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Effect of Filament Discharge on Uprightness of Carbon Nanotwists Tightly-Adhered to Substrate

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Making carbon nanofibers stand up in a field electron emitter to obtain a good field emission property when emitters are fabricated by printing on a substrate has been proposed. In the fabrication process of carbon nanotwist (CNTw) field emitters, paste composed of an ethyl cellulose binder and carbon nanotwists (CNTws) is printed on the substrate. Filament discharge (FD) treatment is an excellent technique that makes CNTws stand up because large-area treatment is possible at a low cost. To solve the problems of weak adhesion between CNTws and the substrate and the generation of fragments during FD treatment, we added a silicone binder to the paste at 0.83–0.97%. The variations in the silicone binder content were compared by the scanning electron microscopy (SEM) observation of CNTw emitter surfaces. As the content decreased, the number of upright CNTws increased and the height of upright CNTws became uniform. We confirmed that the crystalline property of CNTws was not changed by the FD treatment when the silicone binder was added. Also, spark from the CNTw emitter was inhibited with the addition of the silicone binder and the field emission current density in the case with the binder was 200 μA/cm^2 higher than that in the case without the binder.

1. Introduction

Electron field emitters using carbon nanotubes (CNTs) have good properties including a low threshold voltage for emission and a high emission current due to the high aspect ratio of CNTs.[1] However, there are still problems with these emitters. For instance, CNTs are damaged by ion bombardment and thus it is difficult to achieve a long CNT lifetime. We have proposed that the use of the carbon nanotwist (CNTw) is a candidate solution to the above problems.[2] The CNTw has a helical structure that has a stack of two carbon nanofibers. The fiber diameter of the CNTw is ~100 nm, about ten times larger than that of multi-walled CNTs. The CNTw is expected to have a high resistance property against ion bombardment and a longer lifetime owing to its large thickness. The CNTw can be grown at a production yield of ~2 g/h using Ni/Sn catalysts and C_2H_2/N_2 gases.[2] This is good for the industrial application of CNTws.

Making electron emitters stand up on a substrate is a good means of enhancing the field emission properties. There are some stand-up methods including the use of adhesive tape[3] and filament discharge (FD) treatment.[4] Making CNTws stand up using adhesive tape is a simple and inexpensive method, but problems include surface contamination and difficulty in using it for large-area treatment. FD can treat larger surface areas in one operation than the use of adhesive tape, and does not leave any foreign particles on the surface. Three main effects appear when CNTws are treated by FD: (1) Uprightness of CNTws. It is presumed that the gradient force generated in the plasma-substrate interface lifts CNTw tips. (2) Relocation of CNTws. In this phenomenon FD exfoliates CNTws from their original position of being bonded to the substrate and spreads them to other areas by gas flow. (3) Etching of CNTws.[4] As this continues, the tip heights of CNTws become uniform, resulting in a uniform electron field emission. Using this FD treatment, we have examined stand-up CNTws on a substrate and the conditions for their manufacture including treatment time and ambient gas. Since there are no foreign particles left after FD treatment, the electric field on a CNTw tip is not necessarily too high and uniform emission is obtained. The only problem with an FD-treated CNTw emitter is the spark caused during field emission. The reason for this is the concentration of an electric field on CNTw fragments.

In this study, we added a silicone binder to a paste composed of CNTws and an organic binder, and printed it on a substrate. The use of this silicone binder is expected to improve the adhesion of CNTws to the substrate and prevent fragment generation. The silicone binder we used (Shin-Etsu Chemical SIM-260) is prepared from a compound with siloxane bonds. The binding energy of the siloxane bond (Si–O) is 444 kJ/mol larger than that of the C–C bond (356 kJ/mol). Therefore, adding the silicone binder to the paste is considered to increase the resistance against the etching effect on CNTws by FD treatment. In the experiment, we examined the effects of FD treatment on the uprightness of CNTws and their field emission properties. The CNTw crystalline properties before and after FD treatment were analyzed by Raman spectroscopy. The states of upright CNTws treated under different experimental conditions were compared by scanning electron microscopy (SEM) observation. Since the amount of silicone binder was too small to be controlled manually, we varied the CNTw amount in the paste from 2.5 to 20 phr (per hundred resin) instead. By doing this, the weight ratio of the silicone binder to the paste can be relatively controlled.

2. Experimental Methods

2.1 Fabrication of CNTw emitter

CNTws were synthesized by catalytic chemical vapor deposition (CVD). Briefly, Ni and Sn liquid catalysts (Kojundo Chemical Laboratory) were dropped on a graphite substrate and dried at 400 °C for 10 min. The catalytic substrate was placed in a CVD chamber, and the chamber temperature was raised to 650 °C, while N_2 gas was introduced at a flow rate of 1400 ml/min. After reaching

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