A Comparative Study of Cobalt Catalyst Behavior between Silica and Quartz Substrates for Single-Walled Carbon Nanotube Growth*

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The cobalt (Co) catalyst behavior for SWNT growth on thermal oxidized silica and single-crystalline quartz by using alcohol chemical vapor deposition (CVD) was compared. The influence of the nature of substrate surface was analyzed from the size and density of both catalyst nanoparticles and SWNTs. The Co nanoparticles, on the quartz substrate after growth, had a mean diameter of about 5.9 nm which was larger than that (2.1 nm) on the silica substrate. Randomly dispersed SWNTs with a higher density were obtained on silica, while aligned SWNTs with a lower density were achieved on ST-cut quartz. The lower density of the nanoparticles on the quartz substrate can be attributed to a larger surface diffusion length of Co atoms in comparison with the silica surface.


Keywords: Carbon nanotubes; Co-catalyst; Diffusion length; Silica; ST-cut quartz

I. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) [1] have been attracting considerable interest in the fields of electronic, electrochemical and optoelectronic applications [2–6] due to their unique structure and prominent mechanical, thermal, electrical and optical properties [6, 7].

However, the present technical obstacles of fabricating practical scalable SWNT based circuits arise not only from controlling the chirality of SWNTs but also from positioning or integrating specific SWNTs on particular substrates in a designed way.

The catalyzed chemical vapor deposition (CVD) currently provides a marvelous method for the synthesis of SWNTs [8, 9]. Under particular CVD conditions the SWNTs can be grown on the surface of special interest. In CVD, the nature of the substrate surface usually has a great influence on SWNT growth. The choice of the supporting materials as well as the catalyst species is also of great importance, since the growth properties of SWNT strongly depend on the substrates, catalysts and/or the interaction between them. However, as a result of the high-temperature process during CVD growth, only a few substrates can be directly used as the supporting substrates for SWNT growth.

Typically, insulating materials, such as silica [10–12], alumina [8, 9, 13, 14], magnesia [15–17], quartz crystal [18, 19], etc., have been successfully used as catalyst supports in SWNT synthesis. To some extent, the main structure difference of the substrates above can be attributed to amorphous and crystalline configuration of the surfaces.

Many works have recently been focused on controlled SWNT growth with aligned structures for application on such crystal substrates. However, there are few researches investigating the different behaviors of the catalyst nanoparticles on different crystallinity of substrates. Accordingly, to investigate the controllability of CVD growth of SWNTs for future applications, it is interesting and necessary to compare the acting role of the support surface on the catalytic nanoparticles.

In this paper, we present the comparison of the behaviors of cobalt (Co) nanoparticles during the CVD process and the thus growth behaviors of SWNTs on amorphous silica and single-crystalline quartz. The influence of the nature of substrate surface was analyzed from the size and density of both catalyst particles and SWNTs. Studies of the growth reveal important relationships among the catalyst size and density, the SWNT growth morphology, and the substrate surface configuration.

II. EXPERIMENT

The substrate species used for SWNT growth were silica (a thermally grown SiO$_2$ layer on silicon, 100 nm thick) and single-crystal quartz (ST-cut wafer, the normal to the plane lies 42°45’ from the y axis [0 1 1 0]). Co catalyst was deposited on the cleaned substrates with a nominal thickness of 0.02 nm by resistive-heating evaporation at a pressure of 2–3×10$^{-3}$ Pa. Then the substrates were transferred into a horizontal quartz tube furnace (38 mm in inner diameter) and heated to 850°C in air. After 5-minute annealing in air, the furnace was evacuated by a rotary pump. SWNTs were grown by introducing a 50 sccm Ar/H$_2$ (H$_2$ 3% by volume) bubbling through ethanol under 300 Torr for 5 minutes. The Co deposition and CVD conditions were optimized to selectively grow SWNTs [20, 21]. Raman spectroscopy (JASCO NRS-3200), scanning electron microscopy (SEM, LEO 1530) and atomic force microscopy in the tapping mode (AFM, JPK Nanowizard) were mainly used to evaluate the catalyst and grown SWNTs. Raman spectra (not shown here) of the samples show obviously radial breathing mode (100–300 cm$^{-1}$) and G band peak structures (~1590 cm$^{-1}$) of the carbon nanotubes indicating the successfully synthesis of SWNTs.

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III. RESULTS AND DISCUSSION

Figure 1(a) and (b) show the typical low-energy (0.5 keV) SEM images of SWNTs with different growth morphologies synthesized on the silica and quartz, respectively. In general, due to the electron-beam-induced current phenomenon in the silica substrate [22], SWNTs have a bright contrast in SEM images when they contact with the surfaces. Thus, a number of nanotubes can be seen in Fig. 1 with a high bright contrast.

On the Co-catalyzed silica substrate, pristine SWNTs, ranging from isolated and randomly orientated nanotubes to interconnecting networks with a higher density, were easily obtained. Moreover, most of them were showing bent structures. By contrast, on quartz, straightly aligned SWNTs with a lower density were successfully produced. The strong preference for the SWNT alignment was in the \(x\) direction [2 1 1 0] due to anisotropic van der Waals interactions between SWNTs and the ordering arrangement of atoms (either Si or O atoms or SiO\(_4\) reactive sites) on the crystal surface [18, 19, 23]. Besides, on quartz substrates, there was a certain portion of SWNTs showing some deviation from the preferential growth direction. In our case, even under optimal growth conditions it was not possible to obtain 100\% perfect alignment of SWNTs. The obvious disruption in alignment significantly and typically occurs at the early growth stage before SWNTs find the preferable direction or when they grow to such a length that they encounter other catalyst particles, nanotubes or defects on the surface in growth area [23]. The shorter nanotubes shown in Fig. 1(b) were not aligned very well.

The experimental results indicate that the different nature of the substrate gives rise to the distinct growth morphology of the SWNTs. It is known that the growth properties of SWNTs in CVD, such as the diameter, length, chirality and density, show a strong relationship with the size, life time and distribution of catalyst nanoparticles [24]. Therefore, the discrepancy of the SWNT growth morphology on both kinds of the substrates to some extent reflects the different performance of the Co catalyst on such substrates.

Figure 2 shows the AFM images of the distinct morphologies of the Co catalyst and the nanotubes synthesized on silica [Fig. 2(a)] and quartz [Fig. 2(b)], corresponding to the same sample used in Fig. 1. It can be seen again that SWNTs on silica were unevenly dispersed, while SWNTs on quartz were easily aligned along the crystalline direction. The typical diameters of the SWNTs were usually around 1-2 nm evaluated by AFM. The insets in each image show the height profiles of representative SWNTs of 1.5 nm on silica and 1.2 nm on quartz.
It is found that coarsening of Co nanoparticles supported on quartz, which could decrease the probability of the bundles. Thus, the probability of nanotubes binding together via van der Waals force is higher on silica.

The catalyst nanoparticles are also clearly visible in the AFM images of the samples after CVD process shown in Fig. 2. The nanoparticle size was analyzed by the height of the nanoparticles in the AFM images. By comparing the histograms with their Gaussian fitting curves of Co nanoparticle size obtained from Figs. 2(a) and 2(b), respectively, we found that the mean diameter of the nanoparticles on silica was about 2.1 $\pm$ 0.1 nm showing a smaller size than that on crystal quartz (5.9$\pm$0.1 nm) [see Fig. 4, upper part], while the density of Co nanoparticles was 172 $\mu$m$^{-2}$ on silica which was higher than that (48 $\mu$m$^{-2}$) on quartz crystal. The nanoparticle size as well as the full width at half maximum (FWHM) of the size distribution was increased from silica to crystal quartz while the density decreased. Although the density of nanotubes on silica was higher than quartz shown in SEM images (Fig. 1), the number of nanotubes was much smaller than that of nanoparticles in a given area on both of the substrates by comparing them in the AFM images (Fig. 2), i.e., the yield of nanotubes is low.

Since catalyst size is very critical in CVD because it is closely related to nanotube diameter, and the diameter of the nanotubes is usually governed by the size of the catalyst particles [24], we examined the Co nanoparticle formation process by AFM after short term annealing or CVD growth. Annealing in air has the advantage of removing the organic contaminant from the supporting substrates and preventing the Co atoms agglomerating to large particles compared with vacuum or inert gas ambience condition where larger particles quickly formed [26]. In our experiment the catalyst nanoparticles were invisible just after Co deposition. Moreover, after a short time of annealing in air (5 minutes), AFM images showed that the sample surface morphologies were also indistinguishable comparing with the catalyst supported substrates before annealing, or bare silica or quartz crystal surface.

However, after 5-minute CVD growth, the Co nanoparticles were obviously visible on both of the substrates [see AFM images in Figs. 2(a) and 2(b), corresponding to silica and quartz, respectively]. The CVD growth process (bubbling method) resulted in the formation of Co nanoparticles along with many nanotubes. Normally, Ar/H$_2$ gas treatment plays an important role to the agglomeration of the catalyst nanoparticles during the heat process [26]. Therefore, the Ar/H$_2$ gas from our bubbling gas should contribute to the formation of the Co particles with certain sizes and density distributions on both substrates.

For comparison with CVD growth, after annealing the sample in air, instead of 5-minute CVD growth, we also performed Ar/H$_2$ treatment of the sample in the furnace for 5 minutes. The annealing time, pressure and temperature were the same as the bubbling CVD growth process. It is found that coarsening of Co nanoparticles supported on both of the substrates took place immediately after annealing in Ar/H$_2$ gas ambience for 5 minutes (see AFM images in Fig. 3). Thus, annealing in Ar/H$_2$ caused rapid formation of the Co nanoparticles on both substrates.

The histograms and corresponding Gaussian fitting curves of the Co nanoparticle sizes for both of the substrates are shown in the insets in Fig. 3. The value of the Co particle size on silica was found to have a mean size of 1.6 $\pm$ 0.1 nm with a higher density compared to 4.1 $\pm$ 0.1 nm on quartz. The density of Co particles on silica was about 120 $\mu$m$^{-2}$ which was approximately 4 times as large as that on ST-cut quartz (31 $\mu$m$^{-2}$). This relative large difference of the size and density of Co nanoparticles between silica and quartz before CVD is well consistent with the results of Fig. 2 which was obtained after CVD. For both cases, i.e., after CVD and treated in Ar/H$_2$, under the same amount of Co deposition, the smaller size should account for the higher density of the nanoparticles on silica. These experimen-

![Fig. 3: AFM images of Co catalyst nanoparticles on silica (a) and single-crystalline quartz (b) after annealing in Ar/H$_2$ at 850$^\circ$C and 300 Torr for 5 minutes. The insets in each image show the corresponding nanoparticle size distribution. The black arrow shown in (b) indicates a crack where several nanoparticles accumulated.](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))
samples treated in Ar/H\textsubscript{2} gas corresponding to Figs. 2 and 3, respectively. Overall, the diameter of the Co nanoparticles on silica was narrower and presented a relatively uniform size distribution character on silica than that on quartz. Meanwhile, after CVD, the catalyst sizes on both of substrates were larger than that before CVD. The size of catalyst nanoparticles can be increased by the continued agglomeration of small catalyst particles during the CVD process or the enhanced diffusion along the growing nanotube surface [29]. Simultaneously, the dissolution of carbon atoms in the particles and the formation of amorphous carbon or a graphitic carbon shell from excessive carbon species covering on the Co nanoparticle surface could also give rise to the increase of nanoparticle size [24, 27, 30].

It is noted that, after CVD, because of the roughness of our silica sample containing a lot of particles and bent or suspended SWNTs (some SWNTs were vertically grown), bundles and/or nanotube networks [see Fig. 1(a)] which constantly affect the stability of the AFM tips, it was not possible to resolve the SWNTs unambiguously and confirm a clear particle-tube relationship of the silica sample by AFM. However, based on the fact that, the catalytic nanoparticle size gives the upper bound for the nanotube surface [29, 27, 30], we could expect here that, based on diameter \([24, 27, 30]\). Besides, the diffusion length of Co catalyst would be influenced by the extra potential barrier along edges caused by the crystal atomic row direction, steps or terrace on quartz. Consequently, the diffusion process took place more anisotropically on quartz than on silica. Additionally, the defects on quartz, like cracks, holes, etc., would also affect the diffusion process. For instance, nanoparticles were easily accumulated and pinned at the cracks or step edges [see Fig. 3(b), a crack indicated by the black arrow]. This might be the explanation for the relative non-uniform size and density distribution of the Co particles on quartz, thus inhomogeneous morphology of grown SWNTs.
IV. CONCLUSIONS

In conclusion, we compared Co catalyst behavior for SWNT growth on amorphous silica and ST-cut quartz in alcohol CVD. The performance of metal catalysts for SWNT growth largely depended on the crystallinity of the support materials. The mean Co nanoparticle size on silica was smaller and the density of the particle was larger than that on quartz crystal. We proposed different diffusion lengths for Co on both substrates. A higher Co particle density with a smaller size produced a higher density of SWNTs after CVD on the amorphous silica than on quartz crystal surface. The effect of surface topography was examined on the aligned SWNTs on crystal quartz: SWNTs were sometimes bent away from the preferential growth direction when they encountered defects, cracks and catalyst particles.

We believe that the catalyst-substrate interactions should be taken into account in attempting to control nanotube growth, and the appropriate choice of the supporting substrates is vital for future SWNT applications of particular interest.

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