Single-walled carbon nanotube growth at low temperature by alcohol gas source method using Co catalyst: enhancement effects of Al₂O₃ buffer layer on carbon nanotube yield

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Using an alcohol gas source chemical vapor deposition method, we attempted to grow single-walled carbon nanotube (SWCNT) growth using Co catalysts on Al₂O₃ buffer layers. Reducing the growth temperature decreased the optimal ethanol pressure to obtain the highest SWCNT yield. By optimizing the ethanol pressure, we succeeded in growing SWCNTs at 400°C. Irrespective of the growth temperature, SWCNT yields from Co catalysts on Al₂O₃ buffer layers were higher than those on SiO₂/Si substrates, but the enhancing effects of Al₂O₃ buffer layers on SWCNT yield were reduced below 500°C. Taking into account both in-plane X-ray diffraction results and decrease of catalyst aggregation in the low temperature region, we concluded that the density of Co particles suitable for SWCNT growth increased on SiO₂ surface at low temperature, resulting in the reduction of difference in SWCNT yield at low temperature between Al₂O₃ buffer layers and SiO₂/Si substrates.

Key words: single-walled carbon nanotube, CVD, catalyst, Co, low-temperature growth

1. INTRODUCTION

Since a discovery by Iijima,¹ single-walled carbon nanotubes (SWCNTs) have attracted much attention due to their remarkable properties such as ballistic transport,² high mobility,³ and high current carrying density.⁴ Therefore, they offer huge potential for electronics applications such as field effect transistors (FETs),^{5,6} LSI interconnects,^{7,8} and energy conversion devices.^{9,10} To realize SWCNT devices compatible with LSI manufacturing processes, SWCNT synthesis below 400°C is essential to avoid degradation of interlayer dielectric films during SWCNT growth. So far, several groups have reported SWCNT growth at low temperatures.¹²⁻¹⁴ However, only a few studies have been reported for SWCNT growth below 500°C using Co catalysts, although Co has been widely used in catalysts for SWCNT growth by alcohol catalytic CVD (ACCVD).¹⁵⁻²⁰ In particular, low-temperature growth of SWCNTs using Co catalysts on Al₂O₃ buffer layers has scarcely been performed, even though Al₂O₃ buffer layers are recognized to enhance the SWCNT yield in CVD and metal catalysts are frequently supported on Al₂O₃ buffer layers.^{13, 14, 21-24}

In general, it is recognized that metal particles that are a few nanometers (typically 1-3 nm) in diameter act as effective catalysts for SWCNT growth.²⁵ Compared to SiO₂/Si substrates, aggregation of catalyst particles is suppressed on Al₂O₃ buffer layers,²⁶⁻²⁸ and the number of catalyst particles whose sizes are suitable for SWCNT growth increases. However, surface migration distance of catalyst metals should decrease with the reduction of growth temperature, thus, there is a possibility that

Al₂O₃ buffer layers do not enhance SWCNT yield in low-temperature growth, although the increase of SWCNT yield at low temperature is a significant issue for realization of SWCNTs electronic devices.

In this study, we report SWCNT growth at low temperature by an alcohol gas source method using Co catalysts on Al₂O₃ buffer layers. We compared SWCNT yields on Al₂O₃ buffer layers with those on SiO₂/Si substrates and investigated temperature dependence of the enhancement effect of an Al₂O₃ buffer layer on SWCNT yield. Additionally, we characterized Al₂O₃ buffer layers by in-plane X-ray diffraction (XRD), and showed that crystallinity of Al₂O₃ buffer layers did not change remarkably between 400 and 700°C. Based on these results, we discussed the effect of an Al₂O₃ buffer layer on SWCNT growth at low temperature.

2. EXPERIMENTAL METHOD

Co catalysts were deposited on Al₂O₃/SiO₂/Si substrates using electron beam deposition in an ultrahigh vacuum (UHV) chamber. Al₂O₃ buffer layers were formed by depositing Al on SiO₂/Si substrates by rf-sputtering, followed by exposure to air to allow oxidation. The Co and Al thicknesses were 0.2 and 20 nm, respectively; these were monitored with a quartz crystal oscillator. SWCNT growth was performed in a UHV chamber equipped with a stainless steel nozzle for introducing ethanol gas, that is, “gas source type ACCVD.” Details of the setup are given in our previous studies.²⁹⁻³¹ The base pressure of this system was below 1×10^{-6} Pa. The ethanol pressure was controlled with a variable leak valve and monitored by a vacuum ion

gauge, which allowed a minute gas supply and precise control of the ethanol pressure to achieve optimum growth conditions. For SWCNT growth, ethanol gas was supplied directly to the substrate surface for 1 h through the nozzle. The substrate temperature was monitored with a pyrometer (KTL-Pro, LEC Ltd. Tokyo, Japan). The morphology of the grown SWCNTs was characterized using field-emission scanning electron microscopy (FESEM) (JSM-6700F, JEOL, Tokyo, Japan). The accelerating voltage used for SEM observation was 5 kV. Raman spectra of the samples were obtained using a Raman system (RAMANforce, Nanophoton, Osaka, Japan) to evaluate the diameter and chirality of the as-grown SWCNTs. The excitation wavelength used for Raman measurements was 671 nm. Al_2O_3 buffer layers were characterized by in-plane XRD, which was performed at beamline BL6C of the Photon Factory at the High Energy Accelerator Research Organization (KEK) using synchrotron X-ray radiation ($\lambda = 0.12011$ nm) and energy dispersive X-ray spectrometry (EDX) (EMAX, Horiba, Kyoto, Japan).

3. RESULTS AND DISCUSSION

Figure 1(a) and (b) shows SEM images for samples grown at 500°C and 400°C, respectively. The ethanol pressures used to grow these samples were 1×10^{-3} and 1×10^{-4} Pa, respectively; these were optimized for each growth temperature to obtain the highest product yield. Fibrous products were observed on both substrate surfaces, which exhibited web-like structures. Longer fibers were formed at 500°C than at 400°C.

Fig. 1. SEM images of SWCNTs grown with Co catalysts on $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates at (a) 500°C at an ethanol pressure of 1×10^{-3} Pa and (b) 400°C at 1×10^{-4} Pa.

Figure 2(a) and (b) shows Raman spectra of these samples, measured using an excitation wavelength of 671 nm. These spectra showed both G bands at 1594 cm^{-1} and radial breathing mode (RBM) peaks, indicating that SWCNTs were grown under these conditions. In addition, strong RBM peaks were observed at 167 and 176 cm^{-1} for the samples grown at 500°C and 400°C, respectively, that is, the fibrous products shown in Fig. 1 were confirmed as SWCNTs. Considering the relationship between the SWCNT diameter, d , and the wavenumber of its RBM peak, ω , d [nm] = $248/\omega[\text{cm}^{-1}]$,³² some of grown SWCNTs have diameters between 1.40 and 1.49 nm. The G/D ratio of SWCNTs grown at 500°C was 11.2, while that for those grown at 400°C was about 3.6. This indicates that the crystallinity of SWCNTs deteriorated as the growth temperature was reduced.

Fig. 2. (a) Raman spectra in the RBM region and (b) Raman spectra in the high energy region for SWCNTs grown with Co catalysts on $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates at 400°C and 500°C at the optimal ethanol pressures.

Fig. 3. (a) Relationship between the growth temperature and the G/Si intensity ratio for each ethanol pressure for SWCNT growth with Co catalysts on $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates. (b) The relationship between the G/Si intensity ratio and the growth temperature for SWCNTs grown with Co catalysts on $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ and SiO_2/Si substrates at the optimal ethanol pressures.

Considering the morphology of the grown SWCNTs, the intensity ratios of the G bands relative to the Si peak³³ at ~ 520 cm^{-1} (G/Si ratio) roughly correspond to the SWCNT yields. To evaluate the dependence of the SWCNT yield on the growth conditions, we performed Raman measurements of the samples grown under various conditions using a laser with an excitation wavelength of 671 nm. Fig. 3(a) shows the growth temperature dependence of the G/Si ratio, which is shown for each ethanol pressure. At a growth temperature of 700°C, the SWCNT yield (G/Si ratio) reached a maximum at ethanol pressures of 1×10^{-1} and 1×10^{-2} Pa. However, at a growth temperature of 500°C, it peaked at an ethanol pressure of 1×10^{-3} Pa. At 400°C, the SWCNT yield reached a maximum at ethanol pressures of 1×10^{-3} and 1×10^{-4} Pa. A decrease in the optimal ethanol pressure with a reduction in the SWCNT growth temperature was reported for various metal catalysts.^{14,29,34} This could be due to a reduction in the dissociation rate of carbon feedstock molecules on catalyst particles with a decrease in growth temperature, confirming that optimization of the feedstock gas flow is important for low temperature synthesis of SWCNTs. Fig. 3(a) shows that the SWCNT yield reached a maximum at 700°C under the optimal ethanol pressure,

indicating that 700°C was the optimal growth temperature for obtaining the highest yield. Below 500°C, the SWCNT yield was drastically reduced, which is probably due to reduction of catalyst activity at low temperature.

We also investigated the effect of the Al₂O₃ buffer layers on the catalyst activity. Fig. 3(b) shows the G/Si ratios for SWCNTs grown with Co catalysts on Al₂O₃ buffer layers and SiO₂/Si substrates at the optimal ethanol pressures. The data for SWCNTs on SiO₂/Si substrates were taken from our previous study.¹⁹ At growth temperatures between 600°C and 700°C, the G/Si ratios for SWCNTs on Al₂O₃ buffer layers were much higher than those on SiO₂/Si substrates. However, the difference in the G/Si ratios was small, when the growth temperature was below 500°C and above 800°C. Considering that transmittance of 600-700 nm-light for the 20 nm-Al₂O₃ buffer layers were 98-99%,³⁶ the reduction of Si peaks due to Al₂O₃ buffer layers should be negligible in Raman spectra. Therefore, this result indicates that SWCNT yields on Al₂O₃ buffer layers were higher than those on SiO₂/Si substrates, but the enhancement effect of Al₂O₃ buffer layers on SWCNT growth was reduced below 500°C and above 800°C.

Fig. 4. In-plane XRD pattern for an Al₂O₃ buffer layer and those after annealing at 400, 500, 600 and 700°C in a vacuum.

To investigate the reduction in the enhancement effect below 500°C, we performed in-plane XRD measurements on Al₂O₃ buffer layers. Fig. 4 shows an in-plane XRD pattern of an Al₂O₃ buffer layer and those annealed between 400 and 700°C in a vacuum. After annealing, only one broad peak was seen at around 2.5 nm⁻¹, which might be derived from γ -AlO(OH),³⁶ and no distinct peaks corresponding to α - or γ -Al₂O₃³⁷ were observed. This indicates that the Al₂O₃ buffer layer used for SWCNT growth at 400°C was amorphous. Amama et al. reported the influence of the alumina type on the activity of Fe catalyst particles for SWCNT growth at 750°C and showed that amorphous Al₂O₃ was more effective, because aggregation of Fe catalysts was suppressed on amorphous Al₂O₃ buffer layers.³⁸ In our experiment, the enhancement effect of Al₂O₃ buffer layer on SWCNT yield was small below 500°C, even though the Al₂O₃ buffer layer was amorphous. It is generally recognized that Al₂O₃ buffer layers suppress aggregation of catalyst particles.²⁶⁻²⁸ However, in the low temperature region, aggregation of Co catalysts should be reduced even on SiO₂/Si substrates. Consequently, the enhancement effect of the Al₂O₃ buffer layer on the SWCNT yield was remarkably

reduced below 500°C. At a growth temperature of 800°C, the G/Si ratios for the Al₂O₃ buffer layer and the SiO₂/Si substrate were also similar. This might be due to the inward diffusion of the Co catalyst on the Al₂O₃ buffer layer at high temperatures,³⁹ which reduced the amount of Co catalyst on the substrate surface.

We also report high-density growth of SWCNTs at low temperatures. At growth temperatures below 500°C, areas of high-density SWCNT growth were observed on some portions of the Al₂O₃ buffer layer, as shown in Fig. 5(a) and (b), where SWCNTs were grown vertically with a high density. These high-density growth was observed for samples grown under the optimal ethanol pressure, when the growth temperature was 400 and 500°C. The size of each growth area was about several μ m, and their density was about 100/mm², when the growth temperature was 500°C. Although the density decreased drastically at 400°C, these high-density growth was still observed. Considering the fact that such a high-density growth was not observed with Co catalysts on SiO₂/Si substrates, local variations of surface structures in the Al₂O₃ buffer layer might have affected the activity of the Co catalysts, although the mechanism of the high-density growth is currently unclear. By clarifying this mechanism, high-density growth of SWCNTs could be realized at low temperatures.

Fig. 5. Area of high-density growth of SWCNTs grown with Co catalysts on Al₂O₃/SiO₂/Si substrates at (a) 400°C under an ethanol pressure of 1×10^{-4} Pa and (b) 500°C under an ethanol pressure of 1×10^{-3} Pa.

4. CONCLUSION

We achieved SWCNT growth by an alcohol gas source method using Co catalysts on Al₂O₃ buffer layers and obtained web-like SWCNTs even at 400°C. However, the enhancement of the SWCNT yield by the Al₂O₃ buffer layers was reduced below 500°C. In-plane XRD showed that the Al₂O₃ buffer layer was amorphous at 400°C. This indicates that aggregation of Co catalysts was decreased on SiO₂/Si substrates below 500°C, resulting in reduced enhancement of the SWCNT yield on the Al₂O₃ buffer layers.

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