Growth of carbon nanotubes on stainless steel substrates by DC-PECVD

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], they have attracted considerable interest because of their unique physical properties and many potential applications. With the nanometer-size diameter and very large aspect ratio, CNTs exhibit unique electronic properties such as excellent electron emission efficiency and extraordinary mechanical properties. They are the potential building blocks for field emission displays, tips for scanning probe microscopy, X-ray sources using field emission cathode, hydrogen storage, chemical sensors, high-strength mechanical composites, etc. [2–5]. It is reported that X-ray emission properties of the CNT films were measured in the diode configuration, and the turn-on electric field of 3.87 V/μm and field enhancement factor β of about 1737 were obtained from the synthesized CNTs at the gap of 500 μm between the SUS substrate and the anode. These results have not only clarified the effects of the substrate on the growth of CNTs, but also shown the potential of CNTs in field emission applications, especially CNT-based cold-cathode X-ray tubes.

2. Experimental

CNTs had been grown on Ni-coated SUS substrates with a TiN buffer layer by dc plasma enhanced chemical vapor deposition (DC-PECVD). The Ni layer and the TiN buffer layer with a thickness...
of 50 and 1000 Å, respectively, were deposited by using a radio-frequency magnetron sputtering system. It has been reported that the formation of Ni grains during the pretreatment process plays a key role in growing CNTs; when Ni forms alloys such as NiFe, NiCr, etc. (with SUS substrates) or NiSi2 (with Si substrates), other isomers of carbon such as carbon nanotips are formed instead of CNT [13], and therefore TiN buffer layers with excellent electrical conductivity (resistivity ~25 mΩ cm) and high melting point (~3200 °C) [9] are usually added to prevent the reaction between catalyst layers and substrates [14]. To create uniform Ni particles, NH3 gas was introduced for 6 min. During this process, the cathode voltage, the temperature, and the flow rate were kept at ~550 V, 600 °C, and 60 sccm, respectively. The base pressure of the reactor was maintained 3.4 × 10⁻⁶ Torr. Before the CNT growth, we have performed annealing procedures at the temperature of 600 °C in H2 environments. After the pretreatment and annealing processes, CNTs were grown at 600 °C for 15 min using a mixture of acetylene and ammonia with the flow rates of 30 and 100 sccm, respectively. To examine the effects of SUS substrates on the growth of CNTs, CNTs were grown also on Ni-coated Si substrates at the same synthesizing conditions as above.

The morphology, density, and quality of the CNTs were analyzed using field emission scanning electron microscope (FESEM, Hitachi S-4800), a high resolution transmission electron microscope (HRTEM, JEM 2200FS), and Raman spectroscopy (Ar⁺ laser 514 nm, 2.42 eV), respectively. The morphology of Ni particles and Ni catalyst films were investigated using an atomic force microscope (AFM). The field emission properties of the CNT films were measured in the diode configuration in a vacuum chamber with pressure below 3.0 × 10⁻⁷ Torr. The anode was a Mo electrode, and the gap between the SUS substrate and the anode was 500 μm.

3. Results and discussion

Fig. 1(a) and (b) shows the AFM images of the Ni catalyst layers on SUS and Si substrates after the NH3 plasma pretreatment, respectively. The catalyst layers on both substrates were observed to aggregate and form Ni nanoparticles. However, Ni nanoparticles on SUS substrates (Fig. 1(a)) seem to be more uniform in size than those on Si substrates: most nanoparticles on SUS substrates have diameter from 20 to 40 nm while those on Si substrates have from...
10 to 140 nm, although the area uniformity of Ni particles on Si substrates is better compared with that on SUS substrates. We suggest that because of floating voltage in DC-PECVD [15], etching of the Ni layer on the metal substrate could be more effective due to its low resistivity, and therefore the Ni nanoparticles were more uniform. The morphology of surfaces of Ni catalyst layers on the SUS substrates (Fig. 1(a)) seems to be inhomogeneous. To interpret the phenomena, the Ni catalyst layers before the NH$_3$ plasma pretreatment (Fig. 1(c)) were also examined by AFM. Before the NH$_3$ plasma pretreatment, the morphology of the surface of the SUS substrate was inhomogeneous (Fig. 1(c)) and the inhomogeneity is attributed to the non-uniform surface of SUS substrates before the sputtering process.

The diameter of CNTs has been reported to be related to the size of the catalyst particles and the thickness of the catalytic layer [16], and a single CNT was grown on a single nanoparticle below a critical size [17]. This means that the diameters of the CNTs can be controlled by changing the size of Ni nanoparticles during the pretreatment process. Fig. 2(a) and (b) shows SEM images of the CNTs grown on SUS and Si substrates, respectively. The CNTs are well aligned perpendicular to the surface of both substrates, and have lengths of about 1.2 μm. However, the diameters of the CNTs grown on the SUS (Fig. 2(a)) are more uniform than those grown on the Si substrates (Fig. 2(b)). Fig. 3(a) and (d) shows TEM images of the CNTs grown on the SUS and Si substrates, respectively. The diameter of the CNTs grown on the SUS substrates ranges from 10 to 50 nm, and most of them have the diameter of about 30 nm (Table 1). The diameters of the CNTs are much smaller than those previously reported [18]. Although most of the CNTs grown on the Si substrates also have the diameter of about 30 nm, the diameters range from 10 to 140 nm (Table 1). It could be explained by the size uniformity of the Ni catalyst particles on the SUS substrates. Fig. 3(b) and (c) shows TEM images of the CNTs grown on the SUS substrates. The CNTs are multiwalled with the number of walls around 31. The clear walls of CNTs (Fig. 3(c)) show that the crystallinity of CNTs is as good as those previously reported [18].

Fig. 4 shows the Raman spectra of the CNTs grown on both Si and SUS substrates. The Raman spectra of the CNTs grown on both substrates are observed to have two prominent peaks at ~1346 cm$^{-1}$ (noted as D-band) and ~1588 cm$^{-1}$ (noted as G-band) with the intensity ratio $I_D/I_G$ of 0.99, which is related to the size of the sp$^2$ carbon clusters in the graphene sheet or the defect density [19]. We suggest that the $I_D/I_G$ ratio and therefore the quality of CNTs grown by PECVD do not strongly depend on their diameters as well as details of individual CNTs [20].

Fig. 5(a) shows the field emission current density ($J$) as a function of the applied electric field ($E$) from the CNTs film grown on the SUS substrate. The turn-on field, defined as the field for the emission current of 1 μA, was 3.87 V/μm with the gap of 500 μm between the SUS substrate and the Mo anode. According to previous works [6,21], the lowest turn-on electric field for multiwall CNTs was observed to be less than 1 V/μm at the gap of less than 300 μm between substrate and anode. Fig. 5(b) shows the Fowler–Nordheim (F-N) plot of ln($I/V^2$) vs. 1/V for the $J$–$E$ curves shown in Fig. 5(a). The plot shows a linear fit, indicating that the emission current of CNTs follows the F-N behavior. Since the gap between the substrate and the anode was 500 μm, assuming a work function of 5.0 eV for CNT, the field emission factor $β$ is estimated to be about 1737. The CNTs grown on the SUS substrates served as cold cathodes in the X-ray generation in our previous reports [5].
4. Conclusion

We had successfully grown carbon nanotubes on Ni-coated SUS substrates by DC-PECVD. The synthesized CNTs have the diameter of about 30 nm and the length of about 1.2 μm, which were more uniform compared to those grown on Ni-coated Si substrates. It is attributed to Ni catalyst particles on the SUS substrates formed by the pretreatment with NH$_3$ gas before the growth of CNTs, which were more uniform than those on the Si substrates. Field emission properties of the CNT films were measured in the diode configuration, and turn-on electric fields of 3.87 V/μm and field enhancement factor $\beta$ of about 1737 were obtained from the synthesized CNTs. Those results have shown the potential of CNTs in field emission applications, especially CNT-based cold-cathode X-ray tubes.

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