

Effect of Pretreatment on the Deposition of Carbon Nanotubes by Using Atmospheric-Pressure Plasma-Enhanced Chemical-Vapor Deposition

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In this study, carbon nanotubes were grown on NiCr(10 nm)/Cr(100 nm)/glass substrates by using atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) with acetylene (C_2H_2) as the carbon source gas at 400 °C, and the effects of pre-treatment, such as annealing at 400 °C in N_2 and an NH_3/He plasma treatment, on the growth characteristics of the carbon nanotubes were investigated. Carbon nanotubes were grown only on the samples treated with the NH_3/He plasma; nearly no carbon nanotubes were grown on the as-deposited samples or on the samples annealed at 400 °C in N_2 . The carbon nanotubes grown on the sample treated with the NH_3/He plasma appear to be related to enhanced carbon diffusion to the Ni catalyst particles because its the cleaner Ni surface to be cleaner than that of the annealed sample and Ni surface area with nanosized Ni particles is larger than that of the as-deposited sample. Because the grown carbon nanotubes were multi-walled carbon nanotubes with defects on the walls. The inner diameters of the grown carbon nanotubes were 3 ~ 5 nm, and the outer diameters were 20 ~ 40 nm.

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I. INTRODUCTION

Since their first discovery in 1991 [1], carbon nanotubes (CNTs) have been considered for many different applications, such as flat panel displays, power sources, semiconductor devices, electrochemical capacitors, superconductors, etc. [2, 3]. Among these various applications, CNTs are most widely investigated for the possible applications to field-emission display devices due to advantages in the material properties: high aspect ratio with tens of nanometer widths, high strength, high conductivity, etc. [4, 5]. If the CNTs are to be utilized for commercial field-emission displays, multi-walled CNTs need to be grown uniformly on large-area glass substrates and, even more importantly, especially, the CNTs have to be grown at temperatures lower than glass-softening temperature.

CNTs are grown using various methods, such as arc discharges [6], laser ablation of carbon [7, 8], chemical vapor deposition [9], plasma-enhanced chemical-vapor deposition (PECVD) [10], etc. These methods are generally carried out in vacuum; however, these days, methods for growing CNTs by using an atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) are actively being investigated [11]. For appli-

cations to the field-emission display devices, it would be preferable if the CNTs could be grown at atmospheric pressure because that would reduce the cost related to expensive vacuum parts for the extremely large substrate and in-line processing could be used. Also, if a conventional soda-lime glass substrate is to be used, the growth temperature must be lower than the glass-softening temperature of 450 °C, which can be achieved by using PECVD. Before the growth of the CNTs by using PECVD, samples with catalyst layers are generally exposed to N_2 or H_2 plasmas for pre-treatment of the catalyst surfaces by bombarding the surfaces with nitrogen ions, by cleaning the surfaces with hydrogen atoms, etc. The use of a N_2 plasma, instead of a H_2 plasma, is known to promote agglomeration of the Ni catalyst due to the higher momentum and energy transfer to the substrate during the bombardment [12, 14]. A NH_3 plasma is also used for the pre-treatment, and it is known to have a better effect than a N_2 plasma because it is more easily dissociated due to the dissociation energy of N-H (339 kJ/mol) being lower than that of N-N (945 kJ/mol). Also, due to the hydrogen atoms generated during the decomposition of NH_3 , a surface cleaning effect can also be obtained [15, 16].

In this study, CNTs were grown on a NiCr-coated soda-lime glass substrate by using AP-PECVD at 400 °C. A modified dielectric barrier discharge (DBD) was used to generate a plasma atmospheric pressure higher

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than that generated by a conventional DBD and to reduce the growth temperature [17]. Before the growth of the CNTs, the NiCr surface was exposed to the modified DBD using NH₃/He (150 sccm: 8 slm) to understand the pre-treatment effect caused by the NH₃/He atmospheric-pressure plasma. Therefore, in this study, the effects of a pre-treatment using a NH₃/He atmospheric-pressure plasma on the properties of the Ni surface and the growth of the CNT by using AP-PECVD were investigated.

II. EXPERIMENT

Fig. 1 shows the AP-PECVD system used in this study to grow CNTs at atmospheric pressure. As the figure shows, the top electrode was connected to an AC power (20 ~ 30 kHz, 2 kW), and the bottom electrode was grounded. Dielectrics, 3 mm thick, covered both electrodes, and the dielectric on the top of the electrode was perforated to generate a higher density plasma compared to that generated by a conventional DBD and to distribute the reactive gas more uniformly over the substrate. A higher density plasma is believed to be obtained in our modified DBD system by using the electric field sustained in the dielectric of the top electrode to accelerate the electrons in the holes; therefore, an ion-beam-like plasma, in addition to the conventional DBD between the two electrodes, is formed. The substrate temperature was maintained at 400 °C by using a heating block, and the substrate temperature was measured directly by locating and attaching a thermocouple to the surface of the glass substrate. Due to the noise to the thermocouple on the glass substrate during the plasma operation, the temperature of the substrate was maintained by using the thermocouple in the heater. The air-gap distance between the top electrode and the bottom electrode was maintained at 5 mm.

As samples, 100-nm-thick Cr was deposited as an adhesion layer followed by a 10-nm-thick NiCr layer as a catalyst layer without breaking the vacuum on the soda-lime glass substrate by using RF magnetron sputtering at room temperature. Instead of Ni, NiCr was used to grow less dense CNTs on the substrates for a field emitter. The NiCr : Cr(10 nm)/Cr(100 nm) coated glass substrate was inserted in the AP-PECVD chamber and annealed for 8 min at 400 °C in N₂ before the deposition of the CNTs. For the pre-treatment of the NiCr surface, after the annealing in N₂ for 5 min at 400 °C, the samples were exposed to a NH₃(150 sccm)/He(8 slm) atmospheric-pressure plasma generated by using 6 kV of AC power for 3 ~ 5 min at 400 °C. CNTs were deposited on the annealed or pre-treated samples for 4 minutes by using AP-PECVD with C₂H₂(150 sccm)/NH₃(270 sccm)/N₂(100 sccm)/He(8 slm) at 6 kV of AC power while the substrate temperature was kept at 400 °C. He was used to sustain stable atmospheric pressure plasmas, NH₃ and N₂ to activate the substrate surface, and C₂H₂

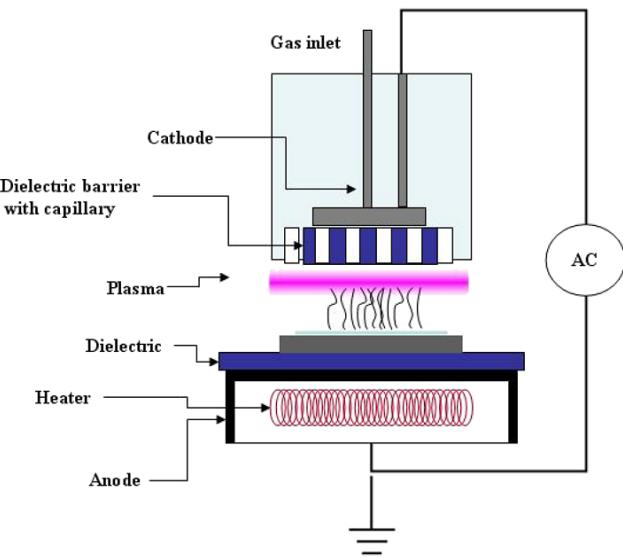


Fig. 1. Schematic diagram of the capillary dielectric discharge-type AP-PECVD system used in this study.

as the carbon source for the CNTs.

The sample's surface roughness before the deposition of CNTs was investigated using an atomic force microscope (AFM, Thermo-Microscopes Inc., CP Research) and the chemical binding states of the NiCr surfaces were investigated using X-ray photoelectron spectrometer (XPS, VG Microtech Inc., ESCA2000). The morphology of the grown CNTs was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700), and the structure was observed using a transmission electron microscope (TEM, Jeol JEM 300F). A Fourier transform Raman spectrometer (FT-Raman, Renishaw RM1000-InVia) was used to analyze the defect states of the grown CNTs.

III. RESULTS AND DISCUSSION

Fig. 2 shows the surface roughness of the NiCr(10 nm)/Cr(100 nm) on the soda-lime glass a substrate measured by AFM and FE-SEM (a) after the deposition of 10-nm-thick NiCr on the 100-nm-thick Cr-deposited soda-lime glass substrate, (b) after annealing at 400 °C in N₂ for 8 min in the AP-PECVD chamber, (c) after annealing at 400 °C in N₂ for 5 min in the AP-PECVD chamber followed by a pre-treatment with a NH₃/He atmospheric-pressure plasma in the same chamber for 3 min and (d) after the pre-treatment with a NH₃/He atmospheric-pressure plasma for 5 min, instead of 3 min used for the condition in (c). 150 sccm of NH₃ and 8 slm of He were used and 6 kV of AC power was applied to generate the NH₃/He atmospheric-pressure plasma, and during the plasma treatment, the substrate temperature was maintained at 400 °C. As in Fig. 2(b) shows, after

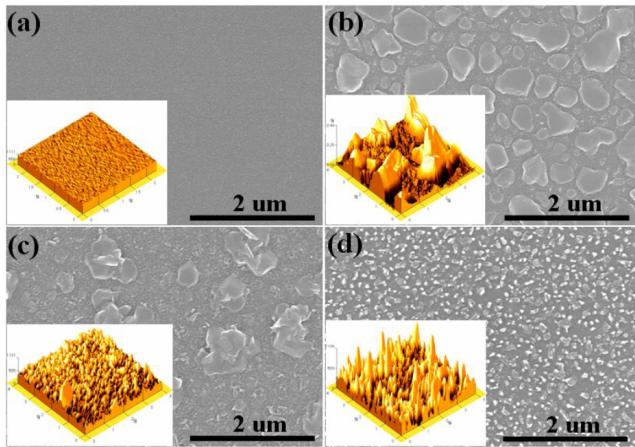


Fig. 2. AFM and SEM images of the NiCr surface (a) after the deposition of 10 nm thick NiCr on the 100 nm thick Cr/soda-lime glass substrate, (b) after annealing at 400 °C in N₂ for 8 min in the AP-PECVD chamber for the NiCr deposited sample, (c) after annealing at 400 °C in N₂ for 5 min followed by a NH₃/He atmospheric pressure plasma treatment for 3 min in the AP-PECVD chamber and (d) after the pre-treatment with a NH₃/He atmospheric pressure plasma for 5 min instead of 3 min as for (c).

the annealing at 400 °C for 8 min, the sample surface appears to have large Ni particles due to the agglomeration of Ni and to the formation of some small Ni particles. The addition of the NH₃/He plasma for 3 min after the annealing at 400 °C for 5 min, as shown in Fig. 2(c), however, increases the number of the smaller nanosized Ni particles, instead of the large Ni particles, and the increase in the pre-treatment time appears to increase the smaller Ni particles further, as shown in Fig. 2(d). The AFM data in Fig. 2 shows that the use of a NH₃/He atmospheric-pressure plasma treatment and an increase in the treatment time during the annealing increases the surface area due to an increase in the number of small nanosized Ni particles.

The chemical composition and the binding states of the NiCr surface of the samples before and after the pretreatment were investigated using XPS. Fig. 3 shows the XPS narrow scan data of (a) Ni and (b) Cr for the sample conditions shown in Fig. 2(a), (b) and (c). The Ni2p_{3/2} binding energies for Ni, NiO, and Ni₂O₃ are located at 852.5 eV, 854.3 eV, and 855.8 eV, respectively; therefore, as shown in Fig. 3(a), the Ni2p_{3/2} peaks at about 853 eV and 855.6 eV appear to be related to Ni and Ni₂O₃. In the case of Cr, the Cr2p_{3/2} binding energies are known to be located at 574.4 eV for Cr, 576.9 eV for Cr₂O₃, 576.3 eV for CrO₂, and 578.3 ~ 579.8 eV for CrO₃. Therefore, the peak at 575.75 eV shown in Fig. 3(b) appears to be related to CrO₂ (or Cr₂O₃) and the peaks at 578.3 eV and 579.7 eV appear to be related to CrO₃. As the figure shows, due to the air exposure of the sample, the as-deposited NiCr appears to be partially oxidized as Ni₂O₃ and CrO₂ (or Cr₂O₃). During the annealing in N₂ at 400

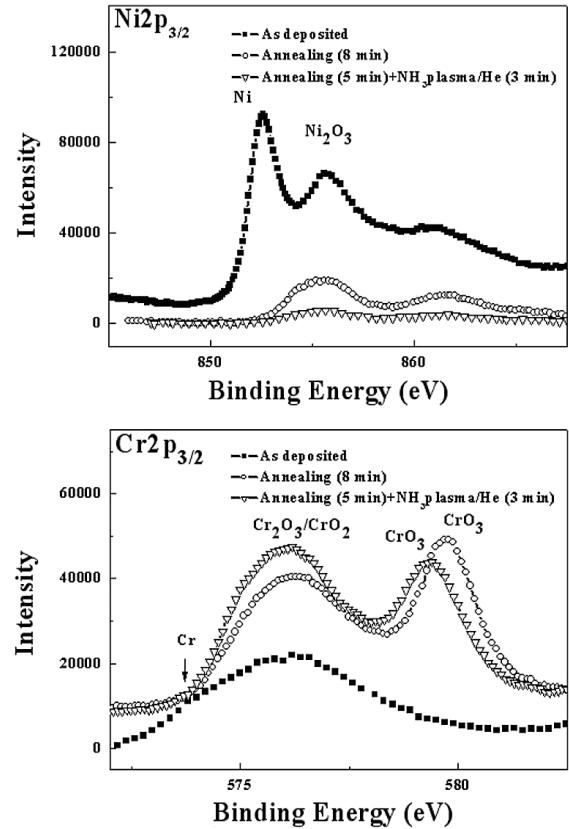


Fig. 3. XPS narrow-scan spectra of (a) Ni2p_{3/2} and (b) Cr2p_{3/2} for the sample surfaces in Fig. 2(a), (b) and (c).

Table 1. Atomic composition, as measured by using XPS, for the NiCr surfaces shown in Fig. 2(a), (b) and (c).

Treatment method	Atomic concentration(%)		
	O	Cr	Ni
As deposited	54.1	19.3	26.6
Annealing (8 min)	63.2	33.4	3.4
Annealing (5 min) + NH ₃ /He plasma (3 min)	60.8	40.0	3.2

°C in the AP-CVD chamber, the remaining metallic Ni and Cr appear to be oxidized further by forming Ni₂O₃ and CrO₂/Cr₂O₃, respectively, and Cr₂O₃ appears to be oxidized further to CrO₃ due to a small air leak to the atmospheric-pressure system. However, when the NH₃/H₂ plasma treatment was used after the annealing in N₂ at 400 °C for 5 min, a decrease of NiCr surface oxidation caused by decrease in Ni₂O₃ (or CrO₃) binding and by an increase in Cr₂O₃/CrO₂ from CrO₃ could be observed.

In the case of Ni shown in Fig. 3(a), the Ni2p_{3/2} peak intensity was lower after annealing at 400 °C for 8 min. and was lower still after exposure to the NH₃/He plasma. When the surface atomic composition was measured by using XPS, as shown in Table 1, a decrease in Ni percent

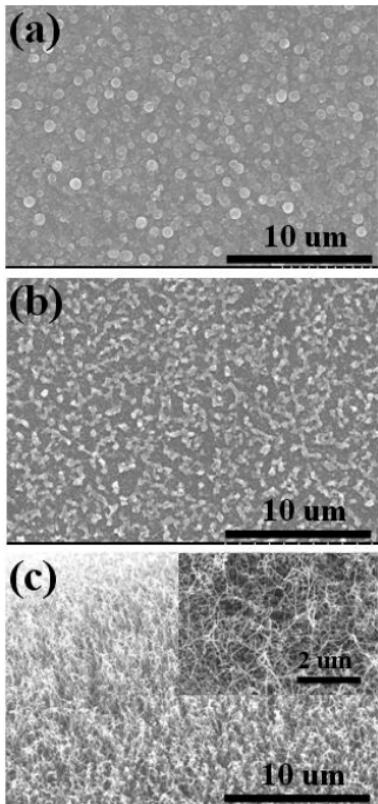


Fig. 4. SEM images of the CNTs grown on the NiCr(10 nm)/Cr(100 nm)/glass substrates. The conditions for (a), (b) and (c) are the same as those in Fig. 2(a), (b) and (c), respectively.

on the NiCr surface could be observed after annealing and after NH_3/He plasma treatment. However, the Cr percent increased after annealing and increased still further after NH_3/He plasma treatment. The decrease in the Ni percent and the increase in the Cr percent on the sample surface with annealing and plasma treatment appear to be related not only to interdiffusion between the NiCr layer on the top and the Cr layer located below but also to the formation of nanosized Ni particles on the surface by the agglomeration of Ni.

Using the NiCr(10 nm)/Cr(100 nm)/glass samples pre-treated under the conditions in Fig. 2(a), (b) and (c), we grew CNTs for 4 min at 400 °C by using APP-PECVD with $\text{C}_2\text{H}_2 : \text{NH}_3 : \text{N}_2 : \text{He}$ (150 sccm : 270 sccm ; 100 sccm : 8 slm), and the SEM images after the growth are shown in Fig. 4(a), (b) and (c), respectively. As the figures shows (a), as-deposited samples and (b) the samples annealed for 8 min have carbon clusters instead of CNTs on the sample surface. However, in the case of the sample treated with the NH_3/He plasma for 3 min after annealing in N_2 at 400 °C for 5 min, “spaghetti-like” 5 ~ 10-nm-long CNTs were observed, as shown in Fig. 4(c).

The samples grown under the conditions in Fig. 4(a), (b) and (c) were also investigated using Raman spec-

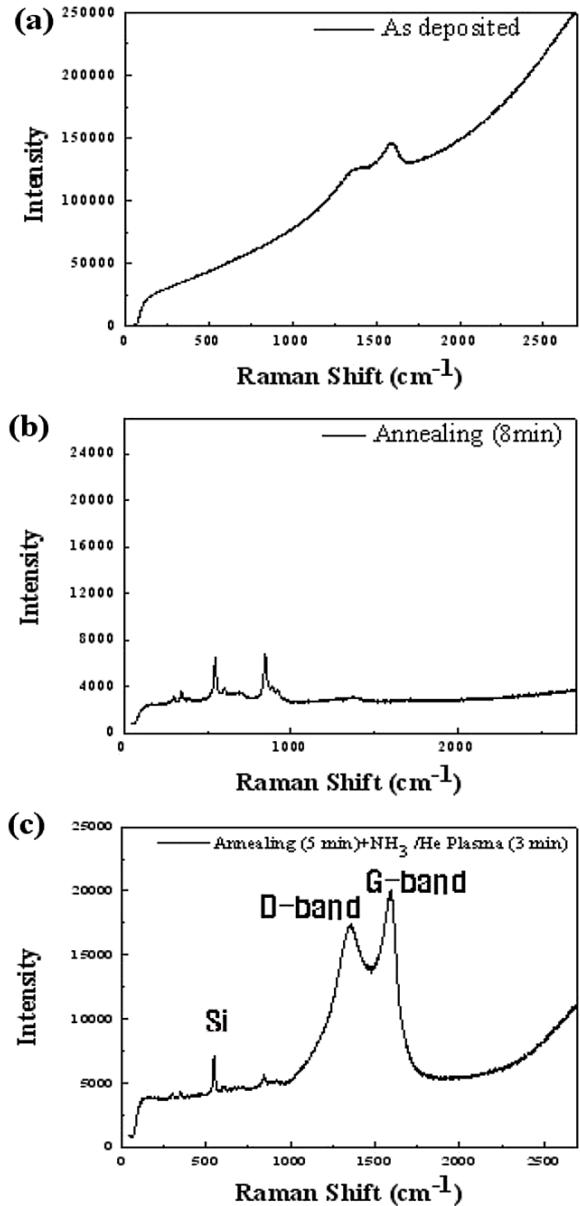


Fig. 5. Raman spectra of the CNTs grown on the NiCr(10 nm)/Cr(100 nm)/glass substrates. The conditions for (a), (b) and (c) are the same as those in Fig. 2(a), (b) and (c), respectively.

troscopy and the results are shown in Fig. 5(a), (b) and (c), respectively. As Fig. 5(a) shows, when CNTs were grown on the as-deposited NiCr/Cr/glass samples without a pre-treatment, very small peaks near 1350 cm⁻¹ and 1588 cm⁻¹ were observed, which appear to correspond to carbonaceous particles with defects and multi-walled CNTs, respectively. However, in the case of the sample annealed at 400 °C for 8 min in N_2 , small peaks near 300, 341, 528, and 1350 cm⁻¹ could be observed. The peaks near 300 cm⁻¹ and 341 cm⁻¹ appear to be related to multi-walled CNTs having an internal diameter of 0.7 ~ 1.0 nm; that is, those peaks appear to

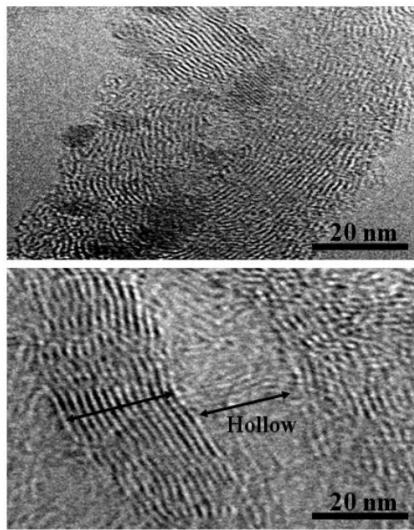


Fig. 6. TEM image of the CNT grown at 400 °C by using AP-PECVD with the NiCr(10 nm)/Cr(100 nm)/glass sample pretreated with a NH₃/He atmospheric pressure plasma for 3 min in the AP-PECVD chamber after annealing in N₂ at 400 °C for 5 min.

be related to RBM peaks observed from 200 ~ 500 cm⁻¹ [18]. The peak near 528 cm⁻¹ appears to be related to silicon from the glass substrate. Therefore, in the case of Fig. 5(a) and (b), even though there are peaks related to the CNTs, their peak intensities are very small; therefore, CNTs were not effectively grown under these conditions. However, in the case of the sample pre-treated by using the NH₃/He plasma after annealing in N₂ at 400 °C for 5 min, even though it does not show the peaks near 400 ~ 1100 cm⁻¹ related to the single-walled CNTs, it does show the large G-band peak at 1588 cm⁻¹ corresponding to the multi-walled CNTs and the D-band peak at 1350 cm⁻¹ corresponding to the defective carbon in the CNTs [19,20].

The growth of CNTs only under the condition of a NH₃/He plasma treatment, as shown in Fig. 4 and 5, appears to be related to the formation of small, nanosized Ni particles on the surface, as shown in Fig. 2(c). Also, it appears to be related to a reduction in the size of oxidized NiCr surface for the enhanced carbon diffusion to the Ni particles as shown in Fig. 3 and Table 1 through nitrogen ion bombardment and hydrogen surface cleaning of the NiCr surface during the plasma treatment. In addition, carbon clusters, instead of CNTs, are observed without N₂ annealing, which appears to be from the nonexistence of nanosized Ni particle before the growth of the CNTs.

The CNTs grown under the conditions shown in Fig. 4(c) were observed using TEM, and the result is shown in Fig. 6. As the figure shows, the grown CNTs had an inner diameter of 3 ~ 5 nm and an outer diameter of 20 ~ 40 nm. Also, as the figure shows, the CNTs had a multi-walled structure with the end of the tubes blocked. The outside wall of the multi-walled CNTs was

rough; therefore, the wall appeared to contain defects consisting of unstable random graphite.

IV. CONCLUSIONS

In this experiment, CNTs were grown at 400 °C, which is lower than the softening temperature of soda-lime glass, by using AP-PECVD with C₂H₂ : NH₃ : N₂ : He (150 sccm : 270 sccm : 100 sccm : 8 slm), and the effect of pre-treatment on the growth characteristics of the CNTs was investigated. The growth of CNTs on NiCr(10 nm)/Cr(100 nm)/soda-lime glass depended significantly on the pre-treatment conditions. CNTs were grown only on the sample pre-treated with a NH₃/He plasma after annealing at 400 °C in N₂ while nearly no CNTs were grown on the samples not treated or annealed in N₂ for 8 min. When the surface morphology and the surface chemical states of the NiCr after the pre-treatments were investigated, the NiCr surface treated with the NH₃/He plasma showed the formation of small Ni particles, an increase in the surface area, and a reduction in NiCr surface oxides formed during the annealing. These were due to nitrogen ion bombardment and hydrogen surface cleaning of the NiCr surface. Therefore, the CNTs grown on the sample treated with the NH₃/He plasma appear to be related to the enhanced carbon diffusion to the Ni particles through the cleaner Ni surface and to a larger Ni surface area for carbon diffusion. The grown CNTs were multi-walled CNTs with defects on the walls. The inner diameters of the CNTs were 3 ~ 5 nm, and the outer diameters of the tubes were 20 ~ 40 nm.

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