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On the Cold Emission Mechanism of Diamond Coated Tips

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Abstract. A formal implementation of the Fowler-Nordheim equation to emission characteristics of diamond coated cold cathodes gives values of the work function which depend on surface curvature of the coating, thus making it incorrect. Experiments with diamond coated Si tips having different coating radii have shown, that their emissivity depends on the radius of the Si tip rather than on the radius of the diamond coating. The emission mechanism of diamond coated conductive tips is considered where electron emission is controlled by the conductive tip-diamond interface. A new definition of an "effective" work function has been proposed which can be used for characterization of emissivity of diamond cold cathodes.

1. INTRODUCTION

At this point in time the field emission mechanism of diamond is still not understood. Several models to explain the field emission properties of diamond were proposed: conduction band emission from a negative electron affinity (NEA) diamond surface [1], emission from defect sub-bands [2], valence band emission from nanoprotusions on the diamond surface [3], and hot-electron emission [4,5]. Some authors have indicated an important role for non-diamond inclusions [4]. Work function values of diamond cold cathodes, reported by different authors, differ by several times. In this paper the problem of a correct evaluation of work function from experimental emission characteristics is considered. Experimental data about the dependency of emission properties of diamond coated pointed cathode on cathode geometry are presented and a field emission mechanism for diamond is discussed.

2. WORK FUNCTION MEASUREMENTS OF DIAMOND COLD EMITTERS

Many estimates of the work function of diamond cold emitters were based on the formal implementation of the Fowler-Nordheim (F-N) equation. The curvature of the diamond surface was used to evaluate the field strength at the surface by use of the expression for the field at the surface of a conductive ellipsoid, where \( F \sim 1/r \) (\( r \) is radius of the curvature). In the case of flat-film diamond cathodes [1,6] a parallel-plate capacitor field \( V/d \) (\( d \) is anode-to-cathode distance) is widely used. Results of these calculations seems to be absurd: the evaluated work function strongly depends on the curvature radius of the diamond! The work function was found to be at a minimum for flat-film cathodes (0.01-0.3 eV [1,6]) and it increases with a decrease of the emitters radius giving 0.37 eV at \( r=3 \) \( \mu \)m, 1.01 eV at \( r=0.4 \) \( \mu \)m [3], and about 5 eV at \( r=35 \) nm [7]. Some work function data obtained from the formal implementation of the F-N equation is given in the Table I.

This data indicates that such a formal approach to the evaluation of the work function of diamond cathodes is not correct. Some of the incorrect assumptions are as follows:
Table I

<table>
<thead>
<tr>
<th>Authors</th>
<th>Material</th>
<th>Curvature radius R</th>
<th>$\phi$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>G.J. Amarasinghe and S.R.P. Silva [6]</td>
<td>a-C:H:N (rf PECVD)</td>
<td>infinite (flat surface)</td>
<td>0.03-0.05</td>
</tr>
<tr>
<td>C. Xie et al. [1]</td>
<td>LA &quot;amorphous diamond&quot;</td>
<td>infinite (flat surface)</td>
<td>0.3</td>
</tr>
<tr>
<td>V.V. Zhirimov et al. [3]</td>
<td>HFCVD diamond</td>
<td>3 $\mu$m</td>
<td>0.37</td>
</tr>
<tr>
<td>V.V. Zhirimov et al. [3]</td>
<td>HFCVD diamond</td>
<td>0.4 $\mu$m</td>
<td>1.01</td>
</tr>
<tr>
<td>J. Liu et al. [7]</td>
<td>MPCVD diamond</td>
<td>35 nm</td>
<td>-5</td>
</tr>
</tbody>
</table>

rf PECVD - radio frequency Plasma Enhanced CVD; LA - laser ablated; HFCVD - hot filament CVD; MPCVD-microwave plasma CVD

1) The use of the "outside" radius of the coating for calculations of field enhancement implies treating diamond as a conductor. In fact, for dielectric materials, field penetrates inside of the insulator affects band bending. If the Debye screening length of the insulator is larger than the thickness of the dielectric coating, the field lines will be concentrated at a conductive base ("core"). This means that the curvature of the conductive base plays a major role in field enhancement.

2) For work function calculations for flat-film diamond cathodes, the macroscopic field of a flat capacitor is commonly used. However, field enhancement also may occur in the insulating film on the conductive surface. This field enhancement may be both due to protrusions at the conductive surface and due to an "antenna effect" of conductive microparticles embedded in the dielectric layer (for example graphite in the diamond film)[4, 8, 9].

3) Emission of equilibrium carriers from the conduction band of diamond is suggested. This is inconsistent with experimental results, which show no successful n-doping of diamond.

It should be noted, however, that such a formal approach may be rather correct if applied to highly boron doped p-type diamond field emitters, which may be considered as a conductive material.

Another approach to the evaluation of the work function of diamond coated cathodes is the assumption that the field lines are concentrated at a conductive "core" inside of the diamond, and thus field enhancement depends not on the curvature of the diamond, but on the curvature of the "core" [5]. Authors [5] have proposed a definition of "effective" work function for the characterization of emission process that depends not only on the surface condition, but also on the dielectric constant, the effective electron mass, Fermi level position etc. The emission process is assumed to be controlled by electron tunneling at the metal-diamond interface (n-type Si also may be treated as a metal here, since at high applied fields, it will always be degenerated near the interface due to band bending). The way of determining the "effective" work function is the following. Since F-N plots of many diamond coated cathodes are linear or nearly linear, we will presume that the process is still tunneling controlled. Next, since the field lines are concentrated at the conductive "core", the "core" curvature should be used for the determination of the field enhancement factor. "Effective" work function is defined as the value of work function, calculated from experimental I-V plot, as if the emitter was metallic with a curvature radius equal to that of the conductive "core". An analytical expression of this "effective" work function may be found from the equalizing of the transmission coefficient of the "virtual" metal emitter to the transmission coefficient for electron tunneling through the metal-diamond interface.

The proposed "effective" work function of a "virtual" metallic field emitter has nothing to do with the solid/vacuum potential height any more, but this value is useful because it is easily obtainable from experimental I-V plots by implementation of the F-N equation. Values of effective work function obtained by this approach are in the range of 2-6 eV [5]. Details of the emission mechanism used in this approach and expressions for the effective work function are given below.

It should be noted that this approach may be easily used for pointed cathodes where field the enhancement factor is a reproducible function of tip radius. However, it is more difficult for flat cathodes since field enhancement in this case depends on the roughness of the interface, on graphite inclusions, etc.

3. SUMMARY OF EXPERIMENTAL DATA.

In Fig. 1 (a) I-V curves are shown which were obtained from three Si tips with curvature radii of 50, 100, and 500 nm, all of which have the same radius of diamond coating (R of 500 nm). A strong dependency of
emissivity on the radius of the Si tip is clearly seen. Fig. 1 (b) gives an example of the emissivity of a sharp Si tip with radius of 25 nm that was first coated with diamond of R=400 nm, and later measured again after being coated with diamond of R=800 nm. Only a small change in the I-V plots of the two different coating radii can be seen. As has been shown [5], emissivity of a Si or Mo tip may be considerably improved by deposition of thin (0.5 μm) diamond coatings, however, if the coating is thick (>2 μm) emissivity drops. The authors explain this thickness dependency in terms of a space charge effect.

![Graph showing I-V plots of Si tips with different curvature radii](image)

**Figure 1:** I-V plots of Si tips with different curvature radii having diamond coatings of the same 500 nm radius (a) and a Si tip (r<25 nm) with diamond coatings of two different radii

### 4. ELECTRON EMISSION FROM DIAMOND

For the case of diamond we will consider a field emitter where emission occurs from the conductive "core" beneath the coating. The electric field will penetrate into the diamond, and the field lines will concentrate at the conductive tip (Fig. 3).

In general, electron emission from diamond in this approach is a three-step process. First, electrons are injected into the conduction band of the diamond from the conductive tip by F-N tunneling. The second step is electron transport to the surface. Various processes can accompany the transport: electron scattering, space-charge effects due to excess of non-equilibrium carriers, impact ionization etc. In this simple model, as a perfect diamond crystal with no traps is considered. The third step is the escape of electrons from diamond into vacuum.

#### 4.2. Field strength and potential distribution inside of a diamond coating

We propose a simple expression for the estimation of the field strength near a tip with radius of curvature of r:

\[
F(x) = F_0(\frac{\alpha}{(r+x)^2} + 1) \quad (1)
\]

where x is the distance from the tip to the anode in the direction normal to anode; \( F_0 = V/d \) (d is anode-to-cathode distance) is uniform field near the anode, \( r \) is curvature radius; \( \alpha = \beta r^2 \) (\( \beta \) is field enhancement factor) \( F_{tip} = \beta F_0 \).

It can be seen, that \( F = \beta F_0 \) at the tip (x=0), and \( F = F_0 \), for large values of x. Also, the \( F(x) \) dependency near the tip follows the conventional field strength law for fields near a charged conductive sphere.

Correspondingly, potential distribution may be obtained by the integration of (1), resulting in:

\[
\phi(x) = V/d \left( \frac{\alpha}{(r+x)} - x \right) \quad (2)
\]

Now, let us consider a conductive tip with a diamond coating. We assume for simplicity a spherical shape for the coating (a 'ball-on-point' geometry). The field inside the diamond may be obtained by the division of \( F(x) \) in (1) by a factor k. The factor k is equal to the dielectric constant of diamond, \( k = \varepsilon = 5.6 \) for the case of an infinity large layer of diamond compared to anode and cathode plate distance, for example; in the case of flat conductive plate with a diamond coating. In the case of a finite-size diamond 'ball', the situation
is more difficult. The field inside of a finite-size dielectric sphere in a uniform field is equal to [10]:
\[ F_I = 3F_0/(c+2), \]
\[ k = (c+2)/3 \]
(\( k = 2.53 \) for diamond). For a concentric sphere geometry, where the electric field is highly non-uniform, \( k = \infty \) again. Thus, the field suppression factor \( k \) is geometry dependent. We can distinguish two limiting cases were the analytical expression may be used. First, if the field outside of the diamond surface is approximately uniform, \( k = 2.53 \) (Fig. 2(a)). If the field is non-uniform, \( k = 5.6 \) (Fig. 2(b)).

The uniform-to-non-uniform geometry transition depends on \( R/r \) ratio: for a small value of \( R \) the field is nonuniform across the coating, and above a certain critical value of \( R \) the field may be considered to be uniform (we assumed here the field to be uniform if \( (1-F_0/F(R)) < 0.2 \)). At a given \( r \), a critical value of diamond ball radius \( R_c \) exists: the field is nearly uniform if \( x > R_c \). Values of \( R_c \) for three different \( r \) values are given in the Table II.

<table>
<thead>
<tr>
<th>( r, \text{nm} )</th>
<th>( R_c, \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
</tr>
</tbody>
</table>

![Figure 2: Two “ball-on-point” geometries: non-uniform field geometry (a) and uniform field geometry (b)](image)

Field strength and potential distribution inside a diamond 'ball' on a conductive tip given for two values of \( k \) are shown in Fig. 3 (a) and (b).

![Figure 3: Field strength (a) and potential distribution (b) inside a diamond 'ball' on a conductive tip](image)

### 4.3 Metal/Diamond interface (MDI)

We consider here the MDI of intrinsic and nitrogen-doped diamond. The Fermi level position for intrinsic diamond may be assumed to be \( -E_d/2 = 2.7 \text{ eV} \). Substitutional nitrogen creates deep donor centers in the band gap of the diamond with an activation energy of \( 1.7 \text{ eV} \). The room-temperature concentration of ionized donors follows the expression [11]:

\[ N_d^+ = n = (N_i N_d/2)^{1/2} \exp \left(-\frac{E_c - E_d}{kT}\right) \]

(3)

For nitrogen concentration \( N_d = 10^{19} \text{ cm}^{-3} \), \( N_d^+ \) is about \( 10^3 \text{ cm}^{-3} \), that corresponds to a depletion width of about 1 meter, i.e. still much larger than diamond layer thickness.

The Fermi level position can be found from the expression [11]:

\[ E_f = \left[ (E_c + E_d)/2 \right] - (kT/2) \ln(2N_i/N_d) \]

(4)

For \( N_d = 10^{17} \text{ cm}^{-3} \), \( E_c - E_f = 1.14 \text{ eV} \) and for \( N_d = 10^{19} \text{ cm}^{-3} \), \( E_c - E_f = 1.08 \text{ eV} \).
Only the case of thin diamond coatings with a thickness <1 μm is considered here. In this case the MDI may be treated as a metal-vacuum interface with a conduction band minimum level instead of a vacuum level. Electrons will "boil off" of the metal into the conduction band of the diamond just as they do from a heated cathode in vacuum.

For undoped diamond the intrinsic electron concentration in the conduction band is [11]:

\[ n_i = (N_c N_v)^{1/2} \exp \left( E_b / kT \right) \]  

(5),

where: \( N_c \) and \( N_v \) are density of states in the conduction and valence bands correspondingly, \( N_c = 2.5 \times 10^{19} \) (\( m_e^*/m_0 \) T/300)^3/2, \( N_v = 2.5 \times 10^{19} (m_n^*/m_0) T/300)^{3/2} \) [11].

The value of the intrinsic carrier concentration calculated from (5) for \( E_g = 5.5 \) eV is insignificantly small. Correspondingly, the depletion width is infinite if compared to the thickness of the diamond. As it was shown for insulative wide band gap materials[12], band bending effects at the interface are very small and the barrier height \( \phi_B \) in this case is given by \( \phi_B = E_c - E_v \) (Fig. 4).

![Diagram of Metal-diamond interface band diagram and illustration of emission process](image)

**Figure 4: Metal-diamond interface band diagram and illustration of emission process**

### 4.4. Electron tunneling into the conduction band of diamond.

We assume here a perfect diamond crystal with a band gap of \( E_g = 5.5 \) eV and dielectric constant \( \varepsilon = 5.6 \). The surface of the diamond is assumed to exhibit NEA, i.e. surface barrier does not affect the emission process. The transmission coefficient of an electron at \( E = E_F \) is [12]:

\[ T = \exp(-B d \phi^{1/2}) = \exp(-B \phi^{3/2} / F) \]  

(5)

We have defined "effective" work function of the diamond-coated emitter as a value, corresponding to the same transmission coefficient of a "virtual" metal emitter at same external field. Using this approach, effective work function can be found from the equation:

\[ B_{m_v} d_{m_v} (E_c - E_F)^{1/2} = B_{m_v} d_{m_v} \phi_{eff}^{3/2} \]  

(6)

where \( d_{m_v} \) is tunneling width of the metal-insulator (diamond) interface, and \( d_{m_v} \) is the tunneling width at the surface (metal-vacuum interface) of a "virtual" metallic emitter with "effective" work function \( \phi_{eff} \).

\[ B_{m_v} = (2\pi)(4/3)(2m)^{1/2} / h; \quad B_{m_v} = B_{m_v} (m^*/m_0)^{1/2}, \quad m^* \text{ is the effective electron mass in diamond, and } m_0 \text{ is the free electron mass. Thus,} \]

\[ \phi_{eff} = (m^*/m_0)^{1/2} (E_c - E_F) \varepsilon^{2/3} \]  

(7)

For diamond, by the substitution of \( m^*/m_0 = 0.2 \) [13] into (7), we obtain:

1. intrinsic diamond (\( E_c - E_F = 2.7 \) eV); \( \phi_{eff} = 4.98 \) eV;  
2. nitrogen doped diamond (\( E_c - E_F = 1.1 \) eV); \( \phi_{eff} = 2.01 \) eV

Data obtained consistent with work function values calculated from experimental I-V plots.[5]. For a more accurate estimation of "effective" work function, space charge effects and the resulting thickness effect must be taken into account.

### 4.5 Electron transport in diamond

#### 4.5.1. Space charge effects.

During the emission process, non-equilibrium, non-compensated negative charge \( Q \) is injected into diamond: \( Q = J t = D \varepsilon / \mu F \) (\( J \) is the current density, \( t \) is the transit time for an electron from the tip to the diamond surface, \( \varepsilon \) is the drift velocity, \( \varepsilon \) is the dielectric constant, \( \mu \) is the drift mobility, and \( D \) is the
thickness of the coating). The accumulation of negative charge makes it more difficult for electrons to tunnel into the diamond (tunneling width increases). Also, for a non-perfect diamond crystal, charging of traps should be taken into account. Space charge effects are dependent on both diamond thickness and current. It may be expected that for thick coatings, space charge effects will dominate and the transition from F-N to space charge limited current will occur at a certain critical thickness.

4.5.2. Electron scattering and impact ionization.

Electron scattering processes have been analyzed in detail by Cutler et al. [12]. Scattering affects the mean free path of electrons in diamond. If the mean free path is large enough for an electron to gain sufficient energy for impact ionization of impurities and lattice atoms, avalanche breakdown may take place. Generated electron-hole pairs will change the band diagram considerably, as it has been shown by Latham and co-workers [8,9]. Emission will no longer be controlled by F-N injection or by bulk transport; surface effects will dominate the emission process.

4.6 Electron escape into vacuum

Usually, a NEA surface for diamond is assumed during the analysis of most emission mechanisms. In this case, the emission is MDI-controlled. However, it is important to note, that NEA is not necessarily required for MDI controlled emission. If only a small positive barrier exists at the DVI, its zero-reduction due to image forces is possible. In Table III values of surface barrier reduction $\Delta \chi$ for different values of external field are given. This effect could be expected only for very thin diamond coatings, since the field strength decreases rapidly with an increase of the distance from the tip (Fig. 5). For thick diamond coatings and positive electron affinity surfaces, quasi-thermionic escape of hot electrons is possible as it have been shown by Latham et al [8,9].

<table>
<thead>
<tr>
<th>$F$, V/cm</th>
<th>$\Delta \chi$, eV</th>
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<tbody>
<tr>
<td>$10^5$</td>
<td>0.1</td>
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<td>$5 \times 10^5$</td>
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References