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Field electron emission properties of vertically aligned carbon nanotubes deposited on a nanostructured porous silicon template: The hidden role of the hydrocarbon/catalyst ratio

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ABSTRACT

We report the observation of the field electron emission (FEE) of vertically aligned carbon nanotubes (VACNT) arrays grown on a nanostructured porous silicon template (NPSiT). VACNT were synthesised by a simple method using modified floated carbon source-catalyst in a two-stage hot filament thermal chemical vapour deposition system. Ferrocene was used as a catalyst in varying amounts from 0.3 to 0.8 g. An optimised NPSiT was used during the synthesis of VACNT. The surface morphology, lattice defects and graphitic structure of VACNT were analysed using a field emission scanning electron microscope and a high-resolution transmission electron microscope. The FEE performance of VACNT as synthesised is significantly affected by the hydrocarbon/catalyst ratio. The turn-on field required to extract a current density of 0.01 mA m^{-2} was 2.80 V μm^{-1}. The threshold field corresponding to a current density of 0.1 mA m^{-2} was 3.30 V μm^{-1}. The maximum current density of 1.2 mA m^{-2} was detected from a sample exhibiting optimum growth conditions. The emission stability and field enhancement factor β are also discussed in this paper.

1. Introduction

From theoretical and experimental studies, we know that carbon nanotubes (CNT) are an extraordinary material. CNT are commonly described as a sheet of graphene rolled into a seamless cylinder with a high aspect ratio. Since the landmark paper by Iijima that reported trials of a novel 1-dimensional (1-D) carbon nanostructure in the early 1990s [1], carbon nanotubes have attracted scientists, the business community and even the general public. Numerous studies have shown that CNT possess many extraordinary chemical, physical, electronic, and thermal properties [2–4]. Consequently, CNT have been proposed for use in many potential commercial applications including as electron field emitters [5,6], additives in lubricant [7,8], gas storage media [9,10] and many other fields. These applications have been pursued vigorously [11,12]. In next-generation display technology, CNT may be used as bright elements to produce perfect visual displays, such as high-definition flat panel displays, flexible-thin-paper displays and others.

A tremendous effort has been made to control the structure and characteristics of CNT by adjusting parameters such as their carbon precursors [13,14], the methods and apparatus used for their generation [15,16], the selection of a catalyst support [17,18], carbon and gas feeding rates [19,20] and other factors [21,22]. From the point of view of applications, a method to simply synthesise well-ordered arrays of VACNT is highly desirable. Chemical vapour deposition (CVD) methods (under certain conditions) are capable of producing better vertically aligned carbon nanotubes (VACNT) than other methods of nanotube production such as arc discharge and laser ablation [23]. It has been suggested that VACNT are easier to obtain when bottom growth occurs during the growth reaction, although VACNT can also be grown through a tip growth mechanism. VACNT consisting of very dense and closely packed CNT grow upwards, away from the substrate surface. This process is known as self-assembly or oriented growth [23]. In certain applications such as FEE, the synthesis of VACNT on a substrate is required. Growing VACNT with specified fine structure elements, including diameter, length, chirality and graphene layers, on a NPSiT is a challenging task. Fundamental questions remain regarding the

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Table 1
Specification of Si wafer used in this experimental work.

Type of Si	*P*-type
Dopant	Boron
Resistivity (Ω cm)	1–10
Crystal orientation	⟨100⟩
Diameter (mm)	100
Thickness (μm)	525 ± 25

hydrocarbon/catalyst ratio process occurring during growth and its suitability for FEE applications.

Recently, several groups have reported the successful growth of VACNT on nanostructured templates. According to previous studies, CNT have the ability to emit cold electrons at relatively low voltages due to their controllable properties such as high aspect ratios, nanometer tip sizes [24], high density and well-ordered orientation [25]. Several groups have reported electron field emission from carbon nanotubes. The first reported field emission (FE) of electrons from isolated single multi-walled nanotubes (MWNT) wax by Rinzler et al. [26], who reported the FE when the nanotube tips were opened. This report was followed by Heer et al. [27], who reported FE from MWNT film. According to Saito et al. [28], CNT possess the following properties that make them favourable for FEE applications: (i) a high aspect ratio, (ii) sharp tips, (iii) high chemical stability and (iv) high mechanical strength. However, approximately 90% of the CNT literature still reports a $\mu A\ cm^{-2}$ order of FE current density, and very few papers report CNT FE above 10 $mA\ cm^{-2}$ operating in ultrahigh vacuum conditions [29–31]. In this paper, we studied vertically aligned carbon nanotubes grown on a nanostructured porous silicon template that emit an FE current density on the order of $mA\ cm^{-2}$ with significant stability over a 3000 s duration.

We systematically investigate the hidden role of the hydrocarbon/catalyst ratio parameter on VACNT synthesis on an NPSiT. By tuning the hydrocarbon/catalyst ratio parameter, we have found optimised conditions for the growth of VACNT that offer better control of the following issues: (i) structural properties, (ii) undesired impurities, and (iii) uniformity and improved FEE performance. These findings enhance our understanding of the structural requirements of VACNT grown on a NPSiT and provide further information on the properties of FEE, including the potential to operate at low voltages, good emission stability and longer emitter lifetimes. We hope this article will provide guidance for future research.

2. Experimental methods and materials

2.1. Preparation of the nanostructured porous silicon template (NPSiT)

A detailed description of the preparation of a NPSiT is reported elsewhere [32,33], and the specifications of the Si wafers used is shown in Table 1. Before beginning our experiments, as a standard process, Si templates were prepared by cutting Si wafers to an area of 20 × 20 mm using a precision diamond cutter. The single-slide polished Si templates were ultrasonically cleaned in a mixture of acetone and methanol in a volume ratio of 1:1 for 5 min at 40 °C, and then thoroughly rinsed in de-ionised (DI) water several times. Si templates were kept at room temperature under controlled ambient (vacuum) overnight to avoid [34] (i) unwanted chemical impurities such as native oxides and (ii) moisture from the environment.

The experimental procedure for the formation of a NPSiT has been presented previously. In detail, the NPSiT was constructed through a custom-made photo-electrochemical anodisation setup, as shown in Fig. 1. The electrochemical-based solution (also known as an electrolyte solution) used in this approach was a mixture of ethanol and concentrated hydrofluoric acid (∼48%) with a volume fraction of 1:1. The photo-electrochemical anodisation setup is composed of a highly acidic resistant polymer such as Teflon, which is subsequently filled with a prepared electrochemical solution. To facilitate anodisation, (i) aluminium foil (serving as an anode) was sealed on the rear side of the Si template to form a good ohmic contact, and (ii) a tungsten electrode (serving as a cathode) was fixed at a 15 mm distance from the front surface of the Si template. An 'o-ring' was placed on the front side of the Si template to ensure that only the selected area was exposed to the electrolyte solution. The etching process was assisted by the illumination of a halogen lamp (120 W) and 20 mA/cm^2 of current density for 30 min. Finally, the NPSiT was rinsed in DI water and blown dry with nitrogen. As a result, the etched surface of the NPSiT appeared 'yellowish' and demonstrated visible light emission under UV light.

2.2. Synthesis of vertically aligned carbon nanotubes (VACNT) deposited on a NPSiT

VACNT deposited on a NPSiT were synthesised using a laboratory-scale method involving a two-stage hot filament thermal chemical vapour deposition (TCVD) system, as illustrated in Fig. 2. The experimental setup/configuration of this approach is described in previous experimental work [35–39]. The samples were prepared by varying the weight of ferrocene used (obtained from Sigma Aldrich) from 0.3 to 0.8 g, while maintaining the weight of camphor oil used at 5 g. The catalyst and the carbon source were placed in separate alumina boats and positioned side-by-side in furnace zone-1. The NPSiT was placed in the centre of furnace zone-2. Zone-2 was heated to 800 °C and was left to stabilise for 10 min, after which it was purged with nitrogen gas (0.05–1.00 L min^{-1}). Then, zone-1 was heated to 180 °C for the precursor vaporisation process. After zone-1 reached the required temperature, the synthesis process continued for 60 min. Nitrogen gas was continuously flowed before, during and after synthesis to prepare an ambient nitrogen environment. Zone-1 was turned off after the synthesis process was complete, and zone-2 was left on for 30 min after the annealing process. The samples were removed for characterisation after the furnaces cooled down to room temperature.

2.3. Characterisation process of VACNT deposited on a NPSiT

A field emission scanning electron microscope (FESEM; Carl Zeiss SMT 40VP) was employed to examine the morphological structure of VACNT. The graphitic and lattice structures of VACNT were examined by a high-resolution transmission electron microscope (HRTEM; JEOL JEM 2100F). To obtain optimal FEE characteristics, FEE measurements were performed in a parallel-plate electrode configuration with stainless steel electrodes (10 × 10 mm sample area), with a cathode-to-anode separation distance of 0.25 mm and in a vacuum environment of 10^{-4} Torr working pressure.

3. Results and discussion

Fig. 4 shows typical field emission scanning electron microscopy (FESEM) top-view images for low and high magnifications of carbon nanotubes with varying amounts of catalyst. The low-magnification images show uniform growth and vertical alignment as the amount of ferrocene increases. The relationship between the growth rate of VACNT and the amount of ferrocene (Fe) used (from 0.3 to 0.8 g with 5 g camphor oil) is shown in Fig. 3. The growth