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CVD Synthesis of Small-Diameter Single-Walled Carbon Nanotubes on Silicon

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Abstract. *A simple process for the chemical vapor deposition of ultra SD single-wall carbon nanotubes has been developed. In this process, an iron nitrate nonahydrate solution in isopropyl alcohol with a concentration of (400 μgr/milt) was used to catalyst nanoparticle formation on an oxidized silicon wafer. The oxide on the substrate was made of a thick layer of wet oxide sandwiched between two thin layers of dry oxide. The process results in semiconducting Single-Walled carbon NanoTubes (SWNTs) with diameters of less than 0.7 nm and more than a 1 ev band gap energy, which are amongst the smallest diameters of SWNTs ever reported.*

INTRODUCTION

Carbon nanotubes are currently the focus of intense research due to their unique properties and potential impact on broad areas of science and technology. The distinctive characteristics of carbon nanotubes arise from their size and atomic structure. For example, a nanotube has high Young's modulus and tensile strength [1] and can be semi-metallic or semiconducting, depending on its chirality and diameter [2]. Utilization of these properties in individual or ensembles of nanotubes has led to advanced scanning probes [3], transistors [4] and electron field-emission sources [5].

An important property of a semiconducting material used for electronic devices is its band gap energy, which in turn determines the electrical properties of the device. A semiconducting carbon nanotube's band gap energy is typically in the order of 0.5 ev, which is low compared to over the 1 ev band gap of common semiconductors. Thus, due to the inverse proportionality of semiconducting nanotubes' band gap to diameter, the synthesis of small diameter SWNTs is desired for many nanoelectronic applications, such as Carbon NanoTube Field Effect Transistors (CNTFETs). In addition, development of controlled synthesis methods to obtain nanotubes with a predetermined diameter, chirality, position and alignment is an important and viable route to potential applications of CNTs. In addition, the most applicable method to control the diameter, and especially the position and alignment of nanotubes, is Chemical Vapor Deposition (CVD). We investigated the CVD synthesis of carbon nanotubes and designed and developed the necessary equipment. In the next step, we modified and adjusted an established process to perform the CVD synthesis of ultra small diameter nanotubes.

EQUIPMENT

The main equipment used is a horizontal gas phase reactor, like many other systems, for the CVD synthesis of carbon nanotubes. The reaction chamber is a quartz tube with a length of 130 cm and diameter of 6 cm (Figure 1). During the growth process, we need to heat the tube up to 750°C and this temperature must be stable and controllable over a distance of a few decimeters in the middle of the tube. In addition, its inside should be isolated from the atmosphere carefully because any oxygen leak can cause an explosion in the tube. Reactants are fed from the gas cabinets

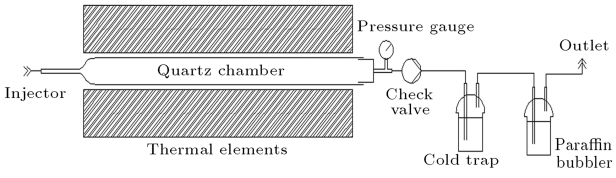

Figure 1. Schematic diagram of reaction chamber.

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through a gas circuit (Figure 2) that controls the flow of each species and provides safety arrangements for using the highly explosive gases. For the CVD synthesis of carbon nanotubes usually, explosive gases are used at a temperature well above their autoignition temperature and safety regulations need to be considered carefully. The most important parts for this are flashback arrestors, which prevent the flashback of gases to the cylinders and the spreading of an explosion. Also, a water bubbler and a paraffin trap are used at the exhaust to cool and neutralize the exhaust gases.

PROCESS

We slightly modified an established easy process for the CVD synthesis of SWNTs [6] to produce SWNTs with the desired diameter. In this process, p-type, $< 111 >$ and polished, silicon wafers were cut to samples of 4 mm $\times$ 8 mm and cleaned using a modified version of standard semiconductor wet cleaning, which was done using the following steps: ultrasonication and then washing by TCE, acetone, methanol, DI water, piranha (H2SO4:H2O2 = 4:1, v/v), DI water, dilute HF solution (%5), DI water, SC1 (NH_4OH:H_2O:H_2O_2 = 1:5:1, v/v), SC_2 (HCl:H_2O:H_2O_2 = 1:6:1, v/v), dilute HF solution (%5), DI Water and drying under N_2 spray. We sandwiched the wet oxide between two layers of thin dry oxides grown on the substrate to have a flat, high quality surface in a short time. For this, we used 15 min of dry oxidation at 1100°C, followed by about 30 min wet and 15 min dry oxidation. Thus, the total thickness of the oxide was determined to be about 500 nm. A solution of iron nitrate nonahydrate in isopropyl alcohol (400 μgr/milt) was prepared. Si substrates were dipped in the solution for 10 sec, rinsed 10 times in n-hexane and dried in air. For CVD, samples were placed in the reactor and heated to 750°C under an argon atmosphere with a flow of 600 sccm. The samples were then annealed for 15 min at 750°C under the flow of argon (600 sccm) and hydrogen (400 sccm). CNT growth was carried out by adding 10 sccm Ethylene for 5 min. Then, the hydrogen and ethylene flow was turned off, the reaction chamber was cooled down overnight under the argon flow and the samples were brought out when the chamber temperature was below 200°C.

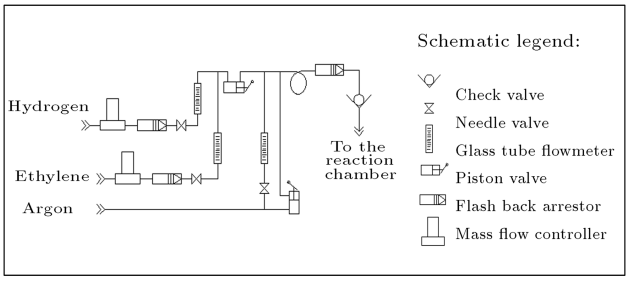

Figure 2. Reactor's schematic diagram of gas circuit.

RESULTS AND DISCUSSION

Some processes based on ferric nitrate nanoparticle formation on silicon dioxide have previously been established to synthesize relatively large diameter (around 5 nm) SWNTs [7]. This study demonstrates the possibility of synthesizing ultra small diameter SWNTs using ferric nitrate catalyst nanoparticles. To achieve this goal, we used a much lower $Fe(NO_3)_3.9H_2O$/isopropyl alcohol concentration and a thick wet oxide sandwiched between two layers of thin dry oxide on the surface of the silicon wafer instead of only wet oxide. In addition, it is essential in this process to cool down grown SWNTs in an inert atmosphere to temperatures below 200°C because ultra small diameter SWNTs burn with oxygen at higher temperatures (the exact burning temperature of a SWNT strongly depends on its defect density and diameter and it is usually between 200°C and 400°C [8]).

Prepared samples were characterized using Atomic Force Microscopy (AFM). For this purpose, we started with a large area scan in an AC mode and continued with low- and high-resolution scans in a DC mode (Figures 3 and 4).

Using high-resolution scans, we can extract the precise values of the carbon nanotube diameter and calculate their chirality vector. Figure 4.b shows various cross- sectional profiles extracted from a typical high resolution scan of the nanotubes. As this Figure demonstrates, their diameter 0.7 nm. Inasmuch as it is proven that the SWNTs' diameter cannot be smaller nm at room temperature. It has been proved theoretically that it is not possible to synthesize SWNTs with a diameter of less than 0.4 nm [9,10], while one can find 0.3 nm thick nanotubes at the most inner layer of MWNTs [11]. Thus, these are some of the thinnest possible single-wall carbon nanotubes, using an iron nitrate solution for nanoparticle formation, which is an inexpensive and useful method for nanoelectronic applications.

The chirality vector of the synthesized nanotubes was calculated from high-resolution scans using the established methods. Figure 4a shows a typical synthesized nanotube, the observed chirality angle of the SWNT is about 43°C (the angle between the parallel lines on the SWNT and the SWNT axle). By applying the correction factors to the image, the accurate angle was calculated to be about 8°C (the correction factor is, $\frac{1}{2}\sqrt{\frac{D}{r+\Delta}}$ where D is the nanotube diameter, r is the AFM tip radius and Δ is the distance between the tip and the nanotube [12]). Using the extracted value of the nanotube diameter (0.69 nm), one can

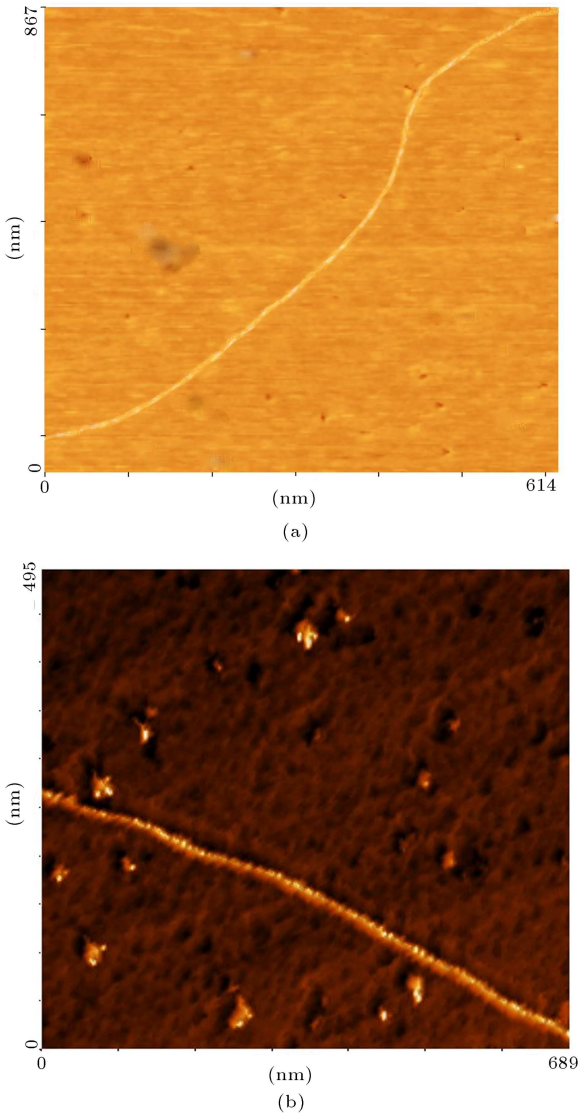

Figure 3. A high resolution scan of the prepared sample. a) A single-wall carbon nanotubes in a topographic image; b) The phase image of a SWNT shows the difference between SWNT and substrate's type of atoms.

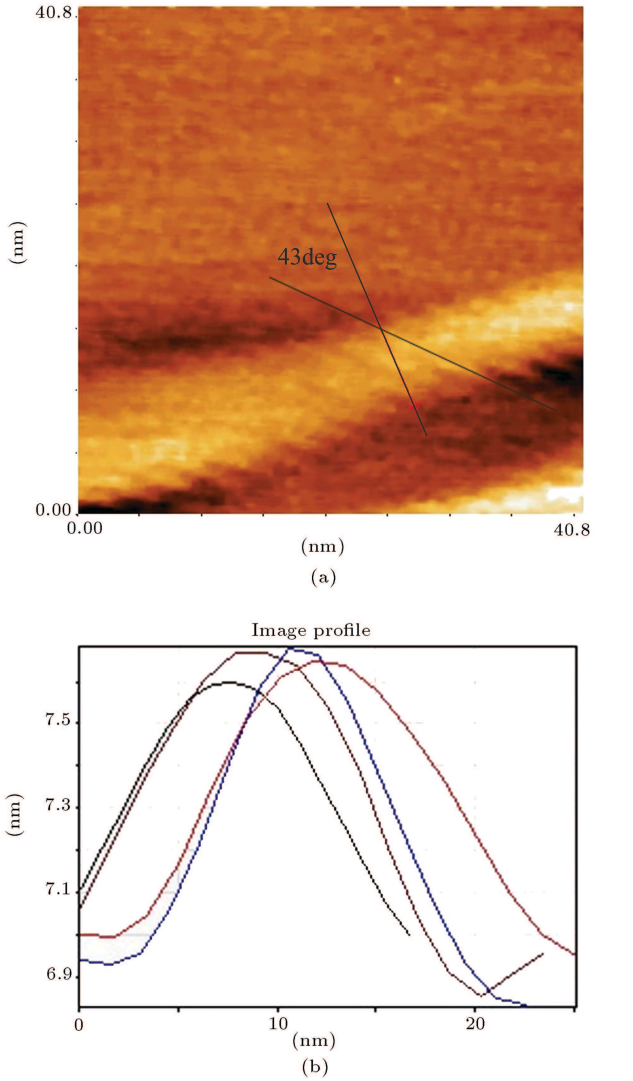

Figure 4. a) A very high resolution scan of a singl-wall carbon nanotube. Chirality and diameter can be extracted from this picture; b) Cross sectional profile of the synthesized nanotubes. The nanotube diameter can be extracted fromt the height of these curves, which is about 0.69 nm. In addition, if we deconvolve the cross sectional curves with the tip profile, we will find the diameter to be about 0.68 nm. Thus, we are sure that the SWNTs have not flattened (maybe due to its small diameter, it is more rigid) and that their diameter is less than 0.7 nm.

calculate the chirality vector that is (9,2). Thus, it is a semiconducting nanotube with a band gap of over 1 ev ($E_g \approx \frac{0.705\text{nm}}{D}$, where E_g is the band gap and D is the nanotubes diameter [13]).

CONCLUSION

A simple method was introduced for the CVD synthesis of ultra small diameter semiconducting Single-Walled carbon NanoTubes (SWNTs). In this method, we placed iron nitrate catalyst nanoparticles on an oxidized silicon substrate, using a dilute solution of iron nitrate nonahydrate in isopropyl alcohol and a thick wet oxide sandwiched between two layers of thin dry oxides. The process was carried out, like common carbon nanotube growth processes, by using ethylene as the carbon containing reactant, hydrogen as the catalyst depoisoner and by paying special attention to the cool-down procedure in order to avoid burning the ultra small diameter nanotubes. It is worth mentioning that if we define the yield of this process as the ratio of the number of SWNTs to the number of nanoparticles, it will be quite low and in an area which was covered by hundreds of nanoparticles, few SWNTs were observed.

Atomic Force Microscopy (AFM) measurements showed that the process resulted in ultra small diameter semiconducting Single-Walled carbon NanoTubes

with diameters of less than 0.7 nm, produced by iron nitrate for the first time. These diameters would correspond to band gap energies of more than 1 ev (as calculated from FM images).

We think that the very low concentration of iron nitrate together with the appropriate surface preparation led to very small catalyst nanoparticles, which in combination with appropriate thermal conditions and gas flow rates resulted in ultra small diameter SWNTs. As discovered, it is also very important to cool down the chamber under an inert ambient to 200°C; perhaps because the very small diameter SWNTs burn so easily at higher temperatures.

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