YARNS AND SHEETS FROM WELL ALLINED MULTI-WALLED CARBON NANOTUBES

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1 Introduction

Carbon nanotubes (CNTs) have been attended to use extensively as components in various nano/micro-system due to their unique physical and chemical properties. The growth technique of CNTs have been developed for suitable their application. In particular, Jiang et al. grew multi-walled CNT (MWCNT) forests that were well-aligned arrays and pulled a yarn from them [1]. Zhang et al. produced transparent conductive MWCNT sheets simply by spinning MWCNTs [2]. In addition, MWCNT sheet films can be produced simply by being continuously drawn out from super-aligned MWCNTs on the substrate. The sheet films were expected to be comparable with single walled CNT (SWCNT) films. Transparent conductive films using SWCNTs have been presented by many studies. CNT films can be produced to be flexible over a wide area and are expected to be applicable in diode [3], field emission [4], strain gauge [5], solar cell [6] and organic light-emitting diodes [7].

In this paper, we reported the growth of spin-capable MWCNTs on iron catalyzed on a SiO_2 wafer by chemical vapor deposition (CVD), using acetylene and hydrogen gases. We fabricated the yarn and sheet from the well aligned MWCNTs and described the production procedure and the properties of the yarn and sheet by spinning MWCNTs.

2 Experiments

2.1 Growth of spin-capable MWCNTs

Well aligned MWCNTs on iron catalyzed on a SiO_2 wafer were grown by CVD, which was performed at 800 ˚C using C_2H_2 and H_2 gas. The iron film was deposited on the SiO_2 wafer by electron-beam deposition and had a thickness of about 5 nm. The iron films were inserted into the CVD chamber and ramped to the set point temperature of 800 ˚C at a ramping rate of 50 ˚C while flowing Ar (400 sccm) and H_2 (20 sccm). The growth of MWCNTs was performed at the same temperature and pressure of about 21 Torr by C_2H_2 gas (100 sccm) to the flow for 30 min. The grown MWCNTs on the substrate was shown in Fig. 1a) and Fig. 1b) shows the high resolution scanning electron microscopy (SEM) image of the grown MWCNTs. The MWCNTs grown on the substrate were ~12 nm of diameter, the height of MWCNT forests was 250~300 μm.

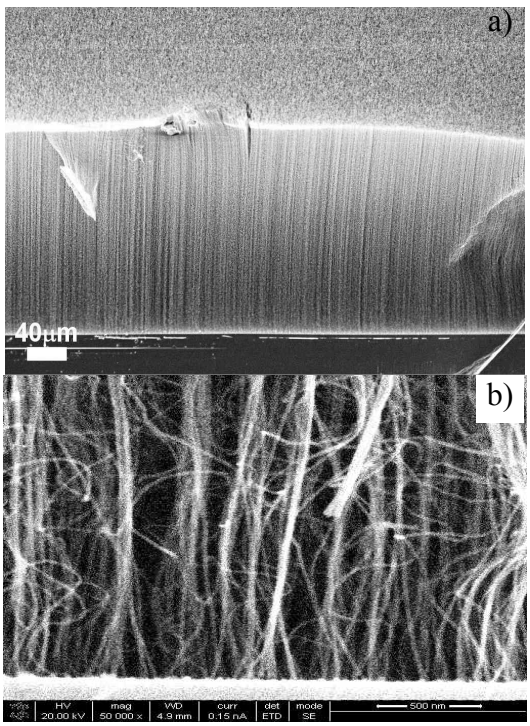

Fig. 1. a) well aligned MWCNTs on the substrate and b) high resolution SEM image

The growth of MWCNTs on the substrate was also performed when the thickness of Fe film were about 3 and 7 nm, respectively. MWCNTs were well grown on both films, as shown in Fig . Unfortunately, both samples were not able to continually spun MWCNTs. The growth for spinning MWCNTs was strongly depended on the thickness of Fe film.

We compared the areal density of MWCNTs grown on the substrates in order to more fully understand how ith is related to: the spinning capability of the forest, the alignment of the MWCNTs in the forest. Spin-capable forests resulting from Fe film have high areal density of $(\sim 1.8\pm 5)\times 10^{10}$ tubes/cm^2. The MWCNTs grown on 30 nm and 70 nm of film thickness have the areal density of $\sim 8.7\times 10^{9}$ and 1.4×10^{10} tubes/cm^2, respectively. The MWCNTs grown on 30 nm and 70 nm of film thickness has lower areal density then the MWCNTs grown on 50 nm of film thickness. When the MWCNTs areal density is low, the MWCNT forests are generally curled or wavy because neighboring tubes are not close enough to have strong Van der Waals interactions between tubes as shown in Fig. 2b) and d). As compared Fig. 1b), Fig. 2b) and d) shows the low density and the declined alignment of MWCNTs.

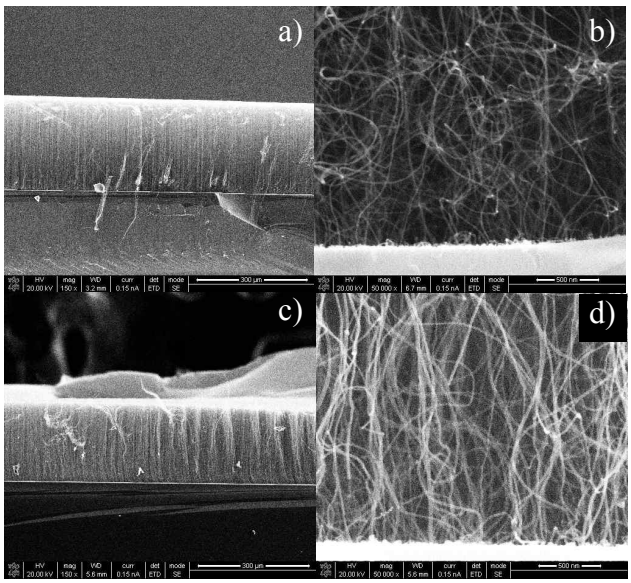

Fig. 2. a) SEM image and b) high resolution image of the MWCNTs grown on the Fe film of 30 nm. c) SEM image and d) high resolution image of the MWCNTs grown on the Fe film of 70 nm.

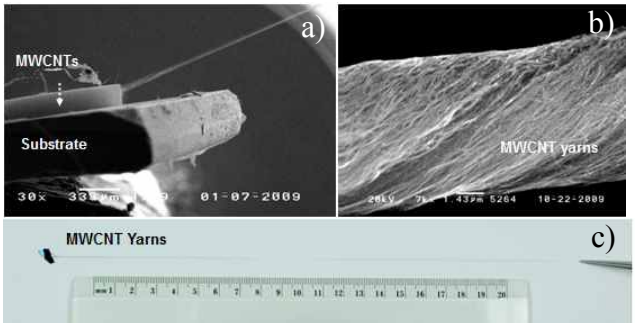

Fig. 3. SEM images of a) yarn from the grown MWCNTs and b) high resolution of MWCNT yarns. c) photo shows the MWCNT yarns

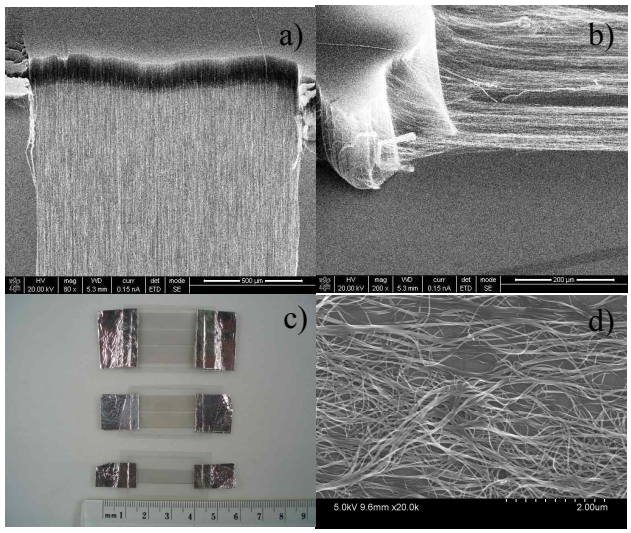

Fig. 4. SEM images shows a) top and b) side view of sheets produced from the well aligned MWCNTs. c) photo and d) SEM image of sheet films.

This suggests that the high areal density promotes alignment of the MWCNTs, perhaps through Van der Waals interactions between growing MWCNTs [9].

2.2 Manufacture of yarn and sheet

As shown in Fig. 3a) the micron-sized MWCNT yarns were produced by twisting MWCNTs. Fig. 3b) shows the SEM image of MWCNT yarns. As shown in Fig. 3c), the photo image shows the MWCNT yarns.

The MWCNT sheets were produced by being continuously pulled out from the grown MWCNTs, as shown in Fig. 4a). Fig. 4b) shows the side view of the sheets from the grown MWCNTs on the substate. The MWCNT sheet films were produced by directly coating MWCNT sheets on a poly ethylen

terephthalate (PET). Alcohol was sprayed over the whole surface of MWCNT sheets, which was then dried at 80 °C for 1 h in an oven. Al foils were then put into contact on both ends of MWCNT sheet with a silver paste. The PET film was also coated on top of MWCNT sheets coated on the PET film. The prepared MWCNT sheet films are shown in Fig. 4c). The SEM image shows the top region of the sheets, as shown in Fig. 4d).

2.3 Electric characterization of yarn and sheet

The MWCNT yarns was immersed in water and the electric resistance of yarn was measured while raising the temperature from 23 °C to boiling point of water as shown in Fig 3. The diameter of yarn is about 100 μm. Black and red allows in Fig. 5 indicated 23 °C and boiling point of water, respectively.

The electric resistance was linearly decreased to boiling point of water. The electric resistance was depended on the temperature of water. An intuitive approach to temperature dependence leads one to expect change in resistance which is proportional to the temperature change:

$$R=R_0[1+\alpha(T-T_0)],$$

where R is the current resistance, R_0 is initial resistance, α is temperature coefficient, T is current temperature and T_0 is initial temperature. The temperature coefficient of MWCNT yarns was calculated to $(-1.2\pm0.3)\times10^{-3}$/°C. We expect that yarn can be applied to temperature sensor.

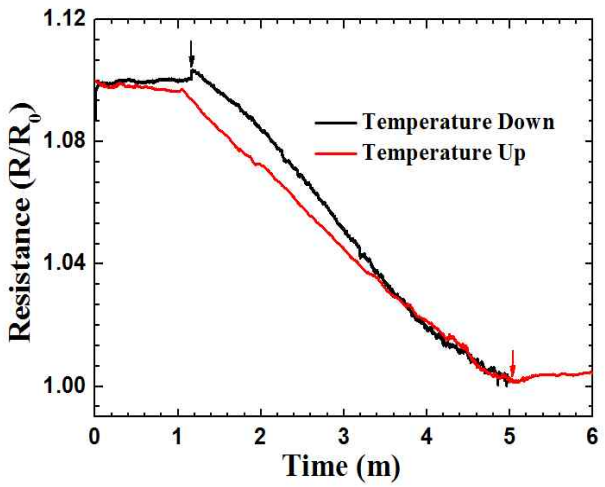

Fig. 5. The electrical resistance variation was depended on the temperature change of water

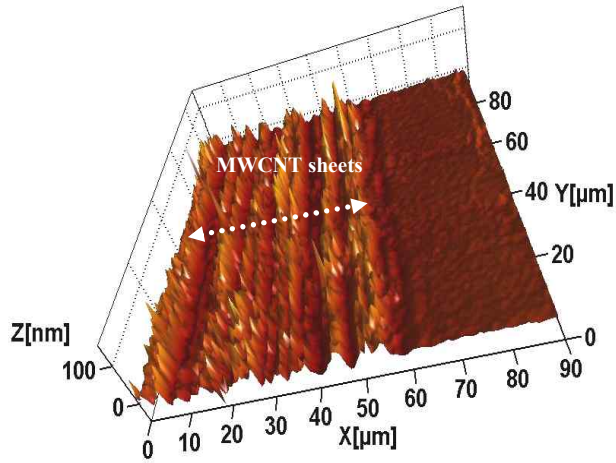

Fig. 6. AFM images of sheets on the substrate.

The morphology of the MWCNT sheets was characterized by atomic force microscope (AFM). The voltage source (Agilent E3634A) was directly connected to both ends of the Al foil electrode on the sheet films, and the current and resistance of the sheet films were measured with a digital multimeter (Agilent 34401A). MWCNT sheet films were fabricated with a uniform density of ~$1.8\pm5\times10^{10}$ tubes/cm^2, sheet resistances of ~699 Ω/sq, and transmittances of 81% to 85% [8].

The AFM images of sheet films are shown in Fig. 6. The thicknesses of the MWCNT sheets were obtained by measuring the heights measured via AFM. The thickness of the sheet was under 100 nm (Fig. 6),

The prepared MWCNT sheet films were heated by supplying DC power. The size of sheet film is 1.15× 0.7 cm^2. The surface temperature of the single sheet films were measured using the infrared thermal camera while a DC voltage was supplied. The defroster in the window of vehicles requires 12 V of driving voltage. The current value of the sheet film was measured to 15.8 mA. The sheet film reached temperature of 56 to 58 °C at an applied voltage of 12 V. The sheet film required ~0.189 W of DC power to increase the sheet temperature to ~58 °C. We propose that the MWCNT sheet films have less sheet resistance and/or electrical resistance spread over the same area as compared to car windows. We measured the temperature of the heat film at an applied voltage of 12 V from outside of –3 °C. As shown in Fig. 7, the film heater was comparable with a car window.

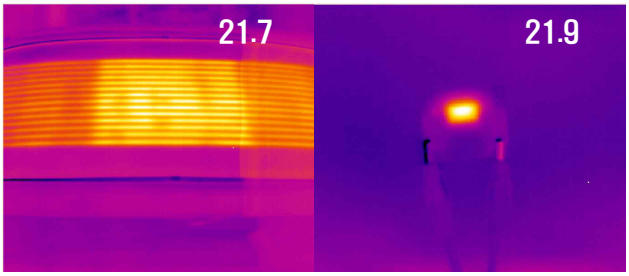

Fig. 7. Comparison of a) car window and b) film heater

3 Summary

The MWCNT yarns and sheets were produced by being continuously pulled out from the vertical-aligned MWCNTs on a substrate. The temperature coefficient of MWCNT yarns was calculated to -1.2×10^{-3}/°C. The MWCNT sheet films have a sheet resistance of ~699 Ω/sq, and transmittance of 81~85 %.

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