Effects of oxygen plasma on optical and electrical characteristics of multiwall carbon nanotubes grown on a four-probe patterned Fe layer

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We report on the fabrication and electrical characterization of aligned multiwall nanotubes (MWNTs) grown on a four-probe patterned catalyst layer. This structure has been designed to directly measure the electrical property of as-grown MWNTs. The temperature-resistance results show that the aligned MWNTs are semiconducting in directions perpendicular to the tube axis and follow the three-dimensional hopping conduction mechanism. Effects of oxygen plasma on the characteristics of the MWNTs are also investigated. Raman spectroscopy results indicate that oxygen plasma treatments can be used to reduce the carbonaceous material in the film. As the exposure time of oxygen plasma increases, the resistance of the aligned MWNTs increases mainly due to the suppression of current conduction through carbonaceous materials. These results suggest that oxygen plasma treatment is effective in improving the film quality of as-grown MWNTs.

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I. INTRODUCTION

Carbon nanotubes (CNTs) are considered highly attractive for applications in nanoelectronics, field emission displays, and sensors due to their excellent electrical and physical properties. In particular, multiwall nanotubes (MWNTs) have been widely investigated because of relatively lower growth temperature and unique aligned structure.

Recently, the fabrication of thin-film transistors and field emission displays using aligned MWNTs have been reported, even though the electrical properties of aligned MWNTs have been investigated less than individual single- or multiwall nanotubes. De Heer et al. showed that aligned MWNTs have anisotrophic electrical properties depending on the direction to the tube axis. The MWNTs used in that study were transferred onto a plastic substrate which may affect the accuracy of the measured results. More recently, Wang et al. reported similar electrical transport properties for aligned MWNTs obtained by inserting Au wires into the MWNTs. This method could cause some physical damage to the MWNTs film.

Aligned MWNTs are typically synthesized by using a chemical vapor deposition (CVD) method, which is suitable for the fabrication of electronic devices. However, during the carbon nanotube growth, other carbonaceous materials such as carbon nanoparticles, graphitic carbons, and amorphous carbon coatings on the MWNTs are simultaneously incorporated in the film. These materials may adversely affect the electrical characteristics of the aligned MWNTs film.

In this article, we propose a method for measuring the electrical characteristics of aligned MWNTs films by patterning the catalytic layer for MWNT growth as a four-point probe. This four-probe method enabled us to perform electrical measurements directly on the as-grown MWNTs without any additional processing. We also investigated the effect of an oxygen plasma on the optical and the electrical characteristics of the aligned MWNTs. The results show that an oxygen plasma treatment improves the film quality by removing carbonaceous materials and thus increases the electrical resistance of the aligned MWNTs.

II. EXPERIMENT

The fabrication steps used in this work are shown in Fig. 1. First, a photoresist was spin coated and patterned by photolithography. A 200 nm thick Au layer was then deposited by thermal evaporation and formed electrode pads after a liftoff process in acetone [Fig. 1(a)]. Then, a 1 μm thick polymethyl (methacrylate) was spin coated and hard baked at 170 °C for 30 min [Fig. 1(b)]. This layer was used to pattern the catalyst regions. The four-probe patterns were defined by electron beam lithography and developed in a 33% solution of methylethlyketone and isopropanol for 7 min. A catalyst (Fe) was then deposited by electron-beam evaporation onto the patterned region and followed by liftoff in acetone [Fig. 1(c)]. Finally, aligned MWNTs were grown in a plasma enhanced chemical vapor deposition (PECVD) system at atmospheric pressure [Fig. 1(d)]. Figure 2 shows geometry of a four-probe-pattern region. The patterns consist of five individual rectangular-shape regions each with an area of 10 × 20 μm². They are separated by 500 nm in order to prevent a leakage current through the thin catalyst film.

An atmospheric pressure plasma “jet” (Atomflo 250D from Surfx Technologies) was used to grow MWNTs. Figure 3 is a schematic drawing of the system used in this work. The substrate was rapidly ramped up to process temperature after purging with 40 slm of helium at room temperature. At process temperature, helium with a flow rate of 25 slm was passed through the plasma source and plasma was generated...
by applying rf power at 13.56 MHz. As a carbon precursor, C2H2 (acetylene) with a flow rate of 1.5 slm was added to the plasma inside the system. The plasma power of 45 W with substrate temperature at 700 °C was used to grow the CNTs. After MWNTs growth, the substrate was cooled down to room temperature in a helium ambient.

To investigate the effect of O2 plasma on the optical and electrical properties, the as-grown MWNTs on the four-probe structure were exposed to O2 plasma using a reactive ion etcher at room temperature. The plasma power was set to 45 W and a chamber pressure to 150 m Torr, respectively. Raman analysis was conducted using a Labram HR micro-Raman spectrometer (JY Horiba). A 632.8 nm He–Ne laser was used for excitations. The electrical characteristics of the aligned MWNTs have been obtained by using the four-probe circuit in ac mode over the temperature range of 2–300 K. A physical property measurement system, manufactured by Quantum Design was used to make the measurements.

### III. RESULTS AND DISCUSSION

#### A. Multiwall carbon nanotube growth

MWNTs typical of those grown on the four-probe structure were characterized using scanning electron microscopy (SEM) and once by high-resolution transmission electron microscopy (HR-TEM). The outer diameter of the as-grown MWNTs was found to range from 10 to 30 nm from the TEM and SEM images. Figure 4 shows a typical SEM image of aligned MWNTs with a forest height of about 50 μm, grown at 700 °C for 3 min on the four-probe patterned Fe catalytic layer. The Fe layer was deposited to be 5 nm thick and sintered in N2 ambient before loading to the PECVD chamber. It is commonly believed that adjacent nanotubes attract and support each other by the van der Waals force and thus the MWNTs grow vertically. The tubes appear to have approximately uniform diameters. The Fe nanoparticles are only found at the bottom suggesting a base growth mechanism dominates here.
We were able to obtain HRTEM analysis once in order to confirm the wall structures of the MWNTs. Figure 5 shows HRTEM images of what we expect are our typical MWNTs. Figure 5(b) clearly shows the tubular nature of the nanotubes where the graphene planes are parallel to the tube axis. It is found that the MWNTs generally consist of 10–20 graphene shells with a hollow region of about 3–8 nm from the TEM analysis.

B. Raman spectroscopy

Raman spectroscopy has been used to characterize the structures of different carbon nanotubes in a nondestructive manner. In this work, micro-Raman spectroscopy was carried out in order to investigate the effect of oxygen plasma on the MWNTs. The Raman spectra gave information on the average properties of the MWNTs in the volume with an illuminated area of a few square microns.

Figure 6 shows Raman spectra in the range of 1200–1500 cm$^{-1}$ for the MWNTs with different exposure times of oxygen plasma. The two main features in the Raman spectra are the $D$ and $G$ peaks at approximately 1330 and 1580 cm$^{-1}$, respectively, as shown in the inset in Fig. 6. The $D$ peak is generally caused by defects in the curved graphite sheet and by the finite sizes of graphite crystallites. The $G$ peak corresponds to the tangential stretching ($E_{2g}$) mode of graphite and indicates the presence of crystalline graphitic structure in the MWNTs. We found that the width of the $D$ peak narrows as the exposure time of oxygen plasma increases while the width of the $G$ peak change slightly with plasma treatment.

Figure 7 shows the full width half maximum (FWHM) values of the $D$ peak and the intensity ratio of $I_G/I_D$ as a function of oxygen plasma treatment time. The FWHM value of the $D$ peak decreases by approximately 15 nm during the initial 20 s of plasma treatment time and then saturates at approximately 65 nm FWHM. The sharper $D$ peaks after the oxygen plasma treatment could be due to the reduced disorder and/or reduced amounts of other carbonaceous materials within the film. These other materials are undoubtedly incorporated in the MWNTs film during the CVD process and could be removed by the O$_2$ plasma more readily than the
MWNTs due to their structural imperfection. The intensity ratio $(I_G/I_D)$ shows a slight increase with the plasma treatment time up to 20 s and then decreases. This, we think, indicates that overexposure to the oxygen plasma can damage the MWNTs as well.

C. Electrical characteristics of the MWNTs

To investigate the effect of oxygen plasma treatment on the electrical properties of the MWNTs, electrical resistances are measured in the temperature range of 2–300 K. The oxygen plasma treatments were performed for 20 and 100 s at 45 W. The MWNTs were also inspected using a SEM in order to confirm that there was little change in their morphology after the O$_2$ plasma treatment.

Figure 8 shows the temperature dependence of the resistance measured from the as-grown MWNTs on the four-probe patterned Fe layer, with different O$_2$ plasma exposure times. For all samples, the four-probe resistance increases as the temperature decreases, showing typical semiconducting characteristics. Since the intrinsic resistance of individual MWNTs is much lower than the measured resistance, the resistance is mainly attributed to electron hopping through tube to tube junctions, approximately perpendicular to the tubes’ axes. For the variable range hopping (VRH) model in the strong localization regime, the low-temperature resistivity $\rho(T)$ is given by

$$\rho(T) = \rho_0 \exp \left( \frac{T_0}{T} \right)^m$$

or

$$\ln \left( \frac{\rho(T)}{\rho_0} \right) = \left( \frac{T_0}{T} \right)^m,$$

where the exponent $m=1/4$, 1/3, and 1/2 for three-dimensional, two-dimensional, and one-dimensional VRH conduction, respectively; and $T_0$ is the Mott characteristic temperature.

In order to analyze the obtained results, we tried to fit the resistance using different $m$ values in Eq. (1) and found that the best fit was obtained using a $T^{-1/4}$ behavior. The choice of $m=1/4$ makes the data fall on straight lines in the low temperature region.

Figure 9 shows $\ln(R/R_0)$ versus $T^{-1/4}$ for the as-grown MWNTs and after O$_2$ plasma treatment for 100 s. The linear increase of $\ln(R/R_0)$ in the lower temperature region supports the validity of the three-dimensional VRH model in the aligned MWNTs. The measured slopes were almost the same for the as-grown and for the plasma treatment for 20 s, giving a $T_0$ of 4.5 K. A smaller value of $T_0$ (2.5 K) was obtained after an O$_2$ plasma treatment for 100 s. The decrease in $T_0$ indicates a degradation in the localization of the electron wave functions, probably due to defects generated in the MWNTs after the excess plasma treatment.

IV. CONCLUSIONS

A four-probe patterned catalyst layer has been developed in order to directly measure the electrical characteristics of as-grown MWNTs. The temperature dependence of the four-probe resistance suggests that the as-grown MWNTs are semiconducting in directions perpendicular to the tube axis and follow the three-dimensional hopping conduction mecha-
nism. Raman spectroscopy results indicate that oxygen plasma treatments are useful for reducing the carbonaceous material in the film. With the oxygen plasma treatment, the resistance of the aligned MWNTs increases mainly due to the suppression of current conduction through these carbonaceous materials. These results suggest that O$_2$ plasma treatment is effective in improving the film quality of as-grown MWNTs.

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