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Synthesis of carbon nanotubes by laser-assisted alcohol chemical vapor deposition

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ABSTRACT

A laser-assisted alcohol chemical vapor deposition (CVD) process was carried out on a quartz substrate without a thick absorption layer, as a result of which, the substrate retained its transparency. The thickness of the carbon nanotube (CNT) film grown with 120 s of laser irradiation was 16.6 μm, which was three orders of magnitude thicker than the CNT film grown without laser irradiation. The area of growth enhancement was nearly the same size as the laser spot, which implies that this method can be used for position-controlled CNT growth. In addition, the laser-assisted method can be used to decrease the process temperature. Raman spectra also showed the enhancement of CNT growth from the higher signal intensity of the G and D bands from the laser-irradiated sample.

1. Introduction

Carbon nanotubes (CNTs) are attracting significant research attention because of their potential applications in micro- and nanodevices owing to their unique properties [1]. For the controlled synthesis of CNTs, various techniques have been developed, such as arc discharge, laser ablation, and chemical vapor deposition (CVD). It is necessary for the synthesized CNTs to satisfy the requirements of the desired application; for example, position-controlled, uniform, dense, or aligned nanotubes may be required for a particular application. Therefore, many investigations have been carried out to achieve these properties using high-throughput CVD methods to grow CNTs on solid substrates. In the CVD process, there are many parameters that can be used to control the growth of CNTs, such as source gases, growth pressure, catalyst species, and the growth temperature. By controlling these parameters, dense and uniform vertically aligned CNTs have been obtained by a CVD process [2–6]. In addition, laser-assisted CVD has recently been shown to be an effective technique for the position-controlled growth of CNTs, with no need for pre-patterning or annealing of the catalyst layer [7–9]. In the laser-assisted CVD growth of CNTs, a focused laser beam directly irradiates the substrate, enabling the growth of CNTs with the intrinsic benefits of localized, fast, and single-step processing. In these laser-assisted CVD processes, the absorption layer needs to be non-transparent in order to efficiently heat the catalyst using the laser. However, this method cannot be applied to a transparent substrate. In this study, we carried out a laser-assisted alcohol CVD process on a substrate without a thick absorption layer, as a result of which, the substrate retained its transparency.

2. Experiments

Laser-assisted alcohol CVD growth of CNTs was carried out in a cylindrical Pyrex chamber. A substrate holder (carbon resistive heater) was located at the center of the chamber. The laser was incident in the direction normal to the substrate surface. The continuous wave (CW) laser used for the irradiation had a wavelength and maximum power of 532 nm and 0.6 W, respectively. The spot size of the laser was 1 mm. Transparent quartz substrates were used for the growth of CNTs. Si substrates were also used as a reference. A single catalyst layer of 6-nm-thick Fe was deposited using DC sputtering at the rate of 0.005 nm/s. The Fe target is cleaned by HF solution before the sputtering. The DC sputtering was conducted under the 10 Pa Ar gas and 1 kV bias voltage. The transparency of the quartz substrate was maintained after the deposition of the catalyst Fe. Subsequently, the substrates were loaded into the growth chamber. The base pressure of the growth chamber before the growth of the CNTs was about 8 kPa. Ethanol gas was provided by resistive heating of liquid ethanol in the growth chamber. The CNTs were grown at various substrate

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temperatures ranging from 450 to 700 °C, with and without laser irradiation under an ethanol gas pressure of 30 kPa. In all samples, the CNTs were grown for 120 s. The thicknesses of the CNT films were measured by laser microscopy (Keyence VK-9700). The Raman spectra were measured using the 532-nm second harmonic line of a YAG laser excited by a semiconductor laser diode, monochromator, and electrically cooled Si detector at room temperature.

3. Results and discussion

Fig. 1 shows images of the sample surface after the deposition of Fe catalyst on (a) a Si substrate, and (b) a quartz substrate. The transparency of the quartz substrate was maintained as shown in (b). We used these substrates for the growth of all CNTs.

Fig. 2 shows images of the sample surfaces after the growth of CNTs on (a) a Si substrate, and (b) a quartz substrate at 600 °C, without laser irradiation. Although an 8.2-μm-thick CNT film was grown on the Si substrate, a very thin CNT film (38 nm) was grown on the quartz substrate. It is considered that the condition of the Fe catalyst on the Si substrate was different from that on the quartz substrate. Fig. 3(a) shows an image of the sample surface after the growth of CNTs on the quartz substrate at 600 °C with laser irradiation. The growth of CNTs at the laser spot was noticeably enhanced. All samples were carried out transmission electron microscope (TEM) measurement and confirmed the growth of CNTs whose diameter was ranging from 0.8 nm to 2 nm. Fig. 3(b) shows a 3D laser microscope image of the sample surface of a CNT film grown by laser irradiation. The scratched line was formed for the measurement of CNT thickness. Fig. 3(c), (d), and (e) shows the cross sections of the laser microscope image outside the laser spot, around the laser spot, and at the center of the laser spot, respectively. The thickness of the CNTs at the center of the laser spot was 16.6 μm, which is three orders of magnitude thicker than CNTs grown without laser irradiation. The diameter of the section of CNT film enhanced by laser irradiation was almost the same as the laser spot size. Therefore, laser irradiation is useful for the position-controlled growth of CNTs without patterning, not only on non-transparent substrates but also on transparent substrates. In addition, the laser-assisted method can be used to decrease the process temperature, which is useful for the growth of CNTs on substrates with low softening points.

The effect of laser irradiation was also observed for CNT growth on the Si substrate. However, the growth mechanism might be different between the Si and quartz substrates. The optical energy of the laser was used for heating the substrate because Si absorbs 532 nm light. However, quartz does not absorb light at this wavelength, and consequently, the optical energy of the laser appears to affect the growth of CNTs directly.

Fig. 4 shows the Raman spectra for (a) the sample as shown in Fig. 2(b) without laser irradiation and (b) the sample as shown in Fig. 3 with laser irradiation. The G and D band signals from the Raman spectra were observed for both samples with and without laser irradiation. These signals were not observed from the substrate before the growth of CNTs; therefore, they were related to the CNTs. The signal at around 500 cm^{-1} is related to the SiO_2

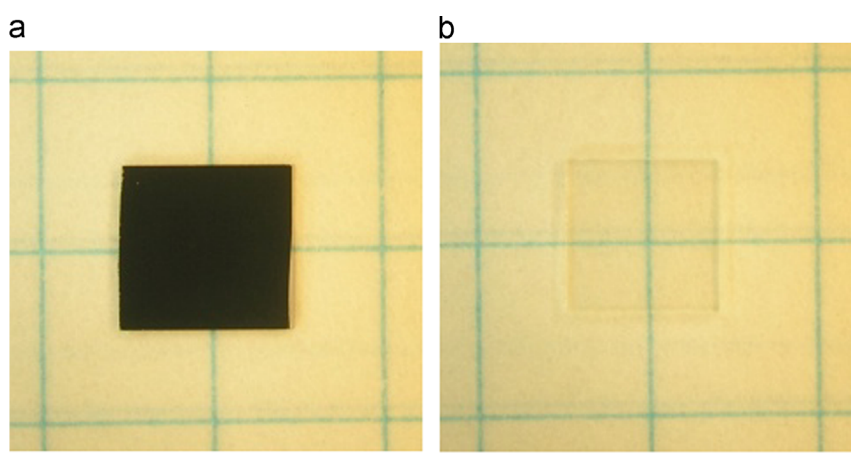

Fig. 1. Photographs of sample surfaces after deposition of Fe catalyst on (a) a Si substrate, and (b) a quartz substrate.

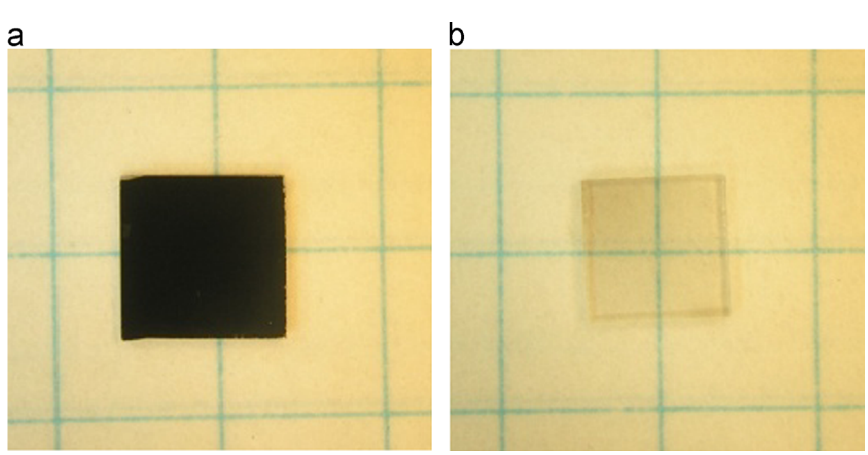

Fig. 2. Photographs of sample surfaces after growth of CNTs on (a) a Si substrate, and (b) a quartz substrate at 600 °C without laser irradiation.