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Sequential tunneling model of field emission through dielectric deposits on nanotips

V. Filip\textsuperscript{a)}

Faculty of Physics, University of Bucharest, P.O. Box MG-11, Bucharest-Magurele 76900, Romania

D. Nicolaescu\textsuperscript{b)}

Nanoelectronics Research Institute, AIST, Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan

M. Tanemura and F. Okuyama

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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A model of sequential (incoherent) tunneling for the electron field emission was built up in order to explain some peculiarities of the electronic emission from relatively thick dielectric layers covering nanometer-range tips, particularly carbon nanotubes. The emission current as a function of applied voltage, dielectric layer thickness, polarizability, and temperature was computed. Various experimentally detected trends were thereby modeled, leading to the conclusion that incoherent tunneling might be a competitive mechanism for electron field emission from dielectric layers on the tips of nanometer-sized cathodes. © 2003 American Vacuum Society. [DOI: 10.1116/1.1596222]

I. INTRODUCTION

It is now well established that huge electric fields are available on supersharp tips, like those of carbon nanotubes (CNTs). The high chemical and structural stability of CNTs allows their field emission operation in relatively high environmental pressures where heavy adsorption on CNT caps is expected, mainly under conditions of high extraction fields.\textsuperscript{3} Electron field emission through relatively thick dielectric layers also takes place when protective and emission stabilizing coatings are applied on high curvature substrates of various natures.\textsuperscript{2–8} As very high field enhancement naturally occurs at CNT tips, such cathodes present particularly interesting quantum effects in the corresponding adsorbate layer.

Saturation effects,\textsuperscript{9} slope-breaking points,\textsuperscript{2,10} and fancy current–voltage characteristics\textsuperscript{3,10–13} are features that could be due to the presence of adsorbates, dielectric coatings, or other structures\textsuperscript{14} on supersharp tips. The present article proposes a model of sequential (incoherent) tunneling for the electron field emission through such dielectric layers. The model should be considered in contrast to the coherent tunneling one. It accounts for the presumable mixing of the electronic waves in a relatively thick coating layer, including deposits that appear after heavy adsorption when operating CNT tips in poor vacuum conditions. The external extraction field, which in the particular case of CNTs is currently enhanced to values of the order of 10 V/nm, is supposed to penetrate the adsorbate/dielectric layer and to form a triangular potential energy well. If the deposit is not too thick, the well may be enough deep and narrow to allow distinct electronic energy levels to appear in the energy gap of the dielectric layer. If no significant barrier is installed at the back interface of the layer then electrons may be supplied to these levels from the emitter, forming a space charge region.\textsuperscript{1,7} The electronic waves entering the well are thus supposed to randomly scatter and rapidly lose their phase memory. Therefore, the tunneling process proceeds from the electronic states of the dielectric layer, not through them (as is the case in coherent tunneling).\textsuperscript{15,16} Any further increase of the extraction field will modify the electronic energy structure of the well and will pass different allowed energies to the Fermi level. This may provide “oscillatory” current–voltage (I–V) characteristics or at least some slope-breaking points followed by saturation regions, as already experimentally detected.\textsuperscript{2,3,9–14} Such parts of negative differential conductivity in the I–V characteristics may be speculated in order to generate high frequency oscillations in some field emission structures obtained through suitable dielectric coatings on very sharp tips.\textsuperscript{7}

The properties of the dielectric layer (thickness, electric polarizability) clearly influence the structure of its electronic states and are thus expected to have important effects on the I–V characteristics. Some of these effects may look quite strange if the dielectric is to be considered only as a simple resistive layer that hinders field electron emission. For example, it is found that adsorbates made of molecules (e.g., water) with high polar moments may both smooth or damp the “oscillations” of the I–V characteristics and strongly stimulate the emission level. Recent careful experiments report such effects\textsuperscript{17} although they are tentatively explained by a mechanism of coherent tunneling field emission only.

The response of the adsorbate field emission to temperature increase is also an important issue. While disregarding adsorption–desorption kinetics our model may partly explain some related experimental results.\textsuperscript{17} It was also found that temperature increase might stabilize the electron field emission from thick adsorbate layers providing confusing data about the cleanliness of the emitting surface.

The electron energy distribution spectra were also computed in our simplified model. While not comparable with

\textsuperscript{a)Electronic mail: filip@digitalnet.ro}

\textsuperscript{b)Author to whom correspondence should be addressed; electronic mail: n-dan@aist.go.jp}
currently available experimental data, these results may form the basis for a more-detailed study.

II. PHYSICAL MODEL

Adsorption phenomena on field emitters have been intensively studied in the past mainly related to field-ion microscopy and to various activation procedures of electron field emission surfaces for better performance.\(^\text{18,19}\) Dielectric coatings on metallic and semiconductor field emitters proved to strongly enhance the electron emission and opened the way for many useful applications.\(^\text{2–8}\) This study recently extended to CNT-based electron sources.

Adsorption phenomena on a surface can be essentially treated as chemical equilibrium between the environmental gas and the adsorbed lattice gas on the surface.\(^\text{20}\) From a more microscopic point of view the equilibrium occurs when the current of gas molecules that come and adsorb on the surface equals the desorbtion current from the surface. The presence of high electric fields near the surface of field emitters may dramatically change the situation. Field polarization and even field ionization of gas molecules frequently occur near the emitting tips.\(^\text{1,18}\) Such charged or polarized molecules crowd into the tip region and significantly enhance the adsorption rate, which is proportional to the local molecular density. For CNTs these effects are even more pronounced, since the electric fields currently attain values of the order of 10 V/nm near the tips.\(^\text{21}\) For example, the density of water molecules (wearing high dipole moments) at 300 K in a region with an electric field of 5 V/nm exceeds more than 1500 times the molecular density at large, faraway from the field action. As the molecules approach the CNT cap they are very likely stripped of some outer electrons and become ionized. This situation increases both the adsorption probability and the activation energy for desorption,\(^\text{18}\) leading to stable multiple molecular layers up to temperatures as high as 900 K.\(^\text{17}\) Under such conditions of “forced” adsorption the formation of layers with thickness up to the order of the CNT diameter seems to be a reasonable hypothesis. On the other hand, the adsorbed layer should generally decrease the field in the neighboring region, so that the molecular crowding, polarization, and ionization phenomena that used to stimulate adsorption may become balanced by desorption events. Thus, the adsorbed layer gradually reaches some equilibrium thickness under the given conditions.

Once the adsorbate deposit or the coating layer is formed, one may expect two distinct electronic behaviors, depending on its thickness. First, if the layer is thick enough, the quantum confinement of the electrons therein is negligible and the adsorbate/coating behaves as a simple dielectric. In this situation, let us suppose that the adsorbed atoms (or molecules) have piled up on the emitter’s tip in a layer of some thickness \(d\) that preserves the original curvature of the cap. Let \(r_0\) be the common value of the radius of curvature for the emitter’s cap and the layer. The potential energy drop in the vacuum gap between the anode (of potential \(V_a\)) and the dielectric termination can be well approximated by \(eFsr_0\),\(^\text{18,21}\) where \(F\) is the electric field in vacuum at the interface with the dielectric and \(s\) is an emitter “self-screening” factor, usually taken at the value of 5.\(^\text{18}\) The electronic potential energy should have an average jump equal to the dielectric layer work function \(\chi\) at the vacuum interface and the potential energy drop in the layer (where the static dielectric constant is \(K_s\)) equals \(eFsd/K_s\). Therefore, considering the contact between the grounded CNT and the adsorbed layer as electrically perfect, the following expression for the extraction field in vacuum is obtained:

\[
F = \frac{V_a}{sr_0} \left(1 + \frac{\chi}{V_a} \left(1 + \frac{d}{sK_sr_0}\right)^{-1}\right).
\]

(1)

The electronic potential energy profile in the region of the layer–vacuum interface could thus be approximated as

\[
W(x) = \begin{cases} 
0, & x < -d, \\
-eF/(K_s)(x + d), & -d < x < 0, \\
-eF\left(x + \frac{d}{K_s}\right) + \chi, & x > 0,
\end{cases}
\]

(2)

where \(x\) is the position measured from the vacuum interface (the positive sense of the axis points towards the vacuum). The origin of the energy scale is taken at the value of the chemical potential of the emitter (electron reservoir). The numerical values for energy are expressed in electron volts throughout this article. An electron coming from the emitter will, therefore, be accelerated in the (relatively high) internal field of the dielectric layer and will most likely escape into the vacuum over the potential barrier, as a hot carrier.

The second case refers to very thin dielectric layers on the emitter’s tip. In this situation, if the external extraction field is large enough, its penetration in the dielectric will determine a spatial confinement. This feature will allow discrete levels in the electronic energy gap of the adsorbate/dielectric layer. The electrons will tunnel into the vacuum through or from such levels, depending on their density. In other words, two possible mechanisms, coherent and incoherent, may be imagined for the electron tunneling through the adsorbates.\(^\text{22,23}\) In a one-particle picture of coherent tunneling,\(^\text{24,25}\) the electrons are supplied from a reservoir with a quasicontinuous energy range (e.g., from the CNT),\(^\text{15}\) and the attempt rate of escape for the electron [defined below, see Eq. (10)] is expressed as a function of the group velocity that also takes quasicontinuous values.\(^\text{25,26}\) The tunneling may take singular high-value resonance peaks when the energy of some of the (sparse) states localized at the vacuum interface coincides with the Fermi level of the reservoir. Modifying the external field changes the energetic structure of the adsorbed atoms/molecules and can bring a localized level at the reservoir’s Fermi energy, thereby fulfilling the resonance condition. In this case, sharp peaks appear in the \(I–V\) characteristics. The resonance energy levels act, therefore, as “holes” in the potential energy barrier of the electrons in the reservoir. The apparition of such resonant states is expected in light atomic/molecular adsorption on the
emission tips. Since the localization of such states is very tight, the \( I - V \) peaks corresponding to resonant levels will be high, sharp, and well separated.

When lots of gas molecules agglomerate randomly on the interface, as is the case for heavier adsorption, the energy levels in the dielectric layer become denser and able to accommodate several electrons on its specific one-particle states (whose density should increase with the amount of adsorbed matter), forming a space charge in the layer.\(^{10-14}\) The electrons coming from the reservoir most likely lose their phase memory through random scattering processes. Thus, the possibility of coherent tunneling dramatically decreases. The quantum states become mixtures to be occupied or sequential.\(^ {22,23}\) The electronic supply for tunneling through the layer is usually termed as incoherent tunneling.\(^ {24}\) Tunneling may then proceed from the discrete states of the space charge in the dielectric layer. This kind of passing the electrons through the layer is usually termed as incoherent or sequential.\(^ {22,23}\) The electronic supply for tunneling takes a discrete character making the resulting \( I - V \) characteristics to have a "noisy-" shaped sequence of closely spaced relatively small peaks, which is different from the incoherent model with a "tightly" spaced sequence of closely spaced relatively high peaks, which is different when compared to the case of resonant tunneling field emission.\(^ {10-14}\) Sometimes, when the dielectric layer is not so thick, the separation between one-electron levels becomes wider and slope-breaking points followed by saturation regions may occur.\(^ {9,11}\)

It is quite clear that the real picture of electronic energy structure in the adsorbate/dielectric layer must lie between the two extremes presented above: a certain potential energy drop may take place in the adsorbed layer and discrete energy levels may appear only near its vacuum surface. For reasons of simplicity we will further examine only the second extreme case, where the confinement quantization extends over the entire adsorbed layer. Also, even if there is no reason to exclude coherent tunneling through a relatively thick randomly structured layer of adsorbates, we will focus on the incoherent (sequential) type of electron field emission only.

As another important approximation, the work function \( \chi \) for the electrons in the dielectric layer will be considered as independent of the external field. Moreover, the one-particle electronic states in the layer will be approximated as those of an infinite triangular well of the form\(^ {27}\)

\[
W_{\text{well}}(x) = \begin{cases} 
- \frac{eF}{K_s}(x+d), & x < 0, \\
\infty, & x > 0.
\end{cases}
\]

(4)

Obviously, this is a crude model intended only to reveal the electron field emission basic features. In fact, the dielectric layer does not behave as a potential energy well for the electrons; its intimate structure may turn the electronic states into complicated bands. However, the most realistic part of the model is the idea of tunneling into the vacuum from the states localized in the layer.\(^ {22,23}\)

While the chosen approach neglects the real continuity condition of the wave function at the emitter–dielectric and dielectric–vacuum interfaces, it allows analytic computation of the electronic wave functions as linear combinations of Airy functions.\(^ {28}\) The corresponding values of the allowed energies may be readily found through conditions of vanishing wave function at \( x = -\infty \) and \( x = 0 \):\(^ {27}\)

\[
E_n = c_n \left( \frac{\hbar eF}{K_s \sqrt{2m}} \right)^{\frac{2}{3}} - \frac{eFd}{K_s}, \quad n = 0, 1, 2, ..., \quad (5)
\]

where \( m \) is the free-electron mass and \( -c_n \) are the negative roots of the Airy function of the first kind. These numbers can be very well approximated as\(^ {28}\)

\[
c_n = \left[ \frac{3\pi}{2} \left( n + \frac{3}{4} \right) \right]^{\frac{2}{3}}, \quad n = 0, 1, 2, ... . \quad (6)
\]

Each electronic quantum state \( n \) of the well should contribute to the total emission current with a specific (elastic) tunneling term \( I_n \) through the dielectric layer–vacuum potential barrier of height \( \chi \):

\[
I_n = 2ef(E_n)D_nv_n . \quad (7)
\]

The meaning of the symbols in Eq. (7) is explained below. Thus, the factor 2 accounts for the spin degeneracy and \( f(E_n) \) is the Fermi–Dirac distribution function describing the occupancy of the discrete energy levels of Eq. (5):

\[
f(E) = \left[ 1 + \exp \left( \frac{E}{k_B T} \right) \right]^{-1} , \quad (8)
\]

where \( k_B \) is the Boltzmann constant. The symbol \( D_n \) in Eq. (7) stands for the transmission coefficient from the energy level \( E_n \) to the vacuum, which for the considered triangular potential barrier takes the form\(^ {29}\)

\[
D_n = \exp \left[ -4 \frac{\sqrt{2m}}{3} \frac{\left( \chi - E_n \right)^{3/2}}{eF} \right] . \quad (9)
\]

(Remember that the origin of the energy scale is taken at the common value of the chemical potential in the emitter and the space charge of the dielectric layer.) The values of the extraction field in vacuum, \( F \), will be given by Eq. (3).

By \( v_n \) in Eq. (7) we denoted the so-called attempt rate of escape for the electron in the quantum state \( n \), that is the
number of times, per unit time, the electron on the energy level $E_n$ hits the dielectric–vacuum interface. This quantity is currently defined as $v_n = V_n / 2I_n$. Here, $v_n$ represents a velocity that corresponds to the classical kinetic energy of the electron at the vacuum interface in the quantum state $n$, namely $E_n + eFd/K_r$, and $I_n$ is the wideness of the well at the $n$th energy level: $I_n = d[1 + E_n/K_r]/(eFd)$. Therefore, in the case of the triangular potential energy well, the following definition of the attempt rate can be inferred:

$$v_n = \sqrt{eF / 2mK_r d} \left( 1 + E_n K_r / eFd \right)^{-1/2}.$$  \hspace{1cm} (10)

The total emission current will thus be obtained as the sum of individual contributions of all the energy levels [see Eq. (7)]:

$$I = 2e \sum_{n=0} \int f(E_n) D_n v_n.$$  \hspace{1cm} (11)

The emission current carried by the electrons that escape with energies in a prescribed grid:

$$\frac{dI}{dE} (E) = 2e \sum_{n=0} \int f(E_n) D_n v_n \delta(E, E_n),$$

$$\delta(E, E_n) = \begin{cases} 1 & \text{if } E = E_n < E + dE, \\ 0 & \text{otherwise}, \end{cases}$$

can be used as a measure of the field emitted electrons energy distribution (FEEED).

When the quantum constraints become less stringent (that is, for large values of $d$ or for low internal fields in the dielectric) the energy levels in the potential well become so dense that the sum in Eq. (12) may be well approximated by the corresponding integral. In order to shift to such an expression it is necessary to introduce a density of states on the energy scale, $dn/dE$. By some straightforward algebra involving Eqs. (5), (6), and (10), one may readily obtain $dn/dE = \pi \hbar v(E)$, so that Eq. (11) becomes

$$I = \frac{2e}{\pi \hbar} \int_{-\infty}^{+\infty} f(E) D(E) dE.$$  \hspace{1cm} (13)

A rather similar expression was previously obtained for the current that tunnels out from the quasicontinuous energy levels of a CNT. The difference consists in the presence of a supplementary factor $S(E)$ in the integral that embeds the details of the energy dispersion relations of the conduction electron in the given CNT. In Eq. (13) this function is actually replaced by the factor 2 originating in the spin degeneracy, so that for the present problem one may write $S(E) = 2$.

Two further remarks should be made on the model described above. First, it is clear that the computations refer to the adsorbed dielectric layer only. No reference was made to the particular electronic structure of the emitter. This approximation has been used when taking the electronic states of the layer as those of the infinite triangular potential energy well. Thus, the special emphasis made on CNT emitters is here related mainly to their peculiar capacity to concentrate huge electric fields on their tips. Only such field values may lead to quantum electron confinement in the adsorbed layers. Nevertheless, for atomically thin adsorbates, the approximation breaks down since the induced energy levels are so sparse that coherent tunneling from the base emitter states becomes dominant. In such cases the coherent tunneling emission mechanism opens the way for the particular electronic structure of the emitter to explicitly influence the emission current.

The second remark regards the potential energy barrier that was used in the computations. It is clearly the simplest possible choice in view of the presently available highly refined theories. The main reason for using such a basic model was the lack of experimental data regarding some real potential energy barrier profile of the adsorbate. Consequently, a generic value of 5 eV was used for the adsorbate/dielectric layer work function throughout the computations performed in this article. The analytical simplicity of the involved mathematics was the other reason for using the triangular barrier model. Nevertheless, it is expected that the main conclusions are, at least qualitatively, independent on such simplifying hypothesis.

### III. NUMERICAL RESULTS AND DISCUSSIONS

Examples of $I–V$ characteristics computed using the sequential (incoherent) tunneling field emission model are illustrated in Fig. 1, where three different values of the dielectric layer thickness are used. The “oscillatory” shape of the characteristics is a result of the selective importance of the tunneling terms $I_n$ defined by Eq. (7) when included in the sum of Eq. (11). If looked at as a function of energy, the highest valued terms of this sum actually define a transparency window for the potential energy barrier. An increasing extraction field will continuously deform the structure of the energy levels allowing them to pass by this transparency.
window of the barrier. When one or several energy levels comes into the window a maximum of the emission current takes place. The voltage separation between these maxima will, therefore, be a function of the layer characteristics (thickness and polarizability). This behavior is outlined in both Figs. 1 and 2. It can be seen that above some small value of $d$ (dependent on the dielectric constant), both the amplitude and the voltage separation of the "oscillations" diminish by increasing the layer thickness or its dielectric constant. This is quite obvious since both such trends lead to increased density of energy levels in the barrier’s transparency window. It is remarkable that a moderately thick layer with a high value dielectric constant ($K_s = 80$, near the value of the pure liquid water) may completely smooth the $I$–$V$ characteristics up to an aspect of a clean emitting surface (see Fig. 2 and its inset where corresponding straight-line characteristics may completely smooth the $I$–$V$ characteristics of Figs. 1 and 2). This indicates that straight-line characteristics in the Fowler–Nordheim representation may be sometimes not enough for deciding about the cleanliness of the emitting surface.

Taking into account the simplicity of our model, one may obviously notice that practical characteristics of electron field emission through relatively thick adsorbates/dielectric coatings and under high extraction fields are not expected to be identically reproduced by results like those of Figs. 1 and 2. However, there is a remarkable resemblance between the behavior of these theoretical curves and the relatively rich set of related experimental results. The peculiarities of the emission characteristics cannot be linked to the electronic structure of the base emitter only. This possibility can be ruled out by comparing the characteristics of clean emitters with those obtained after dielectric coating of the emitters or intentional adsorption on their tips.\cite{Filip et al. 2003, Filip et al. 1997, Filip et al. 1998}

Figure 2 also suggests that the emission current at fixed anode voltage may have some increase with the polarization capability of the dielectric layer. In order to elucidate such dependence we computed the emission current as a function of layer thickness for several values of the parameter $K_s$. The results are depicted in Figs. 3(a)–3(c). First, one may notice the "noisy oscillations" of the current with increasing layer thickness. Their origin is similar to the "oscillations" of the $I$–$V$ characteristics of Figs. 1 and 2: increasing $d$ modifies the energy levels in the potential energy well and passes a sequence of such levels by the transparency window of the barrier. Moreover, a relatively low polarizable adsorbate/coating [Fig. 3(a)] shows essentially, on the average, a tendency of decreasing the emission current. Higher values of $K_s$ may reverse this trend: the emission current may increase up to one order of magnitude when the layer grows to 4–5 nm thick [Figs. 3(b) and 3(c)] and continues with a steady (slightly decreasing) value for higher thicknesses. The curves of Figs. 3(b) and 3(c) suggest a comparison with some of the experimental results of Ref. 17. In the mentioned paper the time variation of the emission current from previously cleaned CNTs was measured during selective adsorption of gas molecules. It was found that among several species present in the measuring chamber, only adsorbed water molecules determine an increase of the current and that the increase rate is strongly stimulated by the partial pressure of the water in the measuring chamber. Assuming a continuous growth of the adsorbed layer in time, one can shift the current–time diagrams into current–thickness ones.
that look very similar to the first part of those in Fig. 3(b). It may be concluded that the polarization state of the adsorbed water molecules is not actually the same as in the liquid phase. The shape or even the structure of each molecule may change in order to decrease its dipole moment and to accommodate the huge electric field on the CNT tip. Therefore, one may expect that the dielectric constant of the adsorbed layer becomes thick enough to cover the entire transparency window with dense energy levels [Fig. 3(a)]. On the contrary, higher dielectric constants will allow denser energy levels in the adsorbate and the aforementioned increasing trend of the emission current with $d$ is more obvious [Figs. 3(b) and 3(c)], as described by Eq. (13).

Such behavior of the emission current with increasing adsorbate thickness cannot be generated by coherent tunneling since the increase of $d$ actually hinders the electronic wave from keeping its phase and diminishes the resonance effect. It can thus be concluded that the experimentally verified enhancement of the emission current with the adsorbate thickness actually confirms our model of incoherent tunneling field emission from adsorbates.

The predicted current response to temperature increase in the incoherent tunneling field emission model may also be a point of interest. Formally, temperature enters the expression of the emission current only through the Fermi–Dirac distribution function. In coherent tunneling field emission the electrons are supplied from the quasicontinuous range of energy levels of the reservoir. Therefore, as the rise in temperature enhances the tail of the distribution above the Fermi level, it is expected that for the same value of the extraction field the resonant tunneling takes place at slightly higher energies where the barrier is thinner. This should obviously imply an increase of the emission current. However, present experimental evidence shows an apparent decrease of the emission current as the temperature rises, mainly for high values of the anodic voltage. Such a trend can also be explained in our model. Since emission takes place from the states localized in the adsorbate, the average occupation number takes basically discrete values $f(E_n)$. If the energy levels $E_n$ are well separated (as might be the case in very high electric fields), then the enhanced tail of the distribution above the Fermi level may fall in an energetic gap and thus the allowed (effective) values of the occupation number may actually decrease. The increase of temperature will, therefore, diminish the emission current in such cases, as can be seen in the examples presented in Fig. 5. We speculate that a more accurate model that would take into account the variation of the layer thickness by thermal desorption would provide a steeper decrease of the emission current with temperature rise, as reported in Ref. 17. When the anode voltage is lower, the density of allowed energy levels in the adsorbate increases closer to a quasicontinuum aspect and the temperature variation of the emission current becomes positive, as expected.

One more observation can be made about the influence of a temperature rise on the current–layer thickness ($I$–$d$) variation [Figs. 6(a) and 6(b)]. In Fig. 6(a) the computed $I$–$d$ diagram for 300 K [as presented in Fig. 3(b)] is compared with the same $I$–$d$ variation at 700 K [Fig. 6(b)]. It can be seen that the higher temperature curve is much smoother than that computed at room temperature. This can be explained as follows. First, Eq. (7) shows that a temperature increase should make the electron tunneling transparency

**Fig. 4.** Detailed comparison of a set of energy levels (including the ground energy) of the triangular potential well with the transparency window. It is intended to explain the increase of the emission current with the layer thickness within the framework of our model. The diagrams were drawn for $K_x = 20$. The energy scale is on the ordinate. The tunneling transparency window at some energy $E$ is computed by summing the values of $I_n$ [given by Eq. (7) and divided by the total emission current] for which $E_n$ [of Eq. (5)] falls between $E$ and $E + dE$. The “relative units” on the abscissa refer to the values of the transparency window. (a) For relatively thin adsorbate layers the current is limited by the unavailability of electronic states in the transparency window. (b)–(c) For thicker layers the energy levels become denser and cover more and more uniformly the transparency window leading to a gradual increase (on the average) of the emission current.

The same conclusion may be reached by examining the emission current given by Eq. (13). For increasing values of $d$ the integration range covers more and more the transparency window of the adsorbate and the current correspondingly increases. When the dielectric constant of the adsorbate is small, the energy levels are well separated and Eq. (13) actually does not hold. The variation of the layer thickness severely perturbs the emission current until the adsorbate layer becomes thick enough to cover the entire transparency window with dense energy levels [Fig. 3(a)].
window wider. Then, by increasing the adsorbate layer thickness, the density of energy levels increases, too. These two effects combined will increase the number of energy levels passing by the transparency window and will make less important any change in current due to modifications in the energy scheme. Obviously, the direct effect of such behavior will be the increase of the temporal stability of the emission current at high operation temperatures up to values similar to those corresponding to clean surfaces. This, in turn, may again mask the real cleanliness status of the emitting surfaces at high temperatures: clean-surface emission stability may be obtained even if desorption left enough adsorbate on the emitter (CNT) caps.

As a final point, we turn to the FEEED corresponding to the emission through thick adsorbates. This may be analyzed through Eq. (12) and is expected to have a comb-teethed shape due to the simplified energetic structure of the localized states in the adsorbate. Clearly, even if reports of structured FEEED peaks for CNTs exist, such a simple shape cannot be expected in practice. The triangular potential well for the adsorbate is too simple to be actually realized. Nevertheless, a more careful analysis that should include a partial heating of the electrons in the adsorbate before tunneling in vacuum might account for various observed effects such as FEEED peak position and displacement with the applied voltage and shape variation of the FEEED peak with temperature. We defer this study for another article.

IV. CONCLUSIONS

The electron field emission from relatively thick layers of coatings or adsorbates on nanometer-sized field emission tips was computed in a simplified model of sequential (incoherent) tunneling from a triangular potential energy well created in the dielectric layer by the external field penetration. Despite its simplicity, the model succeeds in explaining some experimentally observed effects such as current enhancement with layer thickness increase and the high-field decrease of the emission current with increasing temperature. While not precluding coherent tunneling through adsorbate layers, the comparison between the results of the present model and the existing experimental data supports the conclusion that incoherent tunneling might be a competitive electron field emission mechanism for the case of relatively thick adsorbate/coating layers on sharp emitter caps.

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