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A fabrication method for field emitter array of carbon nanotubes with improved carbon nanotube rooting

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ABSTRACT

We have developed a technique for fabrication of a field emitter array (FEA) of carbon nanotubes (CNTs) to obtain a high emission current along with a high current density. The FEA was prepared with many small equidistant circular emitters of randomly oriented multiwall carbon nanotubes. The fabrication of a FEA substrate followed with deposition of titanium nitride (TiN) film on a tantalum (Ta) substrate and circular titanium (Ti) islands on the TiN coated Ta substrate in a DC magnetron sputtering coater. CNTs were dispersed on the substrate and rooted into the circular Ti islands at a high temperature to prepare an array of circular emitters of CNTs. The TiN film was applied on a Ta substrate to make a reaction barrier between the Ta substrate and CNTs in order to root CNTs only into the Ti islands without a reaction with the Ta substrate at the high temperature. A high emission current of 31.7 mA with an effective current density of 34.5 A/cm^2 was drawn at 6.5 V/μm from a FEA having 130 circular emitters in a diameter of 50 μm and with a pitch of 200 μm. The high emission current was ascribed to the good quality rooting of CNTs into the Ti islands and an edge effect, in which a high emission current was expected from the peripheries of the circular emitters.

1. Introduction

Carbon nanotubes (CNTs) were found as excellent sources for electron emission due to their high aspect ratios, and extraordinary electrical, thermal and mechanical properties [1–3]. In spite of the work carried out in the field of CNT emitters, achieving a high emission current is still said to be a challenging job. It is because at a high current operation of an emitter, an emission current is in general limited by disappearance of CNTs from a substrate under a high electric field due to a weak bonding between CNTs and a substrate, a high electrical contact resistance and a low thermal conductivity of a CNT junction [4]. Along with this a screening effect provoked by proximity of CNTs on an emitter also results in the limitation of a high emission current [5]. However this might be avoided if the number density of CNTs is controlled with an adequate intertube distance [5,6]. In order to obtain strong bonding of CNTs with a substrate and to maintain high electrical and thermal conductivities at CNT junctions, our group has presented fabrication techniques based on CNT rooting into a substrate. As a substrate we have selected titanium (Ti) coated tantalum (Ta) foil which was found as reliable material at a high temperature owing to Joule heating at high current operation. The rooting method was applied to prepare continuous film emitter (CFE) and field emitter array (FEA) of randomly oriented CNTs [4,7]. Our rooting technique not only showed a high emission current but also an excellent lifetime of an emitter [7]. The screening effect in a CFE cannot be avoided since rooting technique was applied to randomly oriented pre-prepared CNTs which were dispersed on a substrate. In case of emitters fabricated by CNT dispersion the controlled number density of CNTs with an adequate intertube distance cannot be easily obtained. A FEA, which contains an array of small circular emitters of CNTs, might be an alternative way to enhance an emission current. FEAs of CNTs have already been introduced in our previous study and by other groups to get a higher current density compared to that from a CFE [7,8]. The higher current density was imputed to a strong edge effect [7,8]. The edge effect is defined as an effect that shows a high emission current from the edges of a CNT emitter [7]. This manuscript describes a novel method of FEA fabrication to obtain good quality of CNT rooting into a FEA substrate and strong edge effect so as to extract a high emission current.

2. Fabrication process and experimental methodology

A CFE and FEAs were fabricated using randomly oriented multiwall carbon nanotubes (MWCNTs) synthesized with chemical vapor deposition technique. A CFE was fabricated on a Ti coated Ta substrate which was prepared in a homemade UHV-based DC magnetron sputtering coater as explained in detail elsewhere [7]. A Ti film with a thickness of 2 μm was deposited on a Ta substrate of 100 μm thickness in the coater maintained at an argon (Ar) gas pressure of 1 Pa as measured with a diaphragm gauge [7]. CNTs were dispersed using acetone on

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the substrate after segregation of CNT bundles in an ultrasonic bath of acetone. The dispersed CNTs were rooted into the Ti film using our patented rooting technique discussed in detail elsewhere [4,7]. In the rooting technique a CNT dispersed substrate is heated at a high temperature of ~1200 °C for 30 s to fix CNTs into Ti islands. A base pressure of the rooting chamber was maintained in a lower range of 10^{-7} Pa. The substrate with dispersed CNTs was pre-heated at a lower temperature of ~400 °C for ~30 min for degassing. During the rooting operation at the high temperature the chamber pressure reached in a range of 10^{-4} Pa. The pressure of 10^{-4} Pa was low enough to avoid impurity inclusion and to carry out reaction between CNTs and Ti islands to form titanium carbide (TiC) at CNT junction for the rooting. In a post rooting process non-rooted CNTs were removed by cleaning the emitter surface with a soft brush and a jet of N_2 gas.

Fabrication of a FEA was started with a Ta substrate on which an array of small circular Ti islands with a height of 2 μm, a diameter of 100 μm and a pitch of ~450 μm were deposited. The Ti islands were made using a mask set on the Ta substrate during the Ti sputtering coating carried out under the same conditions as used for the CFE. CNTs were dispersed on the Ti island/Ta substrate using the same method as used for the CFE. The dispersed substrate was heated at the high temperature of ~1200 °C to root the CNTs into the Ti islands for making an array of circular emitters. Fabrication method is shown by a schematic in Fig. 1. Fig. 2 shows an optical microscope image of the FEA after being heated at the high temperature and cleaning with a brush and a jet of N_2 gas. At this high temperature the CNTs not only reacted with the Ti islands but also with the Ta substrate to form tantalum carbide (TaC) which was the cause of undesired rooting of CNTs into the Ta substrate. The rooted CNTs on the Ta substrate could not be removed perfectly even with the N_2 gas jet and brush.

In order to avoid undesired CNT rooting into a Ta substrate a FEA was fabricated at a lower rooting temperature of ~1000 °C. Ti islands for the FEA substrate were deposited using another mask having micro-holes in a diameter of 50 μm and a pitch of 200 μm with the number density of holes equal to 29 holes/mm^2. The low rooting temperature was found insufficient for proper chemical reaction to form TiC at the CNT junctions. At the low temperature the CNTs and CNT bundles were partially rooted into the Ti islands and might result in poor bonding of CNTs with the substrate. After applying the cleaning technique to remove CNTs from the Ta substrate, many non-rooted CNTs were removed from the Ti islands as well. Therefore an effective emission area, which was an area covered with CNTs, on the Ti islands was reduced. As a result of the low CNT coverage and the poor rooting a high emission current could not be extracted from a FEA [7].

In order to solve the above antinomy FEA substrate was modified with deposition of an intermediate titanium nitride (TiN) thin film between a Ta substrate and Ti islands. A TiN film with a thickness of 1 μm was coated on a Ta substrate of 100 μm thickness by using the same magnetron sputtering coater. Argon and nitrogen gases in an optimized pressure ratio of 5:4 and with a total pressure of 1.53 Pa

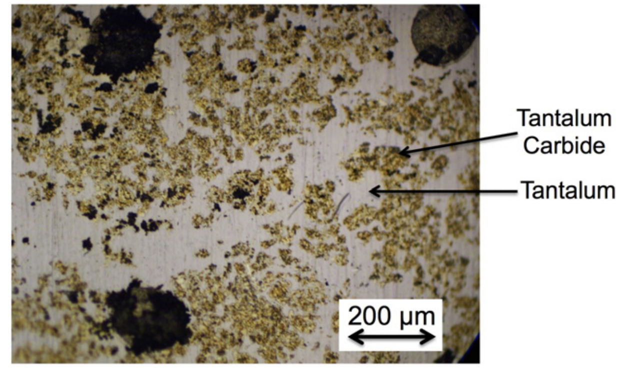

Fig. 2. Undesired TaC formation in a FEA fabricated on a Ta substrate at the high rooting temperature. Circular emitters were prepared in a diameter of 100 μm and a pitch of ~450 μm.

measured with a diaphragm gauge were introduced in the sputtering chamber for stoichiometric TiN film deposition. On the TiN coated Ta substrate, an array pattern of circular Ti islands with a height of 2 μm was deposited using the same mask having holes in a diameter of 50 μm and a pitch of 200 μm. The fabrication procedure for a patterned substrate is illustrated in schematics in Fig. 3 (a)–(c). CNTs were dispersed and rooted into the Ti islands at the high temperature of ~1200 °C to prepare circular emitters of CNTs as shown by schematics in Fig. 3 (d) and (e).

Three emitters including the CFE, the FEA (without the TiN film) rooted at the low temperature of ~1000 °C (FEA-LT) and the FEA (on the TiN film) rooted at the high temperature of ~1200 °C (FEA-HT) were tested in a field emission measurement system. The CFE, FEA-LT and FEA-HT were prepared with substrate areas of 3.1, 3.9 and 4.5 mm^2, respectively. The FEA-LT and FEA-HT contained 114 and 130 circular emitters, respectively. A base pressure of the emission chamber was maintained at 10^{-9} Pa. The emission system consists of a triode system which is an assembly of an emitter acting as a cathode, an accelerating graphite grid and a fluorescent anode screen [7]. An adjustable distance of an emitter surface from the grid was usually set to be 300 ± 10 μm. The emission current measurement setup was detailed elsewhere [7]. The emitted electrons were collected from the graphite grid and the anode screen to get a total emission current from an emitter.

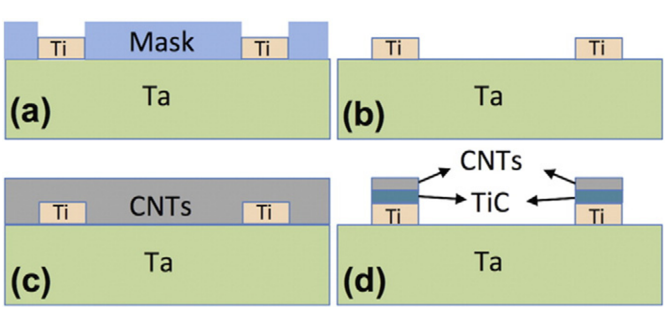

Fig. 1. (a) A mask set on a Ta substrate for deposition of Ti islands. (b) Deposited Ti islands. (c) Dispersion of CNTs on the patterned substrate. (d) FEA after rooting of CNTs into Ti islands at the high temperature.

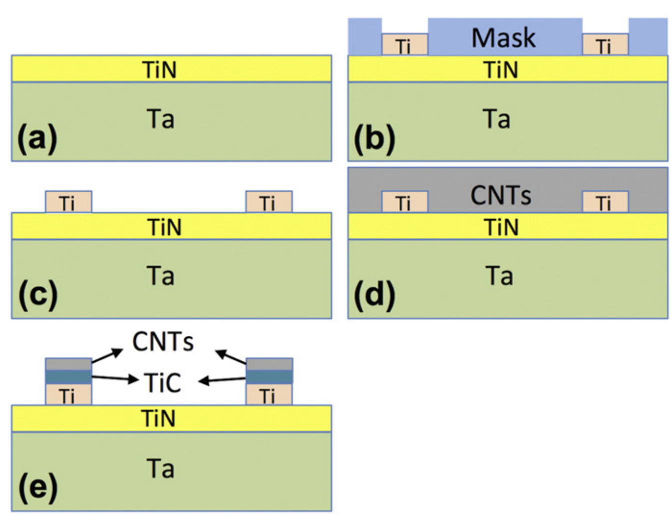

Fig. 3. (a) TiN thin film coating on a Ta substrate. (b) Setting of mask on the TiN coated Ta substrate. (c) Equidistant circular Ti islands deposited on the TiN coated Ta substrate. (d) Dispersion of CNTs on the patterned substrate. (e) FEA containing an array of circular emitters after rooting of CNTs into Ti islands.