour of nanomaterials is important from the basic point of view. However, field emission from nanomaterials has been very attractive field of research due to its technological importance. The current density obtainable for lower and lower turn-on voltage, stability of the current, and life are the main considerations of the study. Ease of synthesis, size and shape, electrical conductivity are also important consideration for a material to be a candidate as an emitter. Finally, ease of fabrication of array of emitters on lithographically patterned substrate decides the applicability of such sources in electronic devices.

3. Nanowires as field emitters

Nanowires of different materials are of immense interest due to their one dimensional structures. Such structures are known to show quantum confinement effects. Nanowires also possess high surface to volume ratio. In particular, nanowires with low threshold and low operating voltage have become potential candidates for field emission display (FED) application. Aligned nanowires with a high packing density can significantly enhance the field emission behaviour. Nanowires possess axial geometry and such nanorods like structures can be grown vertically on flat substrate with desirable density of wires per unit area. Final aim is to form regular array of nanowires with a good uniformity in their aspect ratio (length to radius). This is usually done by growing nanowires on a lithographically patterned substrate. Field emission investigations are carried out on the nanowires grown on the substrate.
3.1 Basic methodology

Most of the nanostructured materials are deposited/coated on flat substrate (nominally 1 cm²) forming broad area electron emitter. The substrate is an electrical conductor/semiconductor. The method of deposition depends on the properties of the material to be deposited. Various methods such as chemical vapour deposition, Arc plasma deposition, pulsed Laser Deposition, electrodeposition, electrochemical deposition, spin coating etc. have been used by researchers. Amongst the various substrates Si is most common as it is suitable for integrating with electronic device technology. This forms the cathode. The anode is indium tin oxide (ITO) coated conducting glass plate with or without phosphor coating. The anode-cathode separation is in the range ~ usually a few microns to a few mm. The anode and the cathode are held separated with the quartz or alumina spacer. This is called the diode configuration. A typical anode cathode system is shown in Fig.2. A holder carrying the anode and the cathode is then mounted in an ultra high vacuum chamber which is subsequently evacuated to a pressure ~ $10^{-7}$-$10^{-8}$ mbar. The high voltage (0-10 kV) from stable DC supply is applied across the anode and the cathode. The current is measured by an electrometer amplifier ($10^{-9}$-$10^{-3}$ A). The current voltage characteristics are measured over a wide range of voltages. Current stability studies are performed by recording the field emission current (at the pre-set value) at regular time intervals. The field emission pattern is observed on the anode screen and recorded if necessary.

![Fig. 2. Schematic of the planar diode configuration arrangement in a vacuum chamber.](image)

3.2 Metallic nanowires

Traditional, Spindt type cathodes consisted of metallic emitters such as W, Mo, and also Si etc but will not be discussed here. Metallic nanowires of Mo, Cu, Co have been used as nanotips for field emission application (Hwang, 2005; Laurent, 2005; Liao, 2005). Field emission characteristics of electrochemically synthesized nickel nanowires on alumina nanoporous template, with oxygen plasma post treatment, have been reported (Joo, 2006). Nickel nanorods arrays have been vertically grown on a Ta-coated Si substrate by electrochemical process (Banerjee, 2011). The authors have reported the experimentally obtained geometrical field enhancement factor from F-N plot to be 4000, agreeing with existing models.
3.3 Inorganic semiconducting nanowires

Wide bandgap semiconductors such as SiC, GaN, ZnO, AlN have attractive physicochemical properties suitable to operate as efficient field emitters in their nanoforms. Field emission characteristics of SiC nanowires and nanorods (Wong, 1999) and GaN nanorods (Kim, 2003) have been investigated. Field emission from SnO$_2$ nanowhiskers, nanogras has been studied (Luo, 2004; Wang, 2005). The 1D SnO$_2$ structures are potentially important in application such as optoelectronics devices and sensors. ZnO is fore-runner amongst the wide band gap materials, so far as the field emission studies are concerned. The field emission properties of ZnO nanowires were first studied by Lee’s group in 2002 (Lee, 2002). In their work, well aligned ZnO nanowires were grown on Si substrate using a metal vapour deposition method. Before growth, nanoscale Co particles (average diameter ~ 6-8 nm) were distributed onto Si substrate as the catalyst. The average length and typical diameter of the ZnO nanowires grown at 550 °C were 13 μm and 50 nm, respectively. The turn-on voltage for the ZnO nanowires was found to be about ~ 6.0 V/μm at a current density of ~ 0.1mA/cm$^2$. The emission current density from the ZnO nanowires reached 1 mA/cm$^2$ at a bias field of 11.0 V/μm.

The ZnO nanoneedle arrays with sharp tips show improved field emission performance (Zhu, 2003). The nanoneedles were grown via selenium-assisted vapour phase deposition. The height and diameter of the nanoneedles were about 3 μm and 100 nm, respectively. The turn-on field was found to be ~ 2.4 V/μm. The emission current density can reach ~ 2.4 mA/cm$^2$ at an applied electric field of ~ 7.0 V/μm. The field emission property of single nanowire was also reported (Dong, 2003). The ZnO nanowires were formed on tungsten substrates using a vapour transport method. In this synthesis gold served as the catalyst during the growth. The lengths of the nanowires were several tens of microns, and their diameters ranging from 25 to 200 nm. Measurement of the I-V current for an individual ZnO nanowire was carried out using a movable Faraday cup. In this research the emission current fluctuations have been studied at different temperatures. ZnO films, nanowires array and nanosheets via seed-layer assisted electrochemical deposition route have been fabricated (Cao, 2007). They found that the ordered ZnO nanowire arrays with high density only show the field emission property a little better than that of the ZnO film because of the local electric field screening effect. The hierarchical ZnO nanowire arrays show good field emission properties due to their high aspect ratio, small radius of curvature, and proper density. Field emission characteristics of ZnO nanowires grown on carbon cloth have been reported (Jo, 2004). ZnO nanowires were synthesized on carbon cloth by vaporization and condensation method. Aligned nanowires carry a lot of importance in their functioning as field emitters. Jamali Sheini et al. (Sheini, 2010) have synthesized aligned ZnO nanowires by annealing gold deposited zinc foil in air at 400°C. Fig. 3 a shows the SEM image of the aligned nanowires. From the field emission studies, the value of the turn-on field corresponding to an emission current density of ~ 0.1 μA/cm$^2$ is found to be ~ 2.4 V/μm and a current density of 100 μA/cm$^2$ is obtained at an applied field of ~ 3.4 V/μm. The field emission current stability investigated over a period of 3 hours at the preset value of 1 μA is found to be good. Attempt has been made to synthesize ZnO nanowires by cathodic electrodeposition of nanostructured ZnO thin films on zinc substrate, followed by annealing in air (Sheini, 2009). The field emission studies showed the value of 1.36 V/μm for drawing the emission current density of ~ 1 μA/cm$^2$ for the best specimen. The field emission was measured in a planar diode configuration. The photoenhanced field emission from Sn doped ZnO nanowires has also been reported by Jamali Sheini et al. (Sheini, 2010).
Fig. 3. (a) An SEM image of aligned ZnO nanowires grown on Au coated Zn Substrate and annealed at 400°C for 4 hours. Reproduced from Materials Chemistry and Physics (Jamali Sheini, 2010) Copyright © 2010, Elsevier.

Fig. 3. (b) An SEM image of as-synthesized ZnO nanowires grown on Zn substrate. Reproduced from Ultramicroscopy (Jamali sheini, 2009) Copyright © 2009. Elsevier.

Fig. 3. (c) A field emission current density-applied field (J–E) plot of the ZnO nanowires and inset showing the corresponding Fowler-Nordheim (F-N) plot. Reproduced from Ultramicroscopy (Jamali sheini, 2009) Copyright © 2009. Elsevier.
Fig. 3. (d) Current versus time (I–t) plot of the ZnO nanowires and inset showing the field emission image. Reproduced from Ultramicroscopy (Jamali sheini, 2009) Copyright © 2009. Elsevier.

Fig. 3 b shows the scanning electron micrograph (SEM) of ZnO nanowires grown on Zn foil by electrodeposition followed by annealing at 400°C for 4 h. The field emission J-E plot and F-N plot are depicted in Fig 3 c and the inset, respectively. Fig. 3 d shows the I-t stability plot and the field emission pattern.

The non-linearity of the F-N plot has been attributed to the semiconducting properties of ZnO. Excellent current stability has been observed with fluctuations within ± 5% of the average value. A good account of electrochemical deposition of ZnO nanowires array has been taken by Zeng et al. (Zeng, 2010). These authors have discussed the effect of doping on the field emission properties. The narrow band gap semiconductors and other semiconducting nanomaterials such as copper sulfide (Cu2S) nanowires arrays have been studied (Chen, 2002). The CuO nanobelts, nanorods, and nanofibres have also been studied by Hsieh et al. (Hsieh, 2003). The MoO3 nanowires and nanobelt structures have been studied by Zhou et al. (Zhou, 2003). One dimensional chalcogenides nanowires have proved to be significant for their novel physical properties and in particular, field emission properties (Datta, 2009). Fig. 4a shows the SEM image of the CdS nanowires synthesized by simple thermal evaporation route on Si substrate.

Fig. 4. (a) An SEM image of as-synthesized CdS nanowires grown on Si substrate by simple thermal evaporation technique.
Fig. 4. (b) Photo-switching properties of the CdS nanowires in current–time (I-t) mode. The turn on field for the emission current density of 0.1 $\mu$A/cm$^2$ is found to be 1.4 V/µm, lower than the reported value for CdS nanostructures. A current density of 27 $\mu$A/cm$^2$ was drawn at an applied field of $\sim$ 2.4 V/µm. Upon illumination with visible light, the CdS nanowires switch to the enhanced emission state and return to the original field emission current after the light source is turned off. Thus it is demonstrated that the CdS nanowires act as photo-field emitter switch. A sequence of current pulses generated due to repetitively switching the light source, on and off, is shown in Fig 4b. The effect has been attributed to the photoconductive property of CdS (band gap 2.4 eV) (Chavan, 2011). Fig. 4c shows the J–E characteristics without and with illumination. Fig 5 shows field emission current stability continuously recorded for 24 hrs at the preset current of 1 $\mu$A. The current is seen to be highly stable. The inset shows field emission image showing the emission spots due to nanowires.

Fig. 4. (c) J–E plots of CdS nanowires with and without light illumination. The high sensitivity and fast response of CdS nanowires points towards possible application of the CdS nanowire field emitters in devices and in pulsed electron beam technology.

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Fig. 5. Current versus time (I–t) plot of the CdS nanowires and inset showing the field emission image.

The number of research articles in the area of the field emission from nanowires and nanomaterials in general is too large to review here. A good account of inorganic nanostructures and their field emission applications has been taken by Fang et al (Fang, 2008). Lanthanum hexaboride (LaB$_6$) is a very well known thermionic electron emitter. Its potential as a field emitter has been recognised by researchers world over. LaB$_6$ nanowires are ideal for applications as electron sources due to their inherent characteristics such as low work function (2.6 eV). Recently it is reported that excellent field electron emission is obtained from single LaB$_6$ nanowire emitter with stability better than the LaB$_6$ needle type emitter or tungsten field emitter (Zhang, 2010). Extremely high emission current density from LaB$_6$ arrays is achieved by Qi et al (Qi, 2008). Field emitter arrays of LaB$_6$ have been fabricated by employing the transfer mold technique (Nakamoto, 2002). LaB$_6$ nanowires have been synthesized using arc plasma synthesis (Late, 2010). More efforts are required to fabricate LaB$_6$ nanowires arrays in a reliable and efficient manner.

4. Future outlook

Nanowire field emitter arrays of various materials will be the area of research interests for some more time. More efforts are required to deliver improved field emitter nanowire arrays as sources in electron tube devices and electron beam accelerators.

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6. References


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This potentially unique work offers various approaches on the implementation of nanowires. As it is widely known, nanotechnology presents the control of matter at the nanoscale and nanodimensions within few nanometers, whereas this exclusive phenomenon enables us to determine novel applications. This book presents an overview of recent and current nanowire application and implementation research worldwide. We examine methods of nanowire synthesis, types of materials used, and applications associated with nanowire research. Wide surveys of global activities in nanowire research are presented, as well.

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