Enhanced Field Emission from Vertically Oriented Graphene by Thin Solid Film Coatings

Michael Bagge-Hansen

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Enhanced Field Emission from Vertically Oriented Graphene by Thin Solid Film Coatings

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Department of Applied Science

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Recent progress and a coordinated national research program have brought considerable effort to bear on the synthesis and application of carbon nanostructures for field emission. At the College of William and Mary, we have developed field emission arrays of vertically oriented graphene (carbon nanosheets, CNS) that have demonstrated promising cathode performance, delivering emission current densities up to 2 mA/mm² and cathode lifetime >800 hours. The work function ($\phi$) of CNS and other carbonaceous cathode materials has been reported to be $\phi$~4.5-5.1 eV. The application of low work function thin films can achieve several orders of magnitude enhancement of field emission.

Initially, the intrinsic CNS field emission was studied. The mean height of the CNS was observed to decrease as a function of operating time at a rate of ~0.05 nm/h (~40 µA/mm²). The erosion mechanism was studied using a unique UHV diode design which allowed line-of-site assessment from the field emission region in the diode to the ion source of a mass spectrometer. The erosion of CNS was found to occur by impingement of hyperthermal H and O neutrals and ions generated at the surface oxide complex of the Cu anode by electron stimulated desorption. Techniques for minimizing this erosion are presented.

The Mo₂C ($\phi$~3.7 eV) beading on CNS at previously reported carbide formation temperatures of ~800°C was circumvented by physical vapor deposition of Mo and vacuum annealing at ~300°C which resulted in a conformal Mo₂C coating and stable field emission of ~50 µA/mm². For a given applied field, the emission current was ~10² greater than uncoated CNS.

ThO₂ thin film coatings were presumed to be even more promising because of a reported work function of $\phi$~2.6 eV. The fundamental behavior of the initial oxidation of polycrystalline Th was studied in UHV (p<1x10⁻¹¹ Torr), followed by studies of thin film coatings on Ir and thermionic emission characteristics. Although a work function of 3.3 eV was determined by a Richard-Dushman plot, activation of the thin film was not achieved at T<1700°C. Rather, the deposited ThO₂ film decomposed, surface diffused and aggregated into stable ThO₂(111) crystallites.

Thin film ThO₂ coatings deposited on CNS initially demonstrated excellent field emission (up to ~2 µA/mm²) and apparently activated spontaneously without significant thermal energy. Fowler-Nordheim plots suggested a work function of $\phi$~2.6 eV. Undesired beading and ThO₂ surface diffusion away from active emission sites resulted in rapidly deteriorating performance at higher field emission currents. Techniques that should provide a more stable ThO₂/CNS conformal coating are presented.

The impact of thin films of Mo₂C and ThO₂ on the magnitude of field emission from carbon nanosheets (CNS) was substantial. For a given field emission current density, J ~2 µA/mm², the necessary applied field for uncoated CNS was ~12 V/µm, but only ~8 V/µm when coated with Mo₂C ($\phi$~3.7 eV) and ~5 V/µm when coated with ThO₂ ($\phi$~2.6 eV). The mechanism for enhanced emission and the stability of the coatings are discussed, with special focus on the activation of ThO₂ thin films. The major limitation observed in these studies has been the difference in surface energy of the graphene and the coatings which resulted in a tendency for the films to bead and separate from active emission sites at elevated currents. Suggested techniques to prevent this unwanted surface diffusion are presented.
To my mom and dad
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CHAPTER 1: INTRODUCTION

J. J. Thompson discovered the electron during his investigation of cathode rays in 1896. One hundred and fourteen years later, the controlled emission of electrons from materials continues to be a subject of significant scientific innovation and technological importance. Cathodes are a critical component in a wide variety of electronic devices and are now omnipresent in virtually all laboratories and industrial facilities. In most applications, cathodes are used to generate stable, modest electron current densities over extended lifetimes, but a rapidly growing subset of applications, especially in vacuum nano- and microelectronics\(^1\), demand very high current densities, significant miniaturization, high frequency modulation, lower thermal budget, instantaneous turn on/off and robustness. Meeting these technological demands has spurred a revival in both cathode design and novel materials research [1-3].

1.1 OVERVIEW OF CATHODE OPERATION

Most contemporary cathodes can be broadly grouped into two types, differentiated by the specific mechanism driving electron emission. Commercially employed cathodes are often operated at high temperature (typically >1100 K) and generate electrons by thermionic emission. At elevated temperature, the classical Fermi-Dirac probability distribution of occupied electron energy states

\(^1\) The term “vacuum microelectronics” is credited to the first meeting of the International Vacuum Microelectronics Conference (IVMC) in Williamsburg, VA in 1988 (see ref 7).
exhibits a Boltzmann tail extending above the Fermi level where electrons in the highest energy states have sufficient energy to exceed the local work function and escape the surface potential to vacuum. The accepted analytical description of thermionic emission is best credited to Richardson and later, Dushman. When operated in a DC loading mode, state-of-the-art thermionic cathodes can sustain current densities >5 A/cm² over lifetimes typically exceeding 10,000 h [4]. Pulsed cathodes have reported emission currents >100 A/cm² [5].

At temperatures required for operation of thermionic cathodes, chemical deterioration or poisoning of the surface is the primary source of failure. Over the operating lifetime, material is also lost to direct evaporation and surface catalyzed reactions with segregating impurities and background gases (typically H₂O, H₂, CO and CO₂). Accordingly, most cathodes are maintained in high vacuum (p<10⁻⁵ Torr). But, many materials traditionally used in the fabrication of thermionic cathodes (e.g. W) are embrittled by thermal cycling and ultimately fail from vibration or thermal shock. Robustness is often achieved by simply increasing the mass of the cathode. Considerable power must be delivered to heat the cathode to the necessary operating temperature either directly by Joule heating or indirectly by proximity to a separate heater element. Further, device components in the near vicinity must be shielded from damage by radiative heat transfer. Thus, miniaturizing thermionic cathodes for use in the next generation of vacuum nanoelectronics entails maintaining adequate cathode robustness and emission area, accommodating thermal expansion of components, integrating
suitable radiation shielding and incorporating the circuitry necessary to deliver sufficient power to the cathode. Moreover, when high frequency modulation of the electron beam is required, the cathode must be either thermally cycled or suitably gated. These demands are at best, cumbersome and, more often, irreconcilable.

In high vacuum, cathodes may also generate substantial electron current densities when in the presence of a strong external electric field (~10^7 V/cm). Field emission is a quantum-mechanical effect; that is, the probability of electrons occupying states near the Fermi level tunneling through the surface potential barrier to vacuum increases exponentially with the local applied field. Though the experimental evidence for field emission goes back more than 250 years [6,7], the foremost theoretical description was given in 1928 by Fowler and Nordheim [8]. Single field emission sources can be fabricated by fashioning (e.g. wet etching) the end of a metal wire into a conical ultra-sharp tip with a radius of curvature <1 μm down to a single atom [9] at the apex. When immersed in a uniform electric field, the local electric field at the apex is substantially (~10^3) increased. This field enhancement by local emission site geometry habilitates practical field emission devices by requiring only reasonable macroscopic fields, provided the cathode-grid spacing is small. Thus, miniaturization down to the nanometer level is now required in field emission cathode design. Further, field emission cathodes are theoretically capable of much higher current densities; e.g., W tips have demonstrated current densities up to ~10^7 A/cm^2 for over 7500
Single tip field emission cathodes are already employed in field emission microscopes and probes in electron microscopy (i.e. SEM, AES, STM, AFM, etc.). Using practical applied fields, however, cathodes for vacuum nanoelectronics applications achieve the necessary total current by an ensemble of tips or field emission arrays (FEAs), that have shown current densities up to \(\sim 10^3 \text{ A/cm}^2\) [2]. Because field emission is very sensitive to the applied field, currents generated by FEAs can be modulated at very high frequency (>500 GHz)—much higher than possible with thermionic cathodes. However, fabricating FEAs with uniform and stable field emission performance has been a major obstacle to widespread commercialization of field emission cathodes to high power/high frequency vacuum nanoelectronics [10]; the nature of these limitations will be discussed further in the next section.
1.2 APPLICATIONS OF FIELD EMISSION ARRAYS

Early vacuum tubes were the backbone of modern electronic communications [11]. As field emission cathodes available at the time required impractical electric fields, thermionic cathodes were almost universally employed. Thus, early vacuum tubes were often very large, fragile, costly to produce (many by hand), and fundamentally limited in frequency modulation by the operating temperature of the cathode. Triode tubes, such as the “lighthouse” design of the 1940s were able to achieve high frequency operation up to 4 GHz [12]. However, the invention of the transistor and the integrated circuit in the 1950s and the subsequent rapid advancement in solid-state electronics ultimately displaced many of these early vacuum tubes, mostly in low power applications. In high power, high frequency applications, vacuum tubes still dominate the technology.

Today, high power vacuum tubes are typically considered for RF amplification in the microwave regime (1 – 300 GHz). Various tube designs exist, ranging from simple triodes to inductive output amplifiers (e.g. travelling wave tubes, klystrons, klystrodes, twystrodes, etc). There are a number of fundamental considerations that make these vacuum tubes desirable over solid-state devices for this operating regime. For instance, the electron velocity in solid-state devices is limited by phonon scattering to $\sim 10^7$ cm/s [2], whereas, in vacuum, the electron velocity can approach $3 \times 10^{10}$ cm/s (light speed). Thus, in high frequency applications, the transit time for charge carriers between the source and the collector in a vacuum tube can be substantially reduced compared to a solid-
state field effect transistor which allows faster theoretical switching speeds: ~300 GHz for monolithic integrated circuits compared to >500 GHz for FEA traveling wave tubes [11]. Further, solid-state devices are sensitive to thermal degradation that significantly restricts operating lifetimes at peak power. Though the required total power density may be generated by using a large number of transistors in parallel, the efficiency obtained and space required are currently not competitive with relatively compact vacuum tubes. Therefore, vacuum tubes remain the technology of choice [13] for high frequency, high power applications in accelerator physics, radar, electronic warfare, and terrestrial and space-based communications.

With the development of solid state electronics also came technologies able to pattern materials at the micrometer scale (e.g. microlithography). This spawned two critical developments in vacuum tube technology [2]. First, the possibility of fashioning vacuum tubes with much smaller dimensions meant that practical voltages could be used to generate the very large electric fields necessary to operate field emission cathodes. Second, ensembles of ultra-sharp structures could be patterned at useful length scales to form field emission arrays. Consequently, it became feasible to replace thermionic cathodes with field emission cathodes and thereby allow major improvements in the efficiency, power density and operating frequency of microwave vacuum tubes and other vacuum nanoelectronics. This goal has not yet been achieved, chiefly because of the poor reliability of FEAs [3].
The first FEA engineering design was introduced by Spindt in 1968 [14], now known as “Spindt cathodes”. These FEAs consist of Mo cones on a Si substrate with a built-in SiO₂/Mo front gate. Similar designs based on Si have also emerged [3]. However, the field emission performance is not uniform from tip to tip. During fabrication slight differences in the geometry of the tips and gates strongly affect the local applied field and, therefore, the tunneling current. Moreover, adsorbates and impurities alter the local surface potential at the tip and perturb the local tunneling current. As a consequence of this non-uniformity, some tips operate at extremely high loads while others do not turn on at all. Those under excessive loads may arc-over, destroying large areas of the array, melting the dielectric oxide to create a short-circuit between the plane of the cathode tips and the gate plane, yielding catastrophic failure (i.e. irrecoverable damage accompanied by near-complete loss of sustainable emission current). Ion bombardment and chemical erosion further alter individual tip geometry as a function of time, often requiring incremental increases in the applied field to maintain the required current density, while simultaneously increasing the probability of catastrophic failure [3]. In the lab, these effects can be partially addressed by operating in ultra-high vacuum (UHV) conditions and by a variety of cathode conditioning schemes; however, commercial vacuum tubes do not maintain UHV conditions and conditioning has not yet proven effective enough to prolong FEA lifetimes and prevent catastrophic failure.
Robust, nanoscale materials are needed to address the intrinsic problems found with Mo and Si FEAs. Over the last few decades, a number of alternatives have emerged [3]. The most promising of these are FEAs fabricated from nanocarbon materials including: diamond-like carbon (DLC), nanotubes, nanohorns, nanowalls, and nanosheets. The C-C sp² and sp³ hybridized bonds inherent in these materials provide substantial chemical and mechanical robustness.

Further, many of these materials can be fabricated in relatively simple, scalable processes (e.g. CVD). The field emission performance of these carbonaceous materials will be discussed in chapter two. At the College of William and Mary, considerable research has been focused on developing carbon nanosheets (CNS) as field emission cathodes [15-18]. Carbon nanosheets are vertically oriented, graphitic sheets (1-7 graphene layers) that often terminate in a single graphene edge. This material has been found to be superior to CNTs in several areas, e.g., supercapacitors, catalysts, and field emission. This dissertation will expand on the field emission performance of CNS, and further explore the possibility of using ultrathin films to enhance field emission, promote emission uniformity and extend the already substantial lifetime of CNS. These efforts hope to establish paradigms for the development of commercially viable, CNS-based, field emission arrays for high power/high frequency microwave vacuum tubes.
1.3 WORK SCOPE AND ORGANIZATION

The following dissertation is broadly organized into seven chapters. Chapter two offers a more complete discussion of the historical and theoretical foundation of this work. Chapter three provides detailed descriptions of the central experimental techniques, nuances of their operation and calibration, and any custom modifications required to obtain the reported results. Chapters 4-6 discuss the results of various experimental efforts. In particular, chapter four expands on the field emission performance of uncoated carbon nanosheets and highlights vacuum-surface effects on long-term performance. Chapter five discusses efforts to enhance field emission performance and stability using thin films of selected transition metal carbides. Chapter six explores the growth and efficacy of thin thorium oxide films for enhancing field emission. Finally, chapter seven outlines a reasonable program of future research and expands the potential applications to include other technologies that may benefit from this work.
2.1 ANALYTICAL DESCRIPTION OF FIELD EMISSION

The development of quantum mechanics in the early 20th century provided the necessary tools to generate analytical descriptions of field emission. Fowler and Nordheim (FN) were first to establish a complete theory based on planar, ideal, metallic surfaces [8]. So successful was FN theory, that in subsequent work, "Fowler-Nordheim tunneling" became synonymous with field emission.

Nonetheless, numerous analytical and theoretical advances have been made in the intervening 83 years. The complete description of these transformations is beyond the scope of this work; however, the following development is a review of the most complete reformulation to date by R. G. Forbes and J. H. B. Deane [19].

Fowler-Nordheim theory essentially involves computing the tunneling probability of an electron in a given state (typically at the Fermi level, \( E_F \)) through an approximated surface potential barrier (Fig. 2.1). The field emission total energy distribution (TED) is then calculated by adding up the number of electrons that penetrate the barrier for a given energy, over all possible energies, \( E < E_F \). In an ideal metal (e.g. Al at 0 K), the population density is highest at the Fermi level. For \( T>0 \) K, the TED is the product of the tunneling probability (transport function) and the supply function (population density). Thus the TED typically exhibits a maximum near \( E_F \) [20]. Finally, the total electron tunneling probability density or field emission current density is computed by integrating the total energy distribution over all occupied states, \( E < E_F \).
Figure 2.1: Generalized schematic of field emission from a metallic surface at T=0 K (blue) and T>0 K (green) under the influence of a strong, uniform applied electric field and corrected for image potential effects. The resulting surface potential is strongly perturbed and is approximated by a rounded, triangular barrier (in red). As the field increases, the barrier narrows and the tunneling electron current increases.
An elementary form of the FN equation can be written:

\[ J = \frac{aF^2}{\phi} \exp \left[ -\frac{b\phi^{3/2}}{F} \right] \text{ A/cm}^2 \]  

(E.2.1)

Where,

\[ a = \frac{e^3}{8\pi\hbar} = 1.54 \times 10^{-6} \text{ A-eV/V}^2 \]

\[ b = \frac{8\pi\sqrt{2m_e}}{3eh} = 6.83 \times 10^7 \text{ V/cm-eV}^{3/2} \]

and \( J \) (A/cm\(^2\)) is the current density, \( F \) (V/cm) is the applied field strength and \( \phi \) (eV) is the work function.

When applied to nanostructured materials, however, the surface potential barrier in this formulation is no longer a suitable approximation; thus, the theoretical current densities are often substantially less (>10\(^2\)) than empirically measured. A correction factor, \( v \), is needed to reduce the effective tunneling barrier:

\[ J = \frac{aF^2}{\phi} \exp \left[ -\frac{v(f)b\phi^{3/2}}{F} \right] \text{ A/cm}^2 \]  

(E.2.2a)

Where,

\[ v(f) \approx 1 - f + \frac{1}{6} f \ln f \]  

(E.2.2b)

\[ f = \left( \frac{e^3}{4\pi\varepsilon_0} \right) \cdot \frac{F}{\phi^2} = (1.44 \times 10^{-7} \text{ eV}^2\text{-cm/V}) \cdot \frac{F}{\phi^2} \]  

(E.2.2c)
and $f$ is the scaled barrier field; that is, $f = F/F_n$, where $F$ is the field from FN theory, and $F_n$ is the real field required to reduce the effective tunneling barrier height such that resulting tunneling probability current more closely fits the actual emission current.

Recent studies of ultra-sharp single W tips have demonstrated that field emission currents of $\sim 35$ nA can be completely confined to a single atom at the apex [9]. When considering an array of field emission sites, as with FEAs, the apex area of tips that contribute to the emission current may be similarly confined to sub-nanometer areas. The effective emission area, $\alpha$, of an FEA is therefore only a small fraction of the total cathode area, $A$. Further, local geometry augments the local applied field and $F$, the macroscopic field, is scaled by $\beta$, the so-called field enhancement factor. Typical values of $\beta$ for carbon nanomaterials are $\sim 10^3$. The final modified FN equation for FEAs can then be written:

$$J = \frac{I}{\alpha} = \frac{a \beta^2 F^2}{\phi} \exp \left[ \frac{-v(f)b\phi^{3/2}}{\beta F} \right] \text{ A/cm}^2 \quad \text{(E.2.3)}$$

Anticipated current densities can be illustrated with an example. For a typical applied field of $F \sim 10^5$ V/cm, local field enhancement of $\beta \sim 10^3$, and a work function of $\phi = 4.5$ eV (typical for a metal) the current density is calculated to be $\sim 5 \times 10^6$ A/cm$^2$. As a reasonable approximation, the emission site area of a typical FEA is estimated to be $\alpha = 1$ nm$^2$ per cathode area $A = 1$ $\mu$m$^2$, so the area fraction is $\sim 10^{-6}$. Therefore, the theoretically expected current density is $J \sim 5$ A/cm$^2$ which
is competitive with existing thermionic cathodes. However, if, by coating or other surface modification, the work function were reduced by 1 eV, to $\phi = 3.5 \text{ eV}$, and all other parameters were unchanged, the current density would increase by more than an order of magnitude.

### 2.2 CARBONACEOUS MATERIALS FOR FIELD EMISSION

The inadequacies of Spindt and other semiconductor-based FEAs (see chap. 1) have motivated research into more robust nanomaterials. A number of fundamental considerations are necessary when evaluating potential FEA cathode materials. First, the material must be easily grown or fashioned into geometries capable of significant field enhancement. Generally, the smaller the radius of curvature for an emission site, the better the field enhancement, $\beta$, thus, ideal field emission sites are obtained at atomic scale tips and edges. However, the process of producing the material must be fully scalable; that is, emission site uniformity must be preserved in commercial production to ensure cathode lifetime and cost must be competitive with or better than solid state devices. Further, when drawing significant current densities through materials with nanometer dimensions, it is important that the thermal and electrical conductivity be high. Thermal variations can be a source of considerable emission instability as surface diffusion and chemical reordering of emission sites changes both the local work function and the field enhancement factor. Elevated temperatures can also cause significant outgassing, both from the cathode and from components in the vicinity. Because of the small dimensions required for vacuum
nanoelectronics, particularly between the cathode and gate, conductance is very low and even small pressure increases from thermally desorbed gases (e.g. H\textsubscript{2}) can rapidly exceed the breakdown threshold of the Paschen curve, precipitating electrical arc-over. Finally, the material must be chemically robust, since vacuum background gases can chemically alter and erode emission sites, i.e. change the work function and enhancement factor. Commercial vacuum tubes need active or passive gettering to maintain UHV conditions, but even so, their long-term operation requires that the surface (at the emission site) must be relatively insensitive to environmental assault from adsorbates, ion and energetic neutral bombardment, and radiation.

Carbon based nanomaterials can potentially satisfy all these requirements. Fabricating carbon FEAs began by using established techniques for growing diamond and diamond-like carbon films by chemical vapor deposition (CVD), and other approaches have since evolved (see [3] and references therein). Diamond and doped-diamond films typically exhibit very good thermal conductivity, resistance to mechanical and chemical attack, relatively sharp protrusions (high $\beta$), and negative electron affinity (NEA) [3]. That is, some diamond films, particularly those terminated in hydrogen, exhibit no potential energy barrier between the conduction band minimum and vacuum; once an electron is excited from the valence band and across the band gap, it is unbound and therefore free to leave the surface [21]. Unfortunately, when applied to FEAs, diamond films suffer from virtually all of the same problems as Spindt cathodes. Foremost is
considerable non-uniformity in the emission sites, likely exacerbated by the role of hydrogen terminations and other adsorbates on the magnitude of the local potential barrier (i.e. NEA). Further, diamond coatings are intrinsically poor electrical conductors. Providing good Ohmic contact with the substrate and establishing sufficient electron transport to emission sites have been a substantial challenge. Various schemes to include sp$^2$ character, dope with nitrogen, and reduce film dimensions have exhibited some success [3]. Individual pyramidal diamond tips have been shown to sustain currents of up to 15 $\mu$A [22], but uniform, stable, high current densities have not yet been realized from large arrays of this material.

Following their discovery by Iijima in 1991 [23], carbon nanotubes (CNTs) were quickly identified as potential field emission cathodes [24]. CNTs demonstrated robustness, superior thermal and electronic transport and <1 nm radius of curvature (single-walled CNTs) [25,26]. Conceptually, CNTs consist of a rolled sheet of sp$^2$ carbon (graphene). Depending on the angle at which the sheet is rolled and joined, it is possible to imagine a large number of different chiral and achiral structures. Different tubes can be placed concentric to one another to form multi-walled CNTs. Further variation occurs at the termination. Tips may be capped by carbon hemispheres (partial fullerenes) and may also incorporate metal impurities. Alternatively, the cap may be absent, leaving an open ring structure that may lie perpendicular to the axis of the CNT, or at some angle. The terminating edges may have dangling bonds or be either arm-chair, zigzag, or
mixed, depending on the orientation of the hexagonal array and chirality (Fig. 2.2A). These various structural permutations often have very different electrical properties including semi-metallic and metallic character. Work function measurements of various CNTs by photoelectron emission spectroscopy, Kelvin probe and F-N calculations, show variations from approximately 3.5–7.3 eV [25-27].
Figure 2.2 (A) Simulations of various terminating structures of a single-walled (5,5) CNT: (a) open-ended, H-terminated, (b) open-ended, arm-chair, (c) capped and (d) slant cut, zigzag edge [28]. (B) Turn-on distribution evinced by luminescent images of a 32 x 32 array of screen-printed CNT bundles (diam. ~200 µm) with increasing applied field (a) 3.33 V/µm, (b) 3.47 V/µm, (c) 3.60 V/µm, (d) 3.73 V/µm [29].
Adsorption further alters the surface/edge states of CNTs [30,31]. As with diamond, hydrogen can significantly influence the field emission performance [32]. Similarly, at higher current densities and over long periods of operation adsorbates may desorb, form complexes and destabilize emission behavior. The synthesis of CNT-FEAs, however, is the primary difficulty. The initial growth of CNTs for FEAs is often done by CVD, but also laser ablation, or arc discharge. In CVD growth, a catalyst is required, such as Fe or Ni. These metals can be patterned onto the substrate and the nanotubes grown in the selected areas. In other fabrication paradigms, the nanotubes are removed, bundled and immersed in a matrix that can be patterned on to ITO or other temperature sensitive substrates. The uniformity of these arrays has been a significant technological hurdle (Fig 2.2 B) [29,33]. In addition to the various structural permutations, edge terminations and adsorbate effects outlined above, height uniformity is also problematic. When an individual CNT extends further from the substrate than others in its vicinity, it experiences a greater applied field, screens other emission sites and effectively prevents efficient, uniform operation of the array [34].

Promising results have been achieved with some patterned arrays. For instance, C. Li. et al. recently reported current densities up to 1.5 A/cm² at applied fields < 5 V/μm and lifetime data for ~140 h at 200 mA/cm² [35]. Although stable high current density CNT-based FEAs are only now emerging, individual CNTs can been readily implemented as field emission cathodes in applications such as electron microscopes. Recent literature has shown individual CNTs capable of
producing a field emission current of 200 nA under an applied field of ~2.7 V/μm with no damage [33].

Carbon nanowalls (CNW) have also emerged as potential field emission cathodes [36-43]. Typically grown using plasma enhanced (PE) CVD, these films consist of roughly vertically oriented graphite flakes. The outboard edges of these flakes vary considerably in thickness (5-50 nm) and are considered candidate edge emitters. Early work by A. N. Obraztsov et al. demonstrated the growth of CNW, ~10-50 nm thick, with DC field emission current densities up to ~5 mA/cm² [36,37]. CNW structures with wall thicknesses of 10-20 nm have also shown repeatable field emission current densities of ~1 mA/cm² [40,41].

Research at the College of William and Mary has produced carbon nanosheets (CNS)—a substantial advancement over existing CNW structures. These carbon nanosheets are grown by PE-CVD for a variety of applications, including field emission cathodes [15-18]. The CNS are also vertically oriented, graphitic sheets, but are much thinner than CNW; wall thickness is typically 1-7 atomic layers (~0.3–3 nm) with terminating structures often only 1 atomic layer (i.e. graphene). These atomically sharp edges provide excellent field emission sites. Graphene is a large two-dimensional array of sp² hybridized carbon. The properties of graphene and multi-layer graphene have been well documented in the recent literature ([44-52], and references therein). These properties are ideal for high current field emission cathodes. Graphene has a reported thermal conductivity of 5000 W/m K, compared to 1000 W/m K for diamond at room
temperature [53]. The breakdown current density for a graphene nanoribbon has been measured at \( \sim 10^8 \text{ A/cm}^2 \) down to ribbon width of 16 nm [54]. Moreover, because electrons in perfect graphene behave like mass-less Dirac fermions, electron transport is theoretically ballistic; that is, electrons are only forward scattered. Electron mobility exceeds 15,000 cm\(^2\)/V-s and is only weakly temperature dependent [47]. Thus, the vertically-oriented graphene terminations of CNS should provide robust field electron emission sources with the potential of delivering very high current densities. The field emission performance of CNS will be discussed further in chapter four.
2.3 THIN FILM COATINGS FOR ENHANCED ELECTRON EMISSION

This section discusses the motivation for using thin films coatings to augment electron emission from cathodes. The general intent is to lower the work function, particularly over the emitting surface area. Since the work function for CNS terminations is so high (usually 4.5 – 5.1 eV), coatings offer a very pragmatic improvement to this issue. This has been done successfully with thermionic cathodes and, to a lesser degree, with field emission cathodes.

2.3.1 MATERIAL WORK FUNCTION

The work function, \( \phi \), of a material is the \textit{minimum} energy required to remove an electron from the interior of a solid to a position just outside the surface (in vacuum) such that it may be considered a free electron [55]. For an ideal metal, the work function is simply the height of the energy barrier between the Fermi level \( E_F \) and vacuum where \( E_{\text{vac}} = 0 \):

\[
\phi = E_{\text{vac}} - E_F \tag{E. 2.4}
\]

The work function, as defined, is illustrated in Figure 2.1. The theoretical origin of the work function arises from fundamental considerations in solid state physics. The most basic model of a solid assumes a perfect three-dimensional periodic array of atoms. The (periodic) potential, \( V \), at each point in the array, \( r \), is found by integrating the charge density over the primitive cell (i.e. each Wigner-Seitz cell) after [55]:

\[
\]
\[ V(r) = -e \int_{\text{cell}} \frac{\rho(r')}{|r-r'|} \, dr' \]  
(E. 2.5a)

Making the multipole expansion yields\(^2\):

\[ V(r) = -e \frac{Q}{r} - e \frac{\mathbf{p} \cdot \hat{r}}{r^2} + \frac{1}{r^5} \]  
(E. 2.5b)

Where, the total charge in the Wigner-Seitz cell is:

\[ Q = \int_{\text{cell}} \rho(r') \, dr' \]  
(E. 2.5c)

and the total dipole moment:

\[ \mathbf{p} = \int_{\text{cell}} \mathbf{r}' \rho(r') \, dr' \]  
(E. 2.5d)

In the interior of a uniform, symmetric and neutral solid, with periodic charge density \( \rho(r') \), the total charge, \( Q \), must equal zero and the dipole moment, \( \mathbf{p} \), must also vanish. Thus, from E. 2.5b, the contribution to the potential at \( r \) decreases \( \sim 1/r^5 \). Therefore, if a surface is introduced as a perfect truncation of the solid's periodicity, the potential would fall off rapidly \( \sim 1/r^5 \) to zero for \( r \) positioned just outside the solid. If \( V(r) \) is zero just outside the solid, and the conduction electrons in the solid are at the Fermi energy, then the energy required to extract an electron would be just the Fermi energy (E. 2.4).

\(^2\) The \( 1/r^3 \) term and \( 1/r^4 \) term have been dropped for clarity; in a (cubic) solid with inversion symmetry, these terms are necessarily zero to preserve symmetry.
It is then tempting to consider approaching the work function of real materials from first principles; however, a number of the above assumptions must be amended. Real surfaces are decidedly not perfect truncations of crystalline solids. The positions of atoms, even in a pure material, are almost always rearranged to minimize the surface energy by relaxation and/or reconstruction. Consequently, the charge density is distorted. The symmetry and neutrality arguments evoked before are no longer valid; that is, the value of $Q$, and $p$ (E.2.5c-d) need not be zero for $r$ near the surface. The presence of a net surface dipole or double layer gives rise to a large local electric field, $V_{surf}$, where the real work function must be the sum of at least two components: the Fermi energy (relative to $E_{vac}$), which represents the binding energy of an electron to the bulk, and the work required to move an electron through the surface double layer:

$$W_s = \int eV_{surf} \, dx$$

(E. 2.6a)

$$\phi = E_{vac} - E_F + W_s$$

(E. 2.6b)

The effect of the double layer is substantial. H. Kawano has produced a remarkable review of work function data [56]. In this work (with more than 1350 references), he demonstrates that the work function, even for near-ideal preparations, is very sensitive to the exact condition of the surface. For example, measurements of polycrystalline metal surfaces can vary by more than 1 eV; moreover, the measured work function of different single crystal faces varies considerably: e.g., $Ta(100) = \sim 4.2$ eV, $Ta(110) = \sim 4.8$ eV. Further, adsorbates can
significantly affect the work function. It is observed, for instance, that
electronegative species (e.g. oxygen) tend to increase the work function (Fig 2.3)
and is thought to increase the net dipole moment (\(p\)) at the surface, and by
extension, \(W_s\). Furthermore, the work function need not be uniform across a
surface. The presence of local defects, adsorbates, and roughness give rise to
an effective work function, which is essentially an average of a spatial distribution
function. Evidently, it is intractable to calculate the work function analytically[56-
58] without precise knowledge of the local charge distribution at the surface of a
solid.
Monolayer coverage

Figure 2.3: The work function change of Pt (111) as a function of adsorbed oxygen [56].
2.3.2 TUNING THE WORK FUNCTION

The effective work function of the active emission area is the appropriate value ($\phi$) in both the Richardson-Dushman equation for thermionic emission and the Fowler-Nordheim equation for field emission (E. 2.3). The substantial change in the work function by the addition of an adsorbed monolayer (ML) suggests that very thin films can lower the effective work function and substantially improve cathode emission behavior.

2.3.2.1 LOW WORK FUNCTION COATINGS FOR THERMIONIC EMISSION

The operating temperature of thermionic cathodes severely limits their efficiency and useful application (see chapter one). Coatings of low work function materials have been used since the 1930s to reduce the operating temperature of thermionic cathodes [4]. These coatings were typically BaO, SrO, BaO/SrO, or ThO$_2$ on a range of substrate materials—often W, Ir, or Ni. Though BaO and SrO coatings can provide very high pulsed emission current densities (>100 A/cm$^2$), they are easily poisoned, and sensitive to ion bombardment and evaporation. These materials (esp. BaO) have subsequently been engineered for dispenser cathodes where BaO is impregnated into the pores of a metal matrix (e.g. W, Os, Ir) and migrates to the surface to form a continuously supplied monolayer of Ba/BaO [59]. Similar approaches have been successful at implementing very high power cathodes from scandate (Sc$_2$O$_3$). Coatings (~500 nm thick) composed of noble metals, including Os, Os-Ru, Ir, and Re, have also been used
to improve efficiency of high power cathodes where they also demonstrate improved emission uniformity [60]. However, these metal coatings often form alloys and interdiffuse with the metal substrate and thus the work function changes drastically as a function of time. LaB$_6$ and CeB$_6$ have also emerged as popular low work function coatings for thermionic cathodes and have reported work functions of $\sim$2.7 eV [56,61]. However, maintaining the stoichiometry of these coatings is problematic.

Before dispenser cathodes were developed, ThO$_2$ was the preferred choice for cathodes providing high DC currents [62,63]. Many instruments, e.g., ion gauges and mass spectrometers, still use ThO$_2$ coatings ($\sim$50 $\mu$m thick) on W and Ir to improve the efficiency of thermionic electron sources, lowering the operating temperature from $\sim$2300 K to $\sim$1700 K. As with most of the oxide cathodes discussed, ThO$_2$ cathodes often require high temperature “activation,” in some cases up to 2000 K which lowers the work function from $\sim$3.2 eV to $\sim$ 2.8 eV. Without access to modern surface science techniques, early cathode research was mostly phenomenological and the atomistic mechanism suggested by thermal activation was not sufficiently addressed. Three theories emerged [4]. (1) Thermal treatment produces free, Th metal atoms which self-dope the thoria film, providing n-type semiconductor behavior. The presence of a strong surface dipole due to excess metal at the surface generating high positive charge at the vacuum interface has also been suggested. (2) Activation opens pores in the material and emission current travels in these pores. (3) Emission may also be
enhanced by surface conduction along the walls of pores and crevices in the film. Of these theories, (1) seems most probable given the thickness of reported coatings and research elaborated elsewhere in this dissertation (chapter 6). Nonetheless, ThO$_2$ coatings offer a robust, low work function coating that has proven (and continued) efficacy in real devices. The possibility of using ThO$_2$ for field emission enhancement is discussed in detail in chapter six.

2.3.2.2 LOW WORK FUNCTION COATINGS FOR FIELD EMISSION

The use of thin solid coatings to enhance the field emission behavior of various carbonaceous cathode materials (see 2.2) is reviewed in table 2.1. Though much of the reported data is for coating of CNTs, some general comments can be made. First, the description of field emission from these materials is not well-approximated by the tunneling diagram in figure 2.1. Rather, electrons must first tunnel through the interface between the CNT to available electronic states in the coating and once again, from the coating to vacuum. This is especially true for oxide coatings [64]. The nature of this two-step barrier is still unclear (see ref. table 2.1); however, if the FN equation (E. 2.3) is preserved, then these corrections are folded into the effective work function. Second, numerous reports have confirmed that the enhancement of field emission is a function of thickness. For example, CNTs coated with TiC for 2 minutes (<8 nm) exhibited improved field emission, while coating for 10 minutes (<40 nm) substantially reduced emission performance when compared with as-grown CNTs [65]. Therefore, potential low work function coatings for enhanced field emission must address
the same material considerations outlined in 1.1.2, but also the ideal thickness and interface with emission sites must be carefully parameterized.

Table 2.1

<table>
<thead>
<tr>
<th>Coating</th>
<th>t (nm)</th>
<th>Subs.</th>
<th>Treatment (if any)</th>
<th>( \frac{J_{\text{COAT}}}{J_{\text{SUB.}}} )</th>
<th>( J_{\text{MAX}} ) (mA/cm²)</th>
<th>F (V/μm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOₓ</td>
<td>~1-2</td>
<td>CNT</td>
<td>acid (pre-t)</td>
<td>3</td>
<td>6</td>
<td>2.5</td>
<td>[64]</td>
</tr>
<tr>
<td>TiC</td>
<td>&lt; 8</td>
<td>CNT</td>
<td>1200 K</td>
<td>6</td>
<td>14</td>
<td>2.5</td>
<td>[65]</td>
</tr>
<tr>
<td>BaO/Sr  𝑂</td>
<td>100</td>
<td>CNT</td>
<td>--</td>
<td>2</td>
<td>2</td>
<td>4.4</td>
<td>[66, 67]</td>
</tr>
<tr>
<td>HfC</td>
<td>5</td>
<td>CNT</td>
<td>1500 K</td>
<td>10</td>
<td>5</td>
<td>4</td>
<td>[68]</td>
</tr>
<tr>
<td>BN</td>
<td>23</td>
<td>CNT</td>
<td>--</td>
<td>( \sim 10^2 )</td>
<td>3</td>
<td>( \sim 45 )</td>
<td>[69]</td>
</tr>
<tr>
<td>Ti, Al, Mo, Ni</td>
<td>30</td>
<td>DIAM.</td>
<td>--</td>
<td>22</td>
<td>1.3</td>
<td>( \sim 20 )</td>
<td>[70]</td>
</tr>
<tr>
<td>Ru 𝑡</td>
<td>&lt; 3</td>
<td>CNT</td>
<td>--</td>
<td>( \sim 10^2 )</td>
<td>2</td>
<td>4</td>
<td>[71]</td>
</tr>
<tr>
<td>HfC</td>
<td>&lt;50</td>
<td>CNT</td>
<td>2100 K</td>
<td>2</td>
<td>0.32</td>
<td>1.3</td>
<td>[72]</td>
</tr>
<tr>
<td>Ti</td>
<td>5</td>
<td>CNT</td>
<td>--</td>
<td>4</td>
<td>0.2</td>
<td>6</td>
<td>[73]</td>
</tr>
<tr>
<td>Ti 𝑡</td>
<td>2</td>
<td>CNW</td>
<td>--</td>
<td>1.6</td>
<td>42</td>
<td>10</td>
<td>[74]</td>
</tr>
<tr>
<td>Au, Ti, Al</td>
<td>5</td>
<td>CNW</td>
<td>--</td>
<td>2.3</td>
<td>30</td>
<td>10</td>
<td>[75]</td>
</tr>
</tbody>
</table>

*Data shown for selected film; †Not a continuous film
CHAPTER 3: EXPERIMENTAL SYSTEMS

This chapter introduces the numerous experimental systems and techniques required for this work. For clarity, these can be broadly grouped into three overlapping classifications: (3.1) the apparatus and techniques used for growth of carbon nanosheets, post-growth thin film coating and processing, (3.2) characterization systems and techniques used to assess surface composition, chemistry, and morphology and (3.3) field emission test systems.

3.1 SAMPLE FABRICATION AND PROCESSING

This section will briefly introduce radio frequency (RF) plasma-enhanced chemical vapor deposition (PE-CVD) for growth of carbon nanosheets (CNS) — a method developed at the College of William Mary. Also described is a UHV physical vapor deposition system developed for thin film coating of CNS.

3.1.1 PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

Carbon nanosheet samples were grown by RF-PECVD as either (1) 3 - 5 mm diameter dots (using Al₂O₃ masks) on 6 x 6 mm² coupons, or (2) blanket samples on 5 x 25 mm² strips. Typical substrates used in these studies were n-type Si (100), and polished polycrystalline Ta (0.5 mm thick). The samples were cleaned in acetone, rinsed in isopropyl alcohol, air-dried and placed on a heated ceramic stage in the center of a stainless steel vacuum growth chamber (Fig. 3.1).

Because the samples must be in uniform contact with the stage for consistent
growth, a heavy stainless steel mask is sometimes used to pin the sample. The system is evacuated by a Al₂O₃-trapped mechanical pump to ~1x10⁻³ Torr. The stage is comprised of a number of parallel Al₂O₃ tubes threaded with 250 µm W wire; this filament is used to heat the stage by applying DC current step-wise up to ~5.2 A, corresponding to a sample temperature of >1000 K. The emissivity, surface area, and mass of different materials and sample geometries necessitate careful temperature calibration. An inductively coupled plasma (RF at 13.56 MHz, 900-1200 W power) is created via a three-turn, coiled, planar Cu external antenna parallel to a quartz window on top of the growth chamber. The system is evacuated to ~2 mTorr and back-filled with a 60/40 H₂/Ar mix via MKS 10 sccm flow controllers for ~10 minutes. Initiating the RF provides glow discharge cleaning by sputtering the sample surfaces. The substrate is then heated to the desired temperature and the gas composition changed to 40% CH₄, 60% H₂ to a total pressure of 100 mTorr. After 20 minutes, the resulting film consists of ~10 nm of graphitic islands that turn vertical at the grain boundaries forming multilayered sp² carbon sheets that are vertically oriented and approximately 600 nm in height [16-18]. The thickness of the sheets averages ~3 layers, often terminating with a single graphene sheet. The synthesis model is detailed in previous work [76]. Recent work [77] has demonstrated that substantial improvements in CNS morphology are achieved by changing the feedstock gas composition from 40% CH₄ to 80% C₂H₂ (balance H₂).
RF power
13.56 MHz
~1kW

Typical conditions:
RF 900-1200 W
CH₄ (C₂H₂) / H₂
900-1200 K
50-500 mTorr
5-120 min

Figure 3.1: A basic schematic of the PE-CVD system and the conditions typically used in the growth of carbon nanosheet field emission arrays (see text). Growth proceeds on any substrate that can be processed above ~1000 K [76].
3.1.2 UHV PHYSICAL VAPOR DEPOSITION OF THIN FILMS

Physical vapor deposition (PVD) is an established technique for vacuum thin film deposition, both in laboratory and industrial settings. A variety of PVD methods exist (e.g. laser ablation, magnetron sputtering and thermal or electron beam evaporation). In all cases, a solid source is used to generate a gas phase flux, emitted more or less along the local surface normal depending on the method, which then impinges and condenses on a static or rotating sample. The evaporative flux density is directly related to the vapor pressure of the source material. The desired evaporative flux density (i.e. deposition rate) is delivered by adjusting the temperature of the source material. In fact, the vapor pressure is nearly exponentially dependent on the surface temperature of the source (Fig. 3.2).

![Graph](image)

Figure 3.2: The vapor pressure of thorium up to the melting point at 2023 K [53].
Simple PVD systems can be constructed by resistively heating a material to high temperature; however, to obtain reasonable flux density, it is often necessary to exceed the melting point of the material. This is often achieved by placing powdered source material in a W, Ta, Cr or ceramic (e.g. Al₂O₃) boat and raising the temperature high enough to provide the desired flux. At temperature, however, the source material must have a much higher vapor pressure than the boat material or contamination can be significant. For this reason, alternative methods must be used for some materials. For example, an electron beam can be focused on to conductive samples, melting the source material by electron bombardment.

A variant of this electron beam method is employed to deposit films for this study, using a modified MDC vacuum products UHV-PVD gun, model e-vap 100. To minimize contamination, no boat is used; rather the source material is fashioned into a thin (~1 mm), uniform rod (Fig. 3.3 A). This rod is positioned concentric to a W thermionic filament, and the electron beam focused electrostatically, using a high voltage field at 2 kV, so that an electron beam current of ~6-10 mA strikes one end of the rod, creating a melt ball (Fig. 3.3 B-C). This generates an evaporative flux which then condenses, line-of-sight, on a sample positioned ~12.5 cm away. As material evaporates, the rod is manually advanced by a linear motion feedthrough. The entire unit (Fig 3.4 A) is mounted to a 2 ¾” CF port on the introduction chamber (p ~ 5 x 10⁻¹⁰ Torr) of two chamber UHV system (see section 3.2.1) and oriented at a 45° downward angle to accommodate the
sample position and chamber geometry. Deposition is therefore at normal incidence using a 45° sample holder.

A particular problem was encountered with the use of Th rod. The 45° downward position effectively cantilevers the source rod which can result in sagging of certain rod materials when heated. Thorium has an elastic modulus similar to Al and sagged significantly at elevated temperature. This prevented proper function of the e-vap-100 since the source rod is in close proximity to a concentric Ta tube used to focus the electron beam—resulting in a short circuit when the source rod sags and makes electrical contact with the tube. Two modifications were made to address this issue. (1) The inner diameter of the Ta focusing tube was increased, while maintaining the outer diameter, by replacing the MDC-supplied tube with a Ta foil, formed into a cylinder and spot welded in place. (2) A boron nitride ceramic sleeve was designed and fabricated to support the rod ~3 mm below the opening of the focusing tube, alleviating much of the cantilever (Fig 3.4. B). The inner diameter of the sleeve is ~1 mm. The outer diameter (O. D.) is tiered: 3.5 mm at the tip, 5 mm in the midsection and 12 mm at the base. The midsection O. D. is approximately equal to the inner diameter of the Ta focusing tube, thus aligning the source rod along the center axis. The small O. D. at the top section removes the possibility of a short circuit developing from metal deposition on the surface of the ceramic. Finally the wide base prevents the BN sleeve from advancing and is held in place by 250 μm W wire (Fig. 3.4 C).
Contamination is also an issue in PVD. The thermionic W filament and the source rod operate at temperatures exceeding 2000 K. Radiative heat transfer to other components in proximity can cause thermal desorption of surface contaminants, including CO, CO₂, and H₂O. Degassing the unit can help reduce this effect, but bulk impurities can repopulate the surface over time. Hence, it is desirable to increase the conductance of the PVD head unit and reduce the surface area of components in vicinity of the hot filament. Both of these objectives were achieved by replacing the solid Ta shield (Fig. 3.4 A) with a Ta mesh (Fig. 3.4 C). The role of the shield in electrostatically focusing the electron beam was unaffected. During deposition the pressure in the system was ~3x10⁻⁸ Torr.

If the surface temperature of the melt ball is known, then the deposition rate can be estimated. The evaporative flux density at the sample, j (atoms/cm²-s) is given for an ideal effusion cell by J. E. Mahan [78] as:

\[ j = \frac{J_\Omega \cos \vartheta}{R^2} \]  \hspace{1cm} (E. 3.1a)

Where,

\[ J_\Omega = \frac{zA \cos \theta}{\pi} \]  \hspace{1cm} (E. 3.1b)

and,

\[ z = \frac{p}{\sqrt{2\pi m kT}} \]  \hspace{1cm} (E. 3.1c)
$z$ is the impingement rate from kinetic theory ($p$ is the partial pressure of an ideal gas, $m$ is the mass of an individual gas phase atom or molecule, $k$ is Boltzmann's constant, and $T$ is temperature). $J_\Omega$ is the flux from an ideal effusion cell where $A$ is the area of the exit aperture and $\theta$ is the angle of the flux with respect to the effusion cell normal. In E.3.1a, $R$ is the distance between the effusion cell aperture and the sample, and $\vartheta$ is the angle between the incoming flux ($J_\Omega$) and the sample normal.

For example, the vapor pressure of Th is given in figure 3.2; at the melting temperature, $T = 2023$ K, $p \sim 8 \times 10^6$ Torr ($1.1 \times 10^{-3}$ Pa), and $m = 3.87 \times 10^{-25}$ kg.

$$z = \frac{1.1 \times 10^{-3}}{\sqrt{2\pi(3.87 \times 10^{-25} \text{ kg})k(2023 \text{ K})}} = 4 \times 10^{19} \text{ m}^{-2} \text{s}^{-1}$$

Along the normal $\vartheta$ and $\theta$ are zero; the aperture is 5 mm in diameter,

$$J_\Omega = \frac{(4 \times 10^{19})(2 \times 10^{-5} \text{ m}^2)(1)}{\pi} = 2.5 \times 10^{14} \text{ s}^{-1}$$

Finally, the impingement rate at the sample, 12.5 cm away is given:

$$j = \frac{(2.5 \times 10^4)(1)}{(125 \text{ cm})^2} = 1.6 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$$

Typically, a monolayer consists of $\sim 10^{15}$ atoms/cm$^2$ and is approximately 0.33 nm thick. Given the impingement rate above and a sticking coefficient of one, a monolayer would form in 10.4 minutes at a deposition rate of $\sim 2$ nm/hr. The actual deposition rates observed in these experiments agree, within an order of
melt ball is at the melting temperature is likely not valid in all cases as the system is not in thermal equilibrium and the temperature at the area of electron impact is substantially higher.

As mentioned above, operation of the PVD unit radiatively heats surrounding components and increases desorption of gases capable of reacting with and contaminating the deposited films. Residual gas analysis has shown that these gases are primarily CO, CO₂ and H₂O (see chapter 6). It is useful to estimate the expected competitive impingement rate of these contaminants by E.3.1c. For example, given a partial pressure of H₂O of p~5×10⁻⁹ Torr (6.7×10⁻⁷ Pa):

\[
z = \frac{p}{\sqrt{2\pi nkT}} \Rightarrow \frac{6.7 \times 10^{-7} \text{Pa}}{\sqrt{2\pi (3 \times 10^{-26}) k(300K)}} \approx 2.4 \times 10^{16} \frac{H₂O}{m^2 / s}
\]

\[
z \approx 2.4 \times 10^{12} \frac{H₂O}{cm^2 / s} \approx 417 \frac{s}{ML}
\]

It is found that a monolayer of H₂O may dissociatively adsorb (likely followed by H₂ desorption) in ~7 minutes, assuming the sticking probability is one. Thus, contamination can be competitive with PVD deposition. Baking the system, reducing surface area and increasing pumping speed can help reduce the effective contamination rate. Also, with some materials it is possible to substantially increase the deposition rate while maintaining the contamination rate, thereby allowing very pure films to be deposited.
Figure 3.3: (A) Th rod (1 mm diameter) cut to ~50 mm length for use as source material in PVD. (B) The PVD gun, with the screen removed and the Th rod advanced past the modified Ta focusing tube. Note the Th melt ball at the end of the rod and its asymmetry due to gravity. (C) Cross-sectional schematic of the rod-fed, electron beam PVD unit employed in these studies (see text).
Figure 3.4: (A) Schematic of the assembled MDC e-vap 100 UHV PVD gun (image reproduced from MDC product manual). Note the rod is seated only at the wire feed adapter and initially extends, unsupported for 50 mm. (B) A boron nitride sleeve, designed to prevent sagging. (C) The modified e-vap 100. Note the position of the BN sleeve and the mesh shield in place of the solid shield in (A).
3.2.1 MAIN ANALYTICAL SYSTEM

The majority of experiments were conducted in a two chamber UHV Multifunctional Electron Energy and Surface Analysis System, hereafter called MESAS (Fig. 3.5). The PVD source described in the previous section is attached to the introduction system \( (p\sim 5\times 10^{-10} \text{ Torr}) \). Samples are introduced through a 4” CF flange. The system is evacuated by two Pfeiffer 60 l/s \( \text{(N}_2\text{)} \) turbo molecular pumps in series and backed by a Pfeiffer molecular drag pumping station. A tungsten coil mounted inside the chamber (not shown) allows radiative heating of samples for degassing. A precision leak valve mounted to the introduction system allows ultrahigh purity (UHP) inlets of Ar for venting the system or \( \text{O}_2 \) for surface adsorption studies. Pressure is measured by a Hasting 2002 Pirani/piezo gauge \( (p > 1\times 10^{-4}) \) and a nude Bayard-Alpert style ionization gauge \( (p > 5\times 10^{-11} \text{ Torr}) \). Sample transfer protocol requires the introduction chamber to be below \( 5\times 10^{-9} \text{ Torr} \) to limit contamination when opened to the main analytical chamber.

A linear motion arm facilitates sample transfer to the main chamber \( (p \sim 5\times 10^{-12} \text{ Torr}) \) for surface studies. The pressure is maintained by an Osaka turbomolecular pump with a pumping speed of 1100 l/s \( \text{(N}_2\text{)} \) and augmented by Ti sublimation and a Perkin-Elmer 400 l/s ion pump in parallel. A nude Bayard-Alpert ionization gauge is also used to measure pressures down to \( \sim 3\times 10^{11} \), below which x-ray and ESD effects require the indicated pressure to be corrected.
The main chamber features an \((x, y, z, \theta)\) carousel, with eight open sample positions. Two of these carousel positions have electrically isolated terminals that are connected to high power vacuum-electrical feedthroughs; this arrangement permits a variety of experiments, particularly \textit{in situ} Joule heating of specially prepared samples. Samples in these studies are mounted in one of three ways (Fig. 3.6) on modified sample holders based on the Phi 590 system. In particular, samples that require heating are spot-welded between two lengths of W wire. One end of each wire is fixed to two poles of the sample holder (see Fig 3.6B). When installed in one of two electrically isolated carousel positions, currents are applied between these two poles. Often the temperature versus current is calibrated in a separate system using a thermocouple and confirmed in the MESAS by infrared (IR) thermometry (Fig. 3.7). In some cases, a separate Pt anode is also mounted in an adjacent carousel position, and thermionic emission currents are measured (Fig 3.7). Samples that do not spot weld, e.g. Cu, Ag, Au, are often encapsulated in a vacuum-fired Ta foil envelope that serves as a miniature oven. The Ta contains a small aperture to the sample for ion bombardment and surface analysis.

The main analytical tools (discussed in detail in the following sections) are Auger electron spectroscopy and field emission energy distribution studies using a Phi 15-255 GAR double pass-cylindrical mirror analyzer (DP-CMA), and thermal desorption spectroscopy and surface absorption studies monitored by residual gas analysis.
Figure 3.5: MESAS schematic. Samples are introduced through a 4\" CF port, pumped down, coated by PVD (if required) and transferred to an 8 position carousel in the main chamber for analysis and processing (see text). Also shown is a photograph of the system.
Figure 3.6: Exploded schematics of a selection of MESAS sample mounting schemes (A) used for securing CNS samples for PVD and AES (B) for Joule heating of samples suspended between two spot weld leads and (C) accommodating larger samples or those that do not require thermal treatment.
Figure 3.7: A series of photographs showing an Ir filament, mounted in a scheme similar to Fig. 3.6B, at elevated temperature from Joule heating. An *ex situ* IR pyrometer is used to evaluate the temperature. A custom anode comprised of a Pt coupon is mounted to a Cu wire and positioned in an adjacent, electrically isolated carousel position to measure thermionic emission current. The anode can be independently biased with respect to the sample.
3.2.2 RESIDUAL GAS ANALYSIS

Residual gas analysis (RGA) is a mass spectrometry technique for assessing the gas phase composition in vacuum. The instruments used in these studies were manufactured by Stanford Research Systems and employ a quadrupole mass spectrometer (QMS). Sampling of the gas phase takes place inside the ionizer head where a thoria coated Ir filament generates electrons (1 mA) by thermionic emission. These electrons are accelerated to ~70 eV by a mesh anode with high transmission. Most of the electrons pass through the anode mesh into a cylindrical volume where they may collide with neutral gas molecules (those that do not, continue on helical orbits until scattered). Some of these collisions result in fragmentation and/or ionization of molecules. For these studies, the ionization cross-section for the gas species of interest (e.g. CH₄, CO, CO₂) is highest near 70 eV [79].

Positively charged ions are then extracted and focused into the mass filter by a negative potential. These positive ions are filtered according to mass-to-charge ratio by passing through a quadrupole field. This field is created by four parallel rods, arranged in a square (as seen in cross-section). Opposite rods are electrically connected; one pair is negatively biased, the other positively biased. A RF sinusoidal potential is superimposed on the DC bias. The positively biased rods strongly influence only the trajectories of the lighter ions, increasing their amplitude of oscillation in the RF field until they collide with the rods, thus serving as a high pass filter. The negatively biased rods strongly influence the
trajectories of heavier ions in the DC field, thus serving as a low pass filter. Tuning the range of these effective high and low pass filters allows the transmitted signal to be restricted to a window of ~1 amu (the ultimate resolution of the QMS is ~0.3 amu). The ion current is then either measured by a Faraday cup, or amplified by a continuous dynode electron multiplier (CDEM). The ion current is directly proportional to the partial pressure of the parent gas molecule.

During data collection, ion current is measured as a function of mass-to-charge ratio (m/e). Certain corrections are required to assess the actual gas phase composition. (1) Different gas species break into unique molecular fragments; the ion current measured for a given ionized molecular fragment must be corrected with a known fragmentation pattern (i.e., the fragmentation cross-section). (2) The ionization efficiency is dependent on molecular structure. That is, the positive ion yield upon 70 eV electron impact must be calibrated for each molecular species. (3) Larger ion species (typically m/e >40 amu) have a lower probability of transmission through the quadrupole filter and the measured intensity must be suitably calibrated and corrected. (4) The gain applied by the CDEM is dependent on the ion species. Typically the gain decreases rapidly with increasing mass (m/e), but can be easily calibrated by simply turning on and off the CDEM and observing the change in the indicated ion current for a given specie of interest. Corrections of all the aforementioned are best done by direct calibration using the gas species of interest, which will also include entrance and exit effects. However, this is not always possible, e.g., metastables and negative
species like atomic oxygen. Where used in this dissertation, corrected partial pressures will be noted. In all other cases, a qualitative or relative assessment was sufficient.

3.2.3 AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) is a surface sensitive technique for obtaining compositional and chemical information to a depth of <10 nm. When an energetic electron (2-10 keV) strikes a solid surface, atoms within the interaction volume can be excited. In some cases, the incident energy adsorbed by an atom in the solid may be greater than the binding energy for a core shell electron within that atom, ejecting the electron and leaving a core-shell vacancy. Because the nucleus is less effectively screened, an electron from a higher orbital will fill the core-shell vacancy. This transition from a higher orbital state into the core vacancy requires the release of energy equal (evoking Koopmans’ theorem as a first approximation) to the difference between the binding energies of the two states [80]. The release of energy requires the creation of a photon (X-ray fluorescence) or the ejection of yet another electron (Auger electron). Figure 3.8 illustrates the production of an Auger electron schematically; an incident, high energy electron inelastically scatters off an atom, ejecting a core, K-shell electron; in this specific example, an L₁ electron drops to fill the K-shell vacancy; the energy released is imparted to another electron in the L₁ state, which leaves the atom with kinetic energy:

\[ E_{KE}(KL_1L_1) = E_{BE}(K) - E_{BE}(L_1) - E_{BE}(L_1) \]  

(E3.2a)
Figure 3.8: The Auger process illustrated schematically (see text). The effect of orbital relaxation is not shown, but requires only a small correction. Figure adapted from [81].

Figure 3.9: The collected electron signal (counts versus kinetic energy) following electron impact at an energy ($E_p$) on a solid surface. Note that the Auger electrons constitute a relatively small cross-section of the total interaction. Figure adapted from [82].
However, a small but measurable error results from evoking Koopmans' theorem.
As each electron (initial core hole and Auger) is removed, the remaining electrons move slightly closer to the nucleus (orbital relaxation) on a time scale faster than the intra-atomic transitions described above and so the apparent binding energy increases for the filling and Auger electrons. A correction factor based on averaging the effect of a nucleus with one more proton (Z+1) simulates the reduced screening that gives rise to orbital relaxation.

\[ E_{KE}(\alpha\beta\gamma) = E_{BE}^{Z}(\alpha) - E_{BE}^{Z}(\beta) - E_{BE}^{Z}(\gamma) - \frac{1}{2} \left[ E_{BE}^{Z+1}(\gamma) - E_{BE}^{Z}(\gamma) + E_{BE}^{Z+1}(\beta) - E_{BE}^{Z}(\beta) \right] \] (E.3.2b)

This correction factor is often small and E.3.2a sufficient in most calculations. It is important to note that the cross-section for Auger production is quite small compared to the total yield (Fig. 3.9). Nonetheless, it is apparent that the kinetic energy of an Auger electron is rigorously dependent on the electronic states of the probed atom. These electronic states and the cross-sections for allowed transitions are characteristic to the atomic number, Z, (Fig 3.10). Furthermore, if the chemical environment of a given atom changes, the relative atomic or molecular orbital energies will change, and so must the kinetic energies of allowed Auger electrons, observed as a shift to higher or lower energy. The cross-section for Auger electrons, for a given transition, may also be affected by the chemical state of the probed atom, allowing AES to probe chemical processes by examining intensity (line-shape) changes. Figure 3.11 illustrates lineshape changes for the C (KLL) transition as a function of chemical environment.
Figure 3.10: AES relative sensitivity (~cross-section) for KLL, LMM, and MNN transitions as a function of atomic number (Z) [83]. Note $E_p = 3$ keV.

Figure 3.11: AES carbon (KLL) transition as a function of chemical environment. Note the significant energy shifts and lineshape changes giving AES both compositional and chemical sensitivity in the near-surface region. [82]
AES is conducted in the MESAS (see 3.2.1) using a double pass cylindrical mirror analyzer (DP-CMA) with a concentric electron gun, and spiraltron™ (electron multiplier). The nominal energy resolution ($\Delta E/E$) is $\sim 0.6\%$. Typical probe parameters are: $E_p = 2-5$ keV, $I_p = 1 \mu$A, beam diameter $\sim 60 \mu$m. The analyzed Auger electrons typically have a range of kinetic energies from 30 – 1000 eV (1 eV/step, and a time constant of 50 ms/step). Calibration of the detector is done by periodically taking a survey of an $\text{Ar}^+$ sputter-cleaned Cu sample and adjusting the energy scale factor such that the measured kinetic energies for the major Cu peaks correlate with known values (Fig. 3.12).

During longer acquisition times it is important to consider how the electron beam may alter the sample or the observed signal. The absorbed electron energy is sufficient to change the surface chemistry and/or composition of some samples, e.g., by electron beam heating or electron stimulated desorption. Thus, the beam must be periodically moved to a distant spot on the sample and a quick analysis performed to confirm that any observed surface chemistry is independent of the electron beam. Further, because the electron beam is generated by a thermionic W filament, operation of this filament causes the generation of contaminants both thermally and by electron stimulated desorption. The radiative heating of components can generate desorption of primarily CO$_2$, CO, and CH$_4$ (Fig. 3.13) which may subsequently adsorb on the sample surface. Finally, during O$_2$ dosing studies, adsorption of O$_2$ on to the W filament has been observed to cause a linear increase in emitted current (change in work function). The Auger intensity
of Au (69 eV) was used to measure this effect because no stable oxide will form on a Au surface (Fig. 3.14).

Figure 3.12: A calibration survey of a clean, polycrystalline Cu coupon over the kinetic energy range of 30-1000 eV. The electronic scale factor is adjusted such that the Cu peak positions are exactly 60, 105, 776, 849, and 920 eV (+/- 0.5 eV).
Figure 3.13: The relative change in the system partial pressures of CH\textsubscript{4}, CO, CO\textsubscript{2} and H\textsubscript{2}O when the electron beam is turned on and off. Note that the partial pressures are only a relative indication and are not normalized. The beaming flux for these gases from the e\textsuperscript{−}gun is significantly greater since the RGA indications are detected after the Boyle's law expansion. The actual total system pressure is <1x10\textsuperscript{-11} Torr.
Figure 3.14: During $O_2$ dosing studies, the Au peak-to-peak intensity for the 69 eV Auger transition is observed to increase linearly over a period of ~50 minutes. The blue and red lines are linear (least squares) fits to the data in black. No oxygen accumulation on the surface was observed, as is expected for Au. Rather the positive slope is a result of increasing primary beam intensity. $O_2$ absorption on the W thermionic filament that generates the primary electron beam may explain the apparent drift in incident current.
If a sample is not homogeneous, AES provides a means of examining variations in concentration with depth. The most direct method is to use the Ar⁺ ion gun to sputter the surface, while iteratively taking AES surveys of the sample. The depth resolution is limited by mixing, roughness and, in some cases, the relatively long minimum acquisition time of AES (~30 s). Further, the sputter yield must be known or calibrated in order to convert sputter time into depth.

Angle-resolved (AR) AES also provides information about compositional variation with depth, particularly for smooth samples. The information depth of measured Auger electrons of a given kinetic energy (and thus a prescribed inelastic mean free path) vary with take-off angle as the distance that must be traversed through the solid from given depth to the surface increases at shallower angles. To achieve angle sensitivity, a rotating, notched drum with a 12° aperture is placed between the two cylinders in the DP-CMA so that only those Auger electrons with trajectories that align with the drum’s aperture are passed to the spiraltron (Fig 3.15). For example, if the 12° aperture was rotated to 0° and 180° positions, the corresponding Auger electron take-off angles are ~90° and ~0°, respectively. The spectra acquired at ~90° take-off angle represents an information depth of ~3 nm for 100 eV electrons; the spectra acquired at ~0° take-off angle represents an information depth of ~0.5 nm. The 12° aperture, however, severely limits the total signal thereby considerably lowering the signal-to-noise ratio for any fixed collection time, so much longer acquisition times are required.
Figure 3.15: A cross-sectional schematic of the DP-CMA, as used during angle-resolved AES. Note the rotating notched drum used to select electrons by their take-off angle, and thus information depth.
3.2.4 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) is conducted in a Hitachi S-4700 equipped with a field emission gun allowing 500,000x magnification and ~1.0 nm spatial resolution. The field emission gun generates a very high brightness (~$10^9$ A/cm$^2$-sr) electron beam (5-30 keV, 10 μA) for probing the sample. This probe is rastered over a small area of the sample and secondary and back-scattered electrons are collected by an Everhart-Thornley detector positioned ~ 45° from the axis of the probe. Higher secondary electron yield near edges and protrusions provides topographic contrast (Fig. 3.16). An analysis of CNS morphology and efforts to correlate contrast in SEM micrographs with potential field emission sites by computational image analysis is discussed in chapter four.

Figure 3.16: Secondary electrons (SE1) created by interaction with a high energy electron probe have increased yield near topographic features primarily due to the increased surface area associated with protrusions [84].
3.2.5 TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a complementary technique used in these studies to corroborate results from AES. The ToF-SIMS instrument at William and Mary is a Phi THRIFT II ToF-SIMS using a Au liquid metal ion gun (LMIG). High energy (~22 keV) Au ions (~2 nA) are formed into a rapidly pulsed beam which is rastered over ~50 x 50 µm² area. The impact of the Au ion ejects atoms and molecular fragments from primarily the top 1-2 monolayers. A small number (typically <2%) of these secondary particles are emitted as ions and are subsequently collected by the time-of-flight mass filter. Each ion is then accelerated across a defined potential. Heavier ions will not accelerate as fast as light ions. The ions then traverse a field free drift tube, allowing the lighter, faster ions to separate from the slower, heavier ions. The detector measures the number of incident ions as a function of time through each measurement pulse; the time-binned results are added for a large number of pulses to accumulate a ToF spectrum. With a calibration factor, it is straightforward to convert the arrival time at the detector to the mass of the ion.

The ToF-SIMS also has a separate Ar⁺ ion gun for sputtering samples. This can be alternated with the Au LMIG to rapidly cycle sputtering and mass spectrometry, providing a very powerful tool for depth profiling. However, calibration is not straightforward. The secondary ion yield in ToF-SIMS is strongly dependent on the surrounding matrix. Therefore, when sputtering non-homogenous, layered samples, significant matrix-dependent calibration is
necessary for quantitative measurement of the composition. The thickness of a film, however, can often be evaluated from the relative changes in ion signals as a function of depth. As with AES depth profiling, the Ar⁺ sputter yield is required to relate the sputter time to thickness, but this can be more easily calibrated by cross-sectional SEM, profilometry of the sputter crater or with reference samples.

3.3 UHV FIELD EMISSION TESTING

In these studies, two UHV systems were used for evaluating the field emission performance of both as-received and coated CNS samples. For clarity, the systems will be designated field emission (FE) system 1 and 2. In all cases, FE testing is accomplished by placing a single sample in a parallel plate, diode configuration. A laser-cut Al₂O₃ spacer ranging in thickness from 125 to 500 μm defines the diode gap. A negative DC bias is applied to the CNS cathode and the resulting field emission current collected by the anode and passed through a picoammeter in series to ground. When extracting very high current densities, it is probable that the cathode and/or the anode temperature may significantly increase. Therefore, the anode geometries used were fashioned out of OFHC Cu and connected to a 19 mm diameter solid Cu, vacuum-electrical feedthrough and cooled, ex situ to 273 K by a circulating chiller or ice water. All test components were cleaned in an ultrasonic bath in acetone for 15 min, rinsed with semiconductor grade isopropanol, and air dried before installation in the systems.
3.3.1 FIELD EMISSION TEST SYSTEM ONE

A dedicated UHV system (Fig. 3.17), containing a modified diode apparatus, was used for field emission testing and simultaneous reaction-product measurement of smaller dot CNS samples (3-5 mm diameter). The system pressure was maintained by a Leybold turbomolecular pump with a nominal pumping speed of 560 l/s (N₂) backed by a Pfeiffer dry diaphragm/molecular drag 60 l/s (N₂) pumping station in parallel with a Varian 60 l/s (N₂) ion pump. The system was typically baked to ~425 K for 48 h after each sample exchange to remove adsorbed water resulting in a base pressure of <4x10⁻¹⁰ Torr. Testing was accomplished by loading a single CNS dot sample into a diode arrangement consisting of a mechanically polished (1200 grit SiC, 1 μm diamond paste) OFHC Cu anode parallel to the sample substrate and separated by a 254 μm thick, “c”-shaped, Al₂O₃ ring (12 mm outside diameter, 6 mm inside diameter) (Fig. 3.18). A compressed spring is used to apply pressure to the backside of the CNS growth substrate, securing the cathode in a parallel plate geometry and providing electrical contact. A relief geometry in the anode surface just outside of the testing area mirrors the gap in the “c”-shaped insulating ring; this opening increases conductance in the parallel plate geometry and is in line-of-sight with a RGA. A custom LABVIEW program allowed simultaneous control of and data acquisition from the RGA, a nude UHV ion gauge connected via a SRS IGC-100 controller, a Spellman 1200 high voltage source, and a Keithley 6485 picoammeter.
Figure 3.17: Schematic of a UHV field emission test system that allows simultaneous field emission and reaction-product measurement.
Figure 3.18: Schematic of a UHV diode apparatus used for field emission testing and simultaneous reaction-product measurement by a RGA in line-of-sight to the gap in the parallel plate testing geometry.
3.3.2 FIELD EMISSION SYSTEM TWO

A second UHV system was used to test larger CNS sample areas (>25 mm²). As with system one, a diode arrangement was employed. Strips of CNS coated substrates (typically 5 mm x 25 mm) were laid on a machined BN block. The block had been hollowed and a large aperture positioned directly under the sample; this configuration increases the conductance for gases that may desorb during FE tests (e.g. H₂). A large Cu block with a polished (1200 grit SiC, 1 μm diamond paste) surface was positioned parallel to the CNS substrate, but perpendicular to its length (Fig 3.19). Two Al₂O₃ spacers (0.75 mm thick) were placed under each end of the Cu bar to define the diode gap. A custom LABVIEW™ program was used to control a Glassman high voltage source (0-6 kV) and a Keithley 6485 picoammeter. Field emission tests were conducted in DC and ramping modes.
Figure 3.19: Schematic and photograph of a UHV diode apparatus used for field emission testing of larger CNS strips in test system two.
CHAPTER 4: FIELD EMISSION FROM CARBON NANOSHEETS

4.1 MORPHOLOGY OF CARBON NANOSHEETS

Carbon nanosheet (CNS) FEAs are grown by radio frequency plasma-enhanced chemical vapor deposition (RF PE-CVD) (see section 3.1.1). The growth of CNS [85] begins with a base layer of graphite sheets parallel with the substrate surface to about ~10-15 nm thick (~40 layers of ABA stacking) and then the growth turns vertically upward at the grain boundaries (Fig. 4.1). This is predominantly controlled by Volmer-Weber island growth where the thickness of the base layer increases until the islands impinge on each other (r_i ~ 8-10 nm), so the lateral growth is approximately the same as the vertical growth. The probability of vertical growth is then greatly enhanced by the electric field and the higher probability of carbon atoms forming sp^2 bonds to the growing edge compared to the much weaker tetragonalization bonding on the sheet surface [86]. Energetic hydrogen atoms and ions in the plasma impact the growing walls, sputtering away most weakly bound adatoms and amorphous C, thus contributing to the verticality of the growth. The resulting CNS films consist of thin, multilayered (average ~ 2) carbon sheets that are vertically oriented and approximately 600 nm in height (for a 20 min. growth). The height of the growth can be adjusted by growth time so that CNS heights exceeding 1 μm have been achieved. The morphology of carbon nanosheets has been characterized primarily by SEM, but also (in previous work) by high resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy [15-18,87].
following summarizes some pertinent conclusions from these works and expands upon the utility of SEM analysis of CNS.

HR-TEM is the only technique used successfully with CNS that has been capable of true atomic resolution. Micrographs have shown that CNS terminations are ~1-3 atomic layers thick; moreover, diffraction patterns are consistent with highly crystalline graphitic carbon [17].

Raman spectroscopy ($\lambda = 514$ nm) has confirmed that CNS are mostly composed of C-C $sp^2$ hybridized bonding. The ratio of two Raman peak intensities ($D \sim 1350$ cm$^{-1}$/G $\sim 1550$ cm$^{-1}$) has been used to assess CNS quality (i.e. degree of crystallinity). The “D” peak is associated with increased disorder in the carbon array; conversely, the “G” peak is related to the coherence length of graphene domains. That is, if each carbon nanosheet were a perfectly periodic carbon array, the D peak would nearly vanish (except for edge effects). Vacancies, Stone-Wales defects, and dangling bonds terminated with H atoms are believed to be the predominant defect structures. Changing the PE-CVD growth parameters has been shown to affect the $I_D/I_G$ ratio within a range of 0.3 to $>1.0$ [85]. Typical CNS films (as with those in used in this study) had a $I_D/I_G$ ratio $\sim 0.5$. Annealing of the sheets to 1000 °C for 5 minutes generally resulted in improving crystallinity as observed by the $I_D/I_G$ ratio decreasing to 0.25. It is believed that increased disorder in the sheets likely contributes to increased sheet resistance, which is unfavorable to delivering high current densities to edge emission sites;
however, no relationship between field emission performance and $I_D/I_G$ ratio has been conclusively shown.

The CNS schematic in figure 4.1 shows C-H$_x$ terminations on zig-zag or armchair edges, as well as dangling bonds or defect sites, with $x = 1$-$3$ atoms of hydrogen. *Ab initio* density functional theory studies of graphene have simulated an array of bonding sites on a perfect graphene surface and on an array of sites on the edges and found that adsorption energies at these sites can run from 0.5 to 3 eV [88,89]. Temperature desorption spectroscopy (TDS) studies of CNS have confirmed that there is significant hydrogen incorporated during CNS growth, both trapped between the sheets and bonded at edges, defects and tetragonalized surface sites. Surface hydrogen and bulk hydrogen were removed during ramping of CNS samples to 1000°C, but much of the more strongly edge bound hydrogen likely remained in place [85].
4.1.1 SEM ANALYSIS OF CARBON NANOSHEETS

SEM (see section 3.2.4) is the primary tool for assessing the morphology of carbon nanosheets. Figure 4.2 shows top down and cross-sectional SEMs typical for CNS samples grown with CH₄ feedstock. CNS terminations of 1-3 graphene layers (<1 nm) cannot be fully resolved as the maximum spatial resolution of the Hitachi S-4700 is nominally ~1 nm. These dense arrays of ultra-thin edges do display, however, significant contrast (some edges are observed to be brighter than others) which suggests that these bright edges are either protruding further from the substrate and/or are thinner than other edges in the immediate vicinity. As the SEM probe raster over a small region of the sample, the Everhart-Thornley detector integrates the signal (i.e. the total secondary electron yield) associated with each pixel, assigning a relative count, employing an 8-bit, grayscale digitization. That is, there are only 256 possible color values for each pixel: 0 = black, 255 = white. The analog-to-digital converter (DAC) assigns the pixel with the highest signal a value of ~255 and the pixel with the lowest signal a value of ~0; all other signal values are normalized to values between 0-255. The SEM operator can adjust contrast and brightness manually while acquiring images, essentially changing the normalization applied by the DAC.
Figure 4.1: Schematic cross-sectional view of CNS. This dense array of ultrathin edges (1-3 graphene layers) is thought to be an ideal high current field emission array. Note the presence of H at edge terminations.
Figure 4.2: (A) Top view SEM micrograph of a typical CNS cathode (grown with CH₄ feedstock gas). The outboard edges terminate in 1-3 graphene layers and are ideal electron emission sites under an applied field. (B) An approximate cross-sectional view of a CNS film grown on a curved surface. Because the sheets are only 1-3 atomic layers thick, they allow significant electron transmission and appear diaphanous.
When comparing SEM micrographs of CNS materials, it is possible to use quantitative image analysis to develop useful metrics. In particular, a density-based clustering algorithm was written in Matlab™ to identify the size and relative Euclidean separation of CNS edges. The algorithm first identifies pixels above a certain grayscale threshold value (i.e. sufficiently bright). This subset of pixels is then sorted and grouped by spatial position. In order to reduce the effect of noise, the density is used as a means of identifying unique regions, thereby spatially relating clusters of sufficiently bright pixels. When this type of analysis is performed on plan view SEM micrographs, such as in figure 4.2A, the number of unique clusters may be related to the number of edges (Fig 4.3). The brightest edges have the highest secondary and backscattered electron yield and may be correlated with either sharper geometries or sheets that protrude further than those in the vicinity; moreover, it is also likely that the field enhancement of these particular sheets is also augmented by similar geometrical considerations. Thus, such a density-based clustering algorithm has the potential of identifying likely field emission sites based on the relative secondary and backscattered electron yield in the SEM and the associated geometry variation. However, a number of assumptions are necessary in implementing this type of analysis. First, the SEM operator must adjust the initial image to approximately the same contrast and brightness (i.e. maintain the same DAC normalization). The error introduced by this assumption can be substantial, yet can also be somewhat mitigated by either applying an operator protocol or re-normalizing using the output image
histogram. Further, a threshold value must be chosen \textit{a priori} for identifying those pixels that are brightest and ostensibly field emission sites. To choose this value so as to include \textit{only} field emission sites requires some corroborative technique, e.g., UHV STM. With these considerations adequately addressed, quantitative image analysis could provide a means of quickly analyzing and comparing statistically relevant sets of SEM micrographs to extract metrics that may, in turn, be used to form non-obvious correlations with physical parameters such as field emission site area and density. Correlation of the actual emission area and this simulation using Fowler-Nordheim theory is provided in chapter five (see 5.1).

Figure 4.3: A computational contrast analysis of the plan view SEM micrograph in Fig. 4.2A highlighting CNS edges by a density-based clustering algorithm (see text).
Not all CNS edges are expected to contribute to the observed field emission current. Field screening due to relative separation and height, as well as varying field enhancement $\beta$ cause some sheets to turn-on at lower applied fields than others. A Fermi estimate for the probability of imaging an active field emission edge with SEM follows. For typical SEM images at 45k X magnification, the field of view is $\sim 6$ $\mu$m$^2$. By inspecting several similar micrographs, the number of independent, “candidate” emission edges is $\sim 20-50$ (that is, edges that the microscope operator might identify as potential emission sites based on apparent brightness, orientation, and/or thickness). Supposing the operator has a discerning eye, the number of likely emission edges in the field of view will be taken as $3/\mu$m$^2$. In the actual field emission experiments (e.g., chapter 6), the total sample area directly under the anode was $\sim 2.5 \times 10^7$ $\mu$m$^2$. Thus, there are $\sim 8 \times 10^7$ “candidate” edges across the whole sample. During typical SEM analysis, random areas are selected by the operator and individual carbon nanosheets examined more closely, especially at the terminating edge. Acquiring very high spatial resolution images ($\sim 1$ nm) requires careful (i.e. time consuming) adjustments to focus, aperture alignment, and X-Y stigmators. In a typical session, up to 40 random edges might be closely ($>100$ k X magnification) inspected over a given sample (15 min/edge, 10 h operation). As will be shown in later chapters, Fowler-Nordheim analysis for the coated CNS suggests that the upper limit of the estimated emission site area is $a \sim 1 \times 10^{-6}$ cm$^2$ or $1 \times 10^6$ nm$^2$. Although it is possible for field emission to be dominated by single atoms, it is
assumed here that individual emission edges are ultimately resolvable by the SEM (otherwise the probability of imaging would be zero). Thus, if the minimum individual emission site area is \( \sim 5 \text{ nm}^2 \), a total of \( \sim 2 \times 10^5 \) active emission edges exist over the whole tested sample area. Moreover, the probability, \( P \), of imaging an emission edges is given, \( P \sim 2 \times 10^5 / 8 \times 10^7 = 0.25\% \). If 40 random edges are selected, then the probability, \( P_t \), that one of them is an emission edge is given:

\[
P_t \approx 1 - (1 - P)^n = 1 - (1 - 0.0025)^{40} \approx 10\%
\]

Thus, there is only a 10\% probability that 1 out of 40 high resolution images will contain an emission site. Further, to increase the probability to 50\%, over 275 images would have to be acquired (\( \sim 7 \) days of SEM operation)! Even then, it would be unlikely that 1 out of 275 images would appear distinct enough to be unambiguously identified as an active emission site. Clearly, this is only a “back of the envelope” estimate, yet adequately serves to illustrate the improbability that SEM analysis of coated CNS can observe film morphology at emission sites.

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4.1.2 AES ANALYSIS OF CARBON NANOSHEETS

Auger electron spectroscopy has been used extensively in these studies to examine the chemistry and composition of PVD thin film coatings of CNS. Figure 4.4 is a survey of pristine, as-grown CNS for baseline comparison. Two observations from this data are worth emphasizing. First, only the graphitic carbon (KLL) “dolphin peak” is detected at 270 eV; no contaminants (to within ~1 at. %) result from the PE-CVD growth—esp. no oxygen at 510 eV. Second, AES is a three-electron process and cannot, therefore, detect hydrogen. TDS studies (see above) have shown substantial hydrogen incorporation in CNS.

![AES Survey](image)

**Figure 4.4**: Representative AES survey ($E_p = 3$ keV, $I = 1 \mu A$) of CNS. Note that only the C (KLL) transition is visible.
4.2 FIELD EMISSION FROM CARBON NANOSHEETS

Carbon nanosheet cathodes have generated current densities >2 mA/mm² under applied fields of 25 -30 V/µm. The field emission performance (pulsed and DC) and lifetime (> 800 hr) of CNS has been extensively characterized in previous work [85,90,91]; however, it has been difficult to separate the intrinsic field emission performance of CNS from physical processes that evolve during high current testing, e.g., gas desorption/adsorption and erosion. Field emission currents are typically measured in a biased parallel plate configuration with an oxygen-free, high-conductivity (OFHC) copper anode (see section 3.3). The following section will discuss a series of experiments designed to elucidate some of the surface-vacuum processes affecting CNS cathodes during long term, high current operation in a diode configuration. By investigating high current-evolved processes that take place during field emission testing, it may be possible to mitigate detrimental effects through pretreatment, operating protocol, gun design, and/or fundamental materials engineering.

4.2.1 OVERVIEW AND EXPERIMENTAL DETAILS

Carbon nanosheet dot samples were loaded into field emission test system one, with the diode gap line-of-sight to the RGA ionizer (see 3.3.1, Fig. 3.18). This arrangement allowed simultaneous sampling of gas products that were generated during high current testing. The relative composition and abundance of gas products provided valuable insight into some of the surface-vacuum...
effects occurring during field emission from CNS. The system was baked at ~150°C for 48 h to remove most accumulated H2O.

To establish stable field emission behavior, samples were first DC conditioned by slowly increasing the applied voltage (+1 V/s) such that target field emission currents were observed and maintained; typical objectives were 1, 10, 50, 100, 200, 500, and 1000 μA total emission current with stability (< 10 % variation) over hours of continuous operation. During DC emission current testing, I(V), a custom LabVIEW™ program allowed simultaneous control of data acquisition from the RGA, a nude UHV ion gauge (IG), a high voltage source, and a picoammeter. The RGA was set to scan H2, CH4, CO, and CO2 at 2, 16, 28, and 44 amu respectively with electron energy of 70 eV and an ionizer emission current of 1 mA; the continuous dynode electron multiplier (CDEM) was on in all cases with a nominal gain of 984 (with respect to 28 amu). Partial pressures were later adjusted with manufacturer default sensitivities, fragmentation factors and estimates of the mass-specific gain (see chapter 3). Total pressure (IG), partial pressure (RGA) and I(V) data were plotted and correlation coefficients computed using Matlab™. No significant mass spectral peaks were observed above 50 amu either before or during field emission testing.

During field emission testing in a parallel plate geometry, emitted electrons accelerated across the potential (1-5 keV) and struck the copper anode surface. Electron bombardment of Cu in this energy regime is known to create ions, neutrals and excited neutrals by electron stimulated desorption (ESD) [92,93].
Previous work on ESD from copper surfaces indicated that atomic hydrogen is a major component of the total desorption yield [94-96]. It is then likely that atomic hydrogen ions, neutrals and exited neutrals are created at the Cu anode surface and directed back towards the cathode, impinging on the CNS edges and sidewalls. The reaction pathways for H incident on graphite have been established and suggest that atomic hydrogen readily etches carbon surfaces by the creation and subsequent desorption of CH₄ (Fig 4.5) [97-115]. This has not been shown experimentally for graphene. The results discussed below demonstrate that impingement of CNS by H does indeed result in the formation and desorption of methane, removing C from CNS edges and sidewalls. Further, substantial fluxes of CO and CO₂ (greater than CH₄) were also observed, suggesting a similar type of CNS etching by ESD-generated oxygen from the surface copper oxide on the anode (Fig 4.6). Thus, in ultrahigh vacuum (UHV) field emission testing of CNS films, ESD-generated products etch the outboard graphene edges (Fig 4.7). The reaction products observed (CO, CO₂, and CH₄) are at rates similar to other results on graphite and graphite films in the literature.
Figure 4.5: *Ab initio* energy diagram for atomic hydrogen etching of graphene. Sequential hydrogen absorption (a)-(h) leads to cascade production of methane. Note that the only activation barrier is between (a) and (b) and is on the order of 1 eV. If defects already exist, as with as-grown CNS, then this simulation suggests no activation barrier to methane production. From work by C. Kanai, *et al.* [113].
Figure 4.6: Proposed energy diagram for atomic oxygen reactions with graphene. (a)-(b) oxygen may adsorb at defects with no activation barrier, and (c) CO incident on the absorbed O may form CO₂ and desorb. Also, (not shown) it is possible that in (b) further atomic oxygen may result in direct desorption of CO₂ thereby removing carbon from the CNS. Figure adapted from [113].
The OFHC Cu anode was subsequently removed from FE test system one and coated with \~1 \mu m of Au (no stable oxide and very low H concentration) to confirm that the etching occurred by ESD of the Cu anode. The Au-coated Cu anode was re-installed, with a new CNS dot sample, into the UHV diode configuration. The system was evacuated to a base pressure of \(< 4 \times 10^{-10} \text{Torr}\) and the sample DC conditioned up to a field emission current of 400 \(\mu A\). Line-of-sight RGA data was acquired simultaneously and partial pressures compared with those previously observed with the Cu anode.

\[\text{Figure 4.7: Schematic of the UHV diode apparatus used for field emission testing and simultaneous reaction-product measurement by a RGA in line-of-sight to the gap in the parallel plate testing geometry.}\]
4.2.2 PRESENTATION OF DATA COLLECTED DURING FIELD EMISSION AND SIMULTANEOUS, LINE-OF-SIGHT RGA

Typical field emission I(V) data for these samples up to 1 mA total current (Figure 4.8) and the corresponding Fowler-Nordheim plot (inset) demonstrate good linearity and agreement with FN theory (see chapter 2). A linear least-mean-squares fit of the Fowler-Nordheim plot yields a slope, $S \sim -5.3 \times 10^5$, and a y-intercept, $R \sim -22.7$. Using standard Fowler-Nordheim theory, ($\phi$ assumed to be $\sim 4.7$ eV) the field enhancement factor, $\beta$, can be calculated from the slope and gives $\beta \sim 1320$, consistent with analysis of other CNS samples operating at relatively high current [116]. Figure 4.9 shows the analog RGA survey for the UHV system before (solid line) and during DC field emission testing (dashed line) at 70 $\mu$A total field emission current. The predominant residual gas was hydrogen. Before testing, the system routinely pumped down to a total pressure of $p \sim 4 \times 10^{-10}$ Torr ($H_2$). During testing, significant increases can be seen for $H_2(m/e = 2$ amu), $CH_4(m/e = 16$ amu), $CO(m/e = 28$ amu), and $CO_2(m/e = 44$ amu). The absence of $H_2O(m/e = 18$ amu) is both an indication that the bake-out was effective and that the observed gas products are not likely coming from surrounding components. Also, during field emission testing, small but detectable increases at $m/e = 26, 27, 29$ and $30$ amu were observed. It is probable that they represent $C_2H_2$ (acetylene), $C_2H_4$ (ethylene) and $C_2H_6$ (ethane) and/or corresponding fragmentation peaks. Figure 4.10A shows a stepwise increase in the measured field emission current with respect to time. As
the total emission current increases, Figures 4.10B-C show the corresponding H₂ and CH₄ signals measured in the RGA. Similar behavior was observed for CO and CO₂ (not shown). The correlation coefficient between the H₂ and CH₄ signals is 0.99, indicating the production mechanisms for H₂ and CH₄ are closely related; the correlation coefficient between H₂ and the current signal was computed to be 0.98. Therefore, both the production of H₂ and CH₄ must also be intimately tied to current related phenomena; however, the time resolution of the RGA (> 20 ms/mass) is not sufficient to reveal information about reaction kinetics.

Figure 4.8: I(V) behavior during field emission of CNS dot samples in a diode geometry. The inset shows the corresponding Fowler-Nordheim plot.
Figure 4.9: An analog RGA survey (not calibrated) before and during field emission testing at a total emission current of 70 μA. Before testing the total pressure was < 4x10^{-10} Torr (ion gauge). During testing, clear relative increases in the H₂, CH₄, CO, and CO₂ signals can be observed (dashed line).
The linear least-mean-squares fits of RGA data as a function of field emission current are shown in Figure 4.11 with 95% confidence bounds as an indication of the spread in the data. At a total field emission current of 1 mA ($J_e = 0.14 \text{ mA}\cdot\text{mm}^{-2}$), the observed partial pressures were (Torr): $\text{H}_2$ ($2.5 \times 10^{-8}$), $\text{CO}_2$ ($7 \times 10^{-9}$), $\text{CO}$ ($3.5 \times 10^{-9}$), and $\text{CH}_4$ ($2.3 \times 10^{-9}$). Figure 4.12 juxtaposes gas flow rates at 400 $\mu$A total field emission current using a Cu anode with those observed using a Au-coated anode. The background is shown for relative comparison.

Using the Au anode, there are no hyperthermal oxygen atoms or ions and, since this was a Au coating there was also a minimum of hyperthermal H atoms and ions. An order of magnitude reduction was observed for the Au-coated anode in the gas products generated during field emission. Some ESD emission was observed from the Au (greater than the background) because of dissolved hydrogen, but this is minimal since the coating was Ar$^+$ sputter deposited on to the Cu anode.

Figure 4.13 compares Raman spectroscopy ($\lambda = 514 \text{ nm}$) taken before and after 300 h DC field emission testing in the standard diode configuration. The intensity ratio of the D and G peaks, $I_D/I_G = 0.57$ in the as-grown CNS film, increases to $I_D/I_G = 0.81$. Figure 4.14 shows the result of CNS etching by the change in mean height of the sheets shown in cross section by SEM after 200 h continuous (DC) operation in test system two at a field emission current density of 0.04 mA·mm$^{-2}$, as measured at the Cu anode [91]. From the change in the mean height, an etching rate of $\sim 1.7 \times 10^{-3} \text{ nm}\cdot\text{s}^{-1}$ was determined; however, this assessment only
considers edge erosion. Chemical erosion of both edges and sidewalls must also be considered in estimating the full magnitude of carbon-bearing molecules arriving at the mass spectrometer.

Figure 4.10: By adjusting the applied field up to ~8 V/μm, a stepwise field emission current is observed. Simultaneous measurements by the RGA show a corresponding response in the hydrogen and methane products. Similar responses were observed for both CO and CO₂.
Figure 4.11: The linear least mean squares fits (dashed) of RGA data as a function of current with 95% confidence bounds (dotted). The inset shows a linear plot of the data points in the high current regime.
Figure 4.12: The observed gas flow rates at 400 µA total field emission current with a Cu anode and with a Au-coated anode. The background data is taken with no field emission and a total pressure $\sim 4\times10^{-10}$ Torr. The ESD products from the Au coating are just slightly larger than the background of a small residual H in solution.
Figure 4.13: Raman spectra of the CNS cathode before and after 300 h DC field emission testing in a diode configuration. The $I_D/I_G$ ratio is used as a gauge of the relative defect density in the film. After testing the ratio has increased from 0.57 to 0.81 indicating that ESD-generated ions and neutrals have created further defect sites in the CNS. Adapted from [91].
Figure 4.14: SEM micrographs of CNS cross-sections before and after DC field emission testing for 200 h at a current density of 0.04 mA/mm\(^2\). The observed reduction in the mean height of the CNS corresponds to an etching rate of \(\approx\)1.7x10\(^{-3}\) nm/s [91].
4.2.3 DISCUSSION OF RESULTS

Under an applied field, the ultrathin (< 1 nm) outboard graphene edges of CNS films readily emit electrons by field emission. Since the geometrical electric field enhancement is comprised of edges < 3 graphene layers thick, we assume that the tallest of these are the active emission sites, typically yielding ensemble current densities of \( J_e > 140 \mu A \cdot mm^{-2} \) at fields of \( 8 \text{ V} \cdot \text{um}^{-1} \). Once the samples were DC conditioned, the distribution of individual emission sites over the geometric area was homogenized, as evinced by < 5% height variation in cross-sectional SEM analysis and increased long-term emission stability. Erosion of the outboard edges and active emission sites is a significant concern for the long term stability of CNS cathodes. This erosion is likely due to reactions with electron stimulated desorption of hyperthermal atoms from the Cu anode.

4.2.3.1 ELECTRON STIMULATED DESORPTION FROM COPPER

Electron stimulated desorption (ESD) is a process by which an electron flux impinges on a surface adsorbate (atom or molecule), stimulates the adsorbate atoms from the ground state to an electronic excited state, the atoms subsequently desorbs. Excited states may be anti-bonding, metastable or ionic, depending on the system. The Menzel-Gomer-Redhead (MGR) process is the earliest model for ESD and continues to be an accepted description, especially for simple adsorbates (i.e. O, C) on metal surfaces [117]. In this framework, summarized below, the initial excitation occurs through a Frank-Condon transition; that is, the electronic excitation occurs on a timescale of \( \tau \sim 10^{-15} \text{ s} \).
where nuclear motion \( (m_{\text{nucleus}} \gg m_{\text{electron}}, \tau \sim 10^{-13} \text{ s}) \) is considered nearly “frozen”. After the initial electronic excitation, responsive nuclear motion is permitted on a timescale of \( \tau \sim 10^{-13} \text{ s} \). The new potential, possibly repulsive with respect to the surface, of the adsorbate may be converted to translational kinetic energy, but the probability of neutralization/de-excitation strongly affects the yield. The total desorption yield \( (I) \) is then the sum of all possible ESD products: neutrals and metastables \( (i) \), positive ions \( (i^+) \) and negative ions \( (i^-) \) [118]:

\[
I = (i) + (i^+) + (i^-)
\] (E.4.1a)

Thus, if \( \sigma \) is the cross-section for ESD, then

\[
\frac{I}{Ae} = \frac{I_e}{Ae} \sigma N
\] (E.4.1b)

Where \( A \) is the surface area impinged by an electron current \( I_e \) (with charge \( e \)) covered with chemisorbed species with concentration \( N \). The change in \( N \) as function of time is then given:

\[
-\frac{dN}{dt} = \frac{I_e}{Ae} \sigma N
\] (E.4.1c)

Which can be integrated:

\[
\frac{N}{N_0} = \exp\left(-\frac{I_e}{Ae} \sigma N t\right)
\] (E.4.1d)
where $N_0$ is the initial concentration of chemisorbed species. Thus E.4.1d relates the change in surface concentration as a function of time to the impinging electron current and the total ESD cross-section for a given chemisorbed species. However, this discussion does not consider that the chemisorbed layer may continuously be re-supplied by diffusion of impurities from the bulk or readsorption from the environment (residual gases), thus maintaining a sustained ESD yield (E.4.1a). Typical cross-sections are $\sigma \sim 10^{-16} - 10^{-18}$ cm$^2$. The following section provides a review of pertinent literature describing ESD and reaction cross-sections specific to this experiment.

A field emission current of 1 mA incident on to 7 mm$^2$ of Cu anode at 8 V/µm or a flux density of $J_e \sim 8.7 \times 10^{14}$ e$^-$·mm$^{-2}$·s$^{-1}$, had a mean energy of 2 keV. No literature data was found for direct ESD O yields from Cu/CuO, however, one can assume that atomic oxygen reacts with a probability of $\sim 1$ with residual carbon when it contacts the walls of the vacuum chamber, so the yields of carbon bearing gases detected by RGA are somewhat representative. Gómez-Goñi and Mathewson indirectly measured the molecular desorption yields for OFHC Cu at a temperature of 313 K as a function of 300 eV electrons using an RGA [119]. At a dose of $10^{16}$ e$^-$·mm$^{-2}$ over $\sim 1$ hour, they measured yields (molecules/e) for H$_2$ (2 x $10^{-3}$), CO (7 x $10^{-4}$), CO$_2$ (3 x $10^{-4}$), and CH$_4$ (4 x $10^{-5}$). Nishiwaki et al. examined the problem further by juxtaposing RGA-observed ESD yields at 4.3 x $10^{13}$ e$^-$·mm$^{-2}$·s$^{-1}$ (1.5 keV) from OFHC Cu with surface characterization by Auger depth profiling[95]. As-received Cu showed a mean oxide thickness of 6.5 nm.
and total ESD yield of $6.7 \times 10^{-2}$ molecules/e$^-$ at a total dose of $10^{15}$ e$^-\cdot$mm$^2$; the RGA again showed yields (in decreasing order) of H$_2$, CO, CO$_2$, CH$_4$, and H$_2$O. When the oxide layer was reduced to a thickness of 1.6 nm by an aggressive acid treatment, the CO and CO$_2$ yields decreased by an order of magnitude. Further AES work on Cu in UHV shows a constant O(KLL) peak intensity over 70 minutes of electron bombardment with a flux of $\sim 1.2 \times 10^{12}$ e$^-\cdot$mm$^2\cdot$s$^{-1}$ suggesting that ESD-generated oxygen products are not supply limited in typical OFHC Cu surfaces [120]. Watkins and Williams examined ESD of OFHC copper surfaces as a possible UHV cleaning technique [121]. Their results at $\sim 1 \times 10^{-10}$ Torr show that total desorption efficiency and, therefore, the corresponding cross section, did not change significantly as the incident (0.1 $\mu$A-mm$^2$) electron energy was increased from 300 to 2000 eV. Further, no significant temperature dependence in desorption efficiency was observed as the Cu was heated from 293 – 573 K. ESD-generation of hydrogen and oxygen ions, neutrals and excited neutrals likely have higher cross-sections than molecular species, and both have kinetic energies on the order of $\sim 5$ eV, as confirmed by ToF-SIMS studies [94,96,122]. In these studies, the total ESD yield, following electron bombardment, was measured directly with a ToF-SIMS, used in place of an RGA as the line-of-sight mass detector.
4.2.3.2 HYPERTHERMAL ATOM REACTIONS WITH ATOMIC HYDROGEN

A large body of experimental and theoretical work exists on atomic hydrogen interactions with graphite. Early work by Balooch and Olander demonstrated that CH$_4$ was the sole etching product of atomic hydrogen interaction with both the basal and prism planes of pyrolytic graphite below ~773 K, while H$_2$ did not strongly react [98]. The reaction probabilities were higher for the prism plane; at ~393 K, for example, the apparent reaction probability was $4 \times 10^{-3}$ at a flux density of $8 \times 10^{14}$ atoms·mm$^{-2}$·s$^{-1}$. They propose that once the surface was saturated by C-H, subsequent H atoms produced CH$_n$ (n=1-4), finally desorbing when CH$_4$ is formed. Indeed, density functional theory (DFT) calculations have produced similar models of the reaction mechanisms and rates [113,115]. For example, Espinal et al. did DFT calculations based on a single graphene sheet with H occupying any dangling bonds on the periphery. They found that H$_2$ incident on the graphene edge could dissociatively adsorb and exothermically form CH$_4$ [115]. Similarly, Kanai et al. calculated that an activation energy of only 1.17 eV was necessary for atomic hydrogen incident along the normal of the basal plane to etch graphene, producing CH$_4$ (Fig 4.5). Furthermore, atomic hydrogen adsorption at defect sites in graphene required no activation energy; in fact, they also predict no activation energy is necessary for subsequent CH$_4$ formation and desorption in the presence of successive impinging hydrogen atoms. Raman spectroscopy has shown $I_D/I_G = 0.57$ in the as-grown CNS film (Fig. 4.13). After 300 hours DC field emission testing in a diode configuration,
\( I_D/I_G = 0.81 \), suggesting that ESD-generated atomic species may indeed react with and create further defect sites in the CNS film. Further, TDS of CNS to 1273 K has shown that a large amount of hydrogen exists between graphene sheets and on edges [85]. Thus, the combined mechanisms proposed by Espinal et al. and Kanai et al. are consistent with the observed etching and subsequent CH\(_4\) desorption at both the edges and side-walls of outboard graphene features in CNS films. Since the edge cross-sectional area is so small, the substantial increase in the Raman \( I_D/I_G \) ratio strongly suggests a chemical reaction with and erosion of the graphite base and graphene side walls.

Work by Yamada et al. has shown that the chemical erosion yield by H\(^+\) (~2\times10^{-2} \) molecules/H\(^+\) at room temperature) reached a maxima at 1 keV on glassy carbon and pyrolytic graphite (PG-A and HPG) in basal and prism orientations. For all substrates, the yield at 1 keV (6-8 \times10^{-2} \) molecules/H\(^+\)) was greatest at a temperature of 798 K since the saturation concentration of H\(^+\) at the surface is temperature dependent and drives the etching process [99, 100]. D. Manos et al. also observed considerable carbon erosion from a graphite probe cap exposed to RF heated plasma discharges (95% D, 5% H); it was suspected that synergistic effects of fast ions (50-100 keV) H\(^+\)/Ar\(^+\) and/or elevated temperature were substantial enough to provide an erosion yield of 0.3 +/- 0.2 C/ion [123]. Mech et al. have further demonstrated that even low energy H\(^+\) (< 100 eV) is capable of significant CH\(_4\) yields; for example, at room temperature, 50 eV H\(^+\) (~1\times10^{12} \) H\(^+\)-mm\(^{-2}\)-s\(^{-1}\) bombardment of graphite gave a yield of ~6.6\times10^{-3} CH\(_4\)/H\(^+\)
Vietzke et al. have confirmed that hydrogenated amorphous carbon films (a-C:H) bombarded by 2.5 keV H⁺ at 473 K gave a similar yield as graphite: 4x10⁻² CH₄/H⁺ [104]. Synergistic effects due to combined H⁺/H₀ etching of graphite have been shown to increase the yield by at least of factor 2-15, depending on the ratio of ions to neutrals and the mean energy of each [102,103]. In one experiment, combined H⁺/H₀ bombardment of pyrolytic graphite produced yields in excess of 6x10⁻² CH₄/H⁺ [101]. For most ESD processes, the neutral yield is far greater than the ion yield although the kinetic energy may be substantially less (Eₜₚₑₜₑₐ₅₉ ~ 5 eV).

Analysis of RGA data during field emission testing shows substantial increases in the partial pressures of H₂, CO₂, CO, and CH₄ at elevated currents. Some of the observed signal can be attributed to ESD-generated species directly from the anode, but the cross-sections for these molecular products are relatively small and suggest only small corrections to the observed partial pressure. Moreover, if the change in mean cross-sectional height of the CNS cathode (Fig. 4.14) is taken into consideration, it is clear that chemical erosion of the CNS is a viable explanation. Furthermore, atomic hydrogen and oxygen ions generated at the Cu anode are accelerated by the applied field and will most certainly react with the CNS, but the kinetic energy may have only a small effect since no activation energy is required for reactions at defects (Fig. 4.5).
4.2.3.3 HYPERTHERMAL ATOM REACTIONS WITH ATOMIC OXYGEN

Although no molecular oxygen signal is observed, it is likely that most atomic oxygen species will react with the CNS to form CO and/or CO$_2$ (Fig. 4.6). In fact, a number of studies have reported etching yields near unity ($6 \times 10^{-1}$ CO/O$^+$) for O$^+$ incident on graphite[107,124,125]. Similar yields ($\sim 0.5-1.3 \times 10^{-1}$ CO$_x$/O) have been observed for hyperthermal ($\sim 5$ eV) neutral O impinging the basal plane of pyrolytic graphite at room temperature [126,127]. Popov et al. have observed a similar cross-over in field emission testing of CNTs in polymer composites in a parallel plate configuration; however, they attribute the signal entirely to ESD-generated products at the anode [128]. Alternatively, calculations have shown that CO incident with O on graphite can result in CO$_2$ production[129]. In fact, this may be occurring in this work as well. It is clear from the partial pressures of CO and CO$_2$, that during field emission studies, the oxygen reactions with the CNS are much more dominant than with the hydrogen and are the species most responsible for the etching. Initially, the CO was the dominant ESD specie, but eventually, the CO$_2$ became dominant. The CO-CO$_2$ cross-over observed may be because the chemical erosion increases the defect density in the film and the probability of oxygen adsorption. Pristine, as-grown CNS (as measured by AES) does not adsorb oxygen (Fig 4.4), but graphene films with a significant defect density will. The incident CO desorbed from the anode most likely reacts with the adsorbed oxygen on the CNS and desorbs as CO$_2$ (Fig.4.6).
In this work, a similar experiment with a Au-coated anode was used to confirm the role of ESD-generated oxygen products from the Cu anode; Au has no stable oxide, no solubility for oxygen, and only a single adsorbed layer of atomic oxygen. At 400 µA total field emission current, only small increases in CO and CO$_2$ partial pressures were observed with the RGA. In fact, when compared to the Cu anode, an order of magnitude reduction in the generated gas species was observed (Fig. 4.12), suggesting that ESD-generated O products are central to the observed CO and CO$_2$ production using the Cu anode.

4.2.3.4 TOTAL CARBON-BEARING FLUX

At a field emission current density of $J_e = 0.14$ mA/mm$^2$, the partial pressure (corrected, background subtracted) of CH$_4$ at the RGA was $\sim 2.3 \times 10^{-9}$ Torr and the CH$_4$ pumping speed at the ion source ($\sim 81$ l/s), the etching product flux calculated from this partial pressure, $\phi$ (molecules/s), is then $\phi_{CH_4} \approx 6 \times 10^{12}$ molecules/s. Similarly, for CO the flux is $\phi_{CO} \approx 7.4 \times 10^{12}$ molecules/s, and for CO$_2$, $\phi_{CO_2} \approx 1.2 \times 10^{13}$ molecules/s. To leading order, CH$_4$, CO, and CO$_2$ are the sole carbon-bearing gases. Summing the flux of each carbon-bearing gas (and assuming no other source but erosion products), an estimate of the total number of carbon atoms etched per unit time is, $\phi_{carbon} \approx 2.6 \times 10^{13}$ C atoms/s. This number corresponds to an etching rate of $1.2 \times 10^{-1}$ nm/s for a uniform 7 mm$^2$ graphite slab ($\rho = 2.2$ g/cm$^3$) used as a simple analogy to the CNS area exposed to the ESD-generated atomic flux. The etching rate given by the
change in the mean film height in the cross-sectional SEM micrograph (see Fig. 4.14), however, suggests an etching rate of $1.7 \times 10^{-3}$ nm/s, far less than calculations from the RGA partial pressures suggest. The disparity in the two values may be explained by (1) a significant amount of the carbon bearing gases coming not from erosion of the CNS, but directly from the anode, or by (2) the slower erosion of sheet heights compared to the larger area of impact between the sheets. In the first case, the yields of CO, CO$_2$ and CH$_4$ measured by Gómez-Goñi and Mathewson from Cu suggest that up to 25% of the RGA-observed flux in this work may be attributed to that coming from the Cu anode in the diode geometry. In the second case, the outboard CNS edges represent a much smaller area fraction ($\sim 4 \times 10^{-8}$) to the incident ESD flux (see Fig. 4.3) and therefore give only a proportional contribution to the total reaction-product flux. Density functional theory studies of graphene edges have shown much higher chemisorption bonding energies of H atoms on the edges of the sheets ($\sim 5$ eV) which suggest a much slower chemical erosion rate on the outboard CNS edges compared to that from the side-walls [129]. This is consistent with the Raman data (Fig. 4.13) showing a significant increase in defect density after 200h of field emission, presumably from chemical reactions with and erosion of the CNS side-walls during testing. Since the area fraction of outboard CNS edges is small (Fig. 4.3) and effectively defines the film height in the SEM cross-sectional micrographs, the erosion rate presumed by the diminution of CNS film height
must be a significant under-estimate compared to erosion rates of CNS side-walls and base layers with much greater surface area.

4.2.4 SUMMARY REMARKS

Chemical erosion during high current field emission from CNS cathodes has been measured by a line-of-sight RGA monitoring of reaction-products generated in a UHV diode apparatus. Correlation of the field emission current and the CH$_4$, CO$_2$ and CO partial pressures showed that electrons striking the Cu anode surface created hydrogen and oxygen ions, neutrals, and excited neutrals which then etched side walls and edges of the CNS cathode. Etching of the cathode was observed by cross-sectional SEMs of the CNS cathodes before and after >200 h DC emission testing at moderate current densities. Calculations based on both the observed partial pressures of reaction-products and estimates of the ESD desorption yields agree well with values reported in the literature. The field emission experiments were repeated using a Au-coated anode to confirm the ESD of hyperthermal oxygen and hydrogen coming from the Cu anode.

Surface-vacuum effects such as chemical erosion by ESD products can be mitigated in a number of ways. (1) The parallel plate diode geometry can be abandoned in place of a gridded or lensed gun design (e.g. Pierce gun), but this would require precise fabrication and assembly, extensive calibration. (2) The Cu anode can be pretreated by either vacuum-firing (to remove bulk H) or replaced with Au. (3) The CNS can be coated with a thin film that may serve to both
enhance field emission and resist chemical erosion. This latter strategy is explored in the next chapters.
The reported work function of nano-carbon materials is relatively high, 4.6 - 5.1 eV; it is likely that CNS also have a similarly high work function. Selective thin film coatings may offer significant advantages [77,90,91]. The major objective is to retain the field enhancement advantage of nanometer scale emission sites while coating with a thin film of stable carbide or oxide that has a substantially lower work function than hydrogen terminated graphene edges. Carbides are a good film choice for their corrosive resistance, chemical stability and substantially lower work function. In the following section, two experiments will be described. (5.1) discusses Mo carbide coatings on CNS and (5.2) Nb carbide coatings on CNS.

5.1 THIN FILM COATINGS OF MOLYBDENUM CARBIDE

The coating of CNS with Mo, its subsequent formation to Mo$_2$C and its effect on field emission is expanded in the following sections.

Previous researchers have indicated that Mo$_2$C is a stable, conductive material that has a work function of 3.5-3.8 eV [130-133] which is ~1 eV less than that reported for graphite (4.6-5.1 eV) [134,135]. Fowler-Nordheim theory suggests that a reduction in work function of 1 eV may increase field emission by over an order of magnitude (see chapter 2) [8]. Most experimental data published on work function of applicable materials has a large spread in measured values (>1 eV), so it is uncertain what the true values actually are. In the case of Mo$_2$C, the
small variance in the reported work function measurements and the characteristic stability of refractory carbides suggest that this coating is a good candidate for field emission enhancement.

5.1.1 EXPERIMENTAL DETAILS AND RESULTS

The CNS sample sizes utilized in this work were ~3 mm diameter dots (grown through an Al₂O₃ mask) deposited on cleaved 6x6 mm² coupons of n-type (100) Si substrate (Ω = 0.001-0.005 Ohm-cm). Field emission experiments were conducted in test system one (see section 3.3.1).

Samples were loaded into the MESAS introduction chamber for PVD using a Mo source rod (1 mm diam., 99.95%) and coated for ~60 minutes (8 mA, 2 kV). At the melting temperature (T_m = 2623 °C), the vapor pressure of Mo is p ~ 3x10⁻² Torr. From (chap. 3, E3.1A-C) the estimated deposition flux is \( j = 8 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1} \), or a deposition rate of ~1ML/s. The actual deposition rate was determined by SEM analysis after coating and field emission testing of CNS and was found to substantially less than the calculated value, ~3 ML/hr. This discrepancy may arise from increased surface temperature of the melt ball during electron bombardment, impurities in the Mo rod, inconsistent operation of the e-vap 100 (i.e., not maintaining a melt ball), substrate geometry effects. The substrate temperature during PVD increased slightly from radiant heat transfer from the PVD gun to ~75 °C. The pressure in the system during coating was <1x10⁻⁷ Torr,
predominantly because of the system outgassing generated by the radiant heat from the high temperature of the melt.

After coating the CNS with Mo, the sample was moved from the MESAS introduction chamber into the main analysis chamber for thermal treatment and AES analysis. The AES spectra of the Mo coated CNS directly after deposition is shown in figure 5.1B: the as-grown CNS is also shown for comparison. An estimate of the thin film thickness based on the reduction in the C(KLL) intensity indicates approximately three monolayers of Mo coating the CNS surface. This is a very rough estimate because of disordered CNS topography. Standard thermo-chemical data suggests that formation of the Mo$_2$C requires an increase in temperature to $\sim$900°C to achieve stoichiometric carbide [136]. It is apparent, however, that the “dolphin peak” for graphitic/amorphous C (between $\sim$245 and 290 eV) contains the beginning structure of carbide formation (maxima/minima between 263 and 272 eV) [137-139]. Because carbon exists in at least two different chemical environments (graphitic and metal-carbide) the observed C(KLL) lineshape is believed to be the linear combination of (1) the C(KLL) lineshape for a pure metal carbide and (2) the C(KLL) lineshape for the underlying CNS (Fig. 5.1A). This superposition of (1) and (2) is observed in AES survey of Mo/CNS at surprisingly low temperatures, as low as the deposition temperature of $\sim$75°C. Figure 5.1C is the AES spectra after heating the sample in situ (100°C increments for 10 minutes) to 1000°C. The characteristic carbide “triple peak” between 263 and 272 eV (1, above) has become far more
pronounced and indicates substantially more carbide was formed [137-139]. The amount of carbide was determined by deconvolving the C(KLL) peak into (1) and (2) using the method of Baldwin et al., utilizing the asymmetry ratio, AR = i⁺/i⁻ where i⁺ and i⁻ are the positive and negative portions of the major peak in the carbide AES signal. Figure 5.2 is AES spectra of a pure Mo₂C surface (Mo₂C powder 99.98% from Alfa Aesar pressed uniformly into a pure polycrystalline Al substrate) after Ar⁺ sputtering for 10 minutes at 5 kV and 5 μA current. The major peak between 263 and 272 eV is distinct and serves as a calibration of the superimposed carbide signal (1) of the coated CNS (1)+(2). From figure 5.2 we estimated the pure carbide asymmetry ratio, AR = i⁺/i⁻ = 0.7. The fraction of Mo₂C was calculated from the AES spectra at each 100°C interval as I(Mo₂C) = (i⁺) + (i⁺/AR) [138].
Figure 5.1: AES spectra from 170 – 300 eV of (A) CNS as-grown and without coating, (B) CNS with ~3 ML of Mo coating, and (C) Mo/CNS after heating to 1000°C. Note the triple peak structure of Mo₂C superimposed on graphite peak at 272 eV.
Figure 5.2: AES spectra (50 – 600 eV) of stoichiometric Mo$_2$C for calibration. The characteristic triple peak of metal carbides is observed at 250 - 275 eV. The major peak i+ and the i- give an asymmetry ratio of AR = 0.7.
Figure 5.3 is a plot of the variation in AES concentration of the C(KLL) (272 eV), Mo$_2$C, Mo(MNN) (186 eV) and the O(KLL) (510 eV) as a function of temperature. The Mo peak drops rapidly in concert with the increasing Mo$_2$C and becomes steady at ~200°C, suggesting that the reaction to form carbide is virtually complete. The rapid formation of the carbide is to be expected since there are only a few monolayers of Mo on a very rough graphite surface (recall that the Raman intensity ratio I$_D$/I$_G$ ~ 0.5) so the C has many avenues to diffuse toward Mo atoms. The carbide most likely formed from vicinal adventitious C on the surface and in defects. The C and Mo$_2$C peaks remain stable as the temperature is increased to about 400°C where there is a slight increase as a function of temperature. Also, at this point, the Mo(MNN) peak begins to gradually decay. This slope is interpreted as being associated with geometrical changes in the film.

Figures 5.4A-B are SEM micrographs of the Mo-coated CNS sample taken to 1000°C. The underlying graphene/graphite structure is quite stable at 1000°C and does not react with the Mo coating. The stability of sp$^2$ hybridized C has also been observed by Leroy et al. for Mo on carbon nanotubes [136]. During the temperature increase to 1000°C, the Mo$_2$C has aggregated into the form of beads on the order of 10 nm diameter. Figures 5.4C-D show a CNS sample coated under identical conditions, but only heated to 275°C. No beading is detected and the carbide coating appears uniform. A digital superposition of the pure graphite AES signal and the stoichiometric Mo$_2$C AES signal (shown in 5.1)
was constructed to confirm the actual observed signal. The intensities were assigned by weighting the layers of carbide and by weighting the Auger electron contribution of the underlying C signal. The two spectra are shown in figure 5.5A and 5.5B, respectively. In order to match the experimentally observed signal to the superposition, ~2 ML of Mo$_2$C had to be assumed instead of three. A likely reason for the difference is that the irregular geometry of the CNS gives an overestimate of the thickness by the standard uniform film techniques to account for the attenuation of the C peak and the inelastic mean free path of the C(KLL) Auger electrons through the Mo$_2$C overlayer [140].
Figure 5.3: The variation in concentration of the peaks as a function of temperature in 100°C increments up to 1000°C. The formation of the Mo$_2$C begins forming at 100°C, reaches a plateau at 200°C and begins a gradual increase that continues up to 1000°C. In concert with this behavior, there is a precipitous drop in the free Mo signal to 200°C and a gradual decline that continues up to 1000°C. Very little O signal is initially observed and drops off to <1% at temperatures >200°C.
Figure 5.4: (A-B) Scanning electron micrograph showing the beading of the Mo$_2$C at 1000°C. The underlying hexagonal structure is quite stable and does not react with the Mo deposition. The beads are about 10 nm in diameter. (C-D) Scanning electron micrograph of another sample heated to only 275°C. No beading is observed and the Mo$_2$C coating is quite conformal. This procedure is used to produce the coated samples for field emission testing.
Figure 5.5: (A) A weighting factor (17% contribution to the AES signal) was applied to the spectra of the Mo$_2$C (shown in Fig.5.2) and then digitally superimposed on weighted (83%) spectra of uncoated CNS to match to the actual spectra shown in (B). The actual spectra were measured after heating a second sample of Mo/CNS to 275°C for 30 minutes. The Mo not combined with the adventitious C slowly diffuses into the CNS bulk. The digital match required only two Mo monolayers, indicating that a significant fraction of the Mo did not combine.
The Mo₂C/CNS sample was removed and placed in the aforementioned diode cartridge (see 3.3.1) and then installed in UHV field emission test system one for field emission measurements. Figure 5.6A shows I(V) characteristics of the as-grown CNS compared to the carbide-coated sample. A representative CNS sample is plotted that shows a turn on of I=10 µA at an electric field of ~10 V/µm. The CNS current exponentially increased, as predicted by Fowler-Nordheim theory (see chapter 2). The field was increased to ~17 V/µm which gave a current of 120 µA. Current densities with as-grown CNS have been achieved that are greater than 200 mA/cm², but the purpose of this experiment was to show that coatings can substantially improve emission and not to examine high current behavior. High current behavior generates heat and can result in significant morphological changes that alter the emission sites, and therefore the current, somewhat unpredictably. Figure 5.6A shows that Mo₂C/CNS has a much lower turn on, 6 V/µm, and an exponential rise that is quite sharp, both of which are consistent with the expected lower work function. Thus a given value of electric field will result in an emission current from the carbide-coated sample in excess of two orders of magnitude greater than what is measured for the as-grown CNS. This is consistent with Fowler-Nordheim theory. Figure 5.6B presents Fowler Nordheim plots of the Mo₂C coated CNS data for three separate maximum currents from 100 µA to 300 µA compared to as-grown CNS. The Fowler-Nordheim plots of six as-grown CNS (for clarity, only the linear fit is shown with standard deviations indicated by the error bars) also illustrates the
instability of CNS sample behavior. Many CNS Fowler-Nordheim plots demonstrate a characteristic deviation from linearity (typically referred to as an “S” shape) seen in many carbonaceous materials, including CNTs. The coated samples, however, show extraordinary, repeatable linearity over two and a half orders of magnitude in current, seldom seen in any F-N plot of carbon nanomaterials. From the linear least-mean-squares fit, the correlation coefficients (i.e., \( R^2 = 0.999 \)) are indicative of almost perfect F-N behavior and therefore are representative of ideal metallic/free electron theory behavior. Furthermore, excellent repeatability and stability in the coated samples are observed compared to that of the as-grown CNS. The data at 400 \( \mu \)A (not shown) is somewhat altered compared to the lower currents probably because of changes in the emission edges due to current effects. Table 5.1 shows the slope, intercept and correlation coefficient data in tabular form for the carbide coated samples.

<table>
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<tr>
<th></th>
<th>Max Current</th>
<th>Slope</th>
<th>Vertical Intercept</th>
<th>Correlation Coefficient</th>
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</thead>
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<td>400 ( \mu )A</td>
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<td>-22.241</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

Table 5.1
Figure 5.6: (A) I(V) characteristics of the Mo$_2$C/CNS sample heated to only 275°C compared to as-grown CNS. Note the significant improvement in both threshold and the current for a given applied field. (B) Fowler-Nordheim plots for maximum excursions of current to 300 μA for the Mo$_2$C/CNS sample and the linear least-mean-squares fit of six as-grown CNS samples. When fit by linear least-mean-squares, the Mo$_2$C/CNS correlation coefficients are very good ($R^2 = 0.999$).
5.1.2 ANALYSIS OF MOLYBDENUM CARBIDE COATING RESULTS

The ultimate film composition that results from the physical vapor deposition of 3 ML of Mo on CNS with a thermal-vacuum treatment to 275°C is very likely that of Mo$_2$C. Although, Lu et al. have shown that the composition of molybdenum carbide is very complex and quite dependent on environmental factors [141]. XRD data show that the Mo$_2$C film can be formed by annealing of δ-MoC$_{0.67}$ in vacuum for 1h at 1000°C. Lu et al. also suggest that β-Mo$_2$C is more likely to form in an environment of low gaseous hydrogen where 1000°C for 3h gives β-Mo$_2$C. In this work, the AES spectra as a function of temperature clearly shows that the well-known carbide “triple peak” at 272 eV begins to form immediately and is completed at 200°C (Fig. 5.3). The characteristic AES spectra is also consistent with XRD data confirming carbide formation [138, 142]. Because carbide formation is observed at such low temperatures, it is probable that the physically deposited Mo only weakly interacts with the underlying graphene surface and does not break the sp$^2$ bonding, but rather reacts with the nearby more weakly bound adventitious carbon located in amorphous islands or defects. At low temperatures (T <200 °C), the Mo remains localized and alters the hydrogen termination, CH$_x$ where x = 1-3, and then thermally converts to Mo$_2$C, probably by C diffusion to the Mo [143]. Mikhailov et al. suggest that Mo replaces the hydrogen termination on CVD diamond coatings after a 400°C anneal for 1h [144]. They found that the film became ohmic and confirmed that it was stoichiometric Mo$_2$C. Leroy et al. have studied the formation of Mo$_2$C on
CNTs and have found that the formation of the carbide is independent of the chemical nature of the substrate, but requires a formation temperature of 850°C with an activation energy of 3.15 eV [136]. Our observations that the substrate resists carbide formation are completely consistent with this work. The beading that occurs with elevated temperature is further evidence that the substrate does not take part in the reaction with the Mo film (Fig. 5.4). The difference in temperature at which the carbide is formed, i.e., 200°C in this work compared to their 850°C observed by Leroy et al., is most likely a function of the layer thickness, i.e., ~1 nm on a very disordered surface compared to their 30 nm, and the fact that the Mo was deposited in this work by physical vapor deposition at several orders of magnitude lower background pressure (<1x10^-8 Torr). As a consequence, very little O is observed in our films. Further, our film was heated in UHV compared to their He atmosphere, which most certainly would be more likely to have a relatively higher impurity contamination in the resulting film. As suggested by Mihailov et al., C diffusion is highly dependent on the quantity of other interstitials absorbed in the Mo film (concentration dependent) [144].

Molybdenum carbide coatings have been previously studied on Spindt type cathodes with Mo emitters and on hydrogenated diamond-like carbon films [130,144-146]. The thin film work on Spindt cathodes was shown to substantially improve the field emission simply because the thin film coating did not significantly alter the field enhancement factor, but did significantly reduce the work function. The measured work function for graphite and carbon nanotubes is
in the range of 4.6-4.8 eV and that for Mo$_2$C is in the range of 3.5-3.8 eV [130-135].

The I(V) data presented here suggest that many of the CNS emission sites terminated with H have been replaced by Mo and the resulting surface electric field altered to increase the emission current. The lower surface mobility at such low temperatures has likely caused Mo atoms to remain localized close to their initial impact sites; the amorphous C has diffused into and reacted with the Mo. Hence, the resulting carbide is likely to be at the active emission sites. The atomic configuration of the resulting structure must be such that the surface dipole moment formed by the Mo atoms arranged outboard which substantially increased the accelerating field and lowered the effective work function yielding the observed current increase (>10$^2$) and the observed carbide coated CNS turn-on at <6 V/μm [147].

Although field emission from carbon nanotubes (CNT), carbon nanofibers (CNF), carbon nanosheets and other carbon morphological structures has been extensively studied, high current emission is often unstable and non-uniform. Furthermore, application of Fowler-Nordheim theory often results in non-linear plots, suggesting that such materials are not metal-like, even after extensive conditioning or that arrays do not behave in concert like emission from a single source. Transport of the $\pi$-electrons along single graphene sheets and along the axis of CNTs has been reported to be ballistic, but electron emission to vacuum is controlled by electron recombination to a bonded state at the vacuum
interface; the ultimate tunneling from those states controls the emission characteristics [148].

The Fowler-Nordheim plots are quite linear for all current levels studied. At 100 μA current, the linearity was characterized by a correlation coefficient of $R^2 = 0.9999$. This was true for 200 and 300 μA also, but at consecutive runs of 400 μA, the emission site geometry (therefore the surface electric field) appears to have begun to change, slightly. As long as the current level was maintained at a maximum of 300 μA (~43 μA/mm²) or less, the data were repeatable over hundreds of runs. The reason for degradation at ≥400 μA may be the result of Joule heating, electromigration or possibly electron stimulated alteration/erosion of the terminal bonding [149]. The linearity observed in these F-N plots also suggests a Mo₂C metal-like termination compared to a hydrogen covalent termination. In most all CNT and CNS F-N plots, there is a non-linearity, i.e., a slight “S” shape of the curve and often scatter in the data. Some exceptions to this exist, but very few [26]. It is probable that the lower the work function at the active emission sites, the more likely emission occurs in concert as from a single source. Groning et al. reported excellent field emission and F-N linearity from a mixture of Ni/Fe capped and open CNT, but gave justification as to whether the open ended tubes or the capped end were the emitting source [26]. Those authors suggested that the emission was from open ended versions based on the ring like emission pattern, but also offered that this conclusion was uncertain.
A metallic termination or cap would be more consistent with the data reported here.

Since the linearity in this work is so good, the data provide some confidence in the parameters that comprise the F-N equation (E.2.3) \[135, 150, 151\]. It is then reasonable to estimate the emission site area from the slope and y-intercept of the F-N plot. From SEM images, the observed CNS edge width is \(\sim 1\) nm and the average length of edges, estimated by quantitative analysis of SEM images (Fig. 4.3), is \(\sim 50\) nm; thus, an average emitter-site area can be estimated to be \(\sim 50\) nm\(^2\) or \(5 \times 10^{-13}\) cm\(^2\). From the F-N equation (E.2.3), the phenomenological or equivalent emission site area is given by:

\[
\alpha \text{ (cm}^{-1}\text{)} = \frac{\exp(R) \cdot S^2}{ab^2 \phi^2} \approx 3 \times 10^{-9} \text{ cm}^2 \quad (E.5.1)
\]

where, \(R\) is the vertical intercept of the FN plot, \(S\) is the slope, and \(\phi\) we assume to be 3.7 eV for Mo\(_2\)C. It should be noted that the correction factor, \(\nu(f)\), for an applied field of \(\sim 10\) V/\(\mu\)m is \(\nu(f)\sim 1\), and is therefore not further considered in these calculations.

By taking the ratio of the estimated emission area from E.5.1 and the average emission site area from SEM analysis, a rough estimate emerges for the approximate number of emission sites: \(\sim 6000\) emission sites in the 7 mm\(^2\) area. The current that each emitter will carry at a total current of 400 \(\mu\)A (threshold for edge degradation) is then \(\sim 70\) nA. An individual CNT has reportedly been found
to sustain 200 nA with no damage [33]. So, at a more modest emission, this estimate is reasonable. In cross-sectional SEM images of CNS, we observe some variation in height of the emission edges, and many edges that are not as high as others will not contribute to the emission because of electric field screening [26]. The highest and thinnest edges will have the highest $\beta$ factor and will turn on first. If the field is increased beyond this level, some of these emitters will dominate the array and tend to ultimately burn out. A higher field will be required to turn on lower $\beta$ factor emission sites. Carbide coated sheets did not behave in this manner in that they needed only minimal conditioning. The stability of sites was also likely improved so that at current levels of <400 $\mu$A, these emission sites are quite stable and are the only ones that significantly contribute to the emission. In other words, other emitters may turn on at higher electric fields, but do not significantly contribute to the total current. The work function for Mo$_2$C has been consistently found to be $\phi=3.7$ eV. If it is assumed that the past measurements of the work function of Mo$_2$C are reasonably accurate then an average field enhancement factor can be estimated for the Mo$_2$C/CNS.

$$\beta_{Mo2C} = \frac{-b\phi^{3/2}}{S} \approx 530 \tag{E.5.2}$$

Similarly for as-grown CNS, previous studies have suggested $\beta \sim 700$-1000. By comparing the slopes and the change in the field enhancement factor with
addition of a thin film coating, one can verify the relative change in work function. From (E.2.3),

$$\phi_{CNS} = \left( \frac{\beta_{CNS} S_{CNS}}{\beta_{Mo_2C} S_{Mo_2C}} \right)^{\frac{2}{3}} \phi_{Mo_2C}$$  \hspace{1cm} (E.5.3)

For a slope $S_{CNS} \sim 1 \times 10^6$, and $\beta_{CNS}/\beta_{Mo_2C} \sim 1.30$ (i.e. 700/530), $\phi = 4.7$ eV which is in good agreement with that measured for graphite and CNTs. It is probably that the graphite work function measurements were dominated by defects and field induced micro and nanotips that are terminated with hydrogen, so similar values to that of the CNTs are reasonable. Groning et al. determined that the work function of the multi-wall CNT by field emission energy distribution was 5.13 eV and compared that to ordinary graphite [26]. However, it must be emphasized that the slopes of Fowler-Nordheim plots of as-grown CNS samples have demonstrated a wide range (Fig. 5.6B). Calculations of $\beta$ require that both the slope and work function be defined (E.5.2). Because the range of work functions of both Mo$_2$C ($\phi = 3.5-3.8$ eV) and carbonaceous nanomaterials (4.5-5.1 eV) are well-described in the literature, it is reasonable to estimate $\beta$ using this approach. Nonetheless, a work-function independent calculation of $\beta$ from experimental data has not yet been reported. Analytical attempts to calculate $\beta$ in the literature will be discussed briefly in chapter seven.
5.1.3 SUMMARY REMARKS

Carbon nanosheets coated with a thin film of Mo by physical vapor deposition heated in UHV to form Mo$_2$C have provided a lower field emission threshold and substantially greater field emitted current than that for as-grown CNS edge emitter cathodes. The stoichiometric carbide was formed from approximately 2 ML of Mo reacting with vicinal adventitious carbon atoms diffusing to the active emission sites at a low temperature of 200°C. The carbide plateau remained stable to 400°C and then gradually increased as the temperature was raised to 1000°C as the film transitioned from a uniform coating to form islands. It is likely, that the emission sites normally terminated with hydrogen have been replaced by the Mo$_2$C. The carbide termination which has metal-like behavior and a work function ~1 eV less than that of the as-grown CNS also substantially improved the stability and repeatability of the emitted current. The exceptional linearity of F-N plots permitted calculation of the apparent work function for uncoated CNS, a credible emission area and a plausible value for the field enhancement factor.
5.2 THIN FILM COATINGS OF NIOBIUM CARBIDE

Subsequent to experiments with molybdenum coatings, the MESAS system was dedicated to a series of experiments on ultra-pure coatings of Nb by PVD for RF superconducting cavities [152]. The source rod was replaced with Nb (1 mm. diam., 99.95%). This presented an opportunity to compare the success of Mo₂C/CNS with NbₓC/CNS coatings. The reported work function of NbₓC is ~ 4.9 -5.1 eV [153,154]. Because the work function of CNS is likely 4.6-5.1 eV, the field emission performance of NbₓC/CNS was anticipated to be either the same or worse than as-grown CNS. This provided a target of opportunity to examine only the change in β due to a thin film coating (<5 nm) on CNS.

CNS samples (grown by C₂H₂ feedstock) were loaded into the MESAS introduction system for PVD coating with Nb, thermal treatment to form NbₓC, and compositional and chemical characterization by AES. As with the Mo coatings, the formation of the carbide phase was believed to require extensive thermal treatment. A sample was prepared for in situ Joule heating according to the procedure discussed in chapter 3 (see Fig. 3.6B). After Nb coating by PVD for 15 min (~0.75 nm), the sample was thermally treated from room temperature to 900°C (+100°C/step) and held at each successive maximum temperature for 6 minutes. Figure 5.7 shows a series of AES surveys from 50-600 eV as a function of increasing temperature.
Figure 5.7: A family of AES spectra for Nb deposited on CNS and heated stepwise (100 °C/step) up to 900°C. Note the disappearance of the O signal between 600-700°C, the increasing C(KLL) and the increasingly prominent carbide triple peak structure for NbC.
As with the Mo coating, the thermal evolution of the C(KLL) peak is most useful in determining the temperature at which the available adventitious carbon reacts with the deposited metal layer to form a metal-carbide overlayer. As this was only a relative study, no NbC calibration was used to extract quantitative compositional information from the AES data; rather, the i+ excursion of the carbide peak (255-263 eV) in the C(KLL) transition was used as proxy for the relative carbide concentration. Figure 5.8 shows the AES intensity ratios (extracted from Fig. 5.7) of Nb/C and NbC/C as a function of temperature. The steep increase in NbC/C indicates that the carbide phase is primarily formed between 500-600°C, much higher than observed for Mo (~200°C). Further, the Nb/C signal decreases in concert and may be associated with both the increasing C concentration as adventitious carbon diffuses into the deposited metal layer and/or morphological changes, e.g., the formation of islands. The O/C AES intensity ratio (also extracted from figure 5.7) as a function of temperature shows a sharp drop between 500-700°C (Fig. 5.9), approximately in concert with the observed formation of the carbide. It is probable that the O is reacting with H and desorbing as H₂O or adventitious C to produce CO and/or CO₂.

S. Barzilai et al. have shown by magnetron sputtering that Nb films (~8 μm thick) on ATJ™ graphite can be partially (10-25%) converted to Nb₂C and NbC by annealing at 800°C for 1-8 hr and completely converted at 1200°C [155]. The activation energies for Nb₂C and NbC growth were lower than those reported for
bulk material; this is expected for thin films and may scale with film thickness. In fact, L. Huang has recently used NbC as a contact material for CNTs. Nb coatings of ~40 nm were found to convert to NbC by thermal-vacuum treatment to 700°C [154]. Therefore, for this film (t <1 nm) it is reasonable that carbide formation occurs at 500-600°C.

Having established the temperature required for complete carbide formation and removal of O (~750°C), blanket samples of as-grown CNS were coated for 15 min with Nb and heated to 750°C for 3 minutes. SEM characterization was used to determine the morphology of the NbC thin film after thermal treatment. Representative SEM micrographs are shown, with increasing magnification, in figures 5.10 A-D. The thin film formed into highly faceted islands of ~50 nm diameter and ~20 nm height with a coverage of ~25%. The composition of these islands is believed to be NbC, though it is possible that the less stable Nb$_2$C phase may also exist in this C rich system. The formation of crystallites on sp$^2$ carbon is not unexpected at these temperatures since beading or island formation has been observed for many heteroepitaxial systems [156]. Generally, it is energetically favorable for a thin film to form islands. There are two reasons for this:

(1) Mismatch strain, $\varepsilon_m$, between the film and the substrate increases as the film thickness deceases, though the magnitude of the strain depends ultimately on the relative density and phase of the materials at the interface.
(2) The surface free energy associated with the film, substrate, and the interface between the film and the substrate. The formation of islands increases the total surface area, but decreases the area of the film-substrate interface. Therefore (1) is necessarily reduced by island formation and (2) may increase or decrease, depending on the net surface energy per unit area. To discuss the net influence on film geometry, a ratio of (1) and (2) can be expressed [157]:

\[
\zeta = \frac{\gamma}{Me_m^2} \quad (E.5.5a)
\]

where \( \gamma \) is the surface free energy, \( M \) the elastic modulus. E.5.5a represents a ratio, \( \zeta \), of two energy densities: (1) surface free energy and (2) mismatch strain, as discussed above. The energy minimization of the surface requires some geometrical consideration. Following the general discussion by L. B. Freund and S. Suresh, a parameter \( Z \) relates \( \zeta \) to \( V \) the volume of an island [157]:

\[
Z = \frac{\zeta}{V^{\frac{1}{3}}} \quad (E.5.5b)
\]

Figure 5.11 shows a general plot of free energy per unit volume versus aspect ratio \( a \) (height/radius) for various values of \( Z \) and for a fixed island volume. \( Z \) is inversely proportional to the size of the island. At \( a=0 \), the film is flat and uniform. For all \( Z \), the slope is initially negative and indicates that the flat film is always unstable. The minimum free energy for each \( Z \) is associated with an
energetically stable island aspect ratio. It should be noted that the elastic modulus is assumed to be the same for the film and the substrate in this analysis, but generally only shifts the minima to higher or lower aspect ratio [157].

Further island growth proceeds by thermally-activated Oswald ripening where larger islands grow at the expense of smaller, less thermodynamically stable islands.
Figure 5.8: The variation in AES intensity ratios of Nb/C and NbC/C as a function of temperature for Nb PVD on CNS. A steep drop off between 500-600°C in the Nb/C signal correlates well with the formation of NbC. The apparent attenuation of the Nb peak results from taking the ratio with an increasing C concentration and/or from the formation of islands.
Figure 5.9: The variation in O/C AES intensity as a function of temperature for Nb PVD on CNS. A steep drop off between 500-700 °C correlates well with the formation of NbC (Fig. 5.8). It is suspected that O reacts with adventitious C to produce CO and/or CO₂ and desorbs.
Figure 5.10: (A-D) SEM micrographs with increasing magnification of NbC/CNS after heating to 750 °C for 3 minutes. Note the presence of highly faceted islands, likely crystalline NbC, with a coverage of ~25%. The substantial spatial distribution of islands suggests that they are unlikely to uniformly coat active field emission sites.
Figure 5.11: The variation in free energy as a function of aspect ratio (height/radius) for various values of Z (see text). Z scales inversely with island size. At $a=0$ the film is flat and uniform. For all Z, the initial slope is negative and suggests that island formation is generally favorable. Image from [157].
Niobium carbide-coated CNS samples were loaded into field emission test system two for I(V) measurements. The I(V) behavior for the NbC/CNS film demonstrated no change compared to the as-grown CNS (Fig 5.12). Thus, the crystallites formed by thermal treatment do not appear to affect the intrinsic field emission performance of CNS. The result appears to confirm that the addition of material on the sidewalls does not substantially change the work function or field enhancement at emission sites. For thin film enhancement to be successful, uniform and stable films must be formed over the critical emission sites.
Figure 5.12: I(V) plots for NbC/CNS after thermal treatment (750 °C, 3 min.) compared with the as-grown CNS. No substantial change in the field emission behavior is observed. This is expected as SEM analysis showed that the film had formed large NbC crystallites that are not likely to overlap with active emission sites along CNS edges.
Many low work function films are oxides. Thorium dioxide is a low work function coating used extensively for thermionic cathodes. Selection of this material for a field emission coating seems to be a judicious first choice to characterize. Natural thorium ($^{232}$Th) is a mildly radioactive ($\tau \sim 1.4 \times 10^{10}$ yr) metal in the actinide series and decays primarily by $\alpha$($\sim$4 MeV) emission. From room temperature to 1633 K, Th assumes a fcc cubic structure, at temperatures $> 1633$ K, Th goes through a fcc to bcc phase transition and is stable up to the melting temperature, $T_m \sim 2023$ K. Thorium is readily oxidized, forming ThO$_2$. Since Th$^{4+}$ is the only stable oxidation state at room temperature, the stoichiometry of thoria (ThO$_2$) is typically well-defined. Thorium and thoria have been used in a wide range of applications including optical and electronic thin films, nuclear energy, and catalysis [158-161]. In particular, thoria thin films have been used extensively for low work function thermionic cathode coatings, especially when both high power and robustness are required. For example, many ion gauge and mass spectrometer filaments are made of Ir, W or Ta wire or ribbon, electrophoretically coated with $\sim$50 $\mu$m of ThO$_2$. These cathodes are known to be able to survive catastrophic loss of vacuum and exposure to atmospheric ambient pressure.

As-deposited, ThO$_2$ has a reported work function of 3.3 – 3.8 eV, but when heated to $>1700^\circ$C, the effective work function of these ThO$_2$ films decreases considerably to 2.6 – 2.8 eV. W.E. Danforth et al. published some of the most
thorough studies of the thermionic emission properties and thermal “activation” of ThO₂ in the 1950s [62]. However, lack of advanced surface science techniques and limited access to good vacuum facilities prevented any complete understanding of the mechanism for thermal activation. In the 1960s and onwards, research interest in ThO₂ films waned, yet ThO₂ coatings continued to be widely used in industry. Hence, the thermal activation of the ThO₂ remains poorly understood.

As outlined in chapter two, it is generally proposed that the activation of ThO₂ occurs by thermally-induced self-doping. That is, excess Th is formed during thermal treatment that provides n-type semiconductor behavior. Further, it is believed that a Th monolayer is created at the surface, inducing a strong surface dipole that acts to reduce the effective work function. As the diffusivity for O is reportedly much higher than that of Th in bulk ThO₂, it is probable that free Th is created by O diffusion away from the emitting surface, creating a partially reduced surface region [162,163]. As most ThO₂ films are deposited on clean metal filaments, these materials serve as a substantial sink for O diffusion, thereby maintaining an oxygen concentration gradient. Further, most of these studies were conducted with electrophoretically deposited ThO₂, which are porous. The role of impurities and film density is typically not considered, but may contribute to the observed performance.

To further complicate matters, some authors have reported alternative “activation” schemes. Effective work functions of ThO₂ <2.8 eV have been
measured after positive ion bombardment, providing electron current in the reverse direction (i.e. towards the substrate), or placing the cathode in close proximity to another operating, activated thoria cathode.

Despite extensive and continued use of ThO₂ films for enhanced thermionic emission, no study to-date has reported field emission from ThO₂ coatings. By Fowler-Nordheim analysis (see chapter 2), reducing the work function by 1 eV can theoretically increase field emission current density by more than an order of magnitude. Therefore, establishing a thin, stable layer of ThO₂ (φ ~ 2.6-2.8 eV) on CNS (φ ~ 4.6-5.1 eV) would provide considerable improvement to the efficiency (electron emission for a given applied field) of CNS FEAs.

The following chapter describes a series of experiments intended to build a comprehensive understanding of ThO₂ thin films for field emission enhancement. These studies are broadly separated into three sections: (6.1) fundamental studies of Th oxidation and surface chemistry, (6.2) PVD of Th, oxidation, and thermionic emission from very thin films of (<50 nm) ThO₂, and (6.3) PVD deposition of Th on CNS, oxidation, film morphology, and field emission performance.

6.1 THE OXIDATION OF POLYCRYSTALLINE THORIUM

The oxidation mechanism of Th is critical to this study for two reasons. First, oxygen transport is central to the discussion of ThO₂ activation: i.e., the propensity of oxygen to abandon the surface and diffuse into the bulk. Second,
Th is deposited by PVD on selected substrates and subsequently oxidized. The post-PVD processing required to form stoichiometric ThO$_2$ films needed to be established. The oxidation of a bulk sample of natural $\alpha$-Th was used as a first approximation to thin film behavior.

Past studies of the oxidation of $\alpha$-Th have suggested conflicting positions on O$_2$, CO and CO$_2$ dissociative adsorption, the subsequent dissolution of oxygen and carbon into the bulk and the competitive formation of oxide and carbide phases [164-174].

Rivière observed the variation of work function for polycrystalline Th during O$_2$ exposure and proposed that, following dissociative adsorption, O atoms readily diffuse interstitially into the surface of the $\alpha$-Th cubic structure and, as these sites fill, the surface reaches saturation, subsequently transforming to ThO$_2$ [164]. Simultaneous carbon adsorption was not considered.

Later work by Taylor et al. studied the oxidation of single crystal Th (100) surfaces in UHV by low energy electron diffraction (LEED), AES and work function change ($\phi$ decreasing with O adsorption) [165]. As with Rivière’s work, the Th surface was saturated by dissociative adsorption of O$_2$. The LEED patterns of the saturated surface suggested formation of ThO$_2$ islands, producing a sharp diffraction pattern with moderate heating. The oxide (when heated to $>725^\circ$C) was then found to decompose and dissolve into the bulk. Similarly, the Th(100) surface saturated by CO showed a 90% reduction in the O (KLL) peak
after annealing to only ~300°C. The C (KLL) peak however, only diminished ~15%, suggesting both a greater solubility for O in the Th bulk and an oxidation mechanism in which surface carbide formation may inhibit oxide formation.

Bastasz et al. examined the Th(111) surface [166] in UHV and found similar behavior to the Th (100) face examined by Taylor et al. [165]. At high doses of O₂ and of CO (>10 L), a LEED pattern of ThO₂ was formed. At sufficient CO dosing, carbon did not appear to inhibit the formation of oxide domains, as suggested by Taylor et al.

McLean et al. reexamined CO, CO₂, and O₂ adsorption on Th(111) and the subsequent oxidation using both x-ray photoelectron spectroscopy (XPS) and AES [168]. In particular, analysis of XPS during CO adsorption indicated dissociation to form surface oxide and carbide, along with chemically bound CO (through the carbon). Depth profiles by AES and secondary-ion mass spectrometry (SIMS) suggested significant carbon incorporation. Thus, McLean et al. offered a mechanism in which carbon, subsequent to dissociative adsorption, readily diffuses into the bulk while the oxygen remains in the surface region and forms an oxide.

The conflicting results from these works suggest the need for further surface studies of thorium. In particular, the kinetics of carbon, dissociated from low doses of adsorbed CO/CO₂, is unclear. On one hand, carbon appears to have a lower solubility than oxygen in Th bulk and may initially inhibit surface oxide
formation. On the other hand, data also suggest that carbon may be readily incorporated into the Th bulk as the surface oxide forms. In part, these contradictions may arise from extrapolating observations at higher CO/CO₂ dosages and dose rates back to the initial oxidation behavior (<1 L). The following sections present a UHV (<1x10⁻¹¹ Torr) study of the initial oxidation of clean, polycrystalline α-Th from very low doses (<1 L) of background CO/CO₂ and oxygen dissolution behavior corroborated by admitted O₂ from initial oxidation to the formation of stoichiometric ThO₂.

6.1.1 EXPERIMENTAL DETAILS

Thorium rod (99.5%, polycrystalline, 1 mm diam., obtained from Goodfellow Metals, Inc) was cut to ~5 mm length. Further purification of the rod was achieved by electrotransport and high temperature/UHV processing. The exposed cross-sectional surface was polished to a mirror finish by standard metallographic techniques. In order to facilitate in situ resistive heating, one of the ends of each of two ~9 mm lengths of Re wire (99.5%, 0.25 mm diam.) were spot welded ~1 mm apart near the midpoint of the Th rod. The other end of each Re wire was secured to electrically isolated poles on a 304 stainless steel sample holder (see Fig. 3.6B). This suspended the Th rod so that the polished surface normal was at an angle of ~45° off vertical, which is very near the optimal injection into the DPCMA. The entire assembly was cleaned in an ultrasonic bath of electronic grade acetone for 20 minutes, rinsed with HPLC grade isopropanol, and air dried. Calibration of sample temperature (23–1000°C) as a function of
direct current (DC) was accomplished using a K-type thermocouple junction spot welded between the Re wire contacts, around the azimuthal angle of the Th rod, 1-2 mm away from the contact points (Fig.6.1). The assembly was mounted to a high-power, vacuum-electrical feedthrough with thermocouple facility, and installed in a high vacuum chamber (unbaked base pressure ~1x10^{-9} Torr). Currents of 0-5 A DC were delivered by a BK Precision 1796 high current regulated supply and the temperature repeatedly calibrated (±5%) up to 1000°C. The color of the entire rod at temperature appeared to be quite uniform over the 600-1000°C range.

All adsorption experiments were conducted in the MESAS (see section 3.2.1). The sample was first installed in the introduction chamber (ultimate pressure ~5x10^{-10} Torr) and degassed by radiative heating to ~300°C for 2 hours before transfer to the carousel in the main analysis chamber. The design of the carousel allows resistance heating of samples up to 1700°C concurrent with analysis. All data in this study were collected at a base pressure, p<1x10^{-11} Torr.

Auger electron spectroscopy was performed with at an incident electron beam energy of 3 keV, maintaining a constant measured sample absorption current of 1 μA (±5%). The AES spectra were collected with 1.0 eV/step and a time constant of 50 ms/step; in all cases, multiple (2-20) sweeps were averaged in order to improve the signal-to-noise. A confocal Ar⁺ ion gun (5 keV, 1-2 μA, p ~ 7x10^{-8} Torr [Ar]) was used for sputter cleaning and depth profiling; a 2 mm x 2
mm raster was used in order to maintain the sputtered region much larger than the AES analyzed area.

Initial spectra of the Th surface showed O, C, Cl, and S contamination, which were removed, to below the sensitivity of AES (~1 at. %), by alternating heating to 1000°C for 5 minutes and Ar⁺ sputter cleaning for ~30 min cycles. Adsorption studies were performed immediately following 10 cleaning cycles.

The initial oxidation of the clean polycrystalline Th surface at 25°C was studied by monitoring adsorption of background CO and CO₂, which were predominantly generated by operation of the thermionic emission source in the DPCMA's concentric electron gun (see Fig. 3.13). The normalized partial pressures of CO and CO₂ during operation of the electron gun were <1×10⁻¹⁰ Torr as determined by the RGA. Changes in peak-to-peak intensities of the O(KLL) and C (KLL) AES peaks, corrected with published relative sensitivity factors [83], were used to measure the evolving concentration of O and C on the Th surface as a function of time. It is worth emphasizing here that the base pressure of this system was estimated to be ~5×10⁻¹² Torr.

The cleaning procedure was thereafter repeated and the resulting clean polycrystalline Th surface was exposed to ultrahigh purity (99.99%) O₂ (p =1×10⁻⁸ Torr [O₂], ±5%) for one hour, while AES spectra were collected over three kinetic energy ranges (49-72 eV, 205-230 eV, 495-510 eV) to monitor the surface oxidation process through the variation of Th and O peaks (described in detail
below). All peak-to-peak intensities were converted to relative concentrations using published relative sensitivity factors [83].

AR-AES data were taken for clean polycrystalline Th exposed to 48 h of background contamination by CO/CO₂ and fully oxidized Th by admitted O₂. The information depth of measured Auger electrons of a given kinetic energy (and thus a prescribed inelastic mean free path) vary with take-off angle as the distance that must be traversed through the solid from a given depth to the surface increases at shallower angles. To achieve angle sensitivity, a rotating, notched drum with a 12° aperture is positioned between the two cylinders in the DPCMA such that only those secondary electrons with trajectories that align with the drum’s aperture are passed to the spiraltron. Here, the aperture was rotated to 0° and 180° positions, corresponding to Auger electron take-off angles of ~90° and ~0°, respectively. The spectra acquired at ~90° take-off angle represents an information depth of ~3 nm for 100 eV electrons; the spectra acquired at ~0° take-off angle represents an information depth of ~0.5 nm. The 12° aperture, however, severely limits the total signal thereby considerably lowering the signal-to-noise ratio for any fixed collection time, so longer acquisition times were required.
Figure 6.1: Schematic and photo of Th rod prepared for in situ thermal-vacuum and oxidation studies in the MESAS. Note that the cross-sectional surface was the probed surface in all cases. Re wires were spot welded near the mid-point to enable Joule heating (shown here at T~1000°C). The sample was cleaned by Ar⁺ sputtering and thermal cycling.
The sample was subsequently removed and installed in the ToF-SIMS in order to corroborate the oxide thickness at saturation with estimates from AES, using identical nominal Ar\textsuperscript+ sputter parameters. The ToF-SIMS sputter profile was conducted by alternating analysis using a Au liquid metal ion source (LMIS) (~2 nA, 22 keV) for ~60 s over a random 50 μm raster with sputtering by Ar\textsuperscript+ (1.0 μA, 5 keV) for 10 s using a 2 mm x 2 mm raster. The variation in ThO\textsuperscript+ secondary ion counts, normalized to the total counts for each analysis cycle, as a function of sputtering time serves as a proxy for the ThO\textsubscript{2} oxide profile in ToF-SIMS.

6.1.2 THORIUM OXIDATION STUDY RESULTS

The initial AES trace of a typical polycrystalline α-Th surface, following heating and sputter cleaning, over the kinetic energy range of 30 to 550 eV is shown in figure 6.2. Absence of the O (510 eV) peak and only slight indication of the C (270 eV) peak suggest that the sputtering and annealing procedure was sufficient to produce a clean metal surface (below AES detection limits, ~1 at. %) for subsequent adsorption studies. Previous studies have all shown some residual oxygen peak after cleaning. The major Th Auger peaks are indicated; both the relative intensities and positions correlate well with previous AES spectra of Th reported in the literature [165]. Subsequent SEM analysis showed the average grain size to be ~100 μm (Fig. 6.3).

According to McLean et al. [168], oxidation of Th can occur by dissociative adsorption of CO and CO\textsubscript{2}, yielding an O rich surface as free C is incorporated.
into the bulk (i.e., a decreasing surface C/O ratio). In this work, at <1 L doses, the ratio of C/O increases (Fig. 6.4) over three hours of exposure, indicating that oxygen disappears from the AES probed volume at a rate significantly faster than that of carbon. RGA measurements did not show any evidence for oxygen-bearing species in excess of those arising from the RGA ion source itself. Thus, at these coverages, the chemical potential and/or concentration gradient must drive some of the O into the Th bulk. After three hours of exposure, the C peak shape is indicative [175,176] of spontaneous thorium carbide formation [Fig.6.4 inset]. In order to rule out any electron beam effects, such as electron stimulated desorption or dissociation, the beam was moved to two separate locations on the sample surface immediately after testing. The spectra did not vary with beam position.
Figure 6.2: AES survey ($E_p = 3$ keV) of clean polycrystalline $\alpha$-Th. Carbon (270 eV) and oxygen (510 eV) are not present in detectable quantities.
Figure 6.3: SEM micrograph of the cross-sectional surface of a polycrystalline Th rod used in these studies after thermal treatment and completed experiments. This analysis suggests grain sizes >100 μm.
Figure 6.4: Adsorption and oxidation of Th by CO/CO$_2$ background as monitored by the O (510 eV) and C (270 eV) peak-to-peak intensities in the AES spectra as a function of time. This data was repeated and both sets plotted; the solid line is a linear least-means square fit. The inset shows the C (270 eV) AES peak shape characteristic of carbide formation taken after 3 h CO/CO$_2$ background exposure.
The oxidation kinetics at the surface (25 °C) of clean polycrystalline Th were further investigated by admitting high purity O₂ and increasing the partial pressure to ~1×10⁻⁸ Torr. Our preliminary experiments indicated that, although they are not the highest intensity peaks in the Th spectrum, the overlapping Th(228 eV) and Th(221 eV) peak shape was unaltered by oxygen exposure. Since these peaks are unaltered by changing chemical environment, they are the most reliable and stable measure of Th concentration; hereafter in this discussion, the sum of these peaks will be called “Th(228 eV)”. The AES peak-to-peak intensity of O(510 eV) and Th(228 eV) are plotted versus O₂ dose (Fig. 6.5A). The increase in the O(510 eV) signal coincides with decreasing Th signal as the O concentration in the AES probed volume increases. Interestingly, the slope of the O intensity curve approaches zero at ~15 L, but the Th signal continues to decrease. The O/Th ratio shows that, after ~37 L, the AES probed volume approached 2:1, indicating the formation of stoichiometric ThO₂ (Fig. 6.5B). Figure 6.6 shows the AES survey for ThO₂ after ~37 L O₂. Interpretation of the oxidation kinetics through the variation of the O(510 eV) peak (Fig. 6.5A) becomes problematic at higher doses (>15 L) as the effects of diffusion and incorporation of oxygen into the Th bulk become apparent. Monitoring the absorbed current during AES is not sufficient to claim a constant incident beam current. As the Th metal surface becomes oxidized, the secondary electron emission coefficient changes significantly, altering the observed absorbed current by as much as 30%. As discussed in chapter 3, changes in the emission current,
generated by the electron gun itself, can also occur from oxidation of the thermionic filament surface (decreasing the work function). A small coupon of Au foil (99.9%) was used to help characterize these sample surface and instrument effects (see 3.2.3). Au does not form a stable oxide and therefore will not experience significant change in the secondary electron emission coefficient when exposed to oxygen. The absorbed current through the gold foil from a 3 keV, 1μA e⁻ beam was observed to linearly increase ~25% over 50 minutes (p~1 x 10⁻⁸ Torr [O₂]) and is a reasonable estimate of instrument related error (Fig. 3.14).

Figure 6.5: (A) The variation of the Th (228 eV) and O (510 eV) AES peak-to-peak intensities as a function of O₂ dose, p(O₂)~1x 10⁻⁸ Torr. (B) The ratio of Th (228 eV)/O (510 eV) as a function of O₂ dose. The stoichiometry approaches that of ThO₂ at ~37 L.
Figure 6.6: AES survey (E_p = 3 keV) of ThO_2 created by exposure of Th to ~37 L of O_2. Note that very little C contamination is observed.
It is well-established that Auger lineshapes can yield chemical state information [176] especially in systems involving significant shifts in electron density (as with oxidation). As oxygen dissolves into Th, the qualitative changes in the Th (237 eV) and Th (245 eV) peaks (N\textsubscript{7}O\textsubscript{4}V and N\textsubscript{7}O\textsubscript{5}V transitions, respectively) are significant [165]. However, careful examination of the 50-70 eV range of the observed secondary electron spectrum yields strong quantitative indicators of the degree of oxidation (Fig. 6.5 A-C). Taylor et al. assign the O\textsubscript{5}P\textsubscript{2}V and O\textsubscript{4}P\textsubscript{2}V transitions to the 57 eV and 65 eV peaks [165]. It is observed that the Th (57 eV) peak shifts ~+2 eV when the sample is saturated by >37 L of O\textsubscript{2} relative to the Th (65 eV) peak; moreover, the ratio of the intensity of the Th (57 eV) peak to the Th (65 eV) peak increases as a function of oxygen exposure (Fig. 6.7A). A three dimensional plot of acquired spectra illustrates the continuous evolution of the peak shapes and intensities as a function of time (Fig. 6.5B). For convenience, the local intensity maxima of Th(57 eV) is designated as A and that of Th (65 eV) as C, and a local intensity minimum B in the 50-62 eV range (Fig. 6.7A). Letting \( \alpha=A-B \), \( \beta=C-B \), the ratio \( \alpha/\beta \) serves as an empirical measure of the change in the relative peak heights, and serves as a progress variable for the reaction as the Th surface is oxidized\(^3\). Figure 6.7C demonstrates the aptness of this simple analysis as the trend is analogous to the variation of O/Th shown in figure 6.5B. Similar empirical approaches have been used to analyze AES lineshapes during oxidation of transition metals [177,178].

\(^3\) Please note that \( \alpha \) and \( \beta \) used here are not related to emission site area or enhancement factor used in the description of field emission.
Figure 6.7: (A) The 50-70 eV region of the Th AES spectrum before and after 40 L O₂. Note the changes in the relative peak intensities and position. The local maxima, A and C, and the local minimum, B are indicated for ease of discussion (see text). (B) A three dimensional plot of the same region, illustrating the continuous evolution of the Th peak shapes as a function of oxygen exposure (time). (C) For $\alpha$=A-B, $\beta$=C-B, the ratio $\alpha/\beta$ as a function of oxygen exposure (time). Note the similarity in comparison to figure 6.5B.
Angle-resolved data using the 12° aperture was taken to assess the uniformity of the surface oxide (for clarity, Fig.3.15 is repeated here, Fig. 6.8A). At 180° rotation, only Auger electrons with shallow take-off angle (e_{surf}) pass through the cylinder to the spiraltron™, thereby generating spectra with a much shallower information depth (~0.5 nm) than that obtained at 90° (e_{norm}), ~3 nm. The ratio \( \alpha/\beta \) was used as an empirically-derived measure of the degree of oxidation (Fig. 6.8B). No significant variation was observed for the fully saturated surface (>37 L O_2), suggesting uniform ThO_2 over a depth of at least 2 nm. Both the sputter cleaned Th and partially oxidized Th (48 h background CO + CO_2 exposure) showed lower concentrations of oxygen near the surface suggesting that during the initial stage of oxidation, oxygen atoms diffuse into the Th near-surface region. As discussed above, longer acquisition times were required to obtain reasonable signal-to-noise; therefore, it is expected that some oxygen is observed in the sputter cleaned Th spectra (see Fig. 6.4).
Figure 6.8: (A) A cross-sectional schematic of the DPCMA, as used during angle-resolved AES. Note the rotating notched drum used to select electrons by their take-off angle, and thus information depth. This is a repeat of Fig 3.15 for the reader's convenience. (B) The ratio $\alpha/\beta$ from the AR-AES data as a function of detector angle for polycrystalline Th, Th + 48 background CO/CO$_2$ exposure, and ThO$_2$. The line is eyes-guide only. The oxide appears relatively uniform. The polycrystalline Th and partially oxidized Th data indicate lower surface concentrations of oxygen and further suggest a high solubility of O in Th.
ToF-SIMS and AES depth profiles were used to determine the thickness of the ThO$_2$ layer at saturation (Fig. 6.9). The time to sputter to 50% concentration was used as an estimate of the conventional ThO$_2$/Th interface and was found to be ~100 s. The Ar$^+$ flux (5 keV) was $\sim$1.6 x $10^{14}$ Ar$^+$ cm$^{-2}$ s$^{-1}$. Preliminary experiments with ToF-SIMS sputter depth profiles of ThO$_2$ thin films on Si (film thickness determined by Dektak stylus profilometry) offered an approximate sputter yield of ~0.5 for Ar$^+$ (5 keV) (Fig 6.10). Thus, we estimated the sputter rate in these experiments to be ~0.02 nm s$^{-1}$ and the thickness of the oxide ~ 2 nm.

The structure of the ToF-SIMS depth profile for the Th$^+$ and ThO$^+$ is incredible similar all the way down to the cross-over at the Si interface (Fig 6.10). This suggests complete oxidation throughout the Th film.
Figure 6.9: A comparison of ToF-SIMS and AES sputter depth profiles using Ar⁺ (~1 μA, 5 keV). The variation of ThO⁺ secondary ion counts (normalized to the total counts for each analysis cycle) as a function of sputtering time serves as a proxy for the ThO₂ oxide profile in ToF-SIMS. The variation in the O (510 eV) Auger peak-to-peak intensity is also shown. The profiles appear to correlate well and suggest oxide thickness of ~2 nm (see text).
Figure 6.10: (A) Secondary ion counts (normalized to the total yield) during Ar⁺ sputtering in the ToF-SIMS for ThO₂ deposited on to a Si wafer. (B) A DekTak™ linescan of the resulting sputter crater showing depth of (40 nm). By assuming the Ar⁺ sputter yield of Si ~ 1, the yield for ThO₂ can be estimated to be ~0.5.
Auger data were also acquired during stepwise (+100°C) thermal treatment of the oxidized Th surface up to a maximum temperature of 1000°C. The calibration curve for temperature versus applied DC current is shown in figure 6.11. At each +100°C step, the current was maintained for 5 minutes, after which the current was turned off ~5 min while AES data were collected. During the acquisition of AES data, it is estimated that the temperature of the sample decayed to <150°C over the entire temperature range studied. When the fully oxidized Th sample was heated to 1000°C, the O (KLL) peak-to-peak intensity was found to decrease rapidly between ~550-750°C relative to the Th (228 eV) peak-to-peak intensity (Fig.6.12). No evidence of an increase in oxygen-bearing species was seen in the RGA (the aperture of the RGA is near, but not in line-of-sight to the sample). It is more likely that, at >550°C, oxygen rapidly diffuses into the Th bulk. The C/Th ratio was observed to slightly increase over this temperature range and may correspond to segregation of C from the Th bulk to the surface. It is also possible that the increase in C comes from adsorption of background species, which seems plausible considering there was an observed increase in the partial pressure of CO (+35%) and CO₂ (+27%) from radiant heating of stainless steel vacuum components in the vicinity of the Re heater wire and the Th rod (T= 1000°C)[179].
Figure 6.11: The temperature of the thorium rod as a function of applied DC current, as calibrated by a K-type thermocouple.
Figure 6.12: The AES intensity of O and C (normalized to Th(228eV)) as a function of temperature. The oxygen is observed to rapidly decompose between ~550-750°C and is believed to incorporate into the Th bulk. The slight increase in the C signal is likely due to adsorption of background gases generated by radiant heating of adjacent stainless steel surfaces.
6.1.3 DISCUSSION OF THORIUM OXIDATION RESULTS

The initial and rapid oxidation of polycrystalline Th by very low doses (<1 L) of background CO and CO\(_2\) was observed. The background CO and CO\(_2\) partial pressures were < 1x10\(^{-10}\) Torr. The CO/CO\(_2\) is generated primarily from the concentric electron gun in the DPCMA, where RGA measurements indicate that the flux is predominantly CO and CO\(_2\) (Fig.3.13). Although the total flux is quite small, this beaming effect, unfortunately, is inherent to any instrument with a thermionic cathode that is line-of-sight to the sample. In this work, dissociative adsorption of very low instrument-related doses of CO/CO\(_2\) resulted in the competitive formation of both carbide and sub-oxide: the carbide localized to the surface and the sub-oxide forming a broader vertical concentration profile. From the increasing rate at which carbon accumulates at the surface (Fig.6.4), it is most likely that some of the oxygen resulting from dissociation of both adsorbed CO and CO\(_2\), readily diffuses into interstitial sites in the near-surface Th cubic structure, as suggested by Rivière [164]. Indeed, the ARAES data for Th after 48 h background CO/CO\(_2\) exposure confirms the expected oxygen concentration gradient in the near-surface region (Fig. 6.8B). The carbon occupies surface and near surface sites, and forms thorium carbide as confirmed by the carbide lineshape [175,176] in the C (270 eV) AES spectra (Fig 6.4 inset). Unfortunately, there is insufficient data to suggest the stoichiometry of this carbide phase. Figure 6.13 presents a schematic of the proposed initial oxidation mechanism.
Figure 6.13: Schematic of the proposed initial oxidation mechanism by very low doses (<1L) of CO/CO₂ (generated by operation of the electron gun). Both C and O accumulate on the surface but O at a slower rate because some O incorporates in a manner originally proposed by Rivière [164].
With continued CO/CO₂ exposure, it is likely that, as interstitial sites fill, oxygen dissolution into the Th bulk is reduced, thereby connecting these observations to those of McLean et al. [168]. Indeed, at a CO dose of 2 L and CO₂ dose of 6 L, McLean et al. noted a carbide lineshape in the C (270 eV) AES spectra; however, as the dose was increased to >10 L, they observed a growing graphitic component to the C (270 eV) lineshape. Furthermore, they report that the O/C ratio (from XPS analysis) appears to have increased over this regime: e.g. atomic ratios (O/C) of 1.2 for 10 L CO and 2.9 for 10 L of CO₂. McLean et al. conclude that upon dissociative adsorption, carbon diffuses into the bulk leaving oxygen to react, forming the dioxide near the surface. Their depth profiles by AES and SIMS after 10 L CO are consistent with this picture. However, in this work, the initial CO/CO₂ background adsorption (<1 L) data suggests that the initially observed carbide at low doses is spontaneously formed at the surface. As further CO/CO₂ is adsorbed, oxygen may increasingly compete for sites in the near-surface region and may displace or preclude further carbide formation. Consequently, additional CO/CO₂ adsorption generates free carbon that accumulates on the surface and/or providing the increasing graphitic component to the C (270 eV) lineshape and the buried maxima in the C concentration depth profile [168]. It is also probable that the CO/CO₂ dose rate may affect the observed reaction products. In this work, background absorption of CO/CO₂ occurs over much longer times to achieve doses much less than those reported by Mclean et al., allowing for more significant diffusion in the adsorption,
dissolution and oxidation kinetics. The initial preferential formation of Th\textsubscript{x}C\textsubscript{y} (\(\Delta H \sim 31\) kcal/mol) over ThO\textsubscript{2} (\(\Delta H \sim 293\) kcal/mol) suggests a dominant solubility for O atoms in Th at room temperature [180]. After sufficient O diffusion in to the bulk, the decrease in concentration gradient ultimately favored the formation of ThO\textsubscript{2}.

This work demonstrates that full oxidation of the surface region of polycrystalline Th by O\textsubscript{2} (p \(\sim 1.0 \times 10^{-8}\) Torr) occurs only when incorporation of oxygen into the bulk is saturated as interstitial sites in the near-surface region are successively filled. The oxygen/polycrystalline Au experiment to examine the effect of changing Th\textsubscript{x}O\textsubscript{y}/Th\textsubscript{x}C\textsubscript{y} secondary emission and changing filament emission current of the concentric electron gun was quite revealing. This clearly showed that oxygen adsorption on the W filament strongly affects the observed AES intensity when operating over extending periods of time. This instrument-related error was factored out by taking the ratio of peak intensities; full oxidation is observed after >37 L of O\textsubscript{2} resulting in the formation of stoichiometric ThO\textsubscript{2} (Fig 6.5B). Work on single crystal Th (111) showed that doses up to 40 L (O\textsubscript{2}) were insufficient to reach stoichiometric ThO\textsubscript{2} (~80% oxidized), as evaluated by XPS [168]. Grain boundary effects have been ruled out since the average grain size was relatively large (~0.1 mm) and fully annealed which provides a preferred (111) grain orientation. Therefore, the grain boundary density was quite small and unlikely to be a significant factor.
The resulting ThO$_2$ appears quite uniform since ARAES of the saturated Th surface did not show any change in $\alpha/\beta$ with angle (Fig. 6.8B). Sputter depth profiles done during cleaning cycles in this work, as well as those published by McLean et al., demonstrate an abrupt decrease in the O concentration profile as the bottom of the oxide layer is reached. The available oxidation states of Th are limited, suggesting a small range of stoichiometry [158,164,169]; once saturated, additional adsorbed O cannot easily penetrate the fully-formed ThO$_2$ overlayer. This is consistent with the formation of what Rivière called an "equivalent monolayer". Further, both the AES and ToF-SIMS depth profiles are in excellent agreement and suggest the saturated oxide layer is $\sim$2 nm thick (Fig. 6.9). This thickness is consistent with other native metal oxides and our ARAES results.
6.1.4 SUMMARY REMARKS

The AES of the initial oxidation of Th by low doses (<1 L) CO/CO$_2$ suggests that, upon dissociative adsorption, O is readily incorporated into interstitial sites just below the surface while C, with an apparent lower solubility, accumulates on the surface more rapidly and spontaneously forms a surface carbide. As more CO/CO$_2$ is adsorbed, it is likely that oxygen increasingly competes for sites in the near-surface region and may displace or preclude carbide formation. Consequently, further CO/CO$_2$ adsorption generates free carbon that accumulates in a graphitic form and some diffuses into the bulk.

Saturation of polycrystalline Th by dissociative adsorption of O$_2$ and the subsequent formation of ThO$_2$ occurs at a coverage above about 37 L. Analysis of the 50-70 eV region of the secondary electron spectrum yields a simple empirical approach to gauge the degree of Th oxidation. Further, ARAES data supports a high solubility of O in Th, and an oxidation mechanism similar to that suggested by Rivière in which oxygen is incorporated into the near surface Th interstitial sites before full monolayer coverage of the surface is realized. The AES and ToF-SIMS sputter depth profiles of the resulting ThO$_2$ layer indicate an oxide thickness of ~2 nm. A continuous plot of the thermal stability of the ThO$_2$ indicates decomposition and dissolution of the oxide at a temperature of ~550-750°C, a further indication of a significant O solubility in Th.
6.2 HETEROEPITAXIAL GROWTH OF THIN FILM THORIUM OXIDE ON POLYCRYSTALLINE IRIDIUM

As discussed earlier in this chapter, relatively thick ThO₂ coatings (~50 μm) provide a low work function (ϕ~2.6 eV) surface for electron emitters with superior thermal and chemical robustness and have historically been used for enhanced thermionic emission from metal cathodes [181,182]. Though industry concerns for processing even mildly radioactive materials have largely provoked alternative coatings, ThO₂ electrophoretic coatings are still widely used in technical applications such as cathodes for ion gauges, residual gas analyzers and vacuum tubes [158].

Coatings of ~50 μm are too thick to be useful for enhanced field emission from CNS since the geometrical field enhancement provided by <1nm thick edges would be eliminated. Thus, a study was required to assess the efficacy of much thinner low work function coatings (< 100 nm) on selected thermionic and field emission substrates. The following sections discuss work done to characterize the growth of ThO₂ thin films (~ 40 nm thick) deposited by physical vapor deposition (PVD) of Th on polycrystalline Ir. The Th was immediately oxidized by oxygen-bearing background gases to form ThO₂, during deposition at ~340 K. During subsequent thermal treatment, mass transport and crystallite growth resulted in diverse ThO₂ morphologies with apparent sensitivity to the polycrystalline Ir substrate. Strong morphological heterogeneity in the annealed ThO₂ film can be explained by surface energy minimization and the formation of
the ionic, fluorite (CaF$_2$) structure of ThO$_2$ on energetically and topologically different regions of the polycrystalline Ir substrate. Th and O incorporation into the Ir bulk is not suspected. Previous work on Th doped Ir + 0.3%W alloys demonstrated that the solubility limit for Th is likely below 10 wt. ppm [183]. The Th segregated from these Ir alloys by grain boundary diffusion at elevated temperature. At the surface, Th was shown to selectively oxidize, attributed to favorable thermodynamic conditions: $\Delta G = -917$ kJ/mol for the formation of ThO$_2$ as compared to $\Delta G = +77.8$ kJ/mol for IrO$_2$ at 1600 K. Further, a large body of literature on the heteroepitaxial growth of CaF$_2$ on a variety substrates with similar morphological features to that observed for ThO$_2$ on Ir provides appropriate confirmation, e.g. Si(111) [156,184].

A full description of the ThO$_2$/Ir heteroepitaxial system suggests a means to assess the efficacy of very thin films of ThO$_2$ for enhanced electron thermionic and field emission. Substrate choice and surface preparation may yield more conformal and contiguous ThO$_2$ thin film growth better able to resist thermal cycling while providing a uniform, low work function coating. In this work, it is demonstrated that, following high temperature heating, very thin films of ThO$_2$ - grown by PVD can assume a broad range of highly ordered morphologies on polycrystalline Ir. This variety of form may be technologically useful. Following characterization of the film morphology, corresponding thermionic emission data is also presented for these films.
6.2.1 EXPERIMENTAL DETAILS

Iridium ribbon (99.8%, polycrystalline, 0.13 mm x 0.8 mm, obtained from H. Cross Company) was cut to ~12 mm length and both faces of the ribbon polished with 1200 grit SiC paper. To facilitate resistive heating, each end of the Ir ribbon was spot welded to the midpoint of one of two equal ~14 mm lengths of hairpin shaped W/Re(26%) wire (0.38 mm diam). The ends of each W/Re wire were fixed to one of two electrically isolated poles on a 304 stainless steel sample holder (see Fig.3.6B). A C-type thermocouple was then spot welded to the backside, center of the Ir ribbon. The entire assembly was cleaned in an ultrasonic bath of electronic grade acetone for 15 minutes, rinsed with HPLC grade isopropanol and air-dried. The assembly was mounted to a high-power, vacuum-electrical feedthrough with a complimentary thermocouple feedthrough, and installed in a high vacuum chamber (base pressure ~1x10^-10 Torr). Currents of 0-10 A DC were delivered by a BK Precision 1796 high current regulated supply and the temperature calibrated (±5%) up to 2000 K (figure 6.14). An ex situ two-color optical pyrometer (Raytek Marathon MR1SBSF) positioned at a minimum focal distance of ~60 cm with a spot size of ~7 mm^2 proved reasonably consistent with the thermocouple measurements over the region of 1225–2000 K and was later employed for non-contact monitoring of annealing/thermionic emission experiments. The color temperature of the Ir ribbon indicated a moderate thermal gradient from the center of the ribbon to the junction with the...
W/Re support wire. By changing the optical pyrometer's field of view, the thermal gradient along the Ir ribbon was estimated to be $\sim 30$ K/mm.

Figure 6.14: The temperature of the Ir ribbon as a function of applied DC current, as calibrated by a C-type thermocouple and correlated with an ex situ, two-color pyrometer.
The Th PVD coatings and compositional characterization were conducted in the MESAS. The Ir ribbon (thermocouple removed) was installed in the introduction/coating chamber (ultimate pressure \( \sim 5 \times 10^{-10} \text{ Torr} \)) and degassed by radiative heating to 600 K for 2 hours before transfer to the carousel in the main analysis chamber.

Surface composition was characterized by AES. As with the Th oxidation study, the incident electron beam was \( \sim 60 \mu \text{m} \) in diameter when operated at 3 keV, maintaining a constant measured sample absorption current of 1 \( \mu \text{A} \) (\( \pm 5\% \)). The AES spectra were collected at 1.0 eV/step and a time constant of 50 ms/step; in all cases, multiple (5-10) sweeps were averaged in order to improve the signal-to-noise.

Initial analysis of the Ir substrate showed C, O, and N contamination. These impurities were removed to within the sensitivity of AES (~1 at. %) by sequentially heating to \( \sim 1800 \text{ K} \) and \( \text{Ar}^+ \) sputter cleaning (7 min., 5 keV, 1 \( \mu \text{A} \), \( \bar{p} \sim 7 \times 10^{-8} \text{ Torr[Ar]} \)). The annealed Ir ribbon was then transferred back into the introduction/coating chamber. The MDC e-vap-100 was used for PVD of Th (1mm diam. rod, 99.5% Goodfellow Inc.) onto the polycrystalline Ir substrate at an estimated rate of 0.10±0.05 nm/min. The substrate temperature measured during deposition was 340±10 K. The system pressure increased to \( \sim 3 \times 10^{-8} \text{ Torr} \), primarily as system components in proximity to the e-beam hot cathode were radiatively heated and outgassed. ThO\(_2\) films spontaneously formed as the Th film chemically adsorbed oxygen from background gases. Residual gas analysis
within the introduction system was used during deposition to monitor changes in gas composition.

Immediately following coating, the sample was again transferred to the main analysis chamber where AES was used to assess the as-deposited film composition. The ribbon was then resistively heated to 1750 K over a period of ~10 min and thermionic emission data collected by a remote Pt anode (discussed in more detail in section 6.2.3, below), after which, AES was acquired. The process of coating and heating was repeated until additional coating provided no further change to the post-heating Auger spectra. Initial coating times of 5 min were used; this was increased to 10, 15, 30, 45, 60 and finally 90 minutes. After a total of 425 minutes of deposition time and a final thermal treatment up to 2000 K, the ThO₂/Ir ribbon was removed from the UHV system.

The Hitachi S-4700 scanning electron microscopy (SEM) operated at 10 keV (to minimize charging) was used to examine the Ir and ThO₂ film morphology. Sufficient micrographs of various positions and magnifications of the annealed film were collected to build a statistically relevant assessment.

The crystalline structure was investigated using x-ray diffraction (XRD) by a four-circle PANalytical X’Pert PRO-MRD diffractometer. The diffractometer scanned a 2θ range from 20° to 75° in steps of 0.02°. It also used a a Cu Kα source operated at 45 kV and 40 mA with a 0.5° divergence slit, and a 0.1° receiving slit with line-focus mirror primary optics. The secondary optics consisted of a 0.27°
parallel-plate collimator followed by a flat graphite secondary monochromator and a proportional detector.

6.2.2 RESULTS AND DISCUSSION

During deposition of Th by PVD, radiative heating of near-by system components increased outgassing, which resulted in an increase in the total pressure from $5 \times 10^{-10}$ to $\sim 3 \times 10^{-8}$ Torr. Residual gas analysis shown in figure 6.15 illustrates the relative increases in background gases during PVD of Th. Substantial changes in the partial pressures of CO$_2$, CO, CH$_4$, H$_2$O and H$_2$ were observed, consistent with radiative heating. Oxygen-bearing gases incident on the Th coating were dissociatively adsorbed to form ThO$_2$. No significant C concentration was observed by AES in the ThO$_2$ films. This suggests two possible mechanisms: (1) H$_2$O may dissociatively adsorb, oxidize the Th and release hydrogen:

$$\text{Th} + 2 \text{H}_2\text{O} \rightarrow \text{ThO}_2 + 2 \text{H}_2 \uparrow$$

(2) Alternatively, CO$_2$ may dissociatively adsorb, oxidize the Th metal film and release CO:

$$\text{Th} + 2 \text{CO}_2 \rightarrow \text{ThO}_2 + 2 \text{CO} \uparrow$$

The adsorption of H$_2$O is perhaps the more plausible mechanism given the factor of $\sim 3$ smaller H$_2$O signal compared to the CO$_2$ signal. It is usually observed in unbaked systems that the partial pressure of H$_2$O > CO, CO$_2$ [185]. During PVD, the Th metal evaporative flux is not restricted to the substrate and coats a
significant fraction of the chamber's surface area that is line-of-sight to the source; Th on these surfaces produced chemical adsorption pumping (gettering). Further, an increase in the H$_2$ partial pressure over and above expected degassing from an unbaked system was observed.

Figure 6.15: Residual gas analysis of the MESAS introduction/deposition chamber background before and during PVD of Th. Note the substantial increases in CO and CO$_2$ partial pressures due to radiative heating of near-by system components. The indicated partial pressures are not calibrated; the actual total pressure in the system was $p<5\times10^{-8}$ Torr.
The major Auger transitions for Ir and Th sufficiently overlap obscuring direct interpretation of the AES data collected on as-deposited and heated films following progressive PVD coating of ThO$_2$. In order to assess composition, a digital linear combination of previously acquired [186] AES surveys of bulk Ir, Th, and ThO$_2$ was used to model each experimentally acquired survey. The coefficients used in the linear combination were constrained so that the sum of the coefficients was equal to 1. An exhaustive search algorithm varied the coefficients over the allowed ranges in increments of 0.01 as the modeled fits were compared to the experimental data by computing a Pearson correlation coefficient. By maximizing the Pearson correlation coefficient between the model and experimental spectra, the best-fit digital linear combination of component bulk spectra was found. The best-fit coefficients associated with each component bulk spectra (Ir, Th, and ThO$_2$) can be directly related to composition. As an example, figure 6.16 juxtaposes the experimentally acquired AES survey after a total of 245 minutes deposition and heating to 1750 K with the digital linear combination of Ir, Th, and ThO$_2$ AES spectra having 0.39, 0.01, and 0.60, respectively, as the best-fit coefficients. By comparing the modeling results over various kinetic energy windows, it is estimated that the error in the best-fit coefficients is <10%. In every case, however, the best fit suggests <1% pure Th and is consistent with a stoichiometric thorium oxide film on Ir. Figure 6.17 indicates the best-fit coefficients for Ir and ThO$_2$ for each deposition cycle (both as-deposited and post-heating). The scatter in the data is primarily associated
with the variation in the deposition rate, thickness of the as-deposited film and correlated time-temperature dependent transformations. The dashed lines are an eyes-guide only and are generally in good agreement with AES studies of layer plus island (Stranski-Krastanov) growth [80]. As the ThO₂ film coverage and thickness increases, the probability of detecting Auger electrons generated within the Ir substrate is exponentially damped. Consequently, as deposition time increases, the Ir contributions to the as-deposited AES signal shown in figure 6.16 decrease roughly exponentially. The thickness of ThO₂ on the Ir after substantial PVD of ThO₂ was much greater than the 5 nm information depth for AES and therefore completely masked the Ir substrate. Heating the film to 1750 K, however, facilitated surface diffusion and coalescence resulting in ThO₂ crystallite formation. At the substrate temperature, no re-evaporation or incorporation in the Ir is suspected. As crystallites formed, neighboring depletion zones exposed the Ir substrate, providing a reemerging Ir Auger signal in the post-heating data. After 245 minutes of deposition, the number of crystallites appeared to have reached steady state and each additional deposition and heating cycle added only minimally to the ThO₂ footprint, with an apparent coverage of 0.6±0.06.
Figure 6.16: Comparison of digital linear combination of Ir, Th, and ThO$_2$ bulk AES spectra with experimental AES data of thin film ThO$_2$ (245 min total deposition time) on polycrystalline Ir after heating to 1750 K. C and N impurities are a result of segregation from the Ir bulk.
Figure 6.17: Approximate contribution of ThO₂ and Ir to the measured AES signal from fitting of the data (see text) as function of PVD time. After each deposition cycle, the sample was heated to ~1750 K. The scatter in the data is from error in the fitting and time-temperature variations in surface composition.
From the more than one hundred SEM micrographs taken from the central region of the ThO$_2$-coated Ir ribbon, four have been selected as representative and are shown in Fig. 6.18A-D. Apparent step edges shown in Fig. 6.18A suggest that the annealed, polycrystalline Ir provides vicinal regions on which step-flow growth of ThO$_2$ is preferred. The highly ordered geometry of the film in this region shows a preponderance of 120° and 60° vertexes. Fig. 6.18B-D illustrate highly polymorphic ThO$_2$ thin film growth. In addition to step-flow growth, other observed forms include: quasi-laminar and triangular hillocks; pyramidal structures on large terrace regions; highly anisotropic growth and coalescence of pyramids; and overlapping regions evoking multiple growth modes, likely during different deposition time domains. Assuming the regions between ThO$_2$ crystallites (depletion zones) are comprised entirely of Ir, we can determine a ThO$_2$ crystallite coverage of 0.58±0.05 from SEM studies which is remarkably consistent with the AES data in figure 6.17; however, monolayer ThO$_2$ coverage in these depletion regions cannot be ruled out. The electron beam diameter (~60 μm) is far too large to examine the depletion zones.

The XRD pattern of ThO$_2$ contains well-resolved diffraction information corresponding to the fluorite crystal lattice with a=5.595 Å in space group Fm3m. Table 6.1 summarizes the XRD results. XRD θ-2θ scans of the Ir ribbon before and after coating shows a preferential orientation of the Ir in the (111) and the (200) directions before coating and a strong (111) orientation of the ThO$_2$ in the coated sample (Fig 6.19). The full width at half maximum (FWHM) intensity of the
ThO$_2$ (111) peak at $28.44^\circ$ is $0.26^\circ$ corresponding to an XRD coherence length of 32 nm along the film growth direction. The XRD data shows reasonable agreement with studies of ThO$_2$ precipitates on Ir alloys [183] and with thin (28 – 578 nm) ThO$_2$ films grown on Si(100) by magnetron sputtering [160].

Table 6.1

<table>
<thead>
<tr>
<th>Lattice plane</th>
<th>Calculation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2\theta$ (°)</td>
<td>d (Å)</td>
</tr>
<tr>
<td>ThO$_2$(111)</td>
<td>27.59</td>
<td>3.230</td>
</tr>
</tbody>
</table>

Table 6.1 Calculated and experimental interlayer distance (d) for a cubic ThO$_2$ thin film.
Figure 6.18: Representative SEM micrographs of the central region of the ThO$_2$-coated Ir ribbon. Observed growth paradigms include: (A) step-flow growth, (B) anisotropic coalescence of pyramidal crystallites, (C) pyramidal crystallites and faceted hillocks, and (D) overlapping regions and evidence for quasi-laminar growth (center).
Figure 6.19: XRD data for the Ir ribbon before and after ThO$_2$ deposition. The 'asymmetry' data is a glancing incidence geometry, and the 'symmetry' data is a $\theta$-2$\theta$ Bragg-Brentano scan. The deposited ThO$_2$ crystallites show a preferential (111) orientation.
For films of ionic crystals, Tasker [187] teaches that (in the absence of significant reconstruction or impurities) the arrangement of charged planes avoids a net dipole along the surface normal, otherwise, as further layers are added, the calculated surface free energy diverges and is infinite [187]. Hence, in experimental and theoretical work on CaF$_2$ films, the $<111>$ direction is preferred because this arrangement ($F^-$, Ca$^{2+}$, F$^-$) produces no net dipole [156,184]. Though this is also the case for the $<110>$ direction, both Tasker and Olmstead [156] remark that stronger interlayer bonding infers a higher surface energy than the (111) termination. By analogy, in the fluorite ThO$_2$ $<111>$ direction, charged planes (O$^2-$, Th$^{4+}$, O$^2-$), terminating with O, likely minimize surface energy (Fig 6.20). ThO$_2$ (111) is then the a priori preferred orientation; the XRD experimental data provides confirmation. Though a wide range of morphologies is observed with the SEM, structures appear nonetheless consistent with a ThO$_2$(111) orientation. Careful analysis of the micrographs in figure 6.18 show pyramids on terrace regions, triangular hillocks at edges and quasi-laminar step-flow regions with 60° and 120° apexes. Equilibrium structures may be predicted by the Wulff construction, but requires knowledge of surface free energies that have yet to be determined for this system [188]. In an analogous system, CaF$_2$(111) on Si(111), however, very similar morphologies to what is shown in 6.17 are found under certain growth conditions [184,189]. Though varying flux and substrate temperature during deposition are essential parameters for controlling the morphology of CaF$_2$ growth, preparation of the substrate is equally critical in
promoting more homogenous films [156]. It is likely that a similar approach could be applied to PVD of ThO₂.

Figure 6.20: Schematic crystal structure of ThO₂(111) on polycrystalline Ir. Note the (O²⁻, Th⁴⁺, O²⁻) stacking along the <111> direction.
Figure 6.21: SEM micrograph of ThO$_2$ on polycrystalline Ir. Apparent polymorphism of the thin film across Ir grain boundaries suggests Ir surface energy anisotropy associated with different grain orientations and surface defects strongly influences growth kinetics.
The heteroepitaxial growth of ThO$_2$ on Ir shows evidence of sensitivity to the surface energy anisotropy of the polycrystalline Ir substrate. As described above, it is likely that highly vicinal regions are dominated by step-flow growth of ThO$_2$ (Fig.6.18A, D), where initial nucleation and growth at step edges and kinks reduces surface energy. As these islands grow out from steps, they may coalesce to form much larger quasi-laminar regions observed, for example, in the central area of figure 6.18D. Large terrace areas exhibit mostly pyramidal crystallites (Fig.6.18C) and, in some cases, anisotropic coalescence of crystallites (Fig.7.18B). Anisotropic coalescence of ThO$_2$ crystallites, as seen in figure 6.18B may be generated by macroscopic roughness of the Ir metal, or possibly, missing row reconstructions described for a variety of Ir orientations, such as Ir(110) [190]. Though pyramidal crystallites are not unexpected in accommodating a (111) orientation following high temperature treatment, it is somewhat surprising that the distance between some structures is large (>200 nm) since this suggests substantial surface mobility of the oxide after uniform deposition during each additional PVD cycle. Beading of oxide films at temperatures well below the reported bulk melting temperature is driven by the release of film stress and/or reduction in the surface free energy; however the mass transport mechanism that underlies this phenomenon is not fully understood. It is unlikely that ThO$_2$ molecules surface diffuse across either the Ir or ThO$_2$, but rather dissociate into Th and O and diffuse independently. The low solubility of Th in Ir inhibits Th diffusion into the Ir substrate [183]. Based on the
propensity of O incorporation in most metals at elevated temperature, incorporation into Ir is a possibility (see chapter 7). The bulk diffusion coefficient for O in ThO$_2$ ($\sim$2.0 x 10^{-8} cm$^2$/s at 1873 K) [191] however, is reportedly much larger than that of Th in ThO$_2$ ($\sim$1.5 x 10^{-17} cm$^2$/s at 1873 K) [163]. Therefore, Th may diffuse primarily across both Ir and ThO$_2$ surfaces, while O moves into and out of ThO$_2$ nucleation sites as the crystals orient and grow in a $<111>$ direction. Computational and further experimental investigations of this mass transport mechanism are necessary; however, slight changes in PVD flux, deposition time, and/or temperature would likely have substantial influence on the resulting film morphology and coverage. This emphasis on kinetics is also apparent in CaF$_2$ heteroepitaxial growth [156]. SEM micrographs of dissimilar ThO$_2$ structures on adjacent Ir grains (Fig. 6.21) indicate that the observed ThO$_2$ morphologies may also be partially stimulated by the Ir crystalline orientation, roughness, and defect density. Different Ir crystalline orientations and surface preparations may promote polymorphic growth if interfacial stresses and surface diffusivities are substantially dissimilar. It is likely that judicious selection of single crystal Ir substrates may yield a much more homogeneous ThO$_2$ thin film growth. Further, by parameterizing the substrate temperature and PVD flux, full control over the structural character of ThO$_2$ thin films is almost certainly achievable.

The heteroepitaxial growth of ThO$_2$ coatings ($\sim$40 nm thick) on polycrystalline Ir has been characterized by AES, XRD, and SEM. Thin films of Th were deposited by PVD; the Th film immediately oxidized, forming ThO$_2$, most likely by
absorption and dissociation of background H$_2$O. Following heating to $\sim$1750 K, surface diffusion resulted in significant morphological heterogeneity with apparent sensitivity to the surface energy anisotropy of the polycrystalline Ir substrate. In addition, XRD confirmed a preferred (111) orientation for the ThO$_2$ fluorite structure that was anticipated both from theory, comparison with previous work [160,183], and analogy to the CaF$_2$ system, where similar morphological features have been reported. Among the morphologies in the ThO$_2$/Ir heteroepitaxial system, quasi-laminar growth was observed and suggests the possibility of improving the efficacy of very thin films of ThO$_2$ for enhanced electron thermionic and field emission by identifying and tuning growth parameters to promote only conformal and contiguous ThO$_2$ thin films better able to resist thermal cycling while providing a uniform, low work function coating.

6.2.3 THERMIONIC EMISSION FROM THORIA ON IRIDIUM

During thermal cycling of the coated iridium filament, as described in 6.2.1, a 1cm$^2$ platinum anode was placed $<$2 cm from the filament. The experimental set-up is shown schematically in figure 6.22 (see Fig. 3.7 for photographs taken during operation). The filament was floated $\sim$25-30V above ground using a series of batteries. The Pt anode was held at $+$230 V, so as to increase the collection efficiency of thermionic emission current from the filament. It was expected that the temperature of the filament would be slightly altered by the change in emissivity after coating with ThO$_2$. Thus, during Joule heating of the filament, the temperature was monitored by an ex situ, two-color pyrometer that had
previously been calibrated (Fig. 6.14) against a C-type thermocouple using the same sample. Figure 6.23 shows the measured thermionic emission current versus temperature for selected ThO₂ deposition times. The thermionic emission current as a function of deposition time is shown in figure 6.24.

Figure 6.22: Schematic of in situ thermionic emission testing in the MESAS. A Pt anode attached to a Cu wire is positioned ~2 cm from the Ir filament. The filament is floated +30 V above ground, and +230 V applied (via an external supply) to the Pt anode. The filament is heated by DC current (0-10 A) to temperatures <2000 K. A thermal gradient is observed along the length of the filament, but the center of the ribbon(~1 mm) had a ΔT of only ~30 K.
Figure 6.23: Thermionic emission current versus temperature for an Ir filament coated for 15-425 minutes with ThO$_2$. For a given temperature, over two orders of magnitude improvement is found with the ThO$_2$ coating compared to clean Ir, despite the significant morphological changes observed by SEM (see 6.2.2).
Figure 6.24: The thermionic emission current as a function of deposition time at a temperature of ~1415°C +/- 15°C. The line is an eyes-guide only. The scatter in the plot likely arises from the error in the temperature (I is ~ exponential with T) and the changing film morphology (i.e. island and crystallite formation).
The Richardson-Dushman equation was used to further the analysis of these films [192]. The thermionic emission current density is given:

\[
J = AT^2 \exp\left(-\frac{\phi}{kT}\right)
\]  

(E.6.1a)

Where \( A \) is the material-specific Richardson constant, \( T \) is temperature in K, \( \phi \) is the work function, and \( k \) is Boltzmann’s constant. A Richardson-Dushman plot shows \( \ln(J/T^2) \) as a function of \( 1/T \). Such plots are shown in figure 6.25 for both the uncoated Ir and after 425 minutes PVD of ThO\(_2\). The slope of the Richardson-Dushman plot, \( S \), is related to the work function:

\[
S = \frac{-\phi}{k}
\]  

(E.6.1b)

Thus, from figure 6.25, \( \phi_{Ir} \sim 4.3 \text{ eV} \) and \( \phi_{ThO_2/Ir} \sim 3.3 \text{ eV} \). However, the known work function for polycrystalline Ir is \( \phi \sim 5.3 \text{ eV} \text{ +/- 0.2 eV} \) [56]. No contaminants were detected with AES. This discrepancy of \( \sim 1 \text{ eV} \) could arise from a number of factors. First, the emission area is assumed to be constant, yet the thermal profile across the filament is a moderate function of temperature; thus the effective emission area must also change as a function of temperature. Second, there may be a slight Schottky effect from the +200 V potential applied between the Pt anode and the filament. To leading order, the error of \( \sim 22\% \) in \( \phi_{Ir} \) is a reasonable approximation of the error expected for \( \phi_{ThO_2/Ir} \). The adjusted value is \( \phi_{ThO_2/Ir} \sim 4.1 \text{ eV} \). As described above, both AES and SEM have shown that the
ThO₂ film forms crystallites with ~60% coverage. The work function of the ThO₂ film is then:

\[ \phi_{\text{ThO}_2} = \frac{4.1eV - 0.4(5.3eV)}{0.6} \approx 3.3eV \]

This is a reasonable value, consistent with as-deposited Thoria.

In another approach, combining E.6.1a for the coated (2) and uncoated (1) filament, the change in work function is given:

\[ \Delta \phi = \phi_2 - \phi_1 = \ln \left( \frac{I_1 A_2}{I_2 A_1} \right) \cdot kT \]  
(E.6.1c)

Where \( I \) is the collected thermionic emission current (again, assuming the emission area is constant). The ratio of \( A_2/A_1 \) requires knowledge of the Richardson constants for each material which can be estimated (E.6.1a) from the difference in y-intercept, \( R \) (Fig.6.25):

\[ \Delta R = R_2 - R_1 = \ln \left( \frac{A_2}{A_1} \right) = -2.3 \Rightarrow \frac{A_2}{A_1} \approx 0.1 \]

Thus, at a temperature of ~1690 K (Fig.6.24), \( I_1=2\times10^{-7}A \), and \( I_2=2\times10^{-6}A \); and \( \Delta \phi = -1 \) eV. This is consistent with the initial analysis of the slope from the Richardson-Dushman plot.

A coating of <40 nm of ThO₂ on Ir with only 60% coverage served to increase the thermionic emission current over two orders of magnitude. Despite heating to
>1500 °C, analysis of the work function suggests that the thoria was not activated.

Figure 6.25: Richardson-Dushman plots for the Ir filament with no coating and with an accumulated 425 minutes of ThO₂ deposition. From SEM analysis, it is known that the ThO₂ forms crystallites with a surface coverage of ~0.6. The linear least-mean-squares fit is shown in both cases and the corresponding best fit slope and y-intercept. The correlation coefficients suggest that these fits are in very good agreement with the data.
6.3 FIELD EMISSION FROM THORIUM OXIDE COATED CARBON NANOSHEETS

Blanket samples were prepared by CNS growth (CH\textsubscript{4} feedstock) on to 5 x 25 mm\textsuperscript{2} polished Ta samples (0.05 μm final polish). An alumina mask was placed over the end of each strip to allow handling of the samples. Thorium was deposited on to the CNS by PVD in the MESAS (see chapter 3). As previously observed with PVD of Th on Ir ribbon, Th readily oxidized to form ThO\textsubscript{2}, most probably by the dissociative adsorption of background H\textsubscript{2}O (see section 6.2). Figure 6.26 shows AES surveys from 30-550 eV of as-grown CNS and two representative ThO\textsubscript{2}/CNS samples with different apparent coating thicknesses: (A) and (B). The surveys shown are all normalized to the C(KLL) peak, thus the increasing peak-to-peak intensity in the O and Th transitions are indicative of a mean increase in the coating thickness. Yet, the thickness at the CNS edge terminations (i.e. potential field emission sites) is not easily defined. As PVD is line-of-sight, the average accumulation on CNS edge terminations likely varies since the sheets are often not precisely aligned with the substrate normal. Further, the coating may not be conformal with the CNS substrate, but rather in the form of islands, as with the Ir (after heating to >1750 K). It should be emphasized that none of the observed oxygen signal is associated with the CNS. When the C(KLL) peak is subtracted, the remaining thoria survey agrees well with the AES data collected after saturation of bulk Th with O\textsubscript{2} to form ThO\textsubscript{2} (Fig.6.6).
The ThO$_2$/CNS samples were subsequently removed from the MESAS system and mounted (per figure 3.19) for field emission testing in test system two. Once the total pressure of the system was $<5 \times 10^{-9}$ Torr, the samples were DC conditioned by incrementally increasing the applied voltage across the diode gap ($\sim 340 \mu$m). Figures 6.27 and 6.28 show the DC conditioning behavior of the as-grown CNS and representative behavior of a single ThO$_2$/CNS sample, respectively. The ThO$_2$/CNS data shown is for a coating equivalent to (A) in figure 6.26. Conditioning was periodically suspended to allow I(V) ramping data to be collected (where indicated). The I(V) data corresponding to the pause at 150 minutes is plotted (in green) in figure 6.29 (A) and represents initial I(V) data for two separate coated samples. Though the I(V) behavior was quite repeatable, when DC operation was resumed, significant conditioning occurred, especially at total emission currents exceeding $\sim 2 \mu$A/mm$^2$. Figure 6.29 (B) is a representative I(V) curve that illustrates the intermediate behavior of (A) as conditioning occurred, eventually stabilizing at (C), the as-grown CNS I(V) behavior. Figure 6.29 (B) is also representative of a sample that was not DC conditioning, but rather ramped to high voltage over a period $<5$ min. Figure 6.29 also shows three dashed curves that appear to correlate very well with the actual data. These curves are numerical plots of the Fowler-Nordheim equation (E.2.3) for $\phi=2.6$ eV (green), 3.8 eV (blue) and 4.7 eV (red), provided that $\alpha$ and $\beta$ are constant ($\alpha=5 \times 10^{-9}$ cm$^2$, $\beta=800$). Values for $\alpha$ and $\beta$ were chosen to provide the
best fit, yet correspond well with values calculated previously (section 5.1) for CNS and Mo₂C-coated CNS.

Figure 6.30 shows the corresponding Fowler-Nordheim plots for (A) and (C). In each case a linear least-mean-squares fit was used to calculate the best-fit.

Table 6.2 summarizes the results of this fitting:

<table>
<thead>
<tr>
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<th>$R^2$</th>
<th>Slope (S)</th>
<th>Y-intercept (R)</th>
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<tr>
<td>CNS</td>
<td>0.95</td>
<td>-1.099x10^6</td>
<td>-23.88</td>
</tr>
<tr>
<td>ThO₂/CNS</td>
<td>0.97</td>
<td>-4.55x10^5</td>
<td>-23.14</td>
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</table>
Figure 6.26: A series of AES surveys showing increasing PVD coverage of ThO$_2$ on CNS. (A) and (B) are two separate representative CNS blanket samples that were subsequently transferred to field emission test system two.
Figure 6.27: Conditioning by continuous (DC) field emission as-grown CNS as a function of time (blue). Also shown is the corresponding applied voltage (green).
Figure 6.28: Conditioning by continuous (DC) field emission ThO₂/CNS sample (A) as a function of time (blue). Also shown is the corresponding applied voltage (green). Conditioning was periodically stopped to collect I(V) ramping data. Note the extensive conditioning that occurred at higher currents (e.g. at ~120, 155, and 170 minutes).
Figure 6.29: Initial I(V) plots for two ThO2/CNS samples (A) that were DC conditioning, after repeated I(V) or without DC conditioning (B) in comparison with (C) the as-grown CNS. The dashed lines are numerical plots of the Fowler-Nordheim equation (E.2.3) (see text for complete description).
Figure 6.30: Fowler-Nordheim plots of as-received CNS and ThO$_2$/CNS corresponding to (A) and (C) in figure 6.26. The linear least-mean-squares fit is also shown. The deviation from linearity in the coated sample corresponds to very low currents before the turn-on of field emission.
As with the Mo₂C coatings (section 5.1), the ThO₂ work function can be determined from E.5.3:

\[ \phi_{\text{ThO}_2} = \left( \frac{\beta_{\text{ThO}_2} S_{\text{ThO}_2}}{\beta_{\text{CNS}} S_{\text{CNS}}} \right)^{\frac{2}{3}} \phi_{\text{CNS}} \]

Where S is the slope (see table 6.2), and assuming no change in \( \beta \) and \( \phi_{\text{CNS}}=4.7\) eV, gives \( \phi_{\text{ThO}_2} = 2.6 \) eV, equivalent to the value reported for activated ThO₂. Calculations of \( \beta \) using E.5.2 also suggest that the change in field enhancement for these thin films is small, but requires that the work function be known. Thus, without a robust analytical model for calculating \( \Delta\beta \), it is reasonable to assume, as a first approximation, that an ultrathin film does not significantly alter the local electric field enhancement. Similarly, it is not obvious that the emission site area should be unchanged by coating the CNS. It is possible that the strong effect of local adsorbates (i.e. Hₓ, x=1-3) on the effective work function of CNS is affected by the application of a thin solid film. Thus, the distribution of turn-on for individual emission sites might be reduced. By comparing the coated samples to adequately DC conditioned CNS, the overall magnitude of \( \Delta\alpha \) may be small.

The initial I(V) behavior of the ThO₂ (Fig.6.28A) was not stable at higher current densities, especially during DC testing. Figure 6.31 illustrates the conditioning behavior for one sample during I(V) tests where the field was repetitively ramped over cycles <5 min. The ThO₂ film quickly deteriorated and the final behavior was
consistent with as-grown CNS. Further, the total system pressure (as measured by an ion gauge) was found to increase from \( \sim 1 \times 10^{-9} \) Torr to \( >1 \times 10^{-8} \) Torr for the as-grown CNS sample at currents \( >40 \mu \text{A} \). Whereas during the initial testing of \( \text{ThO}_2/\text{CNS} \) the pressure increased from \( \sim 1 \times 10^{-9} \) Torr to only \( \sim 3 \times 10^{-9} \) Torr at comparable emission currents. Therefore at higher current densities or over extended periods of DC testing, it is likely that the \( \text{ThO}_2 \) film is removed from emission edges, allowing significant \( \text{H}_2 \) desorption from between the graphene sheets. There are a number of mechanisms by which this deterioration could occur, including: mass transport (i.e. bead formation as with \( \text{ThO}_2 \) on the Ir substrate), thermally-induced evaporation due to Joule heating of emission sites, or erosion from hyperthermal atomic species generated at the anode (chap. 4).

Figures 6.32 shows SEM micrographs taken within field emission tested regions of two \( \text{ThO}_2/\text{CNS} \) samples that provided initial \( \text{I(V)} \) behavior shown in figure 6.29A. Figure 6.32(A-D) also corresponds to the AES survey shown in 6.26A. Similarly, figure 6.32(E-F) corresponds to the survey in 6.26B. From examination of the AES data, it is clear that the SEM images in 6.32(E-F) should represent a thicker coating than that in 6.32(C-D); however, there appears to be no (resolvable) difference in edge thickness. Nonetheless, in both cases, there is ample evidence of beading—both on edges and along sidewalls. This island morphology of the coating extended into untested regions (i.e. those regions not directly underneath the anode) and suggests that beading occurred before field emission testing. It is not clear, however, if the apparent depletion zones
between beads contain a thin layer of ThO$_2$. Further, there is no observable
difference in the edge termination morphology at suspected emission sites that
might correspond with the deterioration seen in the I(V) behavior. This is likely
because the emission area represents such a small area fraction and therefore,
the probability of observing the deterioration in the film with SEM very low (see
chapter 4). It is known from work on BaO dispenser cathodes (see chapter 2)
that a single monolayer can lower the work function as effectively as thicker films.
Thus, it is conceivable that the initial low-current improvement reported here for
ThO$_2$/CNS may be related to 1-2 ML of ThO$_2$ that remains in the areas between
visible ThO$_2$ beads (~5 nm diam.) and, therefore, covered active emission sites.
Thermal or field-induced mass transport may encourage further coalescence and
ultimately reveal the underlying CNS active emission sites.
Figure 6.31: I(V) plots for ThO$_2$/CNS (blue) showing temporal conditioning behavior. The film appears to deteriorate, uncovering the underlying CNS. The ultimate behavior appears very similar to as-grown CNS (black/red).
Figure 6.32: (A-F) SEM micrographs of ThO$_2$ coating at various magnifications. Beading is apparently spontaneous, requiring no thermal activation. (A-D) and (E-F) correspond to coatings (A) and (B), respectively, in the AES data shown in Fig.6.26. There is no apparent change in thickness.
The study of ThO$_2$ on Ir was quite revealing. First, the strong morphological heterogeneity observed on polycrystalline Ir was not observed with ThO$_2$ coatings on CNS. This confirms that the surface energy across the CNS sheets is fairly uniform. Further, it is also probable that the ThO$_2$ orients in the (111) direction as this was the preferential direction driving faceted crystallite formation on the Ir. As shown in figure 6.33, the Th(111) orientation offers a terminating dipole structure. Considerable current density through the film during field emission, the strong local applied electric field, and/or hyperthermal $H_0/H^+$ created by ESD from the Cu anode may substantially reduce the surface of ThO$_2$. In this scenario, the remaining termination would be primarily Th and a net dipole would be induced by the charged layer of Th$^{4+}$ on top of a layer of O$^{2-}$. Such a scenario is consistent with the mechanism proposed for the thermal activation of thicker ThO$_2$ films. This is also consistent with the above Fowler-Nordheim calculations.

Figure 6.33 Schematic of the proposed dipole termination by ThO$_2$ on CNS.
6.4 SUMMARY REMARKS

The field emission from CNS has been significantly enhanced by coating with a thin film of ThO₂. From analysis of the Fowler-Nordheim plots, a reasonable estimate of the work function ($\phi_{\text{ThO}_2} = 2.6$ eV) suggests that initial DC conditioning serves to activate the ThO₂ coating. Previous work (discussed above) has suggested that activation of thoria during high temperature treatment (>1700°C) occurs by the self-doping of the oxide with metallic Th, effectively acting as an n-type semiconductor. While this explains conduction through the film, this scheme is not adequate to explain the reduced work function (from ~3.5 to ~2.6 eV). The necessary corollary to this mechanism is the accumulation of an outboard Th layer. The resulting surface could induce a dipole moment substantial enough to reduce the work function ~1 eV. In these experiments, with much thinner films (<5 nm compared with 50 μm), no thermal treatment was administered post deposition, yet the film is ostensibly activated. It is suggested that reduction of the surface by reactions with ESD products and/or field induced diffusion is responsible for both the observed activation, but ultimately (at higher current densities) it also caused an unwanted breakdown of the thin film and progressive deterioration of enhanced field emission. To be useful in engineering applications, a thin film of ThO₂ on CNS would need to endure thousands of hours of stable operation at moderate to high current densities. The next chapter will discuss proposed work to stabilize ThO₂ films and establish a robust coating suitable for high current density CNS field emission arrays. Also discussed is on-
going work to construct sensible \textit{a priori} models of the activated \( \text{ThO}_2 \) surface, the proposed dipole moment and resulting effective work function change.
7.1 SUMMARY

This dissertation has explored the use of thin solid films for enhanced field emission from carbon nanosheets (CNS). The principle motivation was to increase the efficiency of CNS field emission arrays by selecting coatings of low work function materials. The modified Fowler-Nordheim equation is the accepted analytical description of field emission, relating emission site area ($\alpha$), local field enhancement ($\beta$), and work function ($\phi$) to the total emission current. From this relation, it is anticipated that reducing the work function $\sim$1 eV should provide over an order of magnitude increase in emission current. Carbonaceous nanomaterials, such as CNS, have reported high work functions of $\phi$~4.6-5.1 eV which strongly inhibits the transport of electrons to vacuum. A summary of results of selected low work function carbide and oxide coatings on CNS follow:

- A uniform film of Mo$_2$C ($\phi$$\sim$3.7eV) was established by PVD of Mo on to CNS and only moderate thermal treatment to $\sim$200°C. For a given applied field, Mo$_2$C/CNS demonstrated more than two orders of magnitude increase in field emission current when compared to as-grown CNS. Moreover, the stability of field emission was improved, showing more linearity in the resulting Fowler-Nordheim plots. The performance of the coating deteriorated at higher current densities (>60 $\mu$A/mm$^2$) which indicates degradation of the carbide by the
effects of increased current, electric field, electron stimulated desorption (ESD) and/or sputtering.

• In contrast with the Mo$_2$C coatings, NbC films could not be uniformly grown on CNS because the temperature required to complete carbide formation and remove oxygen (~750°C) also allowed for substantial beading; large crystallites were observed with the SEM on the CNS surface with a coverage of ~25%. Because of this limited coverage, the carbide coverage of the active emission sites was significantly affected so that the field emission performance was unchanged from as-grown CNS.

• Thorium films were deposited by PVD on CNS and instantly oxidized to form ThO$_2$ by adsorption of background gases. During subsequent field emission testing, significant enhancement was observed. For example, the applied field required to produce 40 µA was reduced from ~10 V/µm to ~5 V/µm. Comparison of the Fowler-Nordheim plots of as-grown CNS with ThO$_2$/CNS suggested that the work function of the coating was φ~2.6 eV and is consistent with high temperature “activated” ThO$_2$ used for much thicker coatings (~50 µm) on thermionic cathodes. It is suggested that the activation occurs by reduction of the surface by field-induced diffusion or reactions with ESD products (e.g., H$_0$/H$^+$) generated at the Cu anode surface. However, enhanced emission could not be sustained over prolonged operation at higher current densities. The film was completely removed from active emission sites by the effects of increased current, electric field, or ESD sputtering, exposing
the underlying CNS structure. SEM analysis indicated beading of the film over the entire sample, most likely formed during the initial deposition at ~70°C.

These results clearly demonstrate that thin solid coatings have the potential to provide significant efficiency improvements to CNS FEAs, if the aforementioned effects can be minimized. It is also likely that the improved cathode performance seen with coatings of CNS can be applied to other nanocarbon field emission structures, such as CNTs.

7.2 FUTURE OF APPLIED COATINGS WORK

A number of technological challenges must be addressed before such films can be considered in high current density applications. First, it has been shown that most thin film materials on CNS will form into discrete islands or crystallites. For Mo$_2$C, this occurred at temperatures >300°C; however, with ThO$_2$, beading occurred during deposition at only 70°C. Other materials deposited on CNS, including NbC, ZrC, and Pt, have all demonstrated a propensity to form discrete islands. For field emission applications, this morphology is not ideal. A uniform, stoichiometric film is required to ensure that active emission sites are covered. Films form islands and coalesce to minimize interfacial strain and/or surface free energy, but it is probable that the integrity of the film is compromised by the applied field and high current experienced during field emission and, this degradation may be exacerbated by the diode configuration used in this study. Therefore, while significant enhancements have been observed, the long term
survivability of these thin films is questionable. New methods for increasing the interaction at the interface between the deposited film and the CNS, especially at emission sites, are required. An adhesion or wetting layer of 1-2 ML may mediate the interaction of low work function coatings and CNS by providing a stable interface that firmly localizes subsequent deposition. Tungsten is a well-known wetting layer, but also an aggressive getter and may bead similarly to Mo at elevated temperature and/or current. UHV deposition of W could be rapidly followed by thin film growth of ThO₂ to avoid contamination. Thermal treatment may also be required. Such a scheme is complicated by the likely possibility of forming WC. Moreover, the role of the strongly bound chemisorbed H must be carefully examined, especially at edge terminations where field emission is most probable. Pretreatment of the CNS by chemical functionalization may also help prevent beading of the film. For example, cycling thin film deposition with light ion bombardment (e.g., He⁺) may promote interfacial bonding by creating defect sites in the graphene sp² array to form stable bonds with the deposited material. Finally, further exploration of other low work function coating materials may yet discover a more stable coating choice. For example, thick coatings of Y₂O₃ have been used as a direct replacement for ThO₂ in thermionic cathode applications. Ultimately, some combination of the strategies outlined above may provide a stable coating for CNS (and other nanocarbon materials) capable of surviving high current densities and prolonged operation in high vacuum.
It is also likely that the ultimate measured performance of both CNS and coated CNS cathodes are limited by testing in a diode configuration. Field emission testing in a parallel plate diode configuration has been shown to produce hyperthermal H and O capable of eroding the cathode over prolonged operation. Though the erosion of coated CNS has not been studied, it is likely that this and other processes occurring in the diode gap severely degrade these materials. For instance, the limited gas conductance of the diode gap accumulates desorption products (e.g., H₂) significantly increasing the likelihood of arc-over and damage to the cathode. Studies are required to examine the relative performance of coated CNS in low vacuum environments. However, numerous gated and lensed designs exist that may mitigate many of the problems found in parallel plate configurations. Chief among these is the Pierce gun design that employs a series of precisely angled electrostatic lens to produce a well-collimated electron beam. It is expected that the ultimate performance of both as-grown and coated CNS will improve when implemented in such a design. Furthermore, electrostatic or magnetic deflection of the emitted electron beam can minimize line-of-sight deterioration of the cathode. Though necessary for optimal testing, such complex designs are not conducive to high throughput laboratory sample analysis. Further, the fabrication and optimization required for successfully employing such a design is nontrivial and may substantially mask intrinsic material performance with geometric features of the gun.
7.3 FUTURE BASIC SCIENCE INITIATIVES

This dissertation presented studies that augmented understanding of fundamental processes governing thin film coating of CNS, carbide and/or oxide formation, activation (in the case of ThO₂) and eventual deterioration and failure during field emission testing. The results of these studies provided data critical to the outcome of this work, but have also highlighted areas in need of further investigation. Some of these possible initiatives are discussed below, including some preliminary work.

The activation of ThO₂ films on thermionic cathodes is done by thermal treatment to >1700°C. In this work, very thin films (<40 nm) of ThO₂ were grown on Ir ribbon. The ribbon was then heated up to 1700°C to measure thermionic emission performance. Subsequent SEM analysis indicated that large faceted crystallites had formed at these temperatures. The size, shape, and distribution of these crystallites were highly heterogeneous when comparing different local areas of Ir substrate. Analysis of Richardson-Dushman plots suggested that work function of the ThO₂ was 3.3 eV, and thus, not "activated". The inability to activate this film may be because insufficient thermal energy was provided, or because the material formed islands.

In contrast with the ThO₂/Ir thermionic experiments, ThO₂ on CNS field emission experiments with even thinner films (<5 nm), activation was ostensibly observed.

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* Activation, in this work, is defined as the process that establishes the precise crystalline arrangement of Th and O atoms which provides enhancement (ϕ~2.6-2.8 eV) of the electron emission to vacuum, e.g., a favorable surface dipole moment (see Fig. 6.33).
That is, analysis of Fowler-Nordheim plots suggested a work function of ~2.6 eV, consistent with thermally activated ThO₂. No thermal treatment was provided for these films, thus an alternate mechanism must give rise to activation. It is likely that a combination of electric field-induced mass transport, local Joule heating, and/or reactions with hyperthermal ESD products stimulates activation of ThO₂ at active field emission sites. For example, electron bombardment of the ThO₂ may have preferentially removed oxygen from the terminating layer which would increase the effective dipole moment.

Further studies are required to isolate the activation mechanism of ThO₂ during field emission. Unfortunately, such an experimental undertaking requires identification and relevant interrogation of only active emission sites. The tools to carry out such a study are limited. This type of study may be possible with a combined UHV scanning tunneling microscope and SEM; the probe could be positioned over coated carbon nanosheets and the field emission studied locally. Nonetheless, it is likely that continuous, robust coatings are required to warrant such a study; as discussed above, preventing island formation and coalescence is non-trivial on the low surface energy surface of CNS.

The field enhancement factor (β) is another area of considerable ambiguity. Historically, the field enhancement provided by a sharp tip has been analytically described by evoking some form of the aspect ratio: (height/radius of curvature) [90,91,145,150,193,194]. This approach is largely successful for single tips and some sub-micron structures; however, this approach has questionable
significance for large arrays of tips. The mutual screening provided by adjacent tips can have a substantial effect on the local applied field [193,195]. This has been verified by spatial field emission analysis of large carbon nanotube bundles where emission is dominated only by those tubes on the periphery of the bundles [29]. The screening effect has been considered in some analytical descriptions and the ideal in-plane separation is found to be as much as six times the height of the emitter [196,197].

More importantly, our observations have suggested that changes to the aspect ratio of nanomaterials appear to have little impact on the field enhancement factor. For example, two different feedstocks were used to grow CNS by PE-CVD: CH₄ and C₂H₂. The methane-grown CNS are typically thinner (average termination ~1-3 sheets) than acetylene-grown CNS (average termination ~3-7 sheets) [77,198]. When comparing I(V) behavior of statistically robust data sets, the acetylene-grown CNS cathodes consistently provided better field emission performance than the methane-grown CNS. The composition, bonding, and terminating chemistry of these materials is likely very similar. Thus, considerable work function variation between these materials is not expected and is probably less than 0.5 eV. Two parameters remain to explain the improved field emission performance, the emission site area (α) and the local field enhancement (β). The slope of the Fowler-Nordheim plot is independent of α. By using the slope from a large number of Fowler-Nordheim plots of these materials, it has been shown that for the thicker C₂H₂-grown CNS, β ~1.3 times greater than β for the thinner
CH₄ sheets [198]. This result demonstrates that for this material, β is not sensitive to changes in radius of curvature on the order of a nanometer. Thin film coatings used in these studies were typically 1-3 nm and so β for these films may (by analogy) not be strongly affected by the accompanying change in thickness.

The height of carbon nanosheets is defined as the mean distance from the surface of the growth substrate to the terminating edges. This parameter is controlled by the growth time. Typically, after 20 minutes of growth, using CH₄ feedstock, the height is ~600 nm. Various growth times have been used and field emission data collected, but no correlation has been found between growth time and field emission performance. Therefore, above a certain critical height, it appears that β is not strongly affected by aspect ratio.

To further obscure the discussion of β, quantum-mechanical simulations of single walled carbon nanotubes (SWCNT) using ~8000 atoms have suggested that field penetration can have a much more substantial effect in these carbon nanomaterials than previously anticipated [199]. X. Zheng et al. have reported results of this simulation at various applied fields. At 0 V/μm the work function of the SWCNT was φ=4.5 eV, consistent with experimental work. At 10 and 14 V/μm the effective work function (i.e. the potential barrier height) decreased to φ=3.0 eV and 2.0 eV, respectively [199]. Obviously, such simulations require considerable scrutiny and some experimental verification, but they nonetheless suggest a compelling physical scenario that warrants further study and presents
a non-geometrical argument to explain the field emission behavior of nanocarbon materials.

Finally, the oxidation of Th was accompanied by thermal-vacuum stability data that demonstrated rapid decomposition of surface ThO$_2$ and incorporation of oxygen into bulk Th at a moderate temperature: 500-750°C. This result is surprising considering the thermal stability of bulk ThO$_2$: $T_{\text{melt}} \approx 3390$°C. Available in-house data from this research team was compiled for a variety of metals on which similar native oxide, thermal-vacuum stability studies were carried out. Figure 7.1 shows AES data for thin oxide layers (~5 nm) on Ti, Th, Ni, Mo, and Cu. In each case the intensity of a major metal Auger transition is compared to the intensity of the O(KLL) transition. This ratio is plotted as a function of temperature. In all cases, the oxide decomposed at moderate temperatures and then the surface oxygen signal decreased. Based on AES and TDS data acquired to date, we propose a possible mechanism of O initially desorbing (e.g. as CO, CO$_2$) and, following depletion of adventitious C, incorporation of the remaining O into the bulk. This can be modeled as:

$$MO_2 + C \Rightarrow MO + CO \uparrow$$
$$MO \Rightarrow M + O \downarrow$$

Or, for a pentoxide (e.g., tantalum, niobium):

$$2M_2O_5 + 3C \Rightarrow 4MO + 3CO_2$$
$$MO \Rightarrow M + O \downarrow$$

A Cu$_2$O study representative of this is shown in Appendix 1.

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Figure 7.1: The thermal-vacuum stability of native oxides on Ti, Th, Ni, Mo, and Cu. The ratio of AES peak-to-peak intensities of O(KLL), $I_O$, to an Auger transition for the relevant metal, $I_M$, is plotted versus temperature. Note that the oxides appear to decompose rapidly at fairly moderate temperature. O is most likely incorporated into the bulk, but may also desorb depending on the system and, often, the availability of C.
It is believed that incorporation of oxygen into the bulk is the most likely mechanism driving the reduction of the surface oxide. In the particular case of ThO\textsubscript{2}, virtually no carbon was available to form more volatile CO or CO\textsubscript{2} products. Thus, the oxide most probably decomposed at the interface with the bulk metal. The driving force for this decomposition is of considerable interest. It is very likely to combine effects of concentration gradient, interfacial stress/strain, and chemical potential. To further corroborate these results and to establish kinetic details of the mechanism, \textit{ab initio} studies have been initiated. This work is in the early stages and in collaboration with J.E. Bates at the University of California, Irvine (Dept. of Chemistry). The strategy that has been discussed is to employ molecular dynamics (MD) simulations to evolve an oxide layer in contact with a semi-infinite bulk metal layer. The total anticipated system will be \( \sim 5 \times 8 \) nm in-plane and 20 nm in the z-direction (toward the surface). As a first approximation, a \( \sim 4 \) nm oxide layer will be placed adjacent to the bulk metal (\( \sim 12 \) nm), and the interface abrupt. A minimization routine will be used to initialize atomic interaction at the interface. This starting structure is then passed to the Molecular Dynamics code. In particular the ES+ model (introduced by Streitz and Mintmire) is most apt as it allows metal-metal and metal-oxygen interactions to be adequately described within one formalism by combing the embedded atom model (EAM) and variable charge model (VCM) [200-203]. The EAM component describes the pairwise interatomic short-range potential interactions between a given atom and surrounding atoms in the matrix; the VCM portion performs local
charge density optimization and effectively describes the dynamic bonding as the oxide decomposes at the interface and as oxygen diffuses interstitially through the bulk metal [204]. Thus, the total energy in the ES+ model is given:

\[
E_{total} = \sum_{i}^{N} \left[ F(\rho_i) + \frac{1}{2} \sum_{j \neq i}^{N} \phi_y(\mathbf{r}_{ij}) \right] + \sum_{i}^{N} \left[ q_i \chi_i + \frac{1}{2} \sum_{j \neq i}^{N} q_i q_j V_{ij} \right]
\]  (E.7.1)

Where \( F \) is an embedding function, dependent on the local electron density \( \rho \) around atom \( i \) and \( \phi \) is the pairwise interaction between \( i \) and nearest neighbor \( j \) at a separation \( r \); in the second term, \( q \) is the partial charge associated with atom \( i \), and \( \chi \) and \( V \) are functions that address electrostatic interactions between local charge densities and the ionic charges associated with each atom.

It is projected that real time visualization of the decomposing oxide can be simulated at various temperatures (250 K/step, 300–1300 K). The total simulation times are estimated to be \( 10^5 \)-\( 10^6 \) time-steps and may be performed on the College of William and Mary's 2.3 TFLOPS SciClone cluster. The results of this simulation will then be compared with data in figure 7.1. The model can then be modified so as to improve agreement with experimental results. The nature and implementation of these modifications will likely reveal important details of the driving mechanism for the decomposition of the oxide and the fate of oxygen in the system. The results of this analysis will be of critical interest to the catalysis, microelectronics, and corrosion communities. Further, by analyzing the charge distribution at the oxide (i.e. \( \text{ThO}_2 \))—vacuum interface, it may also be
possible to observe evidence of the formation of a net dipole moment; thereby corroborating the proposed mechanism for activation of enhanced electron emission by thermal treatment.

7.4 BROADENING APPLICATIONS OF CARBON NANOSHEETS

This dissertation has focused specifically on the utility of CNS for high current field emission arrays, but this novel material has been considered for numerous other applications. Some of these are highlighted below:

Studies of thin film deposition on to CNS with low work function materials have demonstrated a strong propensity for these films to form discrete islands uniformly over the sidewalls and edges of CNS. The high surface area of CNS and ability to easily pattern nanoscale materials over this surface is especially useful for the catalysis community; however, the current cost of industrial PE-CVD coatings versus competing catalytic materials will likely reduce the market space for CNS films to very high value-added applications. The nature of these applications remains to be seen, but may include in vivo technologies.

The verticality, high surface to volume ratio, and open structure of CNS has recently been shown to have remarkable import for energy storage technologies. In particular superior dynamic response has been demonstrated using CNS for electrodes in electric double-layer capacitors [205]. On-going work is expanding the energy storage capabilities of CNS into battery technology.
APPENDIX A.

THERMAL-VACUUM STABILITY OF THE SURFACE OXIDE COMPLEX ON Cu

The surface of Cu is technologically important in corrosion and heterogeneous catalysis. Copper catalysts, for example, are used in methanol synthesis, recombination of carbon dioxide and electronic applications [206-208]. In another emergent application, Cu catalysts are being used to facilitate water-gas shift reactions associated with fuel cells where hydrogen is generated by the partial oxidation of hydrocarbons[209,210]. Copper has such broad import to catalytic problems chiefly because the degree of Cu oxidation may vary from a chemisorbed layer to a complete oxidation state of CuO (cupric), providing a spectrum of catalytic behavior that may be tailored to accomplish various catalytic demands. The initial and extensive oxidation of Cu has been thoroughly investigated under a variety of environments [211-213], from high pressure to ultrahigh vacuum (UHV); however, one critical characteristic of the oxides has not been fully studied. There is little information[214,215] on the variation in surface chemistry (i.e. thermal stability) of thin film Cu oxides on Cu over a range of temperature. The predominant native oxide on Cu is Cu$_2$O (cuprous). In bulk or sufficient thickness, this oxide is stable until 1230°C where it begins to decompose [216]; however, a thin film oxide (<5 nm) on bulk Cu, in a low pressure environment, begins to decompose (Cu$_2$O $\rightarrow$ Cu$_2$ + O) at temperatures far lower than 1230°C. Here, the thermal stability is discussed for surface Cu$_2$O
on polycrystalline Cu as well as the variation in surface chemistry over the range of 25 – 900°C in UHV.

Cu coupons (99.998%, polycrystalline) were analyzed using glow discharge mass spectrometry (GDMS) and instrumental gas analysis (IGA) by Evans Analytical Group; identified bulk impurities included (ppm wt.): C(<10), O(<10), N(<10), Ag(9.2), S(5.5), and H(<3). Figure A.1A shows a schematic of the presumed surface oxide complex. The outer layer of the complex is likely comprised of C and other impurities, then a hydroxide layer [217], likely Cu(OH)$_2$, and then the oxide, Cu$_2$O. The oxygen concentration then falls off exponentially to a bulk concentration of <1-10 ppm [218]. Structural analysis by XRD (Fig. 1b) of the polycrystalline Cu samples shows that the (111) orientation is dominant with 44% of normalized intensity, followed by the (110) at 35% and the (100) at 21%.

The sample was prepared for UHV surface analysis by acetone/ethyl alcohol ultrasonic cleaning and subsequent encapsulation in a vacuum-fired Ta foil envelope with a 3 mm aperture. The Ta envelope was fabricated with spot welded W26Re wire on each side for resistive heating and the temperature calibrated (up to 900°C) versus current with a K type thermocouple using a duplicate Cu sample. Auger electron spectroscopy was employed for surface chemical analysis; details of the experimental are discussed in chapter three of this dissertation. The sample was installed into the introduction chamber (base pressure 5x10$^{-10}$ Torr). After sample transfer into the analysis chamber (base
pressure ~5x10^{-12} Torr (N\textsubscript{2})), the sample was heated to 900°C and Ar\textsuperscript{*} (5 keV, ~0.1 \, \mu A/mm\textsuperscript{2}) sputter cleaned until no contaminants were observed in the AES survey (3 keV, 1 \, \mu A), with the exception of a small (<10 at. %) residual C signal. The initial oxidation of the Cu surface was studied by admitting 1x10\textsuperscript{-6} Torr O\textsubscript{2} (99.999\%) into the analysis chamber and recording the ratios of O (KLL) and C (KLL) to Cu (LMM) AES peak-to-peak intensities, corrected with published sensitivity factors [83]. Figure A.2 shows the exposure to 75 minutes or ~45 L (1 L = 1x10^{-6} Torr-s). The ratio of I\textsubscript{O}/I\textsubscript{Cu} increases somewhat linearly for the first 12 minutes (~7 L) exposure and then begins to fall off and linearly increase only gradually for the remainder of the study. The dot-dashed line represents the Cu\textsubscript{2}O saturation level at an I\textsubscript{O}/I\textsubscript{Cu} ratio of ~0.33; the apparent discrepancy with stoichiometry (I\textsubscript{O}/I\textsubscript{Cu} = 0.5) likely results from AES signal from the bulk Cu penetrating the thin oxide layer. The initial linear increase in Fig. A.2 corresponds to an initial sticking coefficient of $s_0 = 0.2$ and is in good agreement with previous work on the (110) face of Cu [212]; though, studies of other Cu orientations, such as the (100) and (111) faces, report a much lower sticking coefficient ($s_0 \sim 10^{-3}$). The good agreement of the calculated initial sticking coefficient suggests that the initial oxidation of the polycrystalline Cu surface may be dominated by the (110) surface, despite representing only 35% of the surface (from XRD). The oxidation rate slowed substantially after 12 minutes (~7 L) and proceeded at a linear rate and may be associated with (1) the completed chemisorbed coverage of the (110) orientation and (2) the much lower adsorption rate of the (100) and the
(111) faces. Over the same period, the C signal slowly diminished most likely from room temperature CO formation and desorption.

The saturation of the polycrystalline Cu surface to Cu$_2$O required a very large exposure of pressure and time. Previous research has shown that room temperature saturation to Cu$_2$O can be achieved by subjecting clean Cu to $\sim$10$^5$ L [213]. To facilitate such exposure, the sample was returned to the introduction chamber where 760 Torr O$_2$ (99.999 %) was admitted for 30 minutes. The introduction system was returned to the $10^{-10}$ Torr base pressure range and the sample transferred back into the analysis chamber for thermal analysis. Figure A.3A shows a family of AES surveys (3 keV, 1 µA) at temperatures taken in 100°C increments up to 900°C. Besides O (503 eV), C (270 eV), Cl (181 eV) and S (152 eV) were observed as surface contaminants immediately after oxidation. Oxygen chemical replacement on surfaces throughout the introduction chamber presented a likely source of Cl, S, and C contamination. As the temperature was increased, the Cl disappeared at 500°C and the C disappeared at 600°C, but S substantially increased.

Figure A.3B shows a sensitivity[83] corrected intensity plot of O, C, Cl, and S normalized to the Cu (LMM) peak at 920 eV, as a function of temperature. At low temperature, the O concentration began to decrease gradually, but dropped precipitously at $\sim$200°C, suggesting decomposition of the hydroxide and the Cu$_2$O. The decrease in the O concentration continued down to a plateau of $\sim$400°C, presumably associated with a more strongly bound chemisorbed layer.
At 600°C, the chemisorbed layer also began to breakup and the oxygen signal again dropped precipitously and completely disappeared by 800°C. This observation is consistent with the rather small formation energy of 1.74 eV of Cu₂O compared to the much stronger O-Cu chemisorbed energy of 4.5 eV ((111) orientation) [213]. At a background pressure of <1x10⁻¹¹ Torr, two different mechanisms appear to be operative. The oxygen initially reacts with the adventitious C in the complex and desorbs as CO via,

$$\text{Cu}_2\text{O} + \text{C} \rightarrow 2\text{Cu} + \text{CO}$$

This was confirmed by temperature desorption spectroscopy and, additionally, that CO on Cu desorbs at room temperature [219]. After the adventitious C was substantially reduced to the bulk level, further reduction of the oxide occurs by dissolution of O into the Cu bulk [214,220]. Some authors have suggested that oxygen may desorb as O₂ [215] and may account from some of the decrease the O signal; however, the solubility of O in Cu has been thoroughly studied. At 700°C the solubility is ~1.5 at. ppm [218], and appears to not vary significantly at low temperatures, and is thus sufficiently large to accommodate incorporation of the oxygen from the decomposing Cu₂O surface oxide. The concentration gradient into the bulk is the driving force for the incorporation.

As observed in other metal surface oxides, the oxide and chemisorbed O layer are a barrier to S segregation[221]. Figure A.3B also shows a dramatically increasing sulfur signal in concert with, and mirror image to, the decreasing
oxygen signal between ~600 – 800°C. When the oxygen dissolves into the bulk, the S freely segregates to the surface, diffuses over the surface and increases to a level of Is/Icu = 0.48, consistent with Cu₂S. Sputter cleaning with Ar⁺ for <5 min removed the S layer consistent with an estimated sulfide formation of ~9 nanometers thick. Reheating the surface repopulates the surface with S by segregation from the bulk, albeit somewhat less in intensity. Alternate heating and sputtering is one way of desulfurizing Cu[222].

In summary, a rather dramatic change in surface chemistry has been observed as a function of temperature and in a low pressure environment where the oxygen can completely disappear from a stable oxide and, at higher temperature, a chemisorbed layer. The oxide/chemisorbed layer serves as a cap on bulk S until about 650°C. When that cap is removed, S readily segregates to the surface. Thus, in conditions of elevated temperature and low pressure, catalytic behavior could be significantly altered by diminishing oxygen and poisoned by sulfur contamination.
Figure A.1: (A) Schematic of the surface oxide complex of copper. The concentration of oxygen exponentially decays to <10 ppm in the bulk. (B) XRD of polycrystalline Cu used in this study.
Figure A.2: Initial oxidation of the Cu sample done at \( p = 1 \times 10^{-8} \) Torr \( (O_2) \) for 75 minutes. First linear region represents saturation of (100) orientation at 12 minutes (~7L).
Figure A.3: (A) Family of AES surveys over the temperature range of 25-900°C. (B) AES intensity variations over 25-900°C normalized to the Cu 920 eV peak.
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Michael’s first interaction with the College of William and Mary was through a mentorship program during his last semester of high school; he worked with Dr. Herbert Funsten (Physics) studying omega meson electro-production. Through this work, Michael met Dr. Dennis Manos and was offered a position as a laboratory technician in William and Mary’s surface characterization lab at the Applied Research Center, located on the campus of Jefferson National Lab (Newport News, VA). Michael subsequently enrolled in the undergraduate physics program at the College.

As an undergraduate at the College of William and Mary, Michael continued to work as a surface characterization technician. He took a semester abroad in his junior year to study physics and materials science at the National University of Singapore. Upon his return, he began work on his senior thesis with Dr. Ron Outlaw. Michael received his Bachelor of Science degree in Physics from the College in May, 2007, with a double major in English Literature.

Michael entered the Ph.D. program in Applied Science in August, 2007 and continued to work for Dr. Outlaw and Dr. Manos on thin film deposition, ultrahigh vacuum surface characterization, and field emission studies of carbon nanosheets. In May, 2009, Michael received his Master of Science degree in Applied Science. He continued his work towards a Ph.D.

Michael has accepted a two-year post-doctoral position at Lawrence Livermore National Lab, Livermore, CA and expects to begin in early May, 2011.