The International Symposium on Micro-Mechanical Engineering
December 1-3, 2003

ISMME2003-105

DIRECT SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES ON SILICON AND QUARTZ BASED SYSTEMS

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A new technique of synthesizing single-walled carbon nanotubes (SWNTs) directly on the surface of Si and quartz substrates is introduced in this report. This technique adopted a liquid based dip-coat method to mount very small amount of catalyst metals on the surface of the substrates with using Mo/Co bimetallic acetate solution. Merits of this approach lie in its easy, costless, and geometry-flexible nature compared with conventional sputtering and deposition approaches. We used alcohol catalytic CVD (ACCVD) method that can produce relatively high quality SWNTs even at low temperature down to 600 °C. This low temperature process contributes to the prevention of agglomeration of catalytic metals on the surface and chemical reaction between catalytic metal and silicon, which helps us to eliminate any kind of intermediating support materials. Thereby synthesized SWNTs on Si and quartz substrates under various CVD conditions are characterized by means of SEM, TEM, Raman scattering, and optical absorbance measurements. The underlying reasons of why our experimental procedure and choice of catalyst worked for the synthesis of SWNTs are discussed through comparative studies. In the end of this report, some possible application of this technique is stated.

Keywords: *Carbon nanotubes, CVD, Alcohol CCVD, Silicon, Direct synthesis.*

INTRODUCTION

The discovery of single-walled carbon nanotubes (SWNTs) in 1993 by Iijima and Ichihashi [1] has so far motivated numerous researches in various fields trying to utilize the remarkable physical properties [2] of this newly found 1-D carbon allotrope. Experimental studies about SWNTs have become possible since the discoveries of laser-furnace [3] and arc-discharge [4] techniques to produce bulk amount of SWNTs, and more scalable CVD technique [5-12] that has now become dominant in the mass synthesis of SWNTs.

In attempting to fabricate SWNT-based devices, an appropriate incorporation of SWNTs into silicon or other material-based systems is strongly desired. So far, several studies have been reported in which carbon nanotubes were synthesized on the substrates using various approaches. Kong et al. [13] and Franklin et al. [14] spun-coated their Fe/Mo catalyst with alumina support particles to form patterned catalytic islands on Si surfaces and synthesized a small amount of SWNTs. Cassell et al. mounted mesoporous alumina/silica on Si substrate to support their Fe/Mo catalyst and generated SWNTs [15]. In other studies the mesoporous silica was coated on Si substrate in the form of a thin film as a supporter, leaded to the production of MWNTs [16-18] or SWNTs [19]. Although it depends on assumed application, these support material is sometimes undesired because this is an additional material that are not essential for the functions of devices: One way to circumvent this is presented by Li et al. [20] who did not use support material but utilized ferritin protein to sparsely locating iron nanoparticles on a flat SiO_2 substrate to synthesize SWNTs.

All studies referred above [13-20] used liquid-based approaches for their catalyst preparation; however, in some reports catalytic metals were mounted on substrates using dry processes such as sputtering or deposition [21-26]. Although selective synthesis of SWNTs on flat Si surface was reported recently [26], these methods prone to form relatively large (i.e. more than 10 nm) agglomerates of catalyst metals and to produce multi-walled carbon nanotubes (MWNTs). For examples, dominant products reported by Nerushev et al. [22] and Yoon et al. [23] were MWNTs, though they reported to have synthesized some amount of SWNTs. Delzeit et al. [21] synthesized SWNTs with relatively high quality and selectivity by pre-depositing 20 nm of Al underlayer on Si surface before depositing 1 nm of Fe/Mo catalyst. However, such underlayer resulted in significant surface roughness due to an agglomeration of Al caused by the heat during CVD. Similar trial was made by Zhang et al. [24] but also accompanied an agglomeration of Al underlayer. Although no SWNTs were produced in case of Si substrate, Hongo et al. [25] sputtered Fe on A-face of Sapphire crystal and synthesized relatively abundant amount of SWNTs at the CVD temperature of 800 °C. In other reports SWNTs were successfully incorporated on a

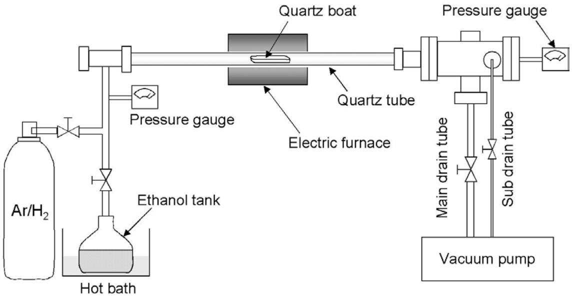

Fig. 1. CVD apparatus for synthesis of SWNTs.

catalyst-patterned substrate as a field-emission transistor (FET) [26, 27]. In their prototypes, very suppressed (one or slightly more) number of SWNTs was grown from catalytic islands of far larger dimensions (3 µm [26] and 100 µm [27]), indicating that there were very few active sites and most catalyst area did not participate. It should be desired to raise the area efficiency of catalyst for future downsizing and concentration of FET density.

We here report a new technique of synthesizing SWNTs directly onto the surface of Si and quartz flat surfaces without using any support or underlayer materials. In this technique, small amount metal catalyst is loaded through a dip coating of a Mo/Co acetate solution, by which very fine dispersion of bimetallic catalyst around a few nanometers were obtained. The alcohol CCVD technique developed by our group [11,12] that can generate relatively high-quality SWNTs even at low temperature of 600 °C [11] was used in order to minimize any side effect caused by the high temperature during CVD process, as discussed later.

EXPERIMENTAL

Catalyst loading on surface of substrates

Detailed description of the catalyst loading process is presented in our previous report [29]. In short, a metal acetate solution is prepared by adding molybdenum acetate $(CH_3COOH)_2$ Mo and cobalt acetate $(CH_3COOH)_2$ Co-$4H_2O$ into ethanol so that the concentration of each metallic species over the total solution is 0.01 wt %. The mixture is then sonicated for 2 hours to dissolve these acetic salts. A substrate piece, appropriately sized, is vertically suspended by a clip connected to a nylon string in the metal acetate solution for 10 min, and then the substrate was drawn-up from the solution at a constant speed of 4 cm/min. Immediately after this, the piece was placed in a furnace kept at 400 °C for 5 min in order to convert metal acetate into metal oxides of bimetallic Mo/Co catalyst on the surface.

CVD procedure

The schematic of our CVD apparatus is shown in Fig. 1. It is composed of an ethanol reservoir, a quartz tube (26 mm i.d., 1 m long), an electric furnace, and a rotary vacuum pump. In the CVD process, the catalyst-loaded substrate is placed on a quartz boat that locates at the central position of the quartz tube as shown in the Fig. 1. While the furnace is being heated up, about 300 sccm of Ar/H_2 gas (3 % H_2) is flowed with remaining only the 'sub drain tube' open. When the furnace reaches the temperature for CVD reaction, Ar/H_2 is stopped and the 'main drain tube' is opened to bring the inside of the quartz tube to vacuum. Subsequently, vapor of ethanol is introduced into the quartz tube so that the pressure just before the entrance of the tube is constant at 10 Torr. After the CVD reaction, ethanol vapor is stopped and the furnace is turned off, before the apparatus is brought back to room temperature with flowing 100 sccm of Ar/H_2.

Measurement and analyses

The SWNTs in 'as-grown' state (i.e. without purification) were analyzed with FE-SEM (Hitachi, S-900), TEM (JEOL 2000EX), and micro Raman scattering (Chromex 501is and Andor DV401-FI for the spectrometer and CCD system, respectively, with an optical system of Seki Technotron STR250). All the Raman spectra shown in this report are an arithmetic average of 10 measurements performed at different locations on the substrate. VIS-NIR absorption spectra were measured with Hitachi U-4000.

RESULTS

Microscopic analyses

Figure 2 shows a SEM image at a broken edge of the quartz substrate after 1 h CVD at 800 ºC. This picture was taken from tilted angle to include the broken

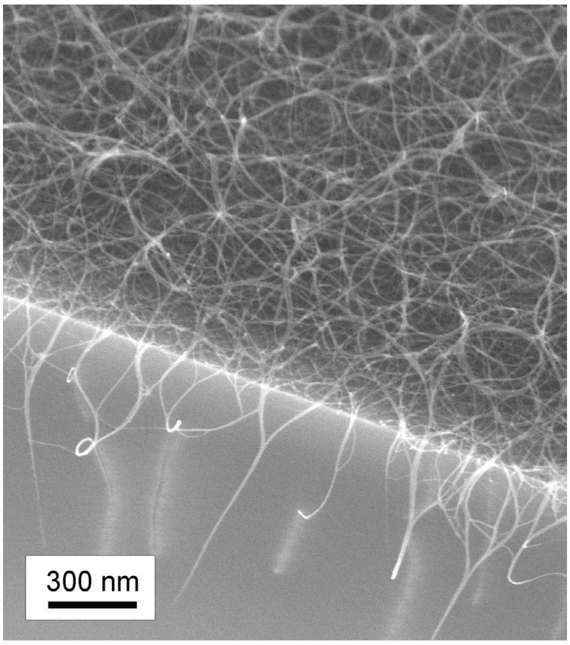

Fig. 2. SEM image of SWNT mat directly synthesized on a quartz substrate [29]. Lower half is the broken cross-section of the substrate. CVD conditions were 800 ºC, 1 h for reaction temperature and time, respectively.

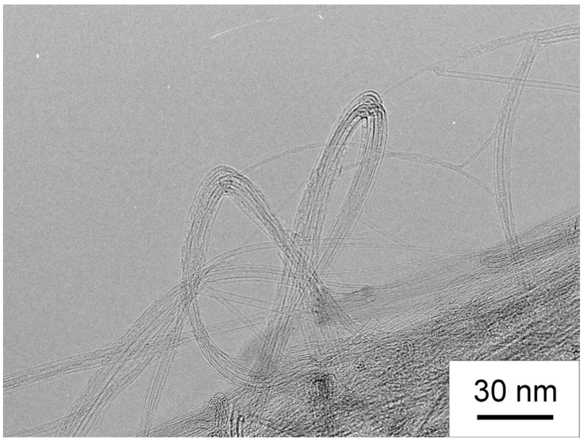

Fig. 3. TEM observations of SWNTs shown in Fig. 2. An edge of SWNT mat was observed. Lower right corner corresponds to the thick mat where the electron transmission is weak and therefore looks darkened.

cross-section in its lower half. This image well exhibits the morphology of the SWNT mat directly synthesized on the quartz surface. SWNTs are randomly oriented and form bundles whose thickness mostly ranges between 7 - 15 nm. In observation around the edge, we were not able to find metallic agglomerates of more than 10 nm that were often observed when catalytic metal was mounted on the surface using sputtering or deposition [21-24]. Detailed characterization on the metal catalyst on the surface is currently in progress by our group.

Although Fig. 2 gives us mesoscopic information about its morphology, the microscopic structure as well as existence of contamination should be confirmed with TEM. We rubbed the blackened quartz surface with a micro-grid and observed an edge of SWNT mat adhered on the grid. Figure 3 shows an image observed with TEM. It was confirmed that the only SWNTs were seen and no multi-walled nanotubes (MWNTs) were recognized. It was also confirmed that the wall of SWNTs was clean and almost free from amorphous carbon or any other impurities. As expected from the SEM observation, most of SWNTs were observed to form bundles: However, some of SWNTs were isolated as exhibited in Fig. 3.

Raman scattering analyses

Raman scattering analysis is a strong tool to characterize obtained SWNTs [30]. The Raman spectra of SWNTs synthesized on Si and quartz substrates are presented in Fig. 4. Detailed interpretations of Raman spectra of SWNTs shall be referred to e.g. Ref. [31]. The CVD reaction times were 10 and 60 min for Si and quartz, respectively. The remarkable peak around 1590 cm^{-1} (G-band) arise from an in-plane oscillation of carbon atoms in the sp2 graphene sheet and less remarkable peak around 1350 cm^{-1} (D-band) reflects degree of defects or dangling bonds contained in the sp2 arrangement of graphene. All the spectra were normalized by the height of G-band peaks.

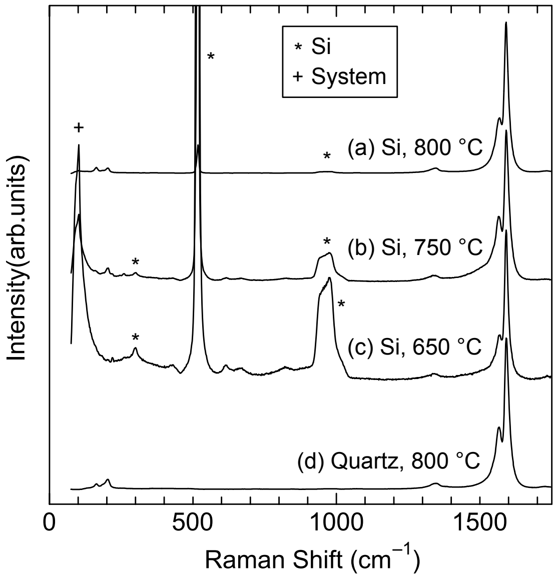

Fig. 4. Raman spectra (taken by 488 nm) of SWNTs grown directly on the Si and quartz substrates under different CVD temperatures. CVD times for Si and quartz are 10 min and 1 h, respectively.

For the case of Si substrates (Fig. 4(a)-(c)), amount of produced SWNTs is estimated from intensity ratio of G-band and Si-derived peak at 960 cm^{-1}. The amount of produced SWNTs drastically increases as the temperature increases; however, above 800 °C the amount decreases again and no SWNTs were detected at the temperature of 900 °C (not shown). This is attributed to the silicide formation caused by the chemical reaction between catalyst metal and silicon, which significantly deteriorates catalytic activity as demonstrated by de los Arcos et al. [32]. In any temperatures, the produced SWNTs retain high quality judging from its high G/D ratio of about 30. Most notably, with our method, SWNTs were synthesized on the Si surface even at the temperature of 650 °C: This is by far the lowest among the previous reports where 800 °C [24,25] or 900 °C (or higher) [13-15,20-23] was employed for SWNT synthesis. This technique is also effective for a quartz substrate and the spectrum (Fig. 4(d)) indicates that SWNTs with sufficiently high quality were obtained.

Figure 5 shows the Raman spectra of 'radial breathing mode' (RBM) of SWNTs synthesized at 800 °C grown on Si and quartz substrates (corresponding to Figs. 4(a) and (d), respectively) measured with 3 different laser wavelengths 488, 514.5, and 633 nm. The RBM is unique to nanotubes and derives from a cyclic boundary condition of the rolled-up graphene sheet, and therefore, planar graphene do not present RBM peaks [2]. On the top of the figure, the Kataura plot [33] calculated using γ_0 = 2.9 eV and a_{c-c} = 0.144 nm [34] is presented with horizontal lines corresponding to each laser energy. Since this is resonant Raman scattering, only limited SWNTs that have a band gap equal to the laser energy can resonantly scatter the incident laser. The peak locations in lower Fig. 5 well agree with those predicted by the Kataura plot and it is recognized that the products for

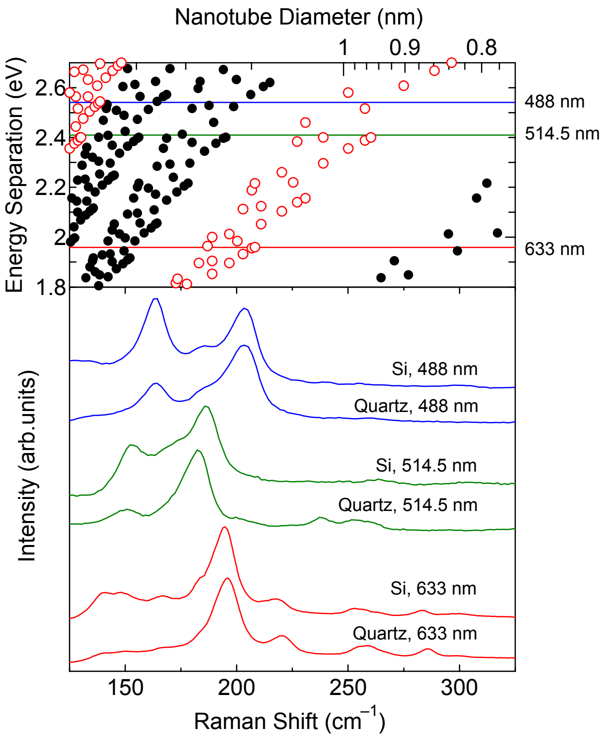

Fig. 5. RBM spectra of SWNTs grown on Si and quartz substrates taken by 3 different lasers, 488, 514.5, and 633 nm. On the top is the Kataura plot where open and solid circles denote energy gaps of metallic and semiconducting SWNTs, respectively. Horizontal lines denote energies of incident lasers.

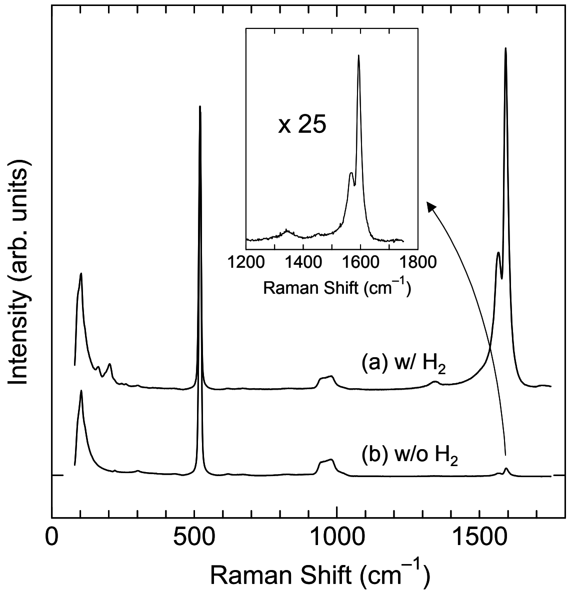

Fig. 6. Raman spectra (taken by 488 nm) of SWNTs synthesized on Si surface when (a) Ar/H_2 (3 % H_2) or (b) Ar was flowed during heat-up of the electric furnace. CVD was performed at 750 ºC for (a) 10 min and (b) 30 min. Inset magnifies G-band in the case of (b).

both cases were a mixture of both metallic and semiconducting nanotubes. Since it is known that the diameter of SWNT is inversely proportional to the RBM shift [31], the diameter distribution is estimated using e.g. the relationship 'd (nm) = 248 / υ (cm^{-1})' [35] where d and υ are diameter and Raman shift of a SWNT, respectively. From Fig. 5, it is recognized that SWNTs grown on Si and quartz surfaces have a diameter distribution of 1.1-1.7 nm, which coincides with the TEM observation in Fig. 3.

DISCUSSION

In the following, some reasons toward our choice of conditions for catalyst preparation and CVD operation are briefly presented and discussed. In the end, possible application of current synthesis technique is stated.

Effect of reduction

We supplied H_2 during heat up of the electric furnace and this is for the purpose of reduction of catalyst metals. Since the catalyst before the CVD is oxidized that has less catalytic activity, one should reduce the catalyst by some way before SWNTs start to grow. Actually, since carbon itself is a good reducer, it is possible to reduce the metal oxides using alcohol vapor. However, since in this case the decomposition speed of alcohol to extract carbon atoms is considered to be slow due to the lower catalytic activity, the amount of SWNTs when catalyst is not reduced prior to the CVD reaction is generally low. This was demonstrated in our previous report using zeolite as a support material [12]. This discussion actually works also in the case of flat substrate: Figure 6 shows the Raman spectra taken by 488 nm from the surface of Si substrate after CVD at 750 ºC. Figure 6(a) is the spectrum when Ar/H_2 (3 % H_2) is supplied during heat-up of electric furnace, and Fig. 6(b) is the spectrum when Ar is used instead of Ar/H_2. The intensity of G-band in case of Fig. 6(a) is about 40 times larger than that of Fig. 6(b), even though the reaction time for Fig. 6(b) was longer than that for Fig. 6(a). This indicates that the amount of SWNTs is drastically controlled by the use of reduction besides changing the time of CVD to control the amount of SWNTs.

Effect of metallic salt

We have employed bimetallic Mo/Co catalyst that exhibits satisfactory performance, as presented thus far. Up to present, various kinds of bimetallic combinations such as Fe/Co [11,12], Mo/Co [36,37], and Mo/Fe [6,8,9,38] impregnated on support powder (e.g. silica, alumina, or MgO.) were employed for the mass synthesis of SWNTs. In some of these studies [8,36-38] the effect of bimetals for an enhancement in SWNT production was discussed.

Figure 7 shows Raman spectra (taken by 488 nm) of a SWNTs grown on quartz substrates with CVD at 800 ºC for 1 h using various catalysts. In Fig. 7(a), our standard acetic Mo/Co catalyst (0.01 wt % each) was used and the spectrum exhibited strong G-band peak at 1590 cm^{-1}, as

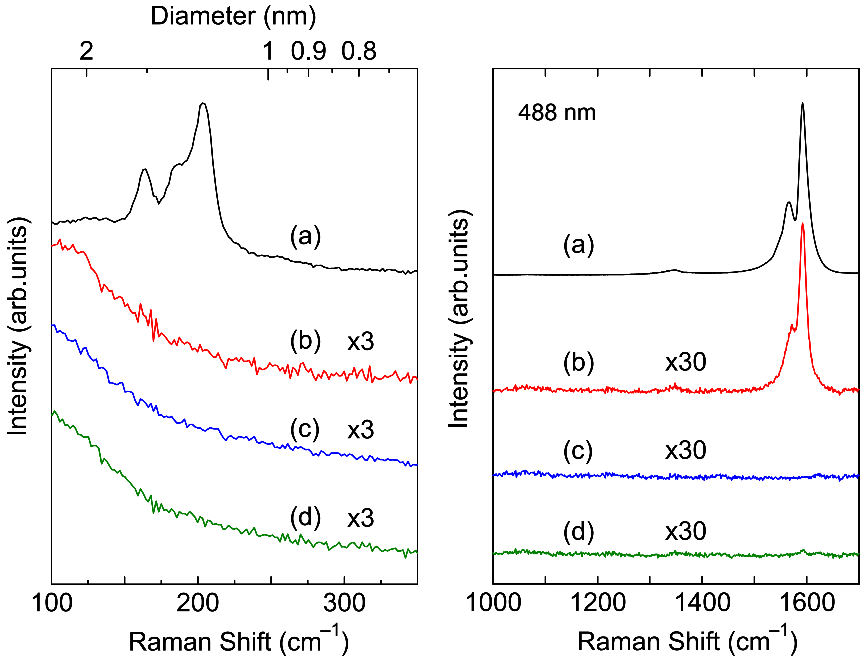

Fig. 7. Raman spectra (taken by 488 nm) of SWNTs generated on quartz substrates from various catalysts, (a) Co acetate and Mo acetate 0.01 wt % each, (b) Co acetate 0.02 wt %, (c) Mo acetate 0.02 wt %, and (d) Co nitrate and Mo acetate 0.01 wt % each. The weight concentration here is defined as a ratio of metallic weight in salt to total solution weight used for the dip-coat process (see experimental section). The right panel shows G-band while left panel exhibits RBM. Indistinct signals below 200 cm^{-1} observed in (b)-(d) are oriented from quartz and our measurement system.

shown before. In case of Fig. 7(b), catalyst of Co 0.02 wt % was used this resulted in far weaker G-band intensity (1/30 of Fig. 7(a)), indicating that much smaller amount of SWNTs was produced with this catalyst. On the other hand, when Mo 0.02 wt % catalyst was employed (Fig. 7(c)), no signal of SWNTs was detected, indicating that monometallic Mo is inactive as a catalyst for SWNTs. Our observations here agrees with the discussion by Alvarez et al. [37] who explained the role of Mo as a stabilizer that prevent Co from agglomerating and therefore to help the catalyst be suitable for SWNT formation. Finally, in case of Fig. 7(d), we used a combination of Molybdenum acetate and cobalt *nitrate* $Co(NO_3)_2$-$6H_2O$. Interestingly, this case again produced no SWNTs. This may be explained by the detailed report by Sun et al. [39] where they prepared cobalt catalysts on silica gel powder through an impregnation of mixture of cobalt (II) nitrate and cobalt (II) acetate salts. They tested various nitrate/acetate ratio from 1:0 (all nitrate) to 0:1 (all acetate) and demonstrated that only when acetate is solely used the fine dispersion of Co particle of around 2 nm were obtained, while when nitrate was used the resultant Co particle became as large as 10 nm. They discussed that this was caused by a strong interaction between metal acetate and SiO_2 support [39]. Although microscopic structure of SiO_2 in our case is different from Ref. [39], since nitrate/acetate ratio is 1.6 in the case of Fig. 7(d), the inertness of the catalyst might be caused by the weakened interaction between metals and SiO_2 surface. However, more careful and detailed investigations on this matter are needed to further discuss the effect of catalyst choice on the synthesis of SWNTs.

Merits and application of current technique

Since generation of SWNTs requires active catalyst of its size comparable to the diameter of a SWNT (i.e. a few nanometers) [5], it is crucially important to mount small amount of catalytic metals on the surface at the same time to prevent them from agglomerating into large particle even under the high temperature during CVD. One obvious merit of our dip-coat technique lies in an easiness of loading very small amount of bimetallic catalyst on the surface partly because one can adjust the concentration of catalyst solution by diluting. In addition, it is confirmed that the catalyst prepared by our method is finely dispersed around a few nanometers after heating up with Ar/H_2 reduction. This good dispersion might be contributed from the strong chemical interaction between metal acetate and SiO_2 base [39], as mentioned above: It is quite plausible that such chemical interaction does not occur in the catalyst loaded by sputtering or deposition processes.

Lowering of CVD temperature is absolutely desired because higher temperature accelerates sintering of catalysts and chemical reaction between catalyst metal and silicon to yield inactive metallic silicide [32]. The alcohol CCVD method employed in this report excels, as already demonstrated in the past reports [11, 12, 19], in

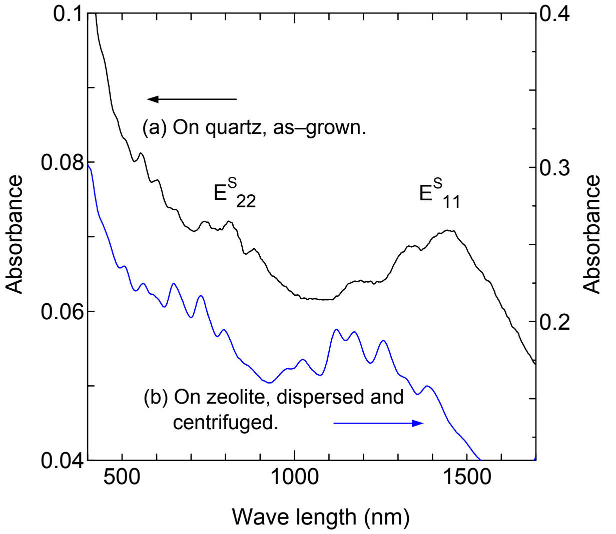

Fig. 8. Optical absorption spectrum of as-grown SWNTs synthesized directly on the surface of quartz, which corresponds to the sample shown in Figs. 2 and 3.

producing relatively high quality SWNTs at low temperature down to 600 ºC. This low temperature process contributes to our direct synthesis technique because, by this, we can be free from conventionally used support materials.

To the best of authors' knowledge, this is the first study to directly synthesize eye-recognizable amount of SWNTs on the surface of quartz substrate. Recently, it is reported that SWNTs exhibits excellent bleached absorption properties due to their strong third-order optical non-linearity ($\chi^{(3)}$) along with an absorption around 1.55 μm that is used in optical telecommunication [40]. These characteristics motivated attempts to apply SWNTs toward optical switching [40] and a mode-lock laser.

The SWNT-synthesized quartz substrate prepared by our technique could be used for such optical applications. An optical absorption spectrum of the specimen shown in Fig. 2 is presented in Fig. 8(a). As a reference, the spectrum of SWNTs synthesized on zeolite support using Fe/Co catalyst [12] was presented in Fig. 8(b), which was suspended in 1 wt % SDS-added D_2O after strong sonication, centrifugation, and decantation of its supernatant based on the procedure in Ref. [41]. In the spectrum in Fig. 8(a), several broad peaks are recognized and this broadening is due to bundling of SWNTs [41]. Sharper peaks are seen when bundles of SWNTs are removed by centrifugation (Fig. 8(b)). Difference in the locations of peaks between Fig. 8(a) and (b) comes from the difference in band-gaps of contained SWNTs (i.e. difference in chirality) in addition to a red shift of the spectrum subjected to Fig. 8(a) due to bundling. There are some recognizable groups of peaks in the spectra. The peaks around 1.45 μm in Fig. 8(a) derives from the first energy gaps of semiconducting tubes E^S_{11}, which corresponds to the peaks around 1.3 μm in the case of Fig. 8(b), and peaks around 800 nm the second energy gaps E^S_{11} [41]. These results assure that the possibility of current technique to be applied to aforementioned optical applications. Up to present, we have been able to synthesize SWNTs directly on the surface of an optical fiber using the same technique, which may also contribute to such SWNT-based optical technologies.

CONCLUSION

We introduced a new method of synthesizing SWNTs with sufficient quality directly on the surface of Si and quartz substrates using dip-coat method for catalyst loading and ACCVD method for CVD process. The SWNTs were synthesized directly on Si surface even at the temperature of 650 °C, which is by far the lower than the reported cases of between 800 to 1000 °C. In case of quartz, abundant amount of SWNTs were produced on the surface to the extent the surface was blackened with SWNTs. The proposed dip-coat method is easy and cost-effective approach that is suitable to mount small amount of catalyst on the surface. The strong interaction between metal acetate and SiO_2 base may help the fine dispersion of catalyst that is sometimes difficult to be achieved by the conventional sputtering or deposition technique, though further elucidation of catalyst formation process is essential. This technique may be applicable to recently proposed SWNT-based optical devices.

ACKNOWLEDGMENTS

Authors thank Mr. H. Tsunakawa for his assistances in TEM operation and T. Sugawara for his advices in SEM operation, both at the University of Tokyo. Part of this work was financially supported by KAKENHI #12450082 and 13555050 from JSPS, and #13GS0019 from MEXT.

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