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Carbon nanohelical coils and nanotubes preparation using metal clusters synthesized by plasma-gas-condensation

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A plasma-gas-condensation type cluster source, which is a combination of sputtering and condensation in an inert gas atmosphere, allowed us to produce nano-scale clusters with the average diameter between 2 and 20 nm. These nanometer sized metal clusters were used for preparing carbon nanohelical coils and nanotubes. The fiber diameter of nanohelical coils produced by a thermal CVD process from Ni clusters were larger than an original cluster size, because the clusters coalesced to form larger clusters on the substrate at 1043 K. The diameter of the nanotubes synthesized by a plasma-enhanced CVD process was almost the same as the cluster size, suggesting that the plasma-enhancement was effective to fabricate nano-sized carbon materials at low temperatures.
Key words: carbon nano-coils, carbon nanotubes, CVD, cluster, plasma-gas-condensation

1. INTRODUCTION

There has been much interest in the syntheses of nanometric metal- and semiconductor-clusters, because their physical and chemical properties are different from those of the bulk solids. Several experimental techniques have been applied to generate and characterize small particles and clusters [1]. Development and improvement of these cluster sources have been strongly desired for a narrower cluster size distribution and more intensive cluster beams. A plasma-gas-condensation (PGC) type cluster source [2-5], which is a combination of sputter vaporization and inert gas condensation techniques, is one of the candidates for this purpose. It is versatile to vaporize transition and refractive metals, and enable to control the cluster size by adjusting the sputter yield, the gas pressure and the volume of cluster growth region.

Many industrial catalysts contain small metal clusters, which form the essential centers where the chemical reactions take place. It is well known that the nano-clusters exhibit different reactivity and selectivity in comparison with the corresponding bulk materials [6]. The aim of this work is to explore the synthesis conditions of the nanometer-sized carbon constructions using such transition metal clusters as nano-catalysts, since it has been desired to obtain the carbon nano coils and carbon nanotubes (CNTs) for industrial applications [7-9].

2. EXPERIMENTAL

Figure 1 shows an overview of the present PGC type cluster deposition apparatus [4,5]. The metal vapor was generated by the DC magnetron sputtering. A continuous Ar gas stream adjusted by a mass flow controller was injected in front of a sputtering target. Clusters nucleated in a high pressure Ar gas atmosphere, P_{Ar} = 0.1 ~ 0.4 kPa, and grew up in the space between the target and the nozzle (the growth region). The length between the target and the nozzle, L_g, could be varied by moving the sputtering source back and forth. He gas was also introduced into the sputtering chamber from the backside of the source to obtain smaller clusters. The cluster beam was extracted through the nozzle (5 mm in diameter) by differential pumping, where we used a powerful mechanical buster pump (MBP) whose exhausting speed was 1200 m^3/h. The cluster beam was further collimated by the three skimmers, whose diameters were 5 mm. The background pressure of 4×10^{-7} Pa was attained in the deposition chamber by three turbo molecular pumps (TMP).

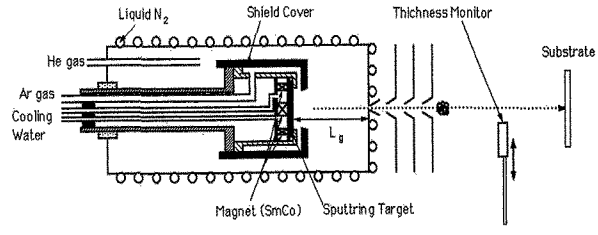

Fig.1 Schematic diagram of plasma-gas-condensation (PGC) type cluster deposition apparatus.

The horizontal reaction tube (quartz, 700 mm length, 26 mm i.d.), having two upper gas inlets and one lower gas outlet, was heated from the outside by a nichrome

wire heater. Al_2O_3, on which the Ni clusters with 5 nm in diameter was deposited by the PGC cluster source, was used as the substrate, and set on the central part of the reaction tube for carbon nano coil preparation. Commercial acetylene was used as the carbon source. A gas mixture of C_2H_2, H_2S, H_2, and N_2 was introduced into the reaction tube through the upper gas inlets. The standard reaction conditions used were as follows: the temperature 1043 K and the reaction time 30 minutes.

The carbon nanotubes were synthesized by the direct-current plasma-enhanced CVD process [9]. A tungsten wire spot-welded to two stainless steel rods was set at a distance of ca. 10 mm from a disc anode. The Pt nano-clusters were deposited by the PGC cluster source as well. Mixtures of C_2H_2 and NH_3 (0.2 and 0.4 Torr, respectively) were introduced into the reaction chamber. The partial pressure ratio of C_2H_2 against NH_3 was kept at 1:2. Application of a negative dc potential (-500V) to the resistively heated W wire induced a glow discharge, growing CNTs on the W wire. The temperature of the sample was 900 K and the reaction time was 20 minutes.

The morphology and microstructure were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). This microscope was equipped with energy-dispersive x-ray spectroscopy (EDS), which was used for compositional analyses. For TEM observation, the tungsten wire with CNTs was directly mounted on a sample holder.

3. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show TEM micrographs of the Ni and Pt clusters deposited on carbon-coated colodion films. These metal clusters were almost spherical and the average cluster size was about 5 nm for Ni and 10 nm for Pt clusters.

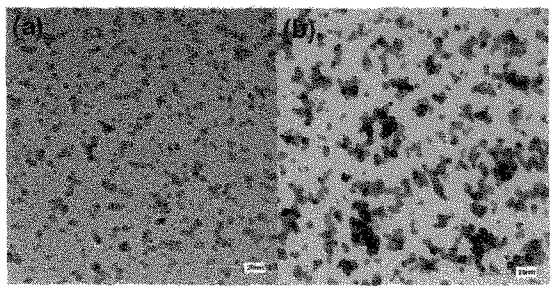

Fig.2 TEM images of (a) Ni and (b) Pt clusters prepared by plasma-gas-condensation cluster source.

Figure 3 shows a typical SEM image of the carbon coils grown by the Ni clusters. The regular carbon coils with an average coil diameter of about 2 μm and an average fiber diameter of about 700 nm were obtained at 1043 K. These regular carbon coils had constant coil pitches of 500 ~ 700 nm without any coil gap and had a coil length of 1 ~ 8 mm for 30 min reaction time. It was observed that the cross-section of the fibers that built up the carbon coils were generally circular or slightly elliptical. Besides the regular carbon coils, twisted carbon coils with a coil diameters of about 0.4 μm were also obtained as shown in Figure 4. The fiber diameter was about 200 nm, which was much larger than the original Ni cluster size (5 nm).

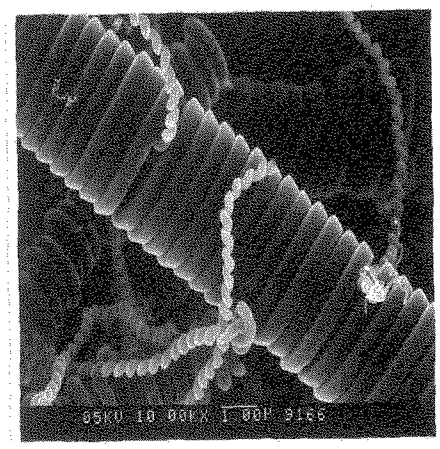

Fig.3 SEM image of carbon coils grown from Ni clusters by thermal CVD process.

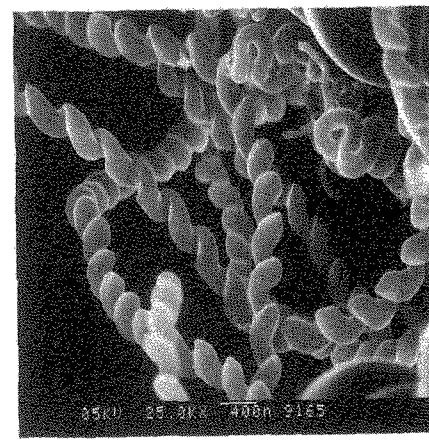

Fig. 4 SEM image of carbon coils grown from Ni clusters by thermal CVD process.

Cluster-cluster coalescence behaviors of monodispersed transition clusters with a mean diameter of 6 ~ 13 nm have been investigated by the electrical transport, magnetic measurement, and TEM observation [10]. TEM observation indicated that the morphology of the cluster was not markedly changed at substrate temperatures below 523 K. Above 523 K, growth or reconstruction of combined clusters was detected by high-resolution TEM images [10]. The interfacial area of coalesced clusters was crystalline, having its own orientation different from those of two connected cluster cores. For the present Ni clusters, it is easily imagined that such cluster-cluster coalescence behaviors should take place, since Ni has lower melting point than Co.

These coalescence behaviors probably caused that the sizes of the carbon coils obtained at 1043 K were larger than the original cluster size.

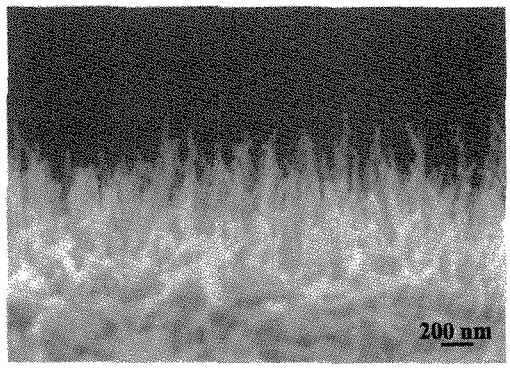

Fig.5 SEM image of carbon nanotubes grown from Pt clusters by dc-plasma-enhanced CVD process.

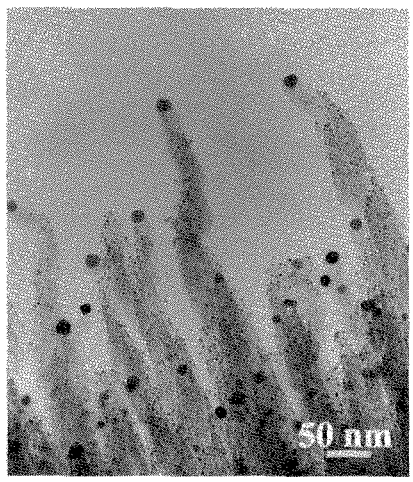

Fig.6 TEM image of carbon nanotubes grown from Pt clusters by dc-plasma-enhanced CVD process.

In order to minimize the cluster-cluster coalescence, we used the direct-current plasma-enhanced CVD process [9]. In this case, we tried to prepare CNTs. When we decreased the reaction temperatures using the plasma-enhanced CVD process, the CNTs were obtained. Figure 5 shows the SEM image of the CNTs grown from the Pt clusters. The diameters of the CNTs in Fig. 5 are about 20 nm and their lengths are rather regular (about 600 nm). The TEM image shown in Figure 6 indicates that the tips of the CNTs are closed and the CNTs encapsulate Pt clusters. The CNTs grown from Pt clusters is of conical shape: the diameters at the top and the bottom are 20 and 40 nm, respectively. It was also found that many Pt clusters were adhered at the surface of the CNTs, which was confirmed by EDS analysis. These results suggest that the carbon coils and/or tubes with the nanometer size could be obtained when the clusters were kept the original size.

4. CONCLUSIONS

Using the nanometer sized metal clusters, carbon nano coils and nanotubes have been grown. The nano coils grown from Ni clusters were larger than an original cluster size, probably because the clusters coalesced to form larger clusters on substrate at 1043 K during the reaction. For the synthesis of carbon nanotubes by a plasma-enhanced CVD process, the diameter of nanotube was almost the same as the cluster size, suggesting that the plasma-enhancement was effective to fabricate nano sized carbon materials.

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References

[1] W. A de Heer, *Rev. Mod. Phys.*, **65**, 611-676 (1993).
[2] H. Haberland, M. Karrais, M. Mall and Y. Thurner, *J. Vac. Sci. Tech. A*, **10**, 3266-3271 (1992).
[3] S. Yamamuro, K. Sumiyama, M. Sakurai and K. Suzuki, *Supramol. Sci.*, **5**, 239-245 (1998).
[4] T. Hihara and K. Sumiyama, *J. Appl. Phys.*, **84**, 5270-5276 (1998).
[5] T. Hihara and K. Sumiyama, *J. Vac. Sci. Technol. B*, **17**, 1923-1929 (1999).
[6] W. Eberhardt, *Surf. Sci.*, **500**, 242-270 (2002).
[7] S. Motojima, M. Kawaguchi, K. Nozaki, H. Iwanaga, *Appl. Phys. Lett.*, **56**, 321-323 (1990).
[8] S. Motojima and X. Chen, *J. Appl. Phys.*, **85**, 3919-3921 (1999).
[9] M. Tanemura, K. Iwata, K. Takahashi, Y. Fujimoto, F. Okuyama, H. Sugie and V. Filip, *J. Appl. Phys.*, **90**, 1529-1533 (2001).
[10] D. L. Peng, T. J. Konno, K. Wakoh, T. Hihara and K. Sumiyama, *Appl. Phys. Lett.*, **78**, 1535-1537 (2001).

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