

Carbon Nanotube Deposition using Helicon Plasma CVD at Low Temperature

Masakazu Muroyama, Kimura Kazuto, Takao Yagi, Kouji Inoue, Ichiro Saito

SONY Corporation,

4-16-1 Okata Atsugi-shi, Kanagawa, 243-0021, JAPAN, Masakazu.Muroyama@jp.sony.com

ABSTRACT

We developed a novel growth method of aligned carbon nanotubes. Aligned carbon nanotubes are grown on a metal catalyst on a glass substrate using biased Helicon plasma chemical vapor deposition (HPECVD) of CH_4/H_2 gases from 400 C to 500 C. The Helicon plasma source is one of the high-density plasma sources and is promising for low temperature carbon deposition. A Ni film was used as a catalyst to reduce the activation energy of the nanotubes' growth. The carbon nanotubes were deposited on the nickel catalysis layer selectively.

1. Objective and Background

Carbon nanotubes are considered to be a promising material for field emission displays (for example, [1]). Preparation of highly purified carbon nanotubes in large quantity, well-aligned nanotubes, and low temperature synthesis are prerequisites for this application. Carbon nanotubes (CNT) and carbon nanofibers (CNF) are formed by various methods, such as arc discharge [2], laser evaporation [3], thermal chemical vapor deposition [4], and plasma enhanced chemical vapor deposition [5].

In this paper, we report a low temperature synthesis of carbon nanotubes using methane and hydrogen. The fabrication

process is based on the biased Helicon plasma chemical vapor deposition with Ni catalyst from 400 C to 500 C. Furthermore, we found that the carbon nanotubes were grown selectively on the catalyst on the substrate. We have carried out the structural analysis to investigate the growth mechanism and measurements for field emission characteristics.

2. RESULTS

A chromium layer was deposited on the glass substrate. A nickel layer was also deposited on the chromium layer as a catalyst for nanotube growth. The silicon oxide and the chromium layer as a top metal were deposited on the nickel pattern. And finally, reactive ion etching technology was used to make an emitter hole structure on this sample.

Vertically aligned carbon nanotubes were selectively grown in the emitter hole using a helicon plasma chemical vapor deposition (HPCVD) system. Methane (CH_4), as a carbon source, and hydrogen (H_2) gases were introduced from the gas introduction ring. RF bias (13.56MHz) was applied to the helicon source to control the gas decomposition. The heater was located with the substrate holder. RF bias (13.56MHz) was also applied to the substrate to control the ion energy.

To characterize the nanotube's

13.1 / Invited

structure, micro-Raman spectra were measured. The Microstructure was investigated scanning electron microscope (SEM) and transmitting electron microscope (TEM).

Macroscopic field emission properties were measured in a parallel plate configuration with ITO patterned on glass as an anode, and an optical fiber of 125 micrometer in diameter as a spacer.

Before carbon nanotube deposition, the nickel layer was treated with NH_3/He or Ar/He plasma for 5 min. The plasma treatment improved the nanotubes growth through the modification of the surface cleanness of the catalyst. After carbon nanotube deposition, these nanotubes were treated with H_2 plasma for 2 min.

The growth of high-density, well-aligned carbon nanotube was demonstrated at 470 C. These carbon nanotube were 2 micrometer in length and 40 nm to 60 nm in diameter. No nanotubes were observed on the top metal layer. The excellent selectivity was achieved by the combination of nickel catalyst and chromium top metals.

The Nickel particle at the top end of the tube was observed as a dark. The graphite sheets were stacked along the Nickel catalyst. A hollow spacing could be observed in a magnified view at the center of the nanotubes.

The Raman spectrum clearly shows the G-peak at 1591 cm^{-1} , which originated from the graphitic sheets. The broad D-peak at 1345 cm^{-1} indicates the existence of a defective graphitic layer, which remains even after the H_2 plasma post treatment.

Field emission measurements were performed with a diode structure. The turn-on voltage was about 7 V/micrometer.

3. Impact

Carbon nanotubes were grown on Ni catalyst using Helicon plasma chemical vapor deposition with RF bias at temperatures ranging from 400 C to 500 C. Vertically aligned carbon nanotubes were obtained selectively on the Ni catalyst. The diameter of the carbon nanotubes was in the range of 40-80 nm. Since the technique we present here is simple for the synthesis of the carbon nanotubes, this technique can be applied for a low temperature process in fabrication of field emission displays.

4. REFERENCES

1. J. Robertson, Proceeding of the Materials Research Society Fall, (1999).
2. C. Journet, WK. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefarant, P. Deniard, R. Lee, J.E. Fischer, *Nature* **75**, 756-8 (1997).
3. W. Zhu, C. Bower, O. Zhou, G. Kochanski, S Jin, *Appl. Phys. Lett.* **75**, 873-5 (1999).
4. S. Fan, G. Michael, G. Chapline, N.R. Franklin, T.W Tomblor, A.M. Cassell, H. Dai, *Science* **283**, 512-4 (1999).
5. S.H Tsai, C.W. Chao, C.L. Lee, H.C. Shih, *Appl. Phys. Lett.* **74**, 3462-4 (1999).