Poster Session 6

G1

Growth of Half-Meter Long Carbon Nanotubes Based on Schulz-Flory Distribution

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The Schulz-Flory distribution is a mathematical function that describes the relative ratios of polymers of different length after a polymerization process, based on their relative probabilities of occurrence. Carbon nanotubes (CNTs) are big carbon molecules which have very high length-to-diameter ratio, somewhat similar to polymer molecules. CNTs are one of the strongest materials ever known. The extraordinary mechanical properties of CNTs renders them promising candidates for superstrong fibers, ballistic armors, and even space elevators. Mass production of CNTs with macroscopical length is the first step to realize their application. Gas-flow-directed chemical vapor deposition on silicon substrates is the most effective method to prepare ultralong CNTs, and sinificant progress has been made in the synthesis of ultralong CNTs. However, the reported longest CNTs was only 20 cm and the number density of ultralong CNTs is usually lower than several CNTs per 100 μm. Besides, it remains a question why their number density decreases so rapidly and how to synthesize meter-long CNTs. Here, we report that the Schulz-Flory distribution can be applied to describe the relative ratios of CNTs of different length produced with a floating chemical vapor deposition process, based on catalyst activity/deactivation probability. With the optimized processing parameters, we successfully synthesized 550-mm-long CNTs, for which the catalyst deactivation probability of single growth step was ultralow. The as-grown CNTs have perfect structures and extraordinary mechanical properties. They even exihibit superlubricity between their intershells. Our finding bridges the Schulz-Flory distribution and the synthesis of one-dimensional nanomaterials for the first time, and sheds new light on the rational design of process toward controlled production of nanotubes/nanowires.

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G2

On the Nitrogen Doping Mechanism in Small Diameter Single Walled Carbon Nanotubes; Impact on Electronic Properties and Growth Selectivity

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Despite numerous studies on nitrogen doped single walled carbon nanotubes (SWCNTs), the structural conformation and stability of nitrogen functionalities in small diameter SWNTs, and their impact on the electronic and mechanical properties of the SWNTs, is incomplete. We report a detailed study on nitrogen doping in SWNTs with diameters in the range of 0.8-1.0 nm. We show that the introduction of nitrogen in the carbon framework significantly alters the stability of certain tubes, opening for the possibility to selectively grow nitrogen doped SWNTs with certain chirality and diameter. At low nitrogen concentration, pyridinic functionalities are readily incorporated and the tubular structure is well pertained. At higher concentrations, pyrrolic functionalities are formed, which leads to significant structural deformation of the nanotubes, and hence a stop in growth of crystalline SWNTs. By correlating the influence of defined nitrogen functionalities on the electronic properties of SWNTs with different chirality we make precise interpretation of experimental Raman data. We show the double resonance G´-peak can be well-correlated to the type of nitrogen doping of SWNTs originating from the p or n-doping nature of the nitrogen incorporation. Our results are supported by experimental and theoretical data.

G3

Loading of Metal Nanoparticle on Oxidation-free Carbon Nanotubes for Fuel Cell Application and their Durability

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CNT have received a great deal of attention as a supporting material for the electrocatalyst in fuel cell due to their highly graphitized surface. However, in returning to the graphitic structure, CNTs lose the metal loading efficiency compared to carbon black. Generally, CNTs are treated by a harsh oxidative treatment with strong acids, but treatment might weaken their inherent durability. We developed the oxidation-free approach, in which CNT surface was wrapped by polybenzimidazoles (PBI). The wrapped PBI on CNT surface functioned as a binding sites for metal loading and, as the results, uniform platinum nanoparticles were loaded homogeneously on CNT.

G4

Fluidized Bed CVD of Submillimeter-Long Carbon Nanotubes Using an Internal Heat-Exchange Reactor

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Low cost production of carbon nanotubes (CNTs) will open many opportunities for the practical applications such as batteries/capacitors. Fluidized bed chemical vapor deposition (FBCVD) has realized mass production of multi-wall CNTs (MWCNTs) at several hundred tons annually per plant, but such CNTs are short, thick, entangled, and thus less conductive. Large-scale, low-cost production of long and thin CNTs are of highly demanded. We previously developed an original FBCVD and realized semi-continuous production of submillimeter-long few-wall CNTs from C_2H_2 at a high yield 70% and short gas residence time $\sim$ 0.3 s [1]. But the high gas feed causes insufficient heating of the bead bed when scaled up. This time, we designed and developed a new FBCVD reactor having an internal heat-exchange and preheating zone and examined its performance in producing submillimter - long CNTs using a reactor with three-times enlarged cross sectional area.

All processes for catalyst (re-)deposition, catalyst reduction, CNT growth, CNT separation, and removal of residual carbons were performed in a single fluidized bed reactor. All the gases except for the catalyst vapor were fed to the outer tube, flown down and preheated by the furnace and the hot effluent gas in the inner tube, and then flown into the inner tube through the distributor at the bottom. Catalyst vapors (aluminum-isopropoxide and ferrocene, carried by 4 vol% O_2/Ar at 20 slm) were fed directly to the bed through the catalyst line penetrating the distributor from the bottom. After catalyst deposition for 4 min, the catalyst was reduced by flowing 26 vol% H_2/ 0.06 vol% H_2O/ Ar at 9.48 slm for 10 min. CVD was performed by flowing 1.1 vol% C_2H_2/ 26 vol% H_2/ 600 ppmv H_2O/ Ar at 9.48 slm for 20 min. CNTs were separated from the beads by vigorously fluidizing the bed by Ar for 10 min. The residual carbon on the beads was removed by flowing 20 vol% O_2/Ar for 5 min. These processes were repeated at 745 C by changing the gas flow.

The bead bed expanded from 3 cm to 12 cm (Fig. 1d) after CVD for 20 min. The CNT yield was increased from 0.25 to 0.82 g/cycle while CNTs retained the submillimter- long array structure. From the transmission electron microscopy (TEM) analysis, we found that the average diameter of the CNTs is 11 nm. We reduced the total supply of Ar carrier for ferrocene to one fifth and the concentration of C_2H_2 to 0.73 vol%, and realized the diameter reduction to 6.5 nm in average. The FBCVD reactor with the internal heat exchanger will realize further scale-up for practical mass production.

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G5

Quality Control of Electric Arc Single-Walled Carbon Nanotubes

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Reliable and rapid measurement of the material purity is central to the progress in the bulk production and purification of single-walled carbon nanotube (SWNT) materials. This talk will focus on the application of solution phase near-IR (NIR) spectroscopy for evaluation of carbon nanotube purity, sample preparation and homogenation. Other popular analytical techniques for characterization of SWNT materials, including thermogravimetric analysis (TGA), Raman spectroscopy, SEM and TEM will be discussed. In addition to recent advances in the purification of carbon nanotubes, I will talk about the SWNT thin film technology and its prospects for energy applications and optoelectronic devices.

G6

Fabrication of carbon nanotube nanogap electrodes by helium-ion sputtering for molecular contacts

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Carbon nanotube nanogap electrodes have been used as electrodes to contact individual large organic molecules. However, the reliable fabrication of a truly nanometer-sized gap remains a challenge with established techniques [1,2]. Recently, successful patterning of graphene with a helium ion beam was demonstrated [3,4]. We now report on using helium ion beam lithography to sputter a nanogap of only (2.8 ± 0.6) nm into single metallic carbon nanotubes embedded in a device geometry. The high reproducibility of the gap size provides us with a reliable nanogap electrode testbed for contacting small organic molecules. To demonstrate its functionality, we present electrical measurements on an oligo(phenylene ethynylene) molecule, a common type of molecular wire.

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G7

Advances in bottom-up assembly of carbon nanotubes and graphene devices

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Over the past few years, we have demonstrated that bottom-up device assembly of nano-carbons using dielectrophoresis (DEP) can achieve ultra-high integration densities, excellent FET device performance and can be combined with sorting to even produce single-chirality SWCNT device arrays. Recently, we have extended the DEP assembly in two main routes.

Firstly, we will present the large-scale assembly of suspended carbon nanotube and graphene devices by bottom-up DEP assembly. Suspended device fabrication is associated with a range of new technological challenges which we have overcome. These devices are ideally suited for sensors and resonator applications.

Secondly, we have succeeded in integrating carbon nanotubes into plasmonic antennae [1], using DEP to place CNTs into a optical cavity formed by a gold nano-disc dimer. In this cavity, we observe plasmonic enhancement of Raman scattering up to 10^4 times.

Finally, I will also discuss how nitrogen-doped SWCNTs can also be assembled individually into devices using DEP. These results further demonstrates the great versatility of the DEP assembly technique for nano-carbon device fabrication [3].

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G8

Controlled Growth of Single-Walled Carbon Nanotubes and Application to CNT-Si Solar Cells

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Chemical reaction process in CVD growth of single-walled carbon nanotubes (SWNTs) will be discussed with diameter controlled CVD growth incorporating nitrogen and molecular dynamics simulations. Then, the structure controlled assembly of SWNTs for SWNT-Si heterojunction solar cells will be discussed.

We found the reversible and repeatable modification of diameter of vertical array of SWNTs by adding acetonitrile (AcN) in ethanol (EtOH) as feedstock of CVD [1-3]. When the nitrogen (N) is involved, the SWNT mean diameter was dramatically reduced from approximately 2.1 nm to less than 1 nm. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic N_2 molecules interior of SWNTs with the content of 1 at %. We address that the nitrogen atoms on the surface of the catalyst particle result in a change from the 'Octopus' to the 'VLS' growth mode predicted by molecular dynamics simulations.

We proposed a water vapor treatment to build up SWNTs to a self-assembled micro-honeycomb network for the application of solar cells [4]. The micro-honeycomb network consists of vertical aggregated SWNT walls and a buckypaper bottom. This hierarchical structure is very efficient to collect holes from the interface of Si. The heterojunction solar cell was fabricated by dry depositing the SWNT film to the 3 mm by 3 mm n-type silicon substrate. The pristine SWNT-Si heterojunction solar cell shows a record-high fill factor of 72 % as well as a power conversion efficiency (PCE) of 6 % without tuning the diameter or height of original vertically aligned SWNTs. The PCE remains stable for months in ambient condition. A PCE exceeding 10 % is achieved in the dry state after dilute nitric acid treatment.

On the other hand, heterojunction solar cells using highly transparent-conductive SWNT films from controlled bundle-diameter and long bundle length [5] are also promising. Here, SWNTs were synthesized by the thermal decomposition of ferrocene vapor in a carbon monoxide atmosphere, with the average diameter of approx. 2 nm. Our preliminary test result shows the highest PCE of 11 % among such CNT-Si design without chemical doping. These solar cells are stable after 6 months.

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G9

Automated carbon nanotube synthesis by water-assisted CVD

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Among many techniques of carbon nanotube (CNT) synthesis available today, chemical vapor deposition (CVD) is the most popular by far due to low cost, ease of set-up, and wide range of nanotube morphologies that can be produced. The throughput of a typical research CVD system, however, is limited to a few runs per day due to time necessary for heating, conditioning, growing, and cooling steps. This makes it difficult and time-consuming to explore the multi-dimensional experimental parameter space that includes temperature, pressure, feedstock composition; catalyst and catalyst support composition. The Adaptive Rapid Experimentation and in-situ Spectroscopy (ARES) CVD system described in this contribution makes over 100 CVD experiments possible in a single day in fully automatic mode, with pre-programmed growth recipes and without user intervention. CNTs are grown in a miniature cold wall CVD reactor, with the same laser used for both thermal activation of the growth process and Raman excitation. Raman spectra are acquired in real time, enabling in-situ analysis of growth kinetics and nanotube characteristics. Further linear regression modeling allowed mapping regions of selectivity towards SWNT and MWNT growth in the complex parameter space of the water-assisted CVD synthesis. This is the first demonstration of automated experimentation combined with regression analysis applied to the CNT synthesis by CVD. This development of the automated rapid serial experimentation is a significant progress towards an autonomous closed-loop learning system: a Robot Scientist.

G10

Simple and scalable aligned nanotube films

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The production of conductive and semitransparent thin films is one of the dominant methods of incorporating carbon nanotubes into useful devices and systems. Over the years this has been done primarily by vacuum filtration or spray deposition from very low concentration surfactant-stabilised suspensions. A recent development is the fabrication of thin films in which the nanotubes are highly aligned in one direction parallel with the surface and such films have been shown to exhibit superior properties, resulting in substantially improved devices and systems. Based on earlier work we have developed a simple and scalable process for the deposition of highly aligned nanotube films. These thin films have excellent properties compared to randomly aligned counterparts produced by other methods, with the addition of several potentially useful characteristics not found in non-aligned films.

G11

Hybrid Carbon Source for Single-Walled Carbon Nanotube Synthesis by Aerosol CVD Method

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We report the results of the enhancement of the film conductivity by tuning the bundle length of single-walled carbon nanotubes (SWCNTs) by applying a double carbon source in the aerosol CVD synthesis reactor. Carbon monoxide plays a role of the carbon source at temperatures below 900 ^{o}C, while ethylene takes over at higher temperatures. The gas composition change in the aerosol CVD reactor allowed us to increase the length of the CNT bundles from 3.4 μm (pure CO system), via 7 μm (CO-H_2 system) to 17 μm by adding C_2H_4 at 900 ^{o}C. The yield of the SWCNTs was increased about 7 times at 1100 ^{o}C, when compared to 900 ^{o}C, preserving the optoelectrical performance of the SWCNT film.

The significant decrease in the sheet resistance at 90% transmittance was observed from 3500 and 7500 ohm/sq. for pure CO system via 1909 and 1709 ohm/sq. for CO-H_2 system to 291 and 358 ohm/sq. in the presence of C_2H_4 at 900 and 1100 ^{o}C, respectively. Treatment of the film with $AuCl_3$ acetonitrile solution allowed us to create the transparent conductive films with the sheet resistance as low as 73 ohm/sq. at an optical transmittance of 90%.

G12

Fabrication and Characterization of Nitrogen-Induced Single-Walled Carbon Nanotubes Field-Effect Transistors

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Carbon nanotube field-effect transistors (CNTFETs) using horizontally aligned single-walled carbon nanotubes is relatively easy with high performance to fabricate devices on desired location and substrate compared with other method.[1] CNTFETs are also expected to enable fabrication complementary circuits with high performance by control of density or carrier type using several techniques. However, there is a major impediment to the introduction of single-walled carbon nanotubes (SWNTs) to these technologies is the lack of reproducibility in SWNT synthesis and CNT-based device.

In this work, we report the synthesis and fabrication of nitrogen-induced horizontally aligned single-walled carbon nanotubes (N-HASWNTs) FETs. The growth of N-HASWNTs using chemical vapor deposition on an r-cut crystal quartz substrate using ethanol and/or acetonitrile,[2] followed by peel off and transfer to a target substrate. Although our N-HASWNT FETs show p-type behaviors, the resulting N-HASWNTs have well-controlled density and a unique morphology, consisting of small diameter nanotubes with narrow diameter distribution (for bandgap control). N-HASWNTs can be This FET simultaneously demonstrates a mobility of 1,284 $cm^2V^{-1}s^{-1}$ and an I_{on}/I_{off} ratio ~ 106. We also demonstrate flexible FETs using N-HASWNT with high performance.

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G13

Synthesis of semiconducting single-wall carbon nanotubes by hydrogen etching

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The most attractive and important application of single-wall carbon nanotubes (SWCNTs) is to fabricate new generation high-performance electronic devices, such as field effect transistors (FETs), integrated circuit, sensors, etc. However, each of these applications requires a pure and high quality sample that contains only or mostly semiconducting SWCNTs (s-SWCNTs). Although post-synthesis separation and in situ selective oxidation techniques have been developed for the selective preparation, the yield (surface growth), quality (more defects, decreased length), and uniformity of the s-SWCNTs obtained are still very poor.

In this presentation, we report high quality, high concentration s-SWCNTs obtained by in situ selective removal of metallic SWCNTs (m-SWCNTs) via hydrogen etching during a floating catalyst chemical vapor deposition process. We found that hydrogen preferentially reacts with m-SWCNTs in the presence of a highly active floating iron catalyst at a synthesis temperature of 1100 °C, while s-SWCNTs are mostly retained. Compared with previously reported oxidative etchants, hydrogen is much milder and does not cause structural defects in the remaining s-SWCNTs. Under an optimum condition, samples containing ~93% s-SWCNTs were obtained in bulk reproducibly. These s-SWCNTs with good structural integrity showed an oxidation resistance temperature of ~800 ºC, the highest value ever reported for SWCNTs. Thin-film transistors using the s-SWCNTs as a channel material showed a high on/off ratio up to 4.0×10^5 and a high carrier mobility of 21.1 $cm^2V^{-1}s^{-1}$. Biosensors fabricated using these s-SWCNTs demonstrated an ultra-low detection limit of 10-18 mol/L for dopamine detection, which is several orders of magnitude lower than values previously reported. The above results indicate that our high quality s-SWCNTs may find application in high-performance FETs, sensors, and other electronic devices.

G14

Growth of Single-walled Carbon Nanotubes from Opened Edges of Carbon Nanotubes

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Chirality control is one of the important topics in the single-walled carbon nanotube (SWNT) growth research field. Although some studies showed chirality selective growth for specific chirality such as (6, 5), it is still difficult to perform chirality control in growth process. It was reported that the epitaxial growth of SWNTs was one of the possible techniques for chirality controlled synthesis [1]. Here, we performed the SWNT growth using the opened edges of SWNTs as the growth template. In advance, horizontally aligned SWNTs (the length was 50 um) were synthesized on crystal quartz substrates from iron catalyst nano-particles [2]. And then horizontally-aligned SWNTs were cut into several shorted SWNTs in length by oxygen plasma etching and SWNTs with opened edges were obtained.

The opened SWNTs were heated in air ambient (at 200 degree C, in 30 min) and water vapor atmosphere (at 400 - 900 degree C). The heating treatments were for the activation of the opened edges [1]. And then, CVD was performed by introduction of ethanol vapor at 800 - 900 degree C. In scanning electron microscopy, the epitaxial growth of SWNTs was observed at approximately 2 % SWNT edges. By repeating epitaxial growth CVD, 10% edges showed the epitaxial growth of SWNTs, totally. We will discuss the mechanism and yield of the repetitive epitaxial growth.

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G15

Synthesis and application of carbon nanocones as CNT substitutes for electron emission and AFM probes

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Carbon nanotubes (CNT) are thought to be an ultimate solution for a variety of applications, including AFM probes and electron emission. But due to various issues related to CNT specificities (e.g. mechanical flexibility, for both the AFM probe and electron emission applications), results are not as good as expected. In this work, we developed a type of objects based on MWCNTs individually coated with pyrolytic carbon, exhibiting unique morphological and textural features.

These morphologically complex carbon objects are produced in a two-step process. The first step requires a catalyst, to grow MWCNTs. During the second step, a multi-texture pyrolytic carbon coating is deposited onto each individual previously-grown MWCNTs. The overall object morphology can be described as a rough-surface microfibre segment ended by a smooth-surface cone at both extremities, with the original CNT protruding at both cone apexes. Hence, the cone apex dimension is equal to that of the supporting MWCNT diameter (few nanometers) whereas the microfibre to which the nanocones are attached allows easy grabbing and handling by micromanipulator tools. The inner structure, texture and nanotexture of the graphenes building the cones were fully described in earlier works [1] and make a quite favorable combination for anticipating optimized performances for applications such as AFM probes and electron emitting tips for TEM high performance electron source (cold-FEG).

Using Focused Ion Beam (FIB), one of these carbon-nanocone–bearing objects was mounted onto a regular but trimmed tungsten FEG emission tip used as support, and then was placed into the electron source (cold FEG type) of a TEM (Hitachi F2000). The resulting performances were outstanding [2], showing improved – or equivalent, for the least – parameters with respect to the best FEG source currently on the market: the beam brightness was up to five times higher, the beam coherence was significantly improved, the energy dispersion of the electron beam was better than 0.3 eV, and the unprecedented current stability make that daily tip flashing is no longer required. This superiority is explained by the mechanical stability brought by the conical shape which makes that the tip exhibits all the benefits of a regular CNT tip as predicted by de Jonge et al [3] without the drawbacks (typically, the tip vibration upon electron emission).

On the other hand, in order to test the performances of the carbon nanocones as AFM probes, several types of substrates were tested, and the results were compared to both the results obtained from usual silicon AFM probes on the one hand, and a variety of commercially available, so-called high resolution (HR) AFM probes (including nanotube-based) on the other hand. The carbon nanocone-based tips prepared at CEMES show good high resolution imaging capabilities, with very few artefacts. They are similar to other HR CNT-based probes regarding the lack of lateral convolution, and compare favorably when imaging close objects, with less sensitivity to water menisci.

For both applications, relatively easy and fast and therefore cost-effective mounting procedures are expected thanks to the unique overall micro/nano morphology, as well superior durability due to the perfection of the graphenes constituting the cones.

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G16

Catalyst control for the selective growth of Semiconductor Single-Walled Carbon Nanotubes

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Novel method to synthesize the single-walled carbon nanotube (SWNT) of semiconductor-type is reported. Selective synthesis of semiconductor-SWNT was reallized by exposing the iron catalyst into the gas ambient containing small amount of H2O just before SWNT growth.
Raman spectra (laser wavelength: 532, 633, 780 nm) from the as-grown SWNT films has suggested the preferential growth of semiconducting SWNTs with small diameter of 0.8-1.1 nm range. Importantly, high selectivity was only achieved when the yield of CNT was low, suggesting the selective growth can be achieved by adjusting the catalyst activity. High performance of field-effect transistor (FET) device was performed by using as-grown CNT film as channel of FET, where high on/off ratio (> 10,000) and mobility (c.a. 10 cm^2/Vs) at a relatively short channel length (5 um). These characterisitics shows that the approach of selective growth can greatly contribute to the widespread electronics application, such as flexible electronics device. To achieve high growth selectivity, and high performance of FET, fine control on catalyst size distribution, furnace ambient, and gas flow in the heating zone is required. Details are presented in this paper.

G17

In situ observation of carbon nanotube re-growth by scanning electron microscopy

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Recently, carbon seeds like nano-diamond, fullerene fragments and nanotube segments have been used to synthesize carbon nanotube (CNT) [1-5]. This new route may produce high purity nanotube free from metal impurities, which will promote the application of nanotubes. In addition, researches on catalysts free nanotube seeds will contribute to understanding on the growth mechanisms of CNT. It has been demonstrated that cloning growth of CNT from seeds with certain chirality was realized [5]. Pretreatment including air oxidation followed by water vapor annealing is proved to be essential. To investigate the process of CNT re-growth so as to better understand it, we conducted re-growth of CNT in the chamber of scanning electron microscope (SEM). Compared with conventional chemical vapor deposition (CVD), the nanotube formation process can be in situ monitored by SEM, which might help to comprehensively evaluate the influence of experimental parameters on its growth.

Since our in situ system is a cold wall CVD, all reaction processes are conducted on the surface of substrate, which is different from conventional hot wall CVD. Therefore, the same condition for conventional CVD cannot be directly used. By varying experimental parameters, the new pretreatment as well as the growth condition suitable for this cold wall system was established, and the re-growth of nanotube from seeds with different chirality in the chamber of SEM was realized. Furthermore, multi-times re-growth of nanotube was also achieved. In situ observation on CNT formation provided a direct evidence for its cloning growth. According to our experimental results, the efficiency of re-growth was closely related with pretreatment conditions and growth parameters, especially the carbon source. We carefully studied the influences of these parameters on the re-growth of CNT. On the basis of these analyses, the growth mechanisms of nanotube synthesized from seed will be discussed.

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G18

Direct Growth of High-Density Carbon Nanotube Arrays on Copper foils toward Thermal Interface Materials

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CNTs are a candidate for future thermal interface materials (TIMs) owing to their high theoretical thermal conductivity (3000 W/m K) and mechanical flexibility. Among introduced approaches for CNT array TIMs, mounting CNT/metal foil/CNT TIMs on devices has advantages not only in avoiding any damage of electrical devices by high CNT growth temperature but also in applying to many devices conveniently. However, typical CNT arrays grown by conventional chemical vapor deposition (CVD) method have thermal conductivity far below the expected values because of their porous structure (mass density < 0.1 g cm^{-3} and porosity > 90%). Previously, targeting at via-interconnects in large-scale integrated circuits (LSIs), we reported sub-μm-tall CNT arrays with a density as high as ~ 1 g/cm^3, grown by CVD at 400 °C with careful control over the nucleation and growth of catalyst particles during sputter deposition [2]. In this work, we target at direct growth of such dense CNT arrays with much larger height of several tens μm on both side of copper foils.

To grow CNTs much taller, we elevated CVD temperature from 400 to 700 °C. At such high temperature, catalyst particles got easily deactivated in the reaction with Cu. Thus we examined diffusion barrier materials used in LSIs. On diffusion barrier preformed on Cu foils, we deposited Ni, Co, and Fe catalysts by sputtering. And then we carried out CVD by feeding C_2H_2/H_2 at a rather low C_2H_2 partial pressure of 0.2 Torr, in order to avoid the catalyst deactivation by carbonization [3]. We evaluated the height and density of CNTs by scanning electron microscopy (SEM) and weight gain method. We found that Ni and Co catalyst worked well at low temperatures ~ 400 °C whereas Fe worked better in growing CNTs tall at a high temperature of ~ 700 °C. Although the mass density of CNT arrays decreased with CVD time and thus their height, a fairly high mass density of 0.22 g cm^{-3} was achieved for a 35-μm-tall CNT array. The 90-μm-thick CNT/Cu/CNT film (35-μm-tall CNT arrays on both sides of a 20-μm-thick Cu foil) would be attractive for TIM applications. We are now evaluating the thermal conductivity of such films.

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G19

Single-walled carbon nanotube growth from Pt catalysts by cold-wall ACCVD

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So far, we have reported single-walled carbon nanotube (SWNT) growth from Pt catalysts in the alcohol gas source method [1]. In this study, we demonstrated that SWNTs grew from Pt under very low ethanol pressure using a conventional cold-wall type chemical vapor deposition (CVD) system and the diameters and chirality of grown SWNTs were investigated using SEM, TEM, Raman and PL.

SWNT growth was carried out on SiO_2/Si substrates at 400-900ºC in a cold-wall type CVD system using Pt as catalysts. When the growth temperature and ethanol gas pressure were 700-900ºC and 1-3 Pa, RBM peaks were observed in the Raman spectra, accompanied with the splitting of G band. From SEM images, high-density web-like structures were observed on the substrates. These results indicate that SWNTs grew under low ethanol pressure even in the conventional CVD system, confirming that the high activity of Pt catalysts. We also estimated the chirality of SWNTs from PL and Raman spectra. Our results showed that diameters of most of SWNTs were below 1.3 nm and that the distribution of chirality was fairly narrow, compared to SWNTs grown from transition metal catalysts.

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G20

Preparation and Properties of PVDF membrane filled with carbon nanotubes

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To investigate the polymer composites with high dielectric constant and excellent electrical conductivity at low filler concentration, we had prepared conductive hybrid ultrafiltration membranes via phase inversion by dispersing carboxyl multi-wall carbon nanotubes (MWCNTs-COOH), ranging from 0 to 10 wt.% in Polyvinylidene Fluoride(PVDF) casting solutions. The membranes had good hydrophilic, high electric conductivity and excellent mechanical properties compared to the pure PVDF film. The electric conductivity and permittivity of pure PVDF film were 10-13 S/cm and 2.8 at 100 HZ respectively, while the valves were both increased with the addition of the MWCNTs content, the statistical percolation threshold for PVDF-MWCNTs membranes was found to be 5 wt.%. When at 5 wt.% MWCNTs, the valves of electric conductivity and permittivity were 10-4 S/cm and 36.5 at 100 HZ respectively, moreover, the contact angle was reduced to 72.3°(the pure PVDF was 80.3°). The morphology of the film was characterized as individual and dispersed uniformly at low MWCNTs contents, whereas it was networked but also aggregated at high filler contents (≥5 wt.%). The mechanical strength of MWCNTs-filled binary films also increased with the increase of MWCNTs content. Our work demonstrated that the MWCNTs played a critical role in determining the structures, morphologies, conductivity and properties of ultrafiltration membranes.

G21

Laser annealing of single-wall carbon nanotubes

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Most carbon nanotube (CNT) synthesis routes carry defects and impurities which are generally addressed by thermal and/or chemical post treatments. However, chemical purification often incurs in further defects, as do mechanical dispersion methods such as ultrasound. Thermal defect elimination requires atmosphere control and time-consuming temperature ramping.

Contrary to previous studies, laser radiation was found to effectively treat both problems, resulting in high-purity and -crystallinity and low-defect CNTs, with a reduced mean interdefect distance. Even mechanically induced defects could be corrected. Super-fast laser radiation times have a leg up on common oven and chemical treatments. Additionally, selective shape and site-specific parameters come into play such as interference patterns. Such arrangements of alternating tube quality, e.g. in a CNT matt, could be interesting for preferred electronic conduction paths and find applications in, e.g., interdigitated electrodes.

As is paramount to the correct evaluation of any CNT study, the starting material and its production method are presented. Then, a study of the laser power and exposure time is discussed, as characterized by Raman spectroscopy, scanning and transmission electron microscopy and thermo-gravimetric analysis. Results are contrasted with previous studies on the effect of laser radiation on CNTs.

G22

Fabrication of infrared solar cell with controllably carrier doped stable semiconducting single-walled carbon nanotube films

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Single-walled carbon nanotubes (SWNTs) are one of the most attractive materials for future high performance solar cells due to their flexible filament-like structures, high carrier mobilities, and tunable bandgap energies by controlling their diameters [1,2]. Multiple exciton generation (MEG) in SWNTs can also be expected. For the fabrication of solar cell with SWNTs, it is necessary to establish a method for carrier type-, density-, and position-controllable doping into SWNTs. Stability of the doping is also another important issue for the practical use of SWNTs in solar cells. Recently, we have demonstrated the controllable and stable n-type carrier doping into semiconducting SWNTs thin films by position selective Cs encapsulation into SWNTs with a plasma ion irradiation method [3]. In this study, the optoelectrical transport properties are investigated for the controllably carrier doped stable semiconducting SWNTs films. It is found that the clear rectifying drain-source current vs. drain-source voltage characteristics can be observed after the position selective Cs encapsulation into semiconducting SWNTs thin films. Furthermore, a short-circuit current and an open-circuit voltage can be also detected under light illumination using a solar simulator. Since pn junctions are formed along the tube axis, carrier loss caused by tube to tube junction can be minimized and high rate power generation can be expected with this pn junction embedded SWNTs solar cells.

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G23

Transfer of chemical vapour deposition grown carbon nanotubes for interconnect applications

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With the increase in current densities through electronic circuitry brought about by miniaturisation, replacements for traditional materials have to be found due to problems arising with electromigration and thermal coefficient of expansion mismatch. Carbon nanotubes (CNT) show promise as a replacement for traditional interconnect materials, such as copper, because they do not suffer from electromigration below a certain size and due to their superior thermal conductivity properties. A method of transposing arrays of multiwall carbon nanotubes (MWCNTs) from their growth substrates to a target metal substrate is demonstrated. MWCNT arrays, typically 300 μm in length, were produced by a chemical vapour deposition process and were shown by Raman spectroscopy to have relatively few defects. MWCNT arrays treated by oxygen plasma followed by a metallisation step were shown to have good adhesion to Sn33Pb67 solder. This paper discusses the solder-MWCNT-solder interconnects manufacturing process and their subsequent electrical characterisation. Using lithography arrays of 100x100 μm were produced and interconnects with average resistance of 5 Ω were achieved.

G24

Relationship between Fe-Catalyzed Single-Walled Carbon Nanotubes and Fe Catalyst Nanoparticles

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It has been well known that single-walled carbon nanotubes (SWCNTs) nucleate and grow on catalytic nanoparticles and the size and crystal structure of the nanoparticles play a key role in determining the chirality of the produced SWCNTs. However, it is often observed that not all nanoparticles actively catalyze growth of SWCNTs in a chemical vapor deposition (CVD) process though they appear to have similar size and structure as active nanoparticles. In addition, the correlation between the nanotube properties and that of active nanoparticles remain under discussion.

In this contribution, we have performed a comprehensive statistical analysis of morphology, size and chemical compositions of a large number of nanoparticles, including both catalytically active and inactive ones, by means of aberration-corrected high-resolution transmission electron microscopy. SWCNTs were produced by a novel floating-catalyst CVD process with Fe nanoparticles serving as catalysts for CO-disproportionation reaction. It is disclosed that active and inactive nanoparticles show no essential difference in morphology and size distribution. Though the average diameter of active nanoparticles (~3.3 nm) is over three times larger than that of SWCNTs (~1.1 nm), our results have shown that the ratio of a certain SWCNT diameter to that of an active catalyst nanoparticle varies dramatically, ranging from 1:2.2 to 1:4.3. Importantly, we discriminate at least two species of Fe nanoparticles, i.e. oxidized Fe nanoparticles and metallic BCC Fe nanoparticles. It is found that no oxidized Fe nanoparticles, but only BCC Fe nanoparticles are catalytically active for SWCNT growth. Electron diffraction analysis indicates a biased chiral distribution of SWCNTs towards high chiral angles, but no significant preference to a specific chirality is observed.

G25

Synthesis of (6,5) and (6,4) enriched SWNTs by pulse plasma CVD

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Single-walled carbon nanotubes (SWNTs) are promising materials in various fields as they have many novel characteristics. Since SWNTs properties strongly depend on the chirality, it is inevitable to realize the chirality-controlled SWNTs synthesis for the fabrication of next-generation high performance electrical devices. In our study, we use parameter-controlled plasma CVD [1-3] to synthesize SWNTs and narrow down the chirality-distribution by the introduction of pulse plasma CVD.

In order to realize narrow chirality distribution of SWNTs, we optimize the parameters in two steps. Firstly, we adjust parameters of growth temperature and gas pressure to suppress the growth of large diameter SWNTs. Secondly, we optimize the time sequence of pulse plasma such as “on” and “off” time to increase the selectivity of (6,5) and (6,4) SWNTs. Through the careful optimizations, we have realized highly enriched growth of (6,5) and (6,4) SWNTs. The detailed effects of plasmas on the selective growth of (6,5) and (6,4) SWNTs are also investigated.

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G26

CaH_2-assisted low temperature synthesis of metallic magnetic nanoparticle-loaded multiwalled carbon nanotubes

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MWCNTs loaded with metallic Ni and Fe NP can be prepared by pyrolyzing nickel stearate or ferrocene, respectively, under a flow of acetylene at 800 - 1100 °C[1].5 In pyrolysis, metallic nanoparticles (NPs) which act as catalysts are formed in-situ via reduction of metal ions by the decomposed organic ligands upon heating.5. Thus, the addition of strong reducing agent which enables the formation of metallic NP catalysts at lower temperatures is expected to accomplish CNT formation at lower temperatures. Several reports in solid state chemistry have shown that CaH_2 is a fairly strong reductant for metal oxides at low temperatures (< 300 °C)[2,3]. Our recent work demonstrated this method can also be applied to reduction of metal organic salts [8]. Metallic Fe and Ni NPs, which are known to be efficient catalysts for MWCNT formation, can be prepared at temperatures as low as 140 ^oC simply by reducing the corresponding metal organic salts with CaH_2[4].

In the current study we have successfully synthesized MWCNTs loaded with Ni or Fe NP by pyrolyzing metal organic salt with CaH_2. The use of CaH_2 enables formation of MWCNTs at 400 °C without using toxic halogen-containing precursors and assistance of plasma. This is about half of the lowest reported temperature in the pyrolysis method and among the lowest formation temperature by the typical CVD methods. The dual roles of CaH_2 are considered to be responsible for such extraordinary low formation temperature; formation of metal NPs which act as catalyst at lower temperatures and enhancement of decomposition of the carbon feedstocks. This work clearly demonstrates that CaH_2 opens a way to low temperature synthesis of MWCNTs loaded with a variety of metal NP able to catalyze CNT growth.

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G27

Novel 3-dimensional nanocomposite of covalently interconnected multiwalled carbon nanotubes using Silicon as an atomic welder

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There is a growing interest in synthesizing three-dimensional (3-D) carbon nanotube structures with multi-functional characteristics. Here, we report the fabrication of a novel composite material consisting of 3-D interconnected multi-walled carbon nanotubes (MWNTs) with Silicon Carbide (SiC) nano- and micro-particles. The materials were synthesized by a two-step process involving the chemical coating of MWNTs with Silicon oxide, followed by Spark Plasma Sintering (SPS). SPS enables the use of high temperatures and pressures that are required for the carbothermal reduction of silica and for the densification of the material into a 3-D composite block. Covalent interconnections of MWNTs are facilitated by a carbon diffusion process resulting in silicon carbide formation as silica coated MWNTs are subjected to high temperatures. The presence of SiC in the sintered composite has been confirmed through Raman spectroscopy, which shows the characteristic peak close to 800 cm^{-1} and also Energy Filtered Transmission Electron Microscopy maps. X-ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy and High Resolution Transmission Electron Microscopy have also been used to characterize the produced material. Interestingly, the thermal property measurements of the sintered composite reveal a high thermal conductivity value (16.72 W/mK) for the material. From the electrical point of view, a 3-D variable range hopping (VRH) electron hopping was observed in the composite.

G28

From 2D to 1D: Localized Laser-Induced Heating In Carbon Nanomaterials

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Highly localized light-induced heating of carbon nanotube forests ("Heat Trap") [1] is an unusual physical property where the generated heat remains locked in place in this otherwise conducting material. This has many potential applications, such as in solar thermionics and light-activated cathodes for multi-electron beam direct-write lithography [2]. Through this effect, temperatures as high as ~ 2,000K have been observed with a laser intensity of less than 10 W/mm^2 from a visible beam [3]. In this work, we study the effect of dimensionality in this phenomenon by using nano carbon of different dimensionalities. Patterned highly ordered pyrolytic graphite was used for comparison with vertically aligned carbon nanotube (VA-CNT) forests. Pseudo-one-dimensional graphene nano-ribbons with widths varying from ~3 μm to ~300 nm were created through focused ion beam patterning on highly ordered pyrolytic graphite (HOPG). VA-CNT forests were synthesized by thermal chemical vapor deposition on Fe/Al_2O_3 thin films on silicon substrates. A focused laser beam was used as the source of irradiation on the specimen at a vacuum level of 10^{-6} Torr. The increase in temperature was observed by monitoring the resulting incandescence and measuring its spectrum using an optical spectrum analyzer. Experiments were also performed on non-patterned HOPG in order to investigate the effect of going from a 2-dimensional to a quasi-1-dimensional system and compare with the behavior in nanotubes.

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