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Research Article

Growth of Pd-Filled Carbon Nanotubes on the Tip of Scanning Probe Microscopy

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We have synthesized Pd-filled carbon nanotubes (CNTs) oriented perpendicular to Si substrates using a microwave plasma-enhanced chemical vapor deposition (MPECVD) for the application of scanning probe microscopy (SPM) tip. Prior to the CVD growth, Al thin film (10 nm) was coated on the substrate as a buffer layer followed by depositing a 5 ~ 40 nm-thick Pd film as a catalyst. The diameter and areal density of CNTs grown depend largely on the initial Pd thickness. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images clearly show that Pd is successfully encapsulated into the CNTs, probably leading to higher conductivity. Using optimum growth conditions, Pd-filled CNTs are successfully grown on the apex of the conventional SPM cantilever.

1. Introduction

Since their discovery by Iijima in 1991 [1], CNTs have successfully been synthesized via various techniques such as arc-discharged method [2], laser vaporization [3], and chemical vapor deposition (CVD) [4]. The advantage of CVD lies in the controlled fabrication at a designated position on the substrate using patterned catalysts. In particular, plasma-enhanced CVD (PECVD) technique can control the growth direction of individual CNTs by electric field [5–7].

Recently, growth of metal-filled CNTs (MF-CNTs) using Pd as the catalyst has been demonstrated and their structure and growth mechanism were investigated [8–10]. The anomalous feature of the Pd-filled CNTs was that they contained a Pd nanowire of the length of micrometer size and diameter of nanometer size. Since Pd has been shown to be particularly useful for achieving reliable ohmic contacts to single walled CNTs (SWCNTs) [11], the Pd-filled CNTs are expected to have higher conductivity from conventional hollow nanotubes. This property has potential application for the conductive tip in scanning probe microscopy (SPM). In addition, Pd, in nanosize and low dimension, is known to change its magnetism from paramagnetic to ferromagnetic [12, 13]. The feature extends the application to the tip of magnetic force microscopy (MFM).

Here, we demonstrate controlled synthesis of Pd-filled CNTs on the Si substrate as well as on the tip apex of SPM probes using the microwave plasma-enhanced chemical vapor deposition (MPECVD). The diameter and density of CNTs are well controlled by changing Pd thickness. The structure is investigated by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (TEM). Raman spectroscopy is also conducted to investigate the quality of the Pd-filled CNTs.

2. Experimental

Pd-filled CNTs were synthesized by using a MPECVD system (CVD-CN-100, Ulvac, Japan). A 10 nm-thick Al film was deposited as a buffer layer on a Si wafer or cantilever. This layer is known to prevent the formation of silicide as well as to support catalyst as nanoparticle [14, 15]. Then Pd of 5–40 nm was deposited as catalyst by sputtering. The mixture

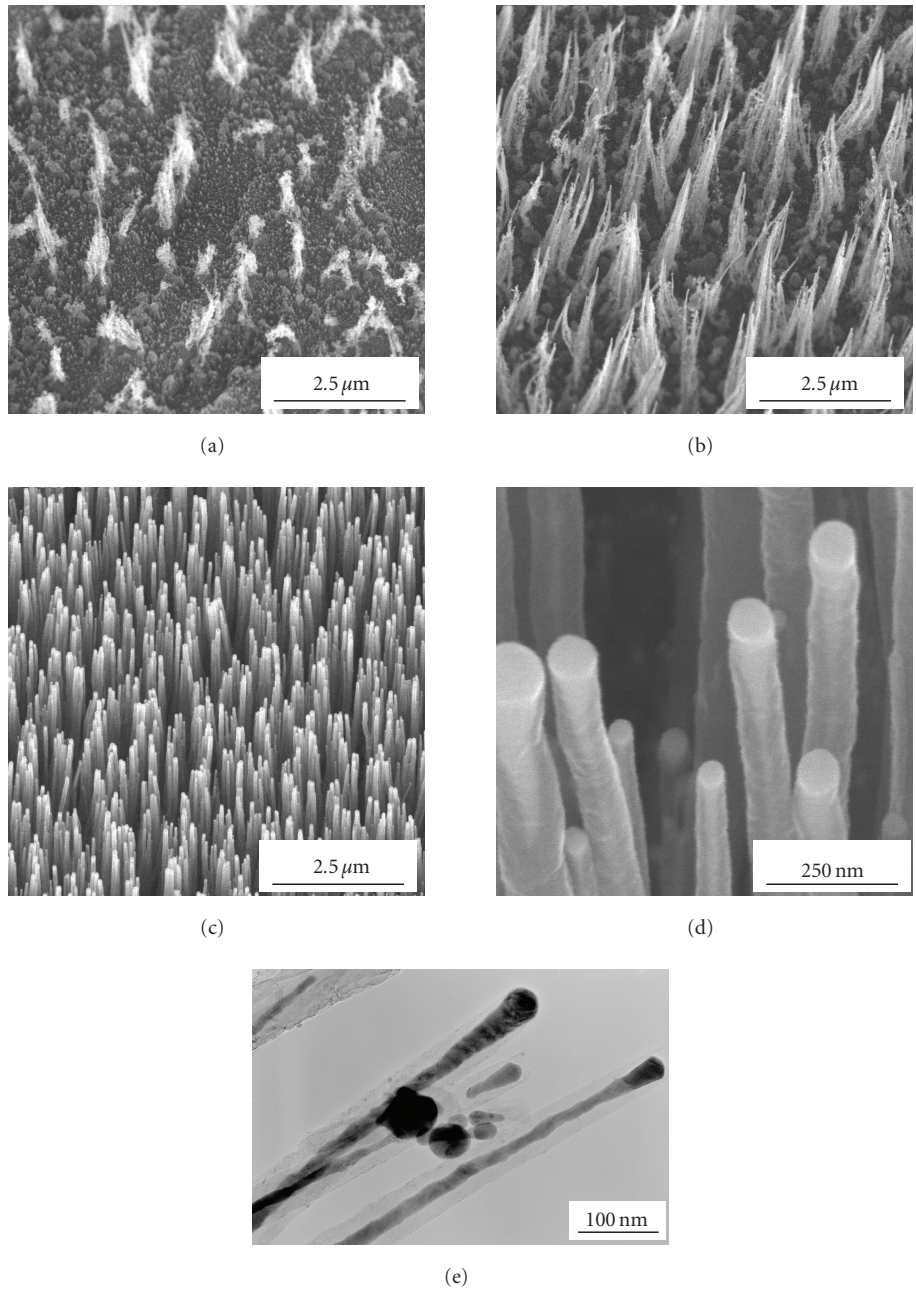


Figure 1: Low magnification SEM images of CNTs grown on (a) Pd (10 nm)/Al (10 nm)/Si, (b) Pd (20 nm)/Al (10 nm)/Si, (c) Pd (40 nm)/Al (10 nm)/Si. (d) High magnification SEM image of the CNTs in Figure 1(c). TEM image of the CNTs in Figure 1(a).

of H_2 and CH_4 gases was used for the CVD growth. The flow ratio of H_2 : CH_4 was kept constant at 80 : 20. Total gas pressure was set at 1.7 torr. We used a microwave of 2.45 GHz and 500 W, and the growth time was 10 minutes. During the growth process, a voltage of 200 V was applied between electrodes. Prior to the CNTs growth, the substrate was exposed to hydrogen plasma for 3 minutes to clean the substrate as well as to activate the catalyst. Hydrogen plasma has a significant annealing effect on Pd particles and alters their morphology [16]. The CNTs grown were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S4700), and high-resolution transmission electron microscopy (TEM, JEOL, JEM2000EX) and Raman spectroscopy (Jovin Yvon, LabRAM HR800) were carried out to determine the structure of the Pd-filled CNTs.

3. Results and Discussion

Figures 1(a)–1(c) show SEM images of CNTs grown with different Pd thickness. The CNTs grown on Pd (10 nm)/Al (10 nm)/Si, as shown in Figure 1(a), were sparsely distributed on the substrate. The CNTs on Pd (20 nm)/Al (10 nm)/Si

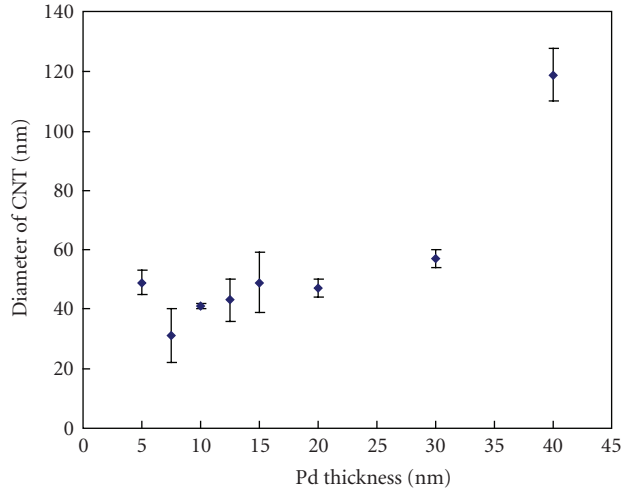


FIGURE 2: Pd thickness dependence of CNTs diameter. Hydrogen cleaning time is 3 minutes. Growth time is 10 minutes.

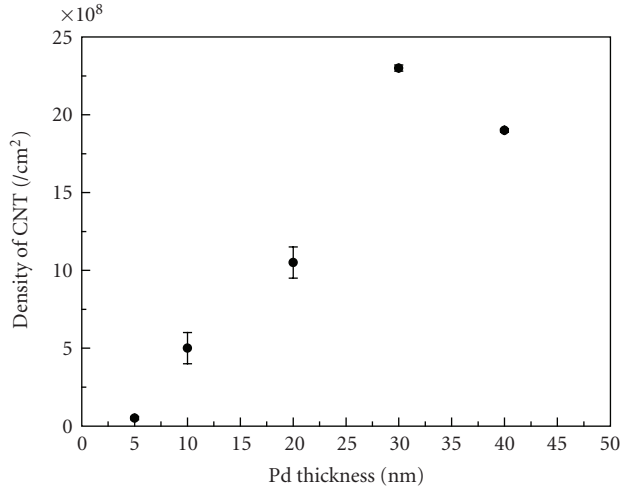


FIGURE 3: Pd thickness dependency of CNTs density. Hydrogen cleaning time is 3 minutes. Growth time is 10 minutes.

in Figure 1(b) and those on Pd (40 nm)/Al (10 nm)/Si in Figure 1(c) are well aligned and homogeneously distributed by the plasma sheath effect in MPECVD [16]. The diameter of the tip of CNTs is approximately 100 nm, and Pd-related materials are visible as bright contrast inside the CNTs as shown in Figure 1(d). TEM image in Figure 1(e) reveals that Pd is encapsulated inside the hollow of CNTs. In previous reports, metals were considered to be encapsulated in the hollows of CNTs by the capillary force [8, 9, 17–20].

Figure 2 shows the diameter of CNTs as a function of Pd thickness. The diameter of CNTs decreases with decreasing Pd thickness. It means that the diameter of CNTs depends on the size of catalyst particles. Thus the diameter can be reduced to approximately 30 nm at a Pd thickness of 7.5 nm. Figure 3 shows the density of CNTs as a function of Pd thickness. The curve was like mountain and it has a peak

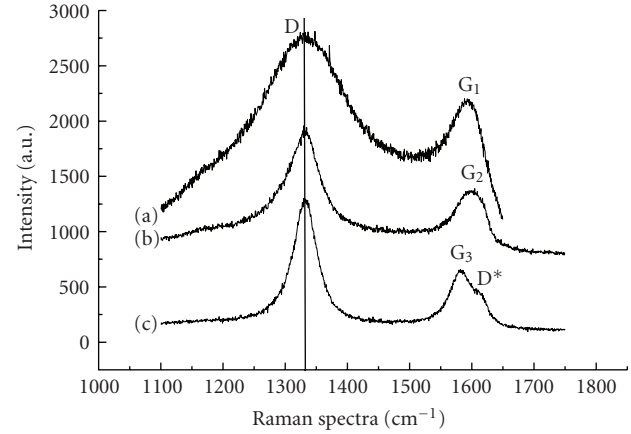
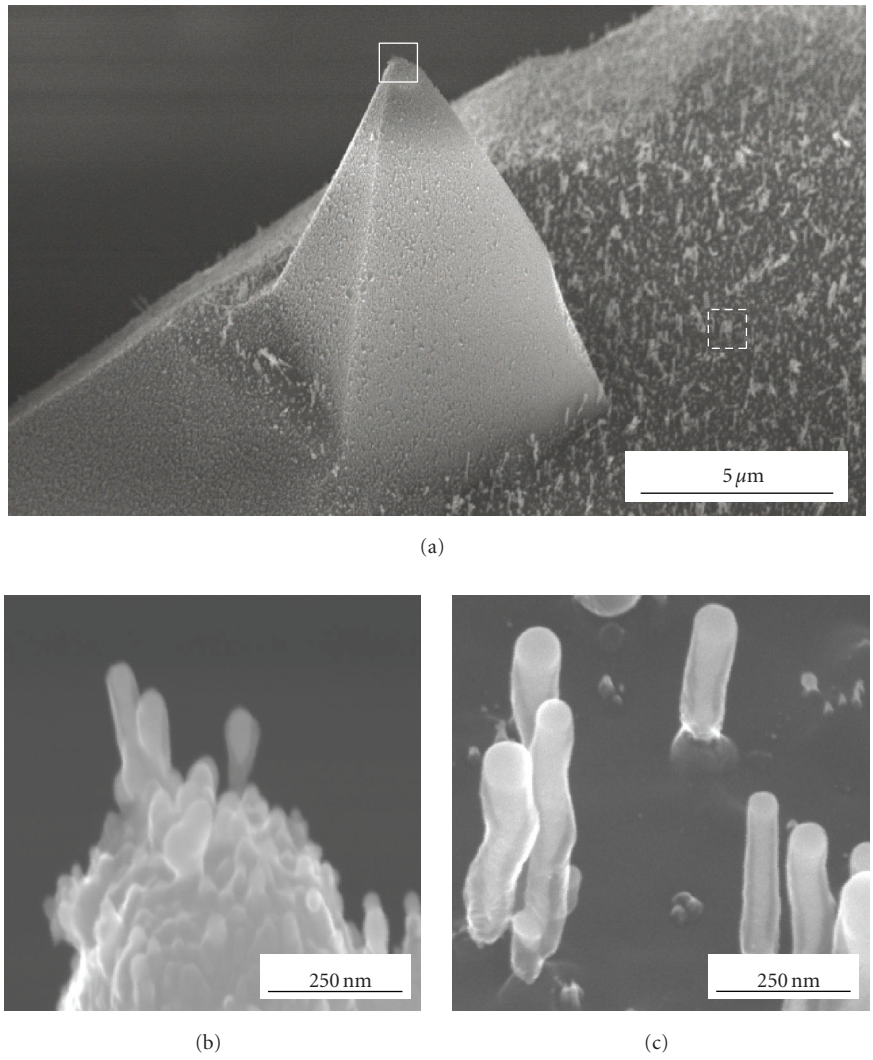


FIGURE 4: Raman spectra of CNTs grown on (a) Pd (1 nm)/Al (10 nm)/Si, (b) Pd (10 nm)/Al (10 nm)/Si, (c) Pd (30 nm)/Al (10 nm)/Si.

at a Pd thickness of 30 nm. CNTs were hardly grown on the substrates with Pd less than 5 nm because Pd was removed from the substrate by plasma etching in MPECVD.

Figure 4 shows Raman spectra of the CNTs grown in different conditions: (a) Pd (1 nm)/Al (10 nm)/Si, remote plasma, (b) Pd (10 nm)/Al (10 nm)/Si, MPECVD, (c) Pd (30 nm)/Al (10 nm)/Si, MPECVD. Remote plasma growth was done for comparison, where Pd was not encapsulated into the whole CNTs. Two strong peaks are observed in all the spectra at around 1350 cm^{-1} (D band) and around 1580–1600 cm^{-1} (G band). G peaks in Figures 4(b) and 4(c) are accompanied by an additional D* peak at around 1610–1620 cm^{-1}. The origin of D and D* bands have been attributed to disorder induced features such as defects generated in the graphitic planes of CNTs, due to curvature [21] and presence of amorphous carbon. On the other hand, G band is a characteristic of graphitic phase corresponding to in-plane vibration of C atoms, which indicates the presence of crystalline graphitic carbon in CNTs [22]. The appearance of D* band in Figures 4(b) and 4(c) agrees with the previous report, indicating the presence of Pd inside the whole CNTs [8, 23]. The intensity ratio of these two bands (I_D/I_G) [24] is considered as a parameter to characterize the quality of disorders in CNTs. The intensity ratios of I_D/I_G in all the spectra are larger than unity, indicating that the Pd-filled CNTs in the present study are multiwall CNTs (MWCNTs) with defective structure.

Since the growth condition is now optimized, growth of Pd-filled CNTs onto the SPM tip apex is performed. The Si cantilever was used as a specimen, and the same preparation, Al (10 nm) and Pd (10 nm) deposition, was conducted. The conditions are optimized to decrease the density of CNT and reduce the number or to produce only one CNT on the apex of tip. Figure 5(a) shows a low-magnified SEM image of CNTs grown on the cantilever surface. It is found that the pyramidal structure keeps its original shape after the growth. This is because the damage was minimized using a metal mesh for shielding from the direct impact of plasma



(a)

(b)

(c)

Figure 5: (a) Low magnification SEM image of CNTs grown on Al (10 nm)/Si cantilever. High magnification SEM images of CNTs at the tip apex (b) and of substrate Si (c).

ions [25]. The CNTs are well aligned and homogeneously distributed on the tip surface (Figure 5(b)) as well as on the cantilever surface (Figure 5(c)). The diameter of CNTs on the apex of tip is estimated to be approximately 50 nm. Figure 5(c) clearly reveals that Pd is encapsulated into the whole CNTs, as is on the Si wafer.

4. Conclusion

Pd-filled CNTs have been synthesized perpendicularly on Pd/Al (10 nm)/Si substrates by MPECVD. The diameter of CNTs has been controlled from 30 nm to 140 nm depending on the Pd thickness. Both SEM and TEM images clearly show that Pd is encapsulated into the whole CNTs. Raman revealed that Pd-filled CNTs were composed of poorly ordered graphene layers. Using optimum growth parameters, we have successfully fabricated Pd-filled CNTs on the apex of SPM probes.

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