Effect of Gas Exposure on Field Emission Properties of Carbon Nanotube Arrays**

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Since the discovery of carbon nanotubes (CNTs) by Iijima,[1] intensive research has been performed to discover their rudimental properties and applications. Among the applications, the field emission display (FED), which was originally proposed by De Heer et al.,[2] is of technological importance. A 4.5 inch (1 inch = 2.5 cm) diode-type FED with arrays of CNTs has been realized recently.[3] Naturally formed CNT emitters with small diameters are very crucial in order to reduce the operation voltage. The superior aspect ratio, electrical conductivity, and mechanical stiffness of CNTs are advantageous over conventional semiconductor and metal emitters in FED applications.[4–6] The field emission properties are correlated with the electronic structure of the CNT, which is determined by the chiral angle and diameter of the CNT.[7,8] In addition, it is possible that intrinsic properties such as electrical resistivity, thermoelectric power, and thermal conductivity can be modified by adsorption and desorption of gas adsorbates.[9–11] Therefore, in order to achieve emission stability and longevity of FEDs, understanding the effect of gas adsorbates on the field emission properties is an important issue both technologically and fundamentally.

The field emission currents can in general be explained by the Fowler–Nordheim (F–N) equation. The F–N plot usually shows two characteristic regions: a moderate field where the current–voltage (I–V) curve fits well to the F–N equation and a high field where the I–V curve deviates from the linear F–N plot due to suppression of the current.[12–14] The origin of current saturation from CNTs in the high-field region has long been argued. Although several mechanisms such as space charge effect, tip–tip interactions, localized states, and gas adsorbates have been proposed, it is still not clear if this suppression is an intrinsic or extrinsic property of the CNT. In this report, the effects of gas exposure on field emission properties are studied over the macroscopic regime using a realistic CNT array with an area of 1.5 cm² covered with millions of vertically aligned CNT emitters. Emission currents were measured under an electric field of up to 4.25 V/µm with the currents ranging from tenths of nanoamperes to a few tenths of milliamperes in order to simulate an operational situation of the FED and study the effects of gas adsorbates in a more realistic regime.

The p-type silicon substrate was cleaned ultrasonically in acetone and subsequently in methanol. A TiN thin film with a thickness of about 100 nm, to enhance the adhesion of Ni film to the substrate, was deposited using radiofrequency (RF) magnetron sputtering at a temperature of 600 °C with a RF power density of 2.5 W/cm². This was followed by Ni thin film deposition with a film thickness of 100 nm at a temperature of 350 °C and a RF power density of 0.25 W/cm².[15] During Ni sputtering, a shadow mask with a hole size of 200 µm was placed on top of the substrate for patterned CNT growth. The shadow mask is used not only for the formation of the array structure but also to concentrate the electric field at the areas where carbon nanotubes are grown.

The morphology and grain size of the Ni thin film play a crucial role in the nucleation of the CNTs and the determination of the CNT diameters. The morphology and grain size of the Ni thin film are controlled by the substrate temperature, RF power, and sputtering time. They are also dependent on the morphology of the underlying TiN thin film. These are described well in detail elsewhere.[16] The Ni-patterned substrate is brought into a quartz chamber of the thermal chemical vapor deposition (CVD) system. The substrate temperature of 700 °C is achieved using halogen lamps with a heating rate of 43 °C/min and an Ar gas flow of 500 sccm while maintaining the chamber pressure at 5 torr. C₂H₂ gas of 100 sccm is then introduced into the chamber. Figure 1a shows the morphology of the grown CNTs, which have two distinct areas. The middle of the circular dot displays well-aligned CNTs, as shown in Figure 1b, and the edge part shows longer CNTs than those at the center (see Fig. 1c). These are multiwalled closed carbon nanotubes with an average diameter of 50 nm. Such morphological changes are related to the different gas kinetics during Ni deposition on the shadow-masked substrate. Since the shadow mask is not tightly attached to the substrate, there is a possibility that Ni particles infiltrate below the mask. The morphology of the Ni film below the mask is expected to be different from that in the center of the circular dot. In fact, the Ni thin film at the edge is thinner than...
in the middle, giving smaller grain sizes at the edge and hence a higher growth rate, in good agreement with the previous report.[17]

An as-grown CNT field emission array (FEA) was transferred into a vacuum chamber at a base pressure of $5 \times 10^{-7}$ torr. The gap between the CNT FEA and an anode deposited as an indium tin oxide (ITO) thin layer (with additional green phosphor layers for emission pattern) was 200 $\mu\text{m}$, separated by a glass spacer. The emission currents fluctuate very rapidly for the initial $I-V$ measurements. This fluctuation can be reduced by applying a high voltage for 30 h (called annealing). This annealing was carried out until the emission currents fluctuated less than 2 %. During high voltage annealing, the emission currents decreased gradually and their fluctuation was reduced. Furthermore, the uniformity in the emission pattern was greatly improved. Figure 1d, obtained after high voltage (HV) annealing, shows the emission pattern at a DC bias of 4.25 V/$\mu\text{m}$. A uniform emission pattern is observed over a large area with a high emission current of 2 mA.

In addition to gas exposure, the emission of air-exposed CNT FEA was characterized. The F–N plot obtained right after loading the FEA into the vacuum system, marked by the empty squares in Figure 2a, shows gross fluctuations, i.e., the emission currents after a complete cycle of the $I-V$ curve are different from the starting values. However, the fluctuations decrease with repeating $I-V$ annealings. The fluctuation in the emission currents is significantly reduced after the third $I-V$ annealing, as shown in Figure 2a. We note that with repetition of the annealings some of the brighter emitters disappeared and uniformity in the emission currents was significantly improved.

The enhancement in field emission is attributed to the removal of extremely sharp CNT emitters by wearing out through resistive heating from high emission currents. This would improve the homogeneous distribution of emitters and result in a change of turn-on voltage. The inset shows that the turn-on voltage increases with repetition of high voltage annealing.

Fig. 2. a) Characteristic F–N curve of the air-exposed CNT FEA measured during rise and fall sweeps. This measurement was repeated three times. The similar $I-V$ curves for oxygen, nitrogen, and hydrogen are shown in (b–d), respectively, for different gas exposure times.
Systematic high voltage annealing diminishes fluctuations. However, the hysteresis—the difference in the emission currents during the “rise” and “fall” sweeps in the voltage scans—persists and becomes more reproducible through the iterative annealing. It implies that the hysteresis is not influenced by the appearance of bright CNT tips. The hysteresis, which is formed during the rise and fall sweeps, stems from the change of the slopes. The first slope, called $S_1$, follows the linear F–N plot, whereas the second slope, called $S_2$, results from suppression of the emission currents at high field. Interestingly, the emission currents increase during the fall sweep, resulting in a monotonic decrease, i.e., a single slope. With repetition of the $I$–$V$ annealing, the current enhancement is not significant in the high field region. The slope $S_1 = b\varphi^{3/2}/\beta$, from the F–N equation, where $b$ is a constant, $\varphi$ is the work function of the tip, and $\beta$ is the geometrical field enhancement factor. This value changes at an early stage of $I$–$V$ annealing and eventually saturates after several repetitions. Even the turn-on voltage, which is defined as the onset of the $S_1$ slope in the F–N plot, varies with repetition of the annealing. This behavior appears almost at the same field strength, 1.8 V/μm, during successive high voltage annealings. This abnormal behavior is in fact a characteristic of carbon nanotube emitters.

The origin of current suppression from the CNT tips has long been argued. Several mechanisms have been proposed. The change of the slope at high field could be induced by the space charges that exist between two electrodes and suppress the emission currents by screening the electric field near the emitters.[18] However, this is not the case here, since the emission currents persistently increase by two orders of magnitude even after suppression. Furthermore, the onset voltage of the current suppression is much lower than that of typical metal tips.[19] There is a possibility that tip–tip interactions may suppress the emission due to screening effects.[20] However, typical CNT arrays do not have such high emitter densities.[12] Localized defect states, which are observed at the apex of the CNTs, may be the cause of the saturation phenomenon. However, the existence of the hysteresis simply negates the possibility of defect states being the origin of the current suppression. Furthermore, transition metals could not be detected on the tip surface of the samples,[21] suggesting that transition metals are not responsible for the current suppression. This suggests that the current suppression is triggered by a different mechanism. Gas adsorbates introduced during the fabrication process are a good candidate for the origin of the current suppression. In order to investigate the effect of gas adsorbates on the field emission properties of the CNT FEA, we next performed gas exposure experiments.

Air is composed of various gases such as nitrogen, oxygen, water vapor, hydrogen, and so on. Therefore, our observations are the integrated results from the above-mentioned gases. In order to distinguish a different gas effect from air, we introduced a single gas species at a time into a vacuum system. Nitrogen, oxygen, and hydrogen gases were used for the experiments. For gas exposures, our system was evacuated first to a base pressure of $5 \times 10^{-7}$ torr. The gases were introduced into the chamber until the pressure increased to $2 \times 10^{-5}$ torr. A high bias voltage of 670 V, with currents of about 0.2–0.3 mA, was applied for 10, 100, 500, and 1000 s. After each exposure, the bias was turned off and the system was again pumped down to a base pressure. $I$–$V$ measurements were then made for each gas exposure time. Since the emission currents fluctuate at a given bias, each data point from Figure 2 was collected by averaging over 500 times for 4 min at a given bias voltage. Figures 2b–d present the change of the F–N plots after three different gas exposures on the CNT FEA. At a short gas-exposure time, the emission behaviors for all cases are similar to those of air-exposed FEA, i.e., current suppression occurs in the rise sweep, whereas a single slope is observed in the fall sweep. However, at 1000 s exposure of oxygen and nitrogen gases, current suppression again occurs even in the fall sweep, although hydrogen gas causes no change in the slope of the fall sweep at that exposure time. We propose here that the fundamental mechanism responsible for this behavior is the adsorption and desorption of gas adsorbates. At a high electric field of $\pm1.8$ V/μm, a large emission current of 0.7 mA/cm$^2$ initiates desorption of adsorbates by Joule heating at the apex of the emitter. In addition, a high local electric field at the tip is expected to accelerate the reactive desorption of gas adsorbates. Gases will be adsorbed not only on the wall surfaces but also at the protruding ends. With increasing voltages, some gases on the tube surface will start desorbing due to Joule heating and even those at the tip will be desorbed at high field, for instance at $\pm1.8$ V/μm, which was evidenced by the fact that the fluctuation of emission currents grows temporarily as the current suppression starts to develop. Since gases are desorbed during the rise sweep, no current suppression will be observed during the fall sweep. However, with large gas exposure times some of the gases will still remain, at least on the tip of the CNTs in the linear F–N region, giving rise again to current suppression, as indicated by the solid triangles in Figure 2b,c. This effect is less obvious in the case of hydrogen gas, with almost no appreciable change for all exposure times. The effect of gas adsorption and desorption is iterative due to the residual gas in the chamber, although the tip morphology could be altered by gas reactions at the tip surface in some cases. This will be discussed later.

Figure 3 shows the changes of some important parameters upon gas-exposure time. $S_1$ changes significantly at short exposure and starts to saturate after even short exposure times, indicating that: i) the surfaces are completely covered at short gas-exposure time and ii) the field enhancement factor and the work function, which are directly related to the slope $S_1$, may be changed at the initial stage of gas adsorption and do not change appreciably for all gases at large gas exposures. The change of $S_2$ is expected to be less prominent than that of $S_1$ because most gases should be desorbed from the CNT surfaces due to resistive heating and a high electric field. In Figure 3c, the variation of the turn-on voltage upon gas exposure, which is directly related to the work function of the
tip, is very similar to that of \( S_1 \). The turn-on voltages of oxygen and nitrogen gases first decrease and saturate at large gas exposure times, whereas that of hydrogen gas decreases initially and increases to saturation at large gas exposures. This behavior is strongly correlated to the electronegativity of the materials, i.e., the electronegativity of oxygen and nitrogen atoms is stronger than that of the carbon atom, whereas that of a hydrogen atom is weaker than that of a carbon atom. It is expected that the adsorbed atoms with strong electronegativity present at the tip edge depress the electron emission, and the larger difference in electronegativity from the carbon atom changes the work function more significantly. This strongly suggests that electron emission occurs through the resonant states of the adsorbed gases. It is very difficult to judge at this moment whether gas adsorbates will increase or decrease the emission current, since gas reaction on the wall surfaces and at the tip of the CNTs may involve degradation of the tip morphology, which will be discussed later.

Figure 3d shows the variation of emission currents in terms of exposure times, where \( I_0 \) (0.2 mA) was measured at 640 V with no gas exposure. The emission currents drop consistently with increasing dosages of oxygen and nitrogen gases, whereas they increase and then saturate for hydrogen gases. This means that oxygen and nitrogen gases neither adsorb physically nor simply cover the surface of CNT emitters. The oxygen molecules exothermically dissociate on the tip edge of CNTs, which is followed by oxidative etching.\[25\] This involves the degradation of the surface morphology, i.e., removal of the cap, leaving an open tip. Once a cap is completely etched away and an open tip is formed, the emission current will be stabilized. This situation may be similar in the case of nitrogen gas. In the case of hydrogen gas, the emission currents do not vary appreciably with repetition of \( I-V \) annealings, as shown in Figure 2d. This, together with the fact that the long gas-exposure time of hydrogen gas in Figure 3d does not result in much change in the emission current, indicates that hydrogen gas merely cleans up the field emitters and stabilizes all other physical parameters, as shown in Figure 3.

For technical purposes, hydrogen gas could be used for activation of the CNT FEA at the initial stage of the \( I-V \) treatment at high field, as it causes the least damage to the CNT morphologies. The role of hydrogen gas from a microscopic point of view is under current investigation. The emission properties of the air-exposed CNT FEA were obtained by integrating the above characteristics. Although air comprises all such molecules, oxygen gas dominates the field emission characteristics of the CNT FEA by changing all the physical parameters more severely than other gases.

To summarize, we have investigated the field emission properties of the CNT FEA by exposing it to various gases. We find that gas adsorbates played a crucial role in the formation of current suppressions at high field. The hysteresis loop during the rise and fall sweeps originates from the presence of gas adsorbates. Oxygen and nitrogen gases show different behaviors compared to hydrogen gas with respect to change of the emission properties. The changes in the slopes, turn-on voltages, and saturation currents at high field are strongly correlated to the electronegativity of the individual species and nature of the adsorption. We conclude that oxygen gas dominates the field emission properties upon adsorption and even degrades the surface morphologies possibly via an oxidative etching process, whereas hydrogen gas affects the field emission properties least—it simply cleans up the surface of the CNT FEA.

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Size-Selective Growth of Nanoscale Tetrathiafulvalene Bromide Crystallites on Platinum Particles**

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We describe the preparation of long (>1.0 μm) nanocrystals of an electronically conductive organic charge transfer salt, tetrathiafulvalene bromide, which are narrowly dispersed in diameter. Our method involves the size-selective electrocrystallization of this salt on platinum catalyst particles supported on a graphite surface. These platinum particles, ranging in diameter from 70 nm to 1.3 μm, were prepared by electrodeposition.[3] The electrocrystallization of tetrathiafulvalene bromide (TTFBr) from a dimethyl acetamide (DMAC) solution was then carried out at this nanostructured surface. (TTF)Br nanocrystals having widths in the range from 30 nm to 600 nm and aspect ratios of 20 or more were formed at the platinum nanoparticles on these surfaces by the electrochemical oxidation of tetrathiafulvalene (TTF) in bromide-containing electrolyte according to the reaction:[4]

\[
\text{TTF} + \text{Br}^- \rightarrow \text{TTF}^+ + \text{Br}^+ + e^-
\]  

(1)

Under the conditions employed in this study, the product of this oxidation was the non-stoichiometric salt (TTF)Br, where x is close to 0.76.[5] The widths of the (TTF)Br₀.76 crystallites (henceforth, (TTF)Br) were directly proportional to the diameter of the platinum particles on which they nucleated and grew. Specifically, the widths of (TTF)Br crystallites were 40–45% of the platinum particle diameter over the entire range indicated above. We believe these observations constitute the first clear demonstration that a nanomaterial can be obtained size-selectively by electrodeposition using size-selected metal particles as electrocatalysts.

Crystalline (TTF)Br is a highly anisotropic material both in terms of its reactivity (with respect to growth and dissolution), and its electrical conductivity. This anisotropy is a manifestation of its crystal structure in which π-stacks of TTF electron acceptors—arrayed along the c-axis of the crystal—are arranged in parallel to an equal number of (incomplete) rows of Br⁻ electron donors.[5] In (TTF)Br electrons are delocalized along these TTF⁺ stacks and the crystal is therefore conductive along the c-axis. The conductivity of single crystals in the direction perpendicular to the stacking direction is much lower. During electrocrystallization, (TTF)Br crystallites grow rapidly in the direction of the c-axis with the result that long, narrow crystallites are produced even at a smooth metal electrode surface.[6,7] However, in all previous studies, the width of these crystallites has been uncontrolled.

We investigated the growth of (TTF)Br crystallites at graphite surfaces covered with platinum nanoparticles ranging in diameter from 70 nm to 1.3 μm. These nanoparticles were prepared using the “slow growth” electrodeposition technique as previously described.[1,2] Briefly, in an aqueous plating solution of 1 mM H₂PtCl₆ (Aldrich, 99.99%) and 0.1 M HCl (Fisher, >99.95%), a sequence of two voltage pulses was applied: The first or nucleation pulse was 5 ms at −0.4 V vs. saturated calomel electrode (SCE) and it was followed by a growth pulse of +0.15 V vs. SCE, which had a duration of between 20 and 120 min. In order to avoid the “electroless” deposition of platinum in this electrolyte,[3] the graphite electrode was anodically protected at +0.5 V vs. SCE during exposure to the electrolyte.[1]

The resulting platinum particle modified graphite electrode was used as the working electrode in a one-compartment glass cell for the (TTF)Br electrocrystallization. The counter electrode was a 1.0 cm² platinum foil and a 1 mm diameter Pt wire was employed as a pseudo-reference electrode. A solution containing 0.1 M tetrabutylammonium bromide (Aldrich, 99%) and 5 mM TTF (Aldrich, 99%) in DMAC (Aldrich, 99.8% anhydrous) was anaerobically transferred to the cell. (TTF)Br crystals were obtained using a train of between 1 and 15 pulses of 0.2 s at +650 mV vs. Pt. Platinum particle growth and TTF(Br) electrocrystallization were carried out under computer control using an EG&G 270M potentiostat.

Shown in Figure 1 are scanning electron micrographs (SEMs) of platinum particles before and after the electrocrystallization of (TTF)Br crystallites. These platinum particles, prepared using the “slow growth” protocol described above...