

**A simple combinatorial method to discover Co-Mo binary catalysts
that grow vertically aligned single-walled carbon nanotubes**

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Abstract

A simple yet versatile combinatorial method to discover binary metal nanoparticle catalysts was developed. In this method, the nominal thickness of component metals can be independently screened for a wide range by simply setting a mask with a slit above a substrate during sputter-deposition. Using this method, we prepared a catalyst library with Mo (0.2– 4 nm) and Co (0.2– 8 nm) thickness profiles on a SiO₂/Si wafer and discovered active catalysts that grow vertically aligned single-walled carbon nanotubes by alcohol catalytic chemical vapor deposition.

Keywords

carbon nanotubes; catalyst; chemical vapor deposition

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1. Introduction

Single-walled carbon nanotubes (SWNTs) are attracting much attention as promising materials for application in nanodevices due to their excellent mechanical, electrical, and chemical properties [1,2]. Many applications such as electron field emission sources [3], field effect transistors [4], molecular wires [5], and chemical sensors [6] have been proposed and are being actively studied. However, several issues in their fabrication process remain to be solved before such applications can be realized.

In the direct growth of SWNTs by chemical vapor deposition (CVD) on substrates, preparation methods of the catalysts become a crucial issue. Aiming at efficient screening of the preparation conditions of carbon nanotube (CNT) catalysts, several studies have used combinatorial approaches involving wet [7–9] and dry [10,11] processes. Wet processes [7–9] such as droplet evaporation are advantageous in preparing and screening a large number of catalyst spots of various precursor materials on a substrate; however, such processes suffer from the non-uniform spatial distribution of catalyst species within each catalyst precursor spot. In contrast, dry processes [10,11] are advantageous in controlling the spatial distribution. Ng et al. [10] fabricated an ensemble of catalysts on a common supporting substrate by using ion-beam deposition with a shadow masking technique. Their catalyst ensemble with discrete composition/thickness variations successfully revealed active catalysts that grew multi-walled CNTs (MWNTs). Christen et al. [11] carefully analyzed the thickness gradients in films formed by pulsed laser deposition, and applied the gradients to fabricate a library of Mo/Fe/Al catalysts. By screening a continuous Fe/Mo profile (i.e., not discrete), they successfully optimized the catalyst condition/thickness and grew vertically aligned MWNTs. Although these works [7-11] demonstrated the effectiveness

of the combinatorial approaches, all of them used special experimental apparatus and/or techniques, and therefore these methods have not been widely used.

We previously developed a simple combinatorial method to screen nominal thickness of deposits [12]. In our Combinatorial Masked Deposition (or CMD) method, a mask with holes is simply placed above a substrate during vapor deposition to dilute the deposition flux, in which the degree of dilution can be controlled by the hole size and the gap between the mask and substrate. By using this CMD method, we discovered in a single experimental run that Co nanoparticles spontaneously forming from a nominal Co submonolayer on SiO₂ can catalyze the growth of high quality SWNTs [13]. In this work, we extended our CMD method to binary systems and examined a Co-Mo binary system, that was previously shown to effectively grow vertically aligned SWNTs [14,15].

2. Experimental

2.1. Preparation of catalyst library by CMD method

A mask with a slit yields thickness profiles of deposits on a substrate in one-dimension perpendicular to the slit. By using the slit-mask, we prepared thickness profiles of two types of deposits independently in two-dimensions on substrate surfaces. Figure 1a shows the mask-substrate layout used to prepare the thickness profiles of Mo and Co. The substrate was a 20-mm-square Si wafer that had a 50-nm-thick thermal oxide layer (SiO₂/Si wafer), which was pretreated with mixed solution of H₂SO₄ aq. (95 wt.%, 10 mL) and H₂O₂ aq. (30 wt.%, 30 mL) for 5 min and then washed with de-ionized water before loading into the sputter-chamber. The mask was a 0.5-mm-thick metal sheet with a 2-mm-wide slit and placed 3.6 mm above the substrate. Mo and Co

was deposited at 0.80 Pa through the slit by using an r.f. magnetron sputtering system with 4 inch targets. In this layout, gas-phase collisions of deposition species during their flight from the slit to the wafer are not negligible, and thus the calculation of solid angle [12] is no longer effective to estimate the deposition rate profiles. In this work, the deposition rate profiles of Mo and Co (Fig. 1b) were derived by growing each metal film for 1 h and measuring the thickness profile by using a surface profiler (KLA Tencor, Alpha-Step 500). The deposition rates decreased exponentially with increasing distances from the slit. Then, the catalyst library with nominal thickness profiles of Mo (0.2- 4 nm) and Co (0.2- 8 nm) was prepared by depositing Mo for 18 s, rotating the substrate by 90 ° under air, and depositing Co for 150 s.

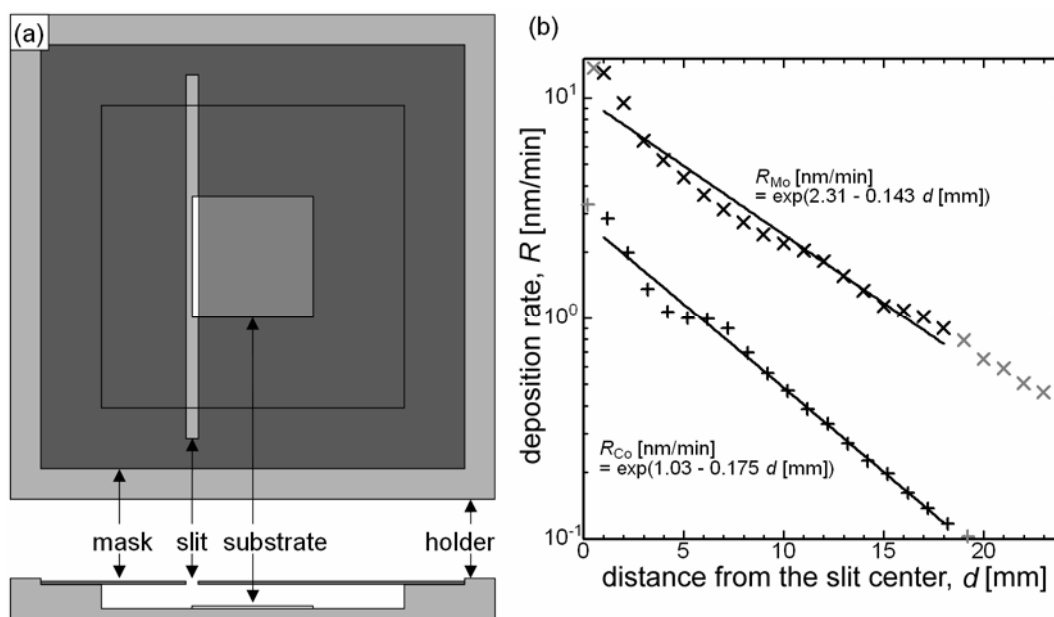


Fig. 1. Schematic explanation of catalyst preparation. (a) Top (top) and side (bottom) views of the mask-wafer layout of CMD to prepare a binary catalyst library on a substrate. (b) The deposition rate profiles of Mo and Co realized by this method.

2.2. Growth and analytical methods of SWNTs

SWNTs were then grown on this library by alcohol catalytic CVD (ACCVD) [16]. Briefly, the library was transferred under air from the sputter-chamber to a hot-wall quartz-glass tubular reactor and heated to a target temperature of 1073 K under a 25 vol.% H₂/Ar flow at 2.7 kPa, kept at that temperature for 10 min, and then SWNTs were grown by flowing pure ethanol vapor at 2.7 kPa for 10 min over the library. Samples of this catalyst library were then characterized by using micro-Raman scattering spectroscopy (Seki Technotron, STR-250), field emission scanning electron microscopy (FE-SEM, Hitachi S-900), and transmission electron microscopy (TEM, JEOL 2000EX).

3. Results and discussion

Figure 2a shows the nominal thickness profiles of Mo and Co of the catalyst library. The library had a physical dimension of 20 mm square, and it had orthogonal thickness profiles. Mo thickness varied from 4 nm (left) to 0.2 nm (right) and Co thickness varied from 8 nm (top) to 0.2 nm (bottom). Figures 2b and 2c are photographs of the catalyst library before and after ACCVD, i.e., before and after the growth of SWNTs, respectively. As for the as-deposited catalyst library with 1-nm-thick Mo/1-nm-thick Co, by X-ray photoelectron spectroscopy, about 30-40 % of Mo and 70-80 % of Co proved to be in the oxidized state. Oxidation probably occurred during exposure to the air during the preparation and transfer processes of the catalyst library and/or during sputter-deposition???. After ACCVD, the color of the library remarkably changed, and certain parts became black, indicating the deposition of carbon species. Points I and II were chosen as typical regions where the color darkened slightly and considerably, respectively.

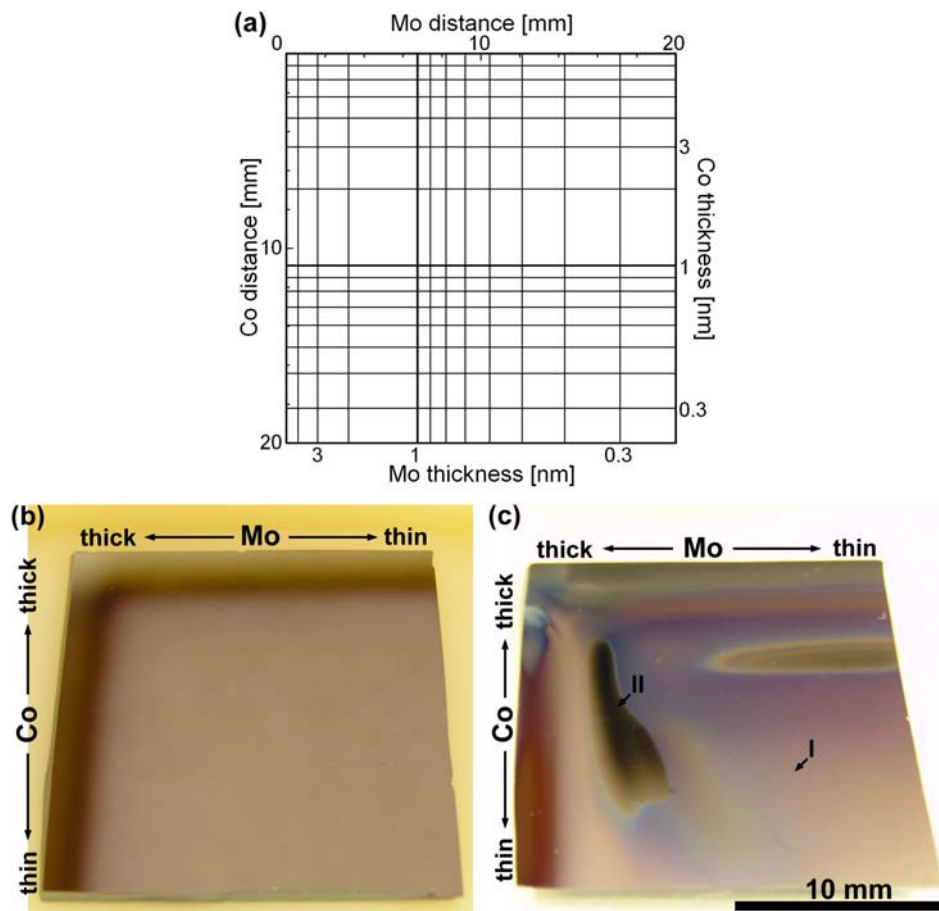


Fig. 2. Nominal thickness profiles of Mo and Co of the catalyst library (a) and photographs of the library before (b) and after (c) ACCVD.

The library was then characterized using micro-Raman scattering measurements at 488-nm excitation. Figure 3a shows typical Raman spectra of samples taken at points I and II in Fig. 2c representing randomly (I) and vertically (II) aligned SWNTs. The sharp, branched peak of the G-band (at 1593 cm^{-1}) with a very small D-band (at around 1350 cm^{-1}) and the radial breathing mode (RBM, at around $150\text{-}280\text{ cm}^{-1}$) at right resonant Raman shifts indicate that SWNTs were the main products. The relatively higher RBM peak at 180 cm^{-1} than the other peaks for point II (compared with that for point I) is characteristic of vertically aligned SWNTs [17].

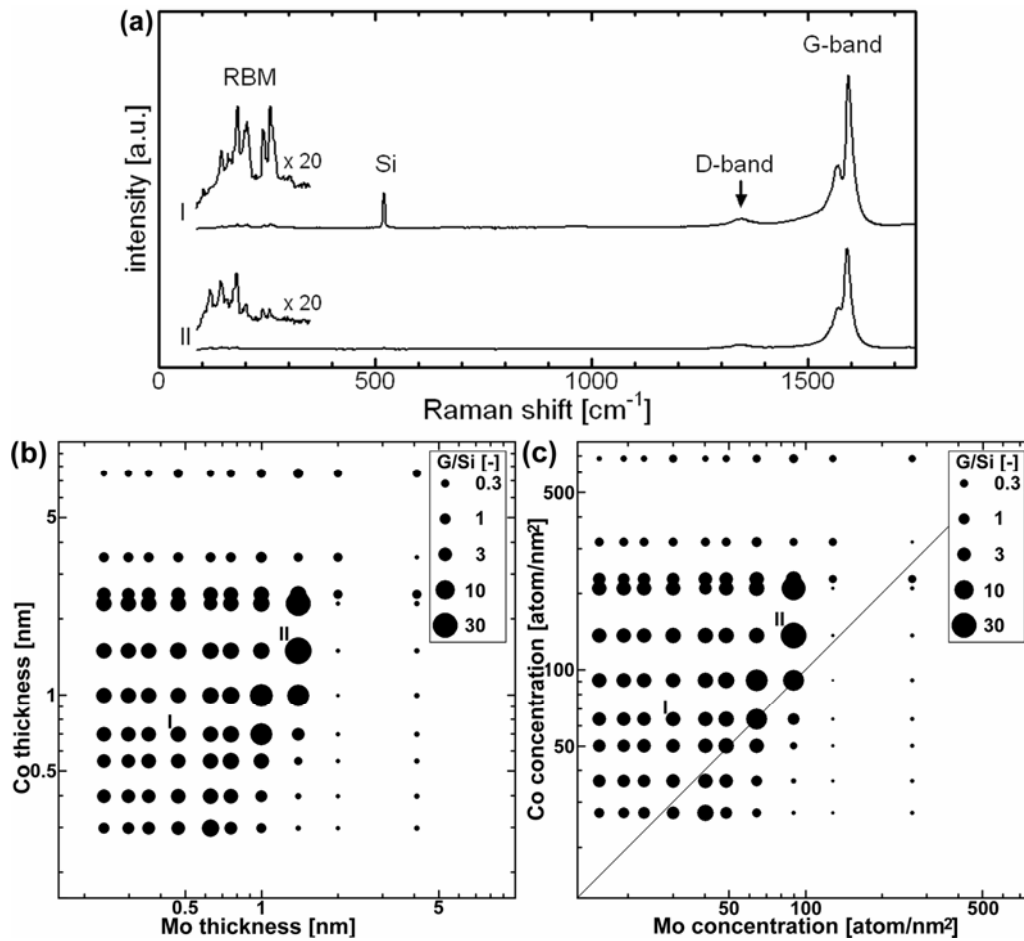


Fig. 3. (a) Typical Raman spectra of randomly (I) and vertically (II) aligned SWNTs at points I and II in Fig 2c. (b,c) Relative yields of CNTs calculated from the peak area ratio of G-band (1593 cm^{-1}) to Si (520 cm^{-1}) mapped against nominal Co/Mo thickness (b) and Co/Mo concentration (c).

The relative yield of CNTs was calculated from the peak area ratio of G-band (1593 cm^{-1}) to Si (520 cm^{-1}) for 100 different points on the library, and then mapped against the nominal Co/Mo thicknesses (Fig. 3b) and the Co/Mo surface concentrations (Fig. 3c). The surface concentrations [atoms/nm^2] were calculated from their nominal thicknesses [nm^3/nm^2], density [kg/m^3], atomic weight [kg/mol], and Avogadro's constant [atoms/mol]. All of these values used were of metallic states because the

degrees of oxidation of Mo and Co in determining the deposition rate profiles was smaller than ?? %. The relative yield varied widely from 0.02 to 40, and the highest yield appeared at point II. It should be noted that there was little difference between the catalyst library with Co deposited on Mo and that with Mo deposited on Co. This indicates that the catalyst metals with thickness around 1 nm were well mixed at the nanometer scale at the CVD temperature of 1073 K.

Figure 3c reveals interesting tendencies; the relative yield was high for points with Co concentration slightly higher than the Mo concentration, and was remarkably lower for points with Mo concentration higher than the Co concentration. This characteristic in stoichiometry indicates that the equivalent amount of Mo and Co were catalytically inactive, and residual Co was catalytically active. This characteristic is consistent with the model previously proposed [15] that the CoMoO_x layer is formed and then the residual Co forms Co nanoparticle catalysts at a high number density on this layer. We do not intend to discuss the mechanism in this work, however, we would like to draw a picture of the possible catalyst structure at point (II). The nominal thickness was 1.5 nm for Co and 1.4 nm for Mo, and the atomic concentration was 140 atom/nm² for Co and 90 atom/nm² for Mo. The residual Co of 50 atom/nm² corresponds to a nominal thickness of 0.5 nm, and if it forms 3-nm-sized hemispherical nanoparticles, their number density becomes as high as 0.07 nm⁻².

However, Herrera et al. [18,19] have proposed another model of Co-Mo catalysts, based on systematic investigations of SWNT production by CO disproportionation. Co-Mo catalysts exhibit their optimal activity and selectivity in forming SWNTs when the Co/Mo molar ratio is as low as 1/3. Herrera et al. concluded that Co and Mo at this low Co/Mo ratio change their state sequentially as follows; they form small clusters of

Mo⁶⁺ species with Co by interaction with Mo in a superficial Co-molybdate-like structure after calcination, Mo and Co retain similar states during subsequent reduction treatment, and after the CO disproportion reaction starts, the Mo oxide species is converted into Mo carbide, and Co are released in the metallic state of high dispersion, which is responsible for the production of SWNT [18]. The reason for the different optimum Co/Mo molar ratios to catalyze SWNTs growth is unclear; the difference might be caused by differences in the SWNTs growth conditions, such as reactant gases, temperature for the H₂ reduction treatment, properties of the support surfaces, and nominal thickness of catalyst precursors.

To make further analysis easier by increasing the area of the target sample, the Co-Mo catalyst with similar conditions to those for point II was supported on another SiO₂/Si wafer, and SWNTs were grown on the catalyst. FE-SEM images of this sample (Fig. 4a) show that the bundles of CNTs were vertically aligned and formed a film approximately 2 μm thick. Many nanoparticles around 5 nm in diameter were clearly evident on the surface (Fig. 4b). Although nanoparticles with diameter similar to that of SWNTs (0.4- 3 nm) probably existed and are believed catalytically active, they cannot be observed by FE-SEM [13]. The bundles were thinner near the substrate interface than in the bulk film, indicating that individual CNTs, which cannot be distinguished by FE-SEM, were separated from the bundles near the interface.

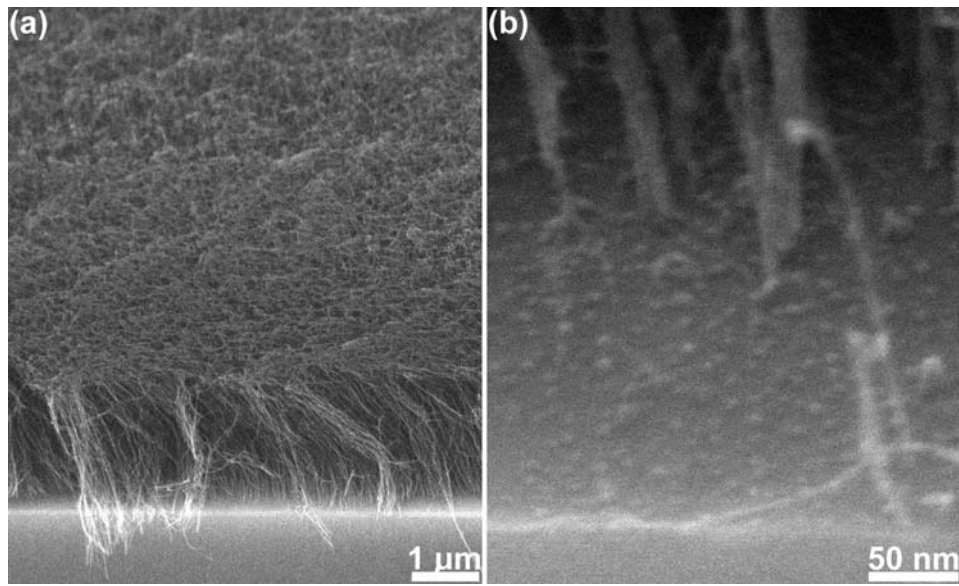


Fig. 4. Cross-sectional FE-SEM images of vertically aligned CNTs taken at 35° from the horizontal.

CNTs were then transferred to a TEM grid for high-resolution observation (HR-TEM). Figure 5 shows HR-TEM images of the as-grown CNTs. The upper-right portion of Fig. 5 shows a thick bundle of CNTs, in which CNTs were parallel to each other. The lower-left portion of Fig. 5 shows a thin bundle, in which individual CNTs are clearly evident. In all of the TEM images, most ($\sim 90\%$) of the CNTs were SWNTs with rather thick diameters of around 3 nm, some ($\sim 10\%$) of the CNTs were double-walled CNTs (DWNTs), and amorphous carbon was also evident. The formation of DWNTs and amorphous carbon was possibly due to the higher ethanol vapor pressure (2.7 kPa) during ACCVD compared with that under standard conditions (1.3 kPa at the inlet of the CVD reactor) [20].

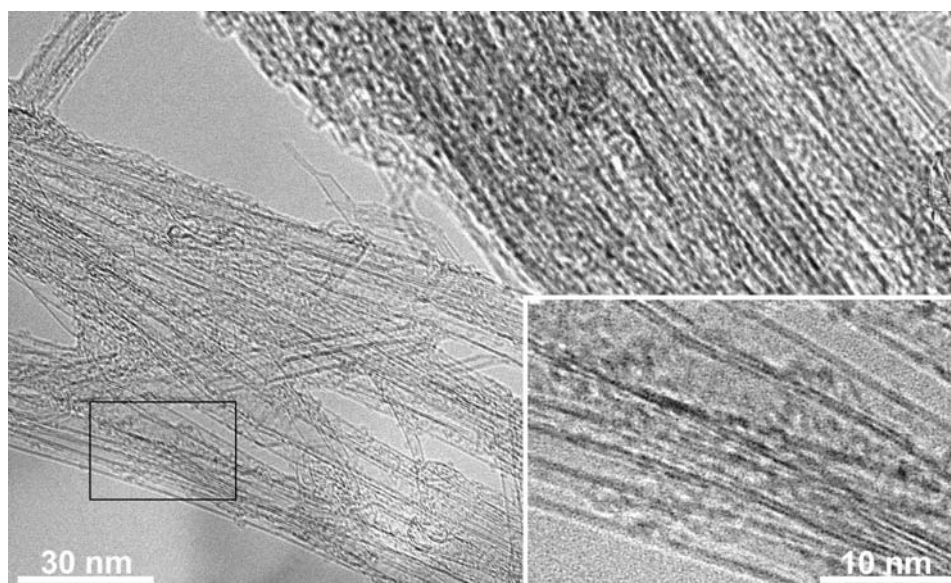


Fig. 5. HR-TEM images of as-grown CNTs. Inset at right shows higher magnification of area enclosed by rectangle at left. The CNTs were primarily SWNTs with some DWNTs and amorphous carbon.

4. Conclusions

Despite of the progress of SWNT growth processes, establishing catalyst preparation methods is still a crucial issue to realize many applications proposed for SWNTs. A simple method to screen binary supported catalysts was developed in which a slit-mask is simply placed above a substrate during vapor deposition of a catalyst precursor. This CMD method proved versatile for discovering active catalysts by using only a minimal number of experiments by successfully growing vertically aligned SWNTs by using Co-Mo catalysts. To realize SWNT-based devices, SWNTs should be grown under widely varied conditions such as substrate material, substrate structure, growth temperature, and precursors. Such wide range of conditions makes the controlled growth of SWNTs difficult because catalyst conditions depend on the growth conditions. Our combinatorial method, which can yield an exhaustive catalyst library on

a substrate, will accelerate the development of SWNTs growth processes.

Acknowledgements

The authors thank Mr. H. Tsunakawa for his assistance in TEM observations.

This work was financially supported in part by JSPS and NEDO of Japan.

References

- [1] Saito R, Dresselhaus G, Dresselhaus MS. Physical Properties of Carbon Nanotubes, London: Imperial College Press, 1998.
- [2] Dresselhaus MS, Dresselhaus G, Avouris P. Carbon Nanotubes, Berlin, Springer, 2001.
- [3] Deheer WA, Chatelain A, Ugarte D. A carbon nanotube field-emission electron source. *Science* 1995; 270(5239): 1179–80.
- [4] Tans SJ, Verschueren ARM, Dekker C. Room-temperature transistor based on a single carbon nanotube. *Nature* 1998; 393(6680): 49–52.
- [5] Cassell AM, Franklin NR, Tomblor TW, Chan EM, Han J, Dai H. Directed growth of free-standing single-walled carbon nanotubes. *J. Am. Chem. Soc.* 1999; 121(34): 7975–6.
- [6] Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, et al. Nanotube molecular wires as chemical sensors. *Science* 2000; 287(5453): 622–625.
- [7] Cassell AM, Verma S, Delzeit L, Meyyappan M, Han J. Combinatorial optimization of heterogeneous catalysts used in the growth of carbon nanotubes. *Langmuir* 2001; 17(2): 260–64.
- [8] Chen B, Parker II G, Han J, Meyyappan M, Cassell AM. Heterogeneous

- single-walled carbon nanotube catalyst discovery and optimization. *Chem. Mater.* 2002; 14(4): 1891–6.
- [9] Kinloch IA, Shaffer MSP, Lam YM, Windle AH. High-throughput screening for carbon nanotube production. *Carbon* 2004; 42(1): 101–10.
- [10] Ng HT, Chen B, Koehne JE, Cassell AM, Li J, Han J, et al. Growth of Carbon Nanotubes: A Combinatorial Method To Study the Effects of Catalysts and Underlayers. *J. Phys. Chem. B* 2003; 107(33): 8484–9.
- [11] Christen HM, Poretzky AA, Cui H, Belay K, Fleming PH, Geohegan DB, et al. Rapid growth of long, vertically aligned carbon nanotubes through efficient catalyst optimization using metal film gradients. *Nano Lett.* 2004; 4(10): 1939–42.
- [12] Noda S, Kajikawa Y, Komiyama H. Combinatorial masked deposition: Simple method to control deposition flux and its spatial distribution. *Appl Surf Sci* 2004; 225(1–4): 372–7.
- [13] Noda S, Tsuji Y, Murakami Y, Maruyama S. Combinatorial method to prepare metal nanoparticles that catalyze the growth of single-walled carbon nanotubes. *Appl Phys Lett* 2005; 86(17): 173106-1–3.
- [14] Murakami Y, Chiashi S, Miyauchi Y, Hu M, Ogura M, Okubo T, et al. Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy. *Chem. Phys. Lett.* 2004; 385(3–4): 298–303.
- [15] Hu M, Murakami Y, Ogura M, Maruyama S, Okubo T. Morphology and chemical state of Co–Mo catalysts for growth of single-walled carbon nanotubes vertically aligned on quartz substrates. *J. Catal.* 2004; 225(1): 230–9.
- [16] Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M. Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol. *Chem. Phys.*

Lett. 2002; 360(3–4): 229–234.

- [17] Murakami Y, Chiashi S, Einarsson E, Maruyama S. Polarization dependence of resonant Raman scattering from vertically aligned single-walled carbon nanotube films. *Phys. Rev. B* 2005; 71(8): 085403-1–8.
- [18] Herrera JE, Balzano L, Borgna A, Alvarez WE, Resasco DE. Relationship between the structure/composition of Co–Mo catalysts and their ability to produce single-walled carbon nanotubes by CO disproportionation. *J. Catal.* 2001; 204(1): 129–45.
- [19] Herrera JE, Resasco DE. Loss of single-walled carbon nanotubes selectivity by disruption of the Co–Mo interaction in the catalyst. *J. Catal.* 2004; 221(2): 354–64.
- [20] Murakami Y, Miyauchi Y, Chiashi S, Maruyama S. Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates. *Chem. Phys. Lett.* 2003; 377(1–2): 49–54.

Figure captions

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