Abstract

Early age discovery of radio, television and computer was realized with invention of thermionic cathode and development of vacuum electronics. Electron source of the vacuum electronic devices are thermionic cathodes. Thermionic cathodes have certain major limitations such as cost effectiveness, high power consumption, bulky size, small life etc. which demands its alternative. Discovery of transistor and integrated microelectronics facilitates versatile, cheap, and robust alternative of vacuum electronics. This allows high frequency operation, low power consumption with low cost and high fabrication yield. Vacuum electronics disappeared completely after invention of transistor and development of integrated microelectronics and semiconductor technology. However, there are certain applications, where these integrated microelectronic devices are impractical and the only one potential solution for these applications are the same vacuum technology that was abandoned earlier. Few of their specialized applications are microwave application, high-power RF transmission, certain military systems, x-ray tubes, modern day electron microscopy etc. These devices are still running with the same vacuum tube principle. These systems are based on nearly ballistic propagation of electron inside a high vacuum tube to achieve desired operation and result such as signal gain, imaging, x-ray generation etc. This again demands other alternative of thermionic cathodes which utilizes same vacuum electronics principle.

With growing demand of device miniaturization, vacuum electronics is also need to be miniaturize similar to the semiconductor technology that obeys Moore’s law. Emerging vacuum microelectronic devices based on field emission source are of much interest due to their unique properties such as high current densities, ballistic electron transport, and temperature independence. Field emitter arrays fabricated with whiskers like shape have optimum field enhancement factor. These properties promote a wide range of applications including field emission displays (FEDs) for flat panel monitors. Initially Spindt type micro tip emitters were proposed as strong field emitter source. Many research groups have developed field emission devices based on nano and micro-structured material such as carbon nanotubes (CNTs), silicon Spindt
emitter, zinc oxide nano rod etc, nano-belts, silicon carbide nano-wires, aluminum nitride nano-needles, silicon nano-wires, tin oxide nano-whiskers etc. Particularly, owing to the excellent thermal properties, good mechanical stiffness and extraordinary electrical properties, CNTs are considered to be potential candidate for numerous technological applications like a CNT field emitter, CNT field effect transistor, atomic force microscope tip, CNT nano tweezers, etc. Out of all these applications, CNTs are considered as a very promising material for electron emitter source in various field emission devices like a microwave amplifier, flat panel display, X-ray tube, etc.

One of the important topics for high power vacuum microelectronics application is to develop a cathode of high emission current density because cathode is the core of a field emitter device. For the development of such a high current density CNT-emitters, it is required to know and tailor the basic parameters which influence their FE behavior. Current density \( J \) of the CNT emitter is governed by the Fowler-Nordheim (F-N) equation,

\[
J = \frac{e^3}{8\pi\hbar\varphi}E^2 \exp \left( -\frac{8\pi\sqrt{2m_e\varphi}}{3\hbar E} \frac{3/2}{3} \right)
\]

Here \( E \) is the enhanced electric field, \( \varphi \) is the work function and rest of the parameters have their usual meaning. As evident from F-N equation, current density \( J \) is strongly dependent on work function \( \varphi \) and enhanced local electric field \( E \). Since CNT inherently possesses the merits of high aspect ratio which attributed to the significant enhancement of the applied electric field at the tip of CNT field emitters. At the same applied electric field, if work function of the CNTs is somehow lowered then it will greatly influence their emission current density.

The aim of the present work is to develop a CNT based cathode or CNT emitter arrays, field emission studies of developed CNT emitter arrays as cathode plate in diode configuration and to study the effects of surface modification, temperature treatment and structural modification on field emission of treated CNT emitter arrays. Work function is a material property and it can be altered using surface modification approach such as low work function decoration, dipolar molecule as
nano particle coating, internal stress release using temperature treatment, etc. Present works summarize the development of carbon nanotubes (CNTs) based cathode and their field emission (FE) along with the optimization and improvement of emission current by work function engineering, temperature treatment and structural engineering. Entire work in this thesis is presented in seven chapters and a summary of each of these chapters is given below.

Chapter 1 initially reviews current scenario, different device development methodologies, CNT based devices such as field emitter, CNT field effect transistor, etc. Later, our device development method will be presented. Section 1.1 gives a detailed description of the literature survey reviewing different device development methodology and suitability of our requirement. Brief introduction of carbon and their allotropes are described. Moreover, brief introduction of carbon nanotubes with complete description of their classification, outstanding properties, different synthesis method, growth mechanism, various characterization techniques and applications will be presented.

Chapter 2 presents introduction of different electron emission techniques such as photo emission, field electron emission, etc. and provides background theoretical knowledge essential to understand the experiments and analysis. The focus of this chapter would be on field emission, however a description of thermal emission, photo emission and secondary emission is also provided.

Chapter 3 gives a detailed description of the experimental methodology employed for development of CNTs based cold cathode. A brief account of the thermal chemical vapor deposition and plasma enhanced chemical vapor deposition used for synthesis of CNTs and development of CNTs based cathode is given. Sputtering used for catalyst coating has also been elaborated. Different characterization tools such as scanning electron microscope, transmission electron microscope, etc. employed to study the morphology and the changes introduced after treatment has also been elaborated. The detailed FE measurement setup and their process steps have been discussed.

Chapter 4 LaB₆ is a traditional low work function material that has well established industrial applications like filaments of thermionic cathodes and is extensively coated on the filament of thermionic cathodes for work function lowering
in different applications. The combined effect of the high aspect-ratio of CNTs and a low work function of the LaB$_6$ is expected to contribute toward the enhanced electric field along with relatively lower work function which may result into a very high current density. These promising features of the LaB$_6$-coated CNT-emitters may exhibit tremendous potential to improve the emission current density from the CNT emitter even at a lower applied electric field. In conventional thermionic cathodes, thick film of LaB$_6$ was coated on the tungsten filaments. However, as per our knowledge, no one has studied the behavior of LaB$_6$ as nano particles (NPs) and decorated them to improve the FE. In this chapter, LaB$_6$ NPs were successfully decorated on the patterned CNT emitter arrays and their effects were studied as comparative change in FE.

Furthermore, thermionic cathodes also employ coating of other low work function material like barium oxide to improve their emission current. Therefore, similar modification on the CNTs emitter surface, by coating them with another low work function material like cesium compound, can be tried as an effective and simple approach to increase the emission current of CNTs. In this chapter, the surface of CNTs has been modified with cesium iodide NPs and its field emission characteristics is presented along with the change in emission current, surface morphology etc. Subsequently, FE results are analyzed in light of effective change in work function due to NPs decoration. Work function of LaB$_6$ NPs decorated CNTs was also estimated using mathematical reverse engineering.

Chapter 5 reports the effect of temperature treatment on FE of bare or pristine CNTs and low work function decorated patterned CNT emitter arrays in different environment such as vacuum and air. CNT emitter arrays had been annealed in vacuum at more than 1000°C. In another study to achieve the optimum result, bare CNTs were temperature treated in oxygen at 400°C because it oxidizes in air above 400°C. Furthermore, cesium iodide nano particles decorated CNTs were vacuum annealed and oxidized CNTs were decorated with LaB$_6$ NPs.

Chapter 6 Owing to their high aspect ratio, CNTs innately keep the merit of very high field enhancement factor. This chapter elucidates the effect of edge effect on FE of patterned CNT emitter arrays. FE measurements of the five different CNT cathodes were carried out at constant cathode to anode spacing. These FE results
show remarkable influence of edge effect on emission current and significant change in turn on electric field. The possible reasons of this were compared and studied in light of Fowler Nordheim equation. Effect of edge length over total growth area and purity on FE of CNTs was analyzed.

Chapter 7 describes the conclusions of the present work and future plans.