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Single-walled carbon nanotube synthesis on SiO_2/Si substrates at very low pressures by the alcohol gas source method using a Pt catalyst

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ABSTRACT

A platinum catalyst was used for single-walled carbon nanotube (SWCNT) growth on SiO_2/Si substrates using an alcohol gas source method, a type of cold-wall chemical vapor deposition. Compared to Co, a conventional transition metal catalyst, the optimal ethanol pressure was considerably reduced in the growth at 700 °C, and SWCNTs could be grown even at an ambient ethanol pressure of 1×10^{-5} Pa. Raman spectroscopy measurements showed that the G/Si ratios of SWCNTs grown at 700 °C with the Pt catalyst under an ethanol pressure between 1×10^{-4} and 1×10^{-1} Pa was larger than that grown with Co catalyst under optimal conditions (700 °C, 1×10^{-1} Pa), indicating that the Pt catalyst is suitable for SWCNT growth under a low ethanol pressure. In addition, the diameter distributions of SWCNTs grown with the Pt catalyst were narrower than those grown with the Co catalyst. Taking into account the results by transmission electron microscopy observation, the diameter reduction was caused by the smaller migration distance of Pt on the substrate. Based on these results, we discuss the growth mechanism of SWCNTs from the Pt catalyst.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted great interest for nanometer-scale electronic devices [1]. At present, catalytic chemical vapor deposition (CVD) is widely used for SWCNT growth because of its ability to control the location, direction and diameter of the SWCNTs [2]. To realize nanotube-based devices compatible with LSI manufacturing processes, SWCNT growth by CVD under low pressure is significant since several processes generally have to be performed in a high vacuum environment for device fabrication, such as ion etching and electrode deposition. In addition, SWCNT growth in a high vacuum is useful for in situ observations during growth, using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

SWCNT growth using CVD under low pressure has been carried out by several groups thus far. For in situ observations, Homma's group carried out carbon nanotube (CNT) growth by low-pressure alcohol CVD at 1–20 Pa [3,4]. Kasumov et al. reported that improvements in the quality of SWCNTs could be attained by reducing the acetylene pressure to 50 Pa in CVD [5]. Shiokawa et al. succeeded in growing SWCNTs by cold-wall CVD using ethanol at 0.05 Pa in an ultra-high vacuum (UHV) chamber [6]. Our group achieved SWCNT growth at an ambient ethanol pressure of 1×10^{-4} Pa with a Co catalyst, adopting an alcohol gas source method in a UHV chamber, a type of cold-wall CVD [7,8]. However, the SWCNT yield decreased significantly in this case, because the growth temperature had to be reduced to 400 °C to obtain SWCNTs under the low ethanol pressure. More recently, we attempted to grow SWCNTs using a Pt catalyst, which has been widely used in practical applications, such as in exhaust systems and fuel cells [9]. Using the alcohol gas source method with a Pt catalyst, we showed that SWCNTs could be grown even at an ambient ethanol pressure of 1×10^{-4} Pa [10]. However, the growth conditions to obtain the higher yield in SWCNT growth with the Pt catalyst were not sufficiently investigated and the properties of the grown SWCNTs have not been clarified.

In this study, we carried out SWCNT growth on SiO_2/Si substrates at 700 °C using a Pt catalyst under various catalyst thicknesses and ethanol pressures. Our results showed that compared to SWCNT growth with Co catalyst, the optimal growth pressure for the Pt catalyst was considerably reduced, while the yield was higher even for an ethanol pressure between 1×10^{-5} and 1×10^{-1} Pa. We also investigated the distribution of SWCNT diameters by Raman measurements and found that the diameter distribution of the SWCNTs was fairly narrower than those grown with the Co catalyst. The usefulness of the Pt catalyst under a low ethanol pressure was demonstrated.

2. Experimental details

SiO_2(100 nm)/Si substrates were used for the SWCNT growth in this work. After deposition of a Pt catalyst by a pulsed arc plasma gun in a UHV chamber (the base pressure was 2×10^{-7} Pa), the substrate temperature was increased to 700 °C under H_2 gas flow at a

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pressure of 1×10^{-3} Pa to prevent oxidation of the catalyst. The Pt thickness was monitored with a quartz crystal oscillator and the nominal thickness was varied between 0.05 and 0.5 nm. The lattice constant of bulk fcc Pt is 0.392 nm, meaning that the deposited Pt had a particle-like structure on the substrates. CNTs were then grown at 700 °C with the alcohol gas source method in a UHV chamber, a type of cold-wall CVD. Ethanol gas was then supplied to the substrate surface for 1 h through a stainless steel nozzle to grow the SWCNTs. In this experiment, the growth temperature was fixed at 700 °C, which was the optimal temperature to obtain the highest yield in the SWCNT growth with the Co catalyst. A variable leak valve controlled the supply of ethanol gas while the ambient pressure was monitored. In this experiment, the ambient pressure was varied between 1×10^{-5} and 1×10^{-1} Pa. For comparison, we also carried out CNT growth using a Co catalyst.

The resulting SWCNTs were characterized by SEM (Hitach; S-3400), TEM (JEOL JEM-3200) and Raman spectroscopy. The excitation wavelengths used for the Raman measurements were 532, 633 and 785 nm. The catalyst size was also investigated by TEM observations, carried out with a 300 kV acceleration voltage. For the TEM observations of catalysts, we used TEM grids composed of SiO_2 membranes 20 nm in thickness (Alliance Biosystems).

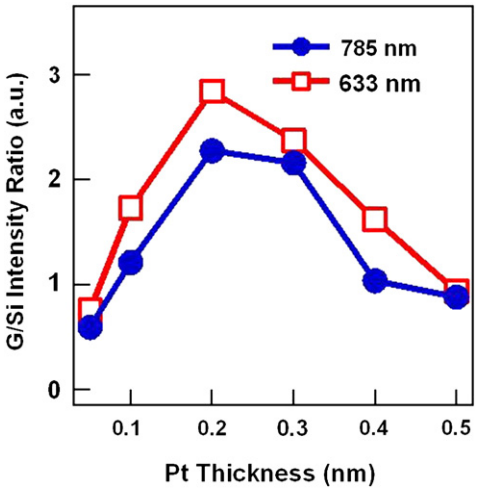

Fig. 1. Ratios of G band peak to Si peak (520 cm^{-1}) (G/Si intensity ratio) in the Raman spectra of SWCNTs grown at 700 °C with the Pt catalyst under an ethanol pressure of 1×10^{-4} Pa as a function of the Pt catalyst thickness. The G/Si intensity ratio in the Raman spectra measured with two different excitation wavelengths of 633 and 785 nm are both plotted.

3. Results and discussion

First, we carried out SWCNT growth with various Pt thicknesses to estimate the optimal catalyst thickness to grow the CNTs. In these series, the growth temperature was set to 700 °C and the ethanol pressure was 1×10^{-4} Pa, since the lower ethanol pressure was suitable for CNT growth with the Pt catalyst [10]. The nominal thickness of the Pt catalyst was varied between 0.05 and 0.5 nm. For the grown SWCNTs, we carried out Raman measurements using two different excitation wavelengths of 633 and 785 nm. Several peaks were observed in the Raman spectra in the radial-breathing mode (RBM) region, confirming that the SWCNTs grew from the Pt catalyst. We also evaluated the G band intensities relative to the Si peak (520 cm^{-1}), the G/Si intensity ratio, to estimate the SWCNT yield. Fig. 1 shows the relationship between the G/Si intensity ratio and the Pt thickness for each excitation wavelength. For both excitation wavelengths, it is clearly seen that the G/Si intensity ratio reached a maximum at 0.2 nm, indicating that the optimal thickness was 0.2 nm to obtain the highest yield with the Pt catalyst.

Using a 0.2 nm thick Pt catalyst, we carried out SWCNT growth under various ethanol pressures. Fig. 2(a), (b) and (c) shows SEM images of the sample surface after the growth at 700 °C with the Pt catalyst under ethanol pressures of 1×10^{-1}, 1×10^{-3}, and 1×10^{-5} Pa, respectively. For reference, SWCNTs grown at 700 °C under 1×10^{-1} Pa using the Co catalyst also of 0.1 nm in thickness, which was the optimal growth pressure to obtain the highest yield in the alcohol gas source method, are shown in Fig. 2(d). At 1×10^{-1} Pa, web-like SWCNTs were formed over the substrate surface using both catalysts and their yields appeared to be similar to each other (Fig. 2(a), (d)). When the ethanol pressure was 1×10^{-3} Pa, the density of SWCNTs grown with the Pt catalyst increased, confirming that the lower ethanol pressure was suitable for SWCNT growth with the Pt catalyst. On the other hand, at 1×10^{-5} Pa, the yield decreased drastically and it was difficult to observe CNTs because of the resolution limitation of our SEM equipment.

The relationship between the G/Si intensity ratio in the Raman spectra and the ethanol pressure is shown in Fig. 2(e) for the Pt and Co catalysts, where the nominal catalyst thickness was also set to be optimal at 0.2 and 0.1 nm for Pt and Co, respectively. For the Co catalyst, the G/Si intensity ratios of SWCNTs grown at both 400 and 700 °C are shown, since the lower growth temperature was suitable for SWCNT growth under the lower ethanol pressure [7]. It is clearly seen that for SWCNT growth with the Pt catalyst, the G/Si intensity ratio reached its maximum at 1×10^{-3} Pa. In contrast, in the growth with the Co catalyst at 700 °C, the G/Si intensity ratio decreased as the ethanol pressure was reduced, and the ratio reached its maximum at 1×10^{-4} Pa at 400 °C, but it was smaller than that for the SWCNTs grown with the Pt catalyst at 700 °C. These results clearly indicate that the optimal growth pressure was considerably lower for the SWCNT growth with the Pt catalyst. It should be noted that the G/Si intensity ratio of the SWCNTs grown with the Pt catalyst in the region between 1×10^{-4} and 1×10^{-1} Pa was larger than that for the SWCNTs grown with the Co catalyst under the optimal condition (1×10^{-1} Pa, 700 °C). Taking into account the SEM results, these results indicate that the yield with the Pt catalyst was superior to that with the Co catalyst in the SWCNT growth under a low ethanol pressure.

To compare the structural quality and properties of the SWCNTs grown using the Pt and Co catalysts, Raman spectra for the SWCNTs grown at 700 °C under optimal ethanol pressures for each catalyst (Pt: 1×10^{-3} Pa, Co: 1×10^{-1} Pa) are shown in Fig. 3(a) and (b). These spectra were measured with an excitation wavelength of 633 nm. In the high frequency regime, strong G bands and weak D bands are observed for both catalysts (Fig. 3(b)), indicating that the crystalline quality of the SWCNTs was fairly good. The G/D ratios of the SWCNTs grown with Pt and Co were about 7.5 and 12.6, respectively. The smaller G/D ratio for the SWCNTs with the Pt catalyst might be due to the lower ethanol pressure during the growth. In the RBM region, several peaks were observed for both catalysts, confirming that the SWCNTs were grown by the alcohol gas source method with the Pt catalyst. It should be noted that there was a marked difference in the RBM region between the Pt and Co catalysts. In the case of the Pt catalyst, the Raman shifts of the grown SWCNTs were distributed between 180 and 360 cm^{-1}, while those grown with the Co catalyst were between 140 and 290 cm^{-1}. Considering that the Raman shift of an RBM peak is roughly inversely proportional to the SWCNT diameter [11], this suggests that smaller-diameter SWCNTs were more likely to grow with the Pt catalyst.

To compare the diameter distribution of the grown SWCNTs using the Pt and Co catalysts in more detail, Raman measurements were carried out using various excitation wavelengths, since the intensities of the RBM peaks are strongly enhanced under resonance conditions. Fig. 3(c), (d) and (e) shows the diameter distributions of SWCNTs grown with the Pt and Co catalysts under the optimal ethanol pressures (Pt: 1×10^{-3} Pa, Co: 1×10^{-1} Pa). The diameters were