Two-step electron tunneling from confined electronic states in a nanoparticle

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Sequential two-step electron tunneling from nanoparticles has been studied from a transport point of view. A steady-state balance equation for the partial electron currents is derived and solved to obtain the stationary level occupancy, which leads to the overall tunneling current as a function of the applied field. Our model explains the steplike features observed in high field tunneling experiments involving composite cathodes that incorporate electronic quantum-confinement regions. In order to assess the validity of our model and to show the apparition of the steplike features in field-emission experiments, we have used the usual diode configuration to obtain current-voltage characteristics from a composite cathode. The theoretical model presented in this paper shows qualitative agreement with the experimental data.

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I. INTRODUCTION

Recent studies of advanced materials have succeeded in obtaining a whole new class of composites such as nanometer-sized particles¹ and nanotubes² with significant potential for electron field-emission (FE) applications. Such materials have generated a great deal of interest due to their unique behavior in FE regimes. While normal emissive materials, such as metals and in most cases semiconductors, exhibit monotonically increasing current-voltage (I - V) characteristics, FE from nanostructured materials often produces results that can be attributed to the underlying quantum confinement of the electrons residing in these cathodes. There are two basic types of FE peculiarities reported thus far from these structures: first, resonant tunneling, where electrons with some resonant values of the energy travel ballistically through nanostructures, and second, the sequential or two-step tunneling, where electrons are first supplied in regions of lower potential energies (energy wells) of the nanostructures before tunneling toward the anode. Inelastic processes are usually involved in the two-step tunneling that lead to quasiequilibrium distributions of electron populations in the potential wells below the emitting surface. Both emission mechanisms can appear in real experiments. Resonant tunneling in FE has been thoroughly investigated both from the theoretical³⁻⁵ and experimental^{6,7} points of view. However, while the existing theoretical models account for the pronounced peaks in the I - V characteristics followed by regions of negative differential resistance (NDR), experimental evidence is scarce due to the special conditions required for the occurrence of resonant tunneling during FE. A more common observation in FE experiments is the steplike I - V characteristic, which can be associated with a two-step tunneling phenomenon. A multitude of examples can be found in the literature where steplike I - V 's appear.^{1,6,8} The explanation behind the peculiar behavior of the I - V characteristics resides in the existence of nanometer-sized particles (or layers) on the sample that produces corresponding nonmonotonic spatial variations in the potential energy. In order to gain a deeper understanding of the quantum-confinement implications in the FE process from nanoparticles, a one-dimensional (1D) two-step FE model is examined in this

study. Field emission measurements were also performed on Au nanoparticles placed on a thin dielectric polymer layer deposited onto an Au substrate. The experimental setup was chosen so that the theoretical assumptions are closely followed and qualitative agreement with the model has been obtained.

II. THEORETICAL MODEL

Many FE experiments and applications involve complex architectures in the form of various conductive or dielectric materials deposited one on top of another. From the point of view of field-emission applications, the governing process is the tunneling of electrons through potential-energy barriers usually created by dielectric layers and by the vacuum interface. Another possible complex cathode configuration is one which contains discrete nanoparticles in its structure. Due to their size, quantization of the electron energy takes place, which we show has important effects on the field-emission characteristics.

The structure examined in our study is simplified to a metallic substrate, which acts as the cathode, on top of which a wide band-gap (WBG) material is deposited. One quantum confining structure (QCS) (e.g., metallic nanoparticle) is placed on top of the dielectric material [see Fig. 1(a)]. The potential energy within the QCS is assumed to be lower than its level in the cathode, so that the dielectric layer plays the role of a barrier which controls the supply of charge from the bulk. Figure 1(b) shows the energy diagram for this idealized system when no electric field is applied in vacuum. To avoid unnecessary technical complications, the present model is based on the common one-dimensional electron-transport approach, which is present in various theoretical studies related to the tunneling phenomenon.^{3-5,7,9} More precisely, although the real system consisting of the bulk Au electrode, the WBG material, and the QCS on top is essentially a three-dimensional (3D) structure, the electron tunneling rates in and out on the QCS will be described using the 1D Wentzel-Kramers-Brillouin (WKB) approximation. Therefore a simple 1D approach for the *energy diagram* of that system is more suited. However, not all the aspects of the system under consideration will be 1D. For example the electron current

FIG. 1. (Color online) (a) Schematics of the idealized system representing a bulk cathode separated from a spherical nanoparticle by a thin WBG material. (b) The potential-energy diagram for the system in (a) (not drawn to scale) at thermodynamic equilibrium with no applied field in vacuum. (c) The potential-energy diagram for the system in (a) after the application of the electric field. The spatial ranges are of the order of few nanometers and the energies extend to a few eV. The origin for the energy scale is set at the Fermi level of the bulk metallic substrate.

from the bulk inside the well will be calculated using the notion of a supply function¹⁰ which uses the “perpendicular” component of the wave vector in the substrate. The emission takes place from the QCS toward the vacuum through a second barrier whose transparency is controlled by the applied electric field. In order to point out the influence of the discrete energy levels on the FE current, a confinement region (nanoparticle) within the heterostructure is modeled as a rectangular asymmetric 1D potential well. The origin of the potential energy is considered to be at the bulk Fermi level. When the system is in thermodynamic equilibrium, there is no electron flow and the Fermi level of the nanoparticle equals that of the bulk. The nanoparticle is assumed as electrically neutral in this state. Given a potential well, the energy levels for the thermodynamic equilibrium case, E_l^0 , can be found in the usual way and considering a Fermi-Dirac statistics, the initial average number of electrons can be calculated as

$$n_0 = 2 \sum_{l=1}^{N_0} f_F(E_l^0, 0), \quad (1)$$

where $f_F(E, \mu) = 1 / \{1 + \exp[(E - \mu) / (k_B T)]\}$ is the Fermi-Dirac distribution, the factor 2 accounts for the spin degeneracy, N_0 is the number of energy levels at equilibrium, and μ is the local chemical potential, which, in thermodynamic equilibrium, equals the bulk Fermi level. Other symbols in Eq. (1) are k_B , the Boltzmann constant and the overall absolute temperature T .

When an electric field F is applied, the thermodynamic equilibrium is broken and an electron flow is established through the system. For a given value of the applied electric field it is assumed that the system reaches a steady nonequilibrium state. As the electrons in the nanoparticle are separated from those of the substrate by a consistent potential barrier, we assume that a *local thermodynamic equilibrium* can be considered in each region. With this hypothesis, a *local chemical potential* can be defined for the electrons contained in the well as a measure of their average number. The electron flow through the system will result in the nanoparticle becoming charged due to excess or depletion of electrons in the potential well. The related charging energy can be described as

$$W_{Ch}(n) = \frac{|n_0 - n|(n - n_0)e^2}{2C}, \quad (2)$$

where n is the average number of electrons inside the well for a given steady-state flow condition (that is, for a given applied field) and C is the electrical capacitance of the nanoparticle and takes values around the capacitance of a conductive spherical nanoparticle of the same diameter. Some remarks regarding the form of Eq. (2) are in order. The one-electron Hamiltonian used in the present model has a position-independent potential energy in the well. In a rigorous treatment, any extra charge introduced in the nanoparticle should produce a potential-energy term that is a solution of the 3D Poisson equation with some specified boundary conditions. While useful for quantitative comparison with experiments, such an approach would greatly complicate the model and would impose a more rigorous 3D approach of the electron transfer at the nanoparticle boundary. Therefore, in order to keep the model as simple as possible, the position-independent charging energy in the well was adopted. However, in order to keep with the rigorous solutions of the Poisson equation, the potential energy resulting from the presence of an extra charge distributed in the well has to be made sensitive to the sign of this addition; an electron depletion in the nanoparticle will give rise to a decrease in the potential-energy term of the electronic Hamiltonian while an electron excess will have the opposite effect. In order to outline this extra-charge sign influence in the Hamiltonian, the product $|n - n_0|(n - n_0)$ has been used in Eq. (2). As the nanoparticle is assumed electrically neutral in the zero-field situation, n_0 represents the number of positive elementary charges in the well.

The application of the external electric field not only removes the thermodynamic equilibrium of the system but also

generates two important effects in the QCS. The first and most common is an overall decrease in the potential barriers together with the well's bottom [see Fig. 1(c)]. This is due to the electric-field penetration into the WBG material, which is obtained from the Gauss theorem by taking into account the electric charge inside the well. Considering a surface area σ for the QCS, transverse on the direction of the electron flow, the internal field F_{int} is obtained as a function of the average number of electrons n , inside the QCS and the external applied field F ,

$$F_{\text{int}}(n, F) = \frac{1}{\varepsilon} \left(F + \frac{e(n_0 - n)}{\varepsilon_0 \sigma} \right), \quad (3)$$

where ε is the relative permittivity of the WBG material. The external field will produce an overall thinning of the potential barriers in the WBG layer and at the vacuum interface. It will not, however, interfere with the well's energy-level distribution or their number. The second influence of the electric field is the change in the number of electrons residing in the nanoparticle. A consequent local charging will occur, as described by Eq. (2). The bottom of the potential well will therefore change due to both these combined effects: field penetration and local charging (which also depends on the applied field). As a result, the number and the positions of the energy levels inside the well will change accordingly with the average number of electrons present inside the well and with the applied field F . Unfortunately such dependence cannot be written in any analytical compact form and has to be obtained numerically, as will be described below.

In the hypothesis of local thermodynamic equilibrium inside the potential well, a Fermi-Dirac distribution of electrons over the available energy levels is assumed. The connection between the average number of electrons and the local chemical potential can be obtained from the sum of the average population of each of the $N(n)$ energy levels, $E_i(n, F)$,

$$n = 2 \sum_{i=1}^{N(n)} f_F[E_i(n, F), \mu]. \quad (4)$$

The above transcendental equation provides the dependence of the chemical potential $\mu(n, F)$ on the average number of electrons inside the potential well and on the applied field F . Due to the discrete structure of the energy spectrum, when n increases there are abrupt shifts in the number of populated energy levels in the well and the obtained n dependence of the chemical potential presents a characteristic staircaselike shape. Figure 2 shows the calculated dependence of the chemical potential (relative to $\chi_1 - F_{\text{int}}d_b$) on the average number of electrons in the well. As the average electron number increases, the well's bottom moves upward followed by the energy levels and the chemical potential is forced to increase every time the maximum population is attained at each predetermined level corresponding to the size of the particle (well). This peculiar shape of the chemical potential has important consequences for the behavior of the current of electrons tunneling out of the well.

Having found the energy levels and the chemical potential for a given electron content of the well, it is now possible to

FIG. 2. (Color online) The variation in the potential-well bottom energy levels and local chemical potential relative to $\chi_1 - F_{\text{int}}d_b$ in the nonthermodynamic equilibrium state with the average number of electrons in the well. For convenience, only a limited number of energy levels have been displayed. $\chi_1 = 4.2$ eV, $\chi_2 = 4.3$ eV, $W_0 = -1$ eV, $d_b = 3$ nm, $d_w = 3$ nm, $C = 3.3 \times 10^{-17}$ F, and $T = 300$ K.

calculate the electron current. A two-step tunneling electron transfer phenomenon is proposed in which steady-state equilibrium is attained between the electron flow from the substrate into the well and from the well, both into the vacuum as a FE current, and back into the substrate. To compute the electron supply current from the bulk substrate, I_{BW} , the well-known kinetic formalism of the supply function (SF) is used.¹⁰ Electrons with energies different from the confinement levels can enter the well through inelastic processes. Such processes are assumed to take place in the barrier region and at the interfaces,

$$I_{BW}(n, F) = e\sigma \int f_{\text{supply}}(E_{\perp}) T_{BW}(n, F, E_{\perp}) dE_{\perp}, \quad (5)$$

where σ is the cross-sectional area of the nanoparticle and $E_{\perp}$ is the so-called “transverse” part of the incoming electron energy. The symbol $f_{\text{supply}}(E_{\perp})$ represents the electron supply function defined as¹⁰

$$f_{\text{supply}}(E_{\perp}) = \frac{m_0 k_B T}{2\pi^2 \hbar^3} \ln(1 + e^{-E_{\perp}/k_B T}), \quad (6)$$

where m_0 is the free-electron mass. $T_{BW}(n, F, E)$ in Eq. (5) is the 1D WKB transmission coefficient for the potential barrier between the bulk substrate and the potential well [see Fig. 1(c)]. For simplicity, σ will be approximated in computations by the square of the potential-well width d_w . The transmission coefficients have been expressed using the WKB approximation through the generic formula

$$T(E) = \exp \left\{ - \int_{x_1}^{x_2} \sqrt{\frac{8m}{\hbar^2} [W(x) - E]} dx \right\}, \quad (7)$$

where $W(x)$ is the potential energy in the 1D potential barrier, x_1 and x_2 are the energy-dependent turning points of the potential barrier, and m is the electron effective mass in the

FIG. 3. (Color online) Electron currents plotted in two representative instances against the average number of electrons in the potential well. The stair points A represent the intersection of the incoming (continuous red line) currents and the outgoing (continuous blue line) current on a vertical stair. The step points B are the corresponding intersections (dashed lines) on a horizontal step. The inset shows a detailed view of the area within the small rectangle for the case of the intersection on a vertical stair. $\chi_1 = 3.8$ eV, $\chi_2 = 4.2$ eV, $W_0 = -2.5$ eV, $d_b = 3$ nm, $d_w = 4$ nm, $C = 4.45 \times 10^{-17}$ F, and $T = 300$ K.

barrier region.¹¹ In order to avoid irrelevant complications by matching Schrödinger's equation solutions across various layers, the effective mass will be held position invariant in the numerical computations. The electron current (or the FE current) from the potential well toward the vacuum can be obtained through the attempt-to-escape frequency formalism,¹²

$$I_{WV}(n, F) = 2e \sum_l f[E_l(n, F), \mu(n, F)] T_{WV}[n, F, E_l(n, F)] \times \nu[n, F, E_l(n, F)], \quad (8)$$

where

$$\nu(n, F, E) = \frac{1}{d_w} \sqrt{\frac{2}{m_0} [E - W_0 - W_{Ch}(n, F)]} \quad (9)$$

is the attempt-to-escape frequency of an electron with energy E inside the well and T_{WV} is the transmission probability through the vacuum barrier. The current in Eq. (8) is obtained through a summation over all the energy levels inside the potential well. Finally, the well-to-bulk current takes the form

$$I_{WB}(n, F) = 4e \sum_l \Phi[E_l(n, F), \mu(n, F)] T_{WB}[n, F, E_l(n, F)] \times \nu[n, F, E_l(n, F)], \quad (10)$$

where

$$\Phi(E, \mu) = f(E, \mu) [1 - f(E, 0)] \quad (11)$$

is the probability for an electron inside the potential well, initially occupying a given energy level E to find an empty level of the same energy in the bulk.

The essential assumption of the present model is that steady-state equilibrium is attained and a balance occurs between the stationary incoming and outgoing electron fluxes

from the QCS. No reverse electron current from the vacuum into the well is allowed. The balance equation can be written as a function of the average number of electrons inside the potential well, n , and of the applied external field F as

$$I_{in}(n, F) = I_{out}(n, F), \quad (12)$$

where $I_{in}(n, F) = I_{BW}(n, F)$ and $I_{out}(n, F) = I_{WV}(n, F) + I_{WB}(n, F)$ are the well's incoming and outgoing currents, respectively. Equation (12) can, in principle, provide a stationary value of the average number of electrons in the QCS for a given external field. Thus, the balance between the incoming and outgoing currents will finally decide the average amount of electrons within the potential well suited to each value of the applied field.

When an electric field is applied to the system, the average electron number in the potential well varies and its structure changes accordingly (Fig. 2). The applied field thus moves the local chemical potential. For example, at high field strengths, when the electron population decreases, the chemical potential approaches the bottom of the potential well. As a consequence of the electron tight confinement in the QCS, the allowed energy levels are well separated and the local chemical potential, as given by Eq. (4), experiences regular jumps. This behavior is further transferred to the currents flowing out of the well as illustrated in Fig. 3 (and in a detailed view in the inset showing an enlarged area of the region within the rectangle in Fig. 3). By contrast, the incoming electron flux from the quasicontinuous spectrum of the substrate will be almost unaffected by the well's quantization. At each value of the field, an intersection of the $I_{in}(n)$ and $I_{out}(n)$ diagrams represents a steady nonequilibrium state determining the value of n . Therefore, by varying the applied field, the balance between the smooth $I_{in}(n)$ and the ridged $I_{out}(n)$ will result in a steplike shape (or at least in some slope discontinuities) of the device's current-field characteristics. Within this framework, the appearance of the stairlike fea-

tures in the FE current can be explained through the two instances highlighted in Fig. 3. The type-A (on a stair of the outgoing current) and type-B (on a step of the outgoing currents) points correspond to situations in which equality between the incoming and outgoing stationary electron fluxes occurs. In the case of a type-A point the equilibrium [i.e., the intersection of the two $I(n)$ diagrams] occurs on a stair of the outgoing current and the intersection point shifts upward (rather slightly) with the applied field. This will therefore lead to a steplike feature in the FE current. By contrast, for the type-B points, the equality occurs on a step of the outgoing current and thus it changes rapidly its position for a slight variation in the applied field. This will correspond to a more or less vertical stair of the FE current. Once the electron population is derived, the FE current can be obtained from Eq. (8) as a function of the applied field only.

It must be stressed out that although this behavior appears similar to what is described as Coulomb blockade in electron field emission (FECB),⁹ the two phenomena differ essentially in their background. In the FECB theory, unlike the classical treatment of the Coulomb blockade,¹³ the ladder-shaped characteristics are mainly an effect of the discreteness of the electric charge and of the local charging of the particle. In the present model, the confinement quantization of the electron energy in the QCS plays the main role, along with the local variations in the number of electrons produced by the strong external field. For this reason, Coulomb-blockade effects are normally observed at low biases and low temperatures,^{14,15} where the local charging energy is not exceeded by the electron thermal energy or by the energy provided by the applied electric field. This effect is typically manifested by blocking the current through the OCS. By contrast, our kinetic model is supposed to be less affected by the temperature change (since the involved energy leaps are hundreds of times larger than the electron thermal energy) and will give rise only to alternating parts of high- and less-bias sensitivity in the characteristics. This description of the FE current is simplified to a stationary flow of electrons driven by chemical-potential differences between adjacent zones assumed in local thermodynamic equilibrium. The emitted current is controlled by the high field applied to the QCS that penetrates into the substrate barrier and leads also to local charging effects.

III. THEORETICAL RESULTS

The first important result of the sequential tunneling model presented in the previous section is the calculated field-emission characteristic as a function of the applied field in vacuum (Fig. 4). As can be seen the steplike shape is obtained for the emission current using the present model. The electric field has been varied from 1 to 3 V/nm and the choice is not arbitrary. For very low values of the applied field the vacuum barrier is too opaque, so that no balance between the incoming and the outgoing currents is possible. On the contrary, for too large value of the field, the QCB is so depleted of electrons that only the very bottom levels in the well (which are much denser) are occupied and the steplike shape of the chemical potential is washed out (see Fig.

FIG. 4. (Color online) Theoretical emission current vs applied-field characteristic obtained from a nanoparticle with $d_w=6$ nm, $d_b=3$ nm, $\chi_1=4.2$ eV, $\chi_2=4.3$ eV, $W_0=-1$ eV, $C=4.45 \times 10^{-17}$ F, and $T=300$ K. Clear steplike features can be observed for small values of the field only to disappear for the larger values due to the strong depletion of the well that leaves only the very bottom (much denser) levels occupied.

4). As a consequence, the features in the characteristic also disappear.

It is interesting to investigate how the properties of the nanoparticle and the WBG potential barrier influence the current-field characteristics. For example, changing the nanoparticle diameter will automatically affect the number and the positions of the energy levels inside the potential well, which will lead to substantial modifications in the current. The results are summarized in Fig. 5. As can be seen, the structure of the diagram changes as the potential well becomes larger [Fig. 5(a)]. The number of steplike features

FIG. 5. (Color online) (a) Field-emission current as a function of the applied electric field for two values of the potential-well width. The potential-barrier thickness is $d_b=3$ nm, $\chi_1=4.2$ eV, $\chi_2=4.3$ eV, $W_0=-3$ eV, $C=4.45 \times 10^{-17}$ F, and $T=300$ K. (b) Field-emission current as a function of the applied electric field for two values of the potential-barrier thickness. $d_w=6$ nm, $\chi_1=4.2$ eV, $\chi_2=4.3$ eV, $W_0=-3$ eV, $C=4.45 \times 10^{-17}$ F, and $T=300$ K.

increases as the potential-well width increases because wider wells have higher densities of available energy levels. For the same reason, at large values of d_w , the chemical potential will be located deeper into the well, electrons facing a thicker vacuum barrier. The current is thus expected to be overall smaller from larger particles. However, a different behavior is obtained if the parameter d_w is maintained constant and the WBG thickness is varied [Fig. 5(b)]. There are again two features to be observed. The first one is the decreasing number of steps as the potential barrier is getting thicker. A thicker barrier toward the substrate means a smaller income of electrons in the QCB and more advanced electron depletion therein. Consequently, the lower and denser energy levels will be occupied and the stairs are again washed out. Also, for a thicker substrate barrier, the emitted current at small fields is lower. Yet the two cases seem to converge toward similar values as the field is increased. This is due to the fact that, at higher fields, the deformation of both the vacuum barrier and the potential-energy barrier in the WBG material increases the electron injection from the bulk, and thus the chemical potentials in the two cases become comparable.

At this point it is worth noting that the average number of electrons in the QCS n is expected to be less than n_0 (the value for the substrate-well thermodynamic equilibrium) for large extraction fields. The well region will therefore be positively charged in such cases. However, when the applied field is small, the value of n may exceed n_0 as well and the QCS becomes negatively charged in the steady state. Therefore, even if for some value of the applied field the equality $n=n_0$ may occur, this *should not* be interpreted as an overall thermodynamic equilibrium situation; as the system is under external field, it is open to electron flows and the thermodynamic equilibrium can be approximately conceived only in very limited regions.

In order to better emphasize the influence of the electron confinement in the QCS on the FE current, the dependence of the current versus the potential-well width has been plotted in Fig. 6. It can be observed that, for narrow wells, for which the confinement is tight and the separation between the energy levels is large, several sharp “oscillations” may appear in the FE current. This is typical of quantum behavior that follows from the (field-induced) shift of the quantized levels in the energy range that is most favored for emission into the vacuum. The effect is rapidly wiped away by the increase in the well width that would sharply decrease the separation between the energy levels. Another feature to be observed in the data of Fig. 6 is the abrupt decrease in the FE current with the increase in the well’s width. As has already been pointed out, this is a consequence of the variation in the local chemical potential in the well. For wider wells, where the energy levels are denser, the steady-state number of electrons will occupy the states with energies close to the bottom of the well. Consequently, the chemical potential approaches the well’s bottom in an energy range where the vacuum barrier is thicker and this will lead to a severe decrease in the FE current.

IV. EXPERIMENTAL DETAILS

The model described in the previous sections has been developed around the idea that various electron-confinement

FIG. 6. (Color online) Field-emission current as a function of the potential-well width d_w for three values of the applied field. $d_b=3$ nm, $\chi_1=4.2$ eV, $\chi_2=4.3$ eV, $W_0=-1$ eV, $C=4.45 \times 10^{-17}$ F, and $T=300$ K.

regions present at the surface of an emitter (e.g., insulated conductive nanoparticles) may interfere in a sequential way with the tunneling transport process to produce the steplike features in the field-emission characteristics. Such circumstances can appear experimentally in various configurations^{1,6,8} but a dedicated experiment is needed to sustain the theoretical model presented above. Therefore, we have devised a FE setup that is able to replicate the apparition of the staircases in the current-voltage diagrams. Using a wet chemistry technique, a structure similar to the one sketched in Fig. 1(a) has been obtained as follows. A microscope glass slide has been covered with a layer of sputtered Au, 100 nm thick, which will represent the bulk electrode in Fig. 1(a). Following the Au deposition, the so-called layer-by-layer (LbL) deposition technique has been used to realize the WBG layer. This technique is a very flexible deposition method, which is template assisted and develops from a solid substrate provided with an electrostatic charge. The requirements for the LbL technique are that the substrate is solvent accessible (i.e., can withstand solvent treatment, a condition that is fulfilled for the case of the Au-covered glass slide) and the presence of some form of charged groups on its surface.^{16–20}

The construction of the WBG layer was realized using two solutions of long-chained weak polyelectrolyte polymers, namely, poly(ethylene imine) (PEI) and poly(acrylic acid) (PAA) purchased from Sigma Aldrich. This choice of solutions made it relatively easy to modify their electrostatic densities by altering the solution’s pH or, alternatively, changing the ionic content thus obtaining two complementary solutions: one which will carry covalently bound cationic groups on the polymer chains and the second which will contain anionic groups. Following the preparation of the two polymer solutions, the following deposition cycle was performed. The Au-covered glass slide was immersed into the first PEI solution, followed by a wash with ultrapure water in order to remove the excess polymer chains on the surface, and then it was immersed in the PAA solution. Each

immersion was 15 min long. Carefully controlling this deposition process, the thickness of the deposited polymer layer can be manipulated to a high degree of accuracy. The last stage in the sample preparation was adding the “impurities” which consisted of Au nanoparticles purchased from Sigma Aldrich with a nominal diameter between 3.5 and 5.5 nm as provided by the manufacturer (transmission electron microscopy).²¹ The starting 2% (w/v) water solution of (1-Mercaptoundec-11-yl)tetra(ethylene glycol) functionalized Au nanoparticles was used to obtain a subsequent solution in ultrapure water of 0.002 (w/v) with pH=13. The high pH value was attained by addition of NaOH and it was performed in order to deprotonate the functionalized Au nanoparticles so that they can be used in the electrostatic-driven multilayer self-assembled LbL procedure. Then, the polymer-coated slide was immersed in the 0.002% functionalized Au nanoparticles solution and left to rest over several hours overnight. The overall thickness of the obtained heterostructure was measured using ellipsometry analysis at a wavelength of 630 nm. Values for the different refraction indexes were outsourced from the scientific literature [PEI, $n=1.454$; PAA, $n=1.43$; poly(ethylene glycol) (PEG), $n=1.475$; Au=0.47].²¹ As a result, the following data was obtained: the first PEI monolayer was reported to be 2.4 nm thick, the PEI/PAA bilayer was calculated to be 3.7 nm thick, the PEI/PAA/PEI LbL films was measured to be 6.2 nm thick, and finally the total PEI/PAA/PEI/Au-nanoparticles film had a thickness of 12.9 nm, a value which is in agreement with the data provided for the Au nanoparticles (diameters in the 3.5–5.5 nm range).²¹

The sample thus prepared was then tested for FE using a simple diode configuration inside a vacuum chamber at a pressure lower than 10^{-6} mbar using a 5-mm-diameter stainless-steel sphere as the anode.²² A clean portion of the deposited Au electrode layer was used to ground the sample and the measurements have been performed at roughly 5 μm anode-to-cathode separation and at the ambient room temperature. The applied anode voltage was increased from 0 V until a current of 1 μA was measured, which was used as a limit in order to protect the sample. Figure 7 shows four consecutive measurements performed over the same point of the sample. As can be seen in the first set, there is a clear sequential tunneling characteristic indicated by the presence of the steplike features in the I - V . In the following cycles the features diminish, indicating that the surface of the sample has undergone significant changes. However, due to the nature of the sample it was impossible to pinpoint the exact nature of these modifications. One can only hypothesize that during the process of FE, the Au nanoparticles present on the soft surface of the dielectric polymer could be subjected to Joule heating thus resulting in a possible shape change (they could even coalesce into larger structures), a fact that would significantly modify the energy-levels distribution and thus affect the I - V characteristic. The migration of the Au nanoparticles on the surface can also be invoked since an increase in the temperature of the area subjected to high electric fields could allow for a certain dynamic of the nanoparticles. Nevertheless, the qualitative comparison between the experimental and theoretical characteristics is possible and it is shown in Fig. 8. One important aspect that should be noted in Fig. 8

FIG. 7. (Color online) Field-emission characteristics measured on a site on the PEI/PAA/PEI/Au-nanoparticles sample at an anode-to-cathode separation of 5 μm . The panels are numbered according to the succession of the emission cycles.

is the difference between the values of theoretical current and the experimental data. This is due to the fact that the theoretical current is obtained from a model which only takes into account a single nanoparticle while the experimental data in Fig. 8(a) was obtained from an extended area covered with Au nanoparticles. Another factor explaining the quantitative discrepancy between theory and experiment lies in the lack of accurate correlation between the anode potential and the local field generated at the surface of each emitting nanoparticle. While quantitative reproduction of experimental results cannot be expected from such a simplified approach, its main merit is the apparition of the steplike features for the room-temperature field-emission experiment described above. We can thus conclude that the data in Fig. 7 support the theoretical model presented in the previous sections and that further refinements of this method could lead to a more quantitative comparison with the experimental data.

V. CONCLUSIONS

A simple one-dimensional model has been constructed to explain the observation of ladder-shaped current-voltage

FIG. 8. (Color online) Qualitative comparison between (a) experimental field-emission measurements and (b) the theoretical model for sequential electron tunneling.

characteristics occurring frequently in experiments of field emission from nanostructures. The peculiar shapes of such diagrams are found to originate in the energy quantization produced by the tight confinement of electrons within nanometer-sized particles, included knowingly or otherwise, in such cathodes. By accounting for the charging effects, a balance between the steady-state electron flows has been shown to govern the steady-state electron content at a given

applied field in the quantum-confinement objects. The theoretical model findings were qualitatively compared against experimental field-emission data. The sample consisted of an Au-covered glass slide on top of which a thin WBG polymer was deposited followed by Au nanoparticles. It was found that the theoretical model was in good qualitative agreement with the experimental data.

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