ON ELECTRON FIELD EMISSION FROM NANOCARBONS

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Introduction

Electron field emission from various carbon nanomaterials has recently attracted much attention for applications. However, although in last decade, considerable progress has been achieved in fabricating the devices based on electron emission from carbon nanotubes (flat panel displays [1]), the current understanding of field emission from carbons is far from the complete picture of the phenomenon widely experimentally studied [2-4]. Here, we analyze the known experimental facts that do not have a reasonable explanation within the framework of conventional ideas on electron field emission and show a need to reconsider the electron field emission occurrence from carbon nanomaterials. We suggest a mechanism [5] which can solve the existing puzzles.

State-of-the-Art in the Field

The electron field emission from nanocarbons is usually supposed to obey the Fowler - Nordheim (FN) law [6]. Following this approximation, the current density J can be written as

$$J(E) = \frac{\eta a}{\varphi}(E_l)^2 \exp\left(-\frac{b\varphi^{3/2}}{E_l}\right), \qquad (1)$$

where the local electric field E_l is connected with the external macroscopic electric field E as $E_l=\beta E$, φ is the work function and β is the field enhancement factor (likely related to the geometry); a=1.54$\times$10^{-6} A eV V^{-2} and b= 6.83$\times$10^{9} eV$^{-3/2}$ V m^{-1} are universal constants. The factor η describes the geometrical efficiency of electron field emission, i.e., it is equal to the ratio of an actual emitting surface area to an overall surface area.

The experimental data are usually treated as follows. The slope of ln(J/E^2) plotted versus $1/E$ gives the value of $\varphi^{3/2}/\beta$, while the ordinate intercept allows one to derive the value of $\eta\beta^2/\varphi$. In order to estimate the work function the measurements on the field emitted electron energy distribution are carried out [7] which, for example, give the value of about 5 eV for carbon nanotubes. This scheme to treat the data might be correct if the perfect linearity of the FN plot is observed. However, the FN representation of electron field emission from nanocarbons usually contains a characteristic knee, which separates two regions with different slopes. The occurrence of the knee was systematically investigated [8], but the suggested explanation of the knee seems to be uncertain. Although the authors [8] convincingly showed that the low-field region could not correspond to the FN emission, to our best knowledge, their study has not been followed and the low-field slope of the FN plot is still used to treat the experimental data. At such treatments, the discussion of the factor η is skipped though its value could be derived from the low field slopes. We have treated different published data in the low field region and found that the factor η varies from paper to paper even reaching the unreasonable value of about 10^6 (Ref. 9). It is obvious, that such an anomalously high η value is only a formal number and cannot correspond to the FN law. Then, the conventional assumption that the low-field region corresponds to the FN field emission and the current saturation occurs at the high-field region appears to be incorrect. As we will see in the low-field region, the field emission current rather approaches the FN regime and the seeming FN behavior is not more than a simulation. The genuine FN regime is realized only in the high-field region above the knee, where the shift of electron states within finite nanocarbon structures under the electric field becomes sufficient to provide this regime.

The other puzzle concerning the field emission from nanocarbons is related to the absolute values of the current measured. The quite high experimental currents are usually explained by introducing the field enhancement occurring at tiplike structures. However, without the absolute measurement of the local fields at a field emitter, all considerations on the enhancement mechanism remained speculative. The recent result on electron holography of field emitting carbon nanotubes [10] filled an existing gap giving the actual value of the fields. It has been obtained, for example, the field emission current 0.54 μA at the local electric field E_l=1.22 V/nm. Taking the emitting area not exceeding about 100 nm^2 (the nanotube tip), we can estimate that the current calculated according to Eq. (1) is tens of orders lower than the experimental value. Another argument against the conventional occurrence of the FN field emission from nanocarbons also comes from the same paper [10]. The authors claimed that the observed current fluctuations did not follow the fluctuations of the local field, which was found to be quite stable. The latter means that the local electric field is not a main cause of the field emission current.

Discussion

Let us return to the knee on the FN representation of the experimental data. The sharp character of the knee separating two regions with the different slopes means that there exists a threshold process in the low-field region, which is responsible for the appearance of the seeming (but not real) FN behavior. In the high-field region, the current can be formally described by Eq. (1) but the mechanism of this field emission requires an additional consideration in order to satisfy the recent experimental data. Summarizing, we have to conclude that the recent results discussed above show an impossibility to describe the experimental current if the field emission occurs under the external local field through the 5 eV barrier between carbon and a vacuum. At the same time, the experiments on the field emitted electron energy distribution show that the electrons really escape the nanocarbon through such a barrier. In order to disprove this apparent contradiction and explain the existence of the knee on the FN plot, we suggest that the electron field emission from nanocarbon occurs as a sequence of some intrinsic threshold field emission followed by the electron tunneling into a vacuum.

Let us dwell on our mechanism in detail. Carbons can exhibit both metallic and semiconducting properties [11]. Then, even carbon nanotubes of metallic type contain semiconducting regions. Due to the contact potential difference the junctions between regions of different types create barriers of low energy. The electron tunneling through such a barrier injects the additional electron into the semiconducting region. Such a tunneling is possible only if the states in the conduction band in the semiconducting region lie below the Fermi level in the metallic region (see the band diagram in Figure 1). Since the external electric field lowers the conduction band (initially lying above the Fermi level), then tunneling may become possible only at a certain threshold field. Actually, because of the finite temperature, tunneling is possible even when the bottom is above the Fermi level, and therefore, the probability to tunnel appears to be not a threshold function of the external field, but a smeared one. The latter effect explains the unreasonable slope of the FN plot at the low field. After the tunneling into the semiconducting region, the electron is trapped there. Being an additional separated charge it creates a local electric field sufficient for the carbon electrons to escape into a vacuum even through the potential barrier of few eV. Summarizing, we consider the electron emission from nanocarbons as two successive processes: (1) Tunneling through the low-energy barrier from the metallic region into the semiconducting region under the external macroscopic electric field and (2) tunneling through the high-energy barrier from the semiconducting region into a vacuum under the Coulomb field of an additional electron appearing in the first process.

The second process itself provides the current independent of the electric field. Taking the electric field of the additional electron to be the Coulomb one and integrating Eq. (1) for different distances between this electron and the surface, we ascertained that this electron could provide the overall tunneling current from one site of the order of tens μA at the work function of 5 eV. This current is much higher than that measured in the experiments. However, as we mentioned before, the second process occurs only as the consequence of the first one. It should be noted that the suggested mechanism implies that after initiating the emission into a vacuum, the trapped electron having created the field sufficient for this emission recombinates with the formed hole. Then, the number of electrons tunneling through the junction between the two regions corresponds to the number of electrons escaping into a vacuum and the resulting emission current is limited by the slowest process – the tunneling through the junction. This current obeys the FN law with the low barrier energy and the external macroscopic (nonenhanced) electric field. At the same time the escape into vacuum occurs in the second process, and therefore, the field emitted electron energy distribution corresponds to the barrier energy of 5 eV.

The knee in the FN plot appears (within the framework of our model) at $E=\varphi/\delta$, where $U=E\delta$ is the lowering of the conduction band within the semiconducting region of size δ at the electric field E. We have found that the sharp knee in the FN plot occurs when

$\varphi >> k_B T$. When φ is comparable with $k_B T$, the knee smears and becomes undetectable. Then, in order to keep the main idea of the knee at room temperature, we have to require φ to be of the order of 1 eV. Since φ and E enter into the expression for tunnelling current in a combination $\varphi^{3/2}/E$, it leads to a need in the field enhancement factor, β, of about 100 at φ~1 eV. Such an enhancement can naturally appear in our model. Indeed, if the alternation of metallic and semiconducting regions occurs within the solid in the external electric field, the magnitude of the field within the semiconducting region is higher than the macroscopic value. This slit enhancement is well known for heterogeneous systems [12]. It leads to the characteristic enhancement of $\beta=\Delta/\delta$, where Δ is the size of the metallic region and can be of the order of 100 (see Ref. 12).

Figure 2 shows the FN plots of field emission current from carbon nanotubes measured in Ref. 19. The fitting according our model is given as well. The slit enhancement of the electric field is taken into account. The fitting parameters (which allow the knee occurrence within the present model at room temperature) are given in Table 1. As one can see, in the case of the nanotubes treated with different duration by hydrogen plasma (Ref. 9), with increase of the treatment time the barrier height (φ) lowers, the size of semiconducting region (δ) decreases and the enhancement factor ($\beta=\Delta/\delta$) increases. Such a parameter behavior seems to be reasonable and self-consistent.

The model can also describe temperature effects in electron field emission from carbon nanotubes during thermal heating recently reported [13]. Such a description is impossible within the framework of conventional ideas on field emission from nanocarbons. We calculated the field emission current according our model and formally extracted (as described in Ref. 2) the effective field enhancement factors in assumption of a conventional one-stage tunneling through the 5 eV barrier. The obtained values are plotted vs. temperature in Figure 3. The values extracted in the same way in Ref. 13 are given in the same Figure. Although, so high values of the field enhancement factor as shown in Fig. 3 (as well as the calculation of the field enhancement in this way) are unreasonable, the comparison of those numbers has sense. Thus, the good agreement seen in Fig. 3 demonstrates that our model can describe electron field emission from nanocarbons in the wide temperature range. Note once again, that such a description is impossible in the framework of conventional field emission models considering tunneling through the 5 eV barrier.

Conclusions

Summarizing, our two-process model on electron field emission from nanocarbons (unlike other existing one-process high-barrier models) can describe the temperature effects together with the knee occurrence at the proper choice of parameters.

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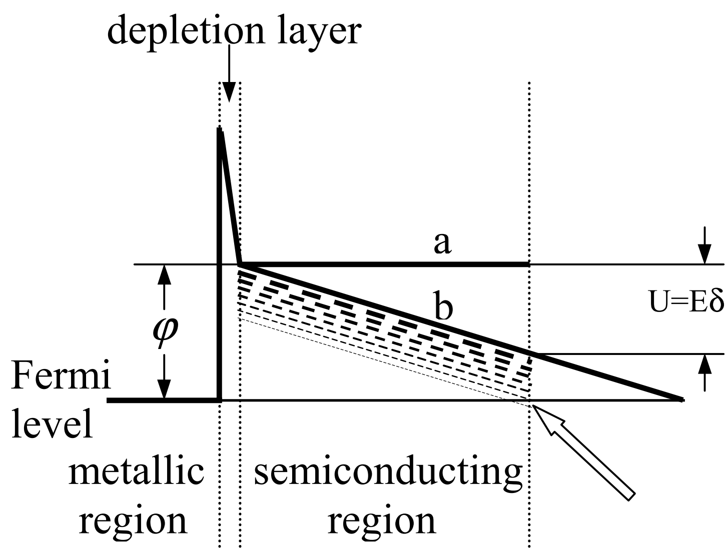

Figure 1. Idealized band diagram illustrating the tunneling from metallic region to semiconducting region with size δ. Lines marked (a) and (b) correspond to the bottom of the conduction band with no electric field applied and with the field *E*, respectively. In the infinite structure tunneling is always possible at any electric field applied. In the finite structure at *T=0* tunneling is possible only if the lowering *U* is bigger than the barrier *φ*. The states, where tunneling is possible, are shown by the arrow.

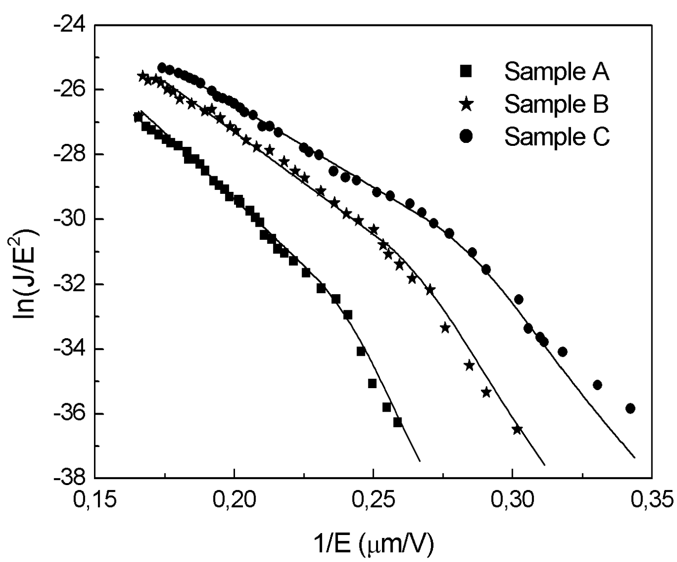

Figure 2. The Fowler-Nordheim plots of field emission current from carbon nanotubes treated by hydrogen plasma (Ref. 9). Solid lines correspond to the fitting made according to the present model, which takes into account the temperature.

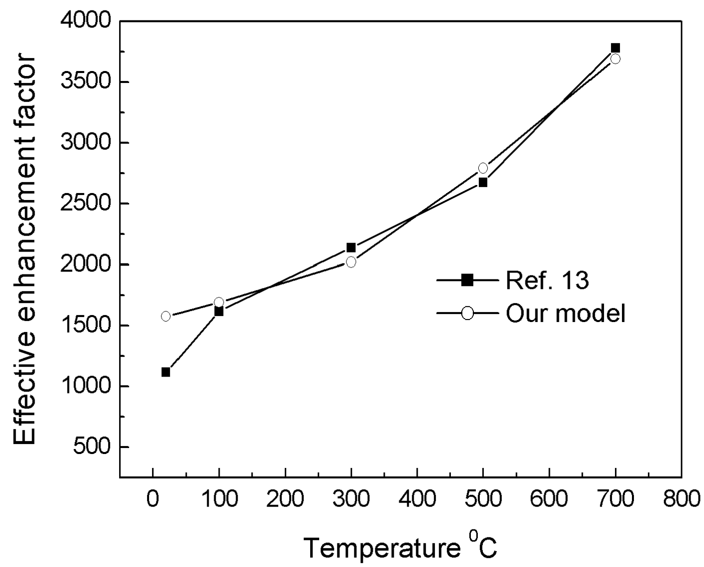

Figure 3. The effective field enhancement factor formally extracted from the FN plot (Ref. 13 and our model for data [13] fitting) in assumption of the Fowler-Nordheim field emission through the 5 eV barrier.

Table I. Fitting parameters for the FN plots of field emission from carbon nanotubes treated by hydrogen plasma. The experimental data for the fitting shown in Fig. 2 were taken from Ref. 9.

	μ, eV	φ, eV	δ, nm	β
Sample A (Ref. 9, 0 min)	0.1	1.20	3.0	100
Sample B (Ref. 9, 2 min)	0.1	1.05	2.8	105
Sample C (Ref. 9, 5 min)	0.1	0.95	2.6	110

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