Modeling of field emission from nanomaterials and nanostructures

Sun, Song

2013

Sun, S. (2013). Modeling of field emission from nanomaterials and nanostructures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54888>

<https://doi.org/10.32657/10356/54888>

Modeling of Field Emission from Nanomaterials and Nanostructures

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

ACKNOWLEDGEMENTS

First and foremost, I must thank my advisor Associate Professor Ang Lay Kee Ricky, for his valuable guidance, consistent support and encouragement throughout the course of my graduate study at Nanyang Technological University in Singapore. From the start of my graduate course till the submission of this dissertation, Dr Ang has been inspirational and is the role model of a hardworking and creative young scientist, who has exhibited lots of passion in his work both in the teaching duties and research. I consider myself privileged to have the opportunity to work with such an outstanding and motivated scientist.

I am grateful to Associate Professor Ng Geok Ing, the Head of the Division of Microelectronics (EEE6). I must also thank Professor Zhu Weiguang, Associate Professor Sun Changqing and Assistant Professor Yu Ting for their support in my qualified examination, Ms. Tan May Ser Serene, the Higher Clerical Officer of the Staff Office S2.2-b3-09, for the usage of their facilities during the course of my work.

It has been a wonderful experience for me to study in the School of Electrical and Electronic Engineering, Division of Microelectronics. I would like to thank my fellow staff and graduate students Dr. Koh Wee Shing, Dr. Wu Lin, Dr. Zhang Peng, Dr. William Chandra, Mr. Liu Yangjie, Mr. Zhu Yinbin, Mr. Kelvin Ooi Jian

ACKNOWLEDGEMENTS

Aun, Mr. Mihir Pant for their support and encouragement during the course of my graduate study.

Many thanks to the laboratory executive Ms. Saw Gwek Keow of the Nanoelectronics Design Laboratory, School of Electrical and Electronic Engineering, Mr. Chow Kam Wah of the Semiconductor Characterization Laboratory 2.

Special thanks to my best friends, Zhang Kaibin, Hu Chen, Li Hailin, Bian Zhiwei, Zhang Junwu and Bian Linyang, who help me to de-stress whenever I am too immerse in my research. My deepest appreciations are for my parents, my brother and my girl friend Ding Yan, who encouraged and supported me in whatever I do throughout my life.

Last but not least, I would like to acknowledge the support of Agency for Science, Technology and Research (A*STAR), Singapore, Nanyang Technological University, Singapore, the Institute of High Performance Computing (IHPC), Singapore, and the IEEE student travel grant for me to attend the 2010 Vacuum Electron Sources Conference in Nanjing, China, and the 2011 IEEE International Conference on Plasma Science, Chicago, USA.

Sun Song

Jun 2013

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SUMMARY

Electron field emission from nanomaterials and nanostructures has remained an area of considerable interest to flat-panel display, compact electron source, electron microscopy, vacuum micro- and nano-electronics. Previously, most of the theoretical developments of the field emission are focused on one-dimensional (1D) classical models and metals. The multi-dimensional models for certain materials with unique electronic properties are relatively undeveloped. However, recent field emission experiments using sharp tips and nanomaterials with unique properties have shown great advances in this area. Hence, this thesis presents the development in the field emission theory on various nanomaterials (graphene and diamond) or nanostructures (sharp tip emitter and triple junction).

Graphene is promised to be an excellent field emission source not only because of the high enhancement on the emission edge, but also due to the unique band structure at low energy level. Many experiments have already verified that graphene can emit high current density at small applied voltage with good stability and compactness. A field emission model is constructed to take into account that graphene is a 2D superlattice instead of a 3D bulk material, and the transmission coefficient through a potential barrier is calculated by Dirac equation. This model predicts a linear current-voltage scaling, which is quite different from the conventional field emission

theory (Fowler-Nordheim law). The subsequent shot noise analysis further verifies our model, where the Fano factor will reach a maximum value of $1/3$.

It is generally argued that the space-charge-effect will be important for a sharp tip emitter. Thus, a simple model to numerically estimate the onset of space-charge-limited (SCL) current at the apex of a sharp tip emitter is proposed. In fact, this onset SCL condition, at which the space charge field is equal to the applied local electrical field at the emitter apex, highly depends on the emitter's geometry. The resultant SCL current is compared with the classical Child-Langmuir law to observe the enhancement due to the cathode surface protrusion.

In practice, the experimentalists try to measure the average enhancement of a sharp tip emitter by fitting the gradient or interpolation of the Fowler-Nordheim plot. However, the gradient and interpolation of the curve vary with respect to anode area, gap spacing as well as emitter's geometry, and it is difficult to justify that the measurement is accurate. Our model establishes a criteria to standardize the measurement of average enhancement for a sharp tip emitter, which can provide a well-defined estimated value.

Lastly, a field emission model from the metal-diamond-vacuum triple junction structure is proposed. According to the diamond surface property and the enhancement at the triple junction point, we modify its band structure from the conventional diamond emitter. The reason for the triple junction structure to reach a low turn on voltage, high current density characteristic is carefully investigated. The resultant emission current density is also compared with the previous experimental data to verify our model.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Field emission (FE) is the emission of electrons from the surface of a material into free space due to the presence of high electric fields. In this phenomenon, electrons with energies below the Fermi level tunnel through the potential barrier at the surface, which is narrowed sufficiently by the high electric field for the electrons to have a non-negligible tunneling probability. Also called cold emission or Fowler-Nordheim tunneling, FE is unique in comparison with thermionic emission [1] or photoemission [2, 3, 4] in which only electrons with sufficient energy to surmount the surface potential barrier are able to escape the condensed phase.

Nowadays field emission is the principal means of generating an electron beam for application in displays based on field emitter arrays, transmitting and scanning electron microscopes, and some vacuum microelectronic devices including FE triodes, amplifiers and microwave frequency devices [5, 6]. Some examples are briefly discussed as follows.

- The traditional cathode ray tube (CRT) equipped with a phosphorescent screen, has been the basic device for translating electronic signals into visual displays, initially in scientific instrumentation (e.g. oscilloscopes) and later in television and computer screens. The modern flat-panel field emission displays generally replace the thermal cathodes of conventional CRT displays with arrays of field emitters, which provide greater life, brightness and focusing ability than the thermionic or photoemission sources.
- Transmission and scanning electron microscopes employ the optical properties of electrons, notably the shorter wavelength, to produce images of very high resolution. These electron microscopes require an electron beam of high brilliance, low divergence and good focusing ability, and they continue to place demands on the development of increasingly sophisticated electron beam technology.
- Transmission electron microscopy (TEM) with its wide-ranging arsenal of tools has long been a powerful method in many areas of research, allowing for sub-nanometer spatial resolution.
- Field ion microscopy (FIM) [7] employed field emission to directly investigate the molecular surface structure of an emitter and its electronic properties. It relies on field emission and produces an image from a gas ionized near the surface by emitted electrons, rather than from the electrons themselves. Consequently the FIM is useful for studying spatial relationships at the surface of metallic solids with atomic resolution, and it is a valuable tool for designing more effective emitters.

Given the importance of field emission to the numerous critical applications, it generally requires the field emitter to be able to emit high current density at low applied voltages. However, classical field emission in pure metals usually occurs in high electric fields: typically higher than 1 gigavolt per meter. Thus, it is crucial for

1.2 Objectives

us to investigate the field emission behaviors for different materials, and to find out the best potential candidate. For example, carbon-based materials such as graphene and diamond (triple junction structure), are believed to be excellent electron sources for field emission.

Besides the material's properties, another way to improve the field emission performance is to change the emitter's geometrical structure by having a sharp tip, or building a complex junction. Both techniques will significantly increase the local electric field at the emission site without actually increasing the applied voltage, and it is essential to operate with a low turn-on voltage. However for sharp tip emitters at high power output, the space charge effect becomes important, which will limit the amount of emission current. Thus, it is important for us to find out the effect of surface protrusion in the space-charge-limited (SCL) regime. On the other hand, the formation of the junction will significantly modify the band structure of the semiconductor, which may further lower the applied voltage. Hence, it also needs careful revision before utilizing in the real applications.

The motivation of this research work is to earn a thorough understanding for the physics of field emission in different nanomaterials (graphene and diamond) and nanostructures (sharp tip emitter and triple junction structure). More details of each topic will be discussed below.

1.2 Objectives

The main objectives of this thesis are summarized as follows:

Firstly, the vertically-aligned single layer graphene sheet may emit high current density at low applied voltage due to the large surface enhancement as well as its unique band structure (here we do not consider the electron beam divergence at the sharp emission edge). The electrons at low energy states obey the linear energy dispersion which mimic the massless Dirac fermion governed by quantum

electro-dynamics (QED). As a result, the tunneling of electrons through a potential barrier exhibits the angle-dependent Klein tunneling phenomenon [8] with a large transmission coefficient. Nevertheless, the physics behind the field emission process of a single layer graphene is not fully developed, and there is no model so far to quantitatively calculate the emission current density due to Klein tunneling. To build such a model, two primary tasks need to be done: 1) the emission current density needs to be re-derived based on the tunneling theory, including the effect of reduction on the dimensionality. 2) the transmission coefficient is angle-dependent and must be solved by a 2D Dirac equation. The resultant current-voltage scaling should be compared with the traditional Fowler-Nordheim (FN) law [9] to demonstrate the differences. In Chapter 3, we will make a first attempt in this direction which includes the shot noise analysis as well.

Secondly, to our knowledge, the emitter is usually fabricated to be a sharp tip, such as Lorentzian shape or Hyperboloid shape, to greatly enhance the local electric field at the emission site. When the applied voltage is sufficiently high, the space charge effects due to the emitted electrons will limit the maximum current flow through the gap. To obtain this limiting current and its corresponding onset condition is the key objective to study the field emission at high power situation. However, the existence models can only manage to solve 1D [10, 11, 12] or 2D cases [13, 14, 15], which are not directly applicable to analyze the sharp tip emitter. Furthermore, the traditional approach to compute the SCL current needs to solve the Poisson equation, which can hardly be simplified in the 3D case [16]. Hence, our main interest is to construct a simple model to calculate the onset SCL condition for a sharp tip emitter without solving the Poisson equation or Schroedinger equation. It is possible to achieve this by tracking the emitted electron trajectories and applying continuity equation near the tip regime. The resultant SCL current should be compared to the 1D Child-Langmuir (CL) Law [10, 11] to observe the enhancement for the 3D structure. Other parameter dependences, such as geometrical sharpness, work

1.3 Potential Impact and Application

function as well as gap spacing, should also be carefully investigated. This topic will be discussed in Chapter 4.

Thirdly, the experimentalists always use the classical FN law to fit the gradient or interpolation of the FN plot in order to obtain the average enhancement of a sharp tip emitter. However for a sharp tip emitter, the emission is nonuniform around the emitter surface (strong emission near the apex and weak emission near the tail) and the electron beam will expand in the vacuum space (the anode area must be large enough to collect all the emission current). Hence, several parameters must be carefully determined in order to define the average enhancement, such as the anode area and the gap spacing [17]. We shall follow a typical experimental set-up to numerically “measure” the average enhancement of a single sharp tip emitter. Our main objective is to establish a criteria for the experimentalists to properly choose the parameters so as to get the accurate enhancement value with the measured data. This topic will be presented in Chapter 5.

Lastly, a quantitative model of the field emission for a metal-diamond-vacuum triple junction has not yet been developed. To construct such a model, the material property of the diamond must be carefully dealt with, e.g. negative electron affinity (NEA) on the diamond (111) surface, the formation of surface state due to the reconstruction, etc. In addition, the potential barrier at the metal-diamond interface as well as the diamond-vacuum interface must be derived base on the semiconductor theory. We shall study the emission process for such a triple junction to achieve a low voltage high current characteristic. The results shall be compared with experimental data [18] for further verification. This topic will be presented in Chapter 6.

1.3 Potential Impact and Application

The above research topics are of substantial interest in many different fields. Our results will not only provide significant theoretical values on material physics and

quantum mechanics, but also help the experimentalist to design the electronic devices for real applications.

The field emission model from single layer graphene could explain the essential physics behind the unusual field emission characteristic (Klein tunneling). The obtained current-voltage scaling could help the experimentalist to develop the next generation display technology base on this material.

If we can create a simple methodology to calculate the onset SCL current from a sharp tip emitter, which avoids the notorious difficulties to solve the 3D Poisson equation, we could directly implement it in PIC (Particle-in-Cell) code package to simulate the real electron gun device, which shall save a lot of computation effort.

By performing the numerical measurement on field emission from a sharp tip emitter, we could get clear about what are the key factors that affect the measurement result in the experiment. After that, we could set up a standard procedure to guide the experimentalist, which will definitely improve the measurement quality.

The field emission model from a triple junction structure would provide a deep understanding on the electron transport mechanism across different mediums. The combined effects of surface state, NEA property and Schottky barrier must be clearly understood before utilizing in the real applications.

1.4 Major Contribution of the Thesis

The major contributions of the thesis are listed as follow:

A quantitative model (see Chapter 3) [19, 20] to calculate the emission current density from a vertically-aligned single layer graphene sheet is developed. The model carefully considered the effect of the reduction on the dimensionality, and the resultant current line density is in the unit of A/m instead of A/m². Our model also illustrates a linear current-voltage scaling by including the Klein tunneling effect particularly for low energy electron near the Fermi energy, which is very different from

1.4 Major Contribution of the Thesis

the FN law, where the current increases exponentially with respect to the applied field. Moreover, a following shot noise analysis further shows the deviation of noise property in graphene field emission from other conventional bulk materials. Under low temperature, the Fano factor will reach a universal maximum value of $1/3$, which is consistent with the experimental data. At high temperature, the Fano factor will exceed this limit and uniformly distributed over a wide range of the applied field.

A simple model (see Chapter 4) [21] is constructed to calculate the onset of SCL current on a single sharp tip emitter of either Lorentzian or Hyperboloid shape. The overall space charge field can be obtained by combining the field emission equation, continuity equation, Newton's law as well as the Gauss's law. The onset SCL condition is reached once the space charge field on the emitter apex matches the local electrical field. The results show a useful scaling that the onset electric field (critical field) multiplies the enhancement value on the emitter apex would be a constant. The protrusive SCL current is compared with the CL law, and the enhancement only depends on the emitter geometry, and independent of the material work function or gap spacing.

By verifying the validity of the experimental approach to measure the average enhancement for a sharp tip emitter, we confirm that the average enhancement can only be obtained by gradient fitting instead of interpolation fitting (see Chapter 5) [22]. We also establish a criteria that the anode area must be large enough to collect all the emission current in order to get the accurate enhancement value. The dependences of the average enhancement on the emitter geometry and gap spacing, are also explored in detail.

A metal-diamond-vacuum triple junction model (see Chapter 6) [23] has been developed to calculate the emission current density. Compare with the conventional diamond emitter, the change in the band structure is clearly illustrated by considering the reduction on the barrier height, the donor level formation, the surface state formation as well as the NEA property on the diamond-vacuum interface. The results

of the emission current density agree very well with the experimental data by including the extra enhancement on the triple point and the reduction on the Schottky barrier height, where the extra enhancement value and the barrier reduction are taken from the experiment. The emission mechanism with light exposure is also briefly discussed.

1.5 Organization of the Thesis

In Chapter 2, first we will present a brief review of the field emission model from the metal, which contains all the background to understand the emission tunneling mechanism in field emission process. Secondly, a review on the electronic property of a single layer graphene is provided, which clearly explains the differences between graphene and other conventional materials. In addition, the unique characteristic of Klein tunneling at low energy level is also discussed. Thirdly, the surface properties of the diamond are generally discussed, and the enhancement on the triple junction point is also provided. These are all the key elements to construct a triple junction field emission model. Lastly, a review on the classical Child-Langmuir law is given, which describes the maximum current flow through a vacuum gap.

In Chapter 3, we will build a field emission model from a vertically-aligned single layer graphene sheet. This model carefully deals with the 2D geometrical structure as well as the unique band structure of a single layer graphene. Furthermore, the shot noise analysis of the developed model is given to compare with the earlier research results.

In Chapter 4, a simple analytical model to calculate the onset SCL current on a single sharp emitter is constructed. Without solving the partial differential equation, the onset SCL condition is obtained for a Lorentzian shape or Hyperboloid shape emitter. The enhancement of the protrusive SCL current with respect to the 1D CL law is also provided.

1.5 Organization of the Thesis

In Chapter 5, we conduct a numerical experiment to simulate the electron field emission from a sharp tip emitter (Lorentzian or Hyperboloid shape). By collecting the emitting current at the anode, we establish the criteria in using Fowler-Nordheim (FN) plot to estimate both the average enhancement and the effective emission area. We will investigate the dependences of the average enhancement on various parameters, such as anode area, gap spacing and geometrical sharpness. The extension of this simple model to a more complicated statistical model to simulate field emission from a cathode consisting of many field emitters is also briefly discussed.

In Chapter 6, a field emission model for a metal-diamond-vacuum triple junction structure will be given. The difference on the band diagram between the triple junction structure and the traditional diamond emitter will be discussed. The emission current results will be compared with the experimental data for verification.

We will summarize and conclude our research work in Chapter 7. Some suggestions for future work will be given.

CHAPTER 2

LITERATURE REVIEW

The field emission (FE) process is a type of electron emission which is due to the quantum mechanical effects - tunneling of electrons into vacuum with a strong applied electrical field. It has recently emerged as an important, high-brightness electron source for generation of coherent radiation [7, 24, 25, 26, 27, 28]. Classically for an one-dimensional isotropic material, e.g. for a flat metal surface at room temperature, the field emission process is known as the Fowler-Nordheim (FN) law [9]. However for other materials such as graphene and diamond, their unique band structures and material properties need to be incorporated in the corresponding field emission theory. Furthermore at high voltage regime, the space charge effect has to be taken into account.

Before looking into the detail field emission mechanism, first it will be necessary to review the general principle of field emission as well as the corresponding material properties which may affect the field emission characteristics. In this chapter, the classical field emission from a flat metal surface is reviewed in Sec. 2.1, followed by the material properties of graphene and diamond in Sec. 2.2 and 2.3 respectively, and lastly the classical 1D Child-Langmuir law is briefly discussed in Sec. 2.4.

2.1 The Classical Field Emission from A Flat Metal Surface

The field emission from a flat metal surface is the simplest model in the field emission study. It contains the basic concepts in the derivation of the emission current density. Hence it is essential for us to understand it before we move to a more complicated model in graphene and diamond.

2.1.1 The Free Electron Theory of Metal

The free-electron theory of metals [29] proposed by Sommerfeld (1928) [30] has provided the basis for practically all the quantum mechanical theories of electron emission from metals. The theory is based on the assumption that the conduction band electrons behave as if they were free particles. In this model the electron state (in the conduction band) is described by a plane wave ψ_k with a wave vector $\vec{k}$, and the energy of the electron is $E = \frac{\hbar^2 k^2}{2m}$. The number of electron states per unit volume with energy between E and $E + dE$ is given by [31]

$$\rho(E) dE \equiv \frac{2}{(2\pi)^3} \iiint d^3k = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE, \quad (2.1)$$

where $\hbar = h/2\pi$ is the reduced Planck's constant and m is the electron rest mass. The probability of an electron state with energy E being occupied (at equilibrium) is given by the Fermi-Dirac distribution function

$$f(E) = \frac{1}{1 + \exp [(E - E_F)/k_B T]}, \quad (2.2)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and E_F is the Fermi energy level.

For the subsequent development of the field emission theory, the number of electrons (under equilibrium conditions) across a unit area (parallel to the y - z plane)

from left to right, per unit time, with total energy between E and $E + dE$ and normal energy $E_x = \frac{\hbar^2 k_x^2}{2m}$ between E_x and $E_x + dE_x$ is given by

$$N(E, E_x) dE dE_x \equiv \frac{2f(E)}{(2\pi)^3} \iiint_{E, E_x} v_x d^3k = \frac{m}{2\pi^2 \hbar^3} f(E) dE dE_x, \quad (2.3)$$

where $N(E, E_x)$ is the number of electron per unit area per unit time, v_x is the velocity of the electron normal to the unit area under consideration, and $[E, E_x]$ indicates the energy states with total energy between E and $E + dE$ and normal energy between E_x and $E_x + dE_x$. Therefore the total number of electrons with normal energy between E_x and $E_x + dE_x$ at equilibrium condition is

$$\begin{aligned} N(E_x) dE_x &= \frac{m dE_x}{2\pi^2 \hbar^3} \int_{E_x}^{\infty} f(E) dE \\ &= \frac{mk_B T}{2\pi^2 \hbar^3} \ln \left[1 + \exp \left(- \frac{E_x - E_F}{k_B T} \right) \right] dE_x. \end{aligned} \quad (2.4)$$

Here for electrons with normal energy E_x far above or below the Fermi energy level E_F , the expression can be simplified, respectively, as

$$\ln \left[1 + \exp \left(- \frac{E_x - E_F}{k_B T} \right) \right] \simeq \begin{cases} \exp [- (E_x - E_F)/k_B T] & \text{if } E_x \gg E_F \\ -(E_x - E_F)/k_B T & \text{if } E_x \ll E_F \end{cases} \quad (2.5)$$

2.1.2 Theoretical Model of Potential Barrier and Current Density

Consider a semi-infinite metal occupying the half-space from $x = -\infty$ to $x \approx 0$. According to the free-electron theory of metals, an electron inside the metal sees a constant (zero) potential. At zero temperature, a certain minimum energy equal to the work function Φ , must be supplied to the metal before an electron can escape from it. From the classical electrostatics, an electron located at a finite distance x from the surface of a perfect conductor is attracted to it, by the well-known “image” force: $-e^2/16\pi\epsilon_0 x$, where e is the electron charge and ϵ_0 is the permittivity of free space. When an external electric field $F > 0$ is applied to the surface, an electrostatic

2.1 The Classical Field Emission from A Flat Metal Surface

force of $-eFx$ is added, and the surface potential profile is given by

$$\begin{aligned} V(x) &\simeq E_F + \Phi - \frac{e^2}{16\pi\epsilon_0 x} - eFx & \text{for } x > x_c \\ &\simeq 0 & \text{for } x < x_c \end{aligned} \quad (2.6)$$

where x_c is determined by $V(x_c) = 0$, and this is indeed the general form of the potential barrier used in most of the field emission models. Here, E_F is usually set to zero as a reference level.

In 1970s, a lot of effort were put into microscopic studies of the potential barrier at a metal-vacuum interface [32, 33, 34, 35, 36, 37], which confirmed that Eq. (2.6) is valid for $x > 3 \text{ \AA}$. The detailed profile of the barrier for $x < 3 \text{ \AA}$ depends on the properties of metal surface under consideration. In the traditional (free-electron) theories of electron emission, it is assumed that Eq. (2.6) remains valid right up to a point x_c such that $V(x_c) = 0$. At large electric field, the potential energy barrier through which the tunneling occurs could be located very close to the cathode-vacuum interface ($x < 3 \text{ \AA}$), where the charge density is quite high due to the “spillover” effects. The classical concept of image charge force in Eq. (2.6) will need to be improved by a density-gradient analysis [38] or the Green function method [39].

As the electric field is negligible inside the metal, it is assumed that the number of electrons with normal energy between E_x and $E_x + dE_x$ impinging on the surface barrier from within the metal is practically identical with its equilibrium value given in Eq. (2.4). Each of these electrons has a probability $\mathcal{T}(E_x)$ to be transmitted through the surface potential barrier given by Eq. (2.6).

For a general analysis of electron emission phenomena, a useful method leading to an analytic expression for the transmission coefficient was developed by Miller and Good (1953) [40], which has been extensively used in the study of electron emission. Their method is a generalization of the ordinary WKB (Wentzel, Kramers and Brillouin) method [41]. Their theory applies to the case of a slowly varying potential barrier, with only two classical turning points. This means that there are

only two real roots of the equation $E_x - V(x) = 0$, when E_x lies below the top of the barrier. We denote them by x_1 and x_2 with $x_1 < x_2$, and the resultant transmission coefficient $\mathcal{T}(E_x)$ can be approximated as

$$\mathcal{T}(E_x) \simeq \exp \left[-2 \int_{x_1}^{x_2} |\Theta(x)| dx \right], \quad (2.7)$$

where $\Theta(x) = \sqrt{\frac{2m}{\hbar^2} [E(x) - V(x)]}$. Recently, a better and more convenient approach to estimate $\mathcal{T}(E_x)$ was suggested by Jensen [42, 43], which performs rather well for a typical potential energy barrier profile as shown in Eq. (2.6).

The resultant emitted current density, e.g. the number of electrons emitted per unit area per unit time, multiplied by the magnitude of the electronic charge, is expressed by the Tsu-Esaki model [44, 45] given by

$$J(F, T) = e \int_0^\infty N(E_x, T) \mathcal{T}(E_x) dE_x, \quad (2.8)$$

where $\mathcal{T}$ is the transmission coefficient [e.g. see Eq. (2.7)], and $N(E_x, T)$ is the total number of electrons [see Eq. (2.4)] which is also known as the electron supply function. Note that if one assumes the validity of the surface barrier given by Eq. (2.6), Eq. (2.7) & (2.8) will provide an estimation of $J(F, T)$ for a given applied field F and temperature T [46].

Although Eq. (2.8) was first derived for the metal, the idea that the current density J can be calculated by integrating the product of the supply function N and transmission probability $\mathcal{T}$, is independent on the material type and dimension [44, 45]. Hence we can always manipulate N and $\mathcal{T}$ base on the material properties and compute the current density J accordingly. We shall apply this equation to calculate the emission current density from a single layer graphene and a diamond-metal-vacuum triple junction in Chapter 3 and Chapter 6 respectively.

2.2 The Electronic Property of Graphene

Graphene is a two-dimensional superlattice which attracts a great deal of attention immediately after its discovery [47]. Its unique band structure results in the observation of a number of very peculiar electronic properties - from anomalous quantum Hall effect to the absence of localization. It also provides a bridge between condensed matter physics and quantum electrodynamics, and opens new perspectives for carbon-based electronics [48].

From Sec. 2.1, we have understood the general principle of field emission from a bulk metal. However the material property of graphene, which will strongly affect its field emission characteristic, is very different from conventional metals. Therefore, the classic Eq. (2.7) to compute the transmission coefficient $\mathcal{T}(E_x)$ cannot be directly used. In order to develop a correct model, it is important to first understand the material properties of graphene. In this section, we will review the band structure as well as the electron transport behavior of a single layer graphene.

2.2.1 The Unique Band Structure of Graphene

Basically, graphene is a honeycomb superlattice which consists two equivalent carbon sublattices A (red) and B (blue) [see Fig. 2.1 (a)]. The structural flexibility of graphene is reflected in its electronic properties. The sp^2 hybridization between one s orbital and two p orbitals leads to a trigonal planar structure with a formation of a σ bond between carbon atoms that are separated by 1.42 Å. The σ bond is responsible for the robustness of the lattice structure in all allotropes. Due to the Pauli principle, these bonds have a filled shell and, hence, form a deep valence band. The unaffected p orbital, which is perpendicular to the planar structure, can bind covalently with neighboring carbon atoms, leading to the formation of a π bond. Since each p orbital has one extra electron, the π bond is half filled.

Figure 2.1: (a) A schematic of the single layer graphene superlattice. (b) A schematic of the single layer graphene band structure, where k and k' denote the two Dirac points.

2.2 The Electronic Property of Graphene

For conventional transition elements, these half filled bands play an essential role in the physics of strongly correlated system due to their strong tight-binding characteristic, leading to strong collective effects, magnetism, and insulating behavior due to correlation gaps or Motttness [49, 50, 51]. However, this point of view appears to be contrasted with the first principle band structure studies [48] of graphene that found it to be a semimetal with unusual electronic excitation, which is proven to be correct by most current experiments [52, 53].

In 1946, P. R. Wallance first worked on the band structure of graphene [54] by a simple nearest neighbor, tight-binding approximation. Due to the quantum-mechanical hopping between these two sets of atoms [see Fig. 2.1 (a)], the energy bands can be expressed as

$$E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t' f(k), \quad (2.9)$$

where $f(k) = 2 \cos(\sqrt{3}k_y a) + 4 \cos(\frac{\sqrt{3}}{2}k_y a) \cos(\frac{3}{2}k_x a)$, $k^2 = k_x^2 + k_y^2$ is the momentum, t is the nearest-neighbor hopping energy, and t' is the next nearest-neighbor hopping energy. The resultant band diagram is depicted in Fig. 2.1 (b), where K and K' are the two points at the corners of the hexagonal Brillouin Zone named the Dirac points. Obviously in neutral graphene, the chemical potential will cross exactly the Dirac points and the band gaps at these locations will vanish. Hence, the graphene material shall exhibit the unusual semimetallic behavior which is different from its allotropes and other semiconductors.

More importantly near these crossing points (at low energy level), quasiparticles exhibit a linear dispersion relation $E = \hbar k v_F$, where E is the particle energy, $\hbar$ is the reduced Plank constant and v_F is the Fermi-velocity, as if they were massless Dirac fermions (for example, photons) described in the quantum eletro-dynamics (QED) [55] but the role of the speed of light is played here by $v_F \approx c/300$. Hence, many of the unusual properties of QED can show up in graphene at much smaller speed, which are quite different from those in the conventional metals and semiconductors where the energy spectrum is approximated by a parabolic dispersion relation $E = \frac{\hbar^2 k^2}{2m}$,

e.g. integer quantum hall effect (IQHE) [52, 53] and unusual mesoscopic effects. For example, zig-zag edge graphene can sustain surface states and resonances that are not presented in the armchair graphene [56, 57], and the boundary condition could strongly affect the conductance of graphene ribbons [58, 59, 60].

2.2.2 The Unique Electron Transport: Klein Tunneling

Another interesting feature of Dirac fermions in graphene is their insensitivity to external electrostatic potentials due to the so-called Klein paradox. Unlike the conventional metals and semiconductors where the electron can transmit through a potential barrier with an exponentially decreased probability as expressed in Eq. (2.7), the Dirac fermions, however, can be transmitted through a classical forbidden region with perfect transmission ($\mathcal{T} = 1$) in certain condition [61, 62]. In fact, recent experiments have already proved the existence of ballistic transport and Klein tunneling inside the single layer graphene [52, 63, 64, 65].

The original meaning of the Klein paradox was published by Klein in 1929 [66], where he calculated the reflection coefficient and transmission coefficient for electrons of energy E , mass m and momentum k incident on a constant potential step V within the context of the relativistic Dirac equation [67]. A paradoxical result arises when letting the potential step $V \rightarrow \infty$ for a fixed E , and the transmission coefficient tends to a non-zero limit. The physical essence of this paradox thus lies in the prediction that according to the Dirac equation, fermions can pass through strong repulsive potentials without the exponential damping expected in the unrelativistic quantum tunneling processes [68].

Since low energy electrons in graphene are assumed to be massless Dirac fermions by examining their cyclotron masses [69, 70], they are proven to obey the 2D Dirac equation. Hence the electron and hole states in graphene are interconnected, exhibiting properties analogous to the charge conjugation symmetry in QED, and the

2.2 The Electronic Property of Graphene

quasiparticles at low energy have to be described by two-component wavefunctions. With this consideration, Katsnelson, *et al.* were the first to address the scattering of electrons in two dimensions by a square barrier along x -direction with barrier height V_0 and barrier width D [8]. By considering the momentum conservation in the y -direction, the resultant transmission coefficient is expressed as,

$$\mathcal{T}(\phi) = \frac{\cos^2 \theta \cos^2 \phi}{[\cos(Dq_x) \cos \phi \cos \theta]^2 + \sin^2(Dq_x)(1 - ss' \sin \phi \sin \theta)^2}, \quad (2.10)$$

where $\phi = \tan^{-1}(k_y/k_x)$ is the incident angle outside the barrier region, $\theta = \tan^{-1}(k_y/q_x)$ is the transmitted angle inside the barrier region, $s = \text{sgn}(E)$ and $s' = \text{sgn}(E - V_0)$, and $q_x = \sqrt{(V_0 - E)^2/(v_F)^2 - k_y^2}$. Note that $\text{sgn}(x)$ is the sign function where $\text{sgn}(x) = 1$ for $x > 0$, $\text{sgn}(x) = 0$ for $x = 0$ and $\text{sgn}(x) = -1$ for $x < 0$.

Obviously, the transmission coefficient $\mathcal{T}(\phi)$ varies at different incident angle ϕ , and it is always perfect transmission at normal incidence ($\phi = 0^\circ$) and zero transmission at parallel incidence ($\phi = 90^\circ$). Furthermore depending on the barrier height and barrier width, for values of Dq_x satisfying the relation $Dq_x = n\pi$ where n is the integer, the barrier again becomes totally transparent. In fact, this result is just a direct manifestation of the Klein paradox and an analogy with QED theory. An electron with energy E propagating in the positive direction originates from the same branch of the electronic spectrum as the hole with energy $-E$ propagating in the opposite direction. This yields that electrons and holes belonging to the same branch have pseudospin pointing in the same direction, which is parallel to the momentum for electrons and antiparallel for holes. Thus due to the matching of states outside and inside the potential barrier, an electron can transmit through a potential barrier as a hole without any impedance, leading to a high transmission probability. More works have been performed to measure the transport properties of graphene for different barrier forms [71, 72, 73], and shown that a slower varying potential is more effective in reflecting electrons at nonzero incident angle.

By combining the Klein tunneling effect and the reduction on the dimensionality, we will investigate the field emission characteristic and its corresponding shot noise behavior from a single layer graphene in Chapter 3.

2.3 Diamond Surface Properties and Triple Junction Enhancement

Diamond is a novel material which has electronic properties superior to other semiconductors [74]. It is another type of carbon allotrope in which the carbon atoms are arranged in the specific type of cubic lattice called diamond cubic. Unlike graphene, the general band structure of diamond is no difference to other semiconductors. However its unusual surface properties, such as negative electron affinity (NEA) as well as the formation of the surface band, make it an ideal electron source in many applications, e.g. cold field emitter, photo cathode and FET transistor.

Similar as graphene in Sec. 2.2, the diamond material properties, such as NEA and surface state, will strongly affect the field emission behavior. Furthermore, the triple junction structure, which involves three types of mediums, is also very different from the traditional field emission structure. Thus, it will be essential to understand the physics before combining them with the general theory in Sec. 2.1. In this section, a brief revision is given on diamond material properties and triple junction enhancement.

2.3.1 The NEA Property and the Surface State of Diamond

There are a few definitions for the electron affinity, e.g. for a single atom and molecule in the gaseous state, it represents the amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion [75]. In solid state physics

2.3 Diamond Surface Properties and Triple Junction Enhancement

however, it is defined as the energy difference E_{ea} between the vacuum energy E_{vac} and the conduction band minimum E_c [76]. If $E_{ea} = E_{vac} - E_c < 0$, which indicates the vacuum energy level is below the conduction band minimum, it is referred as negative electron affinity (NEA).

Early in 1964, NEA was found in the unconstructed natural diamond (111) surface with the vacuum energy 0.3 eV below the conduction band minimum [77]. Soon after, Himpsel [78] demonstrated that diamond has an chemically inert NEA surface which is insensitive to the thermal treatment, and can provide a stable quantum yield as a photo cathode. Later, Geis [79] and Pate [80, 81, 82] further illustrated that its (111) surface is also stable to O_2 , SiO_2 , and solvents by carrying out the capacitance-voltage measurement on the diode or FET device. Compared to other NEA materials, such as LiF (which is a wide gap insulator) or GaAs after complex surface treatments, e.g. Cs plus O (which render the surface chemically sensitive), this chemically inert characteristic guarantees that diamond would be an excellent source in the circuit device and other semiconductor applications.

Another interesting feature is the formation of surface states on the diamond (111) surface. Compared to other semiconductors such as Si and Ge, which have been proven to form intrinsic surface states on their (111) surface in both experiments [83] and pseudopotential calculations [84], for diamond in another hand, the formation of surface states highly depends on the reconstruction techniques on the surface. For an unreconstructed, clean diamond (111) surface, the low energy electron diffraction (LEED) pattern demonstrates an (1×1) symmetry [82], and the subsequent photoemission spectrum shows no surface state has been formed [78]. However, if this unreconstructed surface is further heated to 1225-1275 K to desorb the hydrogen, the surface atoms will be rearranged and form a (2×2) LEED pattern comprising of three nearly equivalent (2×1) domains [82, 85, 86]. These (2×1) domains are essential in the formation of either occupied surface states near the valence band [80] (an energetically

unfavorable situation), or more usefully, unoccupied surface states which centered 1 eV below the conduction band minimum [87].

2.3.2 The Enhancement near a Triple Junction

Triple junction is defined as a junction of metal, dielectric, and vacuum. At the junction, electron emission is favored in the presence of a sufficiently strong electric field due to the field enhancement at the junction [88, 89]. It is generally believed that the electric field at the triple point could be very large, which contributes to a significant enhancement factor [90, 91, 92]. The physics behind this statement is that a first electron, or seed electron, will be produced when a sufficient electric field is presented. This seed electron may undergo rapid multiplication either through impact ionization of neutrals [93], or through secondary emission if this seed electron strikes the dielectric surface with a sufficiently high energy [94]. It has been speculated that near a triple junction, a single electron released from the cathode electrode can initiate a secondary emission avalanche [91]. Fig. 2.2 schematically illustrates the field distribution of a triple junction structure, which can attract the seed electron from cathode to dielectric and lead to secondary emission.

By taking into consideration of the triple junction geometry, the secondary electron emission as well as the electron dynamics, Jordan and Lau [95] investigated the electric field in the immediate vicinity of the triple junction. They assumed that the scale of the electric field, and the impact energy of the electron onto the dielectric, so that a seed electron is likely to initiate multiplication of electrons by secondary emission. The resultant electric field is expressed as

$$E_x + iE_y = -E_0\left(\frac{r}{a}\right)^\delta [x \sin(\delta\phi) + iy \cos(\delta\phi)], \quad (2.11)$$

where δ is the field index, $E_0 = V_g/D$ is the applied electric field with gap spacing D and applied voltage V_g , and $x + iy = re^{i\phi}$. It can also be written as $E_x + iE_y = -iE_0\left(\frac{x-iy}{a}\right)^\delta$. By choosing the proper orientation of the metal and dielectric (by

Figure 2.2: A schematic of the triple junction field distribution.

varying δ), the enhancement value $\beta = |E_x + iE_y|/E_0$ can be computed accordingly, which can go up to as high as 5 to 6, equal to the relative dielectric constant of the dielectric material.

In Chapter 6, a field emission model from a diamond-metal-vacuum triple junction structure will be developed base on the diamond's surface properties and the enhancement at the triple junction.

2.4 SCL Current in Classical Regime

In Sec. 2.1, the field emission theory focuses primarily on the low voltage region without space charge effect, and the emitted electrons are assumed to move freely from cathode to anode. However, if the applied voltage is high enough, the space charge within the gap will certainly limit further emission of electrons, which is very

critical in operating the real solid state devices in high power. In this section, we will briefly review the SCL theory in 1D case.

Since the invention of solid state electronics, nearly every vacuum electronic device, where there is a solid state equivalent was replaced due to the capability to fabricate integrated circuits using solid state technology. With the recent advances of micro-fabrication techniques, vacuum devices can also be integrated on the same platform together with other vacuum or solid state devices. However, vacuum devices are inherently most robust, faster and exhibit excellent radiation hardness. They can also provide higher power for high power microwave source [96], exhibit greater reliability as compared to the solid state equivalent of comparable size.

For some applications especially in high power, the vacuum device is most likely operating in the space-charge-limited (SCL) regime since high current density is required. In the SCL regime, the charged particles across an accelerating gap will experience electrostatic repulsion due to the high density charged particles build-up in the gap, especially near the cathode. Because of the charge's build-up, the electric field is driven to zero near the cathode, and this limits the amount of current that can be transported across the gap.

The classical one-dimensional SCL flow is the maximum electron current density that can be transported across the vacuum gap, which is described as the Child-Langmuir (CL) law. It was first derived by C. D. Child in 1911 who investigated the discharge from a hot calcium oxide (CaO), where electrostatic effect produced by the dominant positive ion species became so large that it limited the amount of current flowing through the discharge tube [10]. Such a movement of the positive ions towards the hot CaO cathode results in the arcing of the discharge tube caused by the sudden heating of the CaO cathode. Subsequently, Irving Langmuir independently derived the same law in 1913 for the SCL electron flow from a hot filament (thermionic cathode) in a vacuum [11].

2.4 SCL Current in Classical Regime

The classic CL law is the maximum current density in a one-dimensional (1D) planar gap assuming the electrons are emitted with zero emission velocity. It is given by

$$J_{CL}(1D) = \frac{4}{9}\epsilon_0\sqrt{\frac{2e}{m}}\frac{V_g^{3/2}}{D^2}, \quad (2.12)$$

where e and m are the charge and mass of the particle, respectively, ϵ_0 is the permittivity of free space, V_g is the gap voltage and D is the gap separation between the cathode and anode. Recently, the unipolar SCL flow has been re-investigated using the Lagrangian flow description [97, 98], the current over-injection approach (similar to the time-average numerical results) [99] and the vacuum capacitance approach [100], which gave the same scaling of $V^{3/2}$ and D^{-2} as predicted. Further contributions such as to extend the 1D planar CL law to multi-dimensional models [13, 14, 15, 16], cylindrical models [101, 102], quantum regime [103, 104, 105, 106], short-pulse models [12, 107, 108] and relativistic models [109, 110, 111, 112] have also been discussed extensively.

With the same SCL definition, our recent developed model [21] to calculate the onset of the SCL current for a sharp tip emitter and the comparison with the classic CL law will be discussed in detail in Chapter 4.

CHAPTER 3

FIELD EMISSION FROM SINGLE LAYER GRAPHENE

3.1 Introduction

Since the first single layer graphene was isolated in 2004 [113], it has rapidly become an active research area due to its unique electronic properties [47]. It is potentially an excellent candidate in a lot of nanoelectronic devices such as composites [114], sensors [115] as well as flat-panel displays [116]. Recently, there have been significant interests in using graphene or graphene composite as an efficient electron source, because of low turn on voltage [117, 118], high current density [118, 119], good stability [119, 120, 121], long lifetime [122], and compactness in a nanogap [123].

However, all the reported experimental findings [117, 118, 119, 120, 121, 122] have simply treated graphene as a bulk material and used the traditional Fowler-Nordheim (FN) law [9] to fit the experimental results by assuming a field enhancement factor β . This approach is not appropriate due to the fact that graphene is a two-dimensional superlattice, which is very different from a traditional bulk material assumed in the derivation of the FN law. Furthermore as introduced in Chapter 2,

3.2 Klein Tunneling Field Emission Model

for graphene, the low energy electrons near the corners of the hexagonal Brillouin zone (Dirac points) have a linear energy dispersion, mimicking the massless Dirac fermion, which exhibit angle dependent Klein tunneling phenomenon [8, 66] leading to a much higher tunneling coefficient as compared to the FN law. Thus, the high current emission from graphene may be due to Klein tunneling, in addition to the large field enhancement assumed in the previous studies.

In this chapter, we are interested to incorporate the effects of the linear energy dispersion and Klein tunneling effect (see Sec. 2.2) into the classical field emission theory (see Sec. 2.1.2) for a single layer vertically-aligned graphene sheet. The details of the field emission model will be discussed in Sec. 3.2, and the subsequent shot noise analysis will be presented in Sec. 3.3. Finally, some conclusion remarks will be given in Sec. 3.4.

3.2 Klein Tunneling Field Emission Model

By considering the reduction of dimensionality for a single layer graphene and including the Klein tunneling effect, we will show later that our model provides a different current-voltage scaling and also a much higher current emission as compared to the FN law. In this model, we have speculated that Klein tunneling phenomenon prevails in the process of tunneling across the barrier on the surface. This is an assumption, thus the model will require verification from future experiments.

3.2.1 Model Schematic and Mathematical Formulation

To fully utilize the large enhancement on the atomically sharp edge, the graphene sheet would have to stand vertically instead of laying laterally flat on the substrate to take that advantage. Thus in our model, we assume a single layer graphene with height H vertically aligned (along x -axis) inside a dc gap of spacing $D \gg H$ with

an applied voltage of V_g as shown in Fig. 3.1. The graphene sheet has a realistic width of $2a = 0.335$ nm (along z -axis) and a length of L (along y -axis), where L is assumed to be infinitely long so that the boundary condition (zig-zag or armchair) on the graphene edge could be ignored. Note that vertically well-aligned graphene single layer considered here has been recently fabricated in arrays with H from 50 to 800 nm [124].

Before presenting our model, it is worthwhile to estimate the value of the field enhancement β on the single layer graphene edge. If we consider a single layer graphene sheet as a knife-edge field emitter with a height of H and a width of $2a = 0.335$ nm, β can be calculated by $\sqrt{(\pi H)/(4a)}$ for $H \gg a$ [125]. For $H = 1$ to 10 μm , the resultant β is about 70 to 220, which is much smaller than the reported values obtained from fitting the measurements with the FN law, such as $\beta = 3000$ for few layers of graphene [117], $\beta = 1200$ for graphene composite [122], and $\beta > 10000$ for doped graphene [118]. Thus, the reported high current emission at low turn-on voltage from graphene may not simply due to large field enhancement, but other reasons that are not captured by the traditional FN law.

Since graphene is a two-dimensional material with linear energy dispersion at low energy, the classical field emission equation (FN law) [9], which is derived for a three-dimension bulk materials with parabolic energy dispersion, could no longer be used. From Eq. (2.8) in Chapter. 2, that the current density J can be calculated by integrating the product of the supply function N and transmission probability $\mathcal{T}$, which is independent on the material type and dimensions. Thus we shall derive the emission current base on this general concept. Assuming that an electron with a two-dimensional momentum $k = \sqrt{k_x^2 + k_y^2}$, incidents on a potential barrier in x -direction where one side is graphene and another side is vacuum, the elementary current density dJ in x -direction can be expressed as [44, 45]:

$$dJ = ev_F \cdot g(k_x) \mathcal{T}(k_x, k_y) f(E) \cos \phi \cdot dk_x, \quad (3.1)$$

3.2 Klein Tunneling Field Emission Model

Figure 3.1: Klein tunneling field emission model of vertically-aligned single layer graphene sheet, where V_g is the applied voltage bias between the anode and the cathode, D is the gap spacing, L and $H(<< D)$ are the length and height of the graphene sheet, respectively.

where e is the electron charge, $v_F \approx 10^6$ m/s is the Fermi-velocity, $\mathcal{T}(k_x, k_y)$ is the Klein tunneling transmission coefficient, $g(k_x) = \int \frac{1}{2\pi^2} dk_y$ is the density of k_x states, $f(E)$ is the standard Fermi-Dirac distribution with linear energy dispersion $E = \hbar v_F k$, and $k_x = k \cos \phi$, $k_y = k \sin \phi$. Further notice that $dk_x dk_y = k dk d\phi$, $k = E/(\hbar v_F)$ and $dk = dE/(\hbar v_F)$, the resultant emission current density can be simply written as

$$J_L = \frac{e}{2\pi^2 \hbar^2 v_F} \int_0^{E_0} \int_{-\pi/2}^{\pi/2} \mathcal{T}(E, \phi) f(E) E \cos \phi \cdot dE \cdot d\phi, \quad (3.2)$$

where J_L is in the unit of A/m instead of A/m², which is a direct result of the reduction on the dimensionality.

In the derivation of Eq. (3.2), we have taken into account that graphene is a two-dimensional structure, so that the integrand is in the form of $dk_x \cdot dk_y$ as compared to $dk_x \cdot dk_y \cdot dk_z$ for a bulk material. The second consideration is to apply the linear energy dispersion $E = \hbar v_F k$ instead of $E = \hbar^2 k^2 / 2m$ to treat the electron as massless Dirac fermion. In addition, the Klein tunneling transmission coefficient $\mathcal{T}(E, \phi)$ depends on both energy E and incident angle ϕ , while for the conventional bulk materials, the transmission coefficient (from Schroedinger's equation) only depends on the energy E [see Eq. (2.7)]. Note that Eq. (3.2) remains valid as long as the electron energy E is small so that the linear energy dispersion $E = \hbar v_F k$ is maintained, and the Klein tunneling effect is important. In our calculations shown below, we have assumed $E_f = 0.1$ eV (unless it is otherwise specified), and the upper limit of the integration E_0 ($= 0.5$ eV) is set to 5 times higher than E_f to avoid numerical errors.

The most difficult part in solving Eq. (3.2) is to calculate the Klein tunneling probability $\mathcal{T}(E, \phi)$ because it will require solving the Dirac equation. Previous works [8, 126, 127] mainly focused on Klein tunneling through a single or multiple square barriers as it is relatively easy to find an analytical solution. However, for field emission, the potential barrier is in a form of $V(x) = V_0 - F \cdot x - Q/x$, where F is the local electric field on the graphene edge, $V_0 \approx 4.66$ eV is set to be the work function of graphene, and Q/x is the image-charge potential with $Q = e^2 / 4\pi\epsilon_0$ is a constant [128].

3.2 Klein Tunneling Field Emission Model

It is noteworthy that F is the local electrical field on the graphene edge which has already included the surface enhancement factor. Using this $V(x)$, we will calculate $\mathcal{T}(E, \phi)$ based on a relativistic WKB (Wentzel-Kramers-Brillouin) method that was recently developed for Dirac equation [129, 130]. This method extends the traditional WKB method from quantum regime to relativistic regime, and it is very suitable to solve the electron tunneling problem through a slow-varying potential barrier, such as $V(x)$ described here, in Dirac equation.

Starting with the Dirac equation $\hat{H}\Psi = E\Psi$, the Hamiltonian of graphene is expressed as $\hat{H} = v_F \cdot (\delta_x p_x + \delta_y p_y) + V(x)$, where δ_x and δ_y are the Pauli's matrices, $p_x = -i\hbar \frac{\partial}{\partial x}$ and $p_y = -i\hbar \frac{\partial}{\partial y}$ are the momentum operators, and $V(x)$ is the potential barrier mentioned above. By considering the conservation of the transverse momentum in y -direction, a solution in the form of $\Psi = e^{ik_y y} \cdot \begin{pmatrix} \psi_A(x) \\ \psi_B(x) \end{pmatrix}$ can be substituted into the Dirac equation to find an expression of wave vector q . In doing so, we can rewrite the Dirac equation into two coupled differential equations: $\psi'_{A,B} = \frac{d}{dx} \begin{bmatrix} \psi_A(x) \\ \psi_B(x) \end{bmatrix} = \frac{1}{\hbar v_F} \cdot \Lambda \cdot \psi_{A,B}$, where Λ is a matrix given by

$$\Lambda = \begin{pmatrix} \hbar v_F k_y & -i(V(x) - E) \\ -i(V(x) - E) & -\hbar v_F k_y \end{pmatrix}. \quad (3.3)$$

Following a series of formulations [130], the wave vector in the WKB form can be found as $q = \sqrt{(\hbar v_F k_y)^2 - (V(x) - E)^2}$, and $q = i\sqrt{(V(x) - E)^2 - (\hbar v_F k_y)^2}$, for $(\hbar v_F k_y)^2 - (V(x) - E)^2 \geq 0$, and $(\hbar v_F k_y)^2 - (V(x) - E)^2 < 0$, respectively, which indicate the classical forbidden and allowed region.

In solving Eq. (3.2) numerically, we define an effective energy of $E_{eff} = \hbar v_F k_x = E \cos \phi$ (which is the actual amount of energy incident on the barrier in x -direction), and an effective potential of $V_{eff} = E_{eff} + \sqrt{(\hbar v_F k_y)^2 - (V(x) - E)^2}$ and $V_{eff} = E_{eff} - \sqrt{(V(x) - E)^2 - (\hbar v_F k_y)^2}$, respectively, for $V_{eff} \geq E_{eff}$ (classical forbidden region) and $V_{eff} < E_{eff}$ (classical allowed region). In doing so, we have transformed the original angle-dependent tunneling problem into a one-dimensional (1D) dual-barrier tunneling problem (as shown in Fig. 3.2) with its four corresponding turning

points (determined at $V_{eff} = E_{eff}$), which are

$$\begin{cases} x_1 = \frac{V_0 - E(1 + \sin \phi) - \sqrt{(V_0 - E(1 + \sin \phi))^2 - 4FQ}}{2F} \\ x_2 = \frac{V_0 - E(1 + \sin \phi) + \sqrt{(V_0 - E(1 + \sin \phi))^2 - 4FQ}}{2F} \\ x_3 = \frac{V_0 - E(1 - \sin \phi) - \sqrt{(V_0 - E(1 - \sin \phi))^2 - 4FQ}}{2F} \\ x_4 = \frac{V_0 - E(1 - \sin \phi) + \sqrt{(V_0 - E(1 - \sin \phi))^2 - 4FQ}}{2F} \end{cases} . \quad (3.4)$$

Thus, we could easily determine the turning points as a function of ϕ and F , and solve for the Klein tunneling coefficient $\mathcal{T}$ based on a standard tunneling problem through a dual-barrier [6, 131]. The detail derivation of Eq. (3.3) and (3.4) will be presented in Appendix A.

3.2.2 Transmission Coefficient and Emission Current

The calculated $\mathcal{T}$ are plotted in Fig. 3.3 (a) for various local field F [V/nm] = 0.01, 0.1, 1 and 10 (left to right). As expected, we have perfect transmission ($\mathcal{T} = 1$) at normal incidence ($\phi = 0^\circ$), and it decreases to 0 at large ϕ approaching 90 degree. Compared to the analytical results of Klein tunneling through a square barrier [8], the continuously varying potential barrier $V(x)$ that we used here will remove other resonance angles with perfect transmission [e.g. $Dq_x = n\pi$ in Eq. (2.10)] except at $\phi = 0^\circ$. The figure also shows that the overall tunneling effect increases (the area under the curve increases) due to the reduction of the barrier's height and width with increasing of local field from $F = 0.01$ V/nm to 10 V/nm.

By substituting $\mathcal{T}$ into Eq. (3.2), we calculate the field emission current line density J_L [A/m] as a function of local electric field $F = 0.2$ to 10 V/nm at $E_f = 0.1$ eV (solid lines) as shown in Fig. 3.3 (b). If one assumes a field enhancement of $\beta = 200$ (for a graphene sheet with a height of $H = 10 \mu\text{m}$), this corresponds to a low turn-on applied field $E_0 = F/\beta$ ranging from $E_0 = 1$ to 50 V/ μm with a high current line density (0.3 to 1.5 A/m). Our model is also showing a current-voltage (J - F) scaling that is very different from the traditional FN law [$J_{FN} = AF^2 \exp(-F/B)$],

3.2 Klein Tunneling Field Emission Model

Figure 3.2: Effective potential profile V_{eff} of a dual-barrier for an electron with an effective energy E_{eff} , and x_1, x_2, x_3, x_4 are the four corresponding turning points at $E_{eff} = V_{eff}$

and also has a much higher current at small $F < 5$ V/nm. For example, at $F = 1$ V/nm, our model gives about $J_L = 0.5$ A/m, while line current density based on FN law [$J_{FN} \times (2a)$] is experimentally small, where $2a = 0.335$ nm is the width of the graphene sheet. At higher $F = 5$ V/nm, our calculated result is $J_L = 1$ A/m, as compared to $J_{FN} \times (2a) = 0.81$ A/m. This unusual behavior clearly indicates that when the low energy electrons of the graphene are treated as massless Dirac fermion, the effect of Klein tunneling will greatly affect the current-voltage scaling, and it can not be explained by FN law. The increment of J at higher temperature T can also be seen when we use $T = 500, 300$, and 5 K (solid line: top to bottom). A calculation with a higher value of $E_f = 0.2$ eV (dashed line) at 300 K is also plotted for comparison.

3.2.3 Emitted Electron Energy Distribution

In Fig. 3.4, we also present the normalized energy distribution of the emitted electron at various values of (a) local field F , (b) temperature T , and (c) Fermi energy E_f . The normalized constant is the peak value obtained at $F = 0.01$ V/nm, $T = 300$ K and $E_f = 0.1$ eV (plotted in solid lines). By increasing F from 0.01 V/nm to 1 V/nm, total amount of emission (area under the curve) will increase due to the reduction of the potential barrier, but the location of the peak remains unchanged [see Fig. 3.4 (a)]. By increasing T from 5 K to 300 K, more electrons with higher energy will emit due to the broadening in the Fermi-Dirac distribution, and thus the peak of the distribution will shift to the left [see Fig. 3.4 (b)]. Lastly, Fig. 3.4 (c) shows that the range of the distribution becomes wider with higher values of E_f , as we have more electrons emitted over a wider energy range.

3.2 Klein Tunneling Field Emission Model

Figure 3.3: (a) Klein Tunneling coefficient $\mathcal{T}$ as a function of incident angle ϕ at various local electric field F . (b) The emission line current density J_L as a function of local field F for $E_f = 0.1$ eV (solid lines) at temperature T [K] = 500, 300, 100 (top to bottom), and $E_f = 0.1$ eV (dashed line) at 300 K.

Figure 3.4: The normalized energy distribution of the emitted electrons for different (a) local field $F = 0.01$ and 1 V/m; (b) temperature $T = 5$ and 300 K; and (c) Fermi energy $E_f = 0.1$ and 0.2 eV. The normalized constant is at $T = 300$ K, $F = 0.01$ V/nm and $E_f = 0.1$ eV (see solid lines).

3.3 Shot Noise of Graphene Field Emission

Shot noise is the fluctuation in the electrical signal due to the discreteness of electron charges, which is important especially for high frequency applications, e.g. microwave tube. In this section, base on the model established in Sec. 3.2 [19], we will continue to investigate the shot noise behavior for low energy electron field emission from a single layer vertically-aligned graphene sheet assuming the emission process is due to Klein tunneling. We will show later that the resultant Fano factor is closely related to temperature T , Fermi energy E_f and local electrical field F . Further more, the universal maximum value of the Fano factor ($\gamma = 1/3$) is recovered at low temperature limit.

3.3.1 Review on Shot Noise Study

Almost a century ago, Schottky pointed out that if electrons are emitted as discrete particles independently of each other, current fluctuation is to be expected with the noise power $S = 2eI$, with e is the electron charge and I is the mean current [132]. This phenomenon, called the "shot effect" by Schottky, was later observed in vacuum tubes [133, 134]. Recent studies of shot noise have been focused on mesoscopic devices [135], which can provide crucial information that is not available in the time-averaged value such as the particle-wave duality of electron transport.

The deviation from the uncorrelated shot noise power ($2eI$) is commonly termed as the Fano factor $\gamma = S/2eI$, where $\gamma < 1$ indicates the suppression of shot noise due to the correlations among the electrons. For electron transport in the mesoscopic devices, the main source of correlation is the Pauli exclusion principle, which provides the effect of quantum partitioning for shot noise suppression observed in many systems, such as ballistic quantum point contact [136, 137], nondegenerate diffusive conductors [138, 139], chaotic system [140] and avalanche photodiodes [141].

Suppression of shot noise due to Coulomb correlation was also studied in ballistic conductors [142, 143, 144].

Compared to the charge transport inside the material, it was first proposed that similar quantum partitioning effect that induces shot noise suppression may also be found in the field emission process [145]. Assuming that the transverse and longitudinal motion of electrons are separable, one can specify the quantum channels associated with transverse modes, and define the scattering states. The equation for the mean current in a phase-coherent conductor attached to two electron reservoirs in which one side is empty is written as

$$I = \frac{e}{\pi\hbar} \int dE \cdot f \mathcal{T}_n, \quad (3.5)$$

where $\mathcal{T}_n$ is the transmission probability associated with n quantum channels at energy E , and f is the electron distribution.

Furthermore, during the electron tunneling process from the surface of the electrode, there is a quantum partitioning effect due to which the shot noise is no longer uncorrelated, and its corresponding spectrum for a two-terminal quantum conductor (e.g. a vacuum gap) for a unidirectional charge injection is given by

$$\begin{aligned} S &= 2 G_0 \sum_n \int dE [f (1 - f) \mathcal{T}_n^2 + f \mathcal{T}_n (1 - \mathcal{T}_n)] \\ &= 2 G_0 \sum_n \int dE [\mathcal{T}_n f (1 - \mathcal{T}_n f)] \\ &\equiv S_T + S_P, \end{aligned} \quad (3.6)$$

where $G_0 = e^2/\pi\hbar$ is the unit of conductance. This formula describes the spectral density of current fluctuations of an electron emitter. It unifies two sources of randomness: (i) the probabilistic occupation of states in the emitter through the function f , and (ii) the probabilistic reflection and transmission at the interface barrier through the probability $\mathcal{T}_n$. The first source of randomness is related to intrinsic thermal agitations of the emitter and can be associated to the first term S_T in Eq. (3.6). It dominates in the absence of partitioning when all transmission

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coefficients $\mathcal{T}_n$ are either 0 or 1, which is interpreted as the *emission shot noise*. The second source of randomness associated with the last term S_P in Eq. (3.6) is caused by quantum partitioning, and the fact that charge is carried by discrete portions (shot effect), so it also named as the *partition shot noise*. Subsequent models have been developed to include more realistic potential profiles [146, 147], space charge effects [148], and 2D model including the consistent field enhancement calculation [149]. A review of the derivations of the mean current [see Eq. (3.5)] and the power spectrum [see Eq. (3.6)] of a two-terminal device will be presented in Appendix B.

3.3.2 Theoretical Model

For graphene, Tworzydło [150] first predicts that the Fano factor of a single barrier structure has a maximum value of $\gamma = 1/3$ at the Dirac point for a short and wide graphene strip, which is coincidentally the same as that of diffusive metals [139, 151]. Recent shot noise measurements in single- and multi-layer graphene samples [152, 153] have shown good agreement with this theoretical predication, and the model has been extended to different systems, such as trapezoid [154], double [155] and multi-barrier structures [156]. It is generally accepted that the sub-Poisson shot noise of graphene is due to the unique band structure at the low energy states near the Dirac point. In other words, the charge carriers are governed by the Dirac equation instead of the Schroedinger equation, which is exactly what we did in Sec. 3.2.

Our model schematic is exactly the same to our previous works illustrated in the Fig. 3.1 [19]. In this model, a single layer graphene with height H is assumed to be vertically aligned (along x -axis) inside a dc gap of spacing $D \gg H$ with an applied voltage of V_g , and it is infinitely long along y -axis to neglect the boundary condition (zig-zag or armchair) on the graphene edge. To calculate the Fano factor γ , the main difficulty is that unlike metals or semiconductors, graphene is a 2D superlattice with linear energy-momentum dispersion at the low energy level. Thus the conventional formulas [145, 148, 149] used to calculate the mean emitted current

I and the power spectra density S for a 3D bulk material can no longer be applied directly. It is necessary for us to re-derive the respective formulas starting from the original definition.

By considering the effects of linear energy dispersion $E = \hbar v_F k$ as well as the Klein tunneling, our previous work has already established the equation to calculate the emission line current density J_L [see Eq. (3.2)]. It is straightforward to obtain the equation for the total emitted current I , which is

$$I = L \times J_L = L \times \frac{e}{2\pi^2 \hbar^2 v_F} \int_0^{E_0} \int_{-\pi/2}^{\pi/2} \mathcal{T}(E, \phi) f(E) E \cos \phi dE d\phi. \quad (3.7)$$

The power spectra density S can be obtained from the scattering and correlation theory [157, 158, 159], given by

$$S = L \times \frac{2e^2}{2\pi^2 \hbar^2 v_F} \int_0^{E_0} \int_{-\pi/2}^{\pi/2} \mathcal{T}(E, \phi) f(E) [1 - \mathcal{T}(E, \phi) f(E)] E \cos \phi dE d\phi, \quad (3.8)$$

where L is the emission length on the graphene edge, e is the electron charge, $\hbar$ is the reduced plank constant, $v_F \approx 10^6$ m/s is the Fermi-velocity of graphene, $f(E)$ is the Fermi-Dirac distribution, and $\mathcal{T}(E, \phi)$ is the Klein tunneling coefficient, which is a function of electron energy E , and incident angle ϕ (in x - y plane). Note that Eq. (3.7) and (3.8) are in the similar format of the original definitions of mean current [see Eq. (3.5)] and power spectrum [see Eq. (3.6)]. The difference is that the integrand is now $dE \cdot d\phi$ instead of dE only due to the Klein tunneling effect. Furthermore, Eqs. (3.7) and (3.8) remain valid as long as the electron energy E is small so that the linear energy dispersion is maintained, and the Klein tunneling effect is important. In our calculations shown below, we have assumed $E_f = 0.1$ eV (unless it is otherwise specified), and the upper limit of the integration E_0 ($= 0.5$ eV) is set to 5 times higher than E_f to avoid numerical errors.

3.3 Shot Noise of Graphene Field Emission

The corresponding Fano factor γ can be calculated by

$$\begin{aligned}
\gamma &= \frac{S}{2eI} = \frac{\int \int \mathcal{T} f(1 - \mathcal{T} f) E \cos \phi dE d\phi}{\int \int \mathcal{T} f E \cos \phi dE d\phi} \\
&= \frac{\int \int \mathcal{T} f(1 - f) E \cos \phi dE d\phi}{\int \int \mathcal{T} f E \cos \phi dE d\phi} + \frac{\int \int \mathcal{T}(1 - \mathcal{T}) f^2 E \cos \phi dE d\phi}{\int \int \mathcal{T} f E \cos \phi dE d\phi} \quad (3.9) \\
&= \gamma_T + \gamma_p,
\end{aligned}$$

Similar as Eq. (3.6), the first term γ_T is mainly affected by the probabilistic occupation of states in the emitter (through the Fermi Dirac distribution $f(E)$). It is very sensitive to the intrinsic thermal agitations of the emitter since $f(1 - f) = -k_B T (\partial f / \partial E)$ and it vanishes at zero temperature. The second term γ_p is closely related to the quantum partitioning and the fact that charge is carried by discrete portions. It only contributes at finite transmission probability other than zero and perfect transmission ($\mathcal{T} \neq 0, 1$) and does not vanishes at zero temperature. Note that γ_p term is exactly equal to the one used in previous works [155, 156] in their calculation of the Fano factor for double- and multi-barrier structures at the low temperature condition.

3.3.3 Result and Discussion

First we need to obtain the transmission coefficient $\mathcal{T}(E, \phi)$, by solving the Dirac equation $\hat{H}\Psi = E\Psi$ numerically with $V(x) = V_0 - F \cdot x - Q/x$, which is the same field emission potential barrier used in Sec. 3.2. In our previous results [19] the angle-dependent $\mathcal{T}(E, \phi)$ was calculated by a relativistic WKB method [129, 130]. Here, we will compare the relativistic WKB method (solid lines) with the transfer matrix method (dashed line) [126, 160, 161] in Fig. 3.5, for various local electric field F [V/nm] = 0.01, 0.1, 1 and 10 at $E_f = 0.1$ eV. The comparison shows that the difference between the two methods is small at small angle and large transmission ($\mathcal{T} > 0.8$).

Figure 3.5: Transmission coefficient $\mathcal{T}$ computed by using the relativistic WKB method (solid line) and the transfer matrix method (dash line). From left to right, F [V/nm] = 0.01, 0.1, 1 and 10 at $E_f = 0.1$ eV.

3.3 Shot Noise of Graphene Field Emission

In general, the transfer matrix method is suited better for the rectangular potential or trapezoid potential. For the smoothly varying potential $V(x)$ used here, it will require a large number of the elementary matrices in order to get the accurate results. The relativistic WKB method is however simple and fast to implement, and still yield a reasonable accuracy. We next compare the calculated Fano factor from both methods. Note that different numerical methods will only change slightly the quantitative value, and have little effect on the overall behavior of the shot noise calculations due to the fact that the transmission probability is small and the temperature T appears, linear to leading order, in both the numerator and denominator.

Figure 3.6 demonstrates the temperature dependence of the Fano factor γ [see Eq. (3.9)] as a function of the local electrical field F at various temperatures $T = 5, 100, 300, 500$ and 1000 K (bottom to top, solid lines), and the Fermi energy E_f is fixed at 0.1 eV. For comparison, we also calculate γ using the transfer matrix method at $T = 5$ K and $E_f = 0.1$ eV (dashed line). At low temperature condition ($T = 5$ K), γ approaches zero at very small electrical field ($F < 10^{-8}$ V/nm) as well as at very high electrical field ($F > 0.1$ V/nm). The maximum value of γ is around 0.326 at $F = 3 \times 10^{-5}$ V/nm which is indeed the expected universal limit predicted before. This finding can be explained by the following reasoning. At low temperature, we have the Fermi distribution $f(E) \approx 1$, $\gamma_T \approx 0$ and thus the shot noise is determined mainly by the second term γ_p . At very small and high electrical field, the transmission coefficient is respectively $\mathcal{T} \approx 0$ and $\mathcal{T} \approx 1$, for which the correlation due to the quantum partition is minimum and thus $\gamma_p \approx 0$. At the intermediate vicinity of $F \approx 10^{-5}$ V/nm, such as $F = 3 \times 10^{-5}$ V/nm, the correlation is maximum and we recover the universal maximum value of $\gamma = 1/3$.

By increasing the temperature T , the first term (γ_T) becomes more dominant due to the change in the Fermi distribution, and the overall Fano factor $\gamma = \gamma_T + \gamma_p$ will exceed $1/3$. In the range of $T = 300$ to 1000 K, γ tends to be uniform regardless

Figure 3.6: The Fano factor γ as a function of the local electric field F at various temperature T [K] = 5, 100, 300, 500 and 1000 (bottom to top, solid lines) at $E_f = 0.1$ eV. The dashed line is the result computed by using the transfer matrix method at $T = 5$ K and $E_f = 0.1$ eV.

of the electrical field F , which clearly indicates that the quantum partition effect (γ_p) is only significant at low temperature condition.

Figure 3.7 demonstrates the Fermi energy dependence of the Fano factor γ as a function of the local electrical field F at $T = 5$ K at different Fermi energy $E_f = 0.1$, 0.15 and 0.2 eV (left to right, solid lines). The comparison with the transfer matrix method is also plotted (dashed line) at $T = 5$ K and $E_f = 0.1$ eV. From the figure, we can easily observe that the results shift to high F as the Fermi energy increases, while the maximum value of γ remains about the same ($\approx 1/3$) regardless of the

3.3 Shot Noise of Graphene Field Emission

Figure 3.7: The Fano factor γ as a function of the local electric field F at various Fermi energy E_f [eV] = 0.1, 0.15 and 0.2 (left to right, solid lines) at $T = 5$ K. The dashed line is the result computed by using the transfer matrix method at $T = 5$ K and $E_f = 0.1$ eV.

Fermi energy level. As mentioned previously, at $T = 5$ K, $\gamma_T \approx 0$ and γ_p plays the major role that the shot noise is mainly due to the quantum partition ($\gamma_p \approx 0$ at both very low and high electric field).

It is worthy to mention that as long as the charge carrier in graphene is described by the Klein tunneling coefficient $\mathcal{T}(E, \phi)$ and governed by the Dirac equation, the maximum value of γ shall never exceed $1/3$ for a static scalar potential barrier, such as $V(x)$ studied here at low temperature regime. Unless a vector potential is added (by applying a magnetic field) and γ shall possibly exceed this limit [162].

3.4 Chapter Summary

In summary, base on the Tsu-Esaki model, we proposed a new field emission model for a single layer graphene by considering the chirality as well as the Klein tunneling effect. First by solving the Dirac equation with a relativistic WKB method, we obtained the angle-dependent Klein tunneling coefficient through a classical field emission potential barrier. After that, the overall emission current density can be calculated by integrating the transmission coefficient and the supply function. The result displays a new J - F relation which indicates that the conventional FN law is no longer valid, and graphene should be classified as a line emission source in the unit of A/m. Under the same geometrical field enhancement factor, our model predicts a much higher emitted current as compared to the FN law at low voltages. Lastly, the emitted electron energy distribution is also briefly discussed.

Next, we continued to carry out the shot noise analysis on this field emission model. The mean emission current and the noise power spectrum are re-derived to include the linear energy dispersion and Klein tunneling effect. We have found that the resultant Fano factor highly depends on both temperature and transmission coefficient, where the universal maximum value ($= 1/3$) is recovered at low temperature limit.

It is worthy to mention that in our model, we assumes that the electrons stay at low energy level so that they obey the linear energy dispersion, and can be treated as massless Dirac fermions. Thus in all our calculations, we use a low temperature and low Fermi-energy condition. Further discussion and future works will be given in Chapter 7.

CHAPTER 4

ONSET OF SCL ON

A SHARP TIP EMITTER

4.1 Introduction

In Chapter 3, the field emission model of vertically-aligned single layer graphene focuses on the low applied voltage regime, where the space charge effect is totally ignored. However, if we continuously increase the applied voltage, eventually it will enter the space-charge-limited (SCL) regime. In Sec. 2.4, we have reviewed that the classical SCL condition for a flat cathode surface is described by the Child-Langmuir (CL) law, where $J_{CL}(1D) = \frac{4}{9}\epsilon_0\sqrt{\frac{2e}{m}}\frac{V_g^{3/2}}{D^2}$ [see Eq. (2.12)], V_g and D are the applied voltage and gap spacing respectively. However, for a nano-scale sharp tip emitter such as graphene sheet [19, 163, 164, 165], it is important to note that the prior models [13, 14] are not applicable as the length scale associated with the emission area on the nanotip is much smaller than the gap spacing, and it has a non-uniform emission profile on the emitting surface. Thus, it is interesting to see if one can develop a simple protrusive CL model to account for the sharpness effect of the cathode, which is absent from the prior 2D CL law developed for a pristine surface. It is generally

argued that the space charge effects can be ignored for a very sharp emitter, so it is also necessary to have a protrusive CL law to determine if such assumption is valid.

The basic approach in the development of the prior 2D CL law is to use the electron density profile obtained from the 1D CL law to estimate the amount of electron current density (from a finite emission area larger than the gap spacing) in order to suppress the electric field at the center of the emitting surface to zero due to the space charge effects. For a sharp emitter, it is clear that these assumptions are not valid as the vacuum electric field on the tip is not uniform and the profile of the emitted electron density is very sensitive to the localized electric field controlled by the geometrical shape of the emitter. The characteristic size of the emission area for the sharp tip is also much smaller than the gap spacing.

Hence in this chapter, we will use the electron density profile obtained from the field emission model (without the space charge effects) to estimate the required emitted current density (or charge density) that is able to produce a sufficient large space charge field to suppress the applied local electric field at the apex of the emitter. At a critical applied field or voltage, we will see that the resultant space charge field will completely suppress the local electric field at the tip's apex to zero, and thus reach the space charge limited condition assumed in the CL law. From our model, this critical applied field E_c will be calculated as a function of work function Φ , gap spacing D and field enhancement β for two geometrical types of emitters: Lorentzian shape [166, 167] and Hyperboloid shape [168]. The corresponding normalized SCL current density μ (in terms of the 1D CL law) can then be calculated at this critical field E_c .

The detail models for emitters of Lorentzian shape and Hyperboloid shape are presented, respectively, in Sec. 4.2 and 4.3. The comparison between these two shapes are shown in Sec. 4.4. Finally, we provide concluding remarks in Sec. 4.5.

4.2 Lorentzian Shape

The Lorentzian model (Fig. 4.1 insert) [166] is a mathematic model frequently used to describe the shape of a field emitter. The apex of the emitter is located at $(x = 0, y = h)$, and the planar cathode and anode is, respectively, at $y = 0$ and $y = D$, where D ($\gg h$) is the gap spacing, h and w is the height and the full-width-at-half-maximum (FWHM) of the emitter, respectively. Unless it is mentioned specifically in the chapter, $D = 10 \mu\text{m}$ and $h = 0.1 \mu\text{m}$ or $h/D = 0.01$ is assumed in the calculation.

4.2.1 Enhancement Profile and Electron Trajectory

The profile of the field enhancement β along the surface of the emitter is characterized by the aspect ratio h/w , which can be expressed as

$$\beta = \frac{\sqrt{X_0^2 + (Y_0 + \epsilon)^2}}{\{[1 - (Y_0 + \epsilon)^2 + X_0^2]^2 + [2X_0(Y_0 + \epsilon)]^2\}^{1/4}}, \quad (4.1)$$

where $\epsilon \approx w/3.464h$, X_0 and Y_0 are the normalized emission points on the emitter surface as shown by Eq. (5) in the reference [167]. Figure 4.1 shows the dependence of β for a Lorentzian type emitter for different values of h/w , as a function of the vertical displacement (Δy) measured from the apex. It is clear that the maximum enhancement factor β_{max} is always at the tip of the emitter, which decreases very rapidly away from the apex, e.g. at $\Delta y > 1 \text{ nm}$, and the enhancement values at the apex are $\beta_{max} = 34.64, 346.4$ and 3464 for $h/w = 10, 100$ and 1000 respectively. Note that ultra-sharp emitter such as $h/w = 1000$ with $h = 0.1 \mu\text{m}$ and $w = 1 \text{ \AA}$ might be difficult to be realized in the laboratory. However we focus on the numerical simulation here, and such parameter is acceptable in the computation.

For a given applied electric field $E_0 = V_g/D$, we can always express the exact local field strength at any points (x_0, y_0) on the emitter surface as $E_s = E_0 \times \beta$. For a given E_s , we can then determine its local emission current density J (without space

Figure 4.1: The local enhancement factor profile for Lorentzian shape at different h/w ratio. The Δy represents the vertical displacement from the apex position. The insert is the schematic of a Lorentzian shape emitter.

4.2 Lorentzian Shape

charge effect) by using the FN law [9] given by

$$J = AE_s^2 e^{-B/E_s} \quad (4.2)$$

where $A = 1.54 \times 10^{-6} \exp(10.4/\sqrt{\Phi})/\Phi$, $B = 6.44 \times 10^9 \Phi^{3/2}$, and Φ [eV] is the material work function. Equation (4.2) clearly indicates that the local emission current density J is very sensitive to the local enhancement factor β . Since β decreases very fast from the apex, the local emission current density J will be much larger near the tip region as compared to the region at the tail. For a work function of $\Phi = 4$ eV, $h/w = 10$, and fixed $E_0 = 10^8$ V/m, we have $\beta_{max} = 34.64$ and $J = 2.9087 \times 10^8$ A/m² at the apex. In comparison, we have $J \approx 0$ at the tail region with $\beta = 1$. This again implies that most emitted electrons will concentrate near to the tip, and it is not necessary to record for the entire emission over a large surface. For Lorentzian shape, we thus ignore all emission points in the region with $\beta < 1$.

Consider electron emission from a given point at the surface of the emitter, carrying a current density J determined by Eq. (4.2), an electron will be accelerated towards the anode, and its trajectory can be determined by the vacuum electric field $\mathbf{E} = E_x + iE_y$ given by [166]

$$E_x + iE_y = \frac{-iE_0[x - i(y + b)]}{\{[a^2 - (y + b)^2 + x^2] - 2ix(y + b)\}^{1/2}}, \quad (4.3)$$

where $a \approx h + \frac{w}{3.464}$ and $b \approx \frac{w}{3.464}(1 + \frac{1}{3.464h/w})$. In Fig. 4.2, we have depicted several emitting electron trajectories emitted from different surface locations (x_0, y_0) such as from the apex (Red line) and the tail with $\beta = 1$ (Cyan line).

4.2.2 The Onset Critical Field

From Fig. 4.2, it is obvious that the electron trajectories will not intersect with each other. This property implies that we may assume the magnitude of the current density $|\vec{J}(x, y)|$ along a given trajectory is approximately equal to the local emission current density $J(x_0, y_0)$ calculated by Eq. (4.2), where (x_0, y_0) is the initial emitting position

Figure 4.2: The emitted electron trajectories (x, y) from various emitting positions (x_0, y_0) (from apex to $\beta = 1$) for Lorentzian shape emitter at $h/w = 10$ and $E_0 = 10^8$ V/m.

4.2 Lorentzian Shape

on the emitter surface. Note that this assumption is generally true in our model since most of electrons are emitted from the emitter apex, where beam spreading is very small. Therefore, the current conservation condition $J(x, y)dx dy = J(x_0, y_0)dx_0 dy_0$ can be approximated by the current continuity equation $J(x, y) = en(x, y)|\vec{v}(x, y)| \approx J(x_0, y_0)$. A convergence study is performed in Sec. 4.4 to check the validity of this assumption. Thus for a given trajectory, we could obtain the electron charge density $n(x, y)$ in the vacuum space by solving $en(x, y)|\vec{v}(x, y)| \approx J(x_0, y_0)$, where the velocity $\vec{v}(x, y)$ is obtained by solving the equation of motion based on the vacuum electric field distribution [see Eq. (4.3)]. It is important to note that in our calculations so far, we have completely ignore the space charge effects in the calculation to obtain the electron density $n(x, y)$, which is to be used later in solving the Gauss law [see Eqs. (4.4) and (4.7)] to estimate the space charge field.

The remaining task is to find out the critical applied electric field E_c at which the SCL condition is reached. For a protrusive shape emitter (Lorentzian or Hyperboloid), we define that the SCL condition is reached when the resulting space charge field E_{sp} (in y -direction due to the vacuum charge density $n(x, y)$) calculated at the apex of the emitter is equal to the applied local electric field $E_s = E_0 \times \beta_{max}$ at the same location ($x_0 = 0, y_0 = h$). By solving the Gauss law, we obtain

$$E_{sp} = \int_0^\infty dx \int_{y(x)}^D dy \frac{(y - h) \rho(x, y)}{\pi \epsilon_0 [x^2 + (y - h)^2]}, \quad (4.4)$$

where $\rho(x, y) = -en(x, y)$, $y(x)$ is the corresponding y -coordinate of the emitting location on surface and $y(0) = h$ represents the emitter apex.

A sample of the calculated values of E_{sp} (solid line) is illustrated in Fig. 4.3 (a) for $\beta_{max} = 34.64$ as a function of applied electric field E_0 . The critical value of $E_0 = E_c$ reaching the SCL condition is obtained by having $E_{sp} = E_s = E_c \times \beta_{max}$ (dash line). For example, in this case, E_c is about $E_c = 0.21$ V/nm (dot line). Initially when the applied electric field E_0 is small, the surface electric field E_s is higher than the space charge field E_{sp} , and thus the space charge effect is not important. When E_0 is

approaching E_c , the space charge effect becomes more and more important, and the total electric field is zero at $E_0 = E_c$ which fulfills the SCL condition. Subsequently by plotting the FN law J_{FN} as a function of E_0 as shown in Fig. 4.3 (b) (solid line), we can easily find the corresponding SCL current density at $E_0 = E_c$ denoted as J_{cL} . The comparison between the calculated J_{cL} and the 1D CL law will be shown later for various values of h/w or β_{max} .

4.3 Hyperboloid Shape

Another well-known mathematical model used for field emitter is the Hyperboloid shape (Fig. 4.4 insert) [168]. In this model, the distance between the emitter apex and the anode is given by $D = a \cos \theta$, where a is the half-foci distance and θ is the tip half-angle. To maintain consistency, we fix the gap spacing $D = 10 \mu\text{m}$ and vary the half-foci distance a to control the sharpness of the emitter. For the ease of formulation, we have used the prolate spheroidal coordinate system: ξ , η and ϕ , where lines of constant ξ and η correspond to the prolate-spheroidal surface and the hyperboloidal surface respectively, and ϕ is the azimuthal angle of rotation about the major axis. The values of $\xi = 1$ and $\xi \gg 1$ denote the location of the apex and the tail of the emitter respectively. Note that the Hyperboloid shape already offers an excellent physical approximation for the experimental geometrical features of a field emission microtip (see Fig. 2 in Ref. [168]).

4.3.1 Enhancement Profile and Electron Trajectory

The corresponding local enhancement factor profile is given by

$$\beta^{-1} = Q_0(\cos \theta) \sqrt{\xi^2 - \cos^2 \theta} \tan \theta, \quad (4.5)$$

where $Q_0(\cos \theta) = (1/2) \ln[(1 + \cos \theta)/(1 - \cos \theta)]$ is the Legendre polynomial of second kind. Figure 4.4 shows the calculated β profile as a function of the vertical

4.3 Hyperboloid Shape

Figure 4.3: For Lorentzian shape at $h/w = 10$ or $\beta_{max} = 34.64$, (a) The overall space charge field E_{sp} (solid line) at the apex as a function of applied electric field E_0 . E_s (dash line) is the surface electric field at the apex and E_c (dot line) is the critical electric field at which $E_{sp} = E_s$. (b) The emission current density at the apex as a function of applied electric field E_0 . J_{FN} (solid line) is calculated using FN law, E_c is the same critical electric field in (a) and the intersection is marked as SCL current J_{cL} .

Figure 4.4: The local enhancement factor profile for Hyperboloid shape at different $\cos \theta$. The Δz represents the vertical displacement from the apex position. The insert is the schematic of a Hyperboloid shape emitter.

4.3 Hyperboloid Shape

displacement Δz measured from the apex at different sharpness conditions. The maximum enhancement β_{max} is again at the apex of the emitter, but it decreases less rapidly compared to the Lorentzian shape. To make the maximum field enhancement comparable to those obtained from the Lorentzian shape, we vary the values of a accordingly in the Hyperboloid model. For example, we shall have $\beta_{max} = 34.786$, 341.51 and 3449.4, at their corresponding a [μm] = 10.04818, 10.00337 and 10.00026 (or $\cos \theta = 0.995205$, 0.999663 and 0.999974). It is noteworthy that Eq. (4.5) is very sensitive to the value of a (or $\cos \theta$), and five or more decimal digits in a (or $\cos \theta$) are necessary to precisely compute the β_{max} value.

With the known β profile, we could calculate the emission current density from the emitter surface using the FN law [see Eq. (4.2)] at any applied electric field E_0 ($E_s = E_0 \times \beta$). Since the emitted electrons also concentrate near the tip region, the effective emission area is limited within tip half angle $\lesssim 20^\circ$, which is enough to include majority of the emitted electrons (more than 95% of the total emission [169]). The tip half angle is defined and calculated in Ref. [170], and will not be discussed here. For example, at $E_0 = 0.1$ V/nm and $\Phi = 4$ eV, we have $\beta_{max} = 34.786$ and $J = 2.7122 \times 10^8$ A/m² at 0° (the apex), while they are $\beta = 2.6895$ and $J \approx 0$ at tip half angle = 20° .

Once the electrons are emitted from the surface, they will be accelerated towards the anode under the influence of the vacuum electric field, which can be determined by taking the derivation of the electric potential field (without space charge field), given by [168]

$$V(\eta) = V_0 \frac{\ln[(1 + \eta)/(1 - \eta)(1 - \eta_1)/(1 + \eta_1)]}{\ln[(1 + \eta_2)/(1 - \eta_2)(1 - \eta_1)/(1 + \eta_1)]}, \quad (4.6)$$

where $\eta_1 = \cos \theta$ is the cathode surface, and $\eta_2 = 0$ is the planar anode. By solving the equation of motion, we obtain the trajectories of the emitted electrons, which are plotted in polar coordinate system (r, z) as shown in Fig. 4.5 for different emitting locations (r_0, z_0) ranging from the apex (Red line) to tip half angle 20° (Cyan line). Here, the apex of the emitter and the planar anode are located, respectively at $(r$

Figure 4.5: The emitted electron trajectories from various emitting positions (r_0, z_0) (from apex to half angle 20°) for Hyperboloid shape emitter at $\cos \theta = 0.995205$ and $E_0 = 10^8$ V/m.

$= 0$, $z = D$) and $z = 0$. Similar to the approach mentioned in Sec. 4.2.1, since the trajectories are not across each other, the magnitude of the current density $J(r, z)$ along the same trajectory is equal to the initial value $J(r_0, z_0)$ calculated at the surface position (r_0, z_0) , and subsequently we could obtain the velocity profile $\vec{v}(r, z)$, and also the electron charge density $n(r, z)$.

4.3.2 The Onset Critical Field

To find out the onset of SCL condition, we use the same approach, and the space charge field (in z -direction due to $n(r, z)$) determined by the Gauss law at the apex

4.4 Further Comparison and Discussion

is

$$E_{sp} = \int_0^\infty dr \int_0^D dz \frac{(D-z)r\rho(r,z)}{2\varepsilon_0[r^2 + (z-D)^2]^{3/2}}. \quad (4.7)$$

Figure 4.6 (a) shows the calculated E_{sp} (solid line) at $\beta_{max} = 34.786$ as a function of applied electric field E_0 . Its intersection with the surface electric field at the emitter apex $E_s = E_0 \times \beta_{max}$ (dash line) defines the critical point $E_c \approx 0.23$ V/nm (dot line), where the SCL condition is fulfilled. Similarly, Fig. 4.6 (b) illustrates the SCL current J_{cL} at this critical E_c .

4.4 Further Comparison and Discussion

Figure 4.7 shows the dependence of the critical applied electric field E_c (solid lines) on the maximum field enhancement factor β_{max} at different work functions $\Phi = 4, 3$ and 2 eV (top to the bottom) for (a) Lorentzian and (b) Hyperboloid shapes. The corresponding h/w ratio and $\cos\theta$ values are also shown in the upper x -axis. Note that in order to hold the assumption in Ref. [167], Lorentzian shape is only valid for $h/w \geq 1$, or $\beta_{max} \geq 3.6055$, and hence the calculations at smaller $h/w < 1$ are not shown. From the figure, we can summarize the following points:

1) For both shapes, as the sharpness (β_{max}) increases, the critical applied field E_c will decrease. For a larger β , a smaller applied electric field E_0 is needed to produce a large surface electric field $E_s = E_0 \times \beta$, which gives larger emission current density J [see Eq. (4.2)]. Thus for a sharper emitter (higher β), a smaller critical electric field E_c is needed to reach SCL condition.

2) For a very sharp emitter ($\beta_{max} \geq 30$), E_c is inversely proportional to β_{max} , which implies that $E_c \times \beta_{max} = \text{constant}$. This is a rather useful scaling because once this *constant* is determined for one specific β_{max} , it will allow us to predict other E_c values at other sharpness conditions. As an example, for Lorentzian

Figure 4.6: For Hyperboloid shape at $\cos \theta = 0.995205$ or $\beta_{max} = 34.786$, (a) The overall space charge field E_{sp} (solid line) at the apex as a function of applied electric field E_0 . E_s (dash line) is the surface electric field at the apex and E_c (dot line) is the critical electric field at which $E_{sp} = E_s$. (b) The emission current density at the apex as a function of applied electric field E_0 . J_{FN} (solid line) is calculated using FN law, E_c is the same critical electric field in (a) and the intersection is marked as SCL current J_{cL} .

4.4 Further Comparison and Discussion

shape, at $\beta_{max} = 34.64$, $E_c = 0.20195$ V/nm and $E_c \times \beta_{max} = 6.9955$ V/nm, while at $\beta_{max} = 346.4$, $E_c = 0.019965$ V/nm and $E_c \times \beta_{max} = 6.9159$ V/nm, where the difference is only 1.13%. Similarly for Hyperboloid shape, we have $E_c = 0.2337$ V/nm for $\beta_{max} = 34.786$, and $E_c = 2.267$ V/ μ m for $\beta_{max} = 3449.4$ and the difference in $E_c \times \beta_{max}$ is only 3.8%.

3) For both shapes, the numerical fitting of E_c will approach to the 1D limit value at small $\beta_{max} \approx 1$, e.g. for Hyperboloid case at $\Phi = 4$ eV (Black line) as shown in Fig. 4.7 (b), the 1D limit is around $E_c = 5.65$ V/nm. This 1D limit value can also be obtained by equating the 1D CL law [see Eq. (2.12)] and the FN law [see Eq. (4.2)] at $\beta_{max} = 1$ (1D flat surface), which gives $E_c = 5.78$ V/nm, with a difference of only 2.21%.

Due to the non-uniform emission of electrons from a protrusive surface, it is necessary to define two parameters to characterize the space charge limit current that occurred at the critical condition E_c . The first one is J_{max} , which is simply the maximum current density emitted from the apex of the emitter. The second one is J_{ave} , which is the average current density (over the effective emission area) calculated by $J_{ave} = \int \vec{J} \cdot \vec{dA} / \int dA$, where dA is the differential area on the emitting surface. Recalled that the effective emission area is, respectively, determined by $\beta \gtrsim 1$ for Lorentzian shape, and within half angle $\lesssim 20^\circ$ for Hyperboloid shape.

In terms of the 1D limit current density J_{1D} (= 1D CL law at the critical condition E_c), the normalized values of J_{max} [$\mu_{max} = J_{max}/J_{1D}$ (dashed lines)], and J_{ave} [$\mu_{ave} = J_{ave}/J_{1D}$ (solid lines)], are plotted in Fig. 4.8 (a) for Lorentzian shape (circle) and Hyperboloid shape (inverted triangle). It is clear that both μ increase with the sharpness characterized by β_{max} , which will converge to a saturated value at large β_{max} . The saturated values are about 20 and 70, respectively, for Lorentzian and Hyperboloid shapes. The convergence is due to the corresponding decreasing

Figure 4.7: The critical applied electric field E_c as a function of emitter sharpness β_{max} and work function Φ [eV] (top to bottom) = 4 (Black), 3 (Red) and 2 (Blue) for (a) Lorentzian and (b) Hyperboloid.

4.4 Further Comparison and Discussion

of the effective emission area when the tip becomes sharper. At the limit case of $\beta_{max} = \infty$ (the emitter looks like an infinitely sharp needle), all electrons will emit from the apex position, we shall have $\mu_{ave} = \mu_{max}$. Note the Hyperboloid shape has a higher value of μ than the Lorentzian shape as the former has a more uniform surface enhancement profile near to the apex (see Fig. 4.1 and Fig. 4.4).

In Fig. 4.8 (a), both μ_{ave} and μ_{max} will approach to unity as β_{max} approaching the 1D limit, especially for the Hyperboloid shape, we have $\mu_{ave} \approx \mu_{max} \approx 1$ at $\beta_{max} \approx 1$. Besides the dependence on the emitter sharpness β_{max} , we also investigate the effects of the gap spacing D ($1 - 100 \mu\text{m}$) and the work function Φ ($2 - 4 \text{ eV}$). Although the absolute magnitude of SCL current density J depends on the specific values of D and Φ , the enhancement factor μ shown in Fig. 4.8 (a) is not sensitive to D and Φ . The maximum variance on μ is within 8% for $D = 1$ to $100 \mu\text{m}$ and 5% for $\Phi = 2$ to 4 eV . In Fig. 4.8 (b), we increase the number of emitting trajectories [see Fig. (4.2) and (4.5)] from the emitter tip to check the convergence of μ_{ave} (solid line: 2 times more and dashed lines: 5 times more) for Lorentzian shape (circle) and Hyperboloid shape (inverted triangle) respectively. The comparison shows good convergence in terms of numerical accuracy which is within 2 to 5% over a wide range of β_{max} , which indicates that our assumption using continuity equation $en(x, y)v(x, y) = J(x_0, y_0)$ is valid to calculate the space charge density $n(x, y)$.

Last but not least, we would like to comment on the two types of geometries that were not studied in this chapter, namely, a perfectly sharp conical shape [171] and knife-edge shape [125]. For a perfectly sharp conical shape, we believe the results should be quite similar to the Hyperboloid shape since they are both cylindrical symmetric about the central axis. The only difference is that the field enhancement is less uniform for the conical shape (enhancement decreases faster as moving away from the apex), and the electron beam will be more concentrated around the emitter tip. Thus, the onset critical field E_c and SCL current enhancement for a conical shape will be less than the Hyperboloid shape. For the knife-edge emitter, it is infinitely

Figure 4.8: (a) The enhancement μ of the protrusive CL model over 1D CL law for J_{ave} (solid lines) and J_{max} (dashed lines) as a function of β_{max} for Lorentzian (circle) and Hyperboloid (inverted triangle) shape. (b) The corresponding deviation of the calculated μ_{ave} shown in (a) for 2 (solid lines) and 5 (dashed lines) times more emitting trajectories from the tip (convergence check).

4.5 Summary

long in the z -direction similar to the Lorentzian shape. Thus, we may speculate that the results will be closer to the Lorentzian shape. However, the knife-edge geometry has two sharp tips (see points B and C in Fig. 1 (a) of Ref. [125]), the onset of SCL condition does not occur at the center of the emitter (point h) but at the two sharp edges, where the total field enhancement is infinite. In terms of the total emission current, it depends on the complete integration of emission current density over the entire emitter surface, which may require a large device-scale simulation and is beyond our scope.

4.5 Summary

In summary, we have proposed a simple method to determine the onset of space charge limited (SCL) current from a protrusive field emitter of either Lorentzian or Hyperboloid shape. The critical applied electric field E_c on the onset of SCL current is calculated and we establish an useful scaling $E_c \times \beta_{max} = \text{constant}$ for a very sharp emitter ($\beta_{max} > 30$). The corresponding SCL current density at the critical applied field is also calculated as a function of the emitter's sharpness characterized by the maximum field enhancement factor β_{max} at the apex of the emitter.

In terms of the 1D CL law, the enhancement factor of this calculated SCL current density μ only depends on β_{max} , and is insensitive to the gap spacing and work function of the emitter. This model should be useful in the quick assessment of SCL electron emission from a sharp tip in applications such as using sharp emitters to produce high current electron beam required for high power microwave sources [172, 173]. In the future, after further verification with well-resolved PIC (Particle-in-Cell) simulation [174], it may be implemented into PIC code package to avoid fine meshing (at the cathode surface) for device-scale simulation. Additional discussion and future works will be given in Chapter 7.

CHAPTER 5

NONUNIFORM EMISSION OF A SHARP TIP EMITTER

5.1 Introduction

Generally for a sharp tip emitter, the field emission (FE) process is commonly described by the well-known Fowler-Nordheim (FN) law given by [9]:

$$J = A\beta^2 E_0^2 \exp\left(-\frac{B}{\beta E_0}\right) \quad (5.1)$$

where J is the current density in A/m², $A = 1.54 \times 10^{-6} \exp(10.4/\sqrt{\Phi})/\Phi$, $B = 6.44 \times 10^9 \Phi^{3/2}$ and Φ is the material work function in eV, β is the electrical field enhancement factor of the sharp tip and is a function of the emitter geometry, and $E_0 = V_g/D$ is the applied electric field with gate voltage V_g and gap spacing D . It is important to note that the FN law is essentially a one-dimensional (1D) model that the field enhancement factor β is arbitrarily added into the model without a consistent 2D or 3D treatment of quantum tunneling. This equation implies that the amount of emitted current density at any position on a given emitting surface is only dependent on the local electric field given by $E_s = \beta E_0$ [see also Eq. (4.2)].

5.1 Introduction

To understand the property of field emission, the FN law has been widely used to analyze experimentally measured field emission data by plotting the FN plot in the form of

$$\ln \frac{J_{ave}}{E_0^2} = \ln(A\beta^2) - \frac{B}{\beta E_0}, \quad (5.2)$$

where $J_{ave} = I_{tot}/S$ is the average emitting current density, I_{tot} is the total emitted current and S is the emission area at the cathode. By measuring the total current I_{tot} for a given area S on the anode as a function of E_0 , followed by plotting $\ln(J_{ave}/E_0^2)$ vs $1/E_0$, we will be able to determine the gradient value of $-B(\Phi)/\beta$ or the interpolation value of $\ln(A\beta^2)$, which are functions of Φ and β . Specifically for a perfectly flat emitting surface with $\beta = 1$, it is straight forward that both the areas of the emitting surface (at cathode) and collecting surface (at anode) are equal, so that the slope or interpolation in FN plot will directly give the value of Φ . In this chapter, we focus only on the low current regime where the applied electric field E_0 is below some threshold value that the space charge effect can be ignored for a sharp emitter [21].

If the cathode is consisting of many sharp emitters (like a field emitter array) or thin films of many sharp features, it will be difficult to use FN plot to characterize the electron field emission data as the analysis will involve all three uncertain parameters, namely emitting area (S), work function (Φ) and enhancement factor (β). In this case, one has to always control or determine 2 out of the 3 parameters from other methods before the analysis. For example, we may solve electrostatic equation to obtain β of a sharp tip, and assume certain emission area based on the sharpness of the tip, and thus be able to determine Φ from the FN plot. We can also use first principal calculation to determine Φ first and to determine β from FN plot. Or we can use the above computational methods to compute Φ and β , and to use FN plot to determine S . The problem becomes more complicated if the emitters are not uniform that we will need a careful statistical model to express the 3 parameters in their average values. The complexity of this issue may explain why there is a large amount of reported β from using FN plot to characterize the experimental field emission data

over a wide range of sharp emitters. Some of the large field enhancement factor with $\beta > 1000$ is even physically not possible according to electrostatic models.

Even for the simplest case of a single sharp tip emitter, where the field enhancement β is not uniform over the protrusive surface, there is a need to define an average field enhancement factor β_{ave} . From the experiment data, in order to determine β_{ave} , we need to first measure the total collected current I_{tot} at the anode of a finite area S_A . After that, we can calculate the average anode current density $J_A = I_{tot}/S_A$ at the corresponding applied electric field E_0 , and use the FN plot [see Eq. (5.2)] followed by fitting the gradient $-B/\beta_{ave}$ or interpolation $\ln(A\beta_{ave}^2)$ to obtain β_{ave} for a given Φ . Note that according to the FN law, the real average emission current density should be expressed as $J_K = I_{tot}/S_K$, where S_K is the actual emission area on the cathode. However in the real experiment, S_K is not directly measurable for a sharp tip emitter, and the anode area S_A is used in the analysis. It is worthy to clarify that the actual average enhancement is an intrinsic property of emitter, which has no relation with external conditions such as anode area and gap spacing. In the other hand, the β_{ave} used in this chapter refers to the "measured" enhancement result in the experiment, whose accuracy will be affected by the anode area.

It is clear that the magnitude of J_A will strongly depend on the anode area S_A , which can actually be chosen arbitrarily in the experiment. In 1996, Gopinath [17] has already pointed out that the space charge limited (SCL) current density depends on the anode/cathode ratio for a cylindrical shape emitter. Therefore, we also speculate that the anode area would affect the enhancement measurement result in the ordinary field emission regime (without space charge effect). For a sharp tip emitter, due to the nonuniform emission feature as well as the beam expansion in the vacuum, S_A could be much larger than S_K . As a result, the gradient and the interpolation of the linear curve [$\ln(J_A/E_0^2)$ vs $1/E_0$] could be affected, and the subsequent fitting values might be inaccurate. Thus, the consistency of the results will need a careful revision

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on the values of S_A to be used, which is expected to be dependent on the geometrical shape of the emitters. Further question like what is the relation between β_{ave} and S_A , will also require some deep investigations.

In this chapter, we will perform a *numerical* experiment to obtain the criteria of using FN law to characterize the field emission from a sharp emitter. We consider a sharp emitter with well-defined shape and known work function, and the electrons are emitted according to the FN law from the cathode to the anode. By collecting the current on the anode, we will perform the analysis based on FN law and investigate the variation of β_{ave} with respect to various geometrical settings, such as gap spacing D and anode area S_A . The detail models for 2 types of emitters used in this chapter namely, Lorentzian shape and Hyperboloid shape are presented, respectively, in Sec. 5.2 and 5.3. Further analysis and discussions are shown in Sec. 5.4. Finally, concluding remarks are presented in Sec. 5.5.

5.2 Lorentzian Shape

A 3D schematic of the Lorentzian shape emitter is illustrated in Fig. 5.1 (a), which is assumed to be infinitely long in the z -direction. A rectangular anode with finite width of $2L$ is proposed to collect the emission current. It is a classical model commonly used to simulate the actual wedge shape emitters formed by GaAs [175], GaN [176], silicon [177] or organic material [178], and can provide simple but good estimation on the field distribution and surface enhancement profile [167]. Nevertheless, it is designed to calculate the fringe fields in the immediate vicinity of the emitter surface, and completely ignore any defect, irregularity, and space charge effect. Thus, the fluctuations in current at constant voltage over time due to charge sputtering and the migration and generation of nanoprotusions will not be included.

The cross section of x - y plane is shown in Fig. 5.1 (b), where h is the height of the emitter in y -direction and w is the full-width-at-half-maximum in x -direction. The

apex of the emitter is located at $(x = 0, y = h)$, and the planar cathode and anode is, respectively, at $y = 0$ and $y = D$. In the figure, L_A is defined as the half anode length to collect the emission line current I_z (A/m), and $L_K = \int dl$ is the corresponding *maximum* arc length on the emitter surface for which beyond the electrons emitted will be outside the collecting area. The collecting area on the anode and emitting area on the cathode, are defined respectively, as $S_A = 2L_A \cdot z$, and $S_K = 2L_K \cdot z$. The total collected current on the anode is $I_{tot} = I_z \cdot z$, where z is infinite in z -direction.

5.2.1 Verification of the Experimental Approach

Recall from Chapter 4 that The surface enhancement profile as well as the vacuum field distribution is expressed in Eq. (5.3) and (5.4) respectively given by [167].

$$\beta = \frac{\sqrt{X_0^2 + (Y_0 + \epsilon)^2}}{\{[1 - (Y_0 + \epsilon)^2 + X_0^2]^2 + [2X_0(Y_0 + \epsilon)]^2\}^{1/4}} \quad (5.3)$$

$$E_x + iE_y = \frac{-iE_0[x - i(y + b)]}{\{[a^2 - (y + b)^2 + x^2] - 2ix(y + b)\}^{1/2}} \quad (5.4)$$

where $a \approx h + \frac{w}{3.464}$, $b \approx \frac{w}{3.464}(1 + \frac{1}{3.464h/w})$, $\epsilon = b/a \approx w/3.464h$ and (X_0, Y_0) are the normalized coordinates of the emitter surface.

With the known surface enhancement profile in Eq. (5.3), we could easily calculate the emission current density $J(X_0, Y_0)$ at every point of the emitter surface (X_0, Y_0) by using Eq. (5.1) at a given applied electric field E_0 . Once an electron emitted into the vacuum, we can simply track the electron trajectory (x, y) by applying Eq. (5.4) as well as Newton's law until it reaches $y = D$ (e.g. see Fig. 4.2). The electrons are considered collected if they are able to fall inside the finite anode area of $2L_A$ in length bounded between $(x = -L_A, y = D)$, and $(x = L_A, y = D)$. The total emission line current I_z that can be collected by the anode is given by

$$I_z = 2 \int_0^{L_K} J \cdot dl \quad (5.5)$$

Note that throughout the chapter, we keep the work function at $\Phi = 4$ eV and $h = 100$ nm $\ll D$.

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Figure 5.1: (a) The 3D schematic of a Lorentzian shape emitter. (b) The cross section schematic of the x - y plane.

Since it is impossible to directly measure the actual emission area S_K on the emitter surface, we define an experimentally measured average current density (based on the collecting area on the anode), which is

$$J_A = \frac{I_{tot}}{S_A} = \frac{I_z}{2L_A} = \frac{\int_0^{L_K} J \cdot dl}{L}. \quad (5.6)$$

The average enhancement β_{ave} is then obtained by plotting $\ln(J_A/E_0^2)$ with respect to $1/E_0$ and fitting the gradient or interpolation. Due to the beam expansion, L_A (or S_A) might be much larger than the real emission length L_K (or S_K). As a result, J_A could be much smaller than the real average emission current density emitted from the cathode given by

$$J_K = \frac{I_{tot}}{S_K} = \frac{I_z}{2 \int dl} = \frac{\int_0^{L_K} J \cdot dl}{\int dl}. \quad (5.7)$$

Thus, it is first necessary to check the validity of replacing J_K with J_A by comparing the β_{ave} results obtained from the FN plot of J_A and J_K as a function of L_A for a case that $h/w = 10$ and $D = 10 \mu\text{m} \gg h = 0.1 \mu\text{m}$ (where $w = 0.01 \mu\text{m} \ll L$).

Apparently from Fig. 5.2 (a), L_A is much larger than L_K (the beam expansion is significant), and L_K increases as L_A becomes larger. However in Fig. 5.2 (b), the calculated β_{ave} values based on gradient fitting of the FN plot of J_A (solid line) and J_K (dash line) agree very well, which imply that it is valid to use L_A (or S_A) and its corresponding J_A to estimate β_{ave} of emitter. The reason will be elaborated later in Sec. 5.2.2. We further confirm that the gradient of the FN plot is rather independent of the applied field E_0 . The error is less than 4 % within the studied range of E_0 , and this clearly indicates that the linear relation of $\ln(J/E_0^2)$ and $1/E_0$ [see Eq. (5.1)] is strictly held in our numerical experiment.

5.2.2 Determine the True Average Enhancement

Theoretically for a fixed set of h , w , and D , the *real* sharpness or average enhancement of the emitter defined as β_c should not vary with the anode property L_A . Thus it

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Figure 5.2: Lorentzian shape emitter at $h/w = 10$: (a) The relation between the real emission area L_K and the anode area L_A . (b) The average enhancement β_{ave} obtained by fitting the gradient of the FN plot using J_A (solid line) and J_K (dashed line).

is important to know the critical L_A (to be controlled by the experimental setting) where its corresponding β_{ave} determined by the FN plot shown in Fig. 5.2(b) is the *real* sharpness β_c . In general, this critical value of L_A mainly depends on the gap spacing D . For a larger D , the electron beam will expand further and we need larger L_A to collect all the electrons emitted from a given emitting surface L_K in order to collect the same amount of total current. Fig. 5.3 (a) illustrated the emission current I_z as a function of L_A at $h/w = 10$ and $E_0 = 10^8$ V/m. As expected, with D increases (from left to right = 1 to 10 μm), larger L_A is required to collect the same amount of current I_z . Since most of the current concentrates near the vicinity of the tip ($\beta \gg 1$) and the emission from the tail ($\beta \approx 1$) can be omitted, the maximum values of I_z are the same regardless the gap spacing D as long as L_A is large enough. A critical value L_c (labeled in the figure) is defined at which the the emission current I_z reaches maximum (all electrons have been collected). For example, we have $L_c \approx 0.13, 0.38$ and 0.57 μm for $D = 1, 5$ and 10 μm , respectively.

The corresponding β_{ave} result at fixed $h/w = 10$ for different D is shown in Fig. 5.3 (b). It is clear that as the anode area L_A approaches to zero, the collected current I_z is mainly from the apex of the emitter, thus we have $\beta_{ave} \approx \beta_{max} = 34.654$, which is the localized field enhancement factor at the emitter apex ($x = 0, y = h$) determined by Eq. (5.3). Here we assume that the size of the anode L_A will not affect the vacuum field distribution [see Eq. (5.4)] and the emitted electron trajectories. Therefore as L_A approaches zero, it will only collect current from the apex and all other electron trajectories will fall out of the anode region, hence β_{ave} will be equal to the apex enhancement. From this figure, we could easily locate $\beta_{ave} = \beta_c \approx 33.37$ at the critical length $L_c \approx 0.13, 0.38$ and 0.57 μm for $D = 1, 5$ and 10 μm , respectively. This value is the *real* average enhancement β_c for $h/w = 10$ and it is independent of the gap spacing. Note that these critical L_c are the *minimum* required anode sizes that one should use in the experiment in order to determine the *real* average

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Figure 5.3: Lorentzian shape emitter: (a) The collected current I_z for various gap spacing D at fixed $h/w = 10$ and $E_0 = 10^8$ V/m, where L_c is the critical anode length at which I_z reaches maximum. (b) The corresponding β_{ave} result, where β_c is the true average enhancement located at L_c . (c) The comparison of β_{ave} obtained by fitting the gradient (solid line) and interpolation (dash line) at $h/w = 10$ and $D = 5$ μm .

enhancement β_c . Thus as long as the value of L is greater or equal than L_c , the estimated $\beta_{ave} \approx \beta_c$ will be valid, and we shall elaborate this further in Sec. 5.4.

From Eq. (5.2), it seems that the average enhancement β_{ave} can be obtained by either fitting the gradient $-B/\beta_{ave}$ or the interpolation $\ln(A\beta_{ave}^2)$. However as we mentioned in Sec. 5.2.1, due to large beam expansion the anode area L_A is much larger than the emission area L_K , and the anode current density J_A [see Eq. (5.6)] is much smaller than the real emission current density J_K [see Eq. (5.7)]. Therefore the FN plot using $\ln(\frac{J_A}{E_0^2})$ vs $\frac{1}{E_0}$ will significantly shift downwards as compared to $\ln(\frac{J_K}{E_0^2})$ vs $\frac{1}{E_0}$, and the interpolation data using J_A will not be valid to obtain β_{ave} . Nevertheless, the gradient values are the same as we proved in Fig. 5.2. In Fig. 5.3 (c), we compare β_{ave} results obtained by fitting the gradient with the result obtained by fitting the interpolation at $D = 5 \mu\text{m}$ using FN plot $\ln(\frac{J_A}{E_0^2})$ vs $\frac{1}{E_0}$. The comparison clearly indicates that the interpolation fitting result (dash line) is much smaller than the gradient fitting result (solid line), and interpolation fitting result (< 1) is not valid to describe the emitter's enhancement value. Hence, we conclude that for a sharp tip emitter, the enhancement value can only be obtained by fitting the gradient.

In Fig. 5.4 (a), we show the calculated results at fixed $D = 5 \mu\text{m}$ and $E_0 = 10^8$ V/m for different sharpness $h/w = 5, 10$ and 15 (bottom to top) with corresponding $\beta_{max} = 17, 35$, and 52 at the emitter apex. Due to larger field enhancement at high h/w , we have more emitted current and thus higher I_z . Similarly to Fig. 5.3 (a), I_z will saturate at large anode area L_A that gives us the critical L_c at about $0.34, 0.38$ and $0.39 \mu\text{m}$ for $h/w = 5, 10$ and 15 . Fig. 5.4 (b) shows the corresponding β_{ave} by gradient fitting, and the *real* field enhancements are about $\beta_c = 17, 33$ and 49 for $h/w = 5, 10$ and 15 respectively. In Fig. 5.4 (c), the β_{ave} results using the gradient fitting (solid line) and interpolation fitting (dash line) at $h/w = 5$ are compared, which implies that the beam expansion is still significant even for a relatively flat emitter ($h/w = 5$).

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Figure 5.4: Lorentzian shape emitter: (a) The collected current I_z for various h/w at fixed $D = 5 \mu\text{m}$ and $E_0 = 10^8 \text{ V/m}$, where L_c is the critical anode length at which I_z reaches maximum. (b) The corresponding β_{ave} result, where β_c is the true average enhancement located at L_c . (c) The comparison of β_{ave} obtained by fitting the gradient (solid line) and interpolation (dash line) at $h/w = 5$ and $D = 5 \mu\text{m}$.

5.2.3 Calculation of the Effective Emission Area

After obtaining β_c , we could directly calculate the effective emission width defined as $L_{eff} = I_z/J_c$, where J_c is calculated by substituting β_c into Eq. (5.1). For the Lorentzian shape emitter, the effective emission width L_{eff} depends on the emitter sharpness characterized by h/w and is independent on the gap spacing D as long as $D \gg h$. For example, we have $L_{eff} \approx 1.49, 0.515$ and $0.28 \text{ \AA}$ for $h/w = 5, 10$ and 15 respectively.

5.3 Hyperboloid Shape

In this section, we will repeat the same approach for the other type of emitter known as hyperboloid emitter, which has a cylindrically symmetry about the z -axis as illustrated in Fig. 5.5 (a). A circular anode with finite radius R is proposed to collect the emission current. Together with the prolate-spheroidal system, this model is able to provide a simple analytical expression of electrical field distribution for Spindt-type and ellipsoid shape nanostructures. Based on the STM and TEM images [179], it shows a much better idealization of the actual emitter structure in contrast to the earlier spherical model [170]. Therefore, it is widely used to simulate the nanorod or nanotube tips such as crystal fiber, carbon nanotube, and metal/metal-oxide nanotip. However, in this model, the mircotip is treated as a smooth hyperboloid surface [168], and hence it may not be accurate enough to estimate an extremely atomic-sharp tip, e.g., TiO_2 nanotip in Ref. [180], which requires to handle the singularity at the emitter apex.

The cross section along the central axis is shown in Fig. 5.5 (b), where the apex of the emitter and the planar anode are located, respectively, at $(r = 0, z = D)$ and $z = 0$. Here, $D = a \cos \theta$ is the distance between the emitter apex and anode, a is the half-foci distance and θ is the tip half angle. R is the finite anode radius to collect the emission current I_{tot} , and (r_m, z_m) is the location on the emitting surface

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for which beyond the electrons emitted will be outside the collecting area $r = R$ at the anode. Thus the collecting area on the flat anode and the actual emitting area on the cathode are, respectively, $S_A = \pi R^2$ and $S_K = 2\pi \int_D^{z_m} r(z) \sqrt{1 + (dr/dz)^2} \cdot dz$.

5.3.1 Verification of the Experimental Approach

Again recall from chapter 4, the surface enhancement profile and the vacuum potential distribution are expressed below respectively.

$$\beta^{-1} = Q_0(\cos \theta) \sqrt{\xi^2 - \cos^2 \theta} \tan \theta \quad (5.8)$$

$$V(\eta) = V_0 \frac{\ln[(1 + \eta)/(1 - \eta)(1 - \eta_1)/(1 + \eta_1)]}{\ln[(1 + \eta_2)/(1 - \eta_2)(1 - \eta_1)/(1 + \eta_1)]} \quad (5.9)$$

where $Q_0(\cos \theta) = (1/2) \ln[(1 + \cos \theta)/(1 - \cos \theta)]$ is the Legendre polynomial of second kind, $\eta_1 = \cos \theta$ is the cathode surface and $\eta_2 = 0$ is the planar anode.

By combining Eqs. (5.1) and (5.8), we can calculate the emission current density $J(r_0, z_0)$ from any point (r_0, z_0) on the emitter surface. By taking the derivative of Eq. (5.9), we obtain the vacuum electric field, and use it together with equation of motion to calculate the electron trajectory (e.g. see Fig. 4.5) and to determine whether it can be collected by the anode area S_A . As a result, the overall emission current I_{tot} collected by the anode is expressed as

$$I_{tot} = 2\pi \int_D^{z_m} J[r(z), z] \cdot r(z) \sqrt{1 + (dr/dz)^2} \cdot dz. \quad (5.10)$$

Due to the beam expansion, the anode area S_A might be much larger than the real emission area S_K , we need to compare the average current density emitted from the cathode surface J_K and its counter part collected on the anode J_A , which are given by

$$J_K = \frac{I_{tot}}{S_K} = \frac{\int_D^{z_m} J[r(z), z] \cdot r(z) \sqrt{1 + (dr/dz)^2} \cdot dz}{\int r(z) \sqrt{1 + (dr/dz)^2} \cdot dz}, \quad (5.11)$$

$$J_A = \frac{I_{tot}}{S_A} = \frac{2 \int_D^{z_m} J[r(z), z] \cdot r(z) \sqrt{1 + (dr/dz)^2} \cdot dz}{R^2} \quad (5.12)$$

Figure 5.5: (a) The 3D schematic of a hyperboloid shape emitter. (b) The cross section schematic along the central axis.

5.3 Hyperboloid Shape

To check the validity of using J_A instead of J_K , to fit the average enhancement β_{ave} , we compare β_{ave} obtained by gradient fitting of the FN plot of J_A (solid line) and J_K (dash line) at $D = 10 \text{ } \mu\text{m}$ and $\cos \theta = D/a = 0.99523$. Fig. 5.6 (a) shows the relationship between S_A and S_K , which illustrates significant beam expansion ($S_K \ll S_A$), while Fig. 5.6 (b) shows good agreement and confirms that it is valid to use J_A to find the field enhancement factor. Note that the maximum enhancement is $\beta_{max} = 34.6654$ when S_A approaching zero (as expected).

5.3.2 Determine the True Average Enhancement

Fig. 5.7 (a) illustrates the total emission current I_{tot} with respect to the anode area S_A for various gap spacing $D = 1, 5$ and $10 \text{ } \mu\text{m}$ (bottom to top) at fixed sharpness $\cos \theta = 0.99523$ and $E_0 = 10^8 \text{ V/m}$. Similarly, we can define a critical anode area $S_c = \pi R_c^2$ (labeled in the figure) where the total current I_{tot} reaches maximum, and this will be the *minimum* anode area to be used in the experiment. For example, we have $S_c [\text{m}^2] = 2.01 \times 10^{-12}$, 4.18×10^{-11} and 2.55×10^{-10} for $D = 1, 5$, and $10 \text{ } \mu\text{m}$ respectively. The corresponding β_{ave} is illustrated in Fig. 5.7 (b) by gradient fitting. At small S_A , we have the $\beta_{ave} \approx \beta_{max} = 34.6654$ which equals to the maximum enhancement on the emitter apex. The *real* average enhancement β_c could be determined at the corresponding S_c , which gives the same $\beta_c \approx 32.05$ (labeled in the figure). Note that β_c only depends on the geometrical sharpness characterized by $\cos \theta$, and independent on the gap spacing. Fig. 5.7 (c) compares the β_{ave} results by gradient fitting (solid line) and interpolation fitting (dashed line), which simply proves that for the sharp tip emitter, the average enhancement can only be obtained by gradient fitting due to the large beam expansion.

Similar to the calculation done for the Lorentzian shape, we see that I_{tot} will saturate at large S_A because most electrons are emitted from the region near the emitter apex. However for the Hyperboloid shape [see Fig. 5.7 (a)], the maximum value of I_{tot} significantly increases with larger gap spacing from $D = 1$ to 5 and 10

Figure 5.6: Hyperboloid shape emitter at $\cos \theta = 0.99523$: (a) The relation between the real emission area S_K and the anode area S_A . (b) The average enhancement β_{ave} obtained by fitting the gradient of FN plot using J_A (solid line) and J_K (dashed line).

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Figure 5.7: Hyperboloid shape emitter: (a) The collected current I_{tot} for various gap spacing at $\cos \theta = 0.99523$ and $E_0 = 10^8$ V/m, where S_c is the critical anode area at which I_{tot} reaches maximum. (b) The corresponding β_{ave} result, where β_c is the true average enhancement located at S_c . (c) The comparison of β_{ave} obtained by fitting the gradient (solid line) and interpolation (dash line) at $\cos \theta = 0.99523$ and $D = 5$ μm.

μm , where $D = 1 \mu\text{m}$ case has a much lower current. In comparison, the Lorentzian shape always has a *same* saturation current which is independent on D as shown in Fig. 5.3 (a). The difference is due to the respective mathematical models used to describe the sharpness of the emitter, which may or may not be sensitive to D . For Lorentzian shape, the enhancement profile is determined by the ratio of h/w , and it is independent of D [see Eq. (5.3)]. Once h/w is fixed for a given h , the sharpness of emitter is determined, and we can study the effects of gap spacing simply by changing D without changing the sharpness of the emitter. Thus, we will have the same maximum current at different D . For the Hyperboloid shape, however, the field enhancement factor given by Eq. (5.8) is governed by both gap spacing D and the half-foci length a (through $\cos \theta = D/a$ relation). In this case, changing D alone will also change the sharpness or field enhancement of the emitter. In order to maintain the same sharpness at larger D , we need to increase a accordingly, which will increase the emission current due to larger emitting area. As a result, the emission current will increase with the gap spacing for Hyperboloid emitter and explains the difference between Fig. 5.3 (a) and Fig. 5.7 (a).

Fig. 5.8 (a) depicts the emission current I_{tot} as a function of anode area S_A at $E_0 = 10^8 \text{ V/nm}$ and $D = 5 \mu\text{m}$ for different sharpness (bottom to top) given by $\cos \theta = 0.9889, 0.99523$ and 0.99704 , where their corresponding maximum field enhancements are $\beta_{max} = 17.2873, 34.6654$ and 51.7668 respectively. As the emitter becomes sharper ($\cos \theta$ increases), the emission current will increase due to larger field enhancement [see Eq. (5.8)]. The critical emission area $S_c [\text{m}^2]$ are found to be $3.63 \times 10^{-11}, 4.18 \times 10^{-11}$ and 4.78×10^{-11} . The calculated β_{ave} is shown in Fig. 5.8 (b), and we could determine the *real* average enhancement β_c at $S_A = S_c$, which gives $\beta_c = 16.62, 32.05$ and 46.21 respectively. Fig. 5.8 (c) compares the β_{ave} obtained from gradient fitting (solid line) and interpolation fitting (dash line) at $\cos \theta = 0.9889$, which again confirms that the later approach is not accurate.

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Figure 5.8: Hyperboloid shape emitter: (a) The collected current I_{tot} for various emitter geometry at $D = 5 \mu m$ and $E_0 = 10^8$ V/m, where S_c is the critical anode area at which I_{tot} reaches maximum. (b) The corresponding β_{ave} result, where β_c is the true average enhancement located at S_c . (c) The comparison of β_{ave} obtained by fitting the gradient (solid line) and interpolation (dash line) at $\cos\theta = 0.9889$ and $D = 5 \mu m$.

5.3.3 Calculation of the Effective Emission Area

Lastly, we calculate the effective emission area defined as $S_{eff} = I_{tot}/J_c$, where J_c can be obtained by substituting β_c into Eq. (5.1). For $\cos \theta = 0.9889, 0.99523$ and 0.99704 at $D = 5 \mu\text{m}$, we have $S_{eff} [\text{m}^2] = 9.60 \times 10^{-15}, 3.78 \times 10^{-15}$ and 2.30×10^{-15} respectively. However unlike the Lorentzian shape where L_{eff} is independent on the gap spacing D , due to the change in the geometrical size (the half-foci length a varies with respect to D to maintain the enhancement profile), $S_{eff} [\text{m}^2] = 1.52 \times 10^{-16}, 3.78 \times 10^{-15}$ and 1.52×10^{-14} for different $D = 1, 5$, and $10 \mu\text{m}$ at fixed sharpness $\cos \theta = 0.99523$.

5.4 Comparison and Discussion

From previous analysis in Sec. 5.2 and 5.3, we have illustrated that the measured average enhancement β_{ave} , obtained by fitting the gradient of FN plot using anode current density $J_A = I_{tot}/S_A$ and Eq. (5.2), varies with respect to the anode area S_A , e.g. see Fig. 5.3 (a) and 5.7 (a). By defining the critical anode area (L_c for the Lorentzian shape and S_c for the Hyperboloid shape) at which the current reaches maximum, we conclude that it is the minimum anode area which is required for the experimental set-up to collect nearly all the emitting current, so that the FN analysis for the emitter will be valid. If the anode area S_A is smaller than the critical value S_c , substantial part of the emitted current is not collected and the corresponding field enhancement result will not be accurate. If $S_A \geq S_c$, according to the FN plot given by $\ln(J_A/E_0^2) = \ln[(I_{tot})/(S_A \cdot E_0^2)] = \ln I_{tot} - \ln S_A - \ln E_0^2$, we see that the second term (a constant) will be cancelled out in the calculation of the gradient, and thus will not influence β_c as long as the first term accounts for all the emitted current. Hence this finding suggests that researchers should use a sufficiently large anode area ($\geq S_c$ calculated here) to collect all the current emitted from a sharp emitter due to beam expansion.

5.4 Comparison and Discussion

Based on the calculated β_c , it is worth while to compare the difference between the Lorentzian and Hyperboloid emitters. From the comparison, we observe that with the same apex enhancement β_{max} , Lorentzian shape always has a slightly larger β_c than the Hyperboloid shape. At $\beta_{max} \approx 17, 35$ and 52 , we have $\beta_c \approx 17, 33$, and 49 for the Lorentzian shape, and $\beta_c \approx 16, 32$ and 46 for the Hyperboloid shape. This is because the field enhancement decreases faster away from the apex for the Lorentzian shape emitter as compared to the Hyperboloid shape emitter (see Fig. 4.1 and 4.4) [21], so the emission current is more concentrated near apex, which will produce a higher β_c . This effect becomes more dominant for sharper tips as shown in Fig. 5.9, which compares the two shapes at large $\beta_{max} \approx 361$ and $D = 5 \mu\text{m}$. Clearly, we have $\beta_c = 264$ at $L_c \approx 0.7 \mu\text{m}$ for the Lorentzian shape (solid line), which is larger than the Hyperboloid shape where $\beta_c = 207$ at $S_c = 2.011 \times 10^2 \mu\text{m}^2$ (dash line).

The model presented here might be convenient to formulate a sharp emitter as a flat surface model with an effective emission area S_{eff} and an enhancement factor β_c . First, we perform an experiment to measure the total collected current I_{tot} at the anode with a size larger than the critical area discussed above. From the obtained I_{tot} , we can use the FN plot to estimate the critical field enhancement factor β_c for which we can calculate the effective emission area by $S_{eff} = I_{tot}/J_c$, where J_c is obtained by substituting β_c into Eq. (5.1). Thus, the field emission from a sharp emitter can be treated as a flat emission model governed by

$$I_{tot} = S_{eff} \cdot A \beta_c^2 E_0^2 \exp\left(-\frac{B}{\beta_c E_0}\right), \quad (5.13)$$

where S_{eff} and β_c are known quantities. Finally this simple model can be further used to calculate emission current at any arbitrary applied field E_0 without performing additional experiment. Note that our model is also valid to formulate the case where the emission is spotty for an imperfect flat surface, e.g. defects are presented on the surface. In such case, the emission spot can be treated as a sharp tip, and the average enhancement can be obtained based on our methodology.

Figure 5.9: The comparison of the β_{ave} results between the Lorentzian shape (Solid line) and the Hyperboloid shape (dashed line) at $\beta_{max} \approx 361$ and $D = 5 \mu\text{m}$, which corresponds to $h/w = 100$ for Lorentzian shape and $\cos\theta = 0.99968$ for Hyperboloid shape. The upper horizontal axis labeled S_A is the anode area for the Hyperboloid shape and the lower horizontal axis labeled L_A is the anode length for the Lorentzian shape.

5.4 Comparison and Discussion

We speculate that this simple model may be useful to create a statistical model for a field emission cathode containing of many field emitters [181, 182], and it is interesting to estimate the overall field enhancement of an array. Assuming that the total emission current can be written as the summation of every single emitter, e.g. $I_{tot} = \sum_{n=1}^N I_n$ where I_n is the current emitted from the n th emitter, and the enhancement can be obtained by fitting the gradient of $\ln[I_{tot}/(S_{tot} \cdot E_0^2)]$ vs $1/E_0$. If all the emitters are identical and uniformly distributed ($I_{tot} = N \times I_1$), the overall enhancement for an array will be the same as a single emitter.

If the emitters are not identical and nonuniformly distributed, then it will require a statistical model with some assumed distribution in terms of the sharpness of the emitter and the spacing of the adjacent emitters. Let us assume the simplest case that all the emitters are identical with $\beta_n = \beta_0$ for $n = 1$ to $N-1$, except for the N th emitter, which has a very large enhancement $\beta_N \gg \beta_0$ and $I_N \gg I_0$. If the number of the emitters N is small such that the sum of the current emitted from all other emitters remains much smaller than the current produced by the sharpest emitter [$I_N \gg (N-1)I_0$], we will have $I_{tot} = (N-1)I_0 + I_N \approx I_N$, and the overall enhancement will be close to β_N . On the another hand if N is very large such that $I_N \ll (N-1)I_0$, $I_{tot} \approx (N-1)I_0$, and the overall enhancement will be close to β_0 . Note that the above analysis totally ignores the field screening and shielding effect [183] between the emitters and the space charge effect, which may actually has a profound effect on the emission properties. A more delicate model will be necessary to study a realistic field emitter array cathode. One possible way is to use the present model to create patches of emitting surface in a particle-in-cell (PIC) code that is able to include both effects of field screening [183] and space charge.

5.5 Summary

In conclusion, we have performed a numerical experiment assuming electrons are emitted from a well-defined field emitter, and use the numerical data to mimic experimental measurements to find the criteria for which the analysis of FN law remains valid to estimate the field enhancement factor and effective emission area. Two types of emitters are studied in this paper, namely Lorentzian shape and Hyperboloid shape. From the analysis, we establish a criteria to determine the critical anode area L_c/S_c for which all the emitting current are collected and it also serves as the minimum anode area that one should use in the real experiment so that the analysis of FN plot is correct. Subsequently, the enhancement factor β_c can be obtained at the appropriate L_c/S_c at specific geometrical condition and gap spacing. Lastly, we may calculate the effective emission area S_{eff} base on the β_c values so that a sharp emitter can be treated as a flat emitting patch, which may be useful to extend to study a field emission cathode consisting of many field emitters. This paper will serve as a baseline on using Fowler-Nordheim (FN) law to characterize the field emission from a single field emitter. Additional discussion and future works will be given in Chapter 7.

CHAPTER 6

FIELD EMISSION FROM TRIPLE JUNCTION

6.1 Introduction

As introduced previously in Sec. 2.3, the negative electron affinity (NEA) characteristic [78, 79] on the diamond (111) surface has led to studies of its field emission properties since it requires little or no field for electron in the diamond conduction band to tunnel into vacuum. However, with a large band gap (5.5 eV), it is almost impossible to directly promote an electron from valence band into conduction band for a intrinsic diamond. To take full advantage of NEA, a source of electrons must be presented either in the conduction band or in a subband near the vacuum energy. Nevertheless, no *n*-type dopant suitable for cold field emission has been reported so far. Hence, a substitutional nitrogen doped type Ib diamond, where the nitrogen forms a deep donor level ~ 1.7 eV below the conduction band, is the best choice [184]. Excellent low-voltage-high-current field emission property has been demonstrated from type Ib N-doped diamond and amorphous diamond-like films on metal substrates [185, 186].

Recently, the experiment [18] has proposed a new mechanism which combines the high electric fields that can be obtained at diamond-metal-vacuum triple junction [88, 89, 95] with the mobile electron surface states that formed on NEA surfaces [78, 80, 83, 84, 87]. The results shows it can emit measurable current density (10^{-4} A/m²) at a gate voltage as low as 0.6 V, which is much smaller than the conventional diamond emitter (around 8 to 10 V) [185]. Such a low turn-on voltage could be utilized in many applications, e.g. flat-panel display. Unfortunately, there is no model to describe the emission mechanism for such a triple junction structure. Hence, we are interested in constructing an analytical formula base on the classical field emission theory (see Sec. 2.1.2) that estimates the emission current density from a triple junction structure using the type Ib diamond.

In this chapter, a brief review of the traditional diamond emitter will be given in Sec. 6.2. Our detailed model and the results will be discussed in Sec. 6.3 and 6.4 respectively. A short summary will be presented in Sec. 6.5.

6.2 Review of the Traditional Diamond Emitter

Before looking at the field emission from the triple junction, it is essential to understand the electron transport mechanism from the metal substrate into the diamond layer for a traditional diamond emitter [see Fig. 6.1 (a)], where the small circles represent the metal particles which roughen the cathode surface for field enhancement. Early in 1996, M. W. Geis etc. had demonstrated the field emission behaviors from various diamond samples, which contain different types of dopant [185]. The results show that for aggregated nitrogen dopant (type Ia diamond), a very deep donor level is formed below the Fermi energy, which is not a favorable situation because if the donor is positively charged, electrons will tunnel to the donor and neutralize it. On the other hand, for substitutional nitrogen dopant (type Ib diamond), the deep donor level is formed well above the Fermi energy (~ 1.7 eV below

6.2 Review of the Traditional Diamond Emitter

the conduction band), which significantly reduced the energy required for electron tunneling into the conduction band, and it can emit a measurable current density (10^{-4} A/m²) at a gate voltage around 8 ~ 10 V for a 100 nm thick diamond substrate. Furthermore, for *p*-type, boron-doped diamond, the electron can hardly emit simply because the Fermi energy is far away from the conduction band. Thus, it is confirmed that the type Ib diamond with substitutional nitrogen dopant offers the best option for the diamond emitter.

In theory it is generally accepted that a Schottky barrier is formed at the metal-diamond interface [185, 187], and the corresponding band structure is illustrated in Fig 6.1 (c) (black curve). In the figure, $\Phi_B \approx 4$ eV is the barrier height at the metal-diamond interface which is equal to the average work function of the metal (Cs and Ni salt) [188]. The deep donor level E_f is formed 1.7 eV below the conduction band E_c for the type Ib diamond ($E_c - E_f = 1.7$ eV, and E_f is assumed to be pinned with large donor concentration). $V_B = V_a + V_b$ is the build-in potential at the junction where V_a is the external applied bias and $V_b = \Phi_B - (E_c - E_f)$ is the fixed difference between the peak of the Schottky barrier and the bottom of the conduction band at $V_a = 0$. Note the definition of V_a and V_b can be found in Figs. 1 (a) and 1 (b) in Ref. [189], are not shown here. At the diamond-vacuum interface, the vacuum energy E_{vac} (red dash line) should be below the conduction band E_c to represent the NEA characteristic, and their difference is determined by the surface treatment techniques in the experiment.

In Ref. [189], Lerner *et al.*, proposed a quantitative model for the traditional diamond emitter by calculating the depletion width of the Schottky barrier, and modeled the small metal particles as spheres of a given radius R . The results agreed quite well with the experimental data. Hence, in our model for the triple junction structure, we will continue to use this methodology.

(black curve) and a triple junction structure (red curve).

6.3 Theoretical Model

Compared to the traditional diamond emitter, there are three major differences in the triple junction structure [see Fig 6.1 (b)], and its corresponding band diagram that is depicted in Fig. 6.1 (c) (red curve). First, as we discussed in Sec. 2.3.2, despite the geometrical enhancement on the metal-diamond interface due to protrusions on the metal substrate, the local electric field at the metal-diamond-vacuum junction can be further increased by an additional factor which can be at most equal to the dielectric constant ($\epsilon_r = 5.68$) of the diamond [95]. Second, the electrons will transport into the diamond surface states E_s instead of the conduction band E_c , where E_s is found to be 1 eV below E_c ($E_s - E_f = 0.7$ eV) [87]. These carriers will go through a lower barrier height $\Phi_{B1} < \Phi_B$, which could be as low as 1 eV to as high as the metal work function Φ_B minus the diamond surface binding energy (0.42 eV) [18]. Finally, besides the Schottky barrier $V_1(r)$ at the depletion region, there may be another barrier $V_2(r)$ formed at the diamond-vacuum interface (NEA surface) as long as $E_c > E_{vac} > E_s$. Obviously, the first two factors will result in a smaller turn-on voltage as compared to the conventional diamond emitter, while the third one tends to have the opposite effect.

Closely following the derivation in Ref. [189, 190, 191], we start by calculating the Schottky barrier $V_1(r)$ with the depletion width ω for the triple junction structure, which requires solving the one-dimensional Poisson equation (in Gaussian unit). Note that we are only interested in the vicinity of the triple junction point as well as the diamond (111) surface regime, therefore the electron tunneling problem can be simplified into a one-dimensional case.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V_1(r)}{\partial r} \right) = -4\pi \frac{\rho(r)}{\epsilon_r \epsilon_0}, \quad (6.1)$$

where $\epsilon_r = 5.68$ is the dielectric constant of diamond and ϵ_0 is the vacuum permittivity. Furthermore, we assume that the cathode is at zero temperature so that there is a constant charge density eN_d within the depletion layer ($\rho = eN_d$), where e

is the unit charge and N_d is the donor concentration. By modeling the metal surface protrusion as spheres with radius R , we have included the geometrical enhancement in our model, and two boundary conditions must be stratified as: $V_1(R) = -\Phi_{B1}$ and $\frac{\partial V_1(r)}{\partial r}|_{r=R+\omega} = 0$. This gives an analytical expression of potential profile $V_1(r)$ expressed in Eq. (6.2),

$$V_1(r) = C_1 - \frac{C_2}{r} - \frac{2\pi e N_d r^2}{3\epsilon_r \epsilon_0}, \text{ where } R < r < R + \omega \quad (6.2)$$

where $C_1 = -\Phi_{B1} + \frac{2\pi e N_d R^2}{3\epsilon_r \epsilon_0} + \frac{4\pi e N_d (R+\omega)^3}{3\epsilon_r \epsilon_0 R}$ and $C_2 = \frac{4\pi e N_d (R+\omega)^3}{3\epsilon_r \epsilon_0}$. Outside the barrier region, we further assume the flat band structure is maintained so that $V_1(R + \omega) = V_B - \Phi_{B1}$. Substituted into Eq. (6.2), we can get the expression of the depletion width ω shown in Eq. (6.3) as a function of the build-in potential V_B , the donor concentration N_d as well as the tip radius R .

$$V_B = \frac{4\pi e N_d \omega^3}{3\epsilon_r \epsilon_0 R} + \frac{2\pi e N_d \omega^2}{\epsilon_r \epsilon_0}, \quad (6.3)$$

The detailed derivation is given in Appendix C.

Next for the second barrier $V_2(r)$ at the diamond-vacuum interface, however, it is difficult to obtain an accurate expression due to the fact that most of the potential drop appears across the diamond layer and is not extended in the vacuum gap [18]. Thus in our model, we use rough estimations expressed as $V_2(r) = \Phi_{B2} - F \cdot r$, where $\Phi_{B2} = E_{vac} - E_s$ is the barrier height, $F = e \cdot V_a / T_d$ is the assumed field strength in the vacuum and $T_d = 100$ nm is the thickness of the diamond slab [185].

6.4 Results and Discussion

Fig. 6.2 (a), (b) and (c) demonstrates the corresponding Schottky barrier profile $V_1(r)$ at different build-in potential V_B ($N_d = 10^{19} \text{ cm}^{-3}$ and $R = 10$ nm), different donor concentration N_d ($V_B = 10$ eV and $R = 10$ nm) and different metal tip radius R ($V_B = 10$ eV and $N_d = 10^{19} \text{ cm}^{-3}$) respectively. Other parameters are set as: $\Phi_{B1} =$

6.4 Results and Discussion

$3 \text{ eV} < \Phi_B$, $V_b = \Phi_{B1} - (E_s - E_f) = 2.3 \text{ eV}$ and the metal fermi energy is set to 6 eV as a reference. In Fig. 6.2 (a), as the build-in voltage V_B increases from 8 eV to 12 eV , which is equivalent to an applied voltage $V_a = V_B - V_b = 5.7 \sim 9.7 \text{ eV}$, the barrier width becomes smaller at the same energy level. Furthermore, the depletion width ω decreases with larger N_d [see Fig. 6.2 (b)] and increases with larger R [see Fig. 6.2 (c)]. An important point is worthy of mention: although ω is closely related to R and N_d , their values are usually fixed in the experiment [185], and the only adjustable parameter is the build-in potential V_B (especially N_d needs to be kept at $\sim 10^{19} \text{ cm}^{-3}$ to pin the deep donor level E_f at 1.7 eV below E_c). Hence, in our model, we will keep a constant tip radius $R = 10 \text{ nm}$ and a donor concentration $N_d = 10^{19} \text{ cm}^{-3}$ to calculate the emission current.

With the known potential barrier profile $V_1(r)$ and $V_2(r)$, we are now able to compute the emission current density J base on the electron tunneling mechanism. Previous work [189] directly used the exact expression of the FN law [9] to estimate the emission current, which was not a deliberate approach due to the fact that the local electric field at the metal tip is not uniform and the potential shape for the Schottky barrier $V_1(r)$ [see Eq. (6.2)] is not the same as the traditional FN form $V(r) = \Phi_{B1} - F \cdot r - Q/r$. Hence, it is necessary to re-derive the numerical expression for the emission current density by applying the general formula, Eq. (2.8).

$$J = \frac{em}{2\pi^2\hbar^3} K_B T \int_0^\infty \mathcal{T}(E) \cdot \ln[1 + \exp(-\frac{E - E_f}{K_B T})] \cdot dE, \quad (6.4)$$

where m is the free electron mass, $\hbar$ is the reduced Plank constant, K_B is the Boltzmann constant, T is the temperature and $\mathcal{T}(E)$ is the corresponding electron tunneling coefficient through either a single barrier [$V_1(r)$ only] or a dual-barrier [$V_1(r)$ and $V_2(r)$], e.g. see Fig. 6.1 (c) the red curve. Compared with the graphene field emission in Eq. (3.2), the transmission coefficient $\mathcal{T}(E)$ only depends on the energy E and has no dependence on the incident angle ϕ , simply because diamond is a conventional semiconductor with a parabolic dispersion $E = \hbar^2 k^2 / 2m$, and is described by the Klein Tunneling.

Figure 6.2: (a) The Schottky barrier profile (solid lines) at different build-in potential V_B at $N_d = 10^{19} \text{ cm}^{-3}$ and $R = 10 \text{ nm}$. From left to right, $V_B = 8, 10$ and 12 eV . (b) The Schottky barrier profile (solid lines) at different donor concentration N_d at $V_B = 10 \text{ eV}$ and $R = 10 \text{ nm}$. From left to right, $N_d = 10^{20}, 10^{19}$ and 10^{18} cm^{-3} . (c) The Schottky barrier profile (solid lines) at different metal tip radius R at $V_B = 10 \text{ eV}$ and $N_d = 10^{19} \text{ cm}^{-3}$. From left to right, $R = 5, 10$ and 15 nm . For all the figures, metal fermi energy (dashed line) is set at 6 eV .

6.4 Results and Discussion

Recall that there are three differences in the triple junction structure: the extra field enhancement factor, the reduction on the Schottky barrier height and the existence of the second barrier. First of all, without including the the additional field enhancement, we only consider the emission with a reduction on the Schottky barrier height ($\Phi_{B1} = 2.5$ eV) and the existence of the second barrier ($\Phi_{B2} = 1$ eV). The result [see Fig. 6.3 (a) dashed line] shows the emission current density J will reach 10^{-4} A/m² at an applied voltage V_a around 4.6 V, which is much smaller compared to the conventional diamond emitter (8 to 10 V) with barrier height $\Phi_B \approx 4$ eV. This proves that a smaller Schottky barrier height does contribute to a smaller turn-on voltage. Nevertheless, the data is still quite large compared to the triple junction experimental value (0.6 V). Thus, it is rational to include an additional enhancement factor ~ 5 at the triple junction. The results are demonstrated in Fig. 6.3 (a) solid lines at different barrier heights (from left to right, $\Phi_{B1} = 2, 2.5$ and 3.5 eV). Obviously, with this additional enhancement, the applied voltage V_a are further scaled by $1/5$, and now it shows very good agreement with the experiment data (for $\Phi_{B1} = 2.5$ eV, the turn-voltage is 0.68 V). Furthermore, the emission current density is insensitive to the second barrier height Φ_{B2} , and the numerical data for $\Phi_{B2} = 1$ eV and $\Phi_{B2} = 0.5$ eV are identical. Hence, we conclude that the extra field enhancement at the triple junction as well as the smaller Schottky barrier height is essential to yield a smaller turn-on voltage, while the existence of the second barrier has very limited effect.

We have also briefly investigated the emission process with and without light exposure. According to the experiment in Ref. [18], once the cathode is exposed to light with photon energy higher than 2 eV (the ionization energy of nitrogen), the photon-generated electrons will neutralize the nitrogen dopant. Thus, the turn-on voltage should shift to a larger value because of the reduction on the donor concentration. However, as the applied voltage increases, the dopant will be re-ionized and it will eventually recover to the emission-in-darkness characteristic at

Figure 6.3: a) The emission current density with (solid lines) and without (dashed line) the extra field enhancement at the triple junction. For solid lines, from left to right, $\Phi_{B1} = 2, 2.5$ and 3.5 eV, $\Phi_{B2} = 1$ eV. For dashed line, $\Phi_{B1} = 2.5$ eV, $\Phi_{B2} = 1$ eV. (b) The emission current density with (dashed line) and without (solid line) light exposure at $\Phi_{B1} = 2.5$ eV, $\Phi_{B2} = 1$ eV.

6.5 Summary

$V_a \approx 3$ V. In our calculation, since the exact relationship between the increment rate of the donor concentration N_d and the applied voltage V_a is unknown, we simply assume a linear relation expressed as $N_d = 10^{19} \cdot (V_a/3) \text{ cm}^{-3}$ for small applied voltage $V_a < 3$ V, and $N_d = 10^{19} \text{ cm}^{-3}$ for $V_a \geq 3$ V. Figure 6.3 (b) shows the fundamental difference between the emission in the darkness (solid line) and the emission in the light (dash line) at $\Phi_{B1} = 2.5$ eV. The turn-on voltage increases to 1.25 V with light exposure, which is comparable to the experimental value 1.6 V.

6.5 Summary

In summary, we have briefly examined the difference of the band structures between the diamond-metal-vacuum triple junction and the conventional diamond emitter. By combining the Schottky barrier model with the NEA property on the diamond surface, a model has been constructed to describe the field emission characteristic for a triple junction, which agrees well with the experimental data. Furthermore, it is found that the field enhancement at the triple junction as well as the reduction on the Schottky barrier height will result in a smaller turn-on voltage. Lastly, the emission process with light exposure will increase the turn-on voltage due to the decrement in the donor concentration. Additional discussion and future works are shown in Chapter 7.

CHAPTER 7

CONCLUSION AND FUTURE RECOMMENDATIONS

7.1 Conclusions

This thesis is focused on the modeling of field emission from various nano-materials and nano-structures. First for a single layer graphene, we investigate the deviation from the traditional FN law by considering the reduction on the dimensionality and the Klein tunneling effect [19]. This is followed by the shot noise analysis of the field emission from a single layer graphene [20]. Next, we look at the Space-charge-limited (SCL) current from a single sharp tip emitter and demonstrate the enhancement on the SCL current compared to the 1D Child-Langmuir (CL) law [21]. Furthermore, we established a criteria [22] to properly measure the average enhancement for a sharp tip emitter, which provides a guild line for the experimentalists. Finally, we build a model for the metal-diamond-vacuum triple junction structure to explain the recent experimental results [23].

7.1.1 Field Emission from Single Layer Graphene

In Chapter 3 [19], a field emission model from a vertically-aligned single layer graphene is presented based on its unique band structure and geometrical dimensionality. Since the low energy electron in the single layer graphene obeys the linear energy dispersion $E = \hbar v_F k$ (where E is the electron energy, $\hbar$ is the reduced plank constant, $V_F = 10^6$ m/s is the fermi velocity, and k is the wavevector) and behaves as massless Dirac fermion, the electron tunneling through a potential barrier can only be described by the angle dependent Klein tunneling. The result of the tunneling coefficient from the 2D Dirac equation shows a perfect transmission at normal incidence as well as a much greater overall transmission probability compared to the conventional material. Furthermore, by taking into consideration that graphene is a two-dimensional superlattice, the total emission current J must be re-derived based on the fundamental concept which has a unit of A/m instead of A/m² (the integrand is in the form of $dk_x dk_y$ instead of $dk_x dk_y dk_z$). Compared with the traditional field emission theory, the current density seems to increase linearly with the local electrical field F , which is quite different from the exponential increment behavior proposed in Fowler-Nordheim (FN) law.

Next, we continued to propose a shot noise analysis to fully understand the field emission characteristic from a single layer graphene [20]. The power spectra density S is derived from the scattering and correlation theory by including the reduction on the dimensionality and Klein tunneling effect, and the Fano factor $\gamma = S/2eI$ is subsequently computed, where e is the electron charge and I is the mean current. The result shows that at low temperature, where the shot noise comes predominantly from the quantum partitioning, the universal maximum value of $\gamma = 1/3$ is recovered at the intermediate value of the local field F , which agrees with earlier research findings [150, 152, 153, 154, 155, 156]. Nevertheless at high temperature, where the shot noise is mainly from thermal agitations, γ exceeds the 1/3 limit and eventually reach as 1 (no shot noise suppression) at extremely high temperature.

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Some key assumptions used in the derivation of the analytical model are summarized. First, this model is only valid for a large graphene sheet, so that the boundary conditions on the emission edges can be ignored (zig-zag or armchair) and we do not need to consider the edge state. Secondly, the graphene sheet is assumed to stand perpendicular on the substrate without rolling or bending, so that the electron will transmit only in the vertical direction without beam expansion and the emission current density can be calculated as proposed. Thirdly, the Hamiltonian [see Eq. (3.3)] used in the 2D Dirac equation is assumed to be from the center of the large graphene sheet, where the lattice hopping between the two atomic sets is unperturbed. Furthermore, the current density from Eq. (3.2) only considered the low energy electron where the linear dispersion is maintained and the carrier exhibits Klein tunneling behavior, so that the Fermi-energy is assumed to be maintained at a low level. Lastly, the model is established on an isolated graphene layer where the layer-layer interactions are totally ignored. This is a reasonable assumption since isolated graphene sheet can now be easily obtained in the experiment.

For the shot noise analysis, besides the assumptions stated above, we further assume that the Fano factors are computed only from the scalar potential [such as the electric potential $V(x)$] without including any vector potential (such as the magnetic field). It is proven that the universal maximum $1/3$ will not be valid once an magnetic field is present [162].

Because of all the assumptions mentioned above, it is difficult to compare our model directly with the experimental measurement due to: 1) In experiment, it is hard to control the direction and shape during the graphene growth, so that the graphene sheet is usually irregular. 2) It is difficult to isolate one graphene layer and make it stand vertically without rolling, the graphene sheets are usually grown in large amounts where the layer-layer interaction is quite significant.

7.1.2 Onset of SCL on a Sharp Tip Emitter

In Chapter 4 [21], we established a model to calculate the onset of space-charge-limited (SCL) current on a single sharp tip emitter of either Lorentzian shape or Hyperboloid shape. The methodology is summarized below: First without considering the space charge effect, by combining the emitter surface enhancement profile [see Eq. (4.1) and (4.5)] with the FN law [see Eq. (4.2)], we compute the emission current density from any point on the emitter surface. Secondly, with the known vacuum electric field [see Eq. (4.3) and (4.6)], we could simply track the electron trajectory and velocity on the vacuum space with Newton's law. Thirdly, since the electron trajectories do not cross each other, we applied the continuity equation to obtain the space charge density in the vacuum space. Lastly, we calculate the overall space charge field E_{sp} on the emitter apex and compare with the surface field $E_s = E_0 \times \beta_{max}$, where E_0 is the applied electrical field and β_{max} is the maximum enhancement value at the emitter apex. The SCL onset condition is satisfied at $E_{sp} = E_s = E_c \times \beta_{max}$, where E_c is the critical applied field.

The result demonstrates an interesting scaling that $E_c \times \beta_{max} = \text{constant}$ for various emitter geometries. This is very useful since it allows us to quickly predict the maximum field that we could apply for a given emitter geometry. Furthermore, compared to the 1D classical CL law, the enhancement μ on the emission current density are also calculated, where μ approaches to unity for a flat emitter (recovering the 1D situation) and reaches a maximum value at high sharpness condition (20 and 70 for Lorentzian shape and Hyperboloid shape respectively). Lorentzian shape has smaller enhancement than Hyperboloid shape because Lorentzian shape is sharper in nature (the enhancement decreases faster away from the apex), the beam is more concentrating at the tip region and it will reach SCL at smaller field.

Some important points are noteworthy: 1) When we track the electrons' trajectories and recording their positions and velocities, we assume that the electrons

leave the cathode surface at zero initial speed. This becomes invalid when an electron beam is injected into the cathode. 2) In our calculation, we totally ignore the carrier-carrier interactions or beam-beam interactions, this could result some deviations in our final result. However, it may take a long time and large computation power to precisely account for the interactions between so many particles, which is beyond the scope of our research. Further work will be performed to resolve this issue. 3) We only focus on the onset of the SCL condition at the emitter apex, and the smooth transitions from the FN law to the SCL limit cannot be illustrated through our method. 4) We define the effective emission area as $\beta \geq 1$ for Lorentzian shape and tip half angle $\leq 20^\circ$ for Hyperboloid shape, because it is easy to determine the integration range on the emitter surface for our simulation. However in the experiment, the enhancement profile is not direct measurable, and it might be more meaningful to define an emission area that emits 90% of the total current (directly measurable), which serves as an critical condition and offers some merit. Nevertheless, such definition will require to precisely locate the cut-off point on the emitter surface to include 90% emission current, which would bring some difficulties in the simulation.

Our model avoids solving the complicated 3D Poisson equation, and it could be useful in the quick assessment of SCL electron emission from a sharp tip in applications such as high power microwave sources [172, 173]. After further verification with well-resolved Particle-in-Cell (PIC) simulation, it may be implemented into gun-code or PIC code to avoid fine meshing (at the cathode surface) for device-scale simulation.

7.1.3 Average Enhancement of a Sharp Tip Emitter

In Chapter 5 [22], we propose a criteria to precisely determine the average enhancement factor for a sharp tip emitter. The initial steps are almost identical as in Chapter 4, where we calculate the emission current density from the emitter surface and track the electron trajectories in the vacuum. However in this case, we limited the anode area S_A which we used to collect the emission current I_{tot} . The

7.1 Conclusions

anode average emission current density J_A is subsequently obtained by dividing I_{tot} with S_A , and the average enhancement β_{ave} are then computed by fitting the gradient $-B/\beta_{ave}$ [or the interpolation $\ln(A\beta_{ave}^2)$] of the FN plot.

In our model, we first check the validity of using the anode area S_A instead of the real emission area S_K on the emitter surface, to calculate the average current density. The result clearly confirms that it is correct to replace S_K with S_A to get the enhancement. The linear curve plotted by FN law will simply shift downward without changing the gradient. Note that in a real laboratory experiment, it is impossible to directly measure S_K for a sharp tip emitter. .

Next, we investigate the effect of the anode area on the enhancement fitting result, and we define the critical anode area S_c at which the emission current I_{tot} reaches maximum (since most of the emission current concentrates near the tip region, S_c must be large enough to cover the tip region). The true average enhancement β_c can then be obtained at corresponding S_c . We also illustrate that S_c varies with the gap spacing D , and with the emitter's geometrical sharpness due to the beam expansion in the vacuum space. Note that similar as Sec. 7.1.2, an effective anode area which collects 90% of the total current may be significant for the experimentalist

Hence in a laboratory experiment, we propose to use an anode area which is large enough to collect all the emission current ($S_{tot} > S_c$) in order to obtain an accurate enhancement value β_c . In addition, we confirm that for a sharp tip emitter, due to the beam expansion and non-uniform emission feature, we can only use the gradient fitting approach to get the correct enhancement factor.

When we limit the total anode area, we still assume the applied electric field $E_0 = V_g/D$ is uniform, which is apparently not valid for a small anode area. Nevertheless, we only wish to demonstrate that at small anode area, the enhancement fitting result is not accurate, and fortunately this assumption will not affect our conclusion. Lastly, although our model is derived for the Lorentzian shape and Hyperboloid shape, the

methodology should be applicable to all protrusive shape emitters, e.g. knife-edge emitter.

7.1.4 Field Emission from Triple Junction

In Chapter 6 [23], a model has been constructed to calculate the emission current density from a metal-diamond-vacuum triple junction structure. Compared to the conventional diamond emitter, there are three major differences in the triple junction band diagram. First by applying proper reconstruction technique in the experiment such as annealing, a surface state E_s will be formed ~ 1 eV below the conduction band E_c . Hence the electron will face a lower barrier height to tunnel from the metal substrate into the diamond layer. Furthermore, besides the geometrical field enhancement on the cathode surface, there exists an addition enhancement factor at the triple junction point due to the secondary electron emission. Lastly as long as $E_c > E_{vac} > E_s$, a second barrier will be formed on the diamond NEA (negative electron affinity) surface, where E_{vac} is the vacuum energy level.

In our model, we illustrated the variation on the Schottky barrier profile $V_1(r)$ with respect to the build-in potential V_B , the donor concentration N_d as well as the metal particle radius R . It is found that the depletion width ω decreases as V_B or N_d increases or R decreases. To compare with the experiment result in Ref. [18], we fixed both R and N_d to obtain the emission current.

Without including the additional field enhancement, the emission current density will reach 10^{-4} A/m² at an applied voltage around 4.6 V, which is much smaller compared to the conventional diamond emitter of 8 to 10 V. However it is still much larger than the triple junction turn-on voltage 0.6 V until we apply an additional field enhancement factor ~ 5 . The result is now 0.68 V which is comparable with the experimental data. We further computed the emission current density with light exposure which manipulates the donor concentration. The turn on voltage will

7.2 Future Recommendations

increase to 1.25 V which again agrees well with the experimental value. We find that the existence of the second barrier on the NEA surface has very limited effect on the emission current density.

7.2 Future Recommendations

Some possible extensions of the topics of this dissertations are given as follows:

The graphene field emission model could be extended for a nano-ribbon structure if the mesoscopic or edge effect is to be considered in the model. The Hamiltonian $\hat{H}$ in the Dirac equation should be modified according to the boundary condition (zig-zag or armchair). This will directly change the transmission coefficient $\mathcal{T}$ because of the possible existence of the edge state and hence affect the shot noise result.

Due to the capability of high current emission at low turn-on voltage from the Klein tunneling model studied here, the space charge effects may become important. A model to show the transition from the Klein tunneling field emission model to the space-charge-limited (SCL) current could be constructed with a multi-dimensional quantum relativistic treatment, to include the effects of extremely small emission area, quantum, and relativistic.

The definition of the local enhancement on the graphene edge seems ambiguous to the experimentalist. A better emission potential profile by solving the 3D Poisson equation may be needed to calculate the enhancement factor on the graphene edge, so that the local electric field can be expressed as $\beta \times E_0$ where E_0 is the applied field, which is more useful in the real laboratory experiment.

The graphene field emission model can be further extended to a multi-layer model by manipulating the Hamiltonian $\hat{H}$ in the Dirac equation, e.g. double-layer graphene, triple-layer graphene. We also speculate that the emission characteristic will recover to classical FN law for the multi-layer graphite as expected for a bulk material.

To extend our onset SCL model to the knife-edge emitter requires comprehensive studies not only because it has two sharp tips (uncertain of the location of the onset SCL condition), but also due to the complexity in the mathematical model. The two sharp edge points have very large field enhancement values approaching infinity (see Eqs. (1) and (4) in Ref. [125]), and careful numerical treatment must be applied. After that, we may even try to extend it to a composite geometry of two ascending metallic protrusions to investigate the effect of multi-sharp tips.

The validity of our onset SCL model in Chapter 4 must be carefully examined with a fine-meshed PIC code. The onset critical applied electric field F_c must be simulated with respect to the emitter's geometry and gap spacing. However, it will require a large number of meshes to simulate an ultra-sharp tip. Thus, great effort must be spent on the PIC code optimization.

In chapter 5, we only focus on the total collected current in the anode. However, it will be interesting to simulate the emitted electron spectrum, which directly illustrates where the electrons are mostly emitted.

The results in Chapter 4 and 5 mainly focus on a single, isolated emitter. However in the real experiment, the emitters are usually fabricated in an array. Hence, it is necessary to extend our model to an array situation by carefully dealing with the electrostatic screening between adjacent emitters.

The field emission model from the triple junction structure can also be extended to a more general case or different dielectric materials: 1) The surface state level and deep donor level can be computed using the first principle method based on the donor concentration. 2) The potential profile at the diamond-vacuum interface can be obtained by solving the Poisson equation for different layer orientation. 3) Under ultra-high electric field, the onset of the SCL condition at the triple point needs to be calculated. Furthermore, a device-scale simulation could be performed to solve the complete 3D Poisson equation, which can provide a more precise result than our simplified model (only solve 1D Poisson equation).

7.2 Future Recommendations

The scope of this thesis focuses primarily on the numerical analysis of field emission from nanomaterials and nanostructures, and most of the results are lack of experimental justifications. In order to make our research more reliable and applicable, it will be necessary to cooperate with the experimental group to verify our theoretical models before implementing in the real device simulation. We are also interested to study more complicated situations, such as electron-photon coupling in nanomaterials and ultra-fast laser excitation on a sharp tip, which could significantly broaden our research scope.

AUTHOR'S PUBLICATIONS

Journal Papers

1. S. Sun, L. K. Ang, D. Shiffler and J. W. Luginsland. “Klein tunnelling model of low energy electron field emission from single-layer graphene sheet”, *Appl. Phys. Lett.*, **99**:013112 (2011).
2. S. Sun and L. K. Ang. “Shot noise of low energy electron field emission due to Klein tunneling”, *J. Appl. Phys.*, **112**:016104 (2012).
3. S. Sun and L. K. Ang “Onset of space charge limited current for field emission from a single sharp tip”, *Phys. Plasma*, **19**:033107 (2012).
4. S. Sun and L. K. Ang. “A Theoretical Study of the Field-Emission from a Diamond-Metal-Vacuum Triple Junction”, *J. Appl. Phys.*, **112**:066102 (2012).
5. S. Sun and L. K. Ang. “Analysis of nonuniform field emission from a sharp tip emitter of Lorentzian or hyperboloid shape”, *J. Appl. Phys.*, **113**:144902 (2013).

Conference Papers

1. S. Sun and L. K. Ang. "Space charge limited field emission from a single sharp field emitter", *8th International Vacuum Electron Sources Conference, Nanjing, China*, P-006 (2010)
2. S. Sun and L. K. Ang. "The Klein tunneling modified field-emission model for a Vertical-aligned single-layer graphene sheet", *38th IEEE International Conference on Plasma Science, Chicago, USA*, IO7B-2 (2011)
3. S. Sun and L. K. Ang. "Two dimensional Child-Langmuir law for a sharp field emitter", *38th IEEE International Conference on Plasma Science, Chicago, USA*, IP1I-53 (2011)
4. S. Sun and L. K. Ang. "Analysis of nonuniform field emission from a Lorentzian or Hyperboloid shape emitter: effective enhancement factor and emission area", *IEEE Pulsed Power & Plasma Science Conference C PPPS 2013, San Francisco, USA*, P4-44 (2013)

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APPENDIX A

FORMULATION OF THE RELATIVISTIC WKB METHODS

A.1 Wave Vector Formulation

In Chapter 3, we see that the low energy electron in the single layer graphene obeys the 2D Dirac equation with a smooth varying potential $V(x)$. Thus it is impossible to analytically match the wavefunction as M. I. Katsnelson did in Ref. [8] for a rectangular barrier. Here we present a simple numerical approximation using a recently developed Wentzel-Kramers-Brillouin (WKB) method [130, 129]. Start with the 2D Dirac equation

$$\hat{H}\Psi = E\Psi, \tag{A.1}$$

The Hamiltonian of graphene is expressed as $\hat{H} = v_F \cdot (\delta_x p_x + \delta_y p_y) + V(x)$ where $V(x) = V_0 - Fx - Q/x$, δ_x and δ_y are the Pauli's matrices expressed as

$$\delta_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \delta_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{A.2}$$

A.1 Wave Vector Formulation

$p_x = -i\hbar \frac{\partial}{\partial x}$ and $p_y = -i\hbar \frac{\partial}{\partial y}$ are the momentum operators. By considering the conservation of the transverse momentum in y -direction, a solution in the form of $\Psi = e^{ik_y y} \cdot \begin{pmatrix} \psi_A(x) \\ \psi_B(x) \end{pmatrix}$ can be substituted into Eq. (A.1) gives

$$\begin{cases} \frac{1}{\hbar v_F}[V(x) - E]\psi_A - i(\frac{d}{dx} + k_y)\psi_B = 0 \\ -i(\frac{d}{dx} - k_y)\psi_A + \frac{1}{\hbar v_F}[V(x) - E]\psi_B = 0 \end{cases} \quad (\text{A.3})$$

which can be equivalently written as two coupled differential equations

$$\begin{cases} \frac{d}{dx}\psi_A = k_y\psi_A - \frac{i}{\hbar v_F}[V(x) - E]\psi_B \\ \frac{d}{dx}\psi_B = -k_y\psi_B - \frac{i}{\hbar v_F}[V(x) - E]\psi_A \end{cases} \quad (\text{A.4})$$

For finding the quasi-classical solution of the above system, it is convenient to write equations (A.4) in the matrix form:

$$\begin{aligned} \Psi' &= \frac{1}{\hbar v_F} \Lambda \Psi, & \Psi &= \begin{pmatrix} \psi_A(x) \\ \psi_B(x) \end{pmatrix} \\ \Lambda &= \begin{pmatrix} \hbar v_F k_y & -i(V(x) - E) \\ -i(V(x) - E) & -\hbar v_F k_y \end{pmatrix} \end{aligned} \quad (\text{A.5})$$

where Ψ' is the derivative of the wave function Ψ , and Λ is indeed Eq. (3.3) mentioned in Chapter 3. Here a constant of $1/\hbar v_F$ remains in the explicit form, the prime denotes the derivative with respect to x . We will regard the solution of the matrix equation (A.5) as the formal expansion in powers of $\hbar v_F$:

$$\begin{aligned} \Psi &= \Phi \exp\left(\int^x y(x) dx\right), & \Phi &= \sum_{n=0}^{\infty} (\hbar v_F)^n \Phi^{(n)}(x) \\ y(x) &= \frac{1}{\hbar v_F} y_{-1}(x) + y_0(x) + \hbar v_F y_1(x) + \cdots \end{aligned} \quad (\text{A.6})$$

where the upper component $\Phi^{(n)}$ of the vector $\Phi^{(n)}(x)$ corresponds to the radial wave function. Note that $\Psi = \Phi \exp(\int^x y(x) dx)$ is very similar to the classical WKB wave function format where $y(x)$ is the wave vector. Hence, our primary task is to find the expression of $y(x)$.

Having submitted Eq. (A.6) into Eq. (A.5), we could obtain:

$$\begin{aligned} \frac{1}{\hbar v_F}(\Lambda - y_{-1}) \sum_{n=0}^{\infty} (\hbar v_F)^n \Phi^{(n)} = & (y_0(x) + \hbar v_F y_1(x) + \dots) \sum_{n=0}^{\infty} (\hbar v_F)^n \Phi^{(n)} \\ & + \sum_{n=0}^{\infty} (\hbar v_F)^n \Phi^{(n)'} \end{aligned} \quad (\text{A.7})$$

Now we equating to zero the coefficients of each power of $\hbar v_F$, we arrived the current system:

$$\begin{aligned} (\Lambda - y_{-1})\Phi^{(0)} &= 0, \\ (\Lambda - y_{-1})\Phi^{(n+1)} &= \Phi^{(n)'} + \sum_{k=0}^n y_{n-k} \Phi^{(k)}, \quad n = 0, 1, \dots \end{aligned} \quad (\text{A.8})$$

Using the equations of the above system by means of the left and right vectors technique, we could easily find the various term y_{-1} , y_0 , For simplicity, we will only use the first term y_{-1} in our paper. Having submitted Eq. (A.5) into Eq. (A.8), we can get:

$$\Lambda \Phi^{(0)} = \begin{bmatrix} \hbar v_F k_y \cdot \Phi_A^{(0)} - i[V(x) - E] \cdot \Phi_B^{(0)} \\ -i[V(x) - E] \cdot \Phi_A^{(0)} - \hbar v_F k_y \cdot \Phi_B^{(0)} \end{bmatrix} = y_{-1} \Phi^{(0)} \quad (\text{A.9})$$

which can be rearranged as two coupled equations:

$$\begin{cases} (\hbar v_F k_y - y_{-1})\Phi_A^{(0)} - i[V(x) - E] \cdot \Phi_B^{(0)} = 0 \\ -i[V(x) - E] \cdot \Phi_A^{(0)} - (\hbar v_F k_y + y_{-1})\Phi_B^{(0)} = 0 \end{cases} \quad (\text{A.10})$$

solve for y_{-1} by eliminating $\Phi_A^{(0)}$ and equating the coefficient of $\Phi_B^{(0)}$ to zero, we can obtain that

$$y_{-1}^2 = (\hbar v_F k_y)^2 - [V(x) - E]^2 \quad (\text{A.11})$$

which is exactly the approximation of the wave vector in Eq. (A.5), and it is proven to be the same expression used in Ref. [8, 71]. Note that Eq. (A.11) is a complete solution and y_{-1} could be either real or imaginary depending on the physical environment.

A.2 The Four Turning Points

For the electron tunneling problem in the single layer graphene, we define an effective energy $E_{eff} = E \cos \phi$, where $E = \hbar v_F k$ is the total electron energy with $k = \sqrt{k_x^2 + k_y^2}$, $k_x = k \cos \phi$ and $k_y = k \sin \phi$. Since the potential barrier $V(x)$ is in the x -direction, E_{eff} is indeed the amount of energy incident on the potential barrier. Now we are looking for the expression of the effective potential V_{eff} so that we can transform the 2D angle-dependence tunneling problem into a classical 1D case.

First if $V_{eff} \geq E_{eff}$, which corresponds to the classically forbidden region, the wave vector y_{-1} in Eq. (A.11) should be real and negative so that the wave function $\Psi = \Phi \exp(\int^x y(x) dx)$ is in the exponential-decay format to be consistent with this physical environment. The relationship between V_{eff} , E_{eff} and the wave vector should obey the linear energy dispersion as

$$\begin{aligned} V_{eff} - E_{eff} = -y_{-1} &= \sqrt{(\hbar v_F k_y)^2 - [V(x) - E]^2}, \\ \text{and} \quad (\hbar v_F k_y)^2 - [V(x) - E]^2 &\geq 0 \end{aligned} \tag{A.12}$$

In another hand, if $V_{eff} < E_{eff}$, which corresponds to the classically allowed region, the wave vector y_{-1} in Eq. (A.11) should be imaginary so that the wave function $\Psi = \Phi \exp(\int^x y(x) dx)$ is an osilating wave. Similarly as Eq. (A.12), we will obtain:

$$\begin{aligned} V_{eff} - E_{eff} = -y_{-1} &= -\sqrt{-y_{-1}^2} = -\sqrt{[V(x) - E]^2 - (\hbar v_F k_y)^2}, \\ \text{and} \quad (\hbar v_F k_y)^2 - [V(x) - E]^2 &< 0 \end{aligned} \tag{A.13}$$

Here, we denote $q = -y_{-1} = \sqrt{(\hbar v_F k_y)^2 - [V(x) - E]^2}$ for the classical forbidden region and $q = -y_{-1} = i\sqrt{[V(x) - E]^2 - (\hbar v_F k_y)^2}$ for the classical allowed region, which is the quantity we used in Chapter 3 [19].

Now for the classical forbidden region ($V_{eff} \geq E_{eff}$), $(\hbar v_F k_y)^2 - [V(x) - E]^2 \geq 0$, which can be equivalently written as:

$$\begin{aligned}
 & [V(x) - E]^2 - (\hbar v_F k_y)^2 \leq 0 \\
 \Rightarrow & [V(x) - E + \hbar v_F k_y][V(x) - E - \hbar v_F k_y] \leq 0 \\
 \Rightarrow & E - \hbar v_F k_y \leq V(x) \leq E + \hbar v_F k_y \\
 \Rightarrow & E(1 - \sin \phi) \leq V(x) \leq E(1 + \sin \phi)
 \end{aligned} \tag{A.14}$$

which is shown as the shadow part in Fig. A.1, and the four tuning points can be easily calculate by $V_{eff} = E_{eff}$ or $(\hbar v_F k_y)^2 - [V(x) - E]^2 = 0$, where $V(x) = V_0 - Fx - Q/x$

$$\left\{ \begin{array}{l} x_1 = \frac{V_0 - E(1 + \sin \phi) - \sqrt{(V_0 - E(1 + \sin \phi))^2 - 4FQ}}{2F} \\ x_2 = \frac{V_0 - E(1 + \sin \phi) + \sqrt{(V_0 - E(1 + \sin \phi))^2 - 4FQ}}{2F} \\ x_3 = \frac{V_0 - E(1 - \sin \phi) - \sqrt{(V_0 - E(1 - \sin \phi))^2 - 4FQ}}{2F} \\ x_4 = \frac{V_0 - E(1 - \sin \phi) + \sqrt{(V_0 - E(1 - \sin \phi))^2 - 4FQ}}{2F} \end{array} \right. . \tag{A.15}$$

which is indeed Eq. (3.4) in Chapter 3. The blank part outside the shadow area is the classical allowed region ($V_{eff} < E_{eff}$) which can be obtained alternatively with $(\hbar v_F k_y)^2 - [V(x) - E]^2 < 0$.

With Eq. (A.12), (A.13) and (A.15), the incident angle ϕ has been absorbed into the expressions of V_{eff} and E_{eff} , and the original angle-dependence tunneling problem has been transform into a 1D classical case, where an electron with energy E_{eff} normally incidents on a double potential barrier V_{eff} , as illustrated in Fig. 3.2.

A.2 The Four Turning Points

Figure A.1: The schematic of the four turning points. The shadow part is the classical forbidden region bound by $E(1 - \sin \phi)$ and $E(1 + \sin \phi)$, and the remaining part is the classical allowed region.

APPENDIX B

REVIEW OF SHOT NOISE OF A TWO TERMINAL DEVICE

Assume conductors with a number of leads which in turn are connect to electron reservoirs (see Fig. 1 in Ref. [192]). The final results are independent of the detailed properties of the states in the reservoirs. According to the quantum statistics, the average current in reservoir α can be expressed as:

$$\langle I_\alpha \rangle = (e/h) \int dE (-df/dE) \times [(M_\alpha - R_{\alpha\alpha})\mu_\alpha - \sum_\beta \mathcal{T}_{\alpha\beta}\mu_\beta] \quad (\text{B.1})$$

where $R_{\alpha\alpha}$ is the total reflection probability in lead α , $\mathcal{T}_{\alpha\beta}$ is the total transmission probability for carriers incident in probe β reaching probe α , f is the equilibrium Fermi function, μ_α is the chemical potential and M_α is the number of channels in reservoir α .

The calculation outlined above gives for the mean-square current in the small frequency interval Δv at probe α by assuming all contacts were connected to a reservoir at chemical potential μ_α ,

$$\langle (I_\alpha)^2 \rangle = 4\Delta v (e^2/h) \int dE f_\alpha (1 - f_\alpha) (M_\alpha - R_{\alpha\alpha}) \quad (\text{B.2})$$

In the equilibrium cross correlations we take into account that the Fermi functions at contact α and β are in general not the same, and write

$$\langle I_\alpha I_\beta \rangle = -2\Delta v kT (e^2/h) \int dE [\mathcal{T}_{\alpha\beta} f_\beta (1 - f_\beta) + \mathcal{T}_{\beta\alpha} f_\alpha (1 - f_\alpha)] \quad (\text{B.3})$$

Next we are ready to investigate fluctuations away from the average current in the presence of transport. By applying Eq. (B.2) and (B.3) and notice that all the fluctuations obey the current conservation condition

$$\langle (\sum_\alpha \Delta I_\alpha)^2 \rangle = \sum_\alpha \langle (\Delta I_\alpha)^2 \rangle + \sum_{\alpha\beta(\alpha \neq \beta)} \langle \Delta I_\alpha \Delta I_\beta \rangle = 0 \quad (\text{B.4})$$

The noise spectra or fluctuations due to transport can be expressed as

$$\begin{aligned} \langle (\Delta I_\alpha)^2 \rangle &= 2\Delta v (e^2/h) \int dE \left[\sum_\gamma \mathcal{T}_{\alpha\gamma} (f_\gamma - f_\alpha) + M_\alpha f_\alpha^2 \right. \\ &\quad \left. - \sum_{\gamma,\delta} f_\gamma f_\delta \text{Tr}(s_{\alpha\gamma}^\dagger s_{\alpha\delta} s_{\alpha\delta}^\dagger s_{\alpha\gamma}) \right] \\ \langle \Delta I_\alpha \Delta I_\beta \rangle &= -2\Delta v (e^2/h) \int dE \sum_{\gamma,\delta} f_\gamma f_\delta \text{Tr}(s_{\alpha\gamma}^\dagger s_{\alpha\delta} s_{\beta\delta}^\dagger s_{\beta\gamma}) \end{aligned} \quad (\text{B.5})$$

where $s_{\alpha\delta}$, $s_{\beta\delta}^\dagger$... etc are the elements in the scattering matrices in Ref. [158, 193].

Next we use the linearity property of the trace and obtain

$$\langle \Delta I_\alpha \Delta I_\beta \rangle = -2\Delta v (e^2/h) \int dE \text{Tr} \left[\left(\sum_\gamma f_\gamma s_{\beta\gamma} s_{\alpha\gamma}^\dagger \right) \times \left(\sum_\delta f_\delta s_{\alpha\delta} s_{\beta\delta}^\dagger \right) \right] \quad (\text{B.6})$$

Eq. (B.6) provides a convenient way of evaluating Eq. (B.5) by noticing that each sum in Eq. (B.6) is zero if the Fermi function f are the same in all reservoir.

Now consider a two terminal device at elevated temperature, let $\alpha = 1$ and $\beta = 2$, the current conservation requires that $\Delta I_1 = -\Delta I_2$. Consequently the mean square flux fluctuations are the same at each probe. The fluctuations can be obtained directly from Eq. (B.2) and (B.5) by applying $M_\alpha - R_{\alpha\alpha} = \sum_{\beta(\neq \alpha)} \mathcal{T}_{\alpha\beta}$

$$\begin{aligned} \langle (\Delta I)^2 \rangle &= 2\Delta v (e^2/h) \int dE \sum_n [\mathcal{T}_n f_1 (1 - f_1) \\ &\quad + \mathcal{T}_n f_2 (1 - f_2) + R_n \mathcal{T}_n (f_1 - f_2)^2] \end{aligned} \quad (\text{B.7})$$

Furthermore, if one terminal is vacuum or if the applied voltage is so large that transmission occurs only from left to right, we can write $f_2 = 0$, such that

$$\begin{aligned}\langle(\Delta I)^2\rangle &= 2\Delta v(e^2/h) \int dE \sum_n [\mathcal{T}_n f_1(1 - f_1) + \mathcal{T}_n(1 - \mathcal{T}_n)f_1^2] \\ &= 2\Delta v(e^2/h) \int dE \mathcal{T}_n f_1(1 - \mathcal{T}_n f_1)\end{aligned}\tag{B.8}$$

As a result, the noise power spectra $S = 2\langle(\Delta I)^2\rangle/\Delta v$ can be obtained from the above equation which is indeed Eq. (3.6) mentioned in Chapter 3.

In fact, Eq. (B.7) and (B.8) can also be viewed using the wave packet approach proposed by Th. Martin and R. Landauer [194]. For a two terminal device, the mean square current fluctuation can be written as

$$\langle(\Delta I)^2\rangle = 2\Delta v(e^2/h) \int dE \langle g^2 - \langle g \rangle^2 \rangle \tag{B.9}$$

where $\langle g^2 - \langle g \rangle^2 \rangle$ is the total deviation on the weight factor. If we assume that the wave packets incident from the right and from the left are synchronized, a transmitted wave packet from the left maps into the same state as a rejected wave packet from the right. In thermal equilibrium, with respective occupation probabilities specified by Fermi distribution functions f_1 and f_2 , there are six possible pulse histories, which are:

1. The probability for a wave packet incident from the left and the right at the same time is $f_1 f_2$, in this case, no current results.
2. The probability that both wave packets are empty is $(1 - f_1)(1 - f_2)$, again, no current is associated with this case.
3. A current +1 is measured when a wave packet incident from the left is transmitted to an empty state on the right. The weight factor for this case is $f_1(1 - f_2)\mathcal{T}$, with $\mathcal{T}$ the transmission probability.
4. A current -1 is measured when a wave packet incident from the right is transmitted to the left, with probability $f_2(1 - f_1)\mathcal{T}$ (the probability for

transmission to the right is the same as the probability for transmission to the left).

5. Same as case 3, except that the wave packet is rejected; no current results, and the weight factor is $f_1(1 - f_2)(1 - \mathcal{T})$.
6. Same as case 4, except that the wave packet is reflected; this yields $f_2(1 - f_1)(1 - \mathcal{T})$.

In cases 1, 2, 5, and 6, the deviation from the average over the set of pulses is $-\mathcal{T}(f_1 - f_2)$ (we have chosen the positive sign for carrier motion from left to right). For case 3 this deviation is $1 - \mathcal{T}(f_1 - f_2)$ and for case 4 the deviation is $1 + \mathcal{T}(f_1 - f_2)$. Now we calculate the expression $\langle g^2 - \langle g \rangle^2 \rangle$ by summing up each mean-square deviation, multiplying by its appropriate weight factor, we could get exactly the same expressions as Eq. (B.7) and (B.8).

APPENDIX C

FORMULATION OF THE SCHOTTKY BARRIER AND CURRENT DENSITY

C.1 Formulation of the Schottky Barrier

We start by writing the 3D Poisson equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V_1(r)}{\partial r} \right) = -4\pi \frac{\rho(r)}{\epsilon_r \epsilon_0}, \quad (\text{C.1})$$

where $\epsilon_r = 5.68$ is the dielectric constant of diamond and ϵ_0 is the vacuum permittivity. Next, by assuming the cathode is at zero temperature, the charge density eN_d within the depletion layer ($\rho = eN_d$) remains a constant, where e is the unit charge and N_d is the donor concentration. The universal solution of Eq. (C.1) can be expressed as:

$$V_1(r) = C_1 - \frac{C_2}{r} - \frac{2\pi e N_d r^2}{3\epsilon_r \epsilon_0}, \quad (\text{C.2})$$

where the parameters C_1 and C_2 need to be determined with proper boundary conditions.

Now considering the metal particles on the substrate as spheres with radius R , the electron transmit from the metal surface into the diamond layer will see a

C.2 Formulation of the Current Density

potential barrier Φ_{B1} , thus we have the first boundary condition $V_1(R) = -\Phi_{B1}$. Furthermore, we assume a flat band structure outside the depletion width ω and the second boundary condition can be obtained as $\frac{\partial V_1(r)}{\partial r}|_{r=R+\omega} = 0$. Substituting into Eq. (C.2), we will get C_1 and C_2 as

$$\begin{aligned} C_1 &= -\Phi_{B1} + \frac{2\pi e N_d R^2}{3\epsilon_r \epsilon_0} + \frac{4\pi e N_d (R + \omega)^3}{3\epsilon_r \epsilon_0 R} \\ C_2 &= \frac{4\pi e N_d (R + \omega)^3}{3\epsilon_r \epsilon_0} \end{aligned} \quad (C.3)$$

The only problem remaining is to determine the depletion width ω . Referring to Fig. 6.1 (c) red curve, by applying a build-in potential V_B , the band energy level will drop to $\Phi_{B1} - V_B$ outside the depletion region. As a result, we shall have $V_1(R + \omega) = V_B - \Phi_{B1}$. Substituting Eq. (C.3) into Eq. (C.2) at $r = R + \omega$, we shall have

$$\begin{aligned} V_1(R + \omega) &= -\Phi_{B1} + \frac{2\pi e N_d R^2}{3\epsilon_r \epsilon_0} + \frac{4\pi e N_d (R + \omega)^3}{3\epsilon_r \epsilon_0 R} \\ &\quad - \frac{4\pi e N_d (R + \omega)^2}{3\epsilon_r \epsilon_0} - \frac{2\pi e N_d (R + \omega)^2}{3\epsilon_r \epsilon_0} \\ &= -\Phi_{B1} + \frac{2\pi e N_d \omega^2}{\epsilon_r \epsilon_0} + \frac{4\pi e N_d \omega^3}{3\epsilon_r \epsilon_0 R} \\ &= V_B - \Phi_{B1} \\ \Leftrightarrow V_B &= \frac{2\pi e N_d \omega^2}{\epsilon_r \epsilon_0} + \frac{4\pi e N_d \omega^3}{3\epsilon_r \epsilon_0 R} \end{aligned} \quad (C.4)$$

which is indeed Eq. (6.3) in Chapter 6.

C.2 Formulation of the Current Density

From the tunneling concept, the element current density dJ through a potential barrier in x -direction between an energy interval E_x and $E_x + \Delta E$ can be expressed as

$$dJ = ev_x \cdot g(k_x) \mathcal{T}(k_x) f(E) \cdot dk_x \quad (C.5)$$

where e is the electron charge, v_x is the carrier speed, $g(k_x)$ is the density of states in k_x direction, $\mathcal{T}(k_x)$ is the corresponding tunneling coefficient and $f(E)$ is the Fermi-Dirac distribution. For a 3D material, $g(k_x)$ can be calculated as

$$g(k_x) = \int \int g'(k_x, k_y, k_z) dk_y dk_z = \int \int \frac{1}{4\pi^3} dk_y dk_z \quad (\text{C.6})$$

where $g'(k_x, k_y, k_z) = \frac{1}{4\pi^3}$ denotes the three-dimensional density of states in the momentum space. Furthermore, the energy dispersion for the conventional material is $E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$, and the velocity $v_x = \frac{1}{\hbar} \frac{dE_x}{dk_x} = \frac{\hbar k_x}{m}$. Substituting into Eq. (C.5), we can obtain

$$dJ = \frac{e}{4\pi^3 \hbar} \mathcal{T}(E_x) dE_x \int \int f(E) dk_y dk_z \quad (\text{C.7})$$

Now using polar coordinate that $k_{||}^2 = k_y^2 + k_z^2$ and $E_{||} = \hbar^2 k_{||}^2 / 2m$, we integrate Eq. (C.7) to obtain the current density as

$$J = \frac{em}{2\pi^2 \hbar^3} \int \mathcal{T}(E_x) dE_x \int f(E) dE_{||} \quad (\text{C.8})$$

Next we put in the Fermi-Dirac distribution $f(E) = \frac{1}{1 + \exp(\frac{E - E_f}{K_B T})}$ and $E = E_x + E_{||}$, the final expression can be obtained as

$$J = \frac{em}{2\pi^2 \hbar^3} K_B T \int \mathcal{T}(E_x) \ln[1 + \exp(-\frac{E_x - E_f}{K_B T})] \cdot dE_x \quad (\text{C.9})$$

Replacing E with E_x , we indeed reach Eq. (6.4).