

## NEW CCVD GENERATION AND CHARACTERIZATION OF SINGLE-WALLED CARBON NANOTUBES

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### ABSTRACT

Bulk amount of single-walled carbon nanotubes (SWNTs) have been generated by laser-oven or arc-discharge techniques, and recently by catalytic chemical vapor deposition (CCVD) technique. CCVD technique is being intensively developed for the possibility of larger-scale production of high quality SWNTs at a low cost. We have demonstrated the high-quality generation of SWNTs by utilizing gas phase alcohols (methanol and ethanol) over iron and cobalt catalytic metal particles supported with zeolite. Compared with conventional CCVD techniques, using hydrocarbons or carbon monoxide over metal catalysts, our products were much purer at low reaction temperature. The product was observed by scanning electron microscope (SEM), transmission electron microscope (TEM) and analyzed by Raman spectroscopy. Figure A-1 shows SWNTs generated from ethanol at 800°C. There were many bundles of SWNTs tangling from the zeolite surface and bundles were made of a few hundred high quality (highly graphitized) SWNTs without any by-products (amorphous carbons, multi-walled carbon nanotubes (MWNTs) and

nanoparticles). Raman spectra revealed that tube diameter decreased with lower temperature, and depended on gas flow rate. The relatively low temperature generation was possible with the minimum temperature of about 550°C with methanol. It seems that hydroxyl radicals, which come from reacting alcohol on catalytic metal particles, remove carbon atoms with a dangling bond, which are the obstacles of high-purity SWNTs. This alcohol CCVD (ACCVD) technique would promote the realization of SWNTs in application devices, and promise the direct growth of SWNTs on conventional semiconductor devices already patterned with aluminum.

In order to create nanotube devices, we tried to generate SWNTs on a silicon wafer. Very small amount of Fe/Co supported with zeolite was located on a silicon wafer, and SWNTs were generated by ACCVD technique from ethanol at 900°C (Fig. A-2). The bundles of SWNTs were growing from the surface of zeolite particles and running on a silicon wafer, because of van der Waals attraction. This is the demonstration of the first step to grow SWNTs on patterned silicon surface.

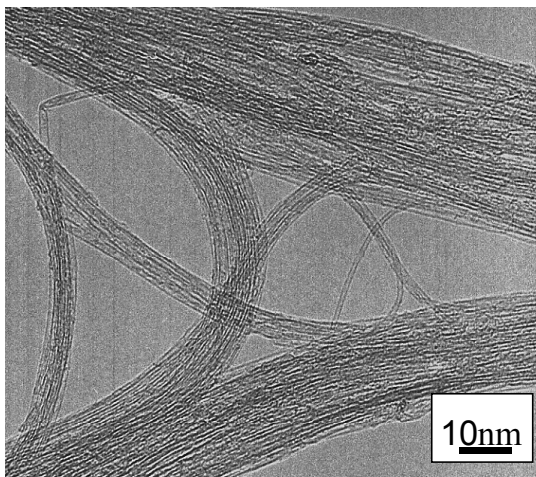


Figure A-1 A transmission electron microscopy (TEM) image of SWNTs generated with the alcohol-CCVD technique.

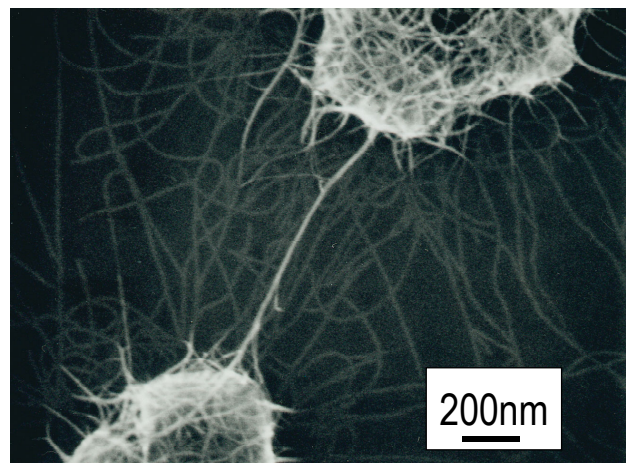


Figure A-2 A scanning electron microscopy (SEM) image of SWNTs grown on a silicon wafer.

## INTRODUCTION

Since the discovery of SWNTs by Iijima *et al* [1], SWNTs have attracted attention and have been studied in many fields. SWNTs have many interesting mechanical, electrical and chemical properties. They have extremely high Young's modulus and superior thermal conductivity along their axes. In electronic conductivity, they can be metallic wires or semi-conductors depending on the chirality.

SWNTs are generated by three techniques; the pulsed laser-oven technique [2], the electric arc-discharge technique [3], and chemical vapor deposition (CVD) technique. In the electric arc-discharge technique, a relatively large amount of SWNTs can be produced but its quality is low, while in the pulsed laser-oven technique, high quality SWNTs can be produced, but the production cost is extremely high. In the last few years, the third technique, CCVD technique is extensively studied, because it has the possibility of a large-scale production. For example, in the HiPco process [4], almost amorphous-free commercial SWNTs were generated using the disproportionation reaction of high-pressure and high-temperature CO with  $\text{Fe}(\text{CO})_5$  as a catalyst seed. But the product has many particles covered with carbon spherical shell and it is dangerous to handle high-pressure and high-temperature CO. On the other hand, highly controlled generation of aligned SWNTs between electrodes on porous silicon surface was also demonstrated [5]. The only problem of this technique for generation on semiconductor devices seems to be the high temperature, such as  $900^\circ\text{C}$ .

We have reported a simple, high-purity and low-temperature synthesis of SWNTs by using a new carbon source molecule, alcohol [6]. The lower reaction temperature and the high-purity features of this alcohol CCVD technique guarantee easy scale-up production at a lower cost. Furthermore, the reaction temperature lower than  $600^\circ\text{C}$  ensures that this technique can be easily applicable for the direct growth of SWNTs on semiconductor devices already patterned with aluminum.

Finally, because this technique is so simple and safe, pure SWNTs can be immediately synthesized at any physics, chemistry or engineering laboratories. The growth of SWNTs on a silicon surface from coarsely dispersed catalyst supported with zeolite particles is demonstrated as the first step for the growth of SWNTs on the patterned semi-conductor devices. We tried to generate SWNTs directly grown from as silicon surface, though only MWNTs were generated in spite of SWNTs.

## EXPERIMENTAL

The metal catalyst supported with zeolite was prepared according to the recipe of Shinohara's group [7,8]. In brief, iron acetate  $(\text{CH}_3\text{CO}_2)_2\text{Fe}$  and cobalt acetate  $(\text{CH}_3\text{CO}_2)_2\text{Co}\cdot 4\text{H}_2\text{O}$  were dissolved in ethanol (typically 20 ml) and mixed with Y type zeolite powder [HSZ-390HUA] (typically 1g). The amount of Fe and Co were 2.5 wt % each. Then, the solution was sonicated for 10 minutes and dried for 24 hours at  $80^\circ\text{C}$ . The resultant white yellow powder on the quartz boat was placed in a quartz tube (i.d. 27 mm) inside of an electric furnace in Fig. 1. While heating up to the desired reaction temperature, more than 200 sccm Ar flow was kept. When the boat reached the desired temperature in about 30 minutes, Ar gas was evacuated and alcohol vapor was supplied to the quartz tube for typically 10 minutes from a room temperature reservoir. Keeping the vacuum pump on, the typical pressure of ethanol in the quartz tube was about 5 Torr. By controlling the reservoir temperature, the vapor pressure was varied. The alcohol gas pressure, flow rate, and the furnace temperature were changed as experimental parameters. After cooling down, the blackened sample on the boat was analyzed with Raman spectrometer, SEM and TEM.

For the generation on a silicon wafer, Fe/Co supported with zeolite particles was dispersed in ethanol and small amount of dispersion liquid (about  $1\mu\text{l}$ ) was dropped onto a silicon wafer ( $10\times 10\text{mm}$ ). In the case of directly generation on a silicon wafer,  $\text{Fe}(\text{NO}_3)_3$  ethanol solution (0.2wt%) was dropped onto a silicon wafer. Then, the wafer was heated ( $600\text{-}900^\circ\text{C}$ ) in an electric oven in Ar

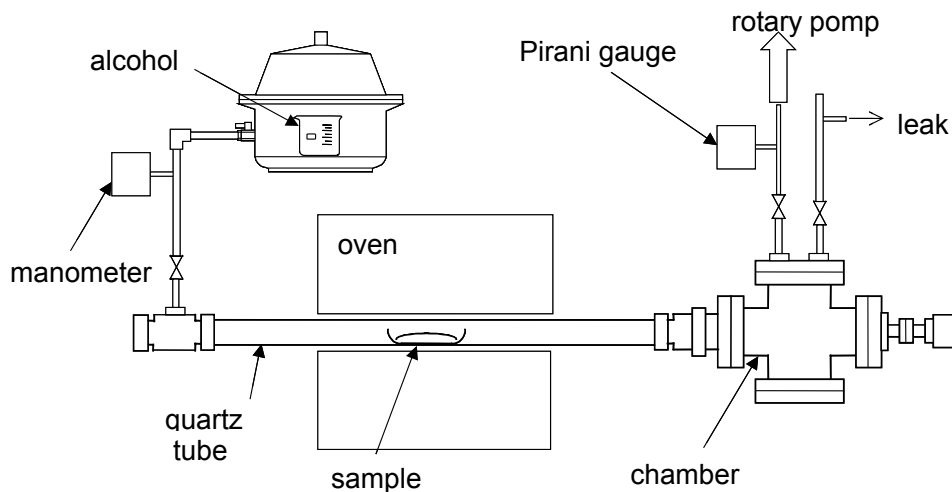


Figure 1 ACCVD experimental apparatus.

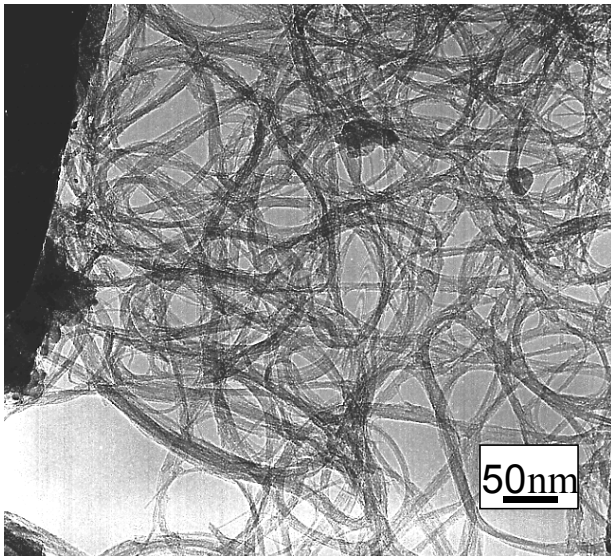


Figure 2 lower magnification TEM image of SWNTs.

atmosphere and ethanol vapor was introduced for 10 min, after evacuation of Ar. After cooled down, the wafer was analyzed by SEM and Raman spectrometer.

## RESULTS AND DISCUSSIONS

### Bulk generation

Figure A-1 shows a TEM image of ‘as grown’ SWNTs from ethanol at 800 °C. The sample was sonicated in ethanol and a drop was evaporated on the microgrid. During careful scan of TEM for several hours, we could not find amorphous carbon, multi-walled carbon nanotubes (MWNTs), carbon nanoparticles or metal particles. Only SWNTs and zeolite particles were observed. Isolated or small bundles of SWNTs, whose diameter are about 1 nm, with clean tube-wall (without amorphous carbon on the surface of its wall) are apparent in Fig. A-1. While SWNTs generated with laser-oven or arc-discharge techniques usually have clean tube-wall, SWNTs from CCVD usually suffers from the imperfect tube wall structure because of imperfect annealing of nanotubes. And, most of samples come with various by-products such as amorphous carbon. We believe that Fig. 1-A is the best clean image of ‘as grown’ SWNTs, ever made.

Figure 2 and Fig. 3 show the lower magnification TEM image and the SEM image of the sample generated in the same condition as in Fig. 1-A. From the lower magnification TEM image in Fig. 2, it can be confirmed that the high-purity image in Fig. A-1 is not the selected special view of the sample. For the SEM image in Fig. 3, small amount of ‘as grown’ sample was placed with the conductive tape for the observation. Web-like growth of bundles of SWNTs from zeolite particles around 300 nm is observed. Again, both from Fig. 2 and Fig. 3, no other structures such as amorphous carbon are observed.

With lower reaction temperature such as 600 °C for ethanol, some view in TEM projection was occupied with SWNTs as in Fig. A-1, but in some spots there were insufficiently annealed short MWNTs with small metal

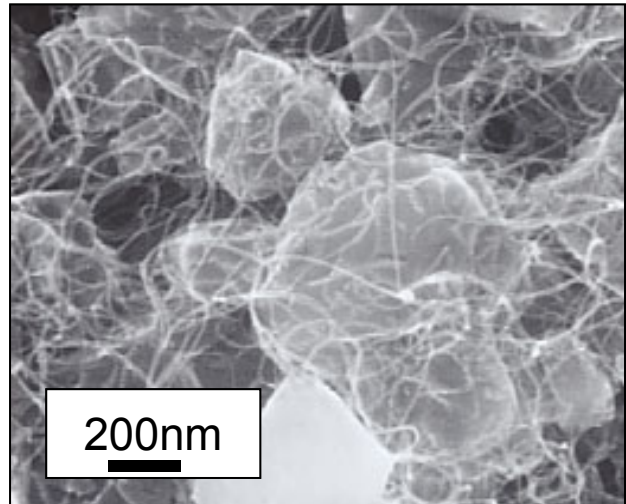


Figure 3 SEM image of SWNTs and zeolites

particles at the end. It seems that the catalyst condition or alcohol gas flow condition was not always perfect for low temperature. By optimizing these conditions, probably the better sample at even lower temperature is possible.

Effects of reaction temperature, reaction pressure, kind of alcohol and catalysts were studied mostly with the Raman measurement [9] by a homemade macro-Raman apparatus with a 50 cm single monochromator and a CCD detector. Figure 4 compares Raman spectra of ‘as grown’ sample from ethanol for various furnace temperatures. The excitation wavelength was 488 nm with an Ar ion laser. The clear radial breathing modes (RBM) (150-300  $\text{cm}^{-1}$ ) and G-band with the zone-holding spread (about 1590  $\text{cm}^{-1}$ ) for all spectra were observed. As a reference, the bottom spectrum was measured from a sample generated with the laser oven technique with Ni/Co (0.6 at% each) loaded graphite. The D-band signal (about 1350  $\text{cm}^{-1}$ ) was quite small for 700 - 900 °C cases but was considerably large for 600 °C case. The D-band increase for 600 °C was probably because of the short MWNTs observed in TEM image. From the expanded RBM signal in Fig. 5, the typical diameter of SWNTs was estimated as about 0.8 - 1.2 nm. Here, the following correlation between diameter  $d$  (nm) and RBM Raman shift  $\lambda$  ( $\text{cm}^{-1}$ )

$$d = 248/\lambda \quad (1)$$

was used for the upper coordinate in Fig. 5 [10]. Compared with the Ni/Co loaded graphite in laser-oven technique (Fig. 5(e)), tube diameter is smaller and more widely distributed. With decrease in the reaction temperature, diameter distribution shifted to the thinner side. At the same time, the BWF line shape [9], which is characteristics of metal SWNTs, are clearly seen for lower temperature samples. From the detailed comparison with Kataura plot [11], it is assigned that Raman peaks around 150-220  $\text{cm}^{-1}$  are semiconductor SWNTs and peaks in 230-300  $\text{cm}^{-1}$  are metallic SWNTs. The temperature dependence of diameter distribution is

very much similar to laser-oven technique [12] even though the absolute value of temperature was much lower in our case.

The dependency of alcohol gas flow rate was also studied. Controlling the temperature of the alcohol reservoir, we changed alcohol gas flow rate. In the case of

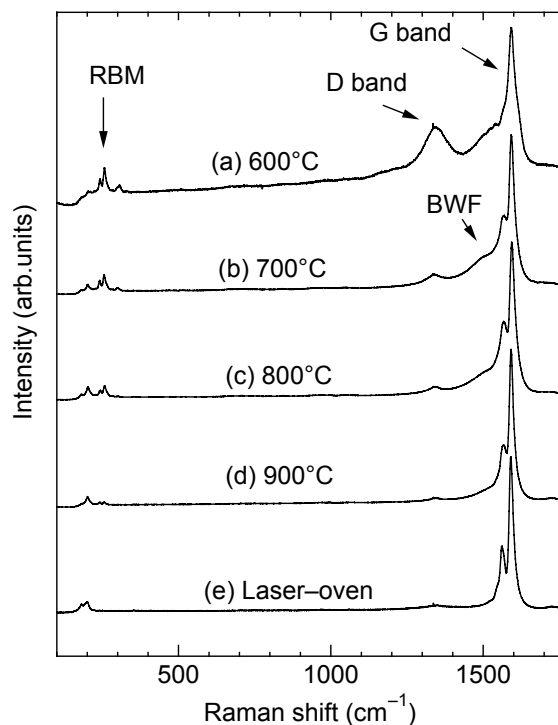


Figure 4 Raman spectra of SWNTs from ethanol.

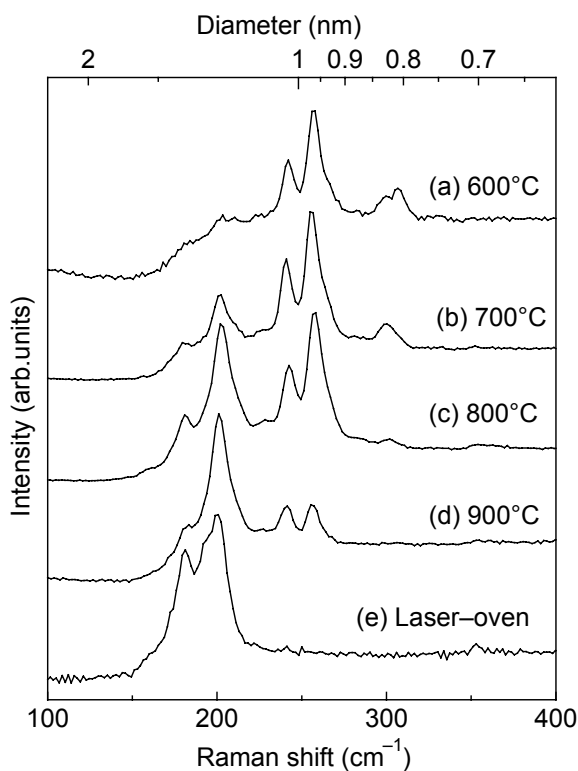


Figure 5 Low frequency of Raman spectra of SWNTs from ethanol.

higher flow rate (about 1840 sccm), the sample contained many amorphous carbon, large metal particles, and MWNTs, and zeolite was covered with thick amorphous carbon layers. These metal particles were larger (5-10 nm) than those in the sample from ethanol at 600 °C (2-3nm). On the other hand, the sample in the lower flow rate condition (about 60 sccm) had few amorphous carbon, few metal particles and no MWNTs. Comparing them with the samples in the standard flow rate condition (about 290 sccm), it was found that with the higher flow rate (higher pressure), the thinner SWNTs were generated. This result shows that the low flow rate or low pressure is the important feature of the generation of high-purity SWNTs.

By replacing the ethanol to methanol in the bulk generation, almost the same Raman spectra as ethanol at 800 °C was observed, but slightly larger diameter nanotubes were enhanced with the methanol case compared with the ethanol case. The Raman spectrum for the lowest temperature case at 550 °C with methanol was very similar to 600 °C case with ethanol, both from the D-band strength and diameter distribution [6]. Even though the D-band peak is considerably large, it is clear that substantial amount of SWNTs was generated at this low temperature. Comparing Raman spectra for ethanol and methanol, it seems that the optimum reaction temperature is about 50 °C lower for methanol case. By TEM observations of the sample from methanol, we found that the bundle size was considerably smaller than the ethanol case, and there were small amount of fine metal particles dispersed in bundles of SWNTs. But the lower temperature generation from methanol is advantageous for nanotube devices, because this low temperature does not damage the aluminum patterns on silicon devices.

We also quickly tried 1-propanol as another alcohol carbon source. Very similar results as ethanol were observed from Raman measurements. The reason why alcohols were much better carbon source for SWNTs compared with hydrocarbons is explained by the role of decomposed OH radicals as follows. It is known that an OH radical efficiently removes the amorphous carbon in the purification process of SWNTs using H<sub>2</sub>O<sub>2</sub>. It is also known that the reaction of OH radical to solid carbon reduces the formation of soot in combustion chemistry [13]. Since an OH radical is decomposed on the catalyst surface from an alcohol molecule, it will attack nearby carbon atoms with a dangling bond to form CO. Then, seeds of amorphous carbon are efficiently removed in its very early stage. We believe that the initial stage of MWNT formation in CCVD process is also initiated from the amorphous carbon attaching to the SWNTs. Hence, the OH radical prohibits the generation of all these side-products, and only the SWNT can survive in this condition.

Comparing with samples generated from ethanol and methanol, it was noticed that the SWNTs with the catalytic metal particles at the end were often found in products for methanol, while in the case of ethanol, such

a structure rarely existed. This difference would mean the difference of growth mechanism between ethanol and methanol. SWNTs are believed to grow up from catalytic metal supported with zeolite particles. If growing SWNTs lift up the metal particles, SWNTs with the metal particles at the end appear. On the contrary, if SWNTs grow from the surface of catalyst metal particles and catalyst metal particles are still fixed on zeolite, SWNTs without metal particles at the end are generated. The difference of growth mechanism would come from the ratio of OH radical to carbon atom decomposed from alcohol.

### Generation on a silicon wafer

The characteristics of ACCVD such as high-purity and low-temperature are very attractive for the

application of nanotube devices. As the first step in this direction, we generated SWNTs on a silicon wafer. Figure A-2 and Fig. 6 show the SWNTs grown on a silicon wafer by ACCVD technique at 900°C. Many bundles of SWNTs were extended from almost all zeolite particles and the length of the bundle reached a few micrometers. The bundles observed as low-contrast image in Figs. A-1 and 6 were running on a silicon wafer, probably because they were attached to silicon surface by van der Waals force. Sometimes, a bundle of SWNTs directly connecting two zeolite catalysts was observed as shown in the center of Fig. A-2. In general, it is very difficult to qualify the dispersed nanotubes on silicon surface. Here, we used the micro-Raman scattering measurements. The Raman spectra in Fig. 7 show that SWNTs were generated on a silicon wafer at 700-900°C, though the

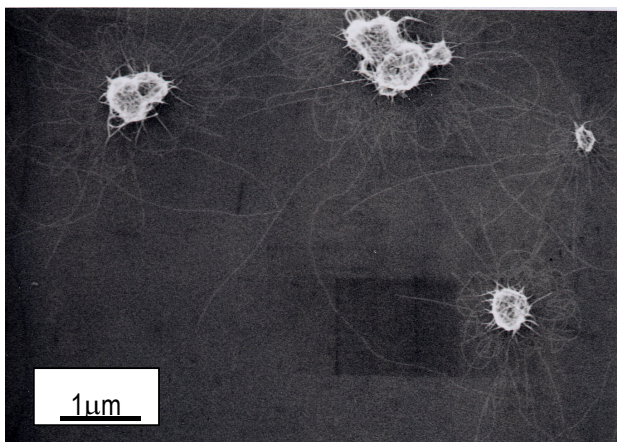


Figure 6 SEM image of SWNTs on a silicon wafer.

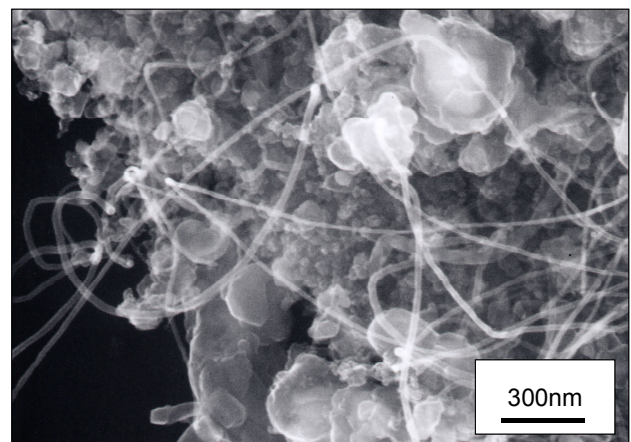


Figure 8 SEM image of MWNTs generated from catalytic metal particles directly located on a silicon wafer.

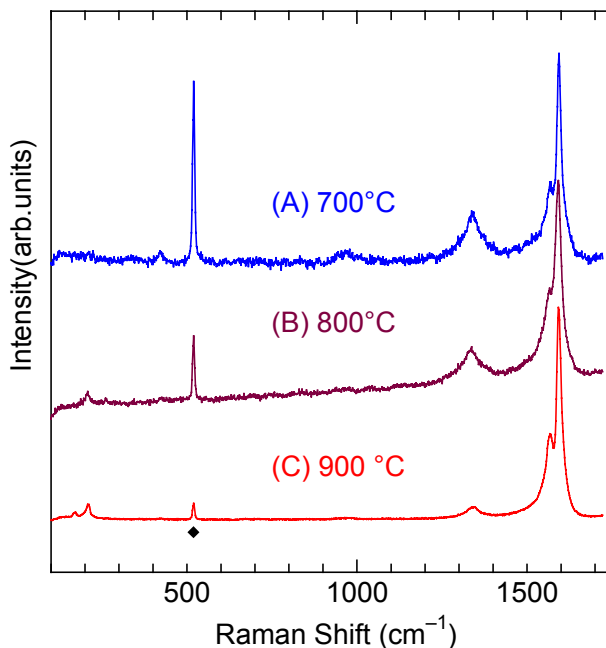


Figure 7 Raman spectra of SWNTs generated from zeolites located on a silicon wafer. The mark ♦ indicates the signal from silicon.

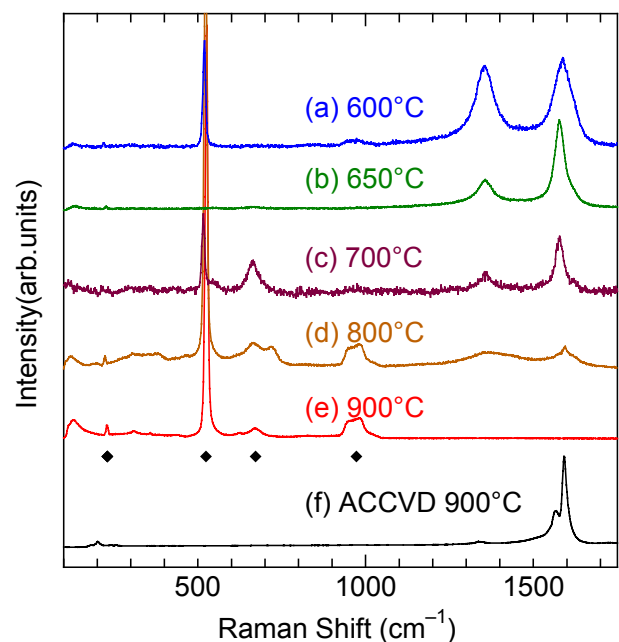


Figure 9 Raman spectra of MWNTs generated from catalytic metal particles directly located on a silicon wafer. The mark ♦ indicates the signal from silicon.

signal intensity of SWNTs relative to silicon background decreased at lower temperatures, which means amount of SWNTs is decreased. Furthermore, at this stage, the D-band signal is significantly large and radial breathing mode is barely distinguishable for low temperature case. However, in principle, if the position of zeolite particles is controlled, SWNTs could be located arbitrarily on a device already patterned.

As the second step to the application of nanotube devices, we tried to generate SWNTs from catalytic metal directly located on a silicon wafer. Tiny amount (typically 2 $\mu$ l) of very dilute solution of Fe(NO<sub>3</sub>)<sub>3</sub> ethanol (0.05wt% Fe) is dropped on silicon surface as the catalyst preparation. From SEM image in Fig. 8, catalytic metal with various sizes and tangling wire structure were observed. Unfortunately, the Raman spectra in Fig. 9 show no evidence of SWNTs, but the wire structures should be MWNTs. The maximum ratio of G-band to D-band was recorded at 650°C. At this stage, SWNTs are not efficiently generated from such metal particles, probably because the metal particles are too large, or because metal is reacted with silicon. Further studies are necessary for the simple growth of SWNTs on silicon surface.

### CONCLUSION

We have demonstrated the generation of SWNTs by catalytic CVD technique using alcohol. High-purity SWNTs were generated at low temperature without any by-products. Changing the reaction temperature and alcohol gas flow rate, the distribution of SWNTs' diameters was controllable. By ACCVD technique, SWNTs were generated on the surface of silicon, for the first step of nanotube devices.

### ACKNOWLEDGEMENT

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