ENHANCEMENT OF CARBON NANOSHEET FIELD EMISSION BY M02C THIN FILM COATINGS

A thesis submitted in partial fulfillment of the requirement for the concentration of Physics from the College of William and Mary in Virginia,

by

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May, 2007

Abstract

Carbon nanosheets, a new morphology of graphite, have shown remarkable promise as field emission cathodes for applications such as microwave tubes and flat panel displays. The sharp emission edges of the sheets are typically 1-3 graphite sheets thick (~1 nm) and thus provide a superior geometry for field emission enhancement. Fowler-Nordheim theory suggests further field emission enhancement is possible by lowering the work function. The effective work function of carbon nanosheets, previously undetermined, was calculated and found to be analogous with that of graphite 4.8 eV. By applying a thin film coating of Mo₂C (ϕ = 3.5 eV), the field enhancement factor from the geometry, β , was reduced by only a factor of two, yet field emission current substantially increased. A molybdenum coating was deposited on a carbon nanosheets sample by physical vapor deposition in very high vacuum ($p \sim 1 \times 10^{-8}$ Torr) and determined to be ~3 monolayers thick by Auger electron spectroscopy. The coated sample was radiatively heated to $T\sim 250^{\circ}$ C to promote molybdenum reaction with adventitious carbon found in defects of the carbon nanosheets' emission edges and the underlying graphite structure. Auger electron spectroscopy and a scanning electron microscope were used to verify the composition and conformity of the coating, respectively. Field emission testing in an ultrahigh vacuum (p ~5x10⁻¹⁰ Torr) diode assembly with 250 μ m spacing showed lowering of the effective work function after the coating procedure and consequently, increased emission current. At an applied field of 9 V/ μ m, the emission current was found to be 100 μ A compared ~0.1 μ A for the carbon nanosheets. A comparison of linear (R^{2} = .999) Fowler-Nordheim plots of coated and uncoated samples yielded values for the work function of uncoated CNS and the fractional emitting area of $\sim 2\%$ for carbon nanosheets. The experimental data of Mo₂C-coated CNS was significantly more repeatable and stable than the uncoated CNS.

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1. Introduction

Throughout the study of electronic materials and their applications there is much interest in understanding and improving electron emission. In the past, the predominant method of electron production for all electronic applications has been by thermionic emission, but that requires high power, relatively large cathode geometry and accommodation of a high thermal budget. Today, research is focused on developing more efficient and reliable electron emitters, such as cold cathodes for flat panel displays and microwave tubes. With the discovery of the carbon nanotube (CNT) in 1991 by Iijima^[1], a great deal of effort has been directed towards establishing the properties of this new material, as well as varieties of this carbon structure. Carbon nanosheets (CNS) are a unique example of such variations. An attempt to grow CNT by plasma enhanced radio frequency chemical vapor deposition (RF PECVD) resulted in ultra-thin (~ 1 nm) sheets of graphite that are vertically oriented ^[2]. Carbon nanosheets have demonstrated superior properties as edge emitters, but field emission may possibly be further optimized by applying thin films that lower the effective work function. Although the effective work function of CNS has not been determined, graphite has a known work function, $\phi \approx 4.6 - 4.8 eV^{[3]}$, which is greater than many metal cathodes ($\phi \cong 4.5 eV$). The Fowler-Nordheim equation predicts that a reduction of 1 eV in the work function translates to an increase of over two orders in current ^[4]. Molybdenum carbide is a robust and stable material with a reported low work function of $\phi \cong 3.5 eV^{[5, 6]}$, thus is a strong candidate for use as a thin film coating. By evaporative deposition (physical vapor deposition) of molybdenum thin film on CNS and heating to form Mo₂C^[7], a reduction in the work function and a substantial increase in field emission is achieved.

1.1. Thermionic Emission

Thermionic emission is a significant and well-understood process in electronic solids. As a cathode is resistively heated, the Fermi-Dirac distribution of states extends to higher energies allowing electron states energetically closer to free space. The work function, ϕ , is the energy required by an electron to move from the Fermi energy to a point outside the surface (free space). Only electrons with energies greater than the sum of the work function and the Fermi energy will leave the surface. Hence, as the temperature of the cathode increases, more electrons are emitted. This behavior is described by the Richardson-Dushman equation^[8]:

$$J = B_0 T^2 \exp\left(-\frac{\phi}{kT}\right) A/cm^2 \qquad (1)$$

Where $B_0 = 1.20 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2}$ is the Richardson-Dushman constant, T is temperature (K) and k is Boltzmann's constant, $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$. This equation, however, does not take into account the quantum affects of an external applied field. A typical example of a thermionic emitter is a 75 – 250µm diameter W wire operated at 1600-2000 K.

Thermionic emission has several limitations; specifically, thermionic emitters require large geometries, have heavy power consumption and produce a large thermal budget. Consequently, with greater mass and heat transport, the turn on time for stable thermionic emission is slow (≈ 1 s). Thus, these cathodes are not as desirable in many modern day applications in which surrounding components are temperature-sensitive, require short response times or miniaturization.

1.2. Field Emission

Applying a high voltage to a metal tip of very small radius of curvature creates a very large local electric field so that electron tunneling can occur through the surface barrier potential. As shown in figure 1, a large electric field creates a finite-width, triangular barrier potential. The height of the barrier is reduced by superimposing image potential forces. If the field is sufficiently large (> 8 V/ μm for CNS), the barrier potential will be narrow enough such that the wave function of some electrons will not completely attenuate. Thus, there is a finite probability that some electrons can tunnel through the barrier and escape to vacuum (field emission). The probability for field emission is described by the Fowler-Nordheim (F-N) equation (2).



Figure 1: An electrostatic potential at a conducting surface with a large applied field and image potential forces shown (T = 0 K).

The F-N equation is based upon the Fermi-Dirac distribution of states in the vicinity of the Fermi energy to model the tunneling (transmission) probability that gives rise to a current density, J:

$$J = \frac{I}{\alpha} = \frac{A \cdot E^2}{\phi \cdot t^2(y)} \exp\left[\frac{-B\phi^{\frac{3}{2}}}{E}v(y)\right] A/cm^2$$
(2)
$$A = 1.54 \times 10^{-6}, B = -6.8 \times 10^9, t^2(y) \cong 1.1, v(y) \cong 0.95 - y^2$$
$$y = 3.79 \times 10^{-4} \frac{E^{\frac{1}{2}}}{\phi}$$

where *E* is the applied field and ϕ is the local work function, I is the emission current and α is the emission area. The local field at the emission site is given by:

$$E_{micro} = \beta E_{macro} = \beta \frac{V}{d}$$

where β is the field enhancement factor, V is the voltage, and d is the spacing.

The current density, as given by equation (2), is governed by three distinct variables: ϕ , the work function, β , the field enhancement factor, and α , the emission area. Although an intrinsic property of any metallic surface, the work function of an experimental material is significantly affected by the chemical, electrical, and physical characteristics of the surface. General examples include nanotips, dislocations, vacancies, inclusions, pits, adsorbed gases, and surface dipole effects. The field enhancement factor of an emitter, β , is largely a function of the atomic or molecular geometry. The sharper the emission tip or edge is, the greater the local applied field and, therefore, the smaller the barrier distance. Though efforts to calculate β have yielded mixed results, there are reliable analytical methods in simplified geometrical models. For example, one very general approximation has been reported ^[9, 10]:

$$\beta = \frac{1}{kr} \tag{3}$$

where k ~5 for most metal tips. The third parameter, α , represents the actual number of emission sites per unit area. This parameter is probably the most difficult to determine because of uncertain atomic defects and varying high β -factor structures e.g., nanotips.

In most cases, efficiency and output are improved by using this "cold" cathode. Without the requirement of high temperatures, field emission cathodes are not subject to oxidation, electro-transport and thermal stresses that degrade thermionic emitters. Cold cathodes do not suffer from the material loss (sublimation) and deformation of thermionic cathodes, therefore greatly improving lifetime and reliability. Furthermore, cold cathodes turn on instantly as soon as the field is applied and stabilize quickly (~1 ms). Thus, cold cathodes are of great utility for many industrial and academic applications. For example, field emission used in flat panel displays is projected to be the next advance in monitors and television screens. Furthermore, field emitters are being developed for traveling wave tubes, microwave tubes and other instruments that require high current sources.

1.3. Graphite and Carbon Nanosheets

In high current applications, refractory metals become preferable for their resistance to thermal shock, limited deformation at high temperature and chemical stability. Graphite, an anisotropic metallic allotrope of carbon, is a particularly promising refractory material because of the strong, planar sigma covalent bonds (~614 kJ/mol)^[11] that give graphite its high melting temperature (~3650 °C)^[3] and chemical stability [Fig 2]. Additionally, sideway overlapping p orbitals form distributed π -bonds parallel to sigma bonds (sp² hybridization). Those π -bonds above and below the carbon plane (p_z) provide the electrons for conduction. Locally weak van der Waals forces bind these honeycomb carbon sheets to an integrated strong cohesive force.

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Thus, π -electrons move easily along the plane between sheets and can be accelerated under an applied field to create a near-ballistic trajectory ^[2].



Figure 2: Graphite crystal structure

Carbon nanosheets (CNS) are formed on virtually any inorganic substrate. As graphite islands grow they eventually meet and grain boundaries form. The disorder of the boundary is the basis for vertical growth, aligning the sigma bonded honeycomb sheets roughly normal to the bulk and substrate, terminating into 1-3 graphite sheets [Fig. 3]. Once the "turn up" occurs, the



Figure 3: Carbon nanosheets are formed from graphene layers orientated normal to the bulk, terminating in 1-3 sheets.

energetic sputtering of H ions and atoms minimizes the weak lateral growth on the hexagonal sheets, thus giving rise to predominantly vertical growth of only a few sheets often terminating in a single graphene sheet.

Although the sheets have only small grains on the order of 100nm, the edge density is very high. Furthermore, the outboard edges of the graphite carbon sheets provide very sharp (r ~ 1 nm) emission sites [Fig. 4], with an accompanying very high field enhancement factor, β , therefore, increasing the emission current, as described by the F-N equation.



Figure 4: Scanning electron microscope images of CNS showing the thickness of the emitting edges, < 1 nm.

An interesting characteristic in CNS is hydrogen bonding at these edges. As hydrogen bonds $(CH, CH_2, and CH_3)$ form terminal sites on the emitting edges of the CNS, different hydrocarbons change the local field [Fig 5a]. Thus, because of the outward positive charge center (surface dipole) the hydrogen termination on CNS may also substantially reduce the effective work function from that of graphite (~ 4.8 *eV*). This same condition, however, may exist in ordinary graphite where the field emission is very likely controlled by dangling bonds and

defects also terminated by hydrogen. Thus, the *effective* work function of CNS must be carefully considered.





Figure 5a: The edge of a nanosheet terminated with H atoms. The edge H adsorbates lower the work function because the form an outboard positive charge center (surface dipole).

Figure 5b: Nanotips (a-b) are generated (c-f) by thermal methods and by high electric fields [12].

The β -factor is also affected by local surface variations. For example, electric field and thermally induced nanotips can be generated on metal cathodes [Fig 5b]. As adsorbate and other species segregate to the surface (usually at elevated temperature), they may form pyramidal structures terminating in a single atom, thus amplifying the field enhancement factor (~ 10²) and increasing the current density. These nanotips, however, are unstable and usually disintegrate under high current.

1.4. Molybdenum Carbide Coating

Refractory metal carbides have long been used as robust coatings in industrial applications—resisting corrosion and wear. Mo_2C is also a conductor that has a particular utility with a reported work function of 3.5 *eV* combined with great thermodynamic stability in ambient conditions.

A coating of molybdenum carbide should reduce the effective CNS work function

 $(\phi_{graphite} \cong 4.6 - 4.8 \ eV)$ to that of the coating $(\phi_{Mo_2C} \cong 3.5 \ eV)$. Unfortunately, the effective work function of CNS has never been measured and may be substantially less than ~4.8 eV because of hydrocarbon terminations on emission edges. Nonetheless, if we assume the effective work function of CNS is greater than 3.5 eV, by equation (5), a sufficiently thin (~1-5 nm) Mo₂C coating should lower the effective work function without drastically lowering the β -factor. The F-N equation suggests that, for constant β , a reduction of 1 eV in ϕ , the work function, should yield an increase of over two orders of magnitude in current. Thus, we can compare F-N plots of intrinsic CNS to Mo₂C coated CNS and from the slope determine whether the thin film coating has, indeed, lowered the work function (5).

2. Theory

2.1. Fowler-Nordheim

The maximum voltage used in CNS field emission testing in this work is 5000V. The separation distance in the diode configuration is $250 \mu m$. A conservative estimate for the field enhancement factor of the CNS is $\beta \sim 1.10^3$. So, at turn on (~8 V/ μm):

$$E_{micro} = \beta E_{macro} = (1000)(8V / \mu m) = 8 \times 10^3 V / \mu m$$

During high current operation

$$\beta E_{macro} = (1000) \frac{5000V}{250 \mu m} = 2 \times 10^4 V / \mu m$$

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but,
$$E <<1 \times 10^7 \frac{V}{\mu m} \Rightarrow 1 \times 10^3 \frac{V}{cm}$$

Then,
$$y_{\text{max}} \cong (3.79 \times 10^{-4}) \cdot \frac{\sqrt{1 \times 10^3 \frac{V}{cm}}}{3eV} \cong 3.99 \times 10^{-3} \Rightarrow v(y) \cong 0.95 - y^2 \approx 0.95$$

The F-N equation is then simplified to:

$$J = \frac{A \cdot E^2}{\phi \cdot 1.1} \exp\left[\frac{-B\phi^{\frac{3}{2}}}{E}(0.95)\right]$$
(4)

Further, the equation can be written as,

$$J = \frac{I}{\alpha} = \frac{C_1 \cdot E^2}{\phi \cdot 1.1} \exp\left[\frac{-C_2 \phi^{\frac{3}{2}}}{E}\right] \text{ where } \alpha \text{ is the emitting area, } C_1 = \frac{A}{1.1} \text{ and } C_2 = 0.95B.$$

If equation (4) is plotted in the form of $\ln \frac{I}{V^2}$ versus $\frac{1}{V}$ a straight line can result.

$$\ln \frac{I}{V^2} = \left(-\frac{C_2 \alpha \phi^{3/2}}{\beta}\right) \frac{1}{V} + \alpha \ln \left(\frac{C_1 \beta^2}{\phi}\right)$$
(5)

where the slope, *m*, is $\left(-\frac{C_2 \alpha \phi^{\frac{3}{2}}}{\beta}\right)$ and the intercept is $\alpha \ln\left(\frac{C_1 \beta^2}{\phi}\right)$.

Equation (3), restated here, suggests that a change in the radius of curvature of the emission tip is directly proportional to a change in the field enhancement factor. Thus, for very thin coatings, the field enhancement factor, β , will vary as:

$$\beta = \frac{1}{kr}$$
(3)
$$\beta + \Delta\beta = \frac{1}{k(r + \Delta r)}$$

$$\frac{\Delta\beta}{\beta} = \frac{1}{(1 + \frac{\Delta r}{r})} - 1$$

So that:

Thus, if
$$\frac{\Delta r}{r} \approx 1 \Rightarrow \Delta \beta = -\frac{1}{2}\beta \Rightarrow 2 \cdot \beta_{final} = \beta_{initial}$$
 (6)

For two linear F-N plots, where (6) is true:

$$\phi_{2} = \left(\frac{\beta_{2}m_{2}}{\beta_{1}m_{1}}\right)^{\frac{2}{3}}\phi_{1} \Rightarrow \phi_{initial} = \left(\frac{2 \cdot m_{initial}}{m_{final}}\right)^{\frac{2}{3}}\phi_{final} \quad (7)$$

However, this assumes that the emitting area, α , is constant. As will be shown, the emitting area of the coating sample is half that of the uncoated sample:

$$2 \cdot \alpha_{initial} = \alpha_{final}$$

$$\phi_2 = \left(\frac{\alpha_1 \beta_2 m_2}{\alpha_2 \beta_1 m_1}\right)^{\frac{2}{3}} \phi_1 \Rightarrow \phi_{initial} = \left(\frac{m_{initial}}{m_{final}}\right)^{\frac{2}{3}} \phi_{final} \quad (8)$$

Also, for a single F-N plot, the y-intercept is given by (5):

$$\alpha \ln \left(\frac{C_1 \beta^2}{\phi} \right) = C_3$$

The square of the slope gives:

$$\left(-\frac{C_2\alpha\phi^{\frac{3}{2}}}{\beta}\right)^2 \Rightarrow [C_2\alpha]^2 \cdot \frac{\phi^3}{\beta^2} = (C_4)^2 \Rightarrow \frac{\beta^2}{\phi} = \frac{[C_2\alpha]^2 \cdot \phi^2}{C_4^2}$$

Then, for constant β , ϕ can be written in terms of only α , the emitting area:

$$\phi = \left[\exp[C_3/\alpha] \frac{C_4^2}{C_1 C_2^2 \alpha^2} \right]^{\frac{1}{2}}$$
(9)

Therefore, given linear F-N plots for coated and uncoated samples, the slopes and vertical intercepts can be used to calculate the intrinsic work function of CNS by (7) and (8) assuming the work function of Mo_2C is 3.5 eV. We these values a calculation for the emission area fraction is then possible by equation (9).

3. Experiment and Data

3.1. Coating Carbon Nanosheets

The coating and analysis of CNS was done in an ultrahigh vacuum (UHV) multifunctional electron and surface analysis system (MESAS) [Fig 6a]. The main system houses a multi-sample carousel and is capable of angle resolved Auger electron spectroscopy (ARAES), angle resolved x-ray photoelectron spectroscopy (ARXPS), temperature desorption spectroscopy (TDS), electron energy loss spectroscopy (EELS), field emission energy distribution (FEED), depth profiling by Ar⁺ sputtering and ultra-high vacuum in the range of ~10⁻¹¹ Torr. The introduction chamber is capable of physical vapor deposition (PVD) and glow discharge cleaning (GDC).

The CNS sample was installed in the introduction chamber. After the chamber was pumped down p~ $1x10^{-9}$ Torr, the sample was radiatively heated (T_{filament} ~ 150°C) to remove adsorbed gases and H₂O acquired in atmosphere. During this heating period, the pressure in the intro chamber increased to p~ $1x10^{-8}$ Torr (H₂O).



Ion Gun

PVD Gun (Evaporation Gun)

Introduction Chamber

Figure 6a: UHV multifunctional electron and surface analysis system



Figure 6b: Schematic of MESA main chamber (left), and the introduction chamber (right) showing PVD (in Red)

After degassing, a UHV PVD gun [Fig 6b, Fig 7] was used to deposit the Mo thin film. It is comprised of a ~1mm diameter rod of molybdenum that is bombarded with 8 mA, 2 kV electrons, forming a liquid drop or melt ball (from surface tension) on the end of the rod. The CNS sample was oriented normal and in proximity to the axis of the molybdenum rod (l =12.5 cm). Molybdenum atoms are evaporated to vacuum from the melt ball because of the vapor pressure ($p \sim 3 \times 10^{-2}$ Torr)^[2] at the melting point (T_m ~ 2620°C)^[3], and deposit on the CNS sample, providing a uniform molybdenum coating. The thickness of the coating is controlled by the exposure time.





3.1.1. Auger Electron Spectroscopy Temperature Study

After the deposition, the sample was transferred to the analysis chamber and heated to provide the necessary thermal energy for molybdenum-carbon bonding. The Mo coated CNS sample was heated from room temperature to 1100°C (temperature suggested from thermochemical data to form Mo₂C) with increasing 100°C, five minute increments. Auger electron spectroscopy (AES) surveys were taken at each interval ($E_e^- = 3 \text{ kV}$, and incident flux, $I = 1\mu A$). The spectrum of uncoated CNS (note the "dolphin shape" of the carbon KLL peak at ~270 eV) is shown in figure 8a. The spectrum of the coated CNS after heating (note the change in the carbon peak from the "dolphin" peak to the characteristic carbide "triple peak" ⁽⁷⁾) is shown in figure 8b. From the AES spectra, we measured peak to peak heights of molybdenum, oxygen, carbon, and molybdenum carbide at each 100°C interval to give a relative assessment of surface composition behavior with temperature [Fig. 9]. The Mo₂C peak was determined by the method of Baldwin et al. ⁽¹³⁾ which will be discussed in detail, later.



Kinetic Energy (eV)

Figure 8a: CNS AES spectra without Mo₂C coating.





Kinetic Energy (eV)

Figure 8b: AES spectra of molybdenum carbide coated CNS after heating to 300°C.



Figure 9: Mo-coated CNS relative surface composition with temperature. At each 100 $^{\circ}$ C interval, an AES survey was taken and the peak to peak height was measured for each species. Dark blue shows the carbon; pink shows molybdenum; yellow shows molybdenum carbide; green shows oxygen. It is clear that the complete Mo₂C was formed at 250 $^{\circ}$ C and additional heat was not needed.

3.1.2. Scanning Electron Microscope

A Hitachi 4700 scanning electron microscope (SEM) was used to determine the evenness of the coating. After heating to 1100°C, the SEM revealed significant beading on the sample surface [Fig 10a]. This suggests that the CNS sheets even at 1100°C are quite stable and do not react with the Mo coating. It is proposed that the Mo reacts only with the adventitious C found in defects in the CNS emission edges and graphite substrate. A second sample was prepared and



Figure 10a: SEM images of Mo2C coated CNS after heating to 1100 C

heated only to 250°C and no beading was observed [Fig 8b]. Thus, the Mo₂C coating formed at 250°C is conformal.



Figure 10b: SEM images of Mo2C coated CNS sample after heating to only 250°C show no beading which suggests a conformal thin film coating

3.2. Molybdenum Carbide Calibration Sample

Proper analysis of AES data requires calibration spectra for all species. The signal from Mo_2C coated CNS is a superposition of the underlying CNS signal and the surface Mo_2C . The data for bare CNS was taken before coating (E_e = 3kV, I = 1µA), but required pure Mo_2C AES spectra to complete the analysis. A 99.9% pure Mo_2C powder from Alfa Aesar was imbedded into a 6 mm² pure Al substrate [Fig 11a]. This was accomplished by uniform compression of the Mo_2C between two identical Al substrates polished to a R_a =7. Aluminum was used as a substrate because the Al AES peaks do not overlap with the Mo or the C peaks. The Al was cleaned in an ultrasonic bath: acetone for 20 minutes and propanol for 20 minutes and then thoroughly dried. A thin layer of the powder was applied to one Al sample and the other Al sample was placed on top and the stacked samples placed between two 2 ¾ " blank stainless steel flanges [Fig 11b]. The flanges were then compressed by tightening the screws. The resulting Mo_2C surface was quite uniform and flat.



Figure 11a: Al sample with uniform, compressed Mo₂C powder coated. The sample is mounted on MESAS sample holder



Figure 11b: Schematic of Mo₂C calibration sample preparation.

One uniformly coated Al sample was placed into the introduction chamber of the MESAS and baked-out at 250°C for 1 hour at a pressure of $p\sim1x10^{-8}$ Torr. The sample was then transferred to the analysis chamber and aligned with the secondary electron elastic peak at 3kV, I=10nA. The sample was then Ar⁺ sputtered ($E_{Ar}^+=5kV$, I = 25 μ A) for 10 minutes. Figure 12 shows the AES spectra of the pure Mo₂C. The triple peaks at Auger electron energies ~ 270 eV



Figure 12: Molybdenum carbide AES spectra after Ar+ sputtering

were consistent with that previously reported in the literature $^{[7, 13]}$. The oxygen peak is most likely associated with the Al₂O₃ surface of the underlying Al substrate. No Al peaks are seen. The major Al LMM peak is at 68 eV which does not overlap with the Mo peaks $^{[15]}$.

3.3. Field Emission Testing

Field emission measurement of the Mo₂C / CNS sample was accomplished with a UHV [Fig 13a] system designed to measure field emission in a diode configuration [Fig 13b, c]. The sample is inset in a 1mm thick Al₂O₃ ceramic ring. A spring-loaded Cu contact (for high electrical conductivity) from the cathode ensures good contact and proper spacing. Two smaller diameter ceramic rings, each 125µm thick, established the 250µm diode spacing between the cathode and anode. A negative voltage was applied to the cathode (0 – 5 kV) and an ammeter measured the current at the anode (V = 0). The Mo₂C sample was mounted in the diode cartridge and installed in the UHV system and pumped down to p ~ 5 x 10⁻¹⁰ Torr. Next, the sample was conditioned by slowly applying a field in 100 +/- 50V increments up to a maximum of ~2 kV. As conditioning induced outgassing of absorbed species and burn-off (sublimation) of emission sites with extremely high enhancement factors with each ramping, the sample began to display stable emission characteristics. After several runs, field emission data was collected.



Figure 13a: UHV Field emission testing chamber



Figure 13b: Schematic of integrated diode (not drawn to scale).



Figure 13c: Diode configuration for FE testing

4. Results and Discussion

4.1. Film Thickness

The carbide formation and coating thickness are essential to gauging the success or failure of this procedure and pertains directly to field emission results. First, a thin film thickness determination method was employed by using AES signal intensities ^[14]. The total AES signal intensity of the substrate material varies exponentially as the thickness of the overlayer increases:

$$I_s = I_{0s} \exp\left(\frac{-x}{\mu_s}\right) \tag{10}$$

where I_s is the experimental substrate signal intensity; I_{0s} is the signal intensity of a clean, infinitely thick substrate; *x* is the overlayer thickness; and μ_s is the mean free path of electrons from the substrate in the overlayer material. Intensity, *I* is the peak to peak height of AE signal / elemental AES sensitivity.

The AES signal intensity was calculated from the peak to peak height of bare, uncoated CNS and that of the unheated, Mo-coated sample. Carbon has an AES sensitivity of ~ $0.2^{[15]}$. Using a mean free path of ~ $10^{-0.2}$ ~0.631 nm ^[16], the initial molybdenum coating had a thickness, *x*, of approximately 0.315 nm; molybdenum has a BCC lattice parameter of 0.315 nm ^[3]. Thus, the initial molybdenum coating was *x* ~3 monolayers thick. Mo₂C is predominantly found in a close-packed hexagonal crystal structure with the carbon atoms located in one half of the available octahedral interstices with lattice parameters a=0.301 nm and c=0.473 nm ^[17]. An estimate of the coating thickness based on the vapor pressure of the melt ball of Mo in the MDV PVD gun at 12.5 cm from the CNS substrate does not agree with the AES results, but this is likely because of incorrect temperature assumptions at the melt ball due to heat conduction down the rod. The AES is a more reliable assessment.

4.2. Carbide Formation

Carbide formation is typically indicated by the transformation of the "dolphin peak" at ~270 eV characteristic of graphite and amorphous carbon [Fig 8a] to the "triple peak" characteristic of the carbide^[7] [Fig 8b]. It is the major peak of the three that was measured (peak to peak) as a function of temperature ^[13]. The relative composition of the sample surface as it was heated is shown in figure 9. After $\sim 250^{\circ}$ C, the carbon to carbide ratio stays the same, but the relative molybdenum signal decreases, suggesting that no more carbide is formed after $\sim 250^{\circ}$ C. Initially, it was presumed from thermo-chemical data that the Mo coating would react with adventitious C (not part of the hexagonal graphite structure), but would require a temperature of $T > 1000^{\circ}C$. SEM results however, show extensive beading resulting from Mo surface diffusion and aggregation of the Mo atoms into an island or bead. The carbide formation as a function of T shows even at 1000°C the sigma covalent bonds in the underlying graphite are too strong to disassociate thermally. Thus, we presume that only adventitious carbon, distributed in the graphite surface (located at defects and disordered islands), bonds with the molybdenum. After all available adventitious carbon has combined with the molybdenum to form Mo_2C (and the temperature is elevated to 1100° C), the remaining molybdenum diffuses into the bulk, thereby reducing the relative Mo signal (note the decline in Mo as a function of temperature [Fig 9]). We



Figure 14: AES signal contribution per monolayer. ^[18]

attempted to add more adventitious carbon to the surface through methane carburization, but no significant advantage was observed, thus indicating surface carbide saturation.

As previously discussed, the AES signal contribution decreases with each successive underlayer ^[14]. Although initially three monolayers, the Mo is now either bound to C, unbound at the surface or diffused into the bulk. Thus, the carbide thickness can only be approximated to be on the same order. With the first three monolayers contributing ~22% of the AES signal [Fig 14], the resulting spectra must then be a superposition of a pure carbide signal [Fig 12] and a clean carbon signal [Fig 8a]. Figure 8b shows the AES spectrum of Mo-coated CNS after heating to 300°C. The 22% weighted carbide signal was digitally superimposed on the 78% weighted



Figure 15: Superposition of 78% weighted CNS AES spectra and 22% weighted Mo₂C AES spectra

carbon signal [Fig 8a] and the result is shown in figure 15. Since there is some loss of Mo from diffusion into the bulk, the assumption of 3 monolayers of Mo₂C is an overestimate, and therefore, accounts for the less pronounced triple peak observed in figure 8b. Figures 8b and 15

are highly correlated, strongly suggesting the experimental AES signal is a superposition of the Mo_2C thin film over a CNS substrate.

4.3. Field Enhancement Factor

If we assume an edge radius equal to the CNS inter-planar spacing to be 0.34 nm ^[3], and we add 3 monolayers of Mo, $a_0 = 0.315$ nm, then we change the radius of the edge by 0.315 nm [Fig 16]. Equation (6) applies:

$$\frac{\Delta r}{r} = -\frac{.315nm}{.34nm} \approx 1$$
$$2 \cdot \beta_{CNS} = \beta_{Mo_2C-CNS}$$

Thus, if the assumption that the Mo₂C coating is approximately the same thickness as that of the initial Mo deposition, then the coating reduces the β by a factor of 2. An assumption of $\beta = 1000$ for CNS then would reduce the Mo₂C- coated CNS to $\beta = 500$.



Figure 16: Idealized CNS edge (C atoms in red) with inter-planar spacing of graphite r ~ .34 nm, coated with d~.31 nm Mo₂C.

4.4. Field Emission

The voltage and current data from field emission testing is graphed in an I-V plot [Fig 17].



Applied Field Strength (V/um)

Figure 17: I-V plot for Mo₂C coated CNS contrasted with uncoated CNS (average of 5 samples). The steeper slope and lower turn-on field for the coated sample indicate a lower work function.

Figure 17 shows the advantages of the coating: the turn-on field is lower for the coated sample, E ~6 V/ μm and the slope is steeper—both indications of a lower work function. The red squares are and average of five uncoated CNS samples with turn-on at E~10 V/ μm . From equation (4) an F-N plot can be constructed. Figure 18 shows the plots of four rampings on a Mo₂C-coated CNS sample at current from 100 to 400 μ A in comparison to an average of five bare CNS runs. A linear fit is shown for each plot. Note that there is some increase in the ϕ of the Mo₂C sample run at 400 μ A most likely due to the conditioning of the dominant emission sites. From the linear fit, the correlation coefficients (i.e. R² = 0.999 for Mo₂C to 200 μ A) are indicative of almost perfect F-N behavior and therefore are representation of ideal metallic and

free electron theory. Furthermore, the repeatability shows strong stability in the coated samples as compared to the CNS. Furthermore, the slopes of these lines can be used to calculate the work function by methods shown in equations (7) and (8) and the emitting area by equation (9).



Sample	Slope (linear fit)	Vertical intercept	Correlation coefficient
CNS	-36363	-17.296	.9954
Mo ₂ C 100 μA	-22914	-14.124	.9997
Mo ₂ C 200 μA	-22913	-14.522	.9998
Mo ₂ C 300 μA	-22155	-14.894	.9989
Mo ₂ C 400 μA	-23702	-14.847	.9973

Figure 18: F-N plots for CNS and molybdenum carbide coated CNS. The data table shows the slope, intercept and correlation coefficient for the linear fit for each data series.

The average slope for the four Mo₂C runs is -22921 and the standard deviation is 10.5%. The slope for CNS is -36362. Assuming a constant α for a thin film (>3 monolayers) by equation (7):

$$\phi_{CNS} = \left(\frac{2 \cdot (-36362)}{-22921}\right)^{\frac{2}{3}} (3.5eV) = 7.6eV$$

Thus, using this method, the work function for CNS is approximately 7.6 eV. This is much higher than expected, but this can be explained by examining the assumptions made. First, the graphene sides of carbon nanotubes have been characterized as semi-metals due to their conduction and valence bands just touching (E_q=0). Thus, the fact that the valence and conduction bands in CNS do not overlap may suggest a higher work function than for metals $(\phi_{avg} \cong 4.5eV)$. Secondly, figure 9 shows the molybdenum peak-to-peak height drop from ~180 at room temperature to ~ 90 at 250°C. Thus, the coating formed at this temperature is a mixture of molybdenum carbide and molybdenum. The emitting area of the carbide coating, therefore, is not equal to that of the CNS, but rather half the emission sites may be occupied by molybdenum. Equation (8) then applies:

$$\phi_{CNS} = \left(\frac{-36362}{-22921}\right)^{\frac{2}{3}} (3.5 eV) = 4.8 eV$$

Thus, using this method, the work function for CNS is approximately the same as that of graphite. This is not altogether unreasonable because the dangling bonds and defects in CNS that are terminated with hydrogen may be similar to that in graphite, i.e. similar β -factors. The work function of Mo₂C is reported from a bulk surface with no in-depth discussion of the enhancement factor. Thus, there is no certainty that ϕ will hold in the CNS geometry. In this treatment, the reported work function of 3.5 eV for Mo₂C is assumed to be correct for the Mo₂C coating and has provided an estimate for the effective work function of CNS.

The emitting area can be determined for CNS and the dispersed area fraction of the surface it represents. For Mo_2C (200µA):

$$\phi = \left[\exp[C_3/\alpha] \frac{C_4^2}{C_1 C_2^2 \alpha^2} \right]^{\frac{1}{2}} = (3.5eV)^2 = \exp(-14.5/\alpha) \cdot \frac{-22913^2}{6 \times 10^9 \cdot \alpha^2}$$

For CNS:
$$(4.8eV)^2 = \exp(-17.3/(2 \cdot \alpha)) \cdot \frac{-36362^2}{6 \times 10^9 (2 \cdot \alpha)^2}$$
$$\alpha \sim 5 \text{ cm}^2$$

The geometrical surface area of CNS is reported to be $1300 \text{ m}^2/\text{g}$ and a 1 cm^2 sample has a mass of m~0.02 mg. Thus, the surface area of CNS is A~260 cm². The fractional emission area is then:

$$\frac{\alpha}{A} = \frac{5cm^2}{260cm^2} \approx 2\%$$

Thus, only about 2% of the surface area is occupied by emission sites for field emission.

5. Summary and Future Work

The formation of conformal Mo₂C thin film on CNS can be achieved at relatively low temperatures, 250°C-300°C. The low work function of Mo₂C (previously reported at 3.5 eV) is much lower than that of the underlying CNS thereby reducing the effective work function of the material, which in turn, significantly increases the field emission. Furthermore, the repeatability and stability are also significantly improved. The comparison of the F-N slopes from uncoated CNS to Mo₂C coated CNS permitted a calculation of ϕ , the work function, for intrinsic CNS and an estimate of the emitting area. Thin film coatings appear to be a promising avenue of research for CNS field emission enhancement and stabilization. However, other coating materials (such as oxides) may be pursued and further research conducted to increase not only the current magnitude, but also the stability and lifetime of CNS. Understanding the barrier mechanism by which bulk CNS electrons interact with such films also remains an exciting frontier to be explored.

6. References

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