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Charging and discharging processes of carbon nanotubes probed by electrostatic force microscopy

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Electrostatic properties of individually separated single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multiwalled carbon nanotubes (MWCNTs) deposited on insulating layers have been investigated by charge injection and electric force microscopy (EFM) experiments. Delocalized charge patterns are observed along the CNTs upon local injection from the EFM tip, corresponding to (i) charge storage in the nanotubes and to (ii) charge trapping in the oxide layer along the nanotubes. The two effects are dissociated easily for CNTs showing abrupt discharge processes in which the charge stored in the CNT are field emitted back to the EFM tip, while trapped oxide charge can subsequently be imaged by EFM, clearly revealing field-enhancement patterns at the CNT caps. The case of continuous discharge processes of SWCNTs, DWCNTs, and MWCNTs is discussed, as well as the evolution of the discharge time constants with respect to the nanotube diameter. © 2006 American Institute of Physics.

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I. INTRODUCTION

The understanding of the electronic behavior of charged carbon nanotubes (CNTs) and of CNTs in a charged environment is a crucial issue in electronic applications such as field-effect transistors or CNT-based nanoelectromechanical devices. Electrostatic force microscopy appears as a dedicated tool to map and study the spatial distributions of electric field and charges at the nanometer scale, but up to now only few studies have applied this technique to carbon nanotubes. For instance, it has been found that CNTs can exhibit a potential barrier leading to charge trapping in CNT loops on insulating surface, confirming the importance of substrate charges around the CNTs in the operation of electronic devices. Up to now, electrostatic imaging and charging issues have been studied mainly in the case of single-walled carbon nanotubes (SWCNTs). One experimental work has so far been published on the charging properties of multiwalled carbon nanotubes.

We present in this paper an extensive discussion about charging effects in carbon nanotubes deposited on oxide (SiO2) layers. The article is organized as follows. We first describe the sample preparation and experimental procedures used for charge injection and detection and characterize both the local charge injection in SiO2 layers and the delocalized charge patterns observed in the case of CNTs. In a second part, we focus on CNTs exhibiting abrupt discharging at nanotube defect points or at the nanotube caps. These field-emission effects enable to easily identify charge storage in the nanotube versus charge storage in the oxide layer along the nanotubes. The field-enhanced charge emission patterns from CNT caps are also analyzed as a function of the CNT cap diameter. In the last part we comment on discharging processes which are not related to abrupt discharging effects of the nanotubes. The continuous discharging of SWCNTs, double-walled carbon nanotubes (DWCNTs), and multiwalled carbon nanotubes (MWCNTs) is discussed, as well as the evolution of the discharge time constants with respect to the nanotube diameter.

II. SAMPLES AND EXPERIMENTS

A. Samples

Purified SWCNTs, DWCNTs, and MWCNTs grown by catalytic carbon vapor deposition were obtained commercially from Nanocyl (Belgium). As-bought nanotubes were placed in dichloromethane solutions, separated by low-power ultrasonication, and finally dispersed by spin coating onto substrates, with a tunable CNT density in the range of 1–10 per μm2. Electrostatic experiments have been performed using doped silicon substrates covered with a 200 nm thermally grown insulating SiO2 layer. Before the CNT deposition, arrays of metal markers have been fabricated using electron beam lithography in order to localize individual nanotubes on surfaces and consist in 30 nm thick platinum squares of 500×500 nm2 size separated by a 5 μm pitch.
shift $\Delta f$ is due to the increase of the tip-substrate capacitance during the linear pass of the tip over the CNT and is thus a capacitive signal induced by the presence of nanotube deposited on the surface. Since capacitive forces are attractive and proportional to $(V_{\text{EFM}})^2$, the corresponding EFM signal is a negative frequency shift, irrespective of the sign of $V_{\text{EFM}}$. Uncharged CNTs are hence always imaged as dark features in EFM images. This, however, no longer holds when the CNTs are charged, because the total electric force also includes a component proportional to the nanotube charge $Q$ and to $V_{\text{EFM}}$. In our experiments, the nanotubes are negatively charged ($V_{\text{inj}} < 0$), and we used negative $V_{\text{EFM}}$ values for charge detection ($V_{\text{EFM}} = -2$ or $-3$ V). Consequently, the additional force component is repulsive and leads to a positive frequency shift imaged as a bright feature in EFM images. Charge and capacitive force gradients, however, compete with each other, so even for $V_{\text{EFM}} V_{\text{inj}} > 0$, charged nanotubes can only be imaged as bright features provided that charge signals predominate over capacitive EFM signals. Such imaging conditions can be reached either for sufficiently charged CNTs, or by lowering the detection bias $V_{\text{EFM}}$. These scanning conditions have been used for all EFM images reported in this article, so that dark and bright features in EFM images will always correspond here to capacitive and charge effects, respectively. Finally, in practice, reference EFM images of the CNTs are always acquired prior to charging experiments as depicted in Fig. 1(a), so as to check the CNT electrostatic state before charging. Charge injection is then performed [Fig. 1(b)] as described above, and the EFM image is finally recorded after charge injection [Fig. 1(c)].

C. Oxide charging

We first characterize the 200 nm thick thermal oxide layers used in this work, which will be later used for comparison with charge injection experiments performed on CNTs. An EFM scan before charging is shown in Fig. 2(a) (10 Hz color scale) and displays no capacitive feature since the SiO$_2$ surface is flat. After injection (here with a tip biased at $V_{\text{inj}} = -5$ V during 2 min), the EFM scan [Fig. 2(b), 10 Hz color scale] exhibits a bright circular spot of maximum positive frequency shift $\sim 7.5$ Hz at the injection point. At a fixed elapsed time $t$ after charge injection, the EFM charge signal is analyzed using a two-dimensional spatial Gaussian distribution law $\Delta f = A/(2\pi\sigma^2)\exp\left[-r^2/2\sigma^2\right]$, where $r$ accounts for surface coordinates, $A$ (in Hz nm$^2$) is the surface integral of the EFM charge signal, and $\sigma^2$ (in nm$^2$) is the squared standard deviation of the charge distribution. $A$ and $\sigma^2$ are thus adjustable parameters which vary as a function of $t$. The diffusion coefficient $D$ of surface charges can be simply obtained by $\sigma^2 - \sigma^2(t=0) = 2Dt$.

The evolution of the fitted parameters $A$ and $\sigma^2$ with $t$ is shown in Fig. 2(c). The surface charge is found to weakly diffuse in the oxide surface with a diffusion coefficient $D \sim (20 \text{ nm})^2/\text{min}$ measured from a linear fit of $\sigma^2$ as a function of time. The EFM signal integral $A$ is also found to slightly decrease within the 25 min time scale of Fig. 2(c).
a larger time scale, almost exponential decays can be observed, with typical decay times of the order of $\sim 40$ min.

### D. CNT charging

First we present charging experiments performed on a 19 nm diameter multiwalled nanotube [topography image in Fig. 3(a)]. The EFM image acquired with $V_{\text{EFM}} = -3$ V before charge injection is shown in Fig. 3(b) and reveals a dark feature corresponding to the capacitive footprint of the uncharged nanotube. Charge injection was made using $V_{\text{inj}} = -5$ V during 2 min at the injection point indicated by the arrow in Fig. 3(a). The delocalization of the injected charge along the MWCNT is visible from the EFM image of Fig. 3(c) (taken after the injection) in which the nanotube is homogeneously bright (positive frequency shift) as a result of the dominant repulsive interaction between the MWCNT negative charge and the negative charge at the biased tip apex. The delocalization of the injected charge over microns along the CNTs is consistent with previous results.\(^5\),\(^6\) From preliminary numerical calculations of the MWCNT charge densities from EFM signals, we estimate the linear charge density to be here $\sim 160 |e|/\mu$m, lower\(^6\) than the value expected from a charging of the CNT-substrate capacitance. The detailed and quantitative analysis of the CNT charge densities will, however, fall beyond the scope of this paper.

The cross sections of EFM signals are displayed in Fig. 3(d) and have been taken at the CNT position indicated by

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**FIG. 2.** (Color online) (a) EFM image (10 Hz color scale, $V_{\text{EFM}} = -3$ V) of a 200 nm thick thermally grown silicon dioxide layer. Since the sample surface is almost flat, no capacitive feature can be seen here. (b) EFM image acquired after a local charge injection ($V_{\text{inj}} = -5$ V for 2 min). The bright circular feature corresponds to a maximum frequency shift $\Delta f \approx +7.5$ Hz. (c) Analysis of the EFM charge signal integral amplitude (circles) and of the EFM charge signal width, as measured from the squared standard deviation $\sigma^2$ (squares) in a Gaussian distribution model.

**FIG. 3.** (Color online) (a) Atomic force microscopy image of MWNT of $\sim 19$ nm diameter on a 200 nm silicon dioxide surface. (b) EFM image ($V_{\text{EFM}} = -3$ V) acquired before charging (10 Hz color scale) with a tip-substrate distance $z \approx 100$ nm. (c) EFM image taken in the same conditions, after a charge injection performed at the point indicated by an arrow in (a), using $V_{\text{inj}} = -5$ V for 2 min. (d) Cross sections of the EFM scans for the cases (b) and (c). The position of the cross section is shown by the horizontal bar in (b). The full width at half minimum (FWHM) of the EFM signals before and after charging (respectively, $\sim 100$ and $440$ nm) is marked by the triangles as a guide to the eye.
the horizontal bar in Fig. 3(b). The full width at half minimum (FWHM) of the EFM signal of the uncharged nanotube equals ~100 nm and is already larger than the apparent CNT diameter in the topography image, as can be seen from the EFM images in Figs. 3(a) and 3(b). This simply illustrates the lower spatial resolution of EFM compared to topography measurements, which is due to the long range of electrostatic forces and the large (80–100 nm) tip-surface distance during EFM data acquisition. A more striking feature is the broadening of the EFM signals when the nanotube is charged (440 nm FWHM), as seen from Fig. 3(d) and from the comparison between Figs. 3(b) and 3(c). This effect does not occur in EFM experiments performed in nanostuctures deposited on conductors,\textsuperscript{11} where the width of EFM signals remains unchanged after charging. The two situations can be explained by the difference in the electrostatic screening induced by the substrate supporting the nanostuctures, as illustrated in Fig. 4. Whatever the nature of the substrate supporting the nanostucture, the EFM capacitive signal stems from the polarization of the nanostucture in the electric field induced by the EFM tip and thus corresponds to an effective dipole oriented perpendicular to the surface, as illustrated in Fig. 4(a). The EFM charge signal, however, strongly depends on the nature of the host substrate. When nanostuctures are deposited on conductors, stored charges are screened by substrate image charges and also behave as surface dipoles oriented perpendicular to the surface\textsuperscript{11} as sketched in Fig. 4(b). In this situation, both charge and capacitive EFM signals consequently display similar variations, and thus identical FWHMs as observed in Ref. 11. In contrast, the use of a 200 nm thick SiO$_2$ layer on the substrate makes the ~100 nm tip-nanostructure distance fairly smaller than the 400 nm separation between the nanostructure charge and its electrostatic image with respect to the substrate. In that case, the nanostructure charge is not screened by the conductive substrate at first order and thus behaves like a charge rather than a dipole [see Fig. 4(c)]. As a result, the nanostructure charge signal is expected to be much more isotropic than the capacitive signal. This effect accounts for the bigger FWHM of the CNT charge signal [EFM image of Fig. 3(c)] compared to the CNT capacitive signal [EFM image of Fig. 3(b)]. Finally, the change observed experimentally in the FWHM of the CNT EFM signal upon charging is a demonstration of the neutral character of the nanotube after its deposition on the silicon dioxide surface and prior to charging experiments, in contrast with experiments performed on conductive substrates, where charge can be transferred between the substrate and the CNTs.\textsuperscript{17} The upper bound of the charge densities prior to charge injection can be obtained from Fig. 3(d). As seen previously, the narrow FWHM of the EFM signal prior to charging indicates that the CNT is almost neutral, as compared with the larger FWHM of the EFM signal measured after charging. More quantitatively, we estimate that the CNT charge—if any—before charge injection experiments corresponds to an EFM signal less than 0.5 Hz, and thus to a maximum $|10 e/\mu m|$ linear charge density.

III. ABRUPT DISCHARGE PROCESSES IN CARBON NANOTUBES

In this section, we review the phenomena associated with abrupt discharge processes in carbon nanotubes. First, we discuss discharging at single/multiple points along the CNT and at the CNT caps, which unambiguously demonstrate charge storage in carbon nanotubes. Then, we report on the field emission of charges to the oxide layer supporting the CNTs and its enhancement at the CNT caps.

A. Abrupt discharges at single and multiple defects

A sudden discharge behavior of the charge injected in a MWCNT is presented in Fig. 5. In Fig. 5(a) the topography of a MWCNT with ~18 nm diameter and ~2.3 $\mu$m length is shown. The point used for charge injection experiments is indicated by the arrow. The EFM signal before charging [Fig. 5(b)] shows a negative frequency shift equal to 1.2 Hz. After the injection ($V_{inj}=-6$ during 3 min) the EFM scan is started from the bottom to the top [Fig. 5(c)]. The nanotube appears as a bright feature with maximum frequency shift +8.2 Hz), but then undergoes three abrupt discharges at the points labeled d1, d2, and d3, each discharge occurring within one scan line. The CNT EFM image was then found stable upon further scanning (no more sudden discharges), indicating that the bright halo surround-

![Image of a cross-section schematics of a neutral CNT placed in the electric field created by the EFM tip biased at $V_{EFM}$. The polarized CNT is detected as a surface dipole. The CNT charge is screened by its electrostatic image with respect to the substrate and is detected as a dipole field.](image-url)
ing the CNT capacitive footprint after the third discharge in Fig. 5(c) is due to charge emitted by the CNT and trapped in the oxide surface. This effect will be discussed in the following. The CNT frequency shifts before and after d1 are compared in Fig. 5(d) and show that the capacitive footprint of the CNT topography can be already clearly identified after the first discharge while the EFM signal was dominated by the CNT charge just after injection.

To associate the discharge locations as specific nanotube points, an injection experiment has been made again at the same nanotube point using $V_{\text{inj}}=-7$ V. The resulting EFM image scanned from top to bottom is shown in Fig. 5(e) and was acquired ~2 h after the scan in Fig. 5(c). Two abrupt discharges are evidenced in Fig. 5(e) and correspond to the discharge points labeled d3 and d2 in Fig. 5(c). This demonstrates that abrupt discharges are induced by specific points along the MWCNT. At the discharge points, the CNT charge is field emitted back to the EFM tip apex which is grounded and intermittently brought into contact with the CNTs during the topography pass. The fact that the discharge occurs during topography imaging will be demonstrated in the next section. Abrupt discharges were observed mainly for MWCNTs with diameter smaller than 25 nm, with a maximum density of discharge points of a few $\mu$m$^{-1}$ in case of multiple discharges.

We assume that the sudden discharge points are related to nanotube defects, such as vacancies and openings in the outer shells, or to metallic catalysts which can remain present inside the nanotube. The presence of defects in the investigated nanotubes has been confirmed by high resolution transmission electron microscopy (HRTEM) studies. Combined EFM and HRTEM experiments would, however, be required to clearly relate the abrupt discharge points to the CNT structural properties.

**B. Abrupt discharges at the CNT caps**

Two examples of sudden discharges at MWCNT caps are evidenced, in the case of an individual MWCNT [Figs. 6(a) and 6(b)] and for a MWCNT network [Figs. 6(c) and 6(d)]. In both cases, the MWCNTs have been charged using $V_{\text{inj}}=-5$ V for 2 min and EFM images acquired from top to bottom. The nanotubes are first observed as negatively charged [bright features in Figs. 6(b) and 6(d)]. In both cases, the MWCNT sudden discharge is seen to occur when the tip gets in intermittent contact with the CNT during the topography scan: discharges in Figs. 6(b) and 6(d) are correlated with the CNT appearance in the topography scans of Figs. 6(a) and 6(c). This demonstrates that the nanotubes are discharged during topography scanning, but not during the EFM data acquisition. Hence, the CNT caps act as efficient discharging points, thus supporting our claim that the abrupt discharge is based on a field-emission process, in which the grounded EFM tip acts as counterelectrode. After the discharge, the nanotubes also exhibit a bright halo as after the discharge in Figs. 5(c) and 5(e), indicating the presence of residual negative charge, which will be discussed in the next section.
FIG. 6. (Color online) (a) AFM topography image of one end of MWCNT with length 1.6 μm and diameter ~21 nm. (b) EFM scan after a charge injection experiment using $V_{\text{inj}}=-5$ V for 2 min. The image is scanned from the top to the bottom as indicated by the arrow. A sudden discharge appears directly at the nanotube cap (4.5 Hz frequency drop). (c) AFM topography image of a part of a MWCNT network (total length >15 μm; diameter at the upper CNT cap ~10 nm). The pixels visible in the topography image are due to a low resolution data acquisition. (d) EFM scan after charge injection with the tip biased at $V_{\text{inj}}=-5$ V. The scan direction is indicated by the arrow. An abrupt discharge is visible at the upper part of the nanotube network.

C. Residual charge emission along CNTs

The EFM images of Figs. 5(c) and 5(e) (after discharge) and of Figs. 6(b) and 6(d) (after discharge at the CNT caps) all display a residual negative charge along the nanotube in the form of a bright halo around the nanotubes. The observation of the halo is due to the different FWHMs of charge and capacitive effects as pointed out in Sec. II D and to the imaging conditions used in this work ($V_{\text{inj}}<V_{\text{EFM}}>0$). The actual issue is to determine whether this negative charge corresponds to electrons still stored in the CNT, or to charge emitted by the CNT and trapped on the oxide surface. If not discussed, the issue of surface charge emission can lead to controversial interpretations of EFM images.5,6 In Figs. 5 and 6, the bright halos observed after charging can be unambiguously attributed to charges trapped on the oxide surface for the following reasons: (i) the residual charge pattern cannot be removed by discharging the nanotube (i.e., performing a charge injection experiment on the CNT using $V_{\text{inj}}=0$ V); (ii) the residual charge pattern decays very slowly with time (at least a few hours) so that no evolution can be observed in the first subsequent EFM images acquired after the abrupt discharge phenomena. This behavior strongly contrasts with that of charge injected in the CNTs, which can be either removed by a local charge injection using $V_{\text{inj}}=0$ V, or abruptly emitted back to the EFM tip as described in the previous section. We finally would like to comment on the decay times of oxide charges stored in the vicinity of the nanotubes, which are found to be much larger than decay times on the bare oxide (~40 min, as seen from Sec. II C). The decay of charge injected in bare thin oxide layers has been proposed to result from the attraction between the oxide charge and their substrate images,12 leading to a gradual move of oxide charges towards the conductive substrate electrode. In our case, the oxide charge near the CNTs is also subjected to an attractive image force from the CNTs themselves. This attractive interaction is consistent with the much longer retention times observed for oxide charge along the CNTs.

D. Enhanced charge emission at the CNT caps

We now report on the charge emission from the nanotube caps. Two examples are shown in Fig. 7. Figure 7(a) shows the topography of a MWCNT with different cap diameters (11 and 27 nm for the lower and upper caps, respectively). The EFM image of the residual charge emission pattern observed after charge and discharge is given in Fig. 7(b) and shows an enhanced charge emission at the smaller cap diameter. In contrast, no significant emission is observed in the vicinity of the upper cap. The frequency scale of the EFM image is 10 Hz. (c) Topography image of a 21 nm diameter MWCNT (d) EFM image (20 Hz frequency scale) after charge injection ($V_{\text{inj}}=-5$ V during 2 min) and the MWCNT discharge. It shows an enhanced charge emission near both caps (+3 Hz; see dark circles) in comparison with the charge emitted along the nanotube (+1.4 Hz frequency shift).
It is known that the field enhancement at the CNT caps depends on the cap shape and on the diameter of the nanotube. It is also considered that MWCNTs have different electron emission parameters than SWCNTs. To test this dependence in our experiments, we plotted in Fig. 8 the ratio of the emitted charge intensities at the CNT cap compared to the CNT side, as a function of the CNT cap diameter. The inset shows a zoom of the data for SWCNTs with diameter <1.6 nm.

IV. CONTINUOUS DISCHARGE OF CNTS

We discuss in this section discharging phenomena which are not related with abrupt discharging processes. We present continuous discharging of SWCNTs, DWCNTs, and MWCNTs and comment on the evolution of the discharge time constants with respect to the nanotube diameter.

A. Continuous fast discharge of SWNTs and DWNTs

Charging experiments are presented in Fig. 9 for a SWCNT with 1 nm diameter. The white squares visible on this image are 500 × 500 nm² metal markers prepared by e-beam lithography and used for the nanotube localization. The EFM scan before injection ($V_{\text{EFM}} = -3 \text{ V}$) is shown in Fig. 9(b). The nanotube and metal markers appear here as dark features, corresponding to uncharged objects. The EFM scan after injection ($V_{\text{ej}} = -5 \text{ V}$ during 3 min) is displayed in Fig. 9(c) and shows the delocalization of the injected charge along the whole SWCNT length ($\sim 30 \mu\text{m}$), while the square metal markers remain uncharged. However, no abrupt discharge occurs in Fig. 9(c). As a consequence, one cannot estimate directly the amount of charge stored in the CNT and the amount of charge trapped on the oxide surface, in contrast with CNTs exhibiting abrupt discharge phenomena as shown in Sec. III. To circumvent this, the CNT has been continuously scanned, and the two first images follow-...
The time between two successive EFM images is 40 min. A discharge—though not abrupt here—is evidenced by comparison of the SWCNT EFM images of Figs. 9c and 9d, respectively. The EFM scan has been taken from left to right, as indicated by the white arrow. The left part of the nanotube appears much brighter than right one, indicating that the nanotube gets gradually discharged during the scan acquisition. Metal markers remain uncharged throughout the scan. (d) EFM image taken 70 min after charging, showing the dark feature associated with the nanotube capacitive signal, surrounded by a faintly bright homogeneous halo. (e) Cross sections at the position labeled 1 in (b) taken before charging, after charging and 70 min after charging. (f) Same plot at the position labeled 2 in (b). The discharge of the CNT during the EFM scan shown in (c) is visible by comparison between the cross sections in (e) and (f).

ing Fig. 9(c) are shown in Figs. 9(d) and 9(e), respectively. The time between two successive EFM images is 40 min. A discharge—though not abrupt here—is evidenced by comparison of the SWCNT EFM images of Figs. 9(c) (5.6 Hz frequency shift at midscan) and 9(d) (4.1 Hz frequency shift at midscan), while no significant change is observed upon further scanning, as seen by comparison of Figs. 9(d) and 9(e), and from the following EFM scans (not shown here). We conclude that the SWCNT in Fig. 9 undergoes a continuous discharge process, in contrast with the abrupt discharge mechanisms presented in Sec. III.

We now discuss the injection experiment performed on 5.5 μm long double-walled nanotube with diameter 1.5 nm [topography scan in Fig. 10(a)]. The EFM scan prior to charging is shown in Fig. 10(b). Both the uncharged DWCNT and metal markers appear as dark features in this image. The data were taken with $V_{\text{EFM}}=-2$ V. The EFM scan has been performed from left to right, as indicated by the white arrow. The left part of the nanotube appears much brighter than right one, indicating that the nanotube gets gradually discharged during the scan acquisition. Metal markers remain uncharged throughout the scan. (d) EFM image taken 70 min after charging, showing the dark feature associated with the nanotube capacitive signal, surrounded by a faintly bright homogeneous halo. (e) Cross sections at the position labeled 1 in (b) taken before charging, after charging and 70 min after charging. (f) Same plot at the position labeled 2 in (b). The discharge of the CNT during the EFM scan shown in (c) is visible by comparison between the cross sections in (e) and (f).
bright, but a clear decrease of the charge can be observed from left to right, as confirmed by the cross sections in Figs. 10(e) and 10(f). In particular, the frequency shift dip associated with the DWCNT is visible in the right part of Fig. 10(c).

To show that this charge decay is due to the CNT discharge, an EFM scan obtained 70 min after charging is shown in Fig. 10(d). The nanotube capacitive footprint is here clearly and homogeneously visible and superimposed on a faintly bright halo. This demonstrates that Fig. 10(c) corresponds to a gradual discharge of the DWCNT with an ~20 min decay time constant, while Fig. 10(d) corresponds to the EFM image of the discharged DWCNT, together with residual surface charges corresponding to the faintly bright halo. The three consecutive charge states of the DWCNT on the oxide surface (neutral DWCNT, charged DWCNT together with oxide charges, and finally oxide charges after the DWCNT discharge) are also evidenced in the frequency shift cross sections in Figs. 10(e) and 10(f). Additionally, the square metal markers in the vicinity of the DWCNT remain unchanged in the EFM images of Figs. 10(b)–10(d) and are thus not affected by the DWCNT and oxide charging.

B. Continuous slow discharge of MWCNTs

Finally, we go back to the case of MWCNTs for which no abrupt discharge could be found. Two examples are presented in Fig. 11. First of all, a ~30 nm diameter MWCNT showing only a weak decay of the total charge signal 13 h after charge injection [see Figs. 11(a) and 11(b)]. In this case, a blurring of the MWCNT charge signal can be observed in Fig. 11(b). This is confirmed by the frequency shift cross section in Fig. 11(c), also showing the resurgence of the MWCNT capacitive frequency shift dip associated with the larger FWHM of the EFM signal 13 h after charge injection. Since the total EFM signal is approximately unchanged between Figs. 11(a) and 11(b), we assume that the observed blurring of the EFM image corresponds to a slow emission of the MWCNT charge to the oxide.

The second example is the 19 nm diameter MWCNT of Fig. 3. EFM images acquired after charging and 90 min after charge injection are shown in Figs. 11(d) and 11(e), respectively. The FWHM of the EFM signal is here unchanged, but the charge signal is weaker in Fig. 11(e) (+4.1 Hz) compared to Fig. 11(f) (+6.4 Hz), which means that the MWCNT is discharging to the EFM tip. No abrupt discharge could, how-
ever, be observed upon continuous scanning between the two scans of Figs. 11(d) and 11(e), demonstrating that the discharge is here continuous and similar to the case of the DWCNT of Fig. 10.

The estimation of decay times associated with continuous discharge processes of CNTs is ~20 min in the case of the SWCNT and DWCNT of Figs. 9 and 10 and ~100 min in the MWCNT of Figs. 11(d) and 11(e). From our experiments, we found that charge decay times increase with the CNT diameter. This is consistent with the case of the larger diameter MWCNT shown in Figs. 11(a) and 11(b) for which the charge is not emitted back to the EFM tip upon continuous scanning, but rather slowly migrates to the oxide surface. The decrease of charge decay times for smaller diameter CNTs may be related either to enhanced field effects due to the CNT curvature, or to the distribution of charge in the CNT shells in the case of MWCNTs. This study, however, falls beyond the scope of this paper.

V. CONCLUSION

We have reviewed in this paper electrostatic force microscopy and charge injection experiments performed on individually separated SWCNTs, DWCNTs, and MWCNTs deposited on thin insulating layers. Charge injection in carbon nanotubes is clearly evidenced from abrupt discharge processes occurring at nanotube specific points or at the nanotube caps, in which the delocalized CNT charge is field emitted back to the EFM tip. CNTs EFM images taken after abrupt discharging also reveal residual charges which are identified as emitted by the CNTs and trapped in the oxide surface along the CNTs. Enhanced emission patterns at the CNT caps have been studied as a function of the CNT diameter. Finally, the issue of oxide versus nanotube charging has been discussed in the case of SWCNTs, DWCNTs, and MWCNTs exhibiting continuous discharge processes.

These experiments show that field-emission phenomena play an important role in the electrostatics of individual CNTs probed by EFM and charge injection experiments, but these charges stored in nanotubes should be dissociated properly from charge emitted by CNTs into the oxide. The detailed charge storage mechanisms of SWCNTs and MWCNTs and their relation with classical electrostatics (i.e., do CNTs charge as capacitors?), however, remain to be clearly established from EFM experiments but require a truly quantitative analysis of the CNT charge states from EFM experiments.

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