AFM Capabilities in Carbon Particles Characterization

P.West, N.Starostin, Pacific Nanotechnology" Inc., 17984 Sky Park Circle, Suite J, Irvine, CA 92614

Abstract

With the current acceleration of developments in the nanotechnology sectors of carbon industry it is preferable for a number of reasons to perform charachterization with atomic force microscopy (AFM) use instead of simply resorting to optical, electron microscopy (SEM/TEM) or dynamic light scattering (DLS). Parameters involving direct measurements of the 3rd dimension, such as height, surface roughness and volume, are possible only with AFM. The range of examples of great scientific interest includes but not limited to visualization and quantitative measurements of single-wall carbon nanotubes and carbon black particles. The point defects on single-walled carbon nanotubes (SWNT) can be seen if labeled by selective electrochemical deposition method. The ability to detect and analyze point defects is very important for quantitative analysis in nanoelectronics development. Not only does particle characterization using AFM provide a resolution comparable to or greater than that of SEM and Raman spectroscopy, it also retains the capacity for both 3-D visualization and direct height and volume measurements.

Introduction

Over the past 20 years Scanning Probe Microscopes (SPM) emerged as an essential material characterization technique in various fields[1,2,3,4,5]. The importance of the SPM was evident as early as 1984 when the Nobel prize was awarded for the Scanning Tunneling Microscope (STM) invention by IBM researchers[1]. Today the Atomic Force Microscope (AFM) is the most commonly used scanning probe microscope for materials characterization[2]. Major advantages of AFM are that it has a combination of high resolution in three dimensions, the sample does not have to conductive, and there is no requirement for a vacuum. The extreme sensitivity of the AFM is derived from a force sensor that establishes the force between the probe and target surface. Forces between the probe and surface in an AFM are typically less than 1 nN/nm. Most of the force sensor in AFMs utilize a light lever, first disclosed in 1929 and then applied to the AFM in 1986.

With an AFM a large variety of topographies and types of materials can be visualized and analyzed. Examples of surface features that may be imaged include: atomic corrugations and terraces on graphite, Single Wall Carbon Nanotube (SWNT), multi wall carbon nanotube, carbon black particles and agglomerates. The ability to detect and analyze point defects on SWNT, especially at very low concentration, provides a quantitative technique in nanoelectronics development[6,7]. This paper demonstrates how AFM can be utilized in characterization of nanoparticle decorating point defects on SWNT.

Nanoparticle characterization with AFM

With the AFM it is possible to directly visualize nanoparticles with sizes ranging from a nanometer up to 10000 nanometers. Sample preparation for nanoparticles characterization with the AFM is relatively simple. A clean, flat surface must be used and the nanoparticles must be dispersed on the sample's surface. It is essential that the nanoparticles have a greater affinity for the surface than for the probe.
There are many properties of nanoparticles that can best be examined by directly visualizing an AFM image of the particles. Examples of properties that are understood best by visualization are shapes, size, dispersion of substrate and surface texture.

Quantitative measurements of nanoparticles
Accurate quantitative measurements are one the strongest points of atomic force microscopy. Height, length and width measurements of particulate can be performed along any direction on the image with very high resolution. In other words complete set of morphological parameters such as size, volume, aspect ratio, surface roughness and particle count can be obtained. Particles Size Distribution (PSD), volume

distribution or any other distribution based on particle count and morphology information can be performed.

In an AFM the resolution in the Z axis, perpendicular to the surface, is different than the resolution in the XY axis, horizontal to the surface. Under ambient conditions, the Z-resolution for most of the commercially available AFMs is on the sub-angstrom level. Resolution along horizontal dimensions, x and y, is established by the diameter of the probe and is on the order of a few nanometers. AFM images are always a convolution o of the probe geometry and sample geometry. However, if the probe is much smaller than the surface features, the distortions from the probe are minimal. Tip artifacts can be recognized and compensated with the help of the software[8].

Comparison to other techniques:

There are four major methods of characterizing nanoparticles: scanning/transmission electron microscopy (SEM/TEM), Dynamic Light Scattering (DLS) and AFM . In general, morphological information, such as area and aspect ratio, as well as surface information, such as texture and roughness parameters, cannot be obtained using ensemble techniques, such as DLS. It is well know that DLS are reliable if the PSD is unimodal, particles are spherical and refractive indices are known. In case of bi-modal PSD, particles of the arbitrary shape or "exotic" particles such as quantum dots, AFM seems to be a better option[9].

With single particle techniques, such as SEM/TEM/AFM, physical parameters for each particle in a set of particles can be recorded and the data set can be processed to generated a statistical distribution (i.e. ensemble-like information) for the entire set of particles. Parameters involving direct measurements of the 3rd dimension, such as height, surface roughness and volume, are possible only with AFM.

A major factor that contributes to microscope single particle analysis and ultimately to the accuracy of measurements is the image quality. TEM is well known for very time-consuming and complicated sample preparation. SEM samples are easier to prepare, however the requirement for conductivity adds some difficulties to it.

Experimental

The SWNT device was fabricated by using standard techniques[9] and then modified in a custom electrochemical cell by selective electrochemical deposition (SED)[6]. Pd metal was a choice for the deposition. The particle decorated SWNT device was imaged in air by AFM (Nano-Rp™, Pacific Nanotechnology Inc.). AFM imaging was done in close contact mode with Si probe (Applied Nanostructures Inc.) inside an acoustic enclosure. NanoRule+™ (Pacific Nanotechnology Inc.) particle measurement software was used to characterize the particles

Results and Discussions

Each SWNT shown on figure1 is grown simultaneously on a single wafer and then decorated by SED.

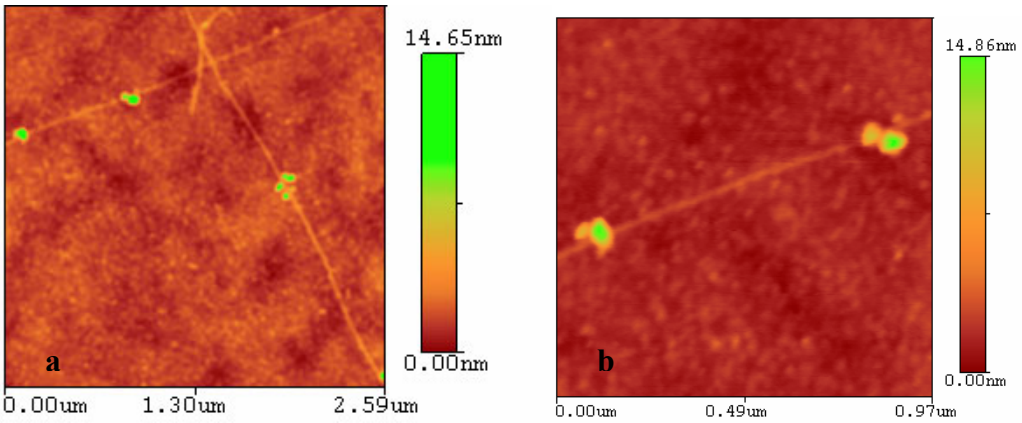

Figure1 demonstrates SED results on SWNT circuits. Three nucleation sites decorated by Pd-particles can be clearly seen on 2.6x2.6scan on figure 1 (a). Close-up image, 970x970nm, of two nucleation sites is shown on the figure 2 (b).

The decoration of the point defect allows to estimate the mean defect density for a particular batch of CVD-grown SWNTs, figure 2. The morphology parameter of every single paricle can be determine as shown on figure 3.

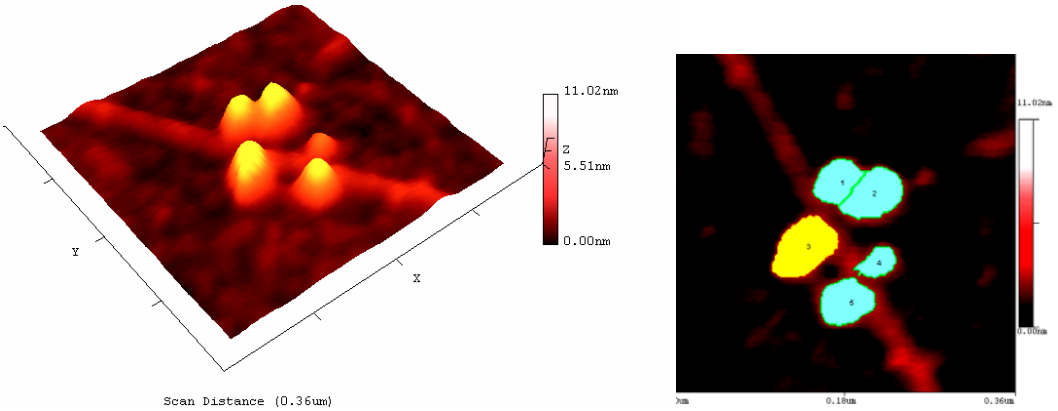

Figure2 shows multiple particle decoration site. 3D view, 360x360nm,is shown on figure 2 (a). Outlined and counted particles are shown on the figure 2 (b).

Total Objects

It...	Area (nm²)	Perimeter (um)	Volume (nm³)	Height (nm)	Max_Height (nm)	Radius (um)	Length (um)	Width (um)	AspectRatio
Total	1.07e+004	0.75	6.51e+004	29.17	46.03	0.13	0.26	0.22	5.93
Avg.	2141.9	0.15	1.30e+004	5.83	9.21	0.025	0.053	0.045	1.19
Max.	3081.6	0.18	1.98e+004	6.52	10.93	0.031	0.071	0.055	1.38
Min	968.98	0.11	4058.2	4.19	6.08	0.017	0.034	0.028	1.03
Range	2112.7	0.078	1.57e+004	2.33	4.85	0.014	0.037	0.027	0.35
St.	716.89	0.028	5338.6	0.88	1.65	0.00490	0.012	0.00987	0.12

Total Particles: 5

Figure 3 shows list of the morphological parameters measure by AFM

The size of the deposited particles is proportional to deposition time of the SED process. It is inversely proportional to positive potential during electrochemical reaction.

Conclusions

AFM is very well suited for both qualitative and quantitative characterization of nanoparticle decoration on SWNTs. The main advantage of AFM is direct height and volume measurements, which allows quantification of the SED process.

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