Growth and properties of Si–N–C–O nanocones and graphitic nanofibers synthesized using three-nanometer diameter iron/platinum nanoparticle-catalyst

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Cone-shaped nanostructures of mixed composition (nanocones) and largely graphitic nanofibers were synthesized on silicon substrates using iron/platinum alloy nanoparticles as the catalyst in a direct-current plasma enhanced chemical vapor deposition reactor. The catalyst nanoparticles were monodisperse in size with an average diameter of 3 (±1) nm. The nanocones were produced on laterally widely dispersed catalyst particles and were oriented perpendicular to the substrate surface with an amorphous internal structure. The nanocones were produced by gas phase mixing and deposition of plasma-sputtered silicon, nitrogen, carbon, and oxygen species on a central backbone nucleated by the Fe–Pt catalyst particle. Field emission measurements showed that a very high turn-on electric field was required for electron emission from the nanocones. In contrast, the graphitic nanofibers that were produced when silicon sputtering and redeposition were minimized had the “stacked-cup” structure, and well-defined voids could be observed within nanofibers nucleated from larger catalyst particles.

I. INTRODUCTION

Growth of isolated and vertically aligned carbon nanofibers (VACNFs) is interesting for fundamental understanding of nanomaterial growth mechanisms and for potential practical applications that include field-emission cathodes for vacuum nanoelectronic devices, highly parallel e-beam lithography, cellular membrane mimics, electrochemical probes of viable cells, and scanning probe tips. Extensive studies using a plasma-enhanced chemical vapor deposition (PECVD) process have demonstrated that VACNF growth is highly deterministic in that a single VACNF can be grown wherever an appropriately sized catalyst particle is formed, generally by using e-beam lithography (EBL) for patterning small evaporated catalyst-metal dots, and complete VACNF arrays can be grown at temperatures ~700°C. The wall structure of VACNFs is quite imperfect compared to concentric hollow carbon nanotubes, consisting of disordered layers of sp²-bonded graphitic carbon with a “bamboo-like” or “stacked-cup” cross-section. The individual VACNFs have a tip radius rₐ typically ~15 nm and heights h of a few microns, depending on the growth duration. Arrays of VACNFs with aspect ratios (h/rₐ) >100 have been grown and are moderately good field emitters as measured by a movable-probe method with threshold fields (for 1 nA current) of 12–60 V/μm.
As device size shrinks, however, scaled-down VACNFs with sharp tips are desired. The growth of VACNFs with smaller tip diameters requires catalyst particles much smaller than those formed by the present EBL-patterned evaporation technique. Consequently, we investigated VACNF growth from very small and nearly monodisperse iron-based nanoparticles\textsuperscript{16} that are two to three orders of magnitude smaller in volume than the EBL-patterned catalyst particles previously used.\textsuperscript{17} Here we report results demonstrating that, as the size of catalyst particles gets smaller, graphitic nanofibers still can be nucleated and grown by the direct-current PECVD (dc-PECVD) process, but their morphology and structure strongly depend on their size and the local packing density of the catalyst nanoparticles.

**II. EXPERIMENTAL**

Iron/platinum (Fe/Pt) alloy nanoparticles were produced following the procedures reported by Sun et al.\textsuperscript{16} The nanoparticles dissolved in hexane were spin-coated on a 5-cm-diameter silicon wafer and dried in air. The concentration of the nanoparticles was controlled by dilution such that the average separation between the nanoparticles was about 300 nm. The Fe/Pt alloy nanoparticles have an average diameter of 3 (±1) nm and a composition of ∼75 at.% iron and ∼25 at.% platinum, as determined using energy dispersive x-ray (EDX) analysis. Each crystalline nanoparticle is stabilized by ligands (oleic acid and oleyl amine). The ligands suppress reactions or aggregation of the nanoparticles in hexane. The wafer then was cut into 0.5 × 1 cm pieces and transferred onto the center of a 5-cm-diameter heating susceptor in the dc-PECVD chamber, which was subsequently evacuated down to ∼30 mtorr. During the following heating stage, a flow of ammonia (99.99%) was maintained in the chamber. After the desired temperature was reached (measured using a thermocouple attached to the bottom of the susceptor), a mixed gas flow of acetylene (99.6%) and ammonia was introduced into the chamber. A dc voltage then was applied between the susceptor which acted as a cathode, and an anode located above it, generating a glow discharge to start the growth process. After growth, the substrate was characterized using a high-resolution field emission scanning electron microscope (FESEM; Hitachi S4700, Japan). The growth products also were scratched off the substrate onto holey carbon grids and imaged using a high-resolution transmission electron microscope (HRTEM; Hitachi HF2000, 200 keV).

Cross-section samples were also prepared for HRTEM imaging. Composition information was acquired using scanning Auger microanalysis (SAM; Physical Electronics Phile80 Nanoprobe, Chanhassen, MN). The primary beam energy was 20 keV at 1 nA current, resulting in a probe beam diameter of 150 Å. To obtain bulk composition information, the growth products were in situ sputter-etched using 3.5 keV Ar ions for 1 min. The etch rate was calibrated at 250 Å/min using a standard SiO\textsubscript{2} film. During the in situ sputter etch, the substrate also was rotated at 1 rpm to increase sputter uniformity and minimize redeposition.\textsuperscript{18} Field-emission properties of the nanocones were measured in a vacuum chamber with a base pressure of 2 × 10\textsuperscript{−6} Torr. A tungsten probe with a tip diameter of about 2 μm was used as an anode. The probe position was computer controlled with a minimum step size of 75 nm in the X-Y-Z directions, and the probe-substrate distance was 3 μm, as determined after field emission measurement.

**III. RESULTS AND DISCUSSION**

Figure 1 shows a FESEM image of well-separated growth products taken at 45° tilt angle. The growth conditions are listed in Table I(a). The growth products have a distinctly cone-shaped morphology and are thus called nanocones to distinguish them from VACNFs. They grow perpendicular to the substrate with a smooth outer surface and with the catalyst nanoparticles forming sharp tips (see Fig. 2), except a few with rounded tips that resulted from losing their nanoparticles and subsequent plasma etching. Table I(b) shows the geometrical parameters of the nanocones at the specific growth conditions listed in Table I(a). For comparison, VACNFs have aspect ratios ranging from 150 to 700 and tip cross-section full angles less than 10°.\textsuperscript{15} As Table I(b) shows, the nanocones have smaller aspect-ratio and larger tip cross-section full-angle than typical VACNFs.

Figure 2(a) shows a nanocone that separated from the substrate and is protruding out of amorphous resin introduced during transmission electron microscope (TEM) cross-section preparation. A Fe/Pt nanoparticle is located at the tip of the nanocone so that its diameter defines the tip sharpness. In contrast to VACNFs, the body of the nanocone lacks a hollow core and is highly defective.
Figure 2(b) shows a section of a nanocone with a round tip and no Fe/Pt nanoparticle attached to it. Figure 2(c) shows another nanocone with its base attached to the silicon substrate. Due to its own amorphous structure, it is difficult to distinguish the nanocone from the surrounding amorphous resin, but its base area has a darker contrast than its body. A HRTEM image [Fig. 2(d)] reveals that the dark contrast is caused by a well-crystallized internal silicon cone, whose structure is continuous with the silicon substrate. The composition of the nanocone, as revealed by SAM in the next paragraph, may further contribute to the contrast difference between the crystalline internal silicon cone and the amorphous nanocone body.

Table II shows composition information acquired using SAM from an as-received nanocone (about three times as large as those shown in Fig. 1) and after 1 min of sputter cleaning (Fig. 3). Because the Auger analysis technique is surface sensitive, Table II reveals the surface composition information of the nanocone for the as-received material and the bulk composition of the cone following the Ar ion sputter cleaning. The table clearly shows that the majority component of the nanocone is silicon, followed by nitrogen, carbon, and oxygen. The silicon must be from the silicon substrate, which is sputtered and etched during the growth process, since there is no active silicon supply gas. Subsequently, the silicon atoms are re-deposited on the growth structure. The silicon substrate etching is further supported by the observation of the silicon cone formed beneath the nanocone [see Figs. 2(c) and 2(d)] since the nanocone behaves like a physical mask, shielding the area it covers from etching during the growth process. The relative compositions of nanocone between the surface and the bulk, however, are different. The surface appears to have a richer composition of nitrogen, carbon, and oxygen than the bulk. This is most likely caused by gas-phase deposition of the ammonia and acetylene gas during the period after turning off the dc glow discharge and complete evacuation, which stops the substrate sputtering and, consequently, the silicon supply. The oxygen could be from both leaking during the growth and exposure to the atmosphere when the sample was taken out of the growth chamber.

Growth of nanocones on the silicon substrate has not been observed without the presence of Fe/Pt nanoparticles. In combination with the TEM data, it is clear that the nanoparticles define nucleation and growth sites for the nanocones. The nanoparticles are crystalline after growth, as shown in Fig. 2(e). In the HRTEM image, the nanoparticle is located on an amorphous holey carbon film, and the crystalline structure of the nanoparticle is clearly seen. Our experiments reveal that the Fe/Pt nanoparticles are highly active and can nucleate nanocones even at temperatures as low as 400 °C. However, the growth rate is low, compared with the nanocones grown at 700 °C. These small nanoparticles do not appear to

![FIG. 2. TEM images of nanocones nucleated by 3-nm Fe–Pt nanoparticles dispersed on a silicon substrate: (a) a nanocone with its tip section hanging over a hole, with the inset showing an enlarged view of the nanoparticle; (b) a nanocone with rounded tip due to plasma etching following loss of its nanoparticle; (c) a nanocone attached on the silicon substrate; (d) the base region of the nanocone in (c); and (e) a catalyst nanoparticle on an amorphous carbon film after nanocone growth.](image)

TABLE I. (a) Growth conditions of the sample in Fig. 1; (b) geometrical parameters of the corresponding nanocones surveyed over ten nanocones. A value of 1.5 nm is used as the tip radius.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>C₂H₂/NH₃ flow rate (sccm)</th>
<th>Current (mA)</th>
<th>Growth time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>3</td>
<td>30/80</td>
<td>100</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Height (nm)</th>
<th>Base diameter (nm)</th>
<th>Ratio of height/tip radius</th>
<th>Ratio of height/base radius</th>
<th>Tip cross-section full angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>163 ± 9 nm</td>
<td>47 ± 3 nm</td>
<td>109 ± 6</td>
<td>7.0 ± 0.4</td>
<td>16.3 ± 0.9</td>
</tr>
</tbody>
</table>
TABLE II. Surface and bulk composition of a nanocone in atomic percent, determined by scanning Auger microanalysis at a location near the center of a nanocone.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Surface</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>42.39</td>
<td>79.78</td>
</tr>
<tr>
<td>N</td>
<td>20.84</td>
<td>10.94</td>
</tr>
<tr>
<td>C</td>
<td>18.37</td>
<td>5.48</td>
</tr>
<tr>
<td>O</td>
<td>18.40</td>
<td>3.80</td>
</tr>
</tbody>
</table>

![SEM image of a nanocone taken at 45° tilt after 1 min sputter cleaning.](image)

break down into smaller nanoparticles during the heating process; thus one nanoparticle nucleates only one nanocone. Their catalytic properties also are retained even after a growth process is terminated and then restarted.

To understand the growth mechanism, we also used the tip of an atomic force microscope (AFM) as a substrate. The small size of the AFM cantilever facilitates easy manipulation in TEM. The pyramid-shaped tip provides edges that can be used as a platform to hold catalyst particles. The wedge-shape of the tip also reduces redeposition of the sputtered silicon on the nanostructures nucleated by the catalyst particles. Concentrated solutions of the Fe–Pt catalyst particles were dropped on the tip and formed a dense layer of catalyst particles on the tip surface, further reducing silicon substrate etching by reducing substrate exposure. As a result, the influence of the substrate sputtering and redeposition was minimized. At the same time, the closely packed Fe–Pt nanoparticles tend to agglomerate into a variety of larger particles at elevated temperature during (or preceding) the dc-PECVD growth, so the dependence on catalyst particle size could be observed. Figures 4(a)–4(c) show TEM images of the nanofibers nucleated by Fe–Pt nanoparticles with different sizes. These images clearly indicate that the catalyst nanoparticles are located at the tips of the nanofibers. These nanofibers are composed of graphitic planes with “cup-like” morphology, which are stacked along their growth axis. For comparison, Fig. 4(d) shows a nanofiber structure nucleated by a pure iron nanoparticle.

The large catalyst particles in Fig. 4 have a “pear” or “tear-drop” shape with their pointed end toward the direction of graphite precipitation, but the small catalyst nanoparticles are nearly round. The graphitic planes in all the nanofibers have curvature similar to their corresponding catalyst particles. Central voids in the carbon fibers can be seen and become more visible in the larger nanofibers nucleated by a 15-nm-diameter Fe–Pt nanoparticle and by a 23-nm-diameter Fe nanoparticle. It has been suggested that the bamboo-like structure is formed when the catalyst particle is pushed upward out of its graphite sheath to the top of the tube by carbon precipitation and thus leaves voids in the structure. This abrupt movement of the catalyst particle has recently been observed via time-resolved in-situ TEM. Our results suggest that the abrupt movement of the catalyst particle and the subsequent void formation are dependent on the size of the catalyst particles: the size of the void increases with that of the catalyst particle. A possible explanation for this is that the stress built up between the catalyst particle and the precipitated graphite is larger for the large catalyst particle; consequently the catalyst particle jumps a larger distance, resulting in a larger void.

The above observations show dramatic differences between the structures due to the influence of silicon substrate etching and redeposition. In an experiment similar to that above but without acetylene present, nanocones were not observed after growth, suggesting that silicon from substrate cannot produce vertical growth and carbon is required for the vertical growth of the nanocone structure. We believe that carbon atoms diffuse through or upon the catalyst nanoparticle and precipitate in graphitic form, accounting for the vertical growth of both nanocone and graphitic nanofiber. However, silicon redeposition and ion bombardment have a strong impact on the graphitic structure during nanocone growth, eventually destroying its crystalline nature. With other elements (N, O) from the gas phase, this surface deposition results in the amorphous structure and cone-like morphology, accounting for the lateral growth of the nanocone structure.

Previous studies revealed a strong influence of the $\text{C}_2\text{H}_2:\text{NH}_3$ ratio on the growth of the carbon nanofibers, which changed from cylinder-like to cone-like morphology with increasing $\text{C}_2\text{H}_2:\text{NH}_3$ ratio. This observation also was explained as a result of competition between vertical growth and lateral growth; the dominance of lateral growth from carbon deposition at high $\text{C}_2\text{H}_2:\text{NH}_3$.
ratio resulted in cone-shaped morphology. Although silicon substrate etching was also observed and silicon was found in the carbon nanofibers structures due to the large catalyst particles and consequently large carbon nanofiber length (a few micrometers), the influence of silicon on the growth morphology was not considered. However, as reported here, nanocones are observed at low C$_2$H$_2$:NH$_3$ ratio (10:80 sccm), strongly suggesting that, as the size of the catalyst particles is reduced, silicon etched from the substrate has a dramatic influence on the morphology, structure, and consequently properties of the nominally carbon nanofiber growth.

Figure 5 shows a current–voltage characteristic of electric field emission measurement on the nanocones, while the inset is a Fowler–Nordheim plot showing a linear behavior indicative of a field emission process. The turn-on voltage for 1 nA current is 270 V/μm, obtained by dividing the applied voltage between the nanocones and the probe anode by their separation. To understand the field emission behavior, field emission simulations were performed using the Lorentz 2D software (Integrated Engineering Software, Inc., Winnipeg, Canada). The simulation gives a turn-on voltage of about 60 V/μm for a pure graphite emitter with dimensions taken from Table I and our measurement conditions, which is much lower than the experimental value for nanocones. However, the calculation is consistent with the field emission behavior of truly graphitic VACNFs of this shape. This is believed to be a direct consequence of the insulating nature of the Si–N–C–O composition of the nanocones, causing high local field required for field emission.

IV. CONCLUSIONS

In summary, cone-shaped nanostructures have been nucleated and grown using 3-nm-diameter Fe/Pt alloy catalyst nanoparticles with high lateral separation on silicon substrates. The nanocones grow perpendicular to the substrate surface and have uniform geometries with a smooth outer surface and the catalyst nanoparticles located at their tips. The silicon substrate is etched during nanocone growth and the resulting Si flux supplies the main component of the nanocone’s composition. On the other hand, graphitic nanofibers are grown using the Fe–Pt catalyst particles as silicon sputtering and redeposition is minimized. The conical shape of the nanocones is thus formed by gas phase deposition of amorphous Si–N–C–O on a core nucleated by the catalyst particle during its growth. However, the nanocone has an amorphous internal structure due to the damaging impact of ion bombardment and silicon deposition during growth. Field emission measurements show that a large turn-on electric field is required for the nanocones to emit electrons.

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REFERENCES


