1. Introduction

Flexible displays such as e-paper[1,2] and flexible light-emitting diodes[3-7] have been in the forefront of flexible electronics technology. The active materials for flexible displays mostly rely on organic semiconductors or inorganic nanomaterials. An organic semiconductor enables facile solution processing of intrinsically flexible active materials but has poor long-term stability. Inorganic nanomaterials such as semiconductor nanowires or nanoribbons ensure robust and highly stable display performances. However, the mass production of nanomaterials and their large-area assembly frequently have major technological challenges. In this regard, carbon materials such as carbon nanotubes (CNTs) and graphene are promising alternatives, owing to their intrinsic flexibility and stretchability, excellent electrical properties, high thermal and chemical stability, and cost-effective mass production.[8-10]

Field emission relies on the electron extraction from a material surface by quantum mechanical tunneling.[11] This simple principle is widely utilized in field emission displays,[12] back-light units,[13] and electron guns.[14] Of these, the field emission display has predominant advantages over other types of displays, particularly in terms of its fast response, low power consumption, and wide viewing angle. Nevertheless, the successful integration of field emission into flexible device architecture remains a technological challenge. This challenge stems from two major limitations: the difficulty of maintaining a vacuum in flexible device architecture and the high-performance requirements of flexible field emission materials. Recent progress in vacuum technology has led to the production of flexible vacuum devices, such as a flexible plasma display panel (PDP).[15,16] In contrast, the development of high-performance, flexible field emission materials with a sufficient field emission current and electrical and mechanical robustness in an extremely deformed geometry has rarely been achieved thus far.

Here we demonstrate the excellent flexible field emission properties of carbon hybrid films made of vertically aligned N-doped carbon nanotubes grown on mechanically compliant reduced graphene films. The bottom-reduced graphene film substrate enables the conformal coating of the hybrid film on flexible device geometry and ensures robust mechanical and electrical contact even in a highly deformed state. The field emission properties are precisely examined in terms of the control of the bending radius, the N-doping level, and the length or wall-number of the carbon nanotubes and analyzed with electric field simulations. This high-performance flexible carbon field emitter is potentially useful for diverse, flexible field emission devices.

Flexible Field Emission of Nitrogen-Doped Carbon Nanotubes/Reduced Graphene Hybrid Films

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The outstanding flexible field emission properties of carbon hybrid films made of vertically aligned N-doped carbon nanotubes grown on mechanically compliant reduced graphene films are demonstrated. The bottom-reduced graphene film substrate enables the conformal coating of the hybrid film on flexible device geometry and ensures robust mechanical and electrical contact even in a highly deformed state. The field emission properties are precisely examined in terms of the control of the bending radius, the N-doping level, and the length or wall-number of the carbon nanotubes and analyzed with electric field simulations. This high-performance flexible carbon field emitter is potentially useful for diverse, flexible field emission devices.

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films, and their field emission properties were systematically characterized under highly deformed states.

2. Results and Discussion

Figure 1a schematically illustrates the flexible field emission devices. The carbon hybrid films were detached from a silicon oxide substrate by hydrofluoric acid (HF) treatment and readily transferred to films made of Au (15 nm) and polycarbonate (PC, 200 μm).[9] The PC substrate ensures optical transparency, mechanical flexibility, and a relatively high glass transition temperature ($T_g = 150$ °C).[10] The thin Au film mediates the electrical contact with the field emission equipment (Supporting Information, Figure S1a). Figure 1b shows a photograph of a hand-bent, flexible field emission device. Because the mechanically compliant reduced graphene film has conformal contact with the underlying Au layer, the carbon hybrid film maintains robust mechanical and electrical contact even in severely deformed geometry.

The performance of flexible field emission devices with an emission area of 1 cm × 1 cm was measured in a vacuum chamber (vacuum pressure: $10^{-6}$ Torr) at room temperature. The anode films were prepared by screen printing phosphor (ZnS:Ag,Cl) on the Au (15 nm)/PC (200 μm) films. The spacing between the N-doped CNT cathode tips and the anode (ZnS:Ag,Cl/Au (15 nm)/PC (200 μm)) was maintained with a flexible PC (800 μm) spacer. For the characterization of the field emission properties, two parameters were measured: the turn-on electric field ($E_{to}$), defined as the magnitude of the applied electric field at a current density of 10 μA·cm$^{-2}$, and the electric field enhancement factor ($\beta$), which is calculated from the Fowler–Nordheim (F–N) plots.[11] Figure 1c shows photographs of the field emission of carbon hybrid field emitters in flat, and concavely and convexly bent morphologies (bending radius: 0.6 cm). The corresponding luminance was measured with a PR650 SpectraColorimeter (Photoscience) on the top of the field emission devices, quantifying the light emission efficiencies.[24] (Supporting Information, Figure S1b). The convexly bent devices clearly show enhanced luminance, whereas the concavely bent devices show degraded luminance at the same electric field.

Figure 2a shows the measured $E_{to}$ values (left axis) and the corresponding $\beta$ values (right axis) of the carbon hybrid films as a function of the bending radius. The length and spacing of six-walled dominant CNTs were maintained at 30 μm and 36 nm, respectively. The positive and negative bending radii correspond to the convex and concave bending, respectively. When the hybrid film was concavely bent, the decrease in the bending radius enhanced the field emission properties. In contrast, the decrease in the convex bending radius degraded the field emission properties (Figure 1d). For a clear explanation of the performance of flexible field emitters, the electric field intensities were theoretically modeled using the program CST EM STUDIO 2006. This program is a dedicated application for the simulation of static and low-frequency electric fields in electronic devices. Figure 2b shows the calculated electric field profiles around the CNT tips for the bending radii of $-0.01$ cm, $\infty$, and $+0.01$ cm. The experimental (dots) and calculated (line) values of the normalized field enhancement factors ($\Delta/\beta_{plane}$) are compared in Figure 2c as a function of the bending radius. This variation in the field emission can be understood in terms of the electric field concentration or dilution around the CNT tips. When the hybrid film is convexly bent, the average spacing between the neighboring
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CNT tips increases. This morphology change lessens the screening effect from the neighboring CNT tips. Therefore, the electric field around CNTs and the corresponding field emission become enhanced. In contrast, when the hybrid film is concavely bent, the average spacing between the CNT tips narrows. This leads to the decrease in the electric field intensity and field emission properties.

The field emission current is inversely proportional to the electron work function (Φ), which is the energy difference between the vacuum and Fermi level, of a field emitter.[11] Accordingly, field emission material with a small work function is generally preferred for the high performance of flexible field emission devices. In this work, N-doping is employed as an effective way to reduce the work function of CNTs.[9,20,25] Figure 3a shows the measured current density versus the applied electric field for six-walled CNT arrays (length: 20 μm) at N-doping levels of 0.0% (squares), 3.0% (circles), 4.6% (upward-facing triangles), 6.2% (diamonds), and 8.0% (left-facing triangles) measured at room temperature. All samples have similar field enhancement factors of 5300–5700. c) Turn-on electric fields (left axis) and work functions (right axis) of the CNT tips as a function of the N-doping level.

Figure 2. a) Turn-on electric fields (left axis) and the corresponding field enhancement factors (right axis) of the hybrid carbon films as a function of the bending radius. b) Calculated electric field intensities at the CNT tips with film bending radii of −0.01 cm, 0 cm, and +0.01 cm. c) Experimental (dots) and calculated (line) field enhancement factors as a function of the bending radius.

Figure 3. a) Current density vs. applied electric field and b) F–N plots for the field emissions of six-walled CNT tips with N-doping levels of 0.0% (squares), 3.0% (circles), 4.6% (upward-facing triangles), 6.2% (diamonds), and 8.0% (left-facing triangles) measured at room temperature. All samples have similar field enhancement factors of 5300–5700. c) Turn-on electric fields (left axis) and work functions (right axis) of the CNT tips as a function of the N-doping level.
(left-facing triangles). Figure 3b shows the corresponding F–N plots for determining the $\beta$ values. The shape (length: 30 μm; diameter: 9.6 nm; average wall-number: 6) and the areal density of the CNTs were precisely maintained via catalyst nanopatterning with block copolymer lithography[9,20–22] and CNT growth time in PECVD.[23] Consequently, the $\beta$ values, determined by the geometry and areal density of the emitters,[20,27] are in a narrow range of 5300–5700, regardless of the N-doping level. In contrast, the $E_{\text{to}}$ value varies greatly with the N-doping level. Because the N-doping provides excess electron carriers,[20,28,29] the work function of CNTs with the N-doping level. Because the N-doping provides the work function decreases with the N-doping level.[25,30] Figure 3c compares F–N plots for determining the $\beta$ value (left-axis) and the $\phi$ value (right-axis) of the N-doped CNTs as a function of the N-doping level. The work functions measured by ultraviolet photoemission spectroscopy (UPS) demonstrate a V shape with a minimum value at the 4.6% doping. The $E_{\text{to}}$ value clearly follows the variation of the work function. This result is in good agreement with the theoretical value generated using the F–N equation (Supporting Information, Figure S2). Moreover, the emission current of 4.6% N-doped CNTs showed a high reliability over 1 month of continuous operation (Supporting Information, Figure S3).

Figure 4 shows the measured $E_{\text{to}}$ value (Figure 4a) and the corresponding $\beta$ value (Figure 4b) of carbon hybrid films as a function of the CNT length and average wall-number. The N-doping level was fixed at 4.6%, and the average spacing between neighboring CNTs was fixed at 36 nm. When the CNTs are relatively short, $E_{\text{to}}$ and $\beta$ values are significantly influenced by the CNT length. However, due to the screening effects of neighboring CNT tips, those parameters become saturated when the CNTs exceed a certain length.[11,12] The field emission properties are also significantly influenced by the wall-number (diameter) of the CNTs. A decrease in the average CNT wall-number improves the shape anisotropy (aspect ratio) of the CNTs. This sharpening of CNT emitters results in an enhanced electric field around the CNT tips. The sharpest double-walled dominant CNT emitter demonstrates the smallest $E_{\text{to}}$ value of 0.4 V·μm$^{-1}$ above 20 μm length.

The electric field intensity around the CNT tips was modeled as a function of the length ($l$), diameter ($d$), and spacing ($s$) of the CNTs. Figure 4c shows the experimental (dots) and calculated (line) field enhancement factors ($\beta/\beta_{\text{max}}$) of the CNT array as a function of $l/(d\cdot s)$. The experimental results from different CNT wall-numbers and lengths can be superposed on a single curve plotted against $l/(d\cdot s)$. A comparison of the theoretical predictions with the experimental data ($d = 9.6 \text{ nm}$, $s = 36 \text{ nm}$) reveals that the calculated $\beta/\beta_{\text{max}}$ value is significantly higher than the experimental values at the same $l/(d\cdot s)$. The calculated $\beta/\beta_{\text{max}}$ values agree with the experimental data when the $l/(d\cdot s)$ value for the simulation is corrected (increased) by a factor of 5. This discrepancy is presumably caused by the non-uniformity of the CNT length, and the curling and bundling of the CNTs. Even though the vertical CNTs grown by PECVD have a relatively uniform length, some longer CNT tips protrude among the other tips. The electric field will be concentrated around these protruding tips, significantly degrading the overall field emission properties. In addition, CNT tips may curl or bundle to form an emitter with a reduced aspect ratio. This non-uniformity of the CNT tips can increase the effective $l/(d\cdot s)$ value of the CNT emitters.

Figure 4. a) Turn-on electric fields ($E_{\text{to}}$) and b) the corresponding field enhancement factors ($\beta$) of the carbon hybrid films as a function of the length and wall-number of the CNT tips. The average spacing between neighboring CNT tips is approximately 36 nm. c) Experimental (dots) and calculated (lines) field enhancement factors ($\beta/\beta_{\text{max}}$) of the CNT emitters as a function of $l/(d\cdot s)$. The calculated field enhancement factors are consistent with the experimental data and have an increment factor of 5.
3. Conclusion

We have demonstrated the excellent field emission properties of flexible carbon hybrid field emitters composed of vertically aligned N-doped CNTs grown on a mechanically compliant graphene film. The influence of the mechanical bending, as well as the N-doping level and nanoscale morphology, of CNT field emitters on the field emission behavior is schematically characterized and analyzed in terms of theoretical electric field calculations. These remarkably flexible carbon field emitters are potentially useful for diverse flexible field emission devices.

4. Experimental Section

Materials: The asymmetric block copolymer polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA), which forms cylindrical nanostructures (molecular weight: PS/PMMA = 46 k/21 k), was purchased from Polymer Source, Inc. The iron source for the e-beam evaporation (purity: 99.95%) was purchased from Thifine. Pure oxygen, hydrogen, and acetylene gases were purchased from Kyungin Chemical Industrial.

Nanopatterned Catalyst Particle Preparation: An aqueous dispersion of graphene oxide was prepared by means of the Hummers method. A film composed of overlapped and stacked graphene oxide platelets was prepared by spin-casting graphene oxide from an aqueous dispersion onto an SiO2 (500 nm)–Si wafer. A random copolymer brush was used to neutralize the graphene oxide surface. A thin film of the block copolymer PS-b-PMMA (molecular weight: PS/PMMA = 46 k/21 k) was spin-cast onto the wafer surface. After high-temperature annealing at 250 °C, the samples were exposed to ultraviolet radiation and rinsed with acetic acid and water to selectively remove the PMMA cylinder cores and to cross-link the PS matrix. An iron catalyst film was deposited (thickness: 0.7–10 nm) onto the block copolymer template by tilted evaporation (tilt angle: 0°–30°). After the deposition process, the remaining PS nanoporous template was lifted off by sonication in toluene.

PECVD Growth of Vertical CNT Arrays: CNT growth was carried out on the prepared catalyst-deposited substrates by catalytic PECVD. The substrate was heated to 600 °C under the flow of a H2/NH3 (100 sccm/0 sccm–50 sccm/50 sccm) gas mixture. When the substrate temperature reached 600 °C, the chamber pressure was adjusted to 5 Torr, and the application of 470 V of DC power produced the plasma. Slow streaming of acetylene gas resulted in the growth of vertical CNT arrays (growth time: 0 min–10 min). The lengths of the CNTs in the resultant arrays were measured with cross-sectional scanning electron micrographs.

Field Emission Measurement: The N-doped CNT arrays grown on reduced graphene films were transferred to Au (15 nm)/PC (200 μm) film. The anode films were prepared by screen printing phosphor (ZnS:Ag,Cd) on the Au (15 nm)/PC (200 μm) films; the phosphor was positioned at the anode parallel to the top surface of the carbon carpet. The spacing between the anode and the top surface of the carbon carpet was set to 800 μm. The field emission properties were measured under a vacuum of 10^{-6} Torr by applying a voltage of 0 to 2000 V between the two electrodes. The luminance was measured with a PR650 SpectraColorimeter (Photo research).

Electric Field Simulation: An electric field simulation of CNT arrays was conducted with the aid of CST EM STUDIO 2006. The CNTs were assumed to be shaped like a straight cylinder with a hemispherical tip, and 145 CNT emitters were included in a hexagonal arrangement. The electric field intensity was taken from the CNT tips, and the field enhancement factor was calculated from the ratio of the local electric field on each CNT tip and the applied electric field on the cathode plane.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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