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Sharpening of carbon nanocone tips during plasma-enhanced chemical vapor growth

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Abstract

In situ tip sharpening of vertically aligned carbon nanocones (VACNCs) was demonstrated. VACNCs were synthesized on patterned catalyst dots of 100 nm in diameter using dc plasma-enhanced chemical vapor deposition. The VACNC tip diameter was found to decrease with growth time. This enables synthesis of ultra-sharp VACNCs even for relatively large catalyst dot sizes, which is quite important for practical applications. We also find that for a given set of growth parameters the diameter of the initially formed catalyst nanoparticle determines the maximum length of the growing VACNC. The mechanism of VACNC growth and sharpening is discussed. © 2001 Published by Elsevier Science B.V.

Vertically aligned carbon nanofibers (VACNFs) with conical shape [1], which we refer to as vertically aligned carbon nanocones (VACNCs), are important for various applications including electron field emitters and probes for scanning microscopy, among others. To date, the crucial advantage of using VACNFs [2–7] or VACNCs versus single- or multi-walled carbon nanotubes is the ability to grow them *deterministically* [1], i.e. their position, height, tip diameter, and, to some extent, shape and orientation can all be controlled, and mechanically and electrically reliable contact to the substrate can be established. VACNCs performance (low field-emission turn-on field, high resolution imaging, etc.) in the above applications improves as the tip diameter decreases. The tip diameter is determined by the size of a catalyst nanoparticle formed during the annealing and pre-etching treatment of a patterned catalyst dot [3,5,7]. The nanoparticle size in turn depends on a number of factors, one of which is the size of the initial catalyst dot. In general, smaller catalyst dots produce smaller nanoparticles, and the fabrication of small diameter dots seems to be necessary for the synthesis of ultra sharp VACNCs.

Commercial production of any technology using VACNCs will require large-scale fabrication techniques. Currently, deep ultra violet

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photolithography can produce minimum feature sizes of the order of 100 nm, whereas a tip radius of curvature of the order of 10 nm or smaller is needed. While electron beam lithography (EBL) is capable of producing these feature sizes, throughput limitations prevent it from being an economically viable production process. Therefore, an important question arises: is it possible to produce VACNCs from ~100 nm catalyst dots with tip radii of much smaller size? In the present letter we address this issue and show that indeed it is possible to produce VACNCs of variable length with a tip radius of curvature an order of magnitude smaller than the initial catalyst dot size.

VACNCs were prepared using dc plasma-enhanced chemical vapor deposition (PECVD) in a vacuum chamber evacuated to a base pressure of $\sim 1 \times 10^{-5}$ Torr. In this work 100 nm catalyst dots were produced using conventional electron-beam lithography, although photolithography already is or soon will be sufficient for this purpose. Ni and Ni–Fe alloy catalysts were deposited on a 10 nm thick Ti layer to prevent silicide formation at the growth temperature (700 °C). For PECVD, a mixture of ~60 sccm of acetylene and 80 sccm of ammonia was used. The total gas pressure during the growth was ~3 Torr, and the dc glow discharge current and voltage were 120 mA and ~550 V, respectively. Post-growth imaging of VACNCs was carried out using a Hitachi S4700 high-resolution scanning electron microscope(SEM).

Our experiments on patterned VACNF and VACNC growth showed that for a 10 nm thick catalyst layer the initial nanoparticle size was about 1/3–1/2 of the dot size and the VACNC tip diameter was roughly equal to the catalyst particle size [3]. However, we have noticed that VACNC tip diameter seemed to decrease as the growth time increased. Unfortunately, there is always a size distribution for the nanoparticles formed and hence for the VACNC tip diameters. In addition, the growth process is sensitive to a number of parameters including the geometry of the sample and of the catalyst pattern. Therefore, even though one can always attempt statistical analysis of average VACNC tip diameters from different samples, it is highly desirable to study the same VACNCs at different times in the growth process. Fortunately, we have found that the VACNC growth process can be terminated, the VACNCs imaged, and growth reinitiated. This allows the study of the growth of individual VACNCs as a function of time.

Fig. 1a–e shows a growth sequence of a VACNC as a function of time. The catalyst nanoparticle, and consequently the VACNC tip diameter, become smaller as the growth proceeds (Fig. 1a–c). At some point during the growth process, the VACNC growth in the vertical direction is terminated and the upper part of the VACNC appears to be severely damaged (Fig. 1d,e). Vertical VACNC growth is terminated due to the loss of the catalyst nanoparticle at the tip of

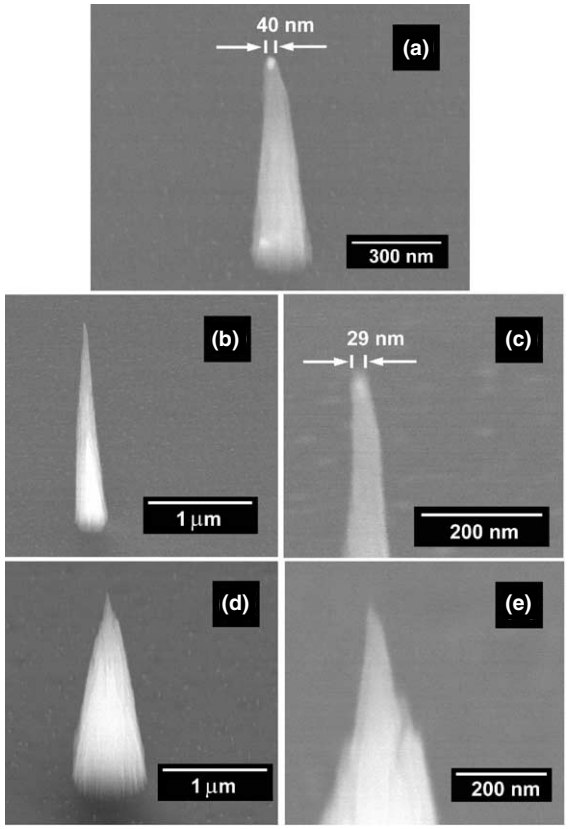

Fig. 1. SEM images of the same VACNC prepared using 10 nm thick Ni–Fe catalyst after total growth time of: (a) 15 min, (b)–(c) 30 min, and (d)–(e) 45 min. Images (c) and (e) are close-ups of the VACNC tip from images (b) and (d), respectively. All images were taken at a tilt angle of ~45°.

the VACNC. We have observed two main mechanisms for the loss of the nanoparticles. First, a nanoparticle can be continuously reduced in size down to zero due to ion sputtering and/or dispersion of the catalyst material within the VACNC during growth. A second mechanism is that a substantial upper part of the VACNC becomes very thin as the catalyst particle size decreases and breaks off from the VACNC base due to intense ion sputtering that can occur at some distance away from the tip [8]. In both cases, the growth in the vertical direction stops but the VACNC tip continues to be bombarded by ions from the plasma, which can lead to its being damaged and etched. We note that despite the fact that vertical VACNC growth is terminated, the lateral growth [1] continues as seen in Fig. 1d.

One consequence of VACNC growth as described above has an implication for the applications that require deterministic production of single VACNCs. In many instances only the VACNC with the largest tip diameter survived a sufficiently long growth process if multiple VACNCs formed from a single catalyst dot. Fig. 2a shows a situation where two VACNCs were initially formed from a single catalyst dot. However, the second VACNC was destroyed during the growth process as seen in Fig. 2b. The second VACNC lost its catalyst particle early in the growth process and its vertical growth was terminated. Consequently, this VACNC was partially etched and completely incorporated into the base of the first VACNC as the lateral growth continued. Despite the possible initial formation of multiple VACNCs, a virtually single VACNC can remain at the end of the growth process. However, this is only true if the vertical growth times of the two VACNCs are vastly different, which requires the diameters of the catalyst nanoparticles to be very different. Thus, it is preferable to have only one catalyst nanoparticle form from each initial catalyst dot.

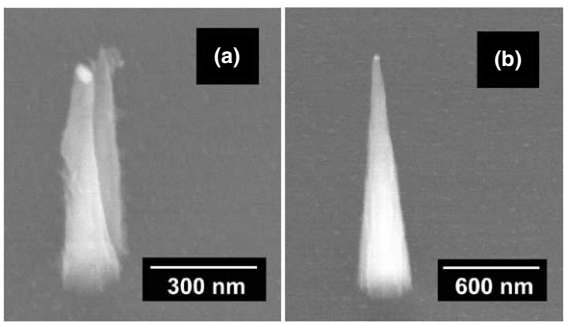

Fig. 2. SEM images showing: (a) formation of multiple VACNCs on a single catalyst dot after 15 min growth time and (b) subsequent transformation into a single VACNC after an additional 15 min of growth (total growth time = 30 min). The presence of the truly single VACNC in (b) was confirmed by observing the structure from different viewing angles. All images were taken at a tilt angle of ~45°.

While the above experiments clearly demonstrate that beneficial sharpening of VACNC tips is possible during the growth process, this phenomenon also places a limit on the length of VACNCs. The vertical growth phase cannot be extended indefinitely. This limitation can be mitigated by forming an initially larger catalyst particle. We note that the VACNC length also will depend on other growth parameters such as growth temperature, pressure, etc., but for otherwise identical experimental conditions, larger particles should yield longer VACNCs.

Formation of larger catalyst nanoparticles is not straightforward. Simply using larger catalyst dot sizes yields multiple nanoparticles rather than one large nanoparticle [3]. Using a thicker (40 nm) Ni–Fe catalyst layer also resulted in formation of multiple nanoparticles for a vast majority of 100 nm catalyst dots. However, the problem can be solved by a proper choice of the catalyst material. In contrast to Ni–Fe, 40 nm thick Ni dots formed single nanoparticles and, consequently, single VACNCs were produced as shown in Fig. 3a. As expected from the deposited catalyst mass considerations, i.e., nanoparticle radius ~(catalyst thickness)$^{1/3}$, a larger (65 nm) nanoparticle was formed for this case as compared to a 40 nm nanoparticle formed from the 10 nm thick Ni–Fe film (Fig. 1a). As a result, the vertical growth was able to continue for longer time (Fig. 3a–e) and consequently a longer VACNC with a sharp tip could be produced (Fig. 3d,e). However, just as in the case of the 10 nm thick Ni–Fe catalyst, if the growth time is too long, the catalyst nanoparticle is removed from the VACNC tip and the vertical growth is terminated (Fig. 3f).

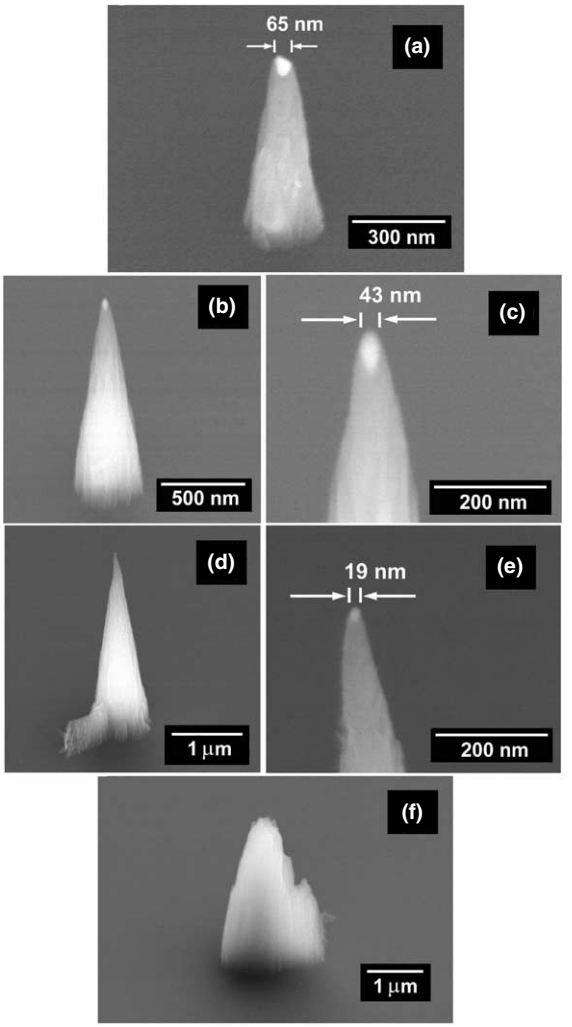

Fig. 3. SEM images of the same VACNC prepared using 40 nm thick Ni catalyst after total growth time of: (a) 15 min, (b)–(c) 30 min, (d)–(e) 60 min, and (f) 90 min. Images (c) and (e) are close-ups of the VACNC tip from images (b) and (d), respectively. All images were taken at a tilt angle of ~45°.

The VACNC length and tip radius of curvature as a function of time for four different VACNCs from the same sample is shown in Fig. 4, where both parameters have an approximate linear growth-time dependence. The error bars are quite small, $< \pm 10\%$, which indicates that good uniformity from one VACNC to another can be achieved. A linear extrapolation of the line in Fig. 4c to zero growth time indicates that the initial radius of the nanoparticle was approximately

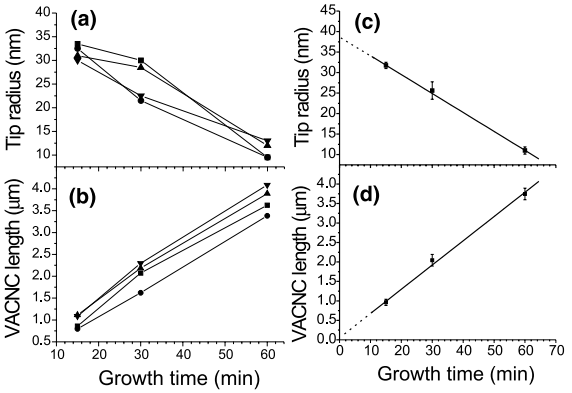

Fig. 4. (a) VACNC tip radius of curvature and (b) VACNC height as a function of time for four VACNCs from the same sample. Averaged values with the error bars for: (c) the VACNC tip radius and (d) height calculated using the data points in (a) and (b).

38 nm. This corresponds reasonably well to the nanoparticle radius (r) calculated from the material's mass conservation: $4/3\pi r^3 = \pi R^2 h$ or $r = (3/4R^2h)^{1/3} = 42$ nm, where $R = 50$ nm is the radius of the catalyst dot and $h = 40$ nm is the Ni thickness. The 'missing' material is probably due to metal interdiffusion and nonspherical shape of the nanoparticle. As can be seen from Fig. 4c, the average VACNC tip radius of curvature at the end of the growth is ~11 nm and for some VACNCs is less than 10 nm. This is within the range of the tip radii of commercial Si tips used in atomic force microscopy. The VACNCs can have even sharper tips by carefully adjusting the growth termination time. Also, if the initial catalyst nanoparticle is made even larger by adjusting the dot size, catalyst thickness, and the type of materials used, synthesis of longer VACNCs can be possible for a given set of the growth parameters, such as plasma power, temperature, gas pressure, ctr.

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