The rapid growth of vertically aligned carbon nanotubes using laser heating

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Abstract
Growth of densely packed vertically aligned carbon nanotubes (VA-CNTs) using laser-induced chemical vapor deposition with visible laser (\(\lambda = 532\) nm) irradiation at room temperature is reported. Using a multiple-catalyst layer (Fe/Al/Cr) on quartz as the substrate and an acetylene–hydrogen mixture as the precursor gas, VA-CNT pillars with 60 \(\mu\)m height and 4 \(\mu\)m diameter were grown at a high rate of around 1 \(\mu\)m s\(^{-1}\) with good reproducibility. It is demonstrated that the fabrication of uniform pillar arrays of VA-CNTs can be achieved with a single irradiation for each pillar using LCVD with no annealing or preprocessing of the substrate. Here, laser fast heating is considered the primary mechanism facilitating the growth of VA-CNT pillars. Field emission characteristics of an array of VA-CNT pillars were then examined to investigate their potential application in vacuum electronic devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

To make effective use of the unique properties [1] of carbon nanotubes (CNTs) for micro- or nanodevices, it is necessary for the CNTs to be grown in such a way that they fit the requirements of the desired application; for example, as position-controlled, uniform, dense or aligned nanotubes. As a representative alignment form, vertically aligned CNTs (VA-CNTs) [2–4] have been investigated by many researchers due to their scientific importance in understanding CNT growth mechanisms [5–8], and also due to their potential application in biological sensors [9, 10], gecko tape [11, 12], yarning [13], interconnects [14, 15] and vacuum electronic devices such as backlight sources [16], x-ray tubes [17] and field emission displays [18, 19]. To grow VA-CNTs, chemical vapor deposition (CVD) methods such as plasma CVD [19] and thermal CVD [20] have been widely employed, resulting in the successful growth of dense and uniform VA-CNTs; position-controlled growth of VA-CNTs was also achieved using prepatterned catalyst layers [20–22]. Although CVD methods have been successfully applied to the growth of CNTs on solid substrates with high throughput, the position-controlled growth of VA-CNTs using these methods also has disadvantages, such as the necessity of prepatterning the catalyst. Furthermore, it has been reported [22] that amorphous carbon has been deposited over the catalyst-free region of the substrate, which can cause problems in the fabrication and/or operation of CNT-based microelectronic devices. In most CVD growth, annealing the catalyst prior to supplying carbon sources is also undertaken as a means of improving the density of effective catalyst nanoparticles [23–25]; the annealing time has significantly varied among reported studies, ranging from a few minutes to overnight [2, 4, 20, 21, 26].

Laser-induced CVD (LCVD) [27, 28] has been shown to be an effective alternative technique for position-controlled growth of CNTs, with no need for prepatterning or annealing of the catalyst layer [29]. In LCVD growth of CNTs [29–37], a focused laser beam directly irradiates the substrate, enabling the growth of CNTs with intrinsic benefits of localized, fast and single-step processing. For example, Kwok and Chiu [33, 34]
demonstrated the deposition of multi-walled CNTs on fused quartz substrates in open air, and Chen et al [35] reported the growth of uniform dot patterns of multi-walled CNTs using graphite coatings, containing iron nitrate and magnesium nitrate as catalysts, on transparent substrates. Recently, the lateral growth of single-walled CNTs on prepatterned SiO2/Si substrates for bridging metal electrodes [36, 37] and the uniform growth of fine CNT structures of the order of a few micrometers in size [38] were also reported. However, the growth of densely packed VA-CNT pillars with a few micrometers in diameter by LCVD has not been reported until now, though successful growth by chamber CVD was demonstrated years ago [20].

In this work, we report the growth of pillar arrays of densely packed VA-CNTs using LCVD at room temperature, with the diameter and maximum height of individual pillars about 4 and 60 μm, respectively, on a multiple-catalyst layer (Fe/Al/Cr) substrate. The growth of each pillar is completed during a single irradiation period without preheating or annealing of the catalyst, and unlike chamber CVD methods no amorphous carbon is found over the non-irradiated area. Subsequent experimental simulations are carried out to verify the effects of laser fast heating on the observed rapid growth of VA-CNT pillars. The field emission characteristics of these VA-CNT pillars are then demonstrated.

2. Experimental details

A substrate with a multiple-catalyst layer consisting of 2/10/500 nm thick Fe/Al/Cr layers, deposited on 1 mm thick quartz using DC sputtering at the rates of 50/190/713 Å min⁻¹ for the Fe/Al/Cr layers, respectively, was used as the target. The relatively thick Cr layer was deposited as a thermal layer that provides uniformly distributed heat to the upper catalyst layers as the laser beam irradiates this Cr layer [38], whereas the Al layer was added to promote CNT growth because without the Al layer CNTs of only very poor density were produced. Although it was reported that Al assisted the formation of an effective catalyst (Fe) during CNT growth [25, 39], its role in the present substrate configuration requires further research. It should be noted, however, that without either of the Al or Cr layer no VA-CNT pillars could be achieved. The substrate was placed inside a stainless steel chamber and irradiated with a continuous wave Nd:YVO4 laser (λ = 532 nm, TEM00) from the backside, as shown in figure 1. To uniformly distribute the laser energy over the spot, the laser beam (diameter = 2.3 mm) was expanded using a beam expander (10×) and cut off with an aperture (d = 11 mm) to collect the central portion only. The laser beam was then directed normally to the target and focused on the Cr surface with an objective lens (5×). Note that, if the laser beam irradiated from the front side on the Fe layer, the process resulted in the production of graphitic material of poor morphological structure instead of CNTs. The laser spot diameter at the Cr surface was around 8 μm, measured using a knife-edge, and the incident laser power, measured before entering the chamber, varied from 91 to 125 mW (the corresponding irradiance ranges from 1.8 to 2.5 × 10⁵ W cm⁻²). It was measured (by a UV/VIS/NIR Spectrophotometer, JASCO V-565) that the combined reflectance of the Cr and quartz surfaces was about 68%. The experiment was carried out at room temperature; however, the temperature of the irradiated surface or near the laser spot could not be measured due to the small spot size.

To grow CNTs, the growth chamber was first evacuated with a rotary pump to a base pressure of about 10⁻² Torr and then the reaction gas, a mixture of a carbon source gas and hydrogen (H₂), was continuously fed into the chamber at flow rates of 100 and 400 sccm, respectively, which led to a chamber pressure of 100 Torr during the growth. Next, the substrate was irradiated by the laser beam; to fabricate a pillar array, the target was translated in a step-and-irradiation pattern using a precision x–y stage. For this study, acetylene (C₂H₂) was selected as the carbon source, as our tests using methane (CH₄) and ethylene (C₂H₄) as the carbon source resulted in no growth of vertically aligned CNTs. The morphological characteristics and detailed wall structures of the VA-CNT pillars were then examined using a scanning electron microscope (SEM; Hitachi S-4700) and a transmission electron microscope (TEM; JEOL 2010), respectively. The structural information on the VA-CNT pillars and a possible formation of carbonaceous materials over non-irradiated regions of the substrate were further analyzed using a confocal Raman spectrometer (WiTec CRM200) with a 532 nm excitation source under ambient air conditions. The field emission properties of the VA-CNT pillars were measured in a high-vacuum system (base pressure = 10⁻⁷ Torr) with a 10 × 10 pillar array for which the center-to-center pitch between pillars was 50 μm. In the system, the VA-CNT sample and a green phosphor plate formed the cathode and anode, respectively, with a spacing of 200 μm and the applied voltage was gradually increased to about 1400 V. Fluorescence due to electron emission was subsequently observed through the chamber window and recorded using a CCD camera.
3. Results and discussion

The CNT patterns produced using LCVD for growth times of 1, 3 and 15 s are shown in figures 2(a)–(c), respectively, where each pattern was produced by a single irradiation. As shown in figure 2(a), CNTs can be grown within 1 s with no delay for annealing. The average growth rate appears to be about 1 μm s⁻¹, as estimated from the SEM images, though the growth rate during the early stage seems to be somewhat higher. Figure 2(c) presents an example of a VA-CNT pillar with a height of about 15 μm, clearly demonstrating that a straight VA-CNT pillar can be grown normal to the substrate surface. It can also be observed that the CNTs are vertically well-aligned along the pillar except at the top and the bottom; the magnified views of the top, middle and bottom regions of the VA-CNT pillar are shown in figures 2(d)–(f), respectively. The CNTs on the top of the pillar (figure 2(d)) reveal a thicket-like morphology with no preferential growth direction. These morphological features possibly imply that, during their initial growth stage, CNTs grow randomly, but due to their high density and growth rate they immediately turn into a VA-CNT pillar (figure 2(c)) (crowding effects [40]). The VA-CNT pillars grow at an almost constant rate of 1 μm s⁻¹ up to about 60 μm height, maintaining a nearly constant diameter (4 μm), but over which it ceases growing for longer laser irradiation (figure 2(g)). The observed growth rate of 1 μm s⁻¹ is comparable to that of CVD methods [41–43]. The saturation of pillar height is possibly attributed to catalyst poisoning effects [44, 45] considering that the VA-CNTs at the bottom of the pillar (figure 2(f)) appear to have lower density than those in the middle (figure 2(e)) and are less straight.

The primary reason we are able to grow the VA-CNT pillar in figure 2(c) is based on the principle of rapidly growing CNTs on a large number of effective catalyst nanoparticles. In chamber CVD methods, it is known that the catalyst heating rate is a central parameter in CNT growth [46–51], especially in producing effective catalyst nanoparticles. Slow catalyst heating leads to the formation of large catalyst particles through sintering [50, 51], which could then result in the growth of other forms of carbon rather than CNTs, whereas fast heating enhances the generation of small catalyst nanoparticles, providing more active sites for CNT growth [48–51]. In addition, in chamber CVD methods, precursor gases are typically supplied to the chamber after the catalyst is heated to a certain required level, the optimal growth temperature, so that a rapid reaction between the carbon source and catalyst can be achieved. However, the precursor gases in LCVD were supplied to the reaction chamber prior to laser heating. Thus, to facilitate the growth of dense VA-CNTs observed in figure 2, proper laser irradiation of the substrate to induce rapid heating of the catalyst is critical, which then produces a large number of effective catalyst nanoparticles and accompanying rapid chemical reactions between the catalyst and the precursor gases.

To examine the effects of heating rate on the growth of VA-CNTs, growths were investigated based on two temporally different irradiation modes, including: (i) a ramp-heating mode in which the laser power was linearly increased to the power level required for CNT growth, denoted by $P_g$, and equal to 108 mW (2.1 × 10^5 W cm⁻²), gas pressure = 100 Torr, flow rates of C2H2 and H2 = 100 and 400 sccm, respectively.

![Figure 2. SEM images of position-controlled CNTs produced using LCVD with growth times of (a) 1 s, (b) 3 s and (c) 15 s. The magnified images show the (d) top, (e) middle and (f) bottom of the VA-CNT pillar in (c). (g) Variation of the height of VA-CNT pillars with respect to irradiation time. Process condition: laser power = 108 mW (2.1 × 10^5 W cm⁻²), gas pressure = 100 Torr, flow rates of C2H2 and H2 = 100 and 400 sccm, respectively.](image-url)
Figure 3. (a) Illustration of ramp-input power with respect to time (slow heating). (b) SEM image of CNTs synthesized by slow heating. (c) Magnified view of (b). Power: 108 mW (\(2.1 \times 10^5\) W cm\(^{-2}\)).

Figure 4. (a) Illustration of step-input power with respect to time (fast heating). (b) SEM image of VA-CNTs synthesized by step-input power. (c) Magnified view of the sidewall of the VA-CNTs shown in (b). Power: 108 mW (\(2.1 \times 10^5\) W cm\(^{-2}\)).

Figure 5. SEM images of the VA-CNT pillars for different laser powers: (a) 91 mW (\(1.8 \times 10^5\) W cm\(^{-2}\)), (b) 99 mW (\(2.0 \times 10^5\) W cm\(^{-2}\)), (c) 108 mW (\(2.1 \times 10^5\) W cm\(^{-2}\)), (d) 117 mW (\(2.3 \times 10^5\) W cm\(^{-2}\)) and (e) 125 mW (\(2.5 \times 10^5\) W cm\(^{-2}\)). (f) Variation of height and diameter of the VA-CNT pillars with respect to the laser power (growth time = 20 s).

Compared with the results for the ramp-heating case, growing VA-CNTs became possible with the step-heating mode due to the fast heating of the catalyst layer with the laser. The rapid heating of the catalyst with an intense laser light is thought to lead to the generation of small Fe nanoparticles by minimizing the sintering time, thus providing a large number of active catalysts for CNT growth. Therefore, the nucleation and growth of CNTs may have occurred immediately on the active Fe catalyst particles under the fast heating condition, thereby leading to the subsequent growth of VA-CNTs. Supporting this consideration, Li et al. [51] suggested that, once metal nanoparticles nucleated carbon nanotubes, further nanoparticle sintering is repressed; the same situation may have happened to the catalytic nanoparticles for the VA-CNTs grown in this study.

Figure 5 shows the structural variation of VA-CNT pillars for different laser powers ranging from 91 to 125 mW at a growth time of 20 s. At the low laser power of 91 mW (\(1.8 \times 10^5\) W cm\(^{-2}\)), a VA-CNT pillar with a relatively small diameter and height of around 2 and 12 \(\mu\)m, respectively, was obtained as shown in figure 5(a); the diameters of VA-CNT pillars increased almost linearly with respect to increasing laser power (see figure 5(f)). On the other hand, the height of the VA-CNT pillars initially increased with laser power up to about 108 mW (\(2.1 \times 10^5\) W cm\(^{-2}\)), but then decreased for higher
laser powers. The height of the tallest pillar in figure 5(c) was around 20 μm. For the higher laser powers of 117 and 125 mW (2.3 and 2.5 × 10^5 W cm^{-2}) in figures 5(d) and (e), respectively, hollow VA-CNT pillars were obtained; for these powers, the temperature increase at the middle of the laser spot may have been too high for the growth of CNTs. Variations of the outer diameter and height of these VA-CNT pillars are summarized in figure 5(f). Thus, to obtain uniformly filled VA-CNT pillars, the laser irradiance should be limited to below 110 mW (2.2 × 10^5 W cm^{-2}) and a laser beam profile needs to be designed (a top-hat or donut shape rather than a Gaussian one) to produce a uniform temperature over the surface. For the experimental conditions in this work, laser power in the range of 100–110 mW (2.0–2.2 × 10^5 W cm^{-2}) is observed to be optimal for growing tall-and-filled VA-CNT pillars.

Figure 6 presents arrays of VA-CNT pillars fabricated using LCVD. Each pillar was grown by laser irradiation for (a) 5 s and (b) 15 s at a laser power of 108 mW (2.1 × 10^5 W cm^{-2}). Insets show the 10 × 10 array patterns.

Figure 7(a) shows a typical optical microscope image of a 2 × 2 pillar array of VA-CNTs. The Raman spectrum of the VA-CNT pillar in figure 7(b) reveals the three characteristic peaks of typical MWCNTs: the G-band signal at 1590 cm^{-1} as a characteristic of graphite, the D-band peak at 1340 cm^{-1} representing defects in the graphite structures and the G’ band at 2700 cm^{-1}, whereas that of the non-irradiated surface shows no peaks. Three-dimensional Raman mapping data (figure 7(c)) shows that the intensity of the G- and D-band signals are clearly distinguished from the surrounding non-irradiated area, thus demonstrating the high locality of the structures produced. The TEM image of a typical VA-CNT sample in figure 7(d) further verifies the MWCNT structure consisting of many carbon layers as shown in the lower inset. The diameter and wall thickness of an individual MWCNT are estimated to be around 10 and 4 nm, respectively. Dislocations and defects are, however, also observed in the TEM image of the MWCNT. In the low magnification TEM image of the VA-CNTs in the upper inset of figure 7(d), it can be observed that the MWCNT diameters are reasonably uniform.

Figure 8 shows the field emission properties of the VA-CNT pillars (10 × 10 array at a size of 500 μm × 500 μm)
represented by the current density ($J$) versus electric field ($E$) plot. A flat fluorescent screen was used as the anode, which was separated from the cathode (VA-CNT pillar array) by a spacing of 200 μm. The emission-current density was obtained by dividing the measured current by the sum of the cross-sectional areas of the entire pillars ($\sim 1.256 \times 10^{-5} \text{ cm}^2$); for example, the current measured for the 1200 V (6 V $\mu$m$^{-1}$) applied field was 4 $\mu$A, corresponding to a current density of 318 mA cm$^{-2}$. This high current density can be attributed to the small pillar diameters [55, 56] and is considered to be further improved if the fabrication process is optimized and/or post-processing of the CNTs, such as plasma treatment [57], is adopted. The inset in figure 8 shows the fluorescence CCD image of the anode due to the field electron emission of the pillar arrays at the condition of 6 V $\mu$m$^{-1}$, which shows high brightness and uniform emission over the array region.

4. Conclusions

We reported the growth of pillar arrays of densely packed VA-CNTs on a multiple-catalyst layer with a minimum feature diameter of 4 μm and an average growth rate of 1 μm s$^{-1}$ using a single-step LCVD. From growth experiments using fast and slow laser heating of a substrate, it could be concluded that laser fast heating is one of the crucial factors enabling the observed growth of VA-CNT pillars. This method can be easily applied for position-controlling VA-CNT patterns at room temperature, with no need for annealing or catalyst prepatterning. No amorphous carbon is found over the non-irradiated area, supporting the high locality of the process. It is thus considered that these VA-CNT pillars have good potential for vacuum electronic devices.

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References

[34] Kwok K and Chiu W K S 2005 Carbon 43 2571
[37] Xiong W, Xhou Y S, Mahjouri-Samani M, Yang W Q, Yi K J, He X N, Liou S H and Lu Y F 2009 Nanotechnology 20 025601
[46] Harris P J F 2007 Carbon 45 229
[52] Dupuis A C 2005 Prog. Mater. Sci. 50 929