Communication

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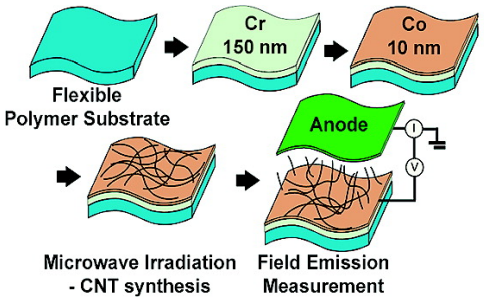

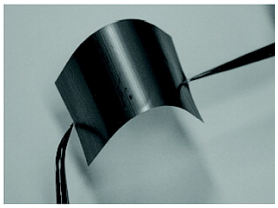

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Fabrication of Flexible Carbon Nanotube Field Emitter Arrays by Direct Microwave Irradiation on Organic Polymer Substrate

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Carbon nanotubes (CNTs) are the material of ever-increasing concern due to their excellent electronic and physicochemical properties.[1] One of the promising applications of CNTs is the electron emitters for field emission displays (FEDs).[1−3] We have reported that flexible field emitters could be fabricated by attaching CNTs onto organic polymer substrates using the self-assembly monolayer (SAM) technique.[3] Although the extension of this technology does not seem to bring in any fundamental difficulty, there are several outstanding problems such as the chemical stability of the substrate against various solvents during the fabrication, and the long-term stability of the attached CNTs.

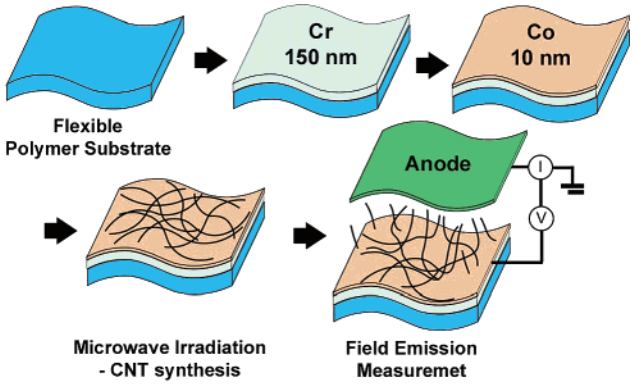
A completely different strategy (direct synthesis of CNTs on flexible substrates) has also been investigated for some time. Plasma-enhanced chemical vapor deposition (PECVD) is the dominant technique in this extreme, but incorporation of high quality CNTs with polymers has been severely limited.[4]

Recently, we have reported the direct synthesis of CNTs on organic polymer substrates by microwave heating of catalysts.[5] Microwave heating, in which the microwave energy is delivered to the materials through molecular interactions with the electromagnetic field, has potential advantages of uniform, rapid, and volumetric heating.[6] Furthermore, selective heating is possible by microwaves due to the difference in dielectric properties of materials.[6] Therefore, only the catalyst particles would be heated to the temperature of CNTs synthesis, without increasing the temperature of the substrate on which the catalysts lie.

In this work, we report the fabrication of flexible field emitter arrays of CNTs and their field emission properties. It is an essential advancement of the microwave synthesis technology to the fabrication of realistic devices with a great commercial value in the years to come. A powerful single-mode microwave radiator was assembled for the fast synthesis of CNTs, typically a few seconds. Since CNTs were synthesized at atmospheric pressure, no vacuum equipment was necessary.

Scheme 1 shows the experimental procedure, and the photograph of the flexible CNTs emitter appears in the Table of Contents. The polymer substrate was the 200 μm thick Teflon sheet, and the roughness was about 30 nm. A thin layer of Cr electrode was deposited onto the substrate by a magnetron sputter. The sputtering chamber was evacuated to a pressure lower than $\sim 10^{-6}$ Torr. Ar gas was introduced into the sputtering chamber, and the working pressure was kept at 5×10^{-3} Torr during the sputtering. RF power was fed to generate plasma, and the thickness of the deposited Cr layer was 150 nm. Co was deposited at 5.5×10^{-2} Torr after base

Scheme 1. Experimental Procedure for the Fabrication of a Flexible CNT Field Emitter



pressure (10^{-6} Torr) was acquired; 700 V dc power was applied to the target until the 10 nm of Co was deposited.

The catalyzed substrate (hereafter, named Co/Cr/Teflon) was placed in a quartz reactor, and microwaves (300 W, single-mode) were irradiated on it with a flowing reactant gas mixture of C_2H_2 (20 sccm) and Ar (80 sccm) for 5 s. The total pressure was kept at 1 atm during the synthesis.

Figure 1a shows the scanning electron microscope (SEM) image of the synthesized CNTs on the Co/Cr/Teflon substrate. The surface of each CNT is clean, and there virtually is no formation of amorphous carbon particles. The transmission electron microscope (TEM) image (Figure 1b) reveals that they are multiwalled CNTs (MWNTs) with well-graphitized walls. The interlayer distance is about 0.35 nm, and each CNT consists of 4−6 walls. The distribution of diameters is narrow in the range of 5−6 nm. We can conclude from these SEM and TEM observations that single-mode irradiation of microwave can synthesize CNTs in a highly uniform and well-crystallized manner in a short time. It is generally known that the diameter of synthesized CNTs is proportional to the size of catalyst particles, so that heat treatment of the thin metal film requires fine control for the formation of monosized catalyst islands.[7] It is rather surprising that we could synthesize highly uniform CNTs without preformation of the monosized catalyst islands. A detailed investigation on the mechanism of microwave synthesis is highly recommended.

The field emission current for the CNTs on the Co/Cr/Teflon was measured. The Cr layer was used as the cathode, and the glass coated with indium tin oxide (ITO, polished, 150 nm) was used as the anode. The space between the field emitter array (FEA) and the anode was 200 μm. Field emission current was measured by a picoampere meter (Keithley 6485) at a pressure of $\sim 10^{-7}$ Torr. Figure 2 shows the field emission current density from the FEA as

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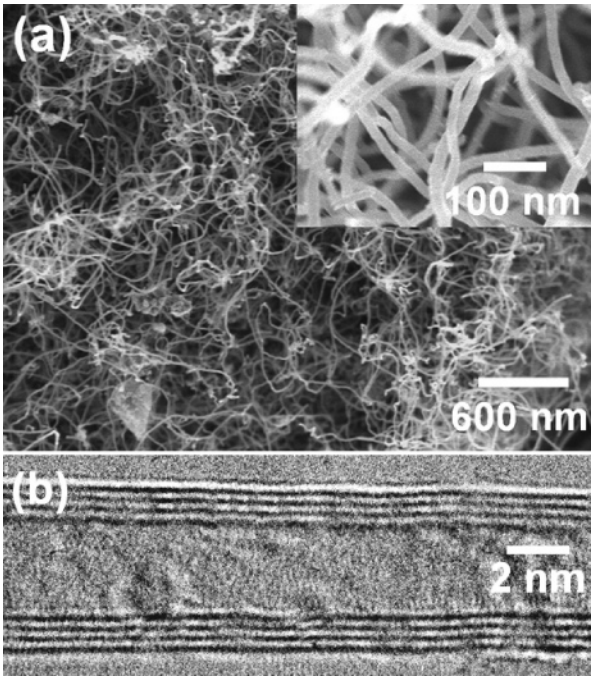

Figure 1. (a) SEM image and (b) TEM image of the CNTs grown on the flexible Co/Cr/Teflon substrate using microwave irradiation (300 W, 5 s) with flowing C_2H_2 (20 sccm) and Ar (80 sccm).

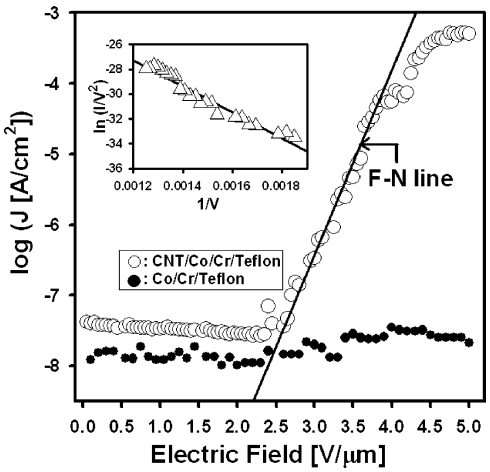

Figure 2. Field emission current density as a function of the applied field. Inset is the Fowler−Nordheim plot for the CNTs grown on the flexible Co/Cr/Teflon substrate.

a function of applied electric field. This $I-V$ curve was obtained after sweeping the voltage several times for the aging of FEA. Field emission did not occur on Co/Cr/Teflon, which is the control sample. It means that the emission current from FEA is primarily due to the CNTs. The E_{to} at the emission current density of 10 μA/cm^2 was 3.6 V/μm. In this work, the turn-on field (E_{to}) is defined as the field required to generate an emission current of 10 μA/cm^2.[8] A CNT-based field emitter should reach 80 μA/cm^2 to be used as a cold emission source.[9] The present sample generated this current density at 4.1 V/μm.

The inset of Figure 2 shows a Fowler−Nordheim (FN) plot of the FN line to analyze the field emission current.[10] The $I-V$ data can be fitted well with the FN model, and it reveals that the emission current of Figure 2 is a typical cold electron emission. The slope of the linear regression is given by $B\phi^{2/3}d/\beta$, where $B = 6.87 \times 10^9$ (V eV$^{-3/2}$ m^{-1}), ϕ is the work function, and d is the distance between the anode and the cathode.[8] The work function of the CNTs in our sample was taken to be that of graphite, 5 eV.[8] The field enhancement factor, β, calculated from the slope of the FN plot, was 1112−1546, depending upon the range of the emission data. These values are in the typical range of MWNTs.[2]

In summary, we synthesized well-graphitized MWNTs directly on flexible polymer substrates using microwave irradiation. The flexible CNT field emitter array thus fabricated showed good field emission properties. Advantages of this technique include no preheating of the catalyst film, atmospheric operation, fast synthesis, and most notably, the ability to synthesize CNTs on polymer substrates. It is an important advance toward flexible field emitters and future plastic electronics incorporated with CNTs.

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