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Growth and field emission of carbon nanotubes on sodalime glass at 550°C using thermal chemical vapor deposition

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Abstract

A low-temperature growth of carbon nanotubes (CNTs) on a sodalime glass substrate at 550°C was achieved by a thermal chemical vapor deposition (CVD) of acetylene gas. Acetylene gas was heated in the first zone of the reactor at 850°C and then brought into the second zone maintained at 550°C for the nanotube growth on the glass substrate. The sodalime glass did not exhibit thermal deformation or material degradation throughout the process. Electron emission sufficient for flat panel displays was observed with the practical range of the applied field, i.e., 1 mA/cm^2 at 5 V/μm. This development is an important progress in the integrated process for the mass production of glass-sealed CNT-based field emission displays (FEDs). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

A carbon nanotube (CNT), since its first discovery in 1991 [1], has been considered for many different technological applications exploiting its unique electrical and mechanical properties. Using CNTs as field emitters in the flat panel display is one of the most promising applications because of their unusually high aspect ratio, mechanical and chemical stability, and good conductance. The CNT-based field emission display (FED) has been demonstrated in several occasions [2–7]. Since sodalime glass is commonly used as a low-cost substrate for the display panel, it is highly desirable to grow CNTs directly on the sodalime glass substrate. However, sodalime glass is known to deform and degrade above 550°C, while the CNTs usually grow only at relatively high temperature (600°C or above) with chemical vapor deposition (CVD) methods [8–13].

Here, we report a low-temperature (550°C) growth of CNTs homogeneously on a large area of sodalime glass substrate by a thermal CVD as well as the observation of a large amount of field emission from as-grown samples. We employed a two-stage heating technique in which the reactants were heated at 850°C in the first heating zone and the CNTs were grown at 550°C in the second heating zone. The configuration and structural characteristics of the CNTs have been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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2. Experimental

A 200 nm thick Ti film was thermally deposited on a 20×30 mm^2 sized sodalime glass substrate using a thermal evaporator under an ambient pressure of 10^{-6} Torr, followed by annealing at 200°C for 20 min in argon gas environment. Then a 100 nm thick catalytic Ni film was thermally deposited on the Ti/sodalime glass substrate. The quartz reactor for the thermal CVD consists of two different temperature zones heated by resistive heating coils, as schematically shown in Fig. 1. The first heating zone was maintained at 850°C and the second heating zone was maintained at 550°C for the CNT growth. The Ni/Ti/sodalime glass substrates were loaded with the face down direction on a quartz boat placed in the second heating zone. Temperature inside the quartz reactor was measured with a pair of thermocouple wires. Argon was passed into the quartz reactor in order to prevent the oxidation of the Ni catalytic film while increasing the temperature. Before growing the CNTs, the Ni catalytic film was pretreated using NH_3 gas with a flow rate of 250 sccm for 20 min at 550°C. The CNTs were grown using C_2H_2 gas with a flow rate of 120 sccm for 10 min at the same temperature. After the growth, the reactor was cooled down to room temperature under Ar ambient. The overall configuration and distribution of CNTs were examined by a SEM (Hitachi S600). A TEM (Philips CM20T, 200 kV) was used to investigate the structure of CNTs. The CNTs separated from the substrate in acetone solution using the ultrasonic treatment were dispersed on a carbon TEM microgrid for the analysis of the structure.

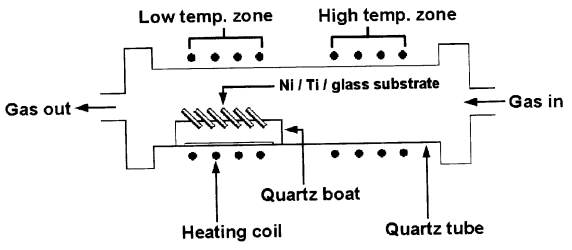

Fig. 1. Schematic diagram of the CVD reactor with two different temperature zones. In the low-temperature zone, the Ni-deposited Ti/sodalime glass substrates are loaded with the face down direction on a quartz boat.

Field emission measurements were carried out for as-grown samples with an electrometer (Keithley 619). The Ti film deposited on sodalime glass played the role of the cathode conducting layer. The distance between the indium tin oxide (ITO) anode and the CNT tip was 150 μm and the emission chamber was maintained at 10^{-6} Torr.

3. Results and discussion

Fig. 2 is the SEM micrographs of the sample. Fig. 2a shows that the CNTs are grown homogeneously on a large area of sodalime glass. The growth direction of CNTs is approximately perpendicular to the substrate. The length of CNTs is about 1 μm. The density of CNTs is much less than that of vertically well-aligned CNTs grown at 950°C [11–13]. Fig. 2b is a top view of CNTs. It reveals that the tip of CNTs are closed and randomly oriented, which is a typical feature for the CNTs grown using thermal CVD method [11–14]. The CNTs have very clean surface without any carbonaceous particles.

No deformation or change in material properties of sodalime glass was observed during or after the whole process. We tried to grow CNTs by various one-stage heating methods at this temperature without success. Our two-stage differential heating method allows us to reduce the CNT growth temperature at least down to 550°C, presumably by having more activated hydrocarbons arrive at catalytic particles in the second heating zone. Even though more study is necessary to elucidate the growth mechanism, this method can be practically applied to achieve the low-temperature growth of CNTs on any substrate.

Fig. 3a shows a TEM image of the sample separated from the substrate. The CNTs are indicated by arrows (1). The diameter of CNTs is in the range of 10–20 nm and that of the inside hollow is about 5 nm. Besides CNTs, carbon nanofibers are also produced as indicated by arrows (2). Noticed that the diameter of carbon nanofibers is in general larger than that of the CNTs. We ob-

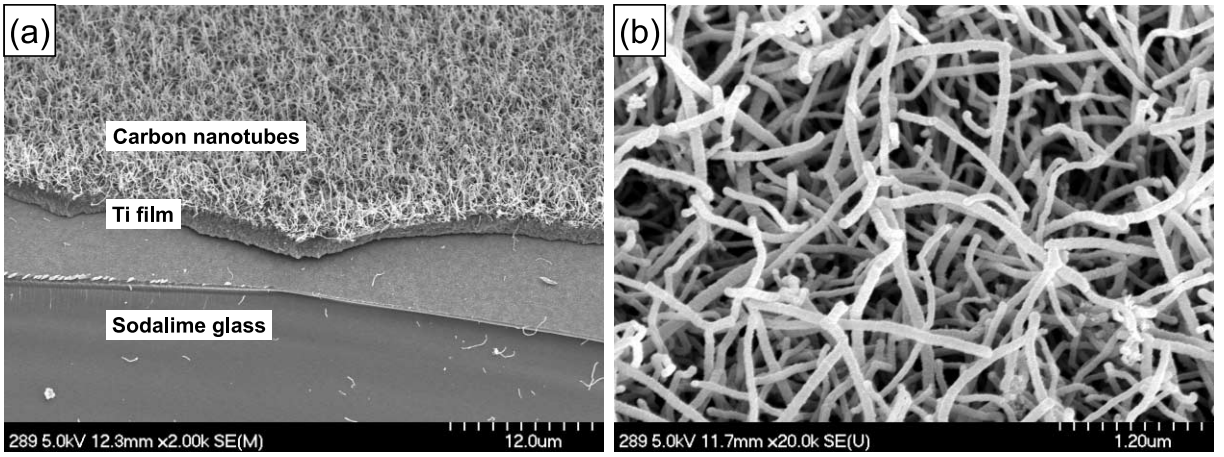

Fig. 2. (a) A SEM micrograph of CNTs grown on Ni-deposited Ti/sodalime glass substrate (20×30 mm^2) at 550°C. (b) A magnified top view of the CNTs.

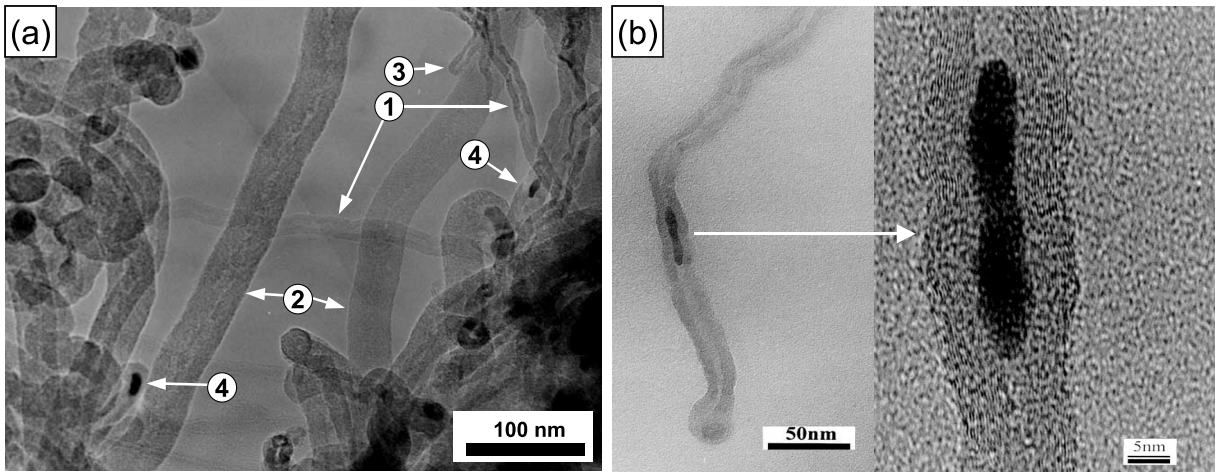

Fig. 3. (a) A TEM image for the CNTs (see arrows (1)) and carbon nanofibers (see arrows (2)). The tips are closed and free of the encapsulated catalytic particles (see arrow (3)). Some of the CNTs encapsulate catalytic particles at the inside of tube (see arrows (4)). (b) A high-resolution TEM image of a CNT encapsulating a Ni particle inside.

served that the growth of nanofibers becomes dominant as the temperature decreases from 550°C to 500°C. The tips of CNTs are all closed. Majority of tips are not encapsulated with any catalytic particles, as indicated by arrow (3). Some of CNTs encapsulate catalytic particles at the tip or inside of tube (see arrows (4)). Fig. 3b is a high-resolution TEM image for a typical CNT. A catalytic particle intercalates inside the tube. The CNT is not straight and the crystallinity of graphitic sheets is not as good as those of grown at 950°C [11–13]. The layers of waving graphitic sheets are separated by ~0.34 nm. The defective graphitic sheets are resulted from the low growth temperature.

We previously reported a low-temperature growth of vertically well-aligned CNTs on Fe-deposited silicon oxide substrate using the same two-stage heating technique at 550°C [14]. The results provide the evidence that the CNTs can be

grown at 550°C regardless of substrates, but the vertical alignment and the yield of CNTs may be influenced by the catalytic species and the substrates. The CNTs grown on Ni-deposited sodalime glass substrate and Fe-deposited silicon oxide substrate at 550°C sometimes encapsulate the catalytic particles at the inside of tube. Encapsulation of catalytic particles indicates an occurrence of capillary action of catalytic particles during the growth of CNTs. It was suggested that the capillary action of quasi-liquid state metal at the temperature below the melting point of bulk phase could be attributed to the size effect of metal at nanometer level and/or the interfacial effect between metal and carbon [15,16].

The present low-temperature growth of CNTs allows an application to the sodalime glass-sealed FED. Fig. 4 illustrates the emission current density from a typical as-grown sample. The bias voltage sweeps were conducted several times and the plot shows the first four sweeps. After the fourth measurement presented in the figure, the current is well stabilized. A relatively large amount of current at the highest voltage in each sweep probably causes some annealing and, after a few sweeps, the structure of the nanotube seems to reach a stable configuration. The turn-on (corresponding to the current density of 0.1 μA/cm^2) applied electric field is about 1.3 V/μm. The emission current density reaches 1 mA/cm^2 at an applied field of about 5 V/μm (i.e., the total bias voltage of 750 V), which produces sufficient brightness when used for the FEDs. Actually, 0.1 mA/cm^2 can produce enough brightness (>1000 cd/m^2) under practical display operating conditions. For comparison, the emission current density of 1–3 mA/cm^2 for the CNTs grown at 950°C was reached at about 4 V/μm [11–13]. The Fowler–Nordheim plot is shown in the inset of Fig. 4. It exhibits a linear behavior in the intermediate range but shows saturation at higher fields in agreement with many other works [17–19]. A remarkable feature in the present measurement is that the field emission is quite robust even though the CNTs are not straight or the crystallinity of graphitic sheets is not perfect. Therefore, the growth of CNTs on sodalime glass at 550°C is an important progress in the integrated process for the mass production of glass-sealed CNT-based FEDs.

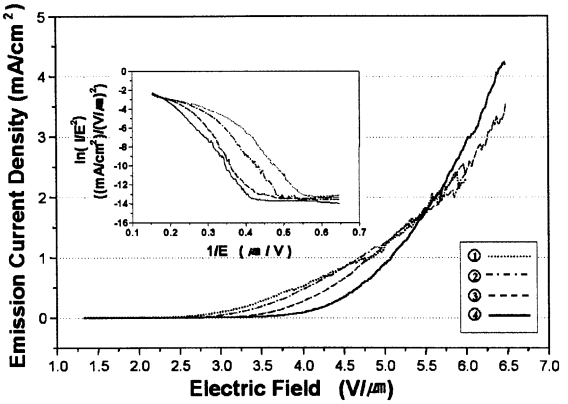

Fig. 4. Emission current density vs applied electric fields. Numbers (1)–(4) indicate four consecutive voltage sweeps. The current is stabilized after the fourth sweep. The inset shows the same result presented in the form of the conventional Fowler–Nordheim plot.

In summary, we have grown the CNTs on Ni-deposited sodalime glass substrate at a low-temperature such as 550°C, by employing the two-stage heating technique that the reactants are heated in the first heating zone at 850°C and then brought into the second heating zone maintained at 550°C for the growth of CNTs. The CNTs are grown approximately toward the vertical direction to the substrate. The diameter of CNTs is in the range 10–20 nm. The CNT is not straight and consisted of waving graphitic sheets. The turn-on applied electric field was about 1.3 V/μm with the current density of 0.1 μA/cm^2. The maximum emission current density is 1 mA/cm^2 at an applied electric field of about 5 V/μm, which provides the sufficient brightness when used for the flat panel displays.

Acknowledgements

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