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Modeling Electron Emission and Surface Effects from Diamond Cathodes

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We developed modeling capabilities, within the Vorpall particle-in-cell code, for three-dimensional (3D) simulations of surface effects and electron emission from semiconductor photocathodes. They include calculation of emission probabilities using general, piece-wise continuous, space-time dependent surface potentials, effective mass and band bending field effects. We applied these models, in combination with previously implemented capabilities for modeling charge generation and transport in diamond, to investigate the emission dependence on applied electric field in the range from approximately 2 MV/m to 17 MV/m along the [100] direction. The simulation results were compared to experimental data. For the considered parameter regime, conservation of transverse electron momentum (in the plane of the emission surface) allows direct emission from only two (parallel to [100]) of the six equivalent lowest conduction band valleys. When the electron affinity χ is the only parameter varied in the simulations, the value $\chi = 0.31$ eV leads to overall qualitative agreement with the probability of emission deduced from experiments. Including band bending in the simulations improves the agreement with the experimental data, particularly at low applied fields, but not significantly. Using surface potentials with different profiles further allows us to investigate the emission as a function of potential barrier height, width, and vacuum level position. However, adding surface patches with different levels of hydrogenation, modeled with position-dependent electron affinity, leads to the closest agreement with the experimental data.

I. INTRODUCTION

High-average current and high-brightness electron beams are needed in advance applications such as ultra-high power Free-Electron Lasers¹ (FELs), electron cooling of hadron accelerators², Energy-Recovery Linac (ERL) light sources³, and lasertron high-efficiency radio-frequency (RF) sources⁴. To address the high brightness requirements for these applications, a new design for a photoinjector with a diamond amplifier was proposed⁵ and is currently being investigated^{6–11}.

The technologically important material properties of diamond have been researched for emission^{12,13} and detector applications. Moreover, diamond is also considered for development of high-flux x-ray monitors in synchrotron beam lines^{14–17}.

The new photoinjector concept has important advantages⁵ (such as the ability to generate high-average current, high-brightness electron beams while providing a very long lifetime) compared to existing metallic and semiconductor photocathodes. The idea of its operation is to first generate a primary beam of electrons (accelerated to about 10 keV) using a conventional photocathode and inject them into diamond. The energetic primary electrons scatter inelastically in diamond, generating secondary electrons. These electrons, and their related holes, relax their energies initially by producing more electron-hole pairs. When the energy of these free charge carriers decreases to values close to the energy gap of diamond, further relaxation of their energy is dominated by scattering with phonons.

In applied electric field, the generated electrons and holes drift in opposite directions and are separated. The secondary electrons are transported towards a diamond surface with a negative electron affinity (NEA). Part of these electrons are then emitted into the accelerat-

ing cavity of an electron gun. The NEA is used to enhance the emission¹⁸ of electrons. Hydrogenation of diamond produces surfaces with NEA. Over two orders of magnitude charge amplification (number of generated secondary electrons emitted relative to the number of primary electrons used as input) could potentially be achieved⁶ using this approach with the design goal to emit ~ 1 nC electron bunches. Recently, O'Donnell *et al.*¹⁹ have also demonstrated electron yield enhancement factor of 200 from NEA lithium-covered diamond surfaces that are air-stable.

Investigation of the phenomena involved in using diamond for generation of amplified electron beams via simulations requires modeling of secondary electron generation, charge transport, and electron emission. Initially, we implemented^{20–22} unified modeling, within the Vorpall²³ computational framework, for the first two types of these processes. Our implementation of secondary electron generation is based on optical models^{24–29} and the charge transport on models for scattering of electrons and holes with phonons³⁰. These capabilities already allow us to investigate charge gain and collection efficiency related to specific experiments.

We have now implemented in Vorpall several models for simulation of electron emission from one 3D domain into another separated by a planar surface. The most general one is the model based on the transfer matrix (TM) method since it allows the calculation of emission probabilities for arbitrary, piece-wise continuous surface potentials. Moreover, it gives us the ability to directly include the effects of transverse momentum conservation and electron effective mass variation when calculating emission probabilities.

To support efficient use of the developed emission models, we have also implemented a general way to specify piece-wise continuous emission surface potentials in

Vorpall input files. The supported syntax allows users of the code to provide space-time varying potentials for the calculation of emission probabilities. This provides the functionality to investigate position-dependent emission behavior and non-uniform emission-surface properties. Time-dependent potentials can be used to study performance evolution of cathodes.

Similarly to the approach implemented to input a surface potential, we implemented the capability to provide a function for modeling the effect of band bending near semiconductor interfaces. The function for the band bending field is parsed and used to calculate the field that charge carriers interact with in the band bending region. We used the newly implemented modeling capabilities to design and run end-to-end simulations to compare with experimental data on emission. The results indicate what surface effects and potential parameters could lead to better agreement with the experiments.

The rest of the paper is organized as follows. First, in Section II, we describe the approach we have developed for end-to-end simulations of charge generation, transport, and emission from diamond. The new emission modeling capabilities are covered in detail. Then, in Section III, we discuss comparison of simulation results with data from experiments¹⁰ designed to deduce the probability of emission as a function of applied field. We provide a summary of the current work and some future directions we are considering in Section IV.

II. MODELING AND SIMULATIONS

In this section, we shortly cover the Vorpall computational framework and then describe the approach we have developed for end-to-end simulations of diamond-amplified electron sources. We discuss in detail the new emission models we implemented and used for the simulations described in the next section.

A. The Vorpall computational framework

The Vorpall²³ computational framework has an extended set of capabilities for simulating electro-magnetics with or without the inclusion of charged particles. Vorpall can currently be used to model the interaction of electromagnetic fields with conducting boundaries, charged particles (of both constant and variable weight), charged fluids, and systems consisting of dielectrics and vacuum regions. The Vorpall framework also has electro-static (ES) solvers that can be used in parallel simulations in combination with pushing particles. In addition, field ionization production of particles and Direct Simulation Monte Carlo treatment of neutral and charged fluids, i.e., self collisions for the particle representations. Vorpall was designed from the beginning for massively parallel runs.

Multiple electromagnetic (EM) algorithms are implemented in Vorpall. The code provides perfectly

matched layer (PML) absorbing³¹ and 2^{nd} order accurate conformal^{32,33} boundary conditions (BC). The PML BCs are effective to reduce numerical errors from reflected waves at boundaries. The conformal BCs can be used to accurately model complex EM structures^{32,33} and also do relativistic particle-in-cell for intense beams. Both, stair step and Dey-Mittra³² boundary algorithms are available. In most finite-difference codes, a curved surface is represented with stair-stepped boundaries, causing first-order errors in the calculation. Furthermore, Vorpall provides a stable finite-difference time-domain algorithm³⁴ for simulations of non-diagonal, anisotropic dielectrics.

The 3D ES particle-in-cell computational capabilities together with the ability to efficiently model domains with multiple dielectrics in parallel have been of particular importance to enable the diamond-amplifier simulations reported here. These algorithms are needed to move particles between scattering events, to specify and maintain fields as in the two types of experiments¹⁰ we simulated.

B. Three-step model for electron emission

The overall approach to model charge generation, transport, and emission that we have implemented corresponds to Spicer's 3-step^{35,36} emission model. A simplified diagram for this model, specialized for diamond, is shown in Fig. 1 together with a representation of the processes involved.

First, creation of (secondary) electrons in the conduction band and holes in the valence band is started by inelastic scattering with highly energetic primary electrons. Next, the free electrons and holes relax their energies via inelastic scattering (creating more electron-hole pairs and/or emission/absorption of phonons). Thus, the electrons drift towards the band bending region (BBR) that ends with a hydrogenated negative electron affinity surface. In the final step, the electrons are emitted or reflected when they attempt to cross the surface.

The surface potential barrier (e.g., the shape shown in Fig. 1) we have considered in the simulations has a similar type as the in the *ab initio* band structure calculations by Sque *et al.*³⁷. Their results for hydrogen-terminated diamond show large (effective) NEA relative to the conduction band minimum (CBM) in bulk^{36,38} and a positive electron affinity relative to the CBM at the surface.

For the results presented here, we used our implementation³⁹ of the Tanuma—Powell—Penn (TPP)²⁴ (see also²⁸ and the references therein) optical model for inelastic scattering leading to secondary electron generation (impact ionization) at 300 K. This corresponds to the first step and represents the first phase of the simulations.

For the low-energy inelastic scattering with phonons we implemented Monte Carlo algorithms based on the models given by Jacoboni and Reggiani³⁰. We have validated that the electron-phonon scattering implementa-

Figure 1. Schematic diagram of the three main processes that should be modeled: (1) generation of electrons in the conduction band, (2) charge transport, and (3) electron emission/reflection at the vacuum interface. One possible shape of the interface potential and a downward band bending region are indicated as well.

tion leads to electron drift velocities that are in agreement with band structure calculations and with experimental data⁴⁰. This low-energy (relative to the secondary electron generation in the first step) electron transport and the emission represent the second phase of the simulations. The particle and field data from the end of the first phase of the simulations represents the input state for the second phase.

C. Modeling electron emission

In Monte Carlo simulations of electron transport, when an electron in a photocathode material attempts to cross its emission surface to move into vacuum, a probability of emission is calculated using the surface potential at the location where the electron hits the surface. Once this probability is known, the electron is emitted or reflected back according to its value (the electron is emitted if the emission probability is higher than the value of a (pseudo) random number generated from a uniform distribution).

The calculation of the emission probability simplifies significantly if the potential is translationally invariant in the emission surface plane. For this case, the potential is a function only of the coordinate along an axis normal to the emission surface. In this study, we use the convention that the x axis is normal to the diamond emission surface. The translational invariance also requires that the transverse electron momentum (in the emission surface plane) is conserved in the emission process (see, e.g., R. L. Bell³⁸). This requirement significantly affects the emission of conduction band electrons from diamond.

We have implemented two different approaches to calculate electron emission probabilities in Vorpall. The first

approach was developed by K. Jensen^{41,42} while the second is based on transfer matrix calculations. In this Subsection, we describe how the probability of emission is calculated in both of these approaches as implemented in Vorpall.

The approach developed by K. Jensen^{41,42} approximates the emission process as an effectively a one-dimensional problem. The one-dimensional approximation works reasonably well for metals. It has been used for a long time⁴³. Furthermore, the electron effective mass is reduced to a scalar value. Neglecting the anisotropy in the effective mass tensor has important implications when modeling electron emission from diamond in 3D simulations.

We implemented code in Vorpall to calculate the emission probability using K. Jensen's approach⁴¹ for two surface potentials. The first is a triangular barrier, extending into vacuum ($x \geq 0$):

$$V(x) = \chi - Fx, \quad (1)$$

(and set to zero inside the emitting material), where χ is the true electron affinity (relative to the conduction band minimum at the surface) and F is the product of the applied field and the fundamental charge (similar to the notation used in K. Jensen⁴⁴). The representation in Eq. (1) is in terms of an electron potential energy. Electron emission using this potential was initially investigated by Fowler and Nordheim⁴⁵. The second potential includes the effect of the image charge:

$$V(x) = \chi - Fx - \frac{Q}{x}, \quad (2)$$

where

$$Q = Q_0 (K_s - 1) / (K_s + 1), \quad (3)$$

with K_s the static dielectric constant of the emitter ($K_s = 5.7$ for diamond), and $Q_0 = q^2 / (16\pi\epsilon_0)$ with q the fundamental charge and ϵ_0 the permittivity of vacuum.

The emission probability for the triangular potential, Eq. (1), in the approximation developed by K. Jensen^{41,42} is given by

$$T_{\Delta}(E_{\parallel}) = \frac{2f(E_{\parallel}, \chi)}{f(E_{\parallel}, \chi) + g(E_{\parallel}, \chi)h(E_{\parallel})}, \quad (4)$$

where $E_{\parallel}$ is the electron kinetic energy normal to the emission surface, $h(E_{\parallel}) = e^{\theta(E_{\parallel})} - (1 - e^{-\theta(E_{\parallel})})/4$, $\theta(E_{\parallel}) = 2\sqrt{2m}(\chi - E_{\parallel})^3$ for $E_{\parallel} < \chi$ (with m the scalar electron effective mass) and $\theta(E_{\parallel}) = 0$ for $E_{\parallel} > \chi$, $f(E_{\parallel}, \chi) = 2\sqrt{E_{\parallel}}|E_{\parallel} - \chi|_+$, $g(E_{\parallel}, \chi) = (E_{\parallel} + |E_{\parallel} - \chi|_+)$, $|E_{\parallel} - \chi|_+ = \sqrt{(E_{\parallel} - \chi)^2 + \gamma_F}$, $\gamma_F = (p_0^2 \hbar^2 F^2 / 2m)^{2/3}$, and $p_0 = 0.51697$. Note that the term transmission coefficient $T(E)$ is often used for

the probability of emission with E denoting the normal energy. Here, we use $T(x)$ and $P(x)$ interchangeably to denote the probability of emission and will use E for the total energy. Thus, we will explicitly indicate what argument x is used for the evaluation of $T(x)$.

The emission probability given by Eq. (4) can be used when the surface potential barrier has a shape close to the triangular one given by Eq. (1). However, since the triangular potential does not vary smoothly, the emission probability $T_{\Delta}(E_{\parallel})$ from Eq. (4) shows a similar behavior at the top of the potential barrier. Thus, $T_{\Delta}(E_{\parallel})$ is a good approximation to a triangular barrier, but is an increasingly poor approximation to $T(E_{\parallel})$ when the barrier top is rounded as for the image charge potential. These issues were addressed in the second method that considers the image charge potential (within the one-dimensional treatment of the emission problem) leading to the following expression for the emission probability^{41,42,44}

$$T_q(E_{\parallel}) = \frac{C(E_{\parallel})}{1 + \exp(2\theta(E_{\parallel}))}, \quad (5)$$

where

$$C(E_{\parallel}) \approx \frac{E_{\parallel}^3}{E_{\parallel}^3 + \frac{1}{2m} \left\{ \frac{\hbar F}{8} \left[\left(\frac{x_o}{x_-} \right)^2 - 1 \right] \right\}^2},$$

with $x_o = \sqrt{Q/F}$ and $x_-(E_{\parallel})$ is the smaller root of the equation $V(x) - E_{\parallel} = 0$, where $V(x)$ is the image charge potential, Eq. (2). Two cases are considered for the evaluation of the function $\theta(E_{\parallel})$ that enters in Eq. (5). For the case of electrons attempting emission with energy lower than the energy $E_o = \chi - 0.5\sqrt{FQ}$, smaller than the maximum of the surface potential, the function is given by:

$$\theta(E_{\parallel}) = \frac{2}{\hbar} \sqrt{2mFL^3G} \left(\frac{x_-(E_{\parallel})}{L} \right), \quad (6)$$

where

$$G(s) = \int_0^{\infty} \frac{\cos^2(\phi) \sin^2(\phi)}{\sqrt{s + \sin^2(\phi)}} d\phi, \quad (7)$$

and $L(E_{\parallel}) = x_+(E_{\parallel}) - x_-(E_{\parallel})$. For the other case of electrons attempting emission with $E_{\parallel} > E_o$, the $\theta(E_{\parallel})$ is expanded to a first order polynomial of $E_{\parallel} - E_o$ in the form

$$\theta(E_{\parallel}) = \theta_o + \left(\frac{\partial \theta}{\partial E_{\parallel}}(E_o) \right) (E_{\parallel} - E_o),$$

in order to have both $\theta(E_{\parallel})$ and $\partial\theta/\partial E_{\parallel}$ smooth for $E_{\parallel} > E_o$ (including the maximum of the potential barrier). Expressions for the calculation of θ_o and $\frac{\partial\theta}{\partial E_{\parallel}}(E_o)$ are given elsewhere⁴¹.

Figure 2. Emission probabilities for diamond parameters with electron affinity $\chi = 300$ meV calculated with the two reduced models (Eqs. (4) and (5)) demonstrate the strong dependence on the external field.

Results obtained by K. Jensen⁴¹ indicate that the model with the triangular potential works well for materials with static dielectric constants $K_s < 2$ while the probability of emission given by the second model with the image charge effect included in the potential provides superior performance when $K_s \gtrsim 2$.

Emission probabilities vs electron energy (the value of $K_s = 5.7$ for diamond was used) and for three different applied fields are shown in Fig. 2. In Fig. 2, the transmission probability $T_{\Delta}(E_{\parallel})$ obtained from Eq. (4), shows a kink when the energy is equal to the top of the potential barrier. This is due to a discontinuity in the first derivative of $T_{\Delta}(E_{\parallel})$ at the top of the barrier; $T_{\Delta}(E_{\parallel})$ is continuous there. The first derivative of $T_q(E_{\parallel})$ for the second model is continuous for all energies.

The reduced emission models considered so far are computationally efficient — once the initialization is done, the evaluation of the emission probabilities is fast. However, the calculation of the emission probability has to be generalized if the electron effective mass tensor is anisotropic, the change of the electron mass has to be taken into account, surface potentials with different shapes than the ones given by Eqs. (4) and (5) are to be investigated, and the transverse momentum during emission has to be explicitly conserved.

All of these effects are of importance for diamond. In particular, since these two emission models do not explicitly take into account the conservation of transverse momentum in the calculation of the emission probability, we introduced it in an ad hoc way in the first algorithm we implemented to simulate electron emission from diamond with them.

To understand why the conservation of transverse mo-

momentum in diamond is important when calculating emission probabilities, consider again the data from the two reduced models in Fig. 2. For the specific case of 10 MV/m external field, the calculated probabilities indicate that if an electron in diamond impacts the vacuum interface with an energy $E_{\parallel} \gtrsim 175$ meV, it will have a non-negligible probability to be emitted that quickly increases towards unity when increasing its energy (for the T_q model, the probability approaches unity for $E_{\parallel}$ close to 230 meV). A histogram of an electron energy distribution from simulations with external field of 10 MV/m indicates that there are a number of electrons with total energies higher than 175 meV and even 230 meV. If only the $T_q(E_{\parallel})$ probability is used to decide which electrons are to be emitted without separately checking if transverse momentum is conserved, all electrons with energies $E_{\parallel} > 230$ meV will be emitted. However, a large number of these electrons cannot be emitted since their transverse momentum cannot be conserved during the emission process.

For a specific case of this limitation, consider again emission of electrons from a (100) diamond surface. Conduction band electrons that are transported in bulk diamond are distributed among six equivalent energy valleys in reciprocal space (two valleys along each of the three coordinate axes in $\mathbf{k}$ space). For example, the energies of electrons in the two valleys along the [010] axis in $\mathbf{k}$ space are approximately given by

$$E_{(010)}(\mathbf{k}) = \frac{\hbar^2}{2m_T} (k_x^2 + k_z^2) + \frac{\hbar^2}{2m_L} (k_y - k_{y0})^2,$$

where m_L and m_T are the electron's longitudinal and transverse effective masses and k_{y0} is the position of the minimum of the energy valley along the [010] direction. For diamond, $|k_{\alpha 0}| \approx 0.73 \times (2\pi/a)$ where $a = 3.57$ Å is the lattice constant (α denotes any of the coordinate axes). For emission from a (100) surface, electrons in the four conduction band valleys along the y and z directions in $\mathbf{k}$ space will have a large transverse momentum that will have to be conserved during emission. Consider again an electron in one of the [010] valleys with a wave vector very close to the conduction band minimum. Its momentum is $\mathbf{p} = \hbar\mathbf{k} \approx \hbar(0, k_{y0}, 0)$. Since it is parallel to the emission surface, it must be conserved during the emission process. However, if we assume that this electron is emitted in vacuum with momentum $p_{vac} = \hbar k_{y0}$ only parallel to the emission surface and equal to the transverse momentum in diamond before emission (in order to satisfy conservation of transverse momentum), then the energy with which this electron must be emitted is

$$E_{vac} = \frac{(\hbar k_{y0})^2}{2m_e},$$

where m_e is now the electron mass in vacuum. For the given diamond parameters, this energy is at least ≈ 6.3 eV. However, the energy with which an electron reaches the emission surface is of the order of 0.1 eV (for external fields of interest not greater than around 30 MV/m

so the applied fields in diamond do not exceed 6 MV/m). For the maximum true NEA measured in experiments on emission from (100) surfaces, an emitted electron can gain an additional energy of 1.7 eV. Thus, for electrons in the four conduction band valleys along the y and z directions in $\mathbf{k}$ space, we cannot satisfy both conservation of energy and transverse momentum during emission. However, electrons in the two valleys along the x direction have a much smaller transverse momentum, since the wave vectors of their valley minima, $\mathbf{k}_0 = (\pm k_{x0}, 0, 0)$, have zero components in the transverse directions. This leads to non negligible probabilities of emission for electrons with energies of the order of 0.1 eV in one of these two valleys.

Figure 3. The surface potential is approximated as a stair-step discretized shape in the transfer matrix method for calculation of the transmission probability. The shown discretization consists of 40 intervals - more than an order of magnitude smaller number than used in the simulations.

In order to explicitly include the conservation of transverse momentum in the calculation of emission probabilities, we also implemented the transfer matrix method^{46–48}. We recently used the TM method in emission studies from GaAs⁴⁹. Moreover, this method allows us to use general, piece-wise continuous surface potentials and the change of the electron mass in the transition from diamond to vacuum. This is done by using a stair-step discretized representation of any surface potential and then solving Schrödinger's equation in each interval. For example, the stair-step discretized representation of the potential energy $V(x)$ across the interface given by Eq. (2) is shown in Fig. 3.

In the transfer matrix approach, the transmission probability is given by

$$T = \left(\frac{k_{tr,\parallel} m_{inc}}{k_{inc,\parallel} m_{tr}} \right) / |P_{11}|^2, \quad (8)$$

where $P = \prod_{i=0}^{n-1} p_i$ with $p_i(k_i, m_i, k_{i+1}, m_{i+1}, \Delta x)$ being 2×2 matrices calculated from the Schrödinger equation in each slice with length Δx , $k_{inc,\parallel}$ and $k_{tr,\parallel}$ are the initial and final electron wave vectors, respectively, along the emission surface normal; similarly m_{inc} and m_{tr} are the initial and final electron masses. We incorporate the effect of the electron mass change in the emission probability calculation using the approximation that the change happens when the emission surface is crossed. For the TM calculation, this leads to the initial k_0, m_0 set to the values in diamond with which an electron attempts to cross the emission surface located at x_0 . All subsequent k_i, m_i , for $i > 0$, are considered to be in vacuum. Thus, m_{inc} is the electron effective mass in diamond along the emission surface normal (the x axis for the case here). Depending on which one of the six equivalent conduction band valleys an electron is when it impacts the vacuum interface, m_{inc} will be equal to either m_L or m_T . For electrons on the [100] valleys in diamond, $m_{inc} = m_L$ and for the other four valleys $m_{inc} = m_T$. The TM approach from Eq. (8) has been applied to calculate transmission probabilities in semiconductor heterojunctions⁴⁷ in order to include the effect of changing the electron mass across subdomains with different effective masses.

Conservation of the electron's transverse crystal momentum and its total energy is explicitly accounted for in the TM method since the values of the (longitudinal) wave vector in each of the slices for $i > 0$ are calculated from

$$k_i = \frac{1}{\hbar} \sqrt{2m_i(E - V(x_i)) - (\hbar k_\perp)^2}, \quad (9)$$

where $E, k_\parallel$, and $k_\perp$ are the electron's total energy, longitudinal and transverse wave vector magnitudes, respectively, in diamond with which it attempts to cross the emission surface. The value of $k_\parallel$ is used to initialize k_0 . For $k_\perp^2 > 2m_i(E - V(x_i))/\hbar^2$ (when transverse momentum cannot be conserved) the wave vector k_i is purely imaginary leading to exponentially small values when calculating the transmission probability (similar to the case of tunneling). Note that the electron total energy is generally given by

$$E = \epsilon(k) + E_V,$$

where $\epsilon(k)$ is the electron energy relative to the bottom of the valley (at energy E_V) it is in. Since for diamond we consider only the lowest conduction band, we can set $E_V = 0$. However, when more conduction bands are considered (or different valleys, non symmetry related, from the same band as in GaAs⁴⁹), E_V can be set to zero only for the lowest conduction band valley.

Since the two reduced 1D models do not generally include conservation of transverse electron momentum, we can directly compare the emission probabilities from the TM method with them only for electrons in diamond on valleys along the [100] axis which is also the direction normal to the emission surface. In this case, the wave vectors

$\mathbf{k}_0 = (\pm k_{0x}, 0, 0)$ of the valley minima have zero transverse components. The electron transverse momentum on these valleys is determined only by their transverse momentum relative to the valley minima. We compare emission probabilities for electrons in [100] valleys calculated with the TM method and with the T_q model, from Eq. (5), in Fig. 4.

However, to better understand how the electron effective mass anisotropy and its change to the isotropic scalar mass in vacuum affect emission probabilities, we consider two cases (in both, the conduction electrons in the emitting material are modeled with a single parabolic band with a minimum at $E_V = 0$). The first case focuses only on the effect of changing the electron effective mass from its value in the emitting material to its different value in vacuum assuming that the emitting material has an isotropic effective mass. Note that an isotropic effective mass is one of the assumptions made in the T_q model, Eq. (5), while the change of the electron mass to its value in vacuum is not included. This leads to the probability of emission given by Eq. (5) to depend only on a single scalar effective mass and the electron normal energy $E_\parallel$, i.e. Eq. (5) has no dependence on the electron's transverse momentum. For the purpose of comparing the emission probabilities with the second case (when the electron effective mass anisotropy for diamond is included), we will assume that the isotropic effective mass in the first case is equal to m_L . Given these assumptions for this first case, we have $E = ((\hbar k_\parallel)^2 + (\hbar k_\perp)^2)/2m_L$, $E_\parallel = (\hbar k_\parallel)^2/2m_L$, $m_{vac} = m_e \neq m_L$, and the longitudinal wave vectors used in the TM method (for a given $k_\perp$) can be determined from the expression:

$$\hbar k_i = \sqrt{2m_i(E_{\parallel, \text{eff}} - V(x_i))}, \quad (10)$$

where

$$E_{\parallel, \text{eff}} \equiv \frac{(\hbar k_\parallel)^2}{2m_L} + \frac{(\hbar k_\perp)^2}{2m_*}, \quad (11)$$

with

$$\frac{1}{m_*} \equiv \frac{1}{m_L} - \frac{1}{m_i}, \quad (12)$$

$m_0 = m_L$, and $m_i = m_e$ for $i > 0$. Since we consider the potential in vacuum, $V(x > x_0)$, when calculating the emission probabilities in the TM method, we always use the initialization $k_0 = k_\parallel$ and $V(x_0) = 0$. Thus, for the isotropic effective mass, Eq. (10) holds even for $i = 0$. For the first case, the emission probabilities from the TM method and the T_q model of Eq. (5) are shown in Fig. 4 (a). Each of the four data sets corresponds to a given value of $k_\perp$ with the probabilities calculated over an interval of $E_\parallel = (\hbar k_\parallel)^2/2m_L$ values (as indicated on the x axis of the plot). Since, the T_q model does not take into account the change of the electron mass, it depends only on $E_\parallel$ and leads to a single data set shown

Figure 4. Comparison of electron emission probabilities from diamond calculated from Eq. (5) evaluated at $E_{\parallel, \text{eff}}(E_{\parallel}, k_{\perp})$ (dashed lines), and from the TM model (solid lines). Each data set shown is for a given value of $k_{\perp}$ and then the probabilities are evaluated for the same range of $E_{\parallel}$ values. The (a) plot is for a “diamond” modeled with an isotropic effective mass. The (b) plot is for the case with the anisotropy of the diamond effective mass included.

with the dashed line for $k_{\perp} = 0$ in Fig. 4 (a). It is in excellent agreement with the corresponding data from the TM calculation, as expected, since for $k_{\perp} = 0$ and an isotropic band, the emission probability calculations in the two models depend only on a scalar effective electron mass and $E_{\parallel}$.

Eq. (10), however, indicates that for a constant $k_{\perp}$, the k_i in the TM method depend on a single, effective, longitudinal energy $E_{\parallel, \text{eff}}$. Since we had an excellent agreement between the two models when $k_{\perp} = 0$, we could expect that if the same effective normal energy is used in the two models, the agreement between them should remain effectively the same. This is indeed the case as seen in Fig. 4 (a) if we use Eq. (5) to evaluate $T_q(E_{\parallel, \text{eff}})$ when

$k_{\perp} \neq 0$. This agreement indicates that we can extend the T_q model to include the change of the electron effective mass during emission (using the same approximation as in the TM method), provided we use Eq. (5) to calculate the emission probability with an argument given by $E_{\parallel, \text{eff}}$. Moreover, the extension preserves conservation of transverse momentum and total energy since these are built in the TM method and will carry over when using $E_{\parallel, \text{eff}}$. This will hold not only for the specific case we considered here when electrons are emitted from the [100] valleys of a “diamond” with an assumed isotropic effective mass but also in the more general case of electrons emitted from a material with cubic symmetry and a parabolic band with its minimum at the Γ point.

The representation given by Eqs. (10) and (11) allows us to better understand the behavior of the calculated emission probabilities shown in Fig. 4 (a) when $k_{\perp}$ increases. Fig. 4 (a) indicates that the onset of essentially non zero emission probabilities occurs at increasing values of $E_{\parallel}$ when $k_{\perp}$ increases. This is due to $m_* < 0$, given by Eq. (12) in the first case when $m_{i>0} = m_e < m_L$ and $E_{\parallel, \text{eff}} < E_{\parallel}$ for $k_{\perp} > 0$ and $i > 0$. This requires an increasingly larger value of the initial $E_{\parallel}$ to reach the threshold of essentially non zero emission probabilities when increasing $k_{\perp}$. This effect is present because we included the change of the electron mass in the calculation of the emission probability and the change is from a larger value in the emitting material to a smaller one in vacuum leading to $m_* < 0$.

For the second case, we include the effect of anisotropy in the electron effective mass in diamond. In the case of emission from [100] valleys again, we now have $E = (\hbar k_{\parallel})^2 / 2m_L + (\hbar k_{\perp})^2 / 2m_T$, $E_{\parallel} = (\hbar k_{\parallel})^2 / 2m_L$, $m_{\text{vac}} = m_e \neq m_L \neq m_T$. The longitudinal wave vectors used in the TM method (for a given $k_{\perp}$) can again be determined from Eq. (10) for $i > 0$. However, in this case the m_* in the effective longitudinal energy, Eq. (11), is given by

$$\frac{1}{m_*} \equiv \frac{1}{m_T} - \frac{1}{m_e}, \quad (13)$$

for all $i > 0$. We now have $m_* > 0$ since $m_T = 0.36m_e$. For $i = 0$, we again initialize $k_0 = k_{\parallel}$ and $m_0 = m_L$ with their values in diamond at the emission surface, $x = x_0$. Due to the anisotropy in the electron effective mass, Eq. (10) now holds only for the slices in vacuum ($i > 0$).

The emission probabilities from the T_q model and the TM approach (which now includes the electron mass anisotropy) are compared in Fig. 4 (b). The $T_q(x)$ model evaluated with $E_{\parallel}$ as its argument corresponds to the data set given for it with $k_{\perp} = 0$ (same as the corresponding data set in Fig. 4 (a)). The data from the TM calculation is also the same as in 4 (a) for $k_{\perp} = 0$ since the effective mass anisotropy is not present when the electron has zero transverse momentum. For $k_{\perp} > 0$ and due to the change of the electron mass effect included in the TM calculation, we use the insight from the first case and evaluate $T_q(E_{\parallel, \text{eff}})$ to compare to the TM results. The agreement between the two models is still very good

for $k_{\perp} = 0.1 \text{ \AA}^{-1}$ but starts to show deviations when increasing $k_{\perp}$ further. In this case, the differences between the two approaches to calculate emission probabilities is due to the presence of anisotropy in the electron effective mass. This effect is included in the TM calculation using the approach we described. However, this approach cannot be directly transferred to the T_q model even when we use $E_{\parallel, \text{eff}}$ for the normal energy in Eq. (5).

For the effective mass anisotropy in diamond, the data in Fig. 4 (b) indicates that the onset of essentially non zero emission probabilities starts at decreasing $E_{\parallel}$ when increasing $k_{\perp}$. This is the opposite behavior relative to the first case shown in Fig. 4 (a). It is readily understood following the same argument: for the specific mass anisotropy, we have $m_{*} > 0$ leading to an increase of the effective normal energy $E_{\parallel, \text{eff}}$ when increasing $k_{\perp}$ for a fixed $E_{\parallel}$. In the TM approach, crossing the diamond-vacuum interfaces leads to redistribution of the electron total energy with the electron effectively gaining normal energy when its transverse mass m_T transitions to the mass in vacuum m_e . A transmission probability that depends both on normal kinetic energy $E_{\parallel}$ and the transverse momentum, $T(E_{\parallel}, k_{\perp})$, has been investigated previously⁵⁰ in the context of Schottky barrier metal-semiconductor contacts.

Our ad hoc implementation of the T_q model in Vorpall does an explicit check to determine if the electron transverse momentum can be conserved during emission. If it can, it then uses the emission probability calculated from T_q to decide if the electron should be emitted or reflected. Otherwise, it directly reflects the electron. In this ad hoc treatment, electrons on non [100] valleys are directly reflected since they never have enough energy to conserve full crystalline momentum during emission. For the TM method, the emission probability is always calculated and used to decide if an electron is emitted or reflected. While all simulation result reported are done with the TM method, the ad hoc algorithm with the T_q probabilities appear to work well for diamond too. This is likely due to the energies with which electrons reach the emission surface (discussed later) that are around 100 meV and the small transverse momentum they have on the two [100] valleys. Under these conditions (approximately $k_{\perp} < 0.1 \text{ \AA}^{-1}$), the probabilities from the TM and the T_q calculations do not show significant differences.

The effective mass change represents a stronger effect on the probability of emission when the relative difference between the effective mass in the photocathode material and in vacuum increases. For example, emission of electrons from the Γ valley of GaAs includes change of the electron mass from $m_{\Gamma} = 0.067m_e$ to the m_e in vacuum⁴⁹.

Note that the TM method allows us to include a more smooth transition for the effective mass from the emitting material to vacuum over a more extended spatial region, similar to the gradual interface for the dielectric constant

Figure 5. The TM allowed us to readily explore a different surface potential (a) and how it affects the emission probabilities (b). The results are for the two limiting values of the external field we considered and for normal incidence.

considered by F. Stern⁵¹. We have considered only a single slice change in the effective mass here, however.

In addition to the surface potential given by Eq. (2), we also investigated electron emission when using another potential function

$$V(x) = V_0 - V_1 \theta(x - d) - Fx, \quad x > 0, \quad (14)$$

where $\theta(x)$ is the Heaviside step function, $V(x) = 0$ for $x \leq 0$ and the emission surface is at $x = 0$. This potential represents a stair-step barrier of height V_0 (relative to the conduction band minimum at the surface) and width d . In absence of applied field F , the vacuum level is at V_1 .

This potential, with no applied field, was proposed by Fisher *et al.*⁵² as an approximation of the surface potential for a GaAs cathode with a Cs-O activation layer. Recent simulations⁴⁹ have shown that using this stair-step potential leads to good agreement with some of the experimental data on electron emission from GaAs. Since the TM method allows us to use any piece-wise continuous function for the potential, we considered how the

emission is affected by the shape and parameters of the surface potential.

A representative stair-step potential is shown in Fig. 5 (a) and its related emission probabilities calculated with the TM method are shown in Fig. 5 (b) for the limiting values of applied fields simulated and normal incidence. The stair-step potential shown in Fig. 5 (a) has parameters $V_0 = 0.35$ eV, $V_1 = 0.18$ eV, and $d = 8$ Å. The emission probabilities calculated with this potential (Fig. 5 (b)) show an onset of emission at lower energies for higher applied field magnitude as expected. For electron energies $E \gtrsim 250$ meV, the emission probabilities at the two different field values are close indicating that the height and width of the stair step potential are the main parameters affecting their values and not the field. In comparison with the emission probabilities calculated with the potential from Eq. (2), the data set with $k_\perp = 0$ shown in Fig. 4, the rise is more gradual (unity is reached over a wider range of energies) while in Fig. 4, the emission probability rises over a narrower range in electron energies.

III. RESULTS

Here, we explain first the simulation set up to model the dependence of the electron emission probability on applied field measured in the experiments done by Wang *et al.*¹⁰. Then, we describe results from the simulations and compare them to the experimental data.

A. Emission probability deduced from experiments

Erdong Wang *et al.*¹⁰ reported an approach to obtain probability of emission vs applied field from experimental data. In the simulations, we varied the external field from 2.1 MV/m to 17.1 MV/m to approximately cover the same range as in the experiments. Each field value corresponds to a separate Vorpil simulation. In all of the results described here, we used the electrostatic (ES) modeling capabilities in Vorpil. In ES-mode simulations, one sets the potential difference across the overall diamond vacuum simulation domain. The values of the fields specified, thus, correspond to the fields established by the ES solver when the charge introduced in the simulations effectively does not lead to screening of the external field. In this case, the values for the field applied in diamond are the corresponding external field values divided by 5.7 (the dielectric constant of diamond). Moreover, the ES solver allows to maintain the potential difference across the simulation domain, similarly to the way the experiments¹⁰ were done.

In these experiments, a probability of emission is deduced from two different types of measurements. In the first type, a transmission-mode experiment, a diamond sample has metal contacts applied to two of its opposite sides and a voltage difference is applied to them. This ef-

fectively represents a capacitor with diamond being the medium between the capacitor plates. A beam of primary electrons with energies of the order of 1 keV are impinging on one of the diamond sides (moving through the metal contacts there), scatter inelastically creating secondary electrons and holes. Part of the generated electrons are transported to the anode on the opposite side of the diamond slab and collected there. This represents the total transmitted charge $Q_{tr}(F)$.

Electron emission is measured in the second type of experiments when the anode is placed in vacuum, in front of the diamond side where electrons are transported to. The cathode is still a metal contact applied at the opposite side of the diamond sample. In this, emission-mode experiment, not all electrons that are transported to the diamond emission surface have enough energy to be emitted. Thus, the total collected charge, Q_{em} , measured at the anode due to emitted electrons collected there is smaller than the total charge Q_{tr} collected in the transmission mode experiments. These two quantities measured in the two types of experiments are used to deduce a probability of emission at the given applied field F :

$$P_{exp}(F) = \frac{Q_{em}(F)}{Q_{tr}(F)}. \quad (15)$$

The total charge collected in the emission experiments is also over a short collection time so any charge accumulation at the emission surface due to reflected electrons does not significantly affect the field applied in diamond.

B. Simulations approach to model experimental data on emission probability

By analogy with the approach to deduce emission probability from the transmission and emission mode experiments, we define a probability of emission from simulations data using the ratio:

$$P_{sim}(F) = \frac{N_{em}(F)}{N_{tr}(F)}, \quad (16)$$

where $N_{em}(F)$ is the number of emitted electrons at the given external field magnitude F and $N_{tr}(F)$ is the number of electrons transported successfully to the emission surface. A typical simulation domain used had lengths of $8 \times 20 \times 20$ μm with $40 \times 30 \times 30$ cells along the x , y , and z axes, respectively. The diamond region had a length of 6.5 μm and the vacuum length was 1.5 μm (some of the simulations were with diamond length of 6.6 μm and vacuum of 1.4 μm).

Each simulation proceeds in two parts. The first part consists of secondary electron and hole generation due to inelastic scattering initiated by primary electrons that impact the diamond on the cathode metal-diamond contact side. In the simulations, we always used 10 primary electrons each with energy of 9 keV. This leads to approximately 6000 secondary electrons that are transported to

the emission surface. We have previously provided³⁹ extensive details of the secondary electron generation phase of the simulations and have also described in detail the charge transport models for diamond we have implemented in Vorpal. Note that not all electrons generated are transported to the emission side of diamond. Some of them are lost to the metal contact at the primary electron impact side due to diffusive expansion³⁹.

The secondary electron generation phase requires a small time step to resolve the inelastic scattering rate. We used $dt \approx 8.3 \times 10^{-17}$ s. However, it completes within several hundred femto seconds. We ran the first phase for 250 fs. The simulation data generated from this phase is used as input to the second, drift-diffusion, simulation phase in which a much larger time step is used. Visualization of the created electrons and holes at the end of the first phase is shown in Fig. 6 (a). Only part of the simulation domain in the transverse directions is shown to focus on the subregion that particles occupy at this stage of their evolution. Each primary electron produces a cascade of secondary electrons and holes. The primary electrons are in red (difficult to see since they are surrounded by the secondary electrons and holes they create via impact ionization), the secondary electrons in yellow, and the holes in blue. Under the applied electric field along the negative x axis, holes are moving to the left side of the simulation domain and collected there. This is the location of the metal contact at the diamond surface. It is at the side of the diamond sample where primary electrons impinge on.

The applied field leads to drift diffusion transport of the electrons towards the emission surface. A distribution at a given time for this state (before emission has started) is shown in Fig. 6 (b). The full size of the simulation domain is shown on all plots of Fig. 6 except in (a). The observer point of view in 6 (b) is similar to the one in the (a) plot and is chosen to clearly display the separation of the holes from the electrons that drift in opposite directions. The (b) plot is from the second stage of the simulations. This stage is dominated by elastic and low-energy (relative to the impact ionization stage) electron scattering processes³⁹ (different types of electron-phonon and charge impurity scattering).

Since the scattering rate of the drift-diffusion phase is several orders of magnitude smaller than in the first (secondary electron generation) phase, we have used a time step of the order of 10^{-15} s in the second phase of the simulations. The particle push algorithm allows for multiple scattering events in a time step. Scattering times are sampled from an exponential distribution. Charged carriers are pushed ballistically between scattering events.

Figure 6. Different phases of particle evolution confirm expected behavior (see text for further details).

We collected emitted electrons over a time interval of approximately 200 ps to obtain $N_{em}(F)$ from the simulations data. The number of transported electrons $N_{tr}(F)$ was estimated by counting the number of electrons in the simulations at a time close to but earlier than the time when emission starts. All of these electrons are transported to the emission surface. When electrons reach the emission surface, the ones with sufficiently high energy (and in the valleys along the [100] direction to allow conservation of transverse momentum) are emitted according to their emission probability.

Visualization of electron emission in the simulations is shown in Fig. 6 (c) with the observer placed in front of the emission surface (on the vacuum side) and looking towards it. The vacuum electrons are in green. This plot is from a simulation with surface-dependent electron affinity $\chi(x = Const, y, z)$, where the emission surface is at a given constant value of x . Note that the vacuum electrons appear in a relatively small stripe for $-y_0 \lesssim y \lesssim y_0$.

This is due to the different values of the electron affinity used in a central stripe region ($\chi = 0.17$ eV) compared to the rest of the emission surface ($\chi = 0.55$ eV). By varying the magnitude of y_0 , we can explore emission from surfaces with different electron affinity coverage, e.g. due to inhomogenous hydrogen coverage. When all the electrons have reached the emission surface and most of them with sufficiently high energy have been emitted, the remaining ones have accumulated at the emission surface as shown in Fig. 6 (d). The observer's point a view is again similar to the one in the (a) and (b) plots. In Fig. 6 (d), the electrons appear as a thin yellow strip perpendicular to the x axis approximately at the location of the emission surface. Due to accumulation of such electrons, the field in diamond will eventually be screened. Then, it will not be possible to transport more electrons to the emission surface unless a sufficient number of the electrons accumulated there are removed.

Over the 200 ps emission time interval simulated and for the surface potentials we have used, almost all of the electrons that have reached the emission surface with sufficiently high energy for emission have been emitted. The remaining electrons have low energies that lead to very small emission probabilities when they hit the emission surface. These electrons accumulate at the surface since the applied electric field pushes them towards the emission surface where they are reflected back most of the time.

C. Electron emission dependence on transverse momentum conservation

To better understand the effect of transverse momentum conservation on electron emission, we consider several dynamic properties of the electrons. Specifically, it is of interest to understand how the number of emitted electrons varies with time, the evolution of electron valley

populations and of the average electron energy.

Figure 7. Time evolution of the number of emitted electrons, valley populations, and the average electron energy for 10.43 MV/m external field confirms emission is from the valleys along the [100] direction only and when the electrons have sufficiently high energy.

Sample results on these quantities are shown in Fig. 7 with data from ES simulations with the TM emission model. The probability of emission was calculated using the surface potential with the image charge given by Eq. (2). Fig. 7 (a) indicates how the total number of emitted electrons increases over time. The fraction of electrons $n_{\parallel}$ on the two [100] valleys and the fraction $n_{\perp}$ of electrons on the four perpendicular valleys are shown in in Fig. 7 (b). Emission is effectively allowed for electrons on the [100] valleys since they have small transverse momentum.

These are the two valleys along the direction normal to the emission surface. Electrons on the perpendicular valleys have large transverse crystalline momentum and cannot be directly emitted given the range of energies with which they reach the emission surface.

The (a) and (b) plots of Fig. 7 confirm the expected behavior. They demonstrate that electrons reaching the emission surface on [100] valleys with sufficient energies are the ones that are emitted first.

This is indicated in Fig. 7 (a) by the fast rise of the number of emitted electrons when emission starts and in Fig. 7 (b) by the fast decrease of the fraction of electrons $n_{\parallel}$ on the two [100] valleys. Note also that Fig. 7 (b) shows the fraction of electrons $n_{\perp}$ on the four perpendicular valleys. This number is effectively unchanged during the time interval of the initial fast rise of the electron emission when the fraction of electrons $n_{\parallel}$ on the [100] valleys rapidly decreases. The electrons on the perpendicular valleys do not have enough energy to be emitted while also conserving their large transverse momentum (in the plane of the emission surface).

After the fast rise of the number of emitted electrons, emission still continues but at a lower rate. This is now due to energetic electrons from the four perpendicular valleys that first experience inter-valley electron-phonon scattering ending in one of the two [100] valleys. Once there, if they still have sufficiently high energies, they can be emitted. This causes the slow decrease of electrons on the four perpendicular valleys as seen in Fig. 7 (b). Finally, Fig. 7 (c) shows the evolution of the average energy of electrons in diamond. Initially, the average energy is around 100 meV. Once emission starts, the electrons with sufficiently high energy on the two [100] are emitted first leading to the fast decrease of the average energy of the remaining electrons in diamond. Then, in the regime of electrons transitioning from the perpendicular valleys to the [100] valleys due to electron-phonon scattering followed by emission, the average energy decreases but again at a lower rate.

Once the electrons remaining in diamond have lowered their average energy close to 40 meV, emission has effectively stopped.

D. Comparison to experimental data

In this subsection, we consider how results from simulations with different modeling approaches compare to ex-

perimental data on the dependence of the probability of emission on applied field. We run simulations with different surface potentials and parameters to understand how they affect the agreement with the experimental data. We also run simulations to investigate band bending and specific inhomogeneous surface effects on the emission probability.

1. Surface potential with the image charge

In the experiments done by Ergong *et al.*¹⁰, four single-crystal, high-purity chemical vapor-deposition diamond samples were prepared with the emission surface hydrogenated to lower the electron affinity. It is expected that the hydrogenation will give effective negative electron affinity. The dependence of the probability of emission on the applied field obtained from the experiments on the four diamond samples is shown in Fig. 8.

Figure 8. Simulation results with the TM emission model using the surface potential with the image charge and constant electron affinities are in qualitative agreement with experimental data from four diamond samples.

Only two of the four similarly prepared diamonds show emission probabilities vs applied field that are close. One of the other diamonds shows higher values while the last one gives lower emission probabilities for each of the applied field values, respectively. This behavior likely indicates that only two of the four diamonds had approximately the same hydrogen coverage while the other two were effectively prepared with different levels of hydrogenation. Furthermore, it is possible that the hydrogen coverage is not uniform across the emission surface - an effect we have started to explore with some of the simulations presented here as well.

However, we start with simulations assuming the diamond emission surface is uniformly hydrogenated (i.e. constant electron affinity for any point on the surface),

the surface potential is given by Eq. (2), and use the TM emission model since it explicitly takes into account conservation of transverse momentum when calculating the probability of emission.

We ran a set of simulations, with results from them also shown in Fig. 8, to determine the electron affinity χ that gives the closest agreement with the experimental data¹⁰. In the simulations, χ is only parameter that is varied. All other parameters are considered to be known.

The set of electron affinities used leads to probabilities of emission from the simulations that span the measured values. For $\chi = 0.35$ eV, all emission probabilities (except one) from the simulations are lower than the experimental data. For $\chi = 0.25$ eV and external field magnitude higher than 8 MV/m, the simulation probabilities exceed all observed ones.

While the simulation probabilities for $\chi \approx 0.3$ eV cover the range of values measured from the four diamonds, the agreement is qualitative. The slope of the probability of emission vs field in the simulations is different than in the experiments. For low field magnitudes, the emission probabilities from the simulations approach zero faster than in the experiments. For high applied fields, the simulations give probabilities that grow faster than in the experiments.

Even within this level of agreement, the electron affinity $\chi = 0.31$ eV from the simulations that leads to emission probabilities closest to the experimental data is in the range of previously deduced from other experiments^{53,54}.

Before proceeding to consider additional effects on emission, we note that the simulation results in Fig. 8 obtained with the TM model are approximately the same as results with electron emission probabilities calculated from K. Jensen's model given by Eq. (5) provided we add an ad-hoc designed algorithm in the code to conserve transverse momentum. This algorithm checks explicitly if transverse momentum can be conserved when an electron is selected for emission with probability calculated from Eq. (5). If its transverse momentum cannot be conserved, it is reflected even though the Monte Carlo approach in the code has used the emission probability value from Eq. (5) to indicate that it should be emitted. For the energies in the simulations, this ad-hoc algorithm effectively sets to zero the emission probabilities of electrons on perpendicular valleys (while in the TM model these electrons have exponentially small probabilities of emission and in practice none of them are emitted). This indicates that the ad-hoc algorithm can be used when electron band valley anisotropy is of importance (as in the case of diamond) together with the reduced model leading to Eq. (5). This is particularly valuable when fast execution is required, e.g. for sufficiently large scale simulations in 3D. For the simulation sizes described here, using the TM model to calculate emission probabilities and running in parallel on 8 or 16 processor Linux cluster (8/16 GB of memory) was sufficient (even when the surface potential had to be recalculated for each electron

emission attempted).

2. Band bending effects

The results presented in the previous subsection did not include energy band bending that develops in semiconductor interface regions. These results give us basis for comparison with simulations that include band bending effects. Moreover, the diamond samples measured in the experiments¹⁰ were high-purity synthetic CVD diamonds produced by Element Six that typically have less than one carbon atom in 200 million replaced by an impurity atom. Thus, at impurity density of the order of 10^{15} cm⁻³ or less and with different hydrogenation levels applied to diamond emission surfaces, the band bending region that develops is still to be determined accurately.

Next, we briefly examine the origin for the development of surface band bending and then consider simulations to explore how given band bending parameters affect electron emission. In these simulations, we treat the band bending region within specific approximations.

In the absence of current flow, band bending near a diamond-vacuum interface in thermal equilibrium develops due to charging of surface states leading to formation of a space-charge layer⁵⁵ beneath the diamond surface. The band bending potential ϕ_S at the diamond-vacuum interface can then be determined from the charge neutrality of the diamond surface solved as an electrostatic problem. The value ϕ_S of the band potential at the surface is needed since it represents one of the two required boundary conditions to solve for the band bending potential ϕ in the BBR. This potential is determined from solving a non-linear Poisson's equation generally given by

$$\nabla \cdot (\epsilon \nabla \phi) = q (n[\phi] - p[\phi] + N_A^-[\phi] - N_D^+[\phi]), \quad (17)$$

where $\epsilon(\mathbf{r})$ is the dielectric constant, n and p are the electron and hole densities in the conduction and valence band, respectively, N_A^- and N_D^+ are the densities of ionized acceptor and donor impurities when present. When periodicity is preserved in the emission surface, the resulting non-linear Poisson equation is effectively one-dimensional. It is then solved with a Neumann boundary condition (bc) in bulk diamond, $\phi'(x \rightarrow \infty) = 0$, and a Dirichlet bc at the diamond surface $\phi(x=0) = \phi_S$. Once $\phi(x)$ is determined, then the effect of band bending on electrons in the conduction band approaching the emission surface can be approximated by applying the additional field $F_{bb}(x) = -\nabla \phi(x)$ when their longitudinal position x is in the BBR.

Emission of electrons in diamond will be enhanced if we could achieve downward band bending as shown on the diagram in Fig. 1. Downward band bending will increase the number of emitted electrons due to two effects. First, it will lower the surface potential barrier relative to the conduction band minimum in bulk diamond and, second, electrons in the BBR will be accelerated towards the emission surface when interacting with the F_{bb} field.

The non-linear Poisson Eq. (17) simplifies when there is only one type of fully ionized impurities, e.g. acceptors, and for a periodic surface the corresponding 1D version becomes:

$$\frac{d^2 U(x)}{dx^2} = \frac{q^2}{\varepsilon k_B T} \left(N_A - \frac{2N_V}{\sqrt{\pi}} F_{1/2}(\eta_V - U(x)) \right), \quad (18)$$

where $\eta_V = (E_V - E_F)/k_B T$ (with E_V the valence band maximum in bulk and E_F the Fermi level, k_B the Boltzmann constant and T the lattice temperature), $U(x) = q\phi(x)/k_B T$, $N_V = 2 \left(\frac{m_{dh} k_B T}{2\pi\hbar^2} \right)^{3/2}$ with m_{dh} a hole-related effective mass, and $F_{1/2}(x) = \int_0^\infty \frac{\sqrt{u}}{1+e^{u-x}} du$.

If the semiconductor is non-degenerate $E_V + 3k_B T \leq E_F \leq E_C - 3k_B T$ (as the high purity CVD diamonds used in the emission experiments), where E_C is the minimum of the conduction band in bulk, the solution of the 1D non-linear Poisson Eq. (18) can be represented in analytic form

$$\text{sgn}(U_S) \int_{U(x)}^{U_S} \frac{du}{F(u, U_F)} = \frac{x}{L_D}, \quad (19)$$

where

$$F(x, y) = \sqrt{e^y (e^{-x} + x - 1) + e^{-y} (e^x - x - 1)},$$

$U_F = (E_i - E_F)/k_B T$ with E_i the Fermi level for the intrinsic semiconductor, $U_S \equiv U(x=0) = q\phi_S/k_B T$, and $L_D = \sqrt{\frac{\varepsilon k_B T}{2q^2 n_i}}$ with n_i the conduction band electron density in the intrinsic case.

Since U_F is calculated from bulk properties as a function of temperature and bulk doping density, we can determine the band bending potential $\phi(x)$ by numerically solving Eq. (19), e.g. by using a bisection algorithm, provided ϕ_S is known.

If the semiconductor is degenerate, as in highly doped GaAs photocathodes, one has to directly solve the 1D non-linear Poisson Eq. (18). It can be solved numerically by a finite difference discretization and then using a Newton-Raphson algorithm to find the roots of the resulting matrix equation.

The value of ϕ_S is determined from the surface charge neutrality condition

$$Q_{ss}(\phi_S) + Q_{sc}(\phi_S) = 0, \quad (20)$$

where $Q_{ss}(\phi_S)$ is the total charge density on surface states and $Q_{sc}(\phi_S)$ is the space-charge density with magnitude determined from $|Q_{sc}(\phi_S)| = |\varepsilon (d\phi/dx)(x=0)|$ where $\phi(x)$ is the solution of the 1D non-linear Poisson equation. In the simplest case of only one type of surface states, e.g. donors with density N_{sd} and energy E_{sd} , the total charge density on surface states is given by $Q_{ss}(\phi_S) = qN_{sd} (1 - 1/(\exp(\beta(E_{sd} - E_F)) + 1))$. Note that for a p -doped semiconductor and downward band bending $\phi_S > 0$ at the surface, with $\phi(x \rightarrow \infty) \rightarrow +0$ in bulk, the space-charge region is negatively charged since

near the surface: $p(x) - N_A = p(x) - p_{bulk} < 0$. For this case, charge neutrality at the surface can be satisfied if there are surface donor states that are positively charged.

The energy of electrons on surface states relative to the valence (or conduction) band at the surface $E_V(x=0)$ is determined from atomic properties and remains fixed⁵⁵. For the case of donor surface states and provided $E_{sd} - E_V(x=0)$ is known from atomic properties, then $E_{sd} - E_F = E_{sd} - E_V(x=0) - q\phi_S + E_V - E_F$ (with $E_V - E_F$ determined from bulk parameters) which allows us to evaluate $Q_{ss}(\phi_S)$ for any given value of ϕ_S and density of surface donors N_{sd} . Then, the band bending potential ϕ_S at the surface can be determined self-consistently by numerically solving for the root of Eq. (20).

We have prototyped code to carry out this approach by numerically solving Eq. (18) for $\phi(x)$ and Eq. (20) for ϕ_S . Results from this code⁵⁶ recover previous calculations⁵⁵ for $\phi(x)$ and the Fermi pinning regime when increasing N_{sd} for the case of GaAs. We are currently considering to add this capability into Vorpall. However, for high purity diamonds, we can further approximate the band bending potential with the quadratic form

$$\phi(x) = \phi_S \left(\frac{x}{d} + 1 \right)^2, \quad (21)$$

where the BBR is defined for the interval $-d < x \leq 0$ with length d , the emission surface at $x=0$, and the vacuum region for $x > 0$. The approximation for the BBR potential from Eq. (21) is straightforward to use in Vorpall since the electric field due to it is expressible as a linear function in a given spatial region. This field can be introduced in the simulations using Vorpall's multi-field functionality. Vorpall allows simulations with multiple fields specified by space-time expressions that could consist of elementary and special functions. These expressions are provided in a Vorpall input file. Vorpall's parser builds abstract syntax trees for all such expressions that can then be evaluated efficiently at each time step and added to requested fields within a given space-time domain.

For the simulations we did with band bending, we specifically considered how the magnitude of the band bending potential energy $W = q\phi_S$ affects the probability of emission. A large range (over a few eV) of values for W have been reported from experiments^{53,54} possibly indicating that W strongly depends on surface coverage preparation. We ran simulations with several values of W and kept $d = 0.1 \mu\text{m}$ constant (such a value for the BBR length was also reported previously from experiments^{53,54}). Generally, d changes when changing ϕ_S as the solution of Eq. (19) for non-degenerate semiconductors indicates. However, we wanted to isolate the effect of W on emission. Moreover, for quadratic band bending, Eq. (21), $d \propto \sqrt{|\phi_S|}$, as discussed by Sze and Ng⁵⁷, leading to relatively small variation of d over the range of W simulated, particularly near the emission surface where the electric field due to the band bending po-

Figure 9. Increasing the band bending magnitude W , while keeping the band bending region length constant at $d = 0.1 \mu\text{m}$, increases the probability of emission (as expected) across the range of external fields. The experimental data and the simulation result without band bending are shown for comparison.

tential is the strongest.

In Fig. 9, we compare results on the probability of emission with different values of the band bending potential magnitude W with a simulation result without band bending and with the experimental data¹⁰ from the four diamond samples.

The simulation without band bending indicate emission probabilities below the measured values (except at the highest applied field); this is the same data set as previously shown in Fig. 8 for $\chi = 0.35 \text{ eV}$. Increasing W leads to increase in the emission probability. This is expected since electrons are accelerated in the BBR and reach the emission surface with higher energies (compared to the no BBR case). In this case, more electrons have sufficiently high energies for emission. The data in Fig. 9 shows that when increasing W from 0.32 eV to 0.96 eV (these are values in the range reported from experimental measurements^{53,54}), the probability of emission moves from below the experimental data to approximately above it. For $W = 0.5 \text{ eV}$, the simulations are within the range of values from the four separate diamond samples measured. Thus, adding band bending in the simulations improves the agreement with experiments. However, the slope of the simulation values still differs from the slope of any of the separate diamond samples. These results indicate that the band bending region effect is important to include in the simulations but other effects are to be considered in the modeling as well before quantitative agreement with the experimental data is achieved.

3. Stair step surface barrier

The simulation results discussed so far in this section used the surface potential with the image charge term given by Eq. (2). The electron affinity is the only parameter of the potential that is varied in the simulations. Values for it can be selected leading to results in the same range as in the experiments. Including downward band bending in the modeling, increases the probability of emission but the agreement with the experimental data remains qualitative.

In Section II, we discussed that a stair step potential was also proposed⁵² and used to study emission from semiconductor photocathodes (GaAs) leading to results in agreement with some of the observed experimental data⁴⁹. Moreover, the TM approach readily allows us to calculate the probability of emission for any piece-wise continuous potential.

Emission probabilities calculated with specific parameters of the stair step potential given by Eq. (14) and two applied fields in the range we study here are shown in Fig. 5. As discussed in Section II, in comparison with the emission probabilities calculated with the image charge potential shown in Fig. 4, the stair step potential leads to probabilities that rise more gradually (unity is reached over a wider range of energies) while in Fig. 2, the emission probability rises from approximately zero to unity over a narrow range in electron energies.

In order to explore how differences in the surface potential affect the comparison with the experimental data, we also run simulations with the stair step potential given by Eq. (14) and parameters in the range considered in Section II. While for the surface barrier with image charge the electron affinity is the only parameter we vary in the simulations, there are three parameters that can be changed when using the stair step potential: the height V_0 of the step relative to the conduction band minimum at the diamond surface, the width of the step, and the position V_1 of the vacuum level. We ran simulations varying all three of these parameters to again consider how the results compare with the experimental data on the probability of emission vs applied field.

A typical set of results from the simulations with the stair step potential is shown in Fig. 10. For comparison, we have also plotted the experimental data from the four diamond samples and one of the simulations with the image charge potential with $\chi = 0.31 \text{ eV}$ (that was shown previously in Fig. 8). To focus only on how the surface barrier type affects emission, all simulation results in Fig. 10 are done without band bending.

We kept the height $V_0 = 0.35 \text{ eV}$ and the width of the potential step at $8 \text{ \AA}$ for the simulation results shown in Fig. 10. We varied only the position of the vacuum level V_1 . Note that V_0 is similar to the electron affinity parameter in the image charge potential.

The results in Fig. 10 indicate that we can again bracket the experimental data when using the stair step barrier and changing only the vacuum level V_1 in the in-

Figure 10. A stair step surface potential with specific parameters could also be used in the simulations to obtain probabilities of emission in the range of observed experimental data.

interval from 0.08 eV to 0.18 eV. The slope of the emission probability vs applied field dependence has changed in comparison with the image charge potential simulations (results for $\chi = 0.31$ eV shown in Fig. 10 to compare with the stair step potential results). However, the level of agreement with the experiments is again qualitative. Simulations with the stair step barrier when varying V_0 and the width of the step do not lead to quantitative agreement with the data from the four diamonds.

4. Effects of electron affinity variation across the emission surface

Given the current level of agreement with the experimental data, it is of interest to understand what other effects could further improve it. The four diamond samples measured also show variation in the probability of emission vs applied field. This variation is likely due to inhomogeneous hydrogen coverage during the emission surface preparation and to surface roughness. Previously, Cui *et al.*¹⁸ considered electron emission from diamond with surfaces with different level of hydrogenation. They interpreted their emission data using graphitic patches that cover a small fraction of the surface. To explore the effect of inhomogeneous surface hydrogenation, we recently prototyped an implementation to model electron emission with surface varying potentials. The initial set of simulation results with this new modeling capability is shown in Fig. 11.

The potential with the image charge given by Eq. (2) is defined to vary across the emission surface through its electron affinity term $\chi(x = \text{Const}, y, z)$ using the form discussed in relation to the simulation visualization shown in Fig. 6. The parameter y_0 was varied in the

Figure 11. Simulation results with surface-dependent electron affinity with the potential from Eq. (2) show the closest agreement with experimental data. The results are from runs with surface patches with different area coverage (apart from the simulation result with constant electron affinity, blue triangles, shown for comparison). The patches are with electron affinities of 0.17 eV (central stripe with given area) and the rest of the emission surface with 0.55 eV.

simulations to select the surface area fraction with the smaller electron affinity of 0.17 eV in the region $-y_0 < y < y_0$ while the rest of the emission surface had a higher electron affinity of 0.55 eV.

Including patches with different electron affinities in the simulations gives the best agreement with the experimental data over the whole range of applied fields so far as the data in Fig. 11 indicate. Area fraction of 0.1 with the lower electron affinity shows results closest to the data from two of the diamond samples measured while the data with area fraction of 0.05 is close to the values from the diamond sample giving the lowest observed emission probabilities.

The results shown in Fig. 11 are representative for the level of agreement with the experimental data that can be reached when using the two electron affinity patch model in the simulations. We are still to perform a systematic study to optimize the parameters of the patch model that lead to the best agreement with the experiments.

Note that the results with the non uniform surface potential described in this subsection are based on the approximation that emission with conservation of transverse momentum is the most dominant process and holds at least locally (the probability of emission is calculated with the potential evaluated at the location on the surface where an electron impacts it). Generally, once the surface potential is not translationally invariant in the emission plane, electrons have non zero probability of emission with a change in their transverse momentum. Quantum mechanical approaches have been developed⁵⁸⁻⁶¹ to study these effects and to model transmission probabil-

ities in the presence of rough surfaces. Periodic variation of the surface potential in the emission plane do indicate⁵⁸ that the dominant emission process (the one with the highest probability) is with conservation of transverse momentum. We are currently investigating these approaches.

We expect that including band bending and surface roughness in the modeling will further improve the agreement with the experimental data although this will increase the parameter space to be explored in the simulations.

IV. SUMMARY

We applied recently implemented electron emission and band bending models, in combination with previously developed capabilities to model secondary electron generation and charge transport in diamond, to perform end-to-end simulations of two types of experiments, transmission and emission, on the diamond-amplifier cathode concept¹⁰. We compared the probability of emission vs applied field from the simulations with the corresponding data from these experiments for electric fields in vacuum in the range from 2.1 MV/m to 17.1 MV/m.

The simulation results indicate a strong dependence of the probability of emission on conservation of transverse momentum. In both, simulations and experiments, the field was applied along the [100] axis. In this setup, electrons have energies that allow emission only from the two lowest conduction energy band valleys parallel to the [100] axis. Electrons on the four perpendicular valleys cannot be emitted directly since they do not have high-enough energies to conserve transverse momentum during emission. However, electrons on perpendicular valleys can transition to parallel valleys due to inelastic electron-phonon inter-valley scattering. Once on parallel valleys, they could be emitted provided they still have sufficiently high energy left. Thus, the emission of electrons that reach the emission surface on perpendicular valleys is delayed relative to the emission of electrons reaching the surface on parallel valleys. The latter could also be emitted with higher energies since they do not lose energy to emit phonons in electron-phonon inter valley scattering transitions. The resulting longer temporal width and larger energy spread of emitted electrons can be reduced either by appropriately tailoring the emission surface or by filtering them where application necessitates.

We used the implemented models to run simulations to compare with results on the probability of emission vs applied field derived from transmission and emission-mode experiments¹⁰. We designed the simulations to explore how two different types of surface potentials (previously considered to model electron emission) affect the comparison with the measured data.

In simulations with the image charge potential, the electron affinity χ is the only free parameter that was varied. Comparison with the experimental data indicates

that $\chi = 0.31$ eV leads to simulation results in the same range. However, the agreement is qualitative. The dependence of the probability of emission on applied field has a different slope in the simulations compared to the experiments.

Using a stair step potential that had three different parameters that can be varied changes the slope of this dependence but the agreement with the experimental data remains qualitative. We can again find parameters for the stair step potential that give results in the same range as in the experiments.

The addition of downward band bending in the modeling using a quadratic approximation increases the probabilities of emission, as expected, but showed small changes in the slope of the probability curves.

The closest agreement with the experimental data was reached when using emission surfaces with a non-uniform surface potential: part of the emission surface had one electron affinity value while the rest was given a different one. We used this as an approach to model non-uniform hydrogen surface coverage since the four diamonds measured showed variation in the probability of emission and their level of hydrogenation is not well understood.

The implemented models already allow us to simulate specific experiments and determine surface properties of interest (e.g. the electron affinity) that lead to agreement (currently qualitative) with the measured data. There are several approaches that we are considering for future development in order to improve the currently implemented modeling capabilities.

The approach we implemented to include the electron mass change when calculating emission probabilities in the TM method can be modified to allow the mass to change over a more extended region rather than the sharp change when the electrons cross the diamond-vacuum interface. This can be done by introducing a smoothly varying function for the electron mass across the interface similar to the approach previously investigated by F. Stern⁵¹ in the context of a gradual dielectric constant change. This approach is more complex to implement since we have to also include the effects of a changing mass (and dielectric constant) in the ES algorithms for pushing electrons and updating the electric field across the extended domain where the mass and the dielectric constant vary.

The band bending potential in thermal equilibrium should be calculated directly by solving the non-linear Poisson equation with the magnitude determined from the charge neutrality of the surface space-charge region as discussed in subsection III D 2. This will allow more accurate treatment of the band bending for degenerate semiconductor photocathodes (e.g., for highly doped GaAs photocathodes) compared to the currently implemented quadratic approximation. Furthermore, it is of interest to include modeling of surface space-charge regions in non-equilibrium⁵⁵ since flow of electrons into the surface layer alters the charge distribution and potential there. It is of importance to add modeling of surface roughness and a

general approach for calculation of emission probabilities with non-uniform surface potentials (including emission with non-conservation of transverse momentum) due to different types of surface coverage¹⁹. Finally, we considered here only direct emission from lowest conduction band valleys. There are other emission processes, such as phonon⁶² and exciton⁶³ assisted ones and emission from localized states^{64,65} that have been used to interpret experimental data. It is of interest to add modeling of these processes as well.

We expect that simulation results with these additional models will allow us to further improve our understanding of the experimental data.

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