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Effect of Gold catalytic layer thickness on growth of single-walled carbon nanotubes using thermal and plasma CVD

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We carried out the carbon nanotubes (CNTs) growth from an Au catalyst with two different kinds of chemical vapor deposition (CVD) methods. In case of thermal CVD (TCVD), high quality single-walled carbon nanotubes (SWNTs) can be grown. On the other hand, only poorly crystallized CNTs are synthesized with plasma CVD (PCVD). Through the parametric investigations, it is found that the hydrogen gas supply which is known as a kind of growth support element in case of normal (Fe, Co, Ni) catalysts causes a significant decrease of SWNTs growth activity in case of Au. Since there is large number of atomic hydrogen reactants decomposed by energetic electrons in plasmas, This negative hydrogen reactants effect on the Au catalyst is supposed to be one possible reason for the unsuccessful growth of SWNTs from the Au catalyst with PCVD.

Keywords: Plasma chemical vapor deposition, Raman, Catalyst activity, Single-walled carbon nanotubes, Thermal chemical vapor deposition

1. Introduction

The unique properties of single-walled carbon nanotubes (SWNTs) [1,2] have motivated intense researches in the fabrication of electronic components [3], field emission sources [4], and hydrogen storage devices [5]. Certain carbon nanotube (CNT) applications require specific dimensions and different levels of homogeneity (e.g. diameter, length, reactivity, crystallinity, purity, and chirality) [6]. Since the composition and morphology of catalyst nanoparticles are critical in determining the structure, length, and yield of nanotubes, different methods and catalysts include superior possibility for the detailed structure control of CNTs. The majority of works reporting the CNTs synthesis has focused on iron family catalysts such as Fe, Co, and Ni.

Catalysis by gold (Au) is a relatively new topic. Although it was considered that Au has no catalytic effects, Haruta et al. reported the high catalytic activity of Au nanoparticles [7]. The main determining factors for formation of active Au species are Au deposition thickness, appropriate metal oxide support, and type of gas pretreatment. Only when the Au atoms are confined to the size of just a few nanometer, they start showing the desired catalytic behavior.

In case of CNTs growth, there are some difficulties using Au as a catalyst due to low ability of Au catalysis to decompose hydrocarbons and also low solubility of carbon atoms in liquid Au (4.7% at 1064 °C) compared with Fe (17% at 1153 °C) [8,9]. Here, we show clear difference of catalytic activity depends on the chemical vapor deposition (CVD) method. Thermal CVD (TCVD) grown materials have a sharp and splitting G band in Raman scattering spectra, which indicates successful growth of SWNTs from the Au catalyst. On the other hand, poorly crystallized CNTs are formed in plasma CVD (PCVD). These difference can be explained by the effect of hydrogen during the growth of CNTs, and particle size difference during the preheating.

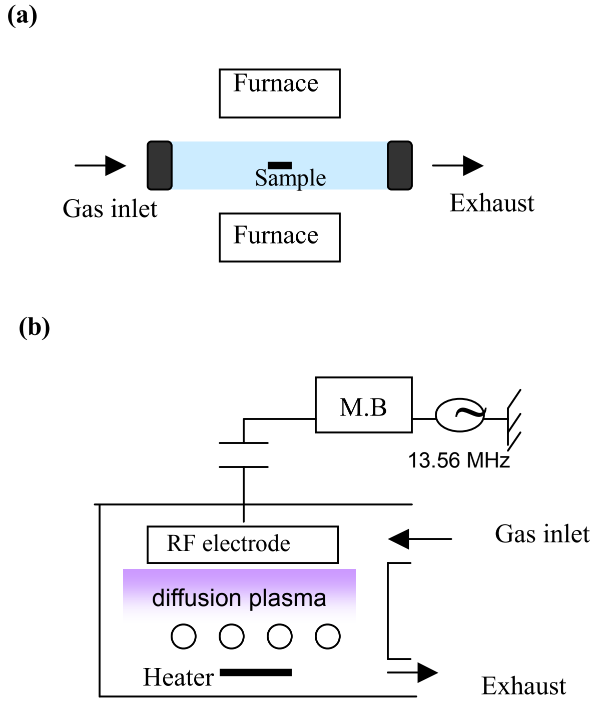

Fig. 1 : Schematic illustration of (a) TCVD and (b) PCVD.

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2. Experimental

TCVD [10-12] and PCVD were used for nanotube growth. Figures 1(a) and (b) show the TCVD and PCVD systems used in the present experiment, respectively.

In case of TCVD (Fig. 1(a)) the catalyst samples (thin catalyst films were deposited on to a silver substrate covered by 20 nm aluminum oxide layer) were placed in the middle of a quartz tube furnace. Before CVD, the catalysts were pretreated in air at 650 ^{o}C for 10 min. Then air was evacuated in order to anneal the catalyst under He or He/H_2 for 10 min. After the reduction, such gas was replaced by ethanol vapor and CVD was performed at 750 ^{o}C for 20 min. In case of PCVD (Fig. 1(b)), a radio frequency (RF, 13.56 MHz) plasma unit is utilized.

The RF power supply system consists of a power generator, a matching box (M.B), and a blocking condenser (B.C). RF power is supplied to an upper electrode and a mesh grid is used as an anode to promote a spatial diffusion of the plasma. A substrate was placed on a heater which is located underneath the lower electrode. At first, the system is pumped down to a base pressure of 1 Pa, and the substrate is heated up to 620 ^{o}C under H_2 at 60 Pa. Methane gas is then introduced for CNTs growth. When total pressure is fixed at 60 Pa, RF power is fed to generate the plasma for 5 min growth time. After CNT growth, methane and hydrogen gases are pumped out and Ar gas is introduced to the system in order to cool down the substrate [13-15]. To characterize the CNTs grown Raman spectroscopy with the laser excitation of 633 nm was used, which is a popular technique for determining the diameter distribution, chirality, and purity of CNTs. An atomic force microscope (AFM) was also used to estimate the diameters of Au nanoparticles from height profile of images obtained in a tapping mode.

3. Results and Discussion

Figure 2(a) shows a Raman spectrum of CNTs grown using PCVD over the Au catalyst, which plots the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (Raman shift) using a laser excitation wavelength of 633 nm. The spectrum gives a clear G band together with a strong D band with a low G/D ratio of 0.79. This suggests that the carbonaceous product formed on the catalyst surface has a low crystallinity. The D peak is prominent due to the condensation of amorphous carbon (a-C) and poorly crystallized CNTs. Figure 2(b) illustrates Raman spectra of SWNTs produced by the TCVD method using the Au catalyst under different hydrogen flow rates. The presence of radial breathing modes (RBM: 100 ~ 300 cm^{-1}) in the spectra verifies that these structures are SWNTs. It is clear that the density of SWNTs decreases by increasing the hydrogen flow rate. Figures 3 indicates the effect of hydrogen gas on CNTs growing over two different catalysts of Fe and Au, which is a graph of G peak intensity versus H_2 flow rate. It is suggested that increasing the H_2 flow rate during growth decreases the G peak intensity in case of the Au catalyst. In case of iron, however, it reversely increases the G intensity. This difference arises from low ability of the Au catalyst to decompose the hydrocarbons. Also it is noticeable that metals such as Au are not versatile catalysts for reactions due to their low ability to adsorb hydrocarbons.

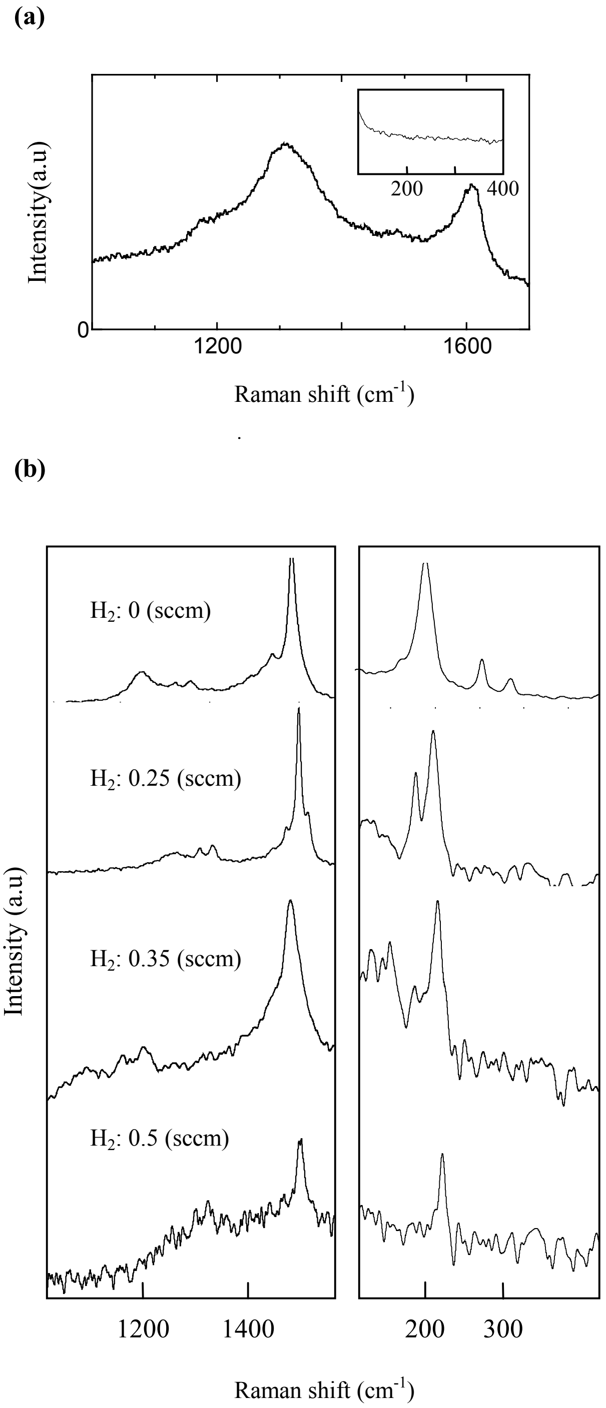

Fig. 2 : Raman spectra of CNTs grown on Au catalyst by (a) PCVD and (b) TCVD at different hydrogen flow rates.

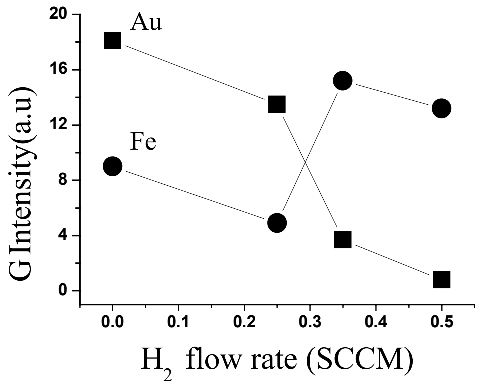

Fig 3 : Effect of hydrogen flow rate on SWNTs growth over Au (closed squares) and Fe (closed circles) catalysts.

It is shown that H_2 plays an undesirable role in etching the considerable amounts of active species which are adsorbed by Au catalyst particles. On the other hand, the Fe catalyst has high ability to adsorb hydrocarbon molecules and hence amounts of hydrocarbon molecules which are adsorbed by the Fe catalyst are much more than those of the Au catalyst. Therefore, hydrogen atoms can etch some amount of reactants which may poison the surface of iron catalyst.

Since PCVD contains large amount of atomic hydrogen due to the strong gas decomposition in a plasma area, high density atomic hydrogen reactants might be one of the failure reasons of growing SWNTs by this method. Another significant difference between TCVD and PCVD is the difference between the Au particles size due to the performance of the preheating step in case of TCVD which can decrease the particle size by evaporation. Figure 4 gives the size distribution of Au particles after pretreatment and after hydrogen annealing. The particle size was estimated from the height profile of AFM topographic images. The Au particle size distribution before PCVD process is shown in Fig. 4(a). It is clear that the particle size distribution is above 7 nm which is not desirable for growing SWNTs over the Au catalyst. On the other hand, it is found that a suitable size of the gold catalyst was obtained for growing SWNTs before TCVD process as shown in Fig. 4(b). This result suggests that preheating in air carried out only for the TCVD experiment is essential in order to make the clean catalyst and decreases the particle size, which is necessary to grow SWNTs.

At the moment there is not a single theory for the role of the pretreatment and reduction on activation and deactivation of the Au catalyst. In our studies the effect of activation on Au catalyst was observed after preheating in air which can decrease the size of Au nanoparticles and enhance the catalytic activity of these nanoparticles.

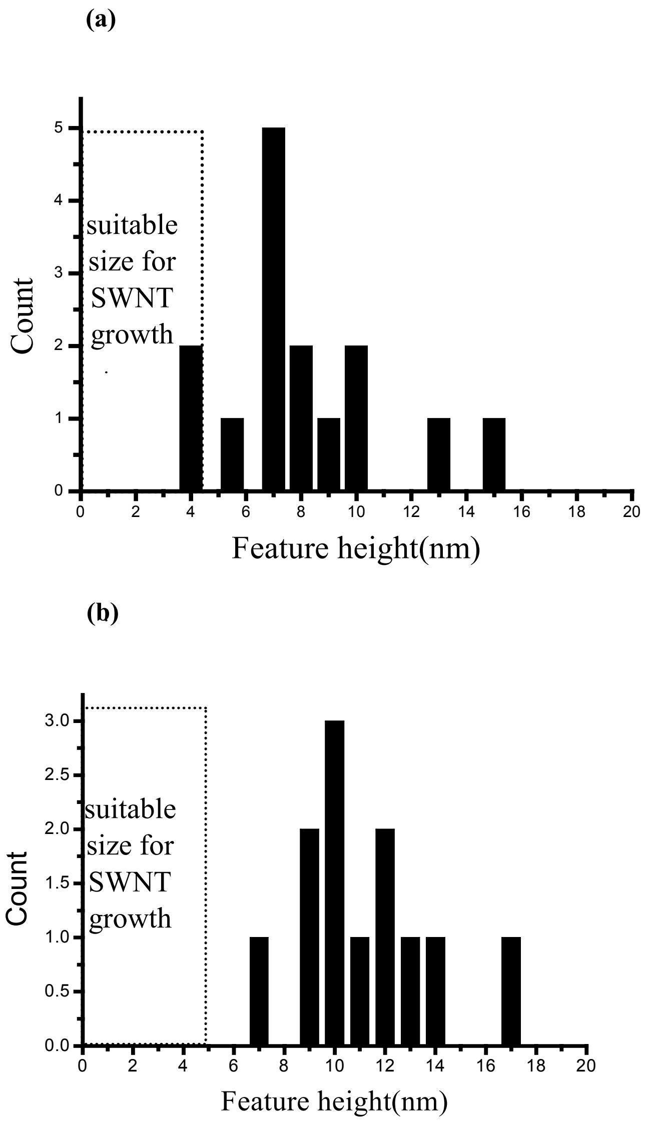

Fig. 4 : (a) Size distribution of Au particles after annealing with H_2 at 620 ^{o}C in case of PCVD and (b) after preheating in air at 650 ^{o}C in case of TCVD.

On the other that we observed that increasing the H_2 concentration while keeping the alcohol vapor pressure constant reduces the yield of SWNTs (Fig.3), providing evidence that hydrogen rich environments are also undesirable and having negative effects on the catalytic activity of Au catalyst.

A major difference between PCVD and TCVD is the much higher concentration of reactive radicals in the former. In our case, because of plasma-assisted decomposition, any H_2 leads to very high H atoms concentration, much more than in TCVD. Thus, the extremely low yield of CNTs observed for PCVD growth strongly suggests the negative effect of H species for SWNTs growth over Au catalyst.

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4. Conclusion

Au catalyzed CNTs growth is precisely investigated with two different kinds of CVD methods, i.e., TCVD and PCVD. The clear and sharply splitting G band peaks and multiple RBM can be observed in higher and lower wave number areas of Raman scattering spectra, respectively, in case of TCVD with Au catalyst. This indicates that high quality Au catalyzed SWNTs can be grown with TCVD. On the other hand, only poorly crystallized CNTs can be produced with PCVD. Based on the parametric study for CNT growth from the Au catalyst, it is found that the hydrogen gas supply which is known as a kind of growth support element in case of normal catalysts (Fe, Co, Ni) causes a significant decrease of SWNTs growth activity in case of Au. Since the large number of atomic hydrogen decomposed by energetic electrons exists in plasmas, this negative hydrogen effect on the Au catalyst can be one possible answer for the unsuccessful growth of SWNTs from the Au catalyst with PCVD. On the other hand, existence of large Au particles (above 5 nm) in the substrate which has the lower catalytic activity to synthesize the CNTs is the other failure reason of CNTs growth by PCVD method.

5. References

[1] S. Ijima: Nature **354**, 56, (1991).

[2] R. Saito, G. Dresslhaus, and M. S. Dresselhaus, physical properties of carbon nanotubes, Imperical college Press, London (1998).

[3] H. T. Soh, C.F. Quate, A. F. Morpurgo, C. M. Marcus, J. Kong, and H. Dai: Appl. Phys. Lett. **75**, 627, (1999)

[4] W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Choi, and J. M. Kim: Appl. Phy. Lett. **75**, 3129, (1999).

[5] H. M. Cheng, Q. H. Yang, and C. Liu: Carbon **39,** 1447, (2001).

[6] A. B. Mendez, J. C. Delgado, A. M. Gomez, M. R. Herrera, A. G. Rodriguez, H. Navarro, M. A. Vidal, H. Terrones, and M. Terrones: Chem. Phys. Lett. **453,** 55, (2008).

[7] M. Haruta, N. Yamada, T. Kobayashi, and S. Ijima: J. Catal. **115,** 301, (1989).

[8] D. Takagi, Y. Homma, H. Hibino, S. Suzuki, and Y. Kobayashi: Nano Lett. **6,** 2642, (2006).

[9] Sreekar Bhaviripudi, Ervin Mile, Stephen A. Steiner III, Aurea T. Zare, Mildred S. Dresselhaus, Angela M. Belcher, and Jing Kong: J. Am. Chem. Soc**.** **129**, 1516, (2007).

[10] S. Maruyama, Y. Shibuta, Chem. Phys. Lett., **382**, 381, (2003).

[11] H. E. Unalan, and M. Chhowalla: Nanotechnol. **16,** 2153, (2005).

[12] S. M. Bachilo, L. Balzano, J. E. Herrera, F. Pompeo , D. E. Resasco, R. B. Weisman, J. Am. Chem. Soc., **125,** 11186, (2003).

[13] T. Kato, R. Hatakeyama, and K. Tohji: Nanotechnol. **17,** 2223, (2006).

[14] T. Kato, G-H. Hirata, R. Hatakeyama, K. Tohji, and K. Motomiya: Chem. Phys. Lett. **381**, 422, (2003).

[15] T. Kato, G-H. Hirata, R. Hatakeyama, and K. Tohji: Jpn. J. Appl. Phys. **43**, 1278, (2004).