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Enhanced and stable electron emission of carbon nanotube emitters with graphitization

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ABSTRACT

The effect of graphite coating on carbon nanotube (CNT) emitter arrays on field emission grown using the resist-assisted patterning (RAP) process was studied. It was found that the electron emission current and the stability of the emission current of graphite-coated CNT emitters were remarkably improved. The enhancement of the electron emission of CNT emitters after graphite coating appears to be due to the effect of graphitization between CNT emitters and the substrate. This graphitization process reduced the field-screening effect, since it unified several grown CNTs as one single emitter and improved adhesion between CNT emitters and the substrate.

1. Introduction

Carbon nanotubes (CNTs) have good properties in electrical, thermal, chemical, and mechanical parts. CNTs are excellent electron emitters for vacuum nano-electronic devices, such as field emission displays (FEDs), X-ray sources, electron guns, and backlight units (BLUs) [1–4]. Since the discovery of electron field emission from CNTs [5], there have been many studies on the electrical, chemical, and structural properties of the electron emission of CNTs [6–8]. The high-performance electron emitters require high emission current density, low driving voltage, long-term stability, and low current fluctuation. The main consideration for the application of CNT emitter arrays is the interface between CNT emitters and the substrate, as it prevents CNT emitters from evaporating at high electron emission currents and ensures stable electron emission. Direct growth of CNTs on a substrate is one way to obtain good adhesion of CNT emitters to the substrate. The resist-assisted patterning (RAP) process with DC plasma-enhanced chemical vapor deposition (DC-PECVD) can be used to improve the interface adhesion [9,10].

In this work, the electron emission properties of CNT emitter arrays were studied using post-treatment technology. We developed a graphitization process on CNT emitters with photo resins. The phase transition of resin to graphite was confirmed with various analyses, resulting in enhanced electron emission. Field emission scanning electron microscopy (FE-SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were used to analyze the structural properties of CNTs, such as the concentration ratio of carbon and their chemical bonding configuration before and after the graphitization process.

2. Experimental

The vertically aligned CNT emitter arrays were grown with a RAP process using the DC-PECVD technique. The growth conditions of CNT emitter arrays are as follows: pressure of 2.0 Torr and temperature of 800 °C in a 40:60 mixture of acetylene (C_2H_2) and ammonia (NH_3), respectively. The CNT emitter arrays were formed from a dot diameter of 3 μm and a dot pitch of 15 μm.

Fig. 1 shows the process flow of graphite treatment after CNT growth with the RAP process. The Ni catalyst was deposited with sputtering on the Si wafer and then patterned with the photoresist patterning process. The Ni layer was etched and then formed in a high-temperature furnace. After forming, the CNTs were grown with an acetylene and ammonia gas mixture using DC-PECVD. After CNT growth with the RAP process, the CNT emitter substrate was coated by resin with the spin-coating technique, and then the substrate was annealed in a furnace at a temperature of more than 800 °C for an hour. During the annealing process, the resin changed

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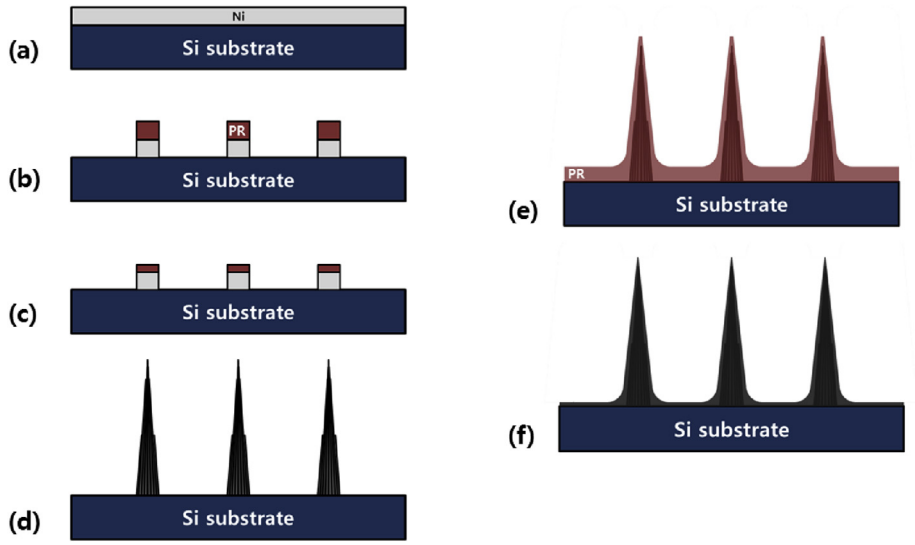

Fig. 1. Process flow for graphite treatment after CNT growth with a resist-assisted patterning (RAP) process. (a) Ni deposition on Si wafer, (b) resist patterning and Ni etch, (c) forming at 600 °C, (d) CNT growth using DC-PECVD, (e) resin coating and (f) annealing at 800 °C in vacuum chamber.

its phase to graphite and strongly adhered to the walls and roots of CNT emitters.

The electron emission current of CNT emitter arrays was measured in DC mode with a diode-type electron emission structure under a pressure of 1×10^{-7} Torr. The distance between the anode and cathode was fixed at 300 μm during the measurement.

3. Results and discussion

Fig. 2 shows SEM images of the CNT emitter arrays before and after the graphitization process. Fig. 2(a) shows as-grown CNT emitter arrays, and Fig. 2(b) and (c) show magnified images. In addition, Fig. 2(d) shows CNT emitter arrays after the graphitization process, and Fig. 2(e) and (f) show magnified images. The thickness of the coated resin is 2.0 μm, and then it reduces to 0.5 μm after annealing in the furnace. The annealing time is 1 h in a vacuum furnace with Ar gas ambient at 800 °C.

In Fig. 2(a), as-grown CNTs show many impurities around the CNT emitter arrays. However, in Fig. 2(d), those impurities are invisible after the graphitization process. The bright impurities on the substrate are one of the arcing sources for high electron emission. By eliminating the arcing source with the graphite coating, the CNT emitter arrays are more stable at high electron emission currents. After the graphitization process, the adhesion between CNTs and the substrate is improved due to the graphite layer formation on the CNT roots. In the SEM image of Fig. 2(c), several CNTs are grown on one dot emitter. However, Fig. 2(f) shows a single emitter on the same dot after the graphitization process.

The CNTs on one dot are unified after the graphitization process, resulting in the formation of a single emitter, as shown in Fig. 3. The graphite layer fills the CNT-to-CNT space during the graphitization process. The formation of the single emitter reduces field screening, resulting in an increased electron emission current. In the case of as-grown CNTs, one dot of numerous emitters is divided into several CNT branches, as shown in Fig. 3(a), which increases the field-screening effect. After graphite treatment, as-grown CNTs turned into single emitters without branches, which are shown in Fig. 3(b). The emitters without branches decreased the field-screening effect through the graphitization process. They also have the advantage of longer stability.

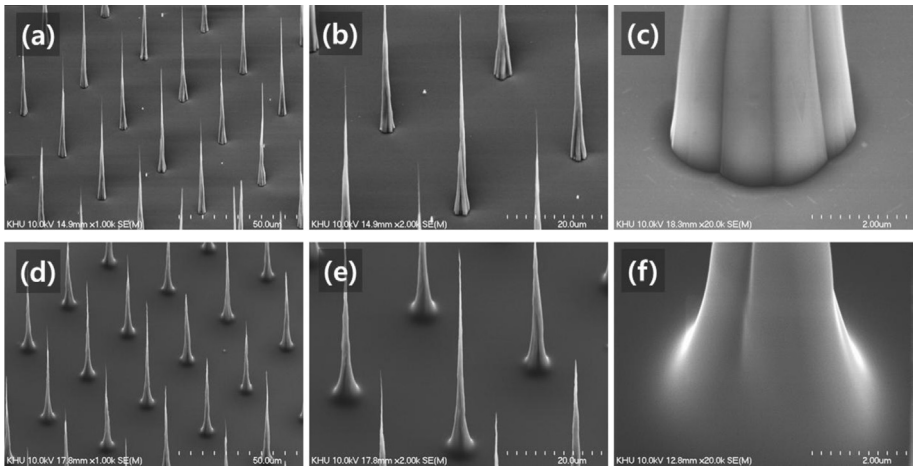

Fig. 2. SEM images of (a) as-grown CNT emitter arrays, (b–c) magnified images of CNT emitter and root of emitter, (d) graphite-coated CNT emitter arrays, and (e–f) magnified images of graphite-coated CNT emitter and root of emitter.