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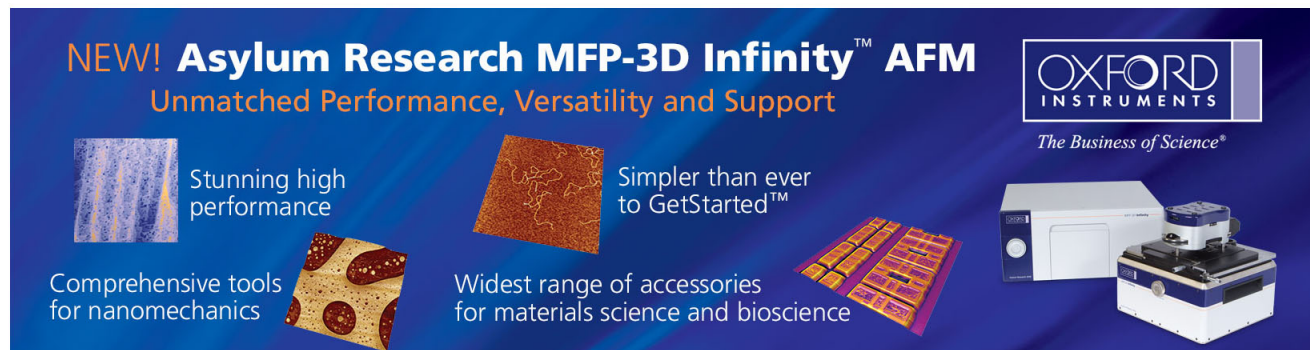AIP Conf. Proc. **685**, 550 (2003); 10.1063/1.1628091

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Role of extrinsic atoms on the morphology and field emission properties of carbon nanotubes

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Extrinsic atoms were doped into multiwalled carbon nanotubes (MWCNTs) using microwave plasma-enhanced chemical vapor deposition. Doped nitrogen atoms alter the original parallel graphenes into highly curved ones including some fullerene-like structures. Doped nitrogen atoms could replace carbon atoms in MWCNTs and therefore increase the electronic density that enhances the electron field emission properties. On the other hand, the incorporation of boron into the carbon network apparently increases the concentration of electron holes that become electron traps and eventually impedes the electron field emission properties. Fowler–Nordheim plots show two different slopes in the curve, indicating that the mechanism of field emission is changed from low to high bias voltages. β values could be increased by an amount of 42% under low bias voltages and 60% under high bias voltages in the N-doped MWCNTs, but decreased by an amount of 8% under low bias region and 68% under high bias voltage in the B-doped MWCNTs. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1579136]

Carbon nanotubes (CNTs) have drawn great attention in the whole scientific world for their superior electronic properties as an electron source for field emission display.[1,2] The characteristic aspect ratio contributes to the excellent field emission behaviors such as much smaller turn-on voltage and larger emission current density than any other field emission devices. In the Fowler–Nordheim[3] coordinates, field enhancement factor β could provide an indicatively physical factor to investigate and compare the results. Similar to other semiconductor materials, extrinsic doping of CNTs could alter and adjust the electronic properties and binding configurations of the CNTs. It is known that the boron-doped nanotubes are intrinsically metallic by the theoretical calculations[4] and conductivity measurements.[5] In this work, both nitrogen and boron atoms are separately doped into multiwalled CNTs (MWCNTs) by a microwave plasma-enhanced chemical vapor deposition (MPECVD) apparatus[6] and the influence of doped atoms on the field emission phenomena is discussed and compared.

MWCNTs were synthesized by the assistance of electroplated Pd catalyst[7] on the tungsten substrate in a MPECVD apparatus with a mixture of methane and hydrogen as precursors.[8] The microwave was generated at the frequency of 2.45 GHz by magnetron and 2.1 kW was used to synthesize MWCNTs. An external dc bias voltage of -350 V was simultaneously applied to the substrate and the synthesis temperature of the substrate was 600–700 °C. The vacuum system was maintained at 14 Torr under the mixed methane

and hydrogen atmosphere. In order to dope nitrogen atoms, MWCNTs were further exposed to nitrogen plasma of 3.1 kW microwave input for 30 min. The B-doped CNTs were produced by a mixture of CNTs and HBO_3 powder under the hydrogen plasma in the MPECVD system. The carbon-based nanostructures were characterized by transmission electron microscopy (TEM), and the chemical analysis was carried out by x-ray photoelectron spectroscopy (XPS). The atomic ratio of the relevant elements was obtained by integrating the core-level peak area, calibrated by the atomic sensitivity factor.[9] The electron field emission properties were measured by a conventional diode method at a pressure of 5×10^{-6} Torr. The Keithley 237 instrument was employed to measure the current density and electric field characteristics. Indium tin oxide glass was made as the anode to receive the emitted electrons with a spacer of 150 μm coverglass to separate from the cathode. The emitted area was fixed at 1 cm^2. The voltage was increased by a step of 10 V/s from 0 to 1100 V. Before the measurement, a voltage of 0–300 V was applied several times to remove contamination adsorbed on tips.

In the total energy calculations using semiempirical Hartree–Fock-based AM1 method,[10,11] the incorporation of nitrogen into graphite-like structures would introduce pentagon defects in the hexagon network. The formation of pentagon would distort and bend the graphite layers, leading to graphenes with high curvatures and cross-linked structures. In addition, basal planes of the graphite layers appear buckled, bent and frequently interlinked. It was also proposed that the fullerene-like structures are able to form in the carbon nitride matrix.[12] In the study of TEM analysis, the basal

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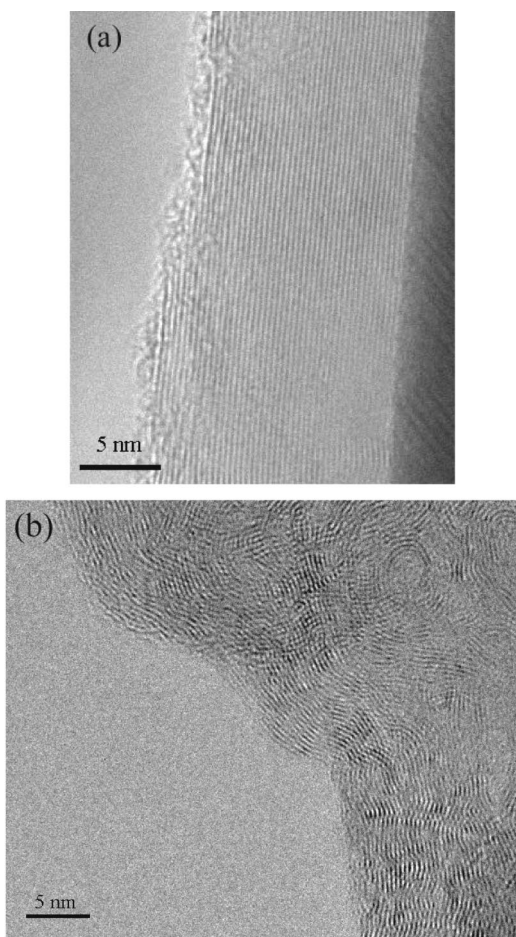
FIG. 1. High-resolution TEM images of (a) MWCNT, and (b) N-doped MWCNT by MPECVD. It is shown that the graphene layers of nitrogen doped MWCNTs appear seriously twisted such as turbostratic graphite layers and otherwise contain some fullerene-like structures inside.
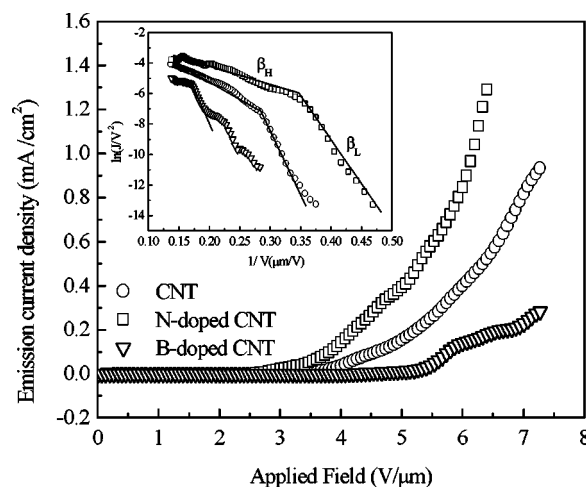

FIG. 2. I–V curves of CNTs for field emission measurements and the insertion for the Fowler–Nordheim plot. The detail field emission properties are listed in Table I.

planes of the graphenes are straight and parallel in the cylindrical MWCNTs, as shown in Fig. 1(a). When nitrogen atoms were doped into CNTs, original ordered parallel layers of the walls are disturbed and highly curved. Consequently some fullerene-like structures also form, as seen in Fig. 1(b). It shows that all the graphene layers of CNTs are affected and appear seriously distorted, similar to the fingerprints of human being.

The N ($1s$) and B ($1s$) core binding energies are detected in the XPS studies. The binding energy around 398–401 eV is corresponding to the nitrogen binding configurations.[13,14] On the basis of the XPS results, the calculated N/C ratio is 22 at. % and B/C ratio is 24 at. % (Table I). In order to evaluate the sp^2/sp^3 ratio of the carbon atoms, we chose to adopt the method of Marten[9] to fit the curve of C ($1s$) core level binding energy. C_1 (284.4 eV) is assigned

as the adventitious carbon and surface free carbon, while C_4 (290.3 eV) is identified as the signal resulting from CO type bonds. The sp^2/sp^3 ratio could be estimated by the method of dividing the integrated peak area of C_2 (285.6 eV) by the peak area of C_3 (287.6 eV).[15] The results are listed in Table I.

Figure 2 is the field emission results of the three types of CNTs and the relevant Fowler–Nordheim plot is shown in the inserted diagram. Because the work function Φ of MWCNTs is difficult to measure, it is assumed to be 4.7 eV according to the work function of pure graphite layers (5 eV), and the field enhancement factor β can be calculated from the slope of the straight line in the Fowler–Nordheim (F–N) plot. It is found that there are two straight lines on the F–N plot and β can be divided into two regions: β_L and β_H under low and high bias voltages, respectively. At low bias voltages, the field emission mechanism obeys the properties of the traditional Fowler–Nordheim equation, while the field emission behavior under high bias voltages deviates from the Fowler–Nordheim equation but still appears a linear relationship on the F–N coordinate. The origin of the deviation from the F–N plot under high bias voltages has long been discussed, and it is commonly explained by the space-charge effect, the presence of localized states at the tip of the emitter, interaction between nanotubes and gas desorption/adsorption on tips.[16–19] The corresponding field emission properties of the different types of CNTs are all compared in Table I. The field emission properties of N-doped CNTs with low onset voltage (2.5 V/μm) and high emission current density (0.4 mA/cm^2 at 5 V/μm) are superior to other types of CNTs.

TABLE I. Relevant atomic ratios, sp^2/sp^3 ratios, field enhancement factor (β_L and β_H), onset voltage, and applied voltage at 1 mA/cm^2 for CNTs doped with nitrogen and boron.

Various types of carbon nanotubes	N/C or B/C atomic ratio (at. %)	sp^2/sp^3 ratio of carbon	Field enhancement factor		Onset voltage (V/μm)	Applied voltage at 1 mA/cm^2 (V/μm)
			β_L	β_H		
MWCNTs	0	2.49	936	3385	3.2	7.26
N-doped MWCNTs	22	2.86	1331	5404	2.5	6.25
B-doped MWCNTs	24	1.30	864	1100	4.6	

When nitrogen atoms incorporated into graphite-like materials, it is easy for them to substitute carbon atoms in the hexagon graphite network due to the small difference of atomic radii for these two atoms. One excess electron is supplied when one nitrogen atom replaces one carbon atom, and the electron concentration in the conduction band can be increased by nitrogen doping into CNTs. The field emission current density is a function of both the tunneling probability of electron depending on the shape of the barrier, and electron supply function depending on the electron concentration in the conduction band. For CNTs, increasing electron concentration is an effective way to enhance the emission properties. N-doped CNTs have even superior emission properties than CNTs. In B-doped CNTs, boron can also replace carbon in the graphite network but produces electron holes in the band structure, which serve as electron traps to make recombination with electron and prevent electron from escaping the CNTs. Both generation of holes and recombination effect can decrease electron supply during emission test, thereby leading to a higher onset voltage (4.6 V/μm), and lower emission current density (0.1 mA/cm^2 at 5.8 V/μm).

In conventional field emitters, β depends on structure geometry of the device, such as the tip radius of curvature, emitter height, statistical distribution of the tip sharpness and so on.[20] But for nanotubes, many reports proposed that β could be affected by other mechanisms in addition to the geometry effect. Because the work function of CNTs is assumed to be a fixed value (4.7 eV), variation of β could be sometimes attributed to other reasons than merely the geometry effect.[21,22] For N-doped CNTs, nitrogen atoms transform concentric graphene cylinders into much more curved and bending layers with some fullerene-like structures inside [Fig. 1(b)]. These locally distorted positions with high curvatures are effective sites to emit electrons. The field amplification effect in these sites is stronger than other smooth places, and β can be enhanced by these sites, such that the N-doped CNTs can have both higher β_L and β_H than CNTs. In addition, binding configuration and local density of states can also have influence on the field emission behaviors. By *ab initio* pseudopotential electronic structure calculation for several edge geometries of the (n, n) single-wall nanotubes,[23] the capped nanotube with π-bonding states localized at the cap and pointing in the tube axis direction are favorable for field emission. In some cases such as pyramidal diamond tips,[24] field emission characteristics can be enhanced by increasing the sp^2 contents. In the studies of carbon nitride materials, it is known that nitrogen atoms could assist the formation of sp^2 bonding by reducing the total energy and approaching more stable states by *ab initio* HF and DF calculations with B3LYP/6-31G(d)//HF/STO-3G methods.[25] These three sp^2/sp^3 ratios (Table I) have the tendency that β increases with increasing sp^2 contents. The π-bonding states of sp^2 binding could enhance the field

emission properties by the assistance of the delocalized electron in the π orbital with higher mobility than the localized electrons in the σ bonds.

In conclusion, nitrogen-doped CNTs prepared by MPECVD can improve β by increasing electron density, locally distorted positions with higher curvatures, and sp^2 contents. The field emission properties of B-doped CNTs, on the other hand, are inferior in performance due to the generation of electron holes and recombination effect of traping electrons.

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