Controlled Growth of Carbon, Boron Nitride, and Zinc Oxide Nanotubes

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Invited Paper

Abstract-Nanotubes represent a unique class of materials in which all atoms are located near the surface. Since electrons flowing through nanotubes are confined near the surface, nanotubes are attractive for sensing biological and chemical molecules. In addition, their tubular structures enable nanofluidic devices that are useful for novel sensing applications. In this paper, we will discuss current applications and the latest advancements on the growth of carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs), and ZnO nanotubes (ZnONTs). First, CNT growth is highly controlled by regulating the effective catalysts and the dissociative adsorption of the hydrocarbon molecules during chemical-vapor deposition growth. Second, we have achieved low temperature growth of vertically aligned BNNTs at 600 °C, the first success of growing pure BNNTs directly on substrates at temperatures about half of those reported so far. Finally, we have developed an original approach for growing ZnONTs without catalyst or template. Robust, controllable growth techniques for nanotubes are necessary in order to fully realize their sensing potential.

Index Terms—Biomedical transducers, chemical transducers, nanotechnology.

I. INTRODUCTION

THE advent of nanomaterial growth has revealed countless new structures and possibilities for sensing technologies. Of particular importance for sensing are nanotubes, a class of materials in which all atoms in a structure are located near the surface. Since current flowing through a tube must take place so close to the surface, nanotubes should have incredible sensitivity when used for sensors. Carbon, boron nitride, and zinc oxide nanotubes have been demonstrated to have properties desirable for application in sensing, but in order to get the most out of the materials, their growth has to be understood and controlled. These three types of nanotubes will be discussed in detail.

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II. CARBON NANOTUBES

A. Overview

The discovery of carbon nanotubes (CNTs) [1] garnered much attention due to their properties, including superior mechanical strength, high electrical and thermal conductivity, and high chemical stability [2], [3]. These properties, together with their size and tubular structure, make CNTs ideal and versatile components for sensing applications. CNTs are a relatively mature nanomaterial and have already been demonstrated in many kinds of sensors.

For example, CNTs' flexibility, high aspect ratio, and extremely small diameter make them perfect modified probes for chemical atomic force microscope (AFM) studies. Wong *et al.* shortened multiwalled carbon nanotubes (MWCNTs) by oxidation, simultaneously forming carboxyl groups at the opened ends. Carboxyl groups can be used to further functionalize the tips and are readily modified in many ways, leading to large sensing possibilities. Mounting these modified MWCNTs to an AFM cantilever tip creates a probe that can elastically bend to protect delicate samples, can access trenches on samples, and shows chemical selectivity. Wong utilized this functionalized MWCNT probe to analyze a patterned self-assembled monolayer (SAM) substrate, demonstrating a measured phase difference between the two different SAM regions on the sample in tapping mode [4].

Lin et al. also put the aspect ratio and small diameter of CNTs to good use by creating arrays of nanoelectrodes for selective and precise glucose detection. In order to fabricate the nanoelectrodes, vertically aligned (VA) CNT arrays were grown on a Cr-coated Si substrate by first electrodepositing Ni catalyst particles and then using a plasma-enhanced (PE) chemical-vapor deposition (CVD) method for CNT growth. In order to preserve the structure and properties of the VA-CNTs, a spin-coated epoxy was applied to a height of half the tube length; the epoxy further served as a dielectric, insulating each tube from its neighbors. Mechanical polishing removed the exposed tube portions, and enzymes were attached to the broken tips using carbodiimide chemistry, ultimately resulting in glucose oxidase (GO_x) functionalized nanoelectrodes. Voltammograms using the arrays were able to preferentially detect hydrogen peroxide, and the high density of electrodes led to a large increase in sensitivity. For an S/N ratio of 3, the limit of detection was 0.08 mM. By functionalizing the CNT nanoelectrodes differently, the array can be easily modified for detection of other chemicals [5].

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Fig. 1. MWCNTs grown at 700 °C by the thermal CVD technique. (a) MWCNT microtowers. (b) Transmission electron micrograph of a MWCNT's sidewalls and channel. (c) Wall of a single MWCNT highlighting the high level of graphitic order.

Field effect transistor (FET) architectures are another possibility for high sensitivity sensors. Besteman *et al.* built FETs using single-walled carbon nanotubes (SWCNTs). The SWCNTs were grown by CVD method on degenerately doped oxide-covered silicon wafers. Gold electrodes with a titanium sticking layer were patterned on the ends of semiconducting tubes by electron-beam lithography, forming the source and the drain of a single SWCNT FET. Sensing took place in an aqueous solution which served as the FET's gate. Next, GO_x enzymes were immobilized on the SWCNTs surface through use of a linking molecule. Only 50 immobilized GO_x molecules were necessary to induce a measurable conductance change in a single SWCNT [6].

Further, the GO_x functionalized FET was extremely sensitive to the pH of the solution, suggesting the ability to detect pH changes as low as 0.1 in a nanoscale sensor [6].

CNT-based sensors need not be limited to the external, however. *In vivo* applications have great potential. For example, CNTs can be used as a shuttle for intracellular transport. Kam *et al.* demonstrated that SWCNTs of various functionalities underwent cellular uptake by an endocytosis mechanism. If the CNTs were properly functionalized, they would chemically target cancerous cells, allowing detection and targeted destruction [7]–[9].

In vivo toxicity studies of functionalized CNTs (fCNTs) performed by Singh *et al.* demonstrated that water soluble fCNTs are significantly less toxic than nonfunctionalized tubes, indicating safe use [10]. In the study, CNTs functionalized with diethylentriaminepentaacetic dianhydride and complexed with ¹¹¹In for tracing were injected into mice. The fCNTs were rapidly cleared from all affected tissues through a renal excretion route with a half-life of 3 to 3.5 hours.

B. Growth

As discussed above, each sensor requires CNTs of specific qualities, be it high crystallinity, particular length, diameter, pattern of growth, number of walls, conducting or semiconducting, etc. To achieve these qualities, the thermal CVD method has many advantages over other growth techniques, including high tube order, high growth density, and variable number of walls. Able to use various hydrocarbon sources and grow higher quality CNTs directly on substrates, it is a powerful and versatile approach. The vapor-liquid-solid (VLS) growth mechanism [11] is well accepted for thermal CVD growth. It includes the decomposition of a carbon precursor on catalyst surfaces, diffusion of released carbon atoms into catalyst particles, and their saturation and segregation in the form of nanotubes. However, it does not provide sufficient details on the precursor decomposition on the catalyst nanoparticles, which is of critical importance for maintaining catalyst activity for continuous growth. We proposed a growth model [12] which is a combination of dissociative adsorption of an acetylene precursor [13] and a solid-core VLS mechanism [11]. According to our model, decomposition of acetylene molecules should balance the diffusion of released carbon atoms to the growth sites. Utilizing this growth model has enabled the growth of highly dense, vertically aligned single-, double- and multi-walled CNTs.

Experimentally, thermal CVD growth of CNTs consists of three steps. First, Fe films are deposited on the substrate. Second, the catalyst-coated substrate is annealed at high temperature to transform the continuous Fe film into the Fe nanoparticles that act as the nucleation sites during nanotube growth. The final step is CNT growth by using a carbon precursor gas. In our case, we used pulsed laser deposition (PLD) [12], [14] to deposit the Fe catalyst film and acetylene as carbon precursor. The acetylene was mixed with carrier gases such as Ar, H₂, or N₂. As shown in Fig. 1(a), high density, vertically aligned MWCNTs can be grown in desired patterns at ~ 700 °C. These MWCNTs are highly ordered and tubular in structure as shown in Fig. 1(b) and (c).

SWCNTs and double-walled carbon nanotubes (DWCNTs) can also be grown using the same growth methods as MWCNTs. However, SWCNT and DWCNT growth require very small catalyst particle size (typically 1–3 nm), high formation energy to overcome the strain of the small diameter, and a limited supply of carbon atoms. To fulfill these requirements, the growth is conducted at higher temperatures (\geq 900 °C) and more stable carbon precursors, such as carbon monoxide [15] and methane [16], are often used to control the carbon supply. By optimizing the catalysts and acetylene supply, we have been able to grow ultra high density, vertically aligned SWCNTs and DWCNTs at temperatures as low as 700 °C [17]. For SWCNTs we used an Al/Fe/Mo (10 nm/0.5 nm/0.1 nm) trilayer catalyst and a



Fig. 2. Growth of vertically aligned SWCNTs. (a) SEM of the SWCNT forest. The sample was tilted 45° during imaging. (b) HRTEM image of SWCNTs. (c) Raman spectrum of SWCNT forests.



Fig. 3. Growth of vertically aligned DWCNTs. (a) Scanning electron micrograph of the DWCNT forest. The sample was tilted at 45° during imaging. (b) HRTEM image of DWCNTs. (c) Raman spectrum of DWCNT forests.

gas mixture of acetylene (10 sccm) and hydrogen (120 sccm). A scanning electron microscope (SEM) image of SWCNTs is shown in Fig. 2(a). The tubes were approximately 170 μ m long in 10 minutes of growth time. The sample consists of almost 100% pure SWCNTs, as is evident in the high resolution transmission electron microscope (HRTEM) image, Fig. 2(b). The diameters range from 0.9 to 2.25 nm as calculated by using the relation [18]

$$\omega(cm^{-1}) = \frac{248}{d(nm)}$$

where ω is the wave number of the Raman shift and d is the diameter of the nanotubes. The SWCNTs' characteristic radial breathing modes and splitting in the Raman spectra are shown in Fig. 2(c).

The growth of DWNCTs was obtained by increasing the supply of acetylene from to 50 sccm and doubling the thickness of the Fe and Mo layers. An SEM image of DWCNTs is shown in Fig. 3(a). These DWCNTs are up to 16 μ m long in one minute of growth. As estimated by HRTEM, these samples contained ~80% DWCNTs with the remainder of the tubes SWCNTs and MWCNTs. The diameters can be as large as 4 nm [Fig. 3(b)], with possible radial breathing mode signals at a Raman shift < 70 cm⁻¹, which are beyond the detection limit of our spectrometer (100 cm⁻¹), as shown in Fig. 3(c). Amorphous carbon was detected at the sidewalls of these DWCNTs which could have contributed to a strong D peak as compared to that in SWCNTs.

The vertical alignment of CNTs described so far is due to the van der Waals forces between the adjacent CNTs [14]. For some devices, individual CNTs that can be vertically aligned are desired as the nanoelectrodes [5] or vertical interconnects. This type of CNT is sometimes referred to as carbon nanofiber due to their relatively disordered structures. Controlled growth of these CNTs can be achieved by plasma-enhanced chemical–vapor deposition (PECVD). In our experiments, we demonstrated that a dual radio frequency PECVD technique [19] provides control over MWCNT diameter and length [20].

A dual RF-PECVD chamber setup consists of two watercooled electrodes each with an RF plasma source generating its own plasma. The top plasma provides control over the primary carbon source gas decomposition, while the bottom provides separate control over substrate biasing. The top plasma is operated in RF mode by adjusting the RF plasma power on the top source; the bottom electrode is an operated dc biasing mode. Precise adjustment of gas flow into the chamber is achieved through the use of a mass flow controller.

MWCNT diameter can be controlled by the adjustment of several parameters, most importantly catalyst thickness. The thickness of the Ni films can be prepared with precision down to the Angstrom level and is responsible for determining the rough size of the catalyst particles formed during growth. At optimum conditions, vertically aligned MWCNTs with uniform diameters can be obtained as shown in Fig. 4.

The catalyst particles serve as the growth sites for the CNTs and remain on the tube tips after growth, as in Fig. 5. As shown, the structural order of our MWCNTs is reasonably high and



Fig. 4. SEM image of MWCNTs grown by the dual RF-PECVD method.



Fig. 5. TEM image of a MWCNT grown by the dual RF-PECVD method. It is characterized by high graphitic order and low amorphous deposition on the walls is evident. The dark region is the Ni catalyst particle.

comparable to those CNTs grown by our thermal CVD. A finer diameter control can also be achieved by adjustment of heater temperature and substrate biasing [20].

MWCNT length is controlled by the duration of the growth. Since PECVD growth is much slower than thermal CVD, the relatively short tubes produced by PECVD are structurally stable enough to remain vertically aligned, an essential trait for many sensing architectures.

In summary, CNTs can be readily grown as SWCNTs, DWCNTs, MWCNTs, vertically aligned forests, and patterned arrays of microtowers. The properties and versatile growth control of CVD grown CNTs makes them readily usable for sensor application.

III. BORON NITRIDE NANOTUBES

A. Overview

Another nanomaterial with sensing potential is boron nitride nanotubes (BNNTs). BNNTs are similar to CNTs in that they are chemically inert. First grown in 1995 [21], BNNTs possess uniform electronic properties: a wide band gap of \sim 5.5 eV regardless of diameter and chirality [22]. In addition, BNNTs are resistant to oxidation up to 800 °C [23], possibly up to 1100 °C [24], and have excellent piezoelectricity [25], [26] and potential hydrogen storage capability [27]. Carbon doping of BNNTs can change the electronic structure, thereby allowing band gap tuning of BNNTs [28]. These properties make BNNTs well recognized as a complement to CNTs in future nanotechnology and are already under intense investigation.

Zhi *et al.*, for example, has performed investigation into modifying BNNTs for applications. In order to make BNNTs soluble in organic liquids, functionalization was needed. CVD grown BNNTs were wrapped noncovalently with the conjugated polymer poly[*m*-phenylenevinylene-*co*-(2,5-dioctoxy-*p*-phenylenevinylene)] (PmPV). This wrapping was accomplished by dissolving PmPV in a solution of BNNTs and chloroform and sonicating for 2 hours at room temperature. The resulting tubes were shortened by the sonication but were soluble in many organic solvents. The strong adhesion of the wrapping is due to noncovalent $\pi - \pi$ interactions between polymer and BNNT and does not affect the band gap [29].

Further work by Zhi investigated covalent functionalization of BNNTs. The approach was based on reactions between the COCl group on stearoyl chloride and the amino groups on the BNNTs. Fourier transform infrared (FTIR) spectra revealed significant differences in the electronic states of the original and functionalized tubes. Cathodoluminescence (CL) and ultraviolet/visible absorption spectra indicated that the long alkyl chains may induce drastic band structure changes [30].

Zhi *et al.* continued their investigation by immobilizing proteins on the BNNTs. Immobilization took place by mixing dispersed BNNTs in a dilute protein solution for many hours. After 120 hours, the protein ferritin was confirmed immobilized, and the ferritin density had no dependence on BNNT size. Immobilization time was drastically reduced by first functionalizing the BNNTs with 1-pyrenebutyric acid N-hydroxysuccinimide ester, lowering the necessary mixing time to 24 hours [31].

Computational study of the effects of covalent bonding on BNNT sidewalls indicates that the band gap decreases as the number of concentrations become two- and six-fold. The six-fold case, in fact, shows *no* discernable energy gap. This opens the possibility of functionalizing BNNTs to metallic states, meaning smooth tuning of the BNNT band gap may be possible [32].

B. Growth

While BNNTs show a lot of promise and their use in sensor technology is underway, there is still a long way to go. One of the continuously biggest obstacles is synthesis of pure BNNTs in bulk quantities. For the past ten years, BNNTs have been grown through arc discharge [33], [34], laser ablation [35], [36], substitution reactions from carbon nanotubes [37], ball-milling [38], and CVD processes [39], [40]. All the preceding methods require high temperatures (> 1100 °C) and the products are dominated by impurities such as amorphous boron nitride powder and catalyst particles. Post treatment of the product is always necessary to extract the useable BNNTs. Recently, our group reported the synthesis of BNNTs directly on substrate at 600 °C by employing a plasma-enhanced pulsed-laser deposition (PE-PLD) technique [41].



Fig. 6. SEM images of BNNT bundles grown directly on a substrate.

The PE-PLD system is composed of an ultra-high vacuum stainless steel chamber and a fourth harmonic generation of a Nd: YAG laser. The process begins with depositing a 12.5 nm Fe film atop an oxidized silicon substrate at room temperature by PLD in vacuum; the thickness is controlled by an in situ monitoring system. The Fe coated substrates are then installed on a heater and sealed inside the vacuum chamber at a base pressure of 2×10^{-2} mbar. The substrates are heated and maintained at 600 °C by a pyrolytic BN heater. Plasma is generated on the substrate surface for 10 minutes by an RF generator (13.56 MHz) that is capacitively coupled to the steel substrate holder, inducing a negative dc voltage on the substrate. During these 10 minutes, Fe nanoparticles are produced on the substrate surface. BNNT deposition is initiated by focusing the laser beam on a high purity hexagonal BN target causing the BN vapor to propagate toward the substrate positioned near the target surface [41].

SEM reveals the BNNTs grown tend to form vertical bundles, as shown in Fig. 6. As clearly indicated by the bases of these bundles, multiple BNNTs are held together at their tips. TEM was used to indicate the microstructure of BNNTs; long, straight, tubular structures were detected (Fig. 7). As shown, some of these BNNTs are still held together but can be easily dispersed by sonication. The PE-PLD produced tubes are made of highly ordered hexagonal phase shells with intershell spacings of 0.33 nm. Furthermore, Fe particles are not found on these BNNTs, indicating a base growth mode.

High purity synthesis of BNNTs directly on substrate has been achieved by PE-PLD at low temperature (600 $^{\circ}$ C). These results encourage future sensor work with BNNTs.

IV. ZINC OXIDE NANOTUBES

A. Overview

Nanotubes composed of oxide and nitride materials are particularly interesting not only due to their tubular structure, but also their hydrophilic natures and wide energy band gaps. Nanotubes of these varieties have led to exciting applications including photochemical cells [42], nanofluidic transistors [43], and DNA sensors [44], all of which have been demonstrated. The DNA sensors using silica nanotubes are based on the FET



Fig. 7. TEM images of PE-PLD grown BNNTs revealing these tubes are highly ordered hexagonal BN shells.

architecture and, theory indicates, could prove sensitive enough to detect single biomolecules, something even the mature CNT technology cannot provide.

TiO₂ [42], GaN [45], silica [46], and ZnO [47], [48] nanotubes have been synthesized by using a multi-step process with templates or by hydrothermal techniques. Of these materials, ZnO nanotubes (ZnONTs) stand out as having multifunctional properties for optical, electronic, and piezoelectric applications. ZnONTs are expected to accomplish the uses of other ZnO nantostructures for applications at the cutting edge of nanoscale.

B. Growth

A high crystallinity of materials is what leads to optimum physical properties and performance. Thus, growth techniques for single crystal ZnO nanotubes are of the utmost importance. We have experimentally proven the direct growth of single crystal ZnO nanotubes without the use of multiple processes, catalysts, or templates [49]. Direct growth of ZnO nanotubes can be explained by the theory of nucleation and vapor-solid crystal growth. According to the theory of nucleation, the probability of nuclei formation is highest at locations with a maximum number of nearest neighbors. For a flat 2-D growth surface, higher binding energies for growth species occur at the edges [50]. For ZnO it is well known that the c-axis growth rate is relatively faster [51], [52]. At decreased growth temperature, the nucleation probability and surface migration will be suppressed [50]. Therefore, if the growth temperatures are low enough to suppress migration along the 2-D surface of the *c*-plane but high enough to sustain the growth along the *c*-axis, the condensation and growth will be limited at the edges of the c-plane of the ZnO and form ZnO nanotubes.

Utilizing this model, we performed a series of experiments to first start the growth of the *c*-surfaces of ZnO nanorods and then





Fig. 8. (a) Experimental setup used in the thermal CVD growth technique. (b) ZnO nanotubes as-grown on substrate number 4.

decrease the growth temperatures for the formation of the nanotubes. We used a simple thermal CVD technique to grow ZnO nanotubes in a horizontal quartz tube vacuum chamber furnace. Precursor material, a mixture of ZnO and graphite powder, was contained in an alumina boat and placed at the closed end of a small quartz tube as shown in Fig. 8(a). A series of oxidized silicon substrates (numbered from positions 1 to 4) were placed downstream from the mixture in the small quartz tube which was then inserted into the vacuum chamber such that the closed end was at the center of the furnace. The temperature of the furnace was ramped up to 1100 °C in vacuum, introducing oxygen into the chamber when the temperature reached ~ 350 °C. The temperature was held at 1100 °C for 30 minutes and the heater was turned off to allow cooling to 600 °C-700 °C in ~30 minutes. Experiments were completed by further cooling the system to room temperature by opening the heating panel of the furnace. According to a calibration experiment, when the furnace center is at 1100 °C, the temperatures of substrates from positions 1 to 4 are about 700 °C, 600 °C, 500 °C, and 420 °C, respectively. After the completion of the experiment, all samples were examined by SEM.

In all the above experiments, we observed that no coating was formed on the substrate at position 1. ZnO nanorods with sharp tips were grown on substrates at positions 2 and 3. We detected ZnONTs only on substrates at position 4 as shown in Fig. 8(b). The diameters of these nanotubes range from ~ 100 to 500 nm near the opened tips. Some of these nanotubes have a single tubular channel as predicted by theory, though some have multiple channels. Formation of these multichannel nanotubes can be explained by defects on the initial growth surfaces. Steps or vacancies may be formed at locations beyond the edges during the process of nucleation and growth. Growth along the c-axis is



Fig. 9. TEM image of a ZnO nanotube with hollow tubular structure.

accompanied by these processes and thus transforms the single channel nanotubes to multichannel structures.

X-ray diffraction, Raman spectroscopy, and photoluminescence indicate that these ZnONTs maintain the same crystal structures of wurtzite ZnO crystals with lattice constants of a = 0.325 nm and c = 0.521 nm. Fig. 9 shows the hollow tubular tip of a ZnO nanotube by low-resolution TEM. High-resolution TEM images (not shown) indicate that these ZnO nanotubes are single crystals with the growth direction aligned to the *c*-axis of ZnO with lattice spacing of 0.526 nm [49].

We have demonstrated a promising route for growth of single crystal ZnONTs without catalysts or templates by simple conventional thermal CVD techniques. As predicted by the theory of nucleation and vapor–solid crystal growth, ZnO nanotubes were grown on the c-surfaces of ZnO nanorods. In theory, we can minimize the height of these nanorod bases to form nanotubes with longer tubular sections. With further refinement of growth techniques, the ease and control of growth of ZnO nanotubes will make them a continually more promising tool for sensing applications.

V. CONCLUSION

Progress in the growth of nanostructures is vitally important to optimize their application, and we have made strides toward more controllable growth. CNTs are a relatively mature nanotube technology with easy and controllable growth leading to a large variety of applications. BNNTs, similar to CNTs but more robust and with their own unique electronic properties, are a promising candidate for sensing. Traditionally, the difficulty of BNNT growth has led to their limited application. However, we have introduced high density growth methods requiring no purification which should help expand their application. ZnO materials stand out because of their hydrophilic natures and wide energy band gaps. We have demonstrated ZnONTs can be grown in single crystals by conventional thermal CVD methods without the use of catalyst or multistep processes. As the growth condition and parameters become better understood and the growth is refined, they will find more use in novel sensing applications.

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