Electron Emission Devices for Energy-Efficient Systems

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1. Introduction

Electron emission has always been an important subject for the research community. This is especially true because this fundamental concept has applications in diverse scientific and industrial fields such as material characterization, lithography, high-frequency radiations, communication, displays, sensors/detector, electronics, defense, and space exploration. Although most of the applications have high vacuum requirement, which makes the equipment assembly bulky, there are very few compatible alternatives available. This is primarily true for high-resolution imaging and lithography. From the electronics point of view, the bulky vacuum tubes were dominated by solid-state transistors due to the edge of miniaturization and the mass production capability at low cost. However, the ballistic or without scattering electron transport in a vacuum tube is still superior to the drift- and diffusion-based transport of electrons in solid transistors. Ballistic electrons in vacuum follow the Newton’s second law of motion, thereby enables ultrafast computation with faster switching speed and power efficiency.[1] Combining the benefits of both vacuum tubes and transistors, recent events in the electron field emission offer miniaturization, mass production at low cost and efficient ballistic transport of electrons in virtual-vacuum or air medium. Although these new developments are exciting and promising, there are drawbacks and challenges that need to be addressed.

As far as fundamentals are concerned, the mechanism of electron emission can be defined by four basic theoretical concepts depending on the energy level of potential barrier height measured from the vacuum level at which electrons reach the vacuum energy level either by overcoming the potential barrier or penetrating through it. A few key mechanisms and a large number of models have been proposed in development stages and been revised as per the new observations. Going further, an extensive range of materials have been studied in the past to discover the perfect emitter material. However, recent developments in electron emission materials highlight a change of research focus from exploring new materials to enhancing the performance of already established potential materials.

Abovementioned discussion highlights the vast scope and depth of research and knowledge available in the electron emission field. It becomes a tedious and time-consuming task to understand the fundamentals of electron emission, the differences between several proposed mechanisms, the application and utilization of theories, the strategies to improve emission performance, and the potential applications, especially for students and beginners.

In this article, we critically analyze the primary theoretical concepts, recent developments in source enhancements, and a wide range of applications with a targeted focus on nano-electronics. This perspective is not aimed to be a comprehensive review of large volume of studies as it is already available in the cited...
references in theories, materials, and applications sections. Rather, we identify the cohort of factors which determine the electron emission using the pre-established theoretical concepts, which can be tailored to enhance emitter performance. As such, we review current research trends focused on improving emitter properties based on material properties and electrodes geometries. Following that a brief overview of the applications in this domain is described, with focused analysis of nanoelectronic applications explored till date. We also offer a future perspective in this field, where newly resurfaced electron emission in air medium is discussed. It potentially has an edge in miniaturization, speed, and energy consumption which could revolutionize the current solid-state transistor.

Considering the vast knowledgebase in this field, scope of the cited literature here is majorly limited to last decade. Figure 1 depicts the scope of this article.

2. Generation and Transport of Electrons (Theory)

The number of electrons contributing to the ultimate emission current depends on two aspects, the number of emitted electrons and the number of transported electrons in vacuum or quasi-vacuum medium. At a fundamental level, the number of emitted electrons is related to the electrode–vacuum interface barrier height and is important to understand how electrons cross the barrier to reach vacuum level from electrode surface. Multiple stimuli are used to achieve the electron emission, such as thermal-energy (thermionic emission), photon (photoemission), ion-electron bombardment (secondary emission), and electric field (field emission). Diverse theories and formulae have been defined to calculate the electron emission under different conditions and a wide range of material are available in this domain. To simplify things here, we discuss the electron emission depending on the barrier height at which electrons escape from the electrode surface. This would provide a good understanding of electron emission mechanisms as shown in Figure 2a.

On the other hand, a limited amount of data is available on the electron transport and trajectories after the emission in vacuum. In this section, we also briefly explain these aspects.

2.1. Electron Emission

2.1.1. Fundamental Thermionic Emission Theory

Thermionic emission is a basic emission process due to thermally excited charges. When electrode is exposed to the elevated

Figure 1. An overview of electronic emission technologies and approaches. The review is divided in three subsections: the theoretical aspects of generation and transfer of the electrons, the current research trends to enhance the source performance, and the range of electron emission applications. (Acronyms: F–N: Fowler–Nordheim tunnelling, SCL: Space-charge limited current).
temperatures, electrons which are bound to the surface obtain energy to overcome potential barrier to reach vacuum level. This basic phenomenon of electron emission is called as thermionic emission or the Edison effect. The expression of thermionic emission is

\[ J = \lambda R A T^2 \exp \left( \frac{-\phi}{kT} \right) \]

(1)

where, \( J \) is the current density, \( \lambda R \) is the material specific correction factor, \( A \) is the Richardson’s constant, \( T \) is the temperature, \( \phi \) is the work function of the electrode, and \( k \) is the Boltzmann’s constant. From the Equation (1) linearity in \( \ln \left( \frac{J}{T^2} \right) \) versus \( \frac{1}{T} \) graph indicates the thermionic emission (other factors being constant) as shown in Figure 2b.\[3\]

2.1.2. Fundamental Schottky Emission Theory

Schottky emission is an electron emission process through field-enhanced thermal activation. When electrode is negatively biased with respect to the surrounding, the energy barrier height at the emitter–vacuum interface may be lowered by the image force. Image force is the effect of electrons approaching electrode–vacuum interface due to increased thermal energy, on the electrode–vacuum interface barrier height. The potential associated with these electrons lowers the barrier height. The barrier-lowering effect due to the image force is called as Schottky effect. As such, electrons near the electrode surface can overcome the energy barrier at lower level to reach the vacuum level. The expression of Schottky emission is

\[ J = A T^2 \exp \left( \frac{\phi - \beta E^2}{kT} \right) \]

(2)

where, \( J \) is the current density at temperature \( T \), \( A \) is the effective Richardson constant, \( \phi \) is the work function of the electrode, \( \beta \) is the relative dielectric constant of the electrode, \( k \) is the Boltzmann’s constant, and \( E \) is the applied electric field. From Equation (2), at a constant temperature linearity in \( \ln(J) \) versus \( E^2/kT \) graph indicates the Schottky Emission\[4,5\] (other factors being constant). A typical graph of Schottky emission is shown in Figure 2c,\[3\] commonly known as “Schottky plot”.

2.1.3. Fundamental Field Emission Theory

Field emission occurs when the energy of an incident electron is less than the potential barrier height and it still tunnels through the barrier provided the tunneling distance is thin enough.
(<100 Å) as predicted by the quantum physics, unlike classical physics where it would reflect. There are two types of field emissions; Fowler–Nordheim (FN) tunneling where electrons tunnel through the triangular region of the potential barrier and direct tunneling where electrons tunnel the full tunneling distance of the potential barrier as shown in Figure 2a. When the electric field is large enough, electrons see a triangular region of the barrier (lower tunneling distance) and emission is due to the FN tunneling. While when the electric field is not large enough, electrons see full tunneling distance and emission is due to the direct tunneling.\(^4\)

The expression of FN tunneling at absolute zero temperature is given as:

\[
J = \frac{A\beta^2 E^2}{\phi} \exp \left( \frac{-B\beta^2}{\beta E} \right)
\]  

(3)

where \(J\) is the current density, \(E\) is the electric field at the cathode, \(\phi\) is the work function of the electrode, \(A = 1.54 \times 10^{-6}\) and \(B = 6.83 \times 10^2\) are the constants, and \(\beta\) is the field enhancement factor. Further Equation (3) can be simplified as:

\[
I = aV^2 \exp \left( -\frac{b}{V} \right)
\]  

(4)

where

\[
a = \left( \frac{A\alpha\beta^2}{1.1\phi} \right) \exp(1.44B \times 10^{-7}\phi^{-1/2})
\]  

(5)

and

\[
b = 0.95B\phi^2/\beta
\]  

(6)

where \(\alpha\) is emitting area. In Equation (4), \(a\) and \(b\) being constants, linearity in \(\ln(V)\) versus \(1/V\) graph indicates the FN tunneling.\(^6\) Direct tunneling is also identified by the same graph by observing linearity at lower voltages (or electric fields).\(^7\) Both FN tunneling and direct tunneling are shown in Figure 2d.\(^7\)

As electric field emission offers an energy-efficient approach, it is the most adopted technique in the field of electron emission. We have observed a gap and confusion regarding some terminologies used in recent literature. Therefore, we would like to expand more on field emission theory to provide clarifications and provide guidelines for future developments in the scope of this review.

Applied electric field \(E\) and field enhancement factor \(\beta\) are the two quantities which can affect the device output from Equation (1). While \(E\) can be adjusted manually, \(\beta\) is given by Equation (7) when \(\phi\) of the electrode is known. Here, \(\beta\) is a unit-less quantity, \(B = 6.83 \times 10^2\) V eV\(^{-3/2}\) cm\(^{-1}\), \(d\) is the distance between anode–cathode in cm, \(\phi\) is the work function in eV, and \(m\) is the slope of the FN plot.\(^8\)

\[
\beta = B\phi^2/m
\]  

(7)

However, analysis by Wang et al.\(^9\) suggests that in case of multiple slopes in the FN plot, \(\beta\) values calculated using Equation (7) are not accurate. In that case, \(\beta\) values can be calculated using the electrode geometry.

In the geometric sense, elongated, tapered, and sharp (hemispherical) electrodes are ideal for field emission due to high aspect ratio and concentrated electric field distribution at the tip.\(^6,10\) Pogorelov et al.\(^6\) have calculated the geometric \(\beta\) value for hemi-ellipsoid model as shown in Equation (8), where \(\beta\) is the length of electrode and \(r\) is the radius of tip curvature.

\[
\beta = \frac{\pi}{\ln(\frac{\pi}{2})} - 2
\]  

(8)

Apart from the field enhancement factor \(\beta\), field factor \(\gamma\) is also considered when evaluating the field enhancement performance of a device. We have observed a confusion in recent literatures regarding the terminologies used for the field enhancement factor \(\beta\) and a field factor \(\gamma\). We underscore the difference between these two quantities here. The field factor \(\gamma\) considers the distance between anode and cathode while calculating field enhancement and thereby it has a unit of cm\(^{-1}\), whereas \(\beta\) which is unit-less and does not consider anode–cathode separation. Further information about field factor \(\gamma\)\(^6\) and its equation\(^11\) can be found in the cited references.

To summarize, electron emission mechanisms are explained here depending on the barrier height at which electrons manage to escape the electrode surface. The difference between thermionic emission, Schottky emission, FN tunneling, and direct tunneling is highlighted with the help of energy-band diagram as shown in Figure 2a. Electron emission can be achieved by multiple stimuli such as thermal, electrical, photon, and ion or electron bombardment. Purely thermionic emission occurs at temperatures generally >1700 K. This temperature can be significantly lowered using the Schottky emission under the influence of electric field. However, electrodes are still hot in Schottky emission process. On a flip side, field emission can provide the cold cathode capability which is certainly an energy-efficient approach. However, to achieve truly energy efficient field emission at lower voltages, electrode geometry has to be controlled precisely down to sub-10 nm scale. Even with the advanced nanofabrication techniques consistency and repeatability of fabrication down to such level is still a challenge.

2.2. Electron Transport

2.2.1. Space Charge Limited Current Theory

Only limited number of electrons emitted by the aforementioned mechanism(s) reaches the collector due to the space charge effect. Emitted electron does not travel instantaneously to the anode; it requires finite amount of time to travel. Due to this, a cloud of electrons forms near the electrode tip creating the negative space charge. This cloud is continuously depleted of electrons going to the collector and replenished by electrons emitted by the emitter. However, not all the emitted electrons reach collector. Due to electron-electron repulsion, they have tendency to diverge in the cloud. Electrons do not converge to reach collector as they become immobilize in the electron cloud or negative space charge. Because of this, current (or electrons) reaching
the collector is limited and the phenomenon is called as space charge-limited (SCL) current.

Before the SCL threshold, all electrons pass without being limited towards the collector. After the SCL threshold, it limits the transport of electrons reaching collector. In this regime, current follows SCL equation formulated by Child and Langmuir for planar sharp electrode in vacuum medium as follows

\[ J = \frac{4e_0}{9} \sqrt{\frac{2eV^{3/2}}{mD^2}} \]  

(9)

where \( J \) is the current density, \( e_0 \) is the permittivity of free space, \( e \) and \( m \) are the charge and mass of electron, respectively, \( V \) is the applied voltage, and \( D \) is the distance between electrodes. SCL current can be identified by the linearity in standard \( I-V \) curve with slope in the range of 1.5–1.7 in vacuum medium for parallel plates.\(^{[12]}\) A revised version of SCL for sharp tip electrodes in vacuum suggests the slope range to be 1.1–1.2.\(^{[13]}\)

Space–charge effect in semiconductors/insulators is different to vacuum and is defined by Mott–Gurney’s theory in the cited reference.\(^{[14]}\)

2.2.2. Mass-Less Approximation Theory

Besides the electron emission and effective current at the collector, another important aspect to consider in vacuum electron emission is the trajectory of electron. Emitting electron trajectories can be regarded same as the electric field lines with the assumption of “zero electron mass.” This phenomenon is known as the electron massless approximation and is used in the simulation of vacuum nano-electronic devices. This theory is more precise when field lines are closer to the straight line. In other words, smaller the curvature of electric field lines, more adequate massless approximation will be. Further information on this can be found in the cited references here.\(^{[13,16]}\)

2.3. Simulators

Theories can be applied and simulated to obtain qualitative solutions to understand device behavior. In the widely used finite element analysis (FEA), larger systems are subdivided into the smaller, simpler parts called as elements. Simple equations are applied to each element which is then combined into a larger system of equations to model the entire device behavior. This approach makes the modeling of complex geometries and irregular shapes easier with further ability to incorporate various material-specific properties. There are multiple FEA tools available such as ANSYS\(^{®}\), CST\(^{®}\), TCAD Sentaurus\(^{®}\), and COMSOL\(^{®}\) where you can perform electromagnetic potential, structural analysis, heat-transfer analysis, practical-transfer analysis, and many other physical phenomena. One great advantage of COMSOL\(^{®}\) and TCAD\(^{®}\) is that they allow “equation-based modeling,” where you can feed your own equations to the simulator to obtain FEA solutions even if they are not preloaded in the software.

However, simulators do not provide the final solution and the practical results can deviate from simulated solutions. In addition, they generate large amount of data and require advanced computer systems to operate it. Despite these issues, it is a nondestructive and cheap way to get insight into device behaviors, and fix obvious issues before fabricating the device. Few recent analytical models in the nanoscale vacuum electron emission devices provide useful guidelines and qualitative solutions to the favorable device designs, material selections, and performance enhancements.\(^{[17–21]}\)

3. Enhancement (Sources)

In the last couple of decades, large number of new materials and composites have been studied to reveal their field emission performance including different metals,\(^{[22–26]}\) semiconductors,\(^{[27–29]}\) metal oxides,\(^{[30–41]}\) sulfides,\(^{[42]}\) carbides,\(^{[43]}\) nitrides,\(^{[44–47]}\) ferrites,\(^{[48]}\) perovskite solids,\(^{[49]}\) hexaborides,\(^{[50–53]}\) and so on. Apart from these materials, low-dimensional materials are getting significant attention recently. As carbon nanotubes (CNTs) have shown exceptional field emission properties due to the high aspect ratios,\(^{[54–58]}\) various other 2D materials\(^{[59–69]}\) have also been used for enhanced field emission performance due to quantum confinement, especially in hybrid electrode designs. In addition to the aforementioned studies, Mittal et al.\(^{[70]}\) presented a comprehensive overview on the development of field emission sources.

In recent years, the focus in this field has moved from exploring new materials, to enhancing the field emission properties for stable and repeatable structures. Field enhancement factor (\(β\)) and work function (\(φ\)) of the electrode are two parameters which strongly influence field emission as stated in the theory section. Different geometries, morphologies, and hybrid designs can modulate \(β\) of anode, thus, it is important to understand surface roughness and morphology of the electrode to accurately estimate field emission current. Commonly observed morphologies are nanorods,\(^{[71]}\) nanowires,\(^{[72,73]}\) nanotubes,\(^{[44]}\) nanosheets,\(^{[41,61]}\) nanoneedles,\(^{[53,74]}\) nanocylinders,\(^{[75]}\) nanoflowers,\(^{[76]}\) nanofiber,\(^{[77,78]}\) nanoterapods,\(^{[68]}\) and nanocrystallites.\(^{[79]}\) The analysis of these studies reveals that although \(β\) is different for different morphologies, it is in the same order of magnitude. In other words, different morphologies have small effect on the overall field emission under same testing conditions. However, for those who need to critically tune the field emission performance, it is important to note the topography of the base substrate. Because growth of electrode material is independent of the substrate, but its ultimate morphology depends on it.\(^{[68,71,73,80]}\) Furthermore, a set of different processing conditions such as temperature, pressure, and RF power (in case of physical depositions) develop different morphologies, which could affect the ultimate field emission.

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3.2. Temperature

Temperature plays a role in two different ways in the process of electron emission: first, the temperature of the electrode during the field emission testing and second, temperature or annealing used as a part of fabrication process, commonly known as “annealing atmosphere engineering.”

The field emission performance of various materials has been investigated at different temperatures, such as CNTs,[81] diamonds,[82] metal oxides,[83–85] 2D materials,[86,87] and SiC.[88] Temperature has a significant effect on the field emission performance, which modulates the work function and turn-on voltage of the emitter as shown in Table 1. The effect of temperature can be further exploited with in situ temperature control to accurately control the performance of field emission devices in extreme temperature applications.

In the annealing atmosphere engineering, electrode materials are annealed at different temperatures during the fabrication. This primarily affects the crystal structure, composition, and electronic properties of the electrode, thereby influencing field emission performance. Studies have shown that annealing atmosphere engineering remarkably improved field emission in TiO$_2$,[89] ZnO,[90] and graphene.[91] In addition, annealing atmosphere engineering can promote adhesion for durable contact between base substrate and the emitters, especially nanotubes; thus, it can increase overall device stability and endurance.[92]

Apart from the above areas where temperature is applied externally, internal Joule heating effects occur at the tip of emitter due to high electric field concentration. This heating contributes to the emission current and must be considered when defining the maximum emission current. On the other hand, the melting of sharp tips has been reported in multiple studies due to excessive Joule heating near the tip region. This damages the emitter tip and degrades the emission current. A few recent studies are cited here which analyzes the effects of self-Joule heating on the emission current and emitter.[93–95]

3.3. Doping

Doping influences the work function by directly altering the interface barrier height; it can either increase or decrease the work function depending on the dopant. It can be used as a tool to achieve enhanced emission current at lower electric field thresholds. Some of the recently used dopants are metals and metal oxides including Au, Pt, Al, Cu, In,[96–100] boron,[82,101] carbon,[75] graphdiyne,[102] silicon,[103] lithium,[104] nitrogen,[74] and tin sulfide.[61] In this context, introducing oxygen vacancy doping for enhanced field emission is gaining significant interest in recent years due to its easy processing. A theoretical model that correlates the change in work function due to oxygen vacancies and a subsequent enhancement of field emission has been developed by Nandy et al.[105] In addition, few other experimental studies demonstrating the effect of oxygen vacancies on field emission have been reported for titanium oxide, zinc oxide, and cupric oxide.[105–108] Apart from these, strontium titanate oxide,[109] tantalum oxide,[110] and hafnium oxide[111] are some of the potential materials which can be explored to understand their field emission response from oxygen-deficient oxides.

3.4. Hybrid Structure

The hybrid or hetero-structures for enhanced field emission is the most commonly reported configuration. The field emission mechanism in a heterostructure is dependent on the intrinsic properties of individual materials, in particular their morphology, work function, and electrical conductivity. As such, a combination of materials with different beneficial properties can render an overall improvement in field emission performance. Hybrid structures are commonly observed in following three types.

3.4.1. By Coating

In this category, a thin layer of different material is coated on the base electrode. Thus, the combination of two different materials with different field emission competencies renders improved field emission electrode. When a material with low work function is coated on a material with high tolerance, the hybrid electrode would have both high field emission and high stability. An example of silicon nanowire and graphene-based hybrid device is shown in Figure 3.[112] Here electron emission occurs in two transport steps: electron transfer from silicon nanowire to graphene, followed by electron emission from graphene to vacuum. Electrons are easily transferred through the downhill potential of Ohmic junction through semiconducting silicon nanowire to metallic graphene. Another point to consider is that the overall field enhancement factor for this cascaded system follows two-stage field enhancement and can be presented as

$$\beta_{\text{Hybrid}} = \beta_{\text{SiNW}} \cdot \beta_{\text{Graphene}}$$  

The Ohmic contact and the two-stage field enhancement together increase the overall field emission performance. A few more recent studies in this domain are cited here[43,67,75,85,108,111–114] and some significant studies are listed in Table 1.

3.4.2. Emitters on Conductive Substrates

Fabricating emitters directly on the conducting base substrate reduces the contact resistance between electrode and substrate. Thereby, it increases the electron injection from substrate when the bias is applied through substrate resulting in higher field emission current. Few recent studies in this domain include CNT on metals,[135,136] CNT on stainless steel,[80] hybrid CNF and RGO on W-wire substrate,[125] AlN on conductive graphite,[137] and CNT on inconel superalloy.[8]

3.4.3. Conductive Adhesion between the Emitter and Substrate

An adhesion layer is required between substrate and electrode when electrodes are not directly grown/fabricated on the substrates, especially in case of CNTs. Conventional adhesive materials are polymer based which are not conductive. In this area, using conductive adhesives is recently getting some attentions to resolve high contact resistance issues, thereby increasing the electron injection, and promote device stability.[138–141]
Table 1. Comparison of field emission enhancement in sources depending on the type of study.

| Parameter | Material system | Methodology | Work function $\phi$ [eV] | Enhancement factor $\beta$ | Turn-on field $E_{\text{on}}$ [V $\mu$m/$\text{Page}^2$]$^a$ | Threshold field $E_{\text{th}}$ [V $\mu$m/$\text{Page}^2$]$^b$ | Anode–cathode spacing [\mu m] | Reference |
|-----------|-----------------|-------------|---------------------------|-----------------------------|---------------------------------|---------------------------------|-----------------------------|-----------|
| Morphology | Titania/titanate on Ti: | Alkali-controlled hydrothermal treatment of Ti surface | $\approx$4.50 | A. 1000 | A. 6.30 | A. 8.90 | 100 | [71] |
| A. 1D nanorods | | | | B. 450 | B. 7.20 | B. 9.00 | | |
| B. Mixture of 1D nanorods and 2D platelets | | | | C. 300 | C. 7.70 | C. 9.10 | | |
| C. 2D platelets | | | | | | | | |
| Morphology | CNT fibers: | Wet spinning of premade CNTs | MWNT $\approx$4.95, SWNT $\approx$5.05 | A. 26000 | A. 0.13 | 1000 | 78 |
| A. $l$ = 3.998 $\mu$m, $r$ = 50 $\mu$m | | | | B. 33000 | B. 0.10 | | |
| B. $l$ = 3.305 $\mu$m, $r$ = 50 $\mu$m | | | | C. 35000 | C. 0.09 | | |
| C. $l$ = 3.804 $\mu$m, $r$ = 22.5 $\mu$m | | | | D. 55000 | D. 0.06 | | |
| D. $l$ = 3.915 $\mu$m, $r$ = 22.5 $\mu$m | | | | | | | | |
| Morphology | NiFe$_2$O$_4$ nanocrystallites | Gas-phase condensation using: | | A. 2.30 | 1000 | [79] |
| A. DC thermal plasma arc (NF–1) | | | | B. 3.75 | | | |
| B. Chemical co-precipitation (NF–2) | | | | | | | | |
| Morphology | SnO$_2$ on graphene oxide: | Hydrothermal synthesis | 4.50 | A. 1158 | A. 7.23 | | [134] |
| A. Allium mongolicum-like | | | | B. 1762 | B. 6.08 | | |
| B. Turfgrass-like | | | | C. 2388 | C. 5.23 | | |
| C. Needle-like | | | | | | | | |
| Morphology, Hybrid | MOS$_2$–reduced graphene oxide (RGO) nanoterapods: | Hydrothermal synthesis | 5.30 (MoS$_2$) | A. 3042 | A. 4.70 | A. 7.00 | 1000 | [68] |
| A. MoS$_2$ | | | | B. 3404 | B. 4.10 | B. 4.2 | |
| B. MoS$_2$–RGO (1%) | | | | C. 3538 | C. 2.80 | C. 3.80 | |
| C. MoS$_2$–RGO (3%) | | | | D. 4128 | D. 2.60 | D. 3.10 (0.1 mA cm$^{-2}$) | |
| D. MoS$_2$–RGO (5%) | | | | E. AGFs on SiO$_2$ | | | | |
| E. AGFs on SiNWs | | | | F. AGFs on SiO$_2$ | | | | |
| F. AGFs on SiNWs | | | | | | | | |
### Table 1. Continued.

| Parameter                   | Material system                              | Methodology              | Work function $\phi$ [eV] | Enhancement factor $\beta$ | Turn-on field $E_{t0}$ [V $\mu$m$^{-1}$] | Threshold field $E_{th}$ [V $\mu$m$^{-1}$] | Anode-cathode spacing [µm] | Reference |
|-----------------------------|---------------------------------------------|--------------------------|---------------------------|---------------------------|-------------------------------------------|-------------------------------------------|---------------------------|-----------|
| Temperature, Hybrid         | VO$_2$-coated ZnO at                        | Low-temperature chemical vapour deposition (CVD) | 5.30 (ZnO), 4.10 (M1-VO$_2$), 3.65 (R-VO$_2$) | A. 3.60 | A. 5.57 | A. 9.75 | 50 | [107] |
|                            | A. 25 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | B. 45 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | C. 65 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | D. 85 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | E. 105 °C                                   |                          |                           |                           |                                           |                            |                           |           |
| Temperature                 | Plasma-treated graphene films               | CVD                      |                           |                           | Increased from 4.00 (RT) to 6.20 (50 K) as temperature decreased | 2671 (at RT) | Decreased from 1.58 (RT) to 0.65 (500 °C) as temperature increased | 700 | [74] |
| Temperature                 | SiC nanoneedles on carbon cloth             | Catalyst-assisted pyrolysis of a polymeric precursor | Decreased from 4.00 (RT) to 2.19 (500 °C) as temperature increased | 4.97 | 8600 | 0.80 | 2.40 (1.0 mA cm$^{-2}$) | 200 | [105] |
| Doping, Morphology          | TiO$_2$ nanotube arrays (TNA) at:           | Liquid-phase reduction strategy using NaBH$_4$ reducing agent | A. 0.014 | A. 5.57 | A. 9.75 | 50 | [107] |
|                            | A. 30 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | B. 50 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | C. 70 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | D. 90 °C                                    |                          |                           |                           |                                           |                            |                           |           |
|                            | E. Pristine TNA                             |                          |                           |                           |                                           |                            |                           |           |
| Doping                      | Cuprous oxide (Cu$_2$O) nanostructures      | Glancing angle deposition | 4.97 | 8600 | 0.80 | 2.40 (1.0 mA cm$^{-2}$) | 200 | [105] |
| Morphology, Doping, Hybrid  | Au capped ZnO:                             | CVD                      | A. 5.04 | A. 1.25 $\times 10^3$ | A. 0.86 | A. 1.30 | 100 | [108] |
|                            | A. Au–ZnO NW                               |                          |                           |                           |                                           |                            |                           |           |
|                            | B. Sharp-tip triangular nanoflake (TNFs) of Au–ZnO | | | | | | |
| Doping                      | Doped-graphene:                            | Freeze drying            | A. 4.25 | A. 1.07 | A. 1.70 | 200 | [99] |
|                            | A. Al-doped                                |                          |                           |                           |                                           |                            |                           |           |
|                            | B. Au-doped                                |                          |                           |                           |                                           |                            |                           |           |
| Doping, Temperature         | Cu-implanted micro-crystalline diamond      | Microwave plasma CVD followed by ion implantation | 26.66 (Undoped), 2.23 (Doped at 600 °C) | 3.10 | 6000 | 1.00 | 150 | [93] |
| Hybrid                      | RGO-coated TiO$_2$ nanotubes               | Anodization               | 3.10 | 6000 | 1.00 | 100 | [67] |
| Hybrid                      | Carbon-coated SiC nanowires                | Chemical vapor reaction   | 3.50 | 5.16 $\times 10^3$ | 0.52 (0.1 mA cm$^{-2}$) | 1.00 (0.9 mA cm$^{-2}$) | 700 | [43] |
| Hybrid                      | GeSn nanoparticles on Si nanopillars       | Epitaxial growth          | $\approx$100 | 65.00 (i = 1.0 µA) | 0.6 | [209] |
| Hybrid                      | Graphene on SiNW                           | CVD, transfer print technique | 5.00 | 9598 | 3.00 (1.0 µA cm$^{-2}$) | 3.30 (10 µA cm$^{-2}$) | 150 | [117] |
| Parameter | Material system | Methodology | Work function $\phi$ [eV] | Enhancement factor $\beta$ | Turn-on field $E_{\text{to}}$ [V $\mu$m$^{-1}$]$^{1/2}$ | Threshold field $E_{\text{th}}$ [V $\mu$m$^{-1}$]$^{1/2}$ | Anode–cathode spacing [µm] | Reference |
|-----------|----------------|-------------|---------------------------|---------------------------|---------------------------------|---------------------------------|---------------------------|-----------|
| Hybrid    | RGO on carbon nanofibers on W wire | CVD, Langmuir–Blodgett method | 5.00 | 16 432.8 | 2.54 | 750 | [125] |
| Hybrid    | Graphene sheets and Ag nanoparticles on TiO$_2$ | Anodization, electrophoretic, and chemical deposition | | | | | | |
| Hybrid    | A. Graphene-wrapped CNT (GWCNT) | CVD, solar reduction technique | A. 4.97 | A. 5300 | A. 0.81 | A. 1.03 | 500 | [131] |
| Hybrid    | B. SnO$_2$ on GWCNT | | B. 4.18 | B. 5821 | B. 0.80 | B. 0.93 | | |
| Hybrid    | C. ZnO on GWCNT | | C. 4.15 | C. 6078 | C. 0.69 | C. 0.77 | | |
| Hybrid    | D. Ru on GWCNT | | D. 4.09 | D. 6958 | D. 0.61 | D. 0.75 | | |
| Hybrid    | A. CuTCNQ (50 nm) on ZnO | Wet chemical method, CVD | A. 2.77 | A. 6559 | A. 1.15 | A. 3.75 | | [210] |
| Hybrid    | B. CuTCNQ (100 nm) on ZnO | | B. 2.77 | B. 4630 | B. 1.57 | B. 4.41 | | |
| Hybrid    | C. AgTCNQ (50 nm) on ZnO | | C. 1.19 | C. 1701 | C. 1.42 | C. 4.13 | | |
| Hybrid    | D. AgTCNQ (100 nm) on ZnO | | D. 1.19 | D. 986 | D. 1.82 | D. 4.78 | | |
| Hybrid    | E. ZnO | | E. 5.30 | E. 7645 | E. 2.01 | E. 5.25 | | |
| Hybrid    | RGO on ZnO nanowires | Spin-coating, plasma etching | 4.60 (Graphene), 5.30 (ZnO) | 10 179 | 1.80 | 4.90 (1.0 mA cm$^{-2}$) | 200 | [120] |
| Hybrid, Doping | Graphene on carbon-doped ZnO | Ion irradiation process, CVD | 4.50 (Graphene), 5.50 (C:ZnO) | 10 866 | 1.36 | 4.30 (1.0 µA cm$^{-2}$) | 100 | [75] |
| Hybrid    | Hexagonal boron nitride (h:BN) on CNT | CVD | 3.20 (h:BN), 5.00 (CNT) | | | | | |
| Hybrid    | TiO$_2$-coated CNTs | Screen-printing, sol-gel/spin-coating | 5.00 (CNT), 3.20 (TiO$_2$) (reduced by 2.00 eV in hybrid structure) | 20 000 | 0.38 | 0.66 | 300 | [129] |
| Hybrid    | Au-coated graphene | CVD, wet-transfer method | | | | | | |
| Hybrid    | A. Al-coated Si substrate – Al on CNT | | A. 0.13 | | A. 0.14 | 100 | | [126] |
| Hybrid    | B. Al-coated Si substrate – Cu on CNT | | B. 0.19 | | B. 0.22 | | | |
| Hybrid    | C. Inconel substrate – Al on CNT | | C. 0.14 | | C. 0.18 | | | |
| Hybrid    | D. Inconel substrate – Cu on CNT | | D. 0.53 | | D. 0.58 | | | |
| Hybrid    | AlN nanowires on conductive graphene sheet substrate | Catalyst-free CVD | | 3.70 | 825 | 4.90 | 6.70 (1.0 mA cm$^{-2}$) | 200 | [137] |
| Hybrid    | Graphene interfacial layer between CNT and metal | Drying process | 4.50 (CNT) | 2,120 | 1.49 | 2.00 | 500 | [139] |
Hybrid design is a practical way of achieving high-performance and stable electrodes, and is a subject of extensive research. Analysis of all the studies in this domain is beyond the scope of this article.

A few conclusive studies highlighting the effect of aforementioned four parameters on field emission properties is shown in Figure 4 and some significant studies in this domain are listed in Table 1.

### 4. Utilization (Applications)

Vacuum field emission devices (VFEDs) have diverse applications in defense, radar, space exploration, telecommunication, medicine, material processing and characterization, and electronics. The aim of this section is to provide a brief overview of the span of applications where electron emission is utilized.

#### 4.1. Electronic

##### 4.1.1. Transistors and Triodes

Design orientation of vacuum channel transistors (VCT) or triodes can be either vertical or planar, depending on the direction of emitter tip. Conventional VCT designs are shown in Figure 5.[142]

In Figure 5a, the emitter is in vertical orientation and this structure is commonly known as Spindt configuration.[143–145] Apart from Spindt configuration, volcano-type structure[146,147] is another common vertical design. Vertical designs offer high performance in electronic devices such as transistors (especially in arrays) which are mainly suitable for large area applications such as displays. On the other hand, planar designs are easy to fabricate and ideal for circuit integration. Due to the benefits planar orientation offer, multiple recent studies are focused on this, with few of the conventional designs shown in Figure 5b–d – back-gate configuration[148–150] (Figure 5b), in-plane double-gate (or multi-gate) configuration[151,152] (Figure 5c), and top-gate configuration[153] (Figure 5d). Apart from these common structures, multi-finger microtriodes[154] and stacks of electrodes structure[155] have been introduced recently.

##### 4.1.2. Other

Apart from transistors or triodes, vacuum field emission electronic devices have applications as diodes[156–160] travelling-wave tube (TWT),[161–163] oscillators,[164,165] klystrons and magnetrons,[166,167] and gyrotrons[165] for high-frequency (RF, GHz, and THz) and high-efficiency applications.

### 4.2. Sensors and Detectors

Vacuum field emission has a wide range of applications in sensors and detectors. A modulation of field emission current is considered for sensing different types of stimuli. For pressure sensors, as an example, an elastic membrane is used as collector. Change in pressure alters the emitter–collector distance, which is reflected in the field emission current down to the sensitivity of 0.16–0.78 nA Pa⁻¹.[168,169] In addition, illumination by ultraviolet

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**Table 1.** Continued.

| Parameter | Material system | Methodology | Work function ϕ [eV] | Threshold field E_th [V/μm] | Turn-on field E_to [V/μm] | Enhancement factor β | Anode–cathode spacing [μm] |
|-----------|----------------|-------------|----------------------|-----------------------------|--------------------------|------------------------|-----------------------------|
| Hybrid    | CNT on Ti substrate | CVD, vacuum brazing | 5.00 | 11,000 | 2,80 | 0.20 (1.0 ± 0.5 μA/cm²) | 500 |
| Hybrid    | CNT on inconel superalloy substrate | Water-assisted CVD | 5.00 | 11,000 | 2,80 | 0.20 (1.0 ± 0.5 μA/cm²) | 500 |
| Hybrid    | CNT on Ti substrate | Plasma-enhanced CVD, photolithography, transfer process | 5.00 | 11,000 | 2,80 | 0.20 (1.0 ± 0.5 μA/cm²) | 500 |

*Turn-on field (E_to) is the macroscopic field at which emitted current density exceeds the background noise level and produces >10 μA cm⁻². For cases where a different value has been used, this has been specifically mentioned. Threshold field (E_th) is the macroscopic field required to produce an emission current density of 10 μA cm⁻². For cases where a different value has been used, this has been specifically mentioned.*
light\textsuperscript{[170]} or external temperature\textsuperscript{[171]} provides extra energy to the emitter that is reflected on the overall field emission current resulting in a photosensor or a temperature sensor. Apart from these sensors, the modulation of field emission current has been used as biosensor for detection of avian influenza\textsuperscript{[172]} ionization guage,\textsuperscript{[86]} gas sensor,\textsuperscript{[173]} and an accelerometer.\textsuperscript{[174]}

Figure 3. Graphene coated silicon nanowires hybrid structure. a) Energy band diagram of hybrid structure. b) Schematic of hybrid structure. Reproduced under terms of the CC-BY licence.\textsuperscript{[112]} Copyright 2015, The Authors, published by Springer Nature.

Figure 4. Effect of different structural and material parameters on field emission current. a) Effect of different morphologies on field emission of carbon nanofibers (CNFs). Reproduced with permission.\textsuperscript{[175]} Copyright 2016, Royal Society of Chemistry. b) Effect of annealing on field emission of copper doped microcrystalline diamond (Cu-MCD). Reproduced with permission.\textsuperscript{[193]} Copyright 2016, Elsevier. c) Effect of gold (Au) and aluminium (Al) doping on field emission of reduced-graphene oxide (rGO). Reproduced with permission.\textsuperscript{[189]} Copyright 2015, Royal Society of Chemistry. d) Effect of tin oxide (SnO\textsubscript{2}), zinc oxide (ZnO), and ruthenium (Ru) coated hybrid structure on field emission of graphene wrapped carbon nanotubes (GWCNTs). Reproduced with permission.\textsuperscript{[131]} Copyright 2014, American Chemical Society.
4.3. Displays and Field Emission Arrays

One of the conventional and significant application of vacuum field emission is in flat panel displays, commonly known as field emission displays (FED). Itoh et al.\cite{177} and Talin et al.\cite{176} have already published in-depth overviews on FEDs. Apart from that green phosphor-based FED has been presented.\cite{177} FED requires large-area field emission sources. In that context, extensive research is ongoing for field emission arrays (FEAs) and gated-field emission arrays\cite{116,147,178,179} to modulate the emission current. Few latest significant studies are silicon-based FEA,\cite{170,171,172} diamond-based FEA,\cite{172} ZnO-based FEA,\cite{178} and CNT-based FEA.\cite{168,179,183}

Field emission displays have been thought to end in past; however, the promise of nanotubes-based FEAs has triggered a large amount of research and development in the area of nano-FEAs also known as nanoemissive displays (NED). NEDs have thought to be the technology of choice for extremely thin, ultra-high-definition, and wide-screen displays.

4.4. Lithography and Imaging

Another prime application of electron emission is in micro-nano lithography and electron imaging. Recently, field emission scanning probe lithography (FE-SPL)\cite{184,185} is getting much attention. Further, the development of field emission sources for high-resolution microscopy is an ongoing research for few decades now. Few of the recent work includes electron sources for ultrafast coherent transmission electron microscopy (TEM),\cite{186} portable absorption imaging of low-Z materials,\cite{187} carbon fiber tips for scanning tunneling microscopy,\cite{188} etc. Apart from above literature, an extensive review article on graphene for electron microscopy is reported by Shao et al.\cite{189}

4.5. Other

Apart from the aforementioned applications, the utilization of VFEDs has extended to X-ray sources,\cite{190} electric solar wind sail,\cite{191} high-frequency pulse generator,\cite{192} fast identification of conduction type of nanomaterials,\cite{193} and an electrostatic ion pump.\cite{194}

5. From Vacuum to Air Medium for Electron Field Emission

All the aforementioned applications are limited to the electron emission and its transport in the vacuum medium. Vacuum encapsulation is necessary to achieve directional and scattering-free electron transport. The scattering-free or ballistic carrier transport in vacuum follows Newton’s second law of motion and thereby has highest momentum of electrons without any resistance. This avoids any delays caused by scattering and maximizes the switching speed. But vacuum tubes require high voltages and are bulky. This is inap in the current pursuit of low power and miniaturized electronics. This is where solid-state transistors dominated the old vacuum tubes. However, going forward vacuum tubes can have remarkable future with miniaturization (especially in electronics). In this section, we provide the outlook of electron emissions, and ways to achieve miniaturization of electron emission devices which can provide competitive edge to solid-state transistors by analyzing the recent developments in vacuum channel transistors (VCTs) operating in air medium.

The first solid-state transistor was invented in Bell Labs in 1947, which soon became a dominant evolution of vacuum tubes. Vacuum tubes despite having an advantage of superior carrier transport became nearly an extinct technology as it could not keep up with the ease of fabrication and miniaturization capabilities of solid-state transistors. However, before its disappearance, researches in vacuum field emission electronics have realized the need to keep up with the competitive edge of solid-state transistors which is mainly the miniaturization. That is the concept of achieving scattering-free carrier transport in air medium or higher pressures at nanoscale was introduced in 1993 by Wong et al.\cite{195} for Au/Ti electrodes by making electrode spacing less than the mean-free path (MFP) of electrons in air. Although it was a successful experimental demonstration, this effort was unprecedented expect mere demonstrations in two decades by Driskill et al.\cite{196} in 1997, Pescini et al.\cite{197} in 2001, and Shojiro et al.\cite{198} in 2007. The concept resurfaced in 2011 by Brimley et al.\cite{199} for iridium/iridium oxide cathode working in atmospheric pressure. However, only after the successful demonstration of MOSFET analogous nanoscale vacuum-channel transistor operating in air by Han et al.\cite{142} it received significant attention. Figure 6 highlights the details of experimental and theoretical demonstrations of field emission at atmospheric temperature and pressure till date.\cite{17–21,31,62,142,196–208} Furthermore, Table 2 highlights the comparison of performance parameters for both field emission and transistor parameters (where applicable).

As for the outlook of electron field emission especially in electronics, following the current developments we believe it is in the air medium. It combines the advantage of both old vacuum tubes and current solid-state transistors. It has an advantage of not only...
Figure 6. Development of emission-based air channel electronics. Timeline for the theoretical and experimental demonstrations of field emission in air medium and its potential application as transistors. (In chronological order) Reproduced with permission.© 1993, IOP Publishing. Reproduced with permission.© 1997, AIP Publishing. Reproduced with permission.© 2001, Wiley-VCH. Reproduced with permission.© 2001, Wiley-VCH. Reproduced with permission.© 2011, AIP Publishing. Reproduced with permission.© 2012, AIP Publishing. Reproduced with permission.© 2012, Springer Nature. Reproduced with permission.© 2014, IEEE. Reproduced with permission.© 2014, Royal Society of Chemistry. Reproduced with permission.© 2017, American Chemical Society. Reproduced with permission.© 2017, Elsevier. Reproduced with permission.© 2018, American Chemical Society.
ballistic transport which can achieve faster switching speeds due to negligible scattering, but also the ease of fabrication and low power operation due to sub-100 nm device structures. Superior scattering-free carrier transport can offer computation in terahertz (460 THz) domain with better power efficiency than solid-state transistors,[1] while the ease of fabrication using standard nanofabrication processes and materials offers a low-cost technology. However, most of the demonstrations in this domain till date are in the proof-of-concept stage and much work is needed to be done before a practical employment.

Same as the conventional VFEDs, devices based on field emission in air channel can be designed in both vertical and planar orientations. The demonstrations with emitter in vertical orientation have potential application in displays and TVs. Considering this, there is a scope for the development of larger area gated vertical emitter arrays operating in air whereas planar devices are ideal for electronic integrated circuit designs. As currently all planar designs are just layered structured, they can eventually be developed in 3D architectures. Although challenging, this would utilize the vertical space in circuits, thereby increasing the number of transistors per volume. Finally, considering the fact that there are multiple successful demonstrations for field emission in air medium, this concept seems to have practical potential to revolutionize the next-generation nanoelectronics which would keep up the Moore’s law for few more decades, and apart from electronics there is a scope to reflect this concept in the other fields of applications as explained in earlier sections.

In summary, we provide a complete overview of the electron emission starting from the fundamental theory, current research directions in source performance enhancements, and its applications in diverse fields with a focus on the applications in electronics. In that context, field emission in air is getting much attention nowadays. Although research is still at an early stage, recent advancements in successful field emission in air medium and its application as transistor provide glimpses that it could one day have a significant influence on the future of the electronics industry, especially where speed, energy, and device weight is paramount.

### Table 2. Comparison of field emission devices operating in air.

| Structure Type | Channel length [nm] | Fabrication Method | Turn-on voltage [V] | Highest current-density/On current [μA] | Field enhancement factor | Threshold voltage [V] | Transconductance [μS] | Subthreshold Slope [V dec⁻¹] | ON/OFF current ratio |
|---------------|---------------------|--------------------|---------------------|----------------------------------------|-------------------------|---------------------|------------------------|-------------------------------|---------------------|
| Planar transistor | 35 | EBL | 0.57 | 1.9 (μA nmV⁻¹) | 22.5 × 10⁹ (m⁻¹) | 36 | 321.85 |
| Planar device | 10 | FIB | 0.46 | 53 | 160 |
| Planar device | 20 | FIB | 2 | 0.0325 |
| Planar transistor | <50 | Top-down silicon technology | 3 | |
| Vertical transistor | 10 | simulation | 1.2 | |
| Planar device | 15 | EBL | sub-10 | ≈10 |
| Vertical nanowires diode | UV lithography 2.9 (μm⁻¹) | 2500 |
| Vertical transistor | 20 | FIB | 0.1 | 0.02 | 500 |
| Planar transistor | 100 | Ashing technique | 3 | 2 | 2.3 | 10⁵ |
| Vertical transistor | 20 | FIB | 0.1 | 0.5 | 0.02 | 500 |
| Planar transistor | 150 | Ashing technique | 10 | 8.9 | 0.2 | 4.2 | 10⁷ |
| Planar triode | 190 | EBL | ≈0.04 | 4 |
| Vertical emitter tips | 30 | EBL, reactive ion etch | 7.5 | 10¹¹ (Am⁻²) | 1.9 × 10⁴ (m⁻¹) |
| Planar diode | <50 | EBL | 45 | 0.100 | 1.05 × 10⁻¹ (m⁻¹) |

a) Turn-on voltage is related to anode/drain voltage and is defined as the point at which electron tunnelling starts; b) Threshold voltage is gate voltage and is defined as the voltage at which drain current modulation is observed.
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Conflict of Interest
The authors declare no conflict of interest.

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