Non-catalytic synthesis of nanostructured carbon films by plasma-enhanced CVD using CO as a carbon source gas

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Abstract: Catalyst-free growth of carbon nanofibers and carbon nanowalls were performed by microwave plasma-enhanced chemical vapor deposition using CO as a carbon source gas. Without an addition of hydrogen, vertically aligned CNFs were synthesized. At the optimal H$_2$ : CO ratio of 8 : 92, carbon nanowalls were synthesized. At higher H$_2$ : CO ratio of 92 : 8, however, polycrystalline diamond films were deposited.

Keywords: Carbon nanofibers, Carbon nanowalls, Carbon monoxide, Plasma-enhanced CVD

1. Introduction

Nanostructured carbon films, such as carbon nanofibers (CNFs) and carbon nanowalls (CNWs), exhibit unique electrical and thermal properties with a high surface area and chemical inertness. An increasing number of potential applications have been reported, such as field emission electron sources, fuel cell electrodes and chemical sensors [1-3]. From the viewpoint of process simplification and product purification, their catalyst-free synthesis is attractive. Here, we try to synthesize nanostructured carbon films without any catalyst materials by microwave plasma-enhanced chemical vapor deposition (PECVD) system. In this study, we utilize CO as a carbon source gas. To our knowledge, few attempts at low-temperature PECVD of CNFs synthesis [4-6] and no attempt for CNWs synthesis using CO as a carbon source have been made. In general, the advantages of low-temperature plasma CVD using CO instead of hydrocarbons as the carbon source gas are as follows: (1) the deposition of amorphous carbon is suppressed even at low temperatures [7, 8]; (2) the CO disproportionation reaction, CO$\rightarrow$CO$_2$+C, is thermodynamically favorable at low temperatures; (3) vibrationally excited molecules are formed which enhance reactions at low temperature, such as CO(v)+CO(w) $\rightarrow$ CO$_2$+C [5, 9, 10]; (4) C$_2$ radicals are known to be formed effectively through the reactions C + CO + M $\rightarrow$ C$_2$O + M and C + C$_2$O $\rightarrow$ C$_2$ + CO and can be precursors for the deposition of functional carbon materials [11, 12]. The effect of CO: H$_2$ and CO: O$_2$ ratio on the morphology of carbon films is investigated.

2. Experimental

The microwave plasma-enhanced CVD system is a modified ASTeX DPA25 plasma applicator in which the quartz discharge tube of a 10-mm or 15-mm inner diameter is used in this study. Borosilicate glass, silicon single crystal wafers, CaF$_2$ and polycarbonate plates (4 mm×4 mm) were used as substrates. Before CNFs synthesis, their surfaces were cleaned by solvent and any catalyst materials were not used in this study. The parameters of the CNFs deposition process were as follows: CO flow rate, 10 sccm; Ar flow rate, 30 sccm; O$_2$ flow rate, 0-1.0 sccm; H$_2$ flow rate, 0-50 sccm; total pressure, 250-400 Pa; microwave power, 60-120 W. Substrate temperature was monitored by the pyrometer (Japan Sensor TMZ9) and was about 800°C. Carbon deposits grown on the substrate were observed by scanning electron microscopy (Hitachi S-4500) and transmission electron microscopy (JEOL JEM-2010F) and analyzed by Raman spectroscopy (JASCO NRS-2100) and FTIR (JEOL JIR-SPX200).

3. Results and Discussion

3.1 CNFs synthesis

Figure 2 shows SEM images of the carbon deposits after 10 minutes of deposition in a CO(10sccm) / Ar(30sccm) / O$_2$(0.07sccm) system. In this case, the H$_2$
flow rate is zero and the CNFs can be synthesized without any catalyst materials. The morphology of carbon deposits is strongly affected by the O₂/CO ratio. Without an addition of oxygen, pillar-like carbon films were formed. When a small amount of O₂ was added to the CO plasma, the morphology of carbon films changed to fibrous structure. At slightly higher O₂ flow rates, however, the deposition rate decreased and no carbon deposits could be observed.

Figure 3 shows SEM images of CNFs grown on different material substrates. The morphologies of the CNFs grown on Si and CaF₂ substrates were almost the same as those grown on the glass substrates. However, CNFs grown on the polycarbonate showed a different morphology. The diameters of the CNFs were increased, fiber-bundling was evident, and the fiber length was diminished. The high affinity that exists between the precursor species and organic materials may result in the formation of large nuclei on the substrates and result in the growth of CNFs with large diameter.

Figure 4 shows TEM images of CNFs grown on the glass substrates at an O₂/CO ratio of 7:1000 at 180°C. The diameters of CNFs were 50-100 nm and no tubular structure was evident (Fig.4(a)). The surfaces of the CNFs were covered with the branching fibers and their nuclei, whose diameters are 5-10 nm. The high-magnification image of the CNF edge is shown in Fig. 4(b). Although it is not clearly seen because they overlapped and their directions were random in relation to the fiber axis, the lattice images of crystalized carbon were partially observed especially in the branching fibers. From this nucleation step for CNF branching, we might know the CNFs nucleation step on the substrates.
3.2 CNWs synthesis

The morphology of carbon deposits is also strongly affected by the H₂/CO ratio. Figure 5 shows SEM image of the carbon materials synthesized in a CO(16 sccm) / H₂(2 sccm) / O₂(0.1 sccm) system after 60 minutes of deposition at substrate temperature of 500°C. In this condition, CNWs were synthesized. Figure 6 shows Raman spectra of the CNWs. As well as G and D-band, the D'-band which is typical in the Raman spectra of CNWs is clearly seen in Fig. 6. Figure 7 and 8 show respectively the SEM and cross-sectional TEM images of CNWs synthesized in a CO(2sccm) / H₂(48sccm) system at 800 °C. The lattice structure of the crystallized carbon layers is clearly seen. At higher H₂ : CO ratio of 4 : 46, however, polycrystalline diamond films were deposited.

4. Conclusion

Catalyst-free growth of nanostructured carbon films were performed by microwave plasma-enhanced chemical vapor deposition using CO as a carbon source gas and carbon nanofibers and carbon nanowalls were synthesized without any catalyst materials. Without an addition of hydrogen, vertically aligned CNFs were synthesized. At the optimal H₂ : CO ratio of 8 : 92, carbon nanowalls were synthesized. At higher H₂ : CO ratio of 92 : 8, however, polycrystalline diamond films were deposited.
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References