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Diamond & Related Materials 15 (2006) 1418 – 1423
DIAMOND AND RELATED MATERIALS
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Localized emission from flat diamond cathodes

Griff L. Bilbro [a,*], Robert J. Nemanich [b]

[a] Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, NC, USA
[b] Department of Physics, North Carolina State University, Raleigh, NC, USA

Received 24 May 2005; accepted 25 October 2005
Available online 13 December 2005

Abstract

We analyze steady-state field emission from an n-type semiconductor under the assumption that its surface presents no barrier for electron emission from the conduction band into the vacuum. We construct a classical Lagrangian field theory for the coupled electric and quasi-fermi potentials and use it to show that uniform emission is unstable against laterally nonuniform perturbations. We use a two-parameter model of normal emission current to show that the Lagrangian of the linearized system is minimal when all electrons are emitted from a single site. In addition to this intensely localized emission, we show the normal electric field at the surface is moderately enhanced at the solitary emission site even though the surface itself is planar. We use the result to explain the isolated emission sites observed in nanocrystalline n-type diamond films.
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Keywords: Negative electron affinity; Nonuniform electron emission; Emission sites; Cold cathode; Lagrangian; Drift diffusion

1. Emission from planar cold cathodes

Diamond and some other materials can exhibit negative electron affinity (NEA). Electrons can be extracted from such diamond surfaces by a relatively low electric field at room temperature [1,2]. For some materials such as nanocrystalline diamond, the electrons are not emitted uniformly but only from small isolated sites. Efforts to develop nanocrystalline cathodes that emit uniformly have improved every measure of material and surface quality except emission uniformity [3].

Previously, we investigated the time dependence of perturbations of a one-dimensional equilibrium solution of the drift diffusion equations [4]. We reported that a zeroth order electric field could make small nonuniformities grow in time, but that theory did not allow us to determine the final, i.e., observable, configuration of the system [4].

In this report we revisit the question of finding a final configuration for the system, but instead of considering time dependent perturbations of the uniform system, we begin with the set of all linearized steady-state solutions and search for the one that is physically realized. We exploit electrostatic boundary conditions at the semiconductor-vacuum interface to analytically simplify expressions for the field energy density and the potential energy density enough to formulate a Lagrangian for the system. Consideration of the resulting Lagrangian action shows that uniform emission is unstable against every lateral nonuniformity. Finally, we show that for material and experimental parameters typical of low-field electron emission from n-type nanocrystalline films at room temperature, the actual minimum of the Lagrangian occurs when all current is emitted from localized sites that are as small as possible and as widely separated as possible.

2. Ideal steady-state emission

Let a planar interface at $z=0$ separate diamond in the half space $z<0$ from vacuum in the half space $z>0$. The electric potential Ψ obeys Poisson's equation which requires the divergence of the electric displacement and the charge density to be equal

$$\nabla\cdot(-\epsilon\nabla\Psi)=\rho \tag{1}$$

where ε is the local dielectric permittivity

$$\epsilon=\epsilon_0, \quad \text{for } z>0 \quad \text{and} \tag{2}$$

$$\epsilon=\epsilon_r\epsilon_0, \quad \text{for } z<0, \tag{3}$$

and ϵ_r is the relative dielectric constant of the semiconductor.

* Corresponding author.
E-mail address: glb@ncsu.edu (G.L. Bilbro).

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doi:10.1016/j.diamond.2005.10.045

For an n-type semiconductor that is electrically neutral at equilibrium,

$$N_D^+ = n_i \exp \frac{-(E_i - E_F)}{k_B T} \tag{4}$$

relates the concentration of ionized donors N_D^+ to the intrinsic electron concentration n_i, the intrinsic level E_i, the Fermi level E_F, and the product of the Boltzmann constant times absolute temperature, assuming that the density of electrons is low enough to obey Boltzmann statistics.

For a steady-state configuration near equilibrium, E_F can be replaced with a local quasifermi level E_{Fn} where both E_i and E_{Fn} vary with location. We can write the perturbed electron density as

$$n = N_D^+ \exp \frac{\Psi - \Phi}{V_T},$$

where $\Psi = -\Delta E_i/q$ and $\Phi = -\Delta E_{Fn}/q$ have the units of volts and represent the changes of E_i and E_{Fn} from their equilibrium values, and $V_T = k_B T \neq q$ is the usual thermal voltage. In this expression, neutrality occurs wherever $\Psi = \Phi$ and equilibrium occurs where both Ψ and Φ also vanish.

In the case of a uniform macroscopic applied field of magnitude E_{vac}, we write the electric potential

$$\Psi = E_{vac} z + \psi \quad \text{for } z > 0,$$

as the sum of the familiar one-dimensional response $E_{vac}z$, which is large for $z \gg 0$, plus a possible non-uniform perturbation ψ which we assume to be small everywhere compared to V_T and to vanish for $z \gg 0$. Now continuity of the zeroth order normal electric displacement requires

$$\Psi = E_{in} z + \psi \quad \text{for } z < 0$$

where

$$E_{in} = \frac{E_{vac}}{\epsilon_r}$$

is familiar from the usual 1-D analysis of such problems. With these choices of Ψ for $z = \pm 0$, the zero of electric potential corresponds to the unperturbed intrinsic level at the interface. Deep within the semiconductor, where ψ vanishes, charge neutrality requires the zeroth order Φ and Ψ to coincide so we write

$$\Phi = E_{in} z + \phi \quad \text{for } z < 0,$$

where ϕ also vanishes for $z \gg 0$ and is small compared to V_T, but allows for a possible perturbation near the surface. With this choice of Φ, the zero of the quasi-fermi potential corresponds to the unperturbed Fermi potential at the interface. We neglect holes, so that the charge density $(N_D^+ - n)q$ becomes

$$\rho = q N_D^+ \left(1 - \exp \frac{\Psi - \Phi}{V_T}\right), \tag{5}$$

where $q > 0$ is the magnitude of the fundamental charge,

In steady state, the charge density does not change with time so that $\partial_{t\rho} = 0$ and

$$\nabla \cdot \vec{J} = 0 \tag{6}$$

everywhere. In quasi-equilibrium, the total current density in the semiconductor is

$$\vec{J} = -qn\vec{v} \quad \text{for } z < 0, \tag{7}$$

where

$$\vec{v} = \mu \nabla \Phi \tag{8}$$

and μ is the mobility of free electrons [5]. We assume that E_{vac} is high enough and electron emission is low enough to neglect all charge in the vacuum, so that $\vec{J} = 0$ and $\rho = 0$ for $z > 0$: Once an electron is emitted, it is swept away before significant charge can accumulate.

3. Lateral non-uniformities

In the vacuum, Ψ is large, but since $\rho = 0$ for $z > 0$ by assumption, Poisson's equation reduces to Laplace's equation

$$\nabla^2 \psi = 0 \tag{9}$$

Both Ψ and Φ are large for $z \ll 0$, but their difference $\Psi - \Phi = \psi - \phi$ is small inside the semiconductor. For $z < 0$, the small magnitude of $\psi - \phi$ allows linearization of the continuity equation

$$\nabla_\phi^2 + \eta \partial_z (\psi - \phi) = 0 \tag{10}$$

and Poisson's equation

$$\nabla^2 \psi - \kappa^2 (\psi - \phi) = 0, \tag{11}$$

where we have defined

$$\kappa = \frac{1}{L_D} = \sqrt{\frac{q N_D^+}{\epsilon_r \epsilon_0 V_T}} \tag{12}$$

and

$$\eta = \frac{E_{in}}{V_T} = \frac{E_{vac}}{\epsilon_r \epsilon_0 V_T} \tag{13}$$

both to have dimensions of reciprocal lengths and units of reciprocal meters in SI.

Eqs. (9) (10), and (11) are satisfied by linear combinations of terms like

$$\psi_{k,out} \sim u_k(x,y) e^{-kz} \text{ in } z > 0, \tag{14}$$

$$\psi_k \sim u_k(x,y) e^{pz} \text{ in } z < 0, \tag{15}$$

$$\phi_k \sim u_k(x,y) e^{pz} \text{ in } z < 0, \tag{16}$$

where $p = p_k$ is a wavenumber in the normal direction z that solves the homogeneous algebraic system

$$\left(-k^2 + p_k^2\right)\psi_k - \kappa^2(\psi_k - \phi_k) = 0, \tag{17}$$

$$\left(-k^2 + p_k^2\right)\phi_k - \eta p_k(\psi_k - \phi_k) = 0, \tag{18}$$

c_k, θ_{xk} and θ_{yk} are constants, $k=\sqrt{k_x^2+k_y^2}$ is the lateral component of the wavevector inside the semiconductor, and

$$u_k(x,y)=\cos(k_x x+\theta_{xk})\cos\left(k_y y+\theta_{yk}\right). \tag{19}$$

Eqs. (17) and (18) have four solutions but only two of them result in finite $\psi(-\infty)$ and $\phi(-\infty)$:

$$p_k=k \text{ with}\frac{\phi_k}{\psi_k}=1, \tag{20}$$

and

$$p_k=\frac{1}{2}\left(\eta+\sqrt{n^2+4\kappa^2+4k^2}\right) \text{ with}\frac{\phi_k}{\psi_k}=\frac{\eta p_k}{\kappa^2}. \tag{21}$$

These two normal wavenumbers are compared in Fig. 1 as functions of k, the lateral wavenumber.

For each k_x, k_y, the general solution therefore contains a linear combination of terms like

$$\psi_{k,\text{out}}\sim c_k e^{-kz}u_k(x,y)$$

$$\psi_k\sim\left(a_k e^{kz}+b_k e^{pkz}\right)u_k(x,y)$$

$$\phi_k\sim\left(a_k e^{kz}-b_k\frac{\eta p_k}{\kappa^2}e^{p_k z}\right)u_k(x,y)$$

for every mode k, if it is to include both solutions 20 and 21 inside the emitter, according to Eqs. (15) and (16).

The coefficients a_k, b_k, and c_k are not independent. The electric potential must satisfy two boundary conditions at the interface: continuity of the normal displacement $-\epsilon\partial_z\psi$ and continuity of the lateral field $-(\partial_x\psi,\partial_y\psi)$ require that

$$\frac{a_k}{c_k}=-\frac{\alpha k}{p_k-k},$$

$$\frac{b_k}{c_k}=1+\frac{\alpha k}{p_k-k},$$

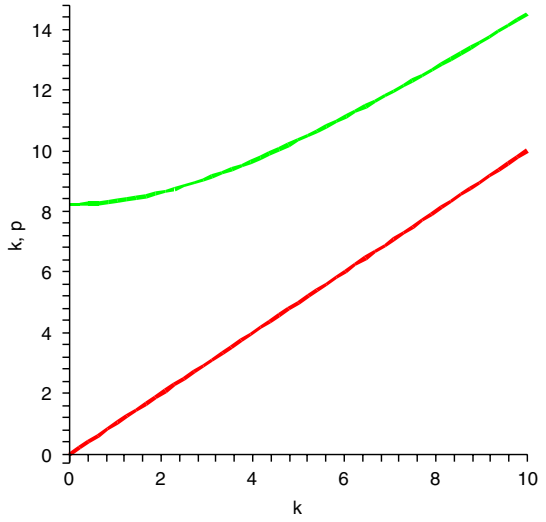

Fig. 1. k and p_k in $(\mu m)^{-1}$ as functions of k in $(\mu m)^{-1}$ for room temperature diamond with $\epsilon_r=5.7$, $N_D^+=10^{14}/cm^3$, and $E_{vac}=1$ V/μm, which correspond to $\kappa=3.49/\mu m$, $\eta=6.75/\mu m$.

where

$$\alpha=\frac{\epsilon_r+1}{\epsilon_r}. \tag{22}$$

These two constraints will be used to rewrite a_k and b_k in terms of c_k.

In terms of the resulting c_k, the general solution of the system is

$$\psi=\sum_{k_x,k_y}c_k u_k(\mathrm{x},\mathrm{y})e^{-kz} \text{ in } z>0, \tag{23}$$

$$\psi=\sum_{k_x,k_y}c_k u_k(x,y)\left[e^{kz}+\frac{\alpha k}{p_k-k}\left(e^{kz}-e^{p_k z}\right)\right] \text{ in } z<0, \tag{24}$$

$$\phi=\sum_{k_x,k_y}c_k u_k(x,y)\left[e^{kz}+\frac{\alpha k}{p_k-k}\left(e^{kz}+\frac{\eta p_k}{\kappa^2}e^{p_k z}\right)\right] \text{ in } z<0, \tag{25}$$

where $u_k(x,y)$, k and p_k depend on k_x, k_y as given by Eqs. (19)–(21), and the c_k have the units of volts.

For any arbitrary set of $\{c_k,\ \theta_{xk},\ \theta_{yk}\}$, Eq. (23) in the vacuum and Eqs. (24) and (25) in the semiconductor satisfy the homogeneous system comprising the linearized electrostatic Eqs. (9) (10), and (11) together with the appropriate boundary conditions at $z=0$ and $|z|=\infty$.

4. Spontaneous non-uniformities

Eq. (1) is equivalent to asserting that the physical Ψ is a variational minimum of an appropriate action functional. This Lagrangian formulation provides an alternative analysis of the system response to E_{vac} that we will use to determine c_k, which are the degrees of freedom remaining after the differential analysis of the previous section. To first order in the small quantities, ψ and ϕ, Eqs. (23) (24), and (25) solve both Poisson's equation and charge continuity equation for $z\neq0$, and satisfy the electrostatic boundary conditions at $z=0$ on normal displacement and tangential field.

The action functional L_{tot} which we now construct is an integral that explicitly excludes the interface, so that our action cannot account for the boundary conditions at the interface. This is of no concern since we will ultimately formulate the minimization in terms of the coefficients c_k, so that our result will satisfy the boundary conditions at $z=0$ because Eqs. (23) (24), and (25) satisfy them.

In the vacuum, the appropriate action is

$$L_{out}=T_{out}=\int_{z>0}\frac{\epsilon_0}{2}|\nabla\psi|^2 d^3r, \tag{26}$$

as can be shown by taking its variation, which is equal to

$$\delta T_{out}=\int_{z>0}\nabla\cdot\left(\frac{\epsilon_0}{2}\frac{\partial}{\partial(\nabla\psi)}|\nabla\psi|^2\right)\delta\psi^3 r$$

$$=-\int_{z>0}\nabla\cdot(\epsilon_0\nabla\psi)\delta\psi^3 r,$$

and which vanishes for arbitrary $\delta\psi$ if and only if Eq. (9) is satisfied. Inside the semiconductor, the action is

$$L_{\text{in}} = T_{\text{in}} - V_{\text{in}}, \tag{27}$$

where the field energy inside the semiconductor

$$T_{\text{in}} = \int_{z<0} \frac{\epsilon_r \epsilon_0}{2} |\nabla\psi|^2 \mathrm{d}^3\mathrm{r},$$

has the same form as T_{out}. The potential energy

$$V_{\text{in}} = -\int_{z<0} \epsilon_r \epsilon_0 \kappa^2 \left(\frac{1}{2}\psi^2 - \psi\phi\right) \mathrm{d}^3\mathrm{r},$$

involves only the potential itself and is independent of $\nabla\tilde{A}$, so its variation

$$\delta V_{\text{in}} = -\int_{z<0} \epsilon_r \epsilon_0 \kappa^2 (\psi - \phi)\delta\psi \mathrm{d}^3\mathrm{r}$$

requires no integration by parts and therefore no special care to exclude the interface.

The observable physical configuration of the system minimizes the Lagrangian combination

$$L_{\text{tot}} = T_{\text{out}} + T_{\text{in}} - V_{\text{in}}, \tag{28}$$

of Eqs. (26) and (27), provided that we restrict ourselves to the ψ and ϕ of Eqs. (23) (24), and (25). The first two terms of Eq. (28) are the integrals of the usual electrostatic field energy density $\frac{1}{2}\vec{D}\cdot\vec{E} = \frac{1}{2}(-\epsilon\nabla\psi)\cdot(-\nabla\psi)$. The last term is the potential energy of the net space charge density, represented by $-\kappa^2(\psi-\phi)$ in Eq. (11), interacting with the local electric potential ψ in the semiconductor.

The first two terms of L_{tot} are positive semi-definite, and they vanish only for constant electric potential; they penalize any change of the potential. In contrast, the third term, $-V_{\text{in}}$, can be negative and this pivotal in our theory: if ψ and ϕ can distort themselves to make this third term in Eq. (28) negative enough to compensate for the increased field energy $T_{\text{out}}+T_{\text{in}}$ of the distortion, then the distorted state is energetically preferred.

In terms of Eqs. (23) and (24), the first two of these integrals are

$$T_{\text{out}} = \frac{\epsilon_0 L^2}{8} \sum_k c_k^2 k, \tag{29}$$

$$T_{\text{in}} = \frac{\epsilon_r \epsilon_0 L^2}{8} \sum_k c_k^2 \left[k + \frac{\alpha^2 k^2}{p_k}\right], \tag{30}$$

which can be combined and simplified into the field energy

$$T_{\text{in}} + T_{\text{out}} = \frac{\epsilon_r \epsilon_0 L^2}{8} \sum_k c_k^2 \frac{\alpha k(\alpha k + 2p_k)}{2p_k}, \tag{31}$$

of the system, where α is defined by Eq. (22).

The potential energy

$$V_{\text{in}} = \frac{\epsilon_r \epsilon_0 L^2}{8} \sum_k c_k^2 \left(\frac{\kappa^2\left[(p_k+\alpha_k)^2 - p_k k\right]}{2p_k k(p_k - k)} + \frac{\alpha\eta k(\alpha k + 2p_k)}{p_k^2 - k^2}\right) \tag{32}$$

can written in terms of the same quantities with Eqs. (25) and (24). Note that $V_{\text{in}} \geq 0$ because $p_k \geq k$, $\alpha > 1$, and the quantities k, η, κ are always positive.

We can combine these results to write the system Lagrangian

$$L_{\text{tot}} = \frac{\epsilon_r \epsilon_0 L^2}{8} \sum_k c_k^2 \left(\frac{\alpha k(\alpha k + 2p_k)}{2p_k} - \frac{\kappa^2\left[(p_k+\alpha k)^2 - p_k k\right]}{2p_k k(p_k - k)} - \frac{\alpha\eta k(\alpha k + 2p_k)}{p_k^2 - k^2}\right). \tag{33}$$

5. Spot emission

Our theory predicts that the perturbations minimize L_{tot} by diverting the uniform current density of the unperturbed state into isolated emission sites, as we now show. For small k, Eq. (33) approaches

$$-\frac{c_k^2 L^2 \epsilon_r \epsilon_0 \kappa^2}{16k}.$$

For large k, Eq. (33) approaches

$$-\frac{c_k^2(\alpha+2)\alpha L^2 \epsilon_r \epsilon_0 k}{16}.$$

Both limits are negative and numerical experiments such as Fig. 2 suggest that the energy of every mode is negative for all combinations of material parameters and experimental conditions in the vicinity of $\epsilon_r = 5.7$, $N_d = 10^{20}/\text{m}^3$, and $E_{\text{vac}} = 10^6$ V/m, which correspond to $\alpha = 1.18$, $\kappa = 3.49/\mu\text{m}$, and $\eta = 6.75/\mu\text{m}$, at room temperature. The energy of any such mode is highest when its amplitude c_k vanishes. We conclude that in any observed equilibrium configuration, the magnitude $|c_k|$ of every

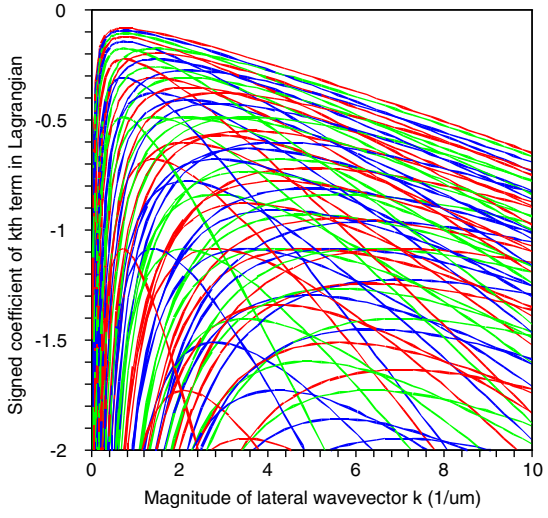

Fig. 2. The normalized coefficient of c_k^2 in the system Lagrangian as a function of k is negative for $\epsilon_r = 5.7$ and all integer combinations of κ and η from 1 to 10, in units of 1/μm, which suggests that the coefficient of c_k^2 is always negative. The energy of any mode with such a negative coefficient is highest when its amplitude c_k vanishes.

mode is as large as feasible and is determined by some constraint on the system. One such constraint is that the actual emitted current must equal the current supplied to the surface by the unperturbed uniform current at $z \ll 0$.

In order to investigate the relation between L_{tot} and electron emission, we introduce a two-parameter model of normal electron emission. A family of normal electron emission patterns that preserves average emission density can be represented along the x axis as a sum

$$j = \sigma\eta V_{\text{T}}\left(1 + 2\sum_{k_x=k_L}^{k_x=k_R}\cos(k_x x)\exp\left(-R^2k_x^2/2\right)\right)$$

over modes of wave number k_x where

$$k_L = 2\pi/L$$

$$k_R = 2\pi/R,$$

$R \leq L$, and $\sigma = qN_{\text{D}}^{+}\mu$ is the usual ohmic conductivity. Any such j is a 1-D array of emission sites with variable radius R, variable pitch L, and fixed average normal emission density $\langle j\rangle = \sigma E_{\text{in}} = \sigma\eta V_{\text{T}}$. This family includes periodic undulations that range from a simple sinusoid at $R = L$ to an array of delta functions for $R \ll L$, as Figs. 3 and 4 show.

The k^{th} coefficient j_k of normally emitted current can be related to the system coefficients c_k, by combining Eqs. (24) (25) (7), and (8) to obtain

$$j_k = c_k\sigma k\left(1 + \alpha\frac{k-\eta}{p_k-k} + \frac{\alpha\eta p_k}{\kappa^2}\frac{p_k-\eta}{p-k}\right)$$

and solving for c_k in terms of j_k. The resulting c_k can be substituted into Eq. (33) to obtain an expression for the total system energy as a function of the R and L of our model emission pattern for a given average emitted current. This

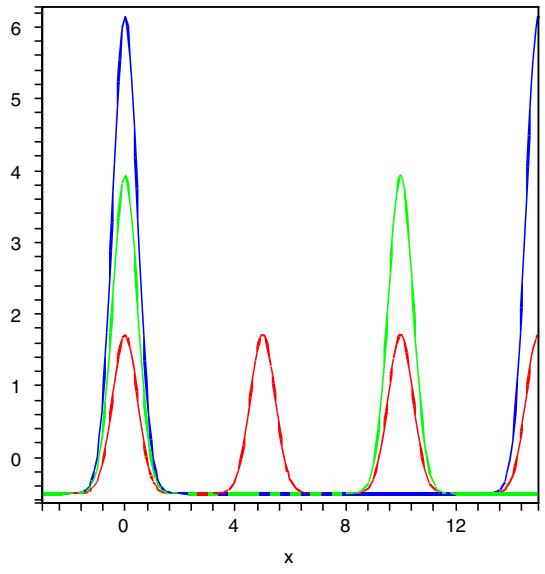

Fig. 3. Cross section of the Gaussian model of normally emitted current density for fixed $R = 2\mu$ and three different values of $L = 5$, 10, 15 in units of microns, shows how the model allows the density, i.e., pitch, of emission sites to be varied.

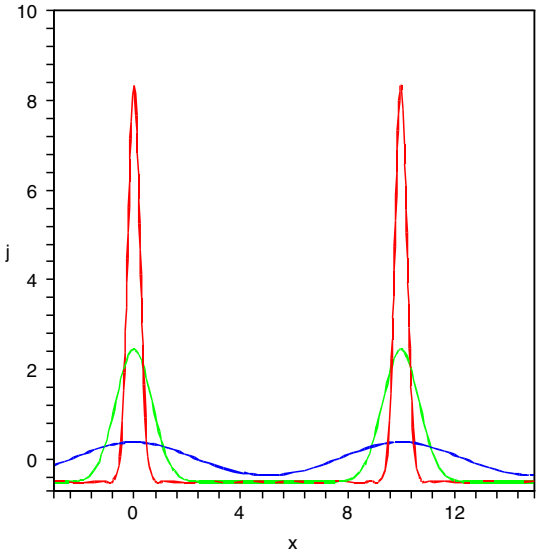

Fig. 4. A cross section of the Gaussian model of normally emitted current density for fixed $L = 10\mu$ and three different values of $R = 1$, 3, 10 in units of microns, shows how the model allows the radius of each emission site to be varied.

energy is a double sum over k_x and k_y, which we plot in Fig. 5. Numerical experiments such as shown in Fig. 5 suggest that the system energy corresponding to the trial emission pattern is minimized by large $L \to \infty$ and small $R \to 0$.

If the minimum system energy occurs for vanishing $R = 0$ and $L = \infty$, then the details of the model j are irrelevant, and we infer that the result is general.

Our model of the normal emission pattern can also be used to investigate the pattern of field enhancement corresponding to the emission pattern. For any finite R and L, the normal electric field can be obtained from the j_k since the first order electric potential just outside the interface for $y = 0$ is

$$\sum_{k_x} c_k\exp(-k_x z)\cos(k_x x)$$

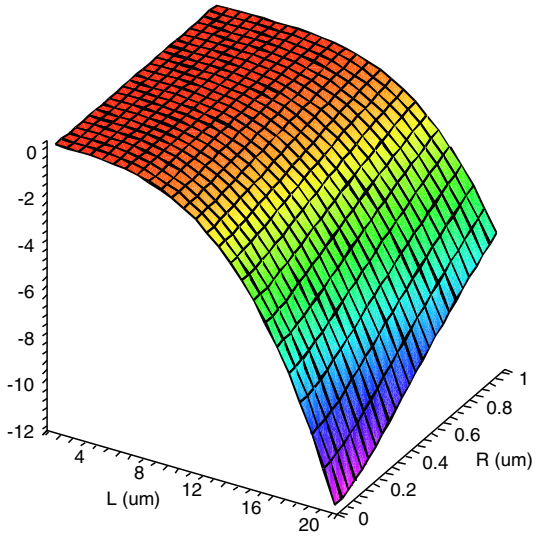

Fig. 5. Normalized L_{tot} as a function of R and L.

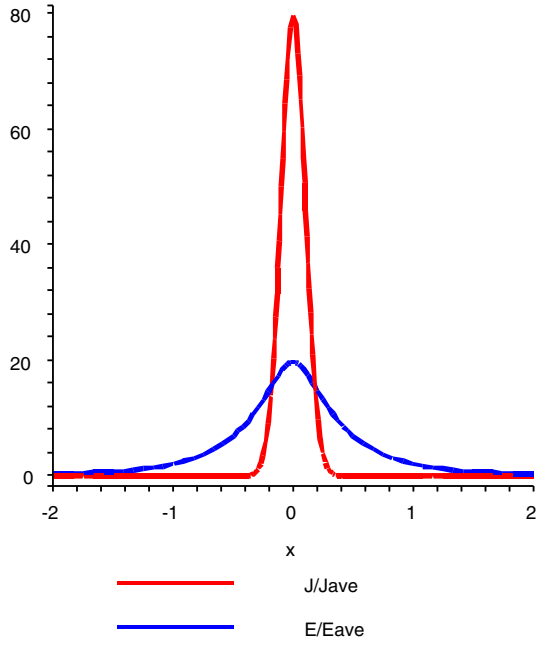

Fig. 6. Normally emitted current density and normal electric field along a cross section through the origin on the interface.

since the $k_y \neq 0$ components can be neglected on this cross section. The normal electric field

$$j = \sigma\eta V_T \left(1 + 2\sum_2 k\cos(kx)\exp\left(-R^2k^2/2\right)\frac{c_k}{j_k}\right)$$

is the z component of Eq. (7) evaluated at $z=0$. The first term $j_0=\sigma\eta V_T$ is the $k=0$ component of j and coincides with unperturbed normal electric field and the cross section of $j(x)/j_0$ of Fig. 6 shows that the electric field is enhanced at the emission site, but not as much as the emitted current.

Fig. 2 shows that the mode energies are least negative at a wavenumber of order κ, which suggests that the corresponding modes are most sensitive to forces neglected in this analysis. If such forces ever make the mode energies positive, this seems most likely to be observable at lateral wavenumbers near $k=\kappa$. Therefore it may be possible to experimentally find a minimum in intensity of the normal electron emission pattern at a lateral period of $2\pi/\kappa \approx 2$ μm.

6. Conclusion

Emission sites have zero radius in the proposed theory. Quantum effects would certainly impose a non-zero minimum, but our physical model also neglects nonlinearities, maximum electron wavenumber, emitter thickness, and surface irregularities. It is not known whether any of these effects restricts the minimum radius to be larger than the quantum limit. Experimentally, the emission site radius is too small to have been measured yet.

Experimentally, NEA is necessary but not sufficient for spot emission, which is always observed for nanocrystalline diamond but not for polycrystalline diamond at red heat. However both exhibit NEA in photoemission studies. In this report, we assume that the material itself is uniform. This assumption is more appropriate for nanocrystaline diamond, and the courser grain boundaries of polycrystalline diamond may obstruct the development of long-range order.

Acknowledgements

This research was supported in part by the ONR MURI on Thermionic Energy Conversion, directed by Dr. Mihal Gross.

References

[1] P.K. Baumann, R.J. Nemanich, Surf. Sci. 409 (1998) 320.
[2] A.T. Sowers, B.L. Ward, S.L. English, R.J. Nemanich, J. Appl. Phys. 86 (October 1 1999) 3973.
[3] F.A.M. Koch, J.M. Garguilo, R.J. Nemanich, S. Gupta, B.R. Weiner, G. Morrell, Diamond Related Mater. 12 (2003) 474.
[4] G.L. Bilbro, R.J. Nemanich, Appl. Phys. Lett. 76 (7) (February 2000) 891.
[5] S.M. Sze, Physics of Semiconducting Devices, 'End of Bibliographic Section, 1981.