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Field emission characteristics of vertically aligned carbon nanotubes with honeycomb configuration grown onto glass substrate with titanium coating

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ABSTRACT

Carbon nanotubes (CNTs) were grown successfully onto a glass substrate using thermal chemical vapor deposition (TCVD) with C_2H_2 gas at 700 °C. The synthesized CNTs exhibited good crystallinity and a vertically aligned morphology. The vertically aligned CNTs (VACNTs) were patterned with a honeycomb configuration using photolithography and characterized using field emission (FE) applications. Owing to the electric field concentration, the FE current density of VACNTs with honeycomb configuration was higher than that of the un-patterned VACNTs. Ti was coated onto the VACNT surface utilizing the relatively lower work function property to enhance the FE current density. The FE current density reached up to 7.0 mA/cm^2 at an applied electric field of 2.5 V/μm. A fluorescent screen was monitored to demonstrate uniform FE VACNTs with a honeycomb configuration. The designed field emitter provided an admirable example for FE applications.

1. Introduction

Numerous relative researches have been conducted since carbon nanotube (CNT) has been used for field emission (FE) applications [1–3] with the main purpose in raising field emission current and lowering the threshold voltage. One of the methods used to enhance FE current involves coating metal oxide onto carbon nanotube such as MgO/CNT or ZnO/CNT [4,5]. Moreover, constructing the CNT configuration to increasingly concentrate the electric field has also been investigated [6,7]. The other method used to enhance FE current involves configuration of the CNT pattern to avoid the screening effect, and therefore concentrating the electric field on the tip of emitter. For example, L. Nilsson et al. reported that when the height of the vertically aligned CNT (VACNT) was fixed, the inter-tube distance to height ratio of a VACNT was approximately 2, a maximum FE current density could be obtained [8].

Using this principle, our previous study showed that VACNT bundle arrays with a hexagon configuration demonstrated a promising field emitter [9]. A VACNT bundle, containing VACNTs with high population density, replaced an un-patterned VACNT to reach the maximum FE current achievement when the inter-tube distance to VACNT height ratio was approximately 2. However, fallen VACNT bundle field emitters sometimes appeared, resulting in obstructing large-area field emitter design development because it is not easy to uniformly grow such a designed architecture without defects in practice.

A honeycomb configuration can be regarded as an anti-hexagon pattern. When VACNT bundles are constructed with a honeycomb configuration as a field emitter [10,11], the applied electric field is concentrated as long as the height of the VACNT bundles is adjusted to an optimal length. From the geometrical structure viewpoint, the VACNTs in a honeycomb configuration are connected with each other and support together to avoid collapse of VACNTs [12]. The honeycomb structure reduces the possibility of collapsed VACNTs. Having an optimal configuration for field emitter applications, this

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designed configuration could be used as a template for coating low work function materials onto this surface. A suitable surface morphology and low work function are the two main influence factors in the Fowler–Nordheim (FN) relation [13]. These approaches could be combined to enrich field emitter performance.

Substrate selection is another important issue for growing VACNTs. Apart from some substrates with high melting (softening) points such as Si, Ni and stainless, growing CNTs onto a glass substrate is a challenge because of the low glass substrate softening point. In general, a comparatively lower growth temperature process is necessary; leading to sometimes sacrificing the crystallinity or surface morphology of CNTs. Sometimes the hollow CNT structure could not be formed, producing a solid fiber structure [14]. In this respect, we found that Corning Eagle^{2000} glass is a suitable glass material for growing VACNTs due to its relatively higher softening point. The growth temperature of VACNT (700 °C) is larger than the melting point of glass substrate (~400 °C). In this experiment, Corning Eagle^{2000} glass substrate has relatively higher softening point (985 °C) and lower cost than other substrates. Related processes for growing patterned VACNTs, such as photolithography and catalyst metal coating can be manipulated on the Eagle^{2000} glass.

This study used thermal chemical vapor deposition (TCVD) to grow VACNTs with a honeycomb configuration onto an Eagle^{2000} glass substrate. VACNTs with good crystallinity and vertically aligned morphology were demonstrated. The relative FE characteristics were examined, showing that VACNTs with a honeycomb configuration manifested excellent FE current density. To further enhance the FE current density, a VACNTs bundle array was used as a template for the Ti coating. Utilizing the low work function property of Ti, the FE current density could reach a higher value [15]. To verify that the designed VACNT exhibited a uniform FE, fluorescent powders were sprayed over graphene as an anode screen. The resultant fluorescent monitor showed a uniform image, confirming the honeycomb configuration exhibited a uniform FE current density. The designed Ti-coated VACNT bundle arrays field emitter with honeycomb configuration could provide a useful platform for FE applications.

2. Materials and methods

Eagle^{2000} glass, 20 mm × 10 mm × 0.8 mm in size, was used as the substrate. The substrate was cleaned using ethanol in an ultrasonic cleaner. A honeycomb pattern 2 μm in width and 5 μm in diameter was developed onto the glass substrate using a standard photolithography process. An Al buffer layer (5 nm) and Fe catalyst layer (3 nm) were coated on the glass substrate using electron beam (e-beam) evaporation. VACNTs with a honeycomb configuration were then synthesized onto the glass substrate using TCVD. The Fe/Al/glass substrate was placed into a quartz tube furnace, with the base pressure about 4×10^{-2} Torr. The glass substrate was annealed at 700 °C for 60 min to form Fe catalyst nanoparticles. Acetylene (C_2H_2) was introduced into the TCVD system for 15 s at a working pressure of 2 torr to grow the 3.5 μm length VACNTs onto the glass substrate as a FE cathode. Ti film with a work function of about 4.3 eV was coated onto the honeycomb VACNT bundle array to enhance FE performance using e-beam evaporation to lower the threshold electric field (Eth). E-beam evaporation system is used in coating Ti metal with the slowly coating rate and rotating holder, which can coat Ti film onto VACNTs bundle arrays homogenously and avoid shadow effects possibly. Ti film was coated onto the VACNTs at thicknesses of 2, 10, 15, and 20 nm, measured using a film thickness gauge in an e-beam evaporation system.

The VANCT surface morphology was observed using scanning electron microscopy (SEM). The internal VACNT and graphene structures were observed using transmission electron microscopy (TEM). The quantitative and qualitative elemental analyses of the Ti film and VACNT were compared using an energy dispersive spectrometer (EDS). Raman spectroscopy was used to examine the structural characteristics of the VACNT and graphene.

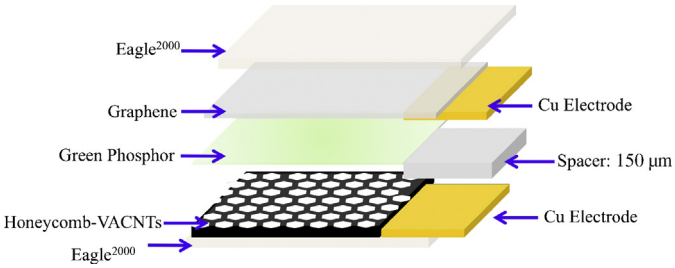

Fig. 1. A schematic drawing of the field emission measurement set-up.

To fabricate the field emitter anode, graphene was used as the electrode material and synthesized onto Cu foil at a size of 20 mm × 10 mm using the TCVD system. A mixed gas that included argon (200 sccm) and hydrogen (4.5 sccm) was introduced into the TCVD system during the annealing process. The Cu foil was annealed at 1000 °C for 60 min. Hydrogen was used to clean the Cu foil surface simultaneously, followed by introducing methane (CH_4) into the quartz tube for 10 min to synthesize graphene onto the Cu foil. After the graphene was synthesized onto the Cu foil, the Cu foil was then etched using $FeCl_3$ solution. The synthesized graphene floated on the $FeCl_3$ solution and was scooped up onto the glass substrate. Phosphor powders were then sprayed uniformly onto the graphene surface as the anode. The chemical composition of the green phosphor powder is $BaMg_2Al_{16}O_{27}$:Eu. The current density-electric field (J–E) curve was measured using a high-vacuum system in parallel electrodes at about 5×10^{-7} Torr. The gap between the anode and cathode (VACNTs) was 150 μm. Because VACNTs in a honeycomb configuration are connected with each other, only a conducting wire is needed to connect to the cathode edge to measure the FE properties. Fig. 1 shows a schematic drawing of the FE measurement set-up. A fluorescent screen was monitored to verify the FE uniformity of the formed field emitter.

3. Results and discussion

Graphene was used as the anode. Fig. 2(a) shows a TEM image of the synthesized graphene. It shows that the graphene exhibited 10 layers and the spacing between adjacent layers was about 0.34 nm. The corresponding Raman spectrum is shown in Fig. 2(b). The 2D band, which could be used to estimate the graphene layers, was fitted with sub-bands matching the number of graphene layers (inset of 2(b)) [16]. According to A.C. Ferrari et al. and L.M. Malard et al. [17,18], the number layers of graphene were identified by corresponding Raman spectrum of 2D band. Multi-layer graphene exhibits the highly oriented pyrolytic graphite (HOPG) properties with increasing graphene layers. There are two small peaks which were fitting from 2D band. Besides, comparing with the study of 2D band by L.M. Malard et al., the full width at half maximum (FWHM) of 2D band we obtained was larger than their result, which indicated that our graphene has more than 4 layers at least. Therefore, the Raman spectrum result is consistent with TEM image of graphene. The G band demonstrated the graphitization of graphene [16]. The indistinct D band, originating from the second-order Raman scattering, presented some defects on the graphene [14].

Fig. 3(a) shows the SEM image, demonstrating that the CNTs were successfully grown onto the glass substrate. The CNTs grew vertically aligned to the glass substrate, with a height of about 3.5 μm, and the inter-tube distance of the honeycomb