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Nitrogen Doping of Single-Walled Carbon Nanotube by Using Mass-Separated Low-Energy Ion Beams

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Mass-separated nitrogen ions with the mass number of 14 were irradiated to the single-walled carbon nanotubes (SWCNTs) under an ultra high-vacuum pressure of $10^{-7}$ Pa for the purpose of achieving nitrogen doping in nanotubes. The incident angle of the ion beam was normal to the target nanotube, and the ion beam energy was 30 eV, which was close to the displacement energy of graphite. The dependence of the structure of SWCNTs on the ion dose was investigated. The ion dose ranged from $2.8 \times 10^{14}$ to $2.2 \times 10^{16}$ ions/cm$^2$. The nitrogen ions are incorporated into graphite sheets of SWCNTs after irradiation at $2.8 \times 10^{16}$ ions/cm$^2$. The graphite structure is distorted and many defects are induced in the nanotube by the nitrogen incorporation. The structure is changed to amorphous after irradiation at $2.2 \times 10^{16}$ ions/cm$^2$. The nitrogen ions with the ion energy of 25 eV are irradiated to the field effect transistor device with the nanotube channel. The n-type characteristic appears upon ion irradiation, and the device exhibits ambipolar behavior. [DOI: 10.1143/JJAP.44.1611]

KEYWORDS: carbon nanotube, SWCNT, doping, low-energy ion beam, ion implantation, CNT-FET

1. Introduction

Carbon nanotubes (CNTs) are expected to have some interesting properties, and the electrical properties of CNTs are significant fundamental interest.1,2 They are predicted to be offering the behavior of metals or semiconductors, which depends on their diameter and chirality. The semiconductive properties of CNTs are attractive for nano scale device applications,3 such as field-effect transistors consisting of CNTs,4–6 and even CNT logic circuits have been reported.7,8 The control of the electron transport properties is important for the electrical application of CNTs, and adding or removing carriers from systems can modulate their resistance. Doping by a gas phase reaction of alkali metals such as potassium or cesium with nanotubes has been reported.9,10 Reversibly intercalating and deintercalating potassium can control the doping level of CNTs. Varying the encapsulated fullerene molecules can modulate the band gap of CNTsencaging fullerenes,11 which were called pea-pods. However, these techniques are not suitable for the device application of CNTs because of thermal unsuitability or difficulty in device production.

Ion implantation at high energy in the MeV order, which is usually used for the doping of Si devices, has some advantages, such as the controllability of dopant species and doping level. However, as the high-energy ions pass through the CNTs, a technique for low-energy ion irradiation to nanotubes is necessary. Mass-separated low-energy ion-beam irradiation is the most suitable method for doping to the CNTs, because it can provide monoenergetic ion species, and because the irradiation parameters are independently controllable. In previous studies using the mass-separated low-energy ion-beam irradiation, the vacuum pressure during irradiation was more than $10^{-5}$ Pa.12,13 However, with low vacuum pressure during irradiation, high-speed neutral species produced by an inelastic collision of fast ions with residual gas molecules also impact and damage the target. We have developed a mass-separated low-energy ion-beam irradiation system under an ultra high vacuum (UHV) of less than $2 \times 10^{-7}$ Pa.14 This system permits irradiation to targets without damage to the target from the impact of high-speed neutral species produced by inelastic collisions of fast ions with residual gas molecules.

In this paper, we report nitrogen ion doping into SWCNTs by mass-separated low-energy nitrogen ions. We also report an investigation of the effect of ion dose on the structure of the SWCNTs, and of the effects of nitrogen ions on the electrical transport in CNT devices.

2. Experimental Methods

Low-energy ion irradiation to SWCNT was carried out by the mass-separated ion beams (MSIB) system. The MSIB system is shown schematically in Fig. 1. Our MSIB system consisted of an ion source, a mass-separation magnet, a transport tube with magnetic lenses, a deflection magnet, deceleration electrodes, and a deposition chamber with a sample-exchange transporter. The plasma-filament ion source, which is operated at a higher discharge current with a longer lifespan than the conventional Freeman ion source, was used as the ion source.15 The ions were extracted from the ion source at approximately 35 kV and mass-separated by means of a sector-type mass analyzer. The ion beam was then focused by a triplet quadrupole magnetic lens. The steering magnet lens in front of the quadrupole lens was used to position beams in a beam transport tube. The ion beam was bent by the deflector magnet, and the fast neutrals, which were produced by inelastic collisions of the fast ions with residual gas molecules, were trapped. After deflection, the ion beam was decelerated by triplet electrodes and irradiated to the target. All magnets and the beam transport tube were floated at an acceleration voltage, and the ion source was biased at a positive voltage with respect to the ground level. The final ion energy was on the basis of the source voltage plus the plasma potential of the ion source with respect to the grounded target.

Commercial SWCNTs, which were produced using the arc discharge plasma of graphite by SES Ltd., (Houston, USA), were used as a target material in this study. The
SWCNTs were dispersed by sonication in hexane, and held with a carbon mesh supported by a copper grid for the observation using a transmission electron microscope (TEM). Field effect transistor (FET) devices based on SWCNTs were also prepared, and the effect of the ion irradiation on their electrical properties was examined. The preparation of the CNT-FET devices was described in detail in our previous report. The distance between the source and drain electrodes was 4 μm.

$^{14}$N$^+$ irradiation to the SWCNT targets was performed. N$_2$ was used as the source gas for the nitrogen ions, and Ar was used as the filament plasma gas. The incident angle of the ion beam was normal to the SWCNT targets. As the displacement energy of graphite was reported to be approximately 25 eV, the ion energies of the nitrogen ion species were 25 or 30 eV. The ion dose ranged from $2.8 \times 10^{14}$ to $2.2 \times 10^{16}$ ions/cm$^2$. The base pressure in the ion irradiation chamber was under $1.0 \times 10^{-8}$ Pa, and the pressure during irradiation was $4 \times 10^{-7}$ Pa. The specimen was not heated during the ion irradiation.

The micro structural characterization of specimens and electron energy loss spectroscopy (EELS) were carried out using an energy-filtering transmission electron microscope (EF-TEM) (Leo, EM-922). The microscope was equipped with an OMEGA-type energy filter, which allows the selection of electrons undergoing certain energy losses.

### Results and Discussion

The structural change of SWCNTs due to ion irradiation was examined by means of TEM. The CNTs before the ion irradiation, of which a TEM micrograph is shown in Fig. 2(a), have clear bundles with a single-walled structure, and the average diameter of tubes is 1.4 nm. The nitrogen ions with the ion energy of 30 eV were irradiated to the SWCNT bundles. TEM micrographs of the SWCNTs after ion irradiation doses of $2.8 \times 10^{14}$, $1.7 \times 10^{15}$, and $2.2 \times 10^{16}$ ions/cm$^2$ were shown in Figs. 2(b), (c), and (d), respectively. The CNTs still have a clear single-walled structure after the ion irradiation dose of $2.8 \times 10^{14}$ ions/cm$^2$. However, after the ion irradiation dose of $1.7 \times 10^{15}$ ions/cm$^2$, many amorphous carbons were observed around bundles of SWCNTs. The bundle structure of SWCNTs disappeared and was changed to an amorphous structure after the ion irradiation dose of $2.2 \times 10^{16}$ ions/cm$^2$.

The number of carbon atoms in a carbon hexagonal ring unit is two (Fig. 3). The lattice parameter of the graphite $a$ axis is 0.246 nm. Therefore, the number of carbon atoms in the unit area of the graphite sheet is obtained according to the formula $2/(\sqrt{3}/2 \times a^2) = 3.8 \times 10^{15}$ atoms/cm$^2$. The number of carbon atoms in a SWCNT with diameter $d$ is $3.8 \times 10^{15} \times \pi \times 1.4 \times 10^{-7} \times L = 1.7 \times 10^9 \times L$ atoms. Bundles consist of approximately twenty SWCNTs, and the diameter of a bundle is 12.5 nm according to the TEM observation. Therefore, the number of carbon atoms in the unit area of the SWCNT bundles is $1.7 \times 10^9 \times L \times 20/(12.5 \times 10^{-7} \times L) = 2.7 \times 10^{16}$ atoms/cm$^2$. The ion doses used in this study were $2.8 \times 10^{14}$, $1.7 \times 10^{15}$, and $2.2 \times 10^{16}$ ions/cm$^2$. Therefore, the atomic ratio of irradiated nitrogen to carbon in the CNTs was in the order of approximately 10$^{-2}$ to 1. As the structure of CNTs after the irradiation of $2.2 \times 10^{16}$ ions/cm$^2$ dose was amorphous according to the TEM observation, many strains or defects are induced into the graphitic structure in CNTs by the nitrogen irradiation.

EELS analyses were performed on the SWCNTs to investigate the effects of the ion irradiation. EEL spectra in the carbon K-edge of the SWCNTs after ion irradiation doses of $2.8 \times 10^{14}$, $1.7 \times 10^{15}$, and $2.2 \times 10^{16}$ ions/cm$^2$ are shown in Fig. 4(a). EELS K-edge spectrum of the SWCNTs without ion irradiation is also shown in Fig. 4(a). The peak at 292 eV can be attributed to the transition from 1s to the $\pi^*$ state, and the shoulder at 284 eV is related to the transition from 1s to the $\sigma^*$ state. The presence of the $\pi^*$ peak indicates the existence of carbon $sp^2$ or $sp$ bonds in the structure. The subpeaks between 300 and 325 eV indicate the near-edge structure of carbon. The spectrum of SWCNTs without irradiation is similar to that of graphite, and the presence of these peaks clearly indicates that the carbon atoms of SWCNTs are ordered in a graphite-like manner. The $\pi^*$ and $\sigma^*$ peaks were slightly broadened after the ion irradiation.
A dose of $2 \times 10^{14}$ ions/cm$^2$, and this is caused by the distortion of the graphite structure due to the incorporation of nitrogen ions in the SWCNTs. The $\pi^*$ and $\sigma^*$ peaks were broadened further according to the ion irradiation, and the spectra were close to those of amorphous carbon at the ion dose of $2.2 \times 10^{16}$ ions/cm$^2$. This result agrees well with the TEM observations.

EELS spectra of the nitrogen K-edge of the SWCNTs after ion irradiation of $2 \times 10^{14}$, $1 \times 10^{15}$, and $2 \times 10^{16}$ ions/cm$^2$ dose are shown in Fig. 4(b). In the spectra from SWCNTs after the irradiation at $2 \times 10^{14}$ ions/cm$^2$, it is impossible to detect the nitrogen due to its dilution, which is mentioned above. The nitrogen peak appears slightly from the specimen after the irradiation at $1 \times 10^{15}$ ions/cm$^2$, but is clearly detected from the specimen with an irradiation dose at $2.2 \times 10^{16}$ ions/cm$^2$. The peak at 398 eV is attributed to the transition from $1s$ to the $\pi^*$ state, and the peak at 405 eV arises from the transition from $1s$ to the $\sigma^*$ state. It is clarified that the nitrogen bonded in an $sp^2$-like manner in the SWCNTs.

An FET device based on SWCNTs was fabricated and the electrical properties were investigated. The dependence of the drain current on the gate bias of the CNT-FET device
FET exhibits p-type conduction due to the absorption of carbon atoms in the unit area of one SWCNT is varied between 3.3 \times 10^{12} \text{ atoms/cm}^2. The number of carbon atoms in the unit area of one SWCNT is 3.8 \times 10^{15} \times \pi \approx 1.2 \times 10^{16} \text{ atoms/cm}^2. Therefore, the atomic ratio of irradiated nitrogen to carbon in a CNT is 450 ppm.

Annealing of CNT-FET devices after the ion irradiation was not performed. The drain current at the negative gate bias decreases and the drain current at the positive gate bias increases in comparison with those in the specimen before the ion irradiation. The n-type characteristic clearly appeared in the positive gate bias region, and this FET exhibits ambipolar behavior. We consider that the n-type characteristic of CNT is induced by the nitrogen incorporation into the SWCNTs.

4. Conclusions

We have succeeded in the ion doping of carbon nanotubes by means of a mass-separated ion beam technique under the ultra-high vacuum conditions. The nitrogen ions with the mass number of 14 were irradiated to the single-walled carbon nanotubes at the ion energy of 30 eV, which was close to the displacement energy of graphite. The nanotubes maintain their single-walled structure, with some distortions and defects occurring after the ion irradiation of 2.8 \times 10^{14} \text{ ions/cm}^2 due to the nitrogen incorporation into the nanotube. The structure is changed to an amorphous one after the higher dose irradiation of 2.2 \times 10^{16} \text{ ions/cm}^2. The field effect transistor device with the nanotube channel shows p-type conduction in as prepared specimen. The n-type characteristic appears upon nitrogen ion irradiation with the energy of 25 eV, and the device exhibits ambipolar behavior.