Synthesis, electrical and magnetic characterization of core–shell silicon carbo-nitride coated carbon nanotubes

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We demonstrate synthesis, electrical and magnetic characterization of silicon carbo-nitride (SiCN) coated multiwalled carbon nanotubes in a core–shell structure. The core formed by a carbon nanotube had a diameter in the range of 10–100 nm. The shell was synthesized by pyrolysis of an SiCN precursor on the surface of carbon nanotubes. Electrical resistivity of an individual composite nanotube was measured to be $\approx 2.55 \times 10^3$ Ω cm. The magnetic measurements performed by a superconducting quantum interference device on the composite nanotubes in the temperature range of 5–300 K show a reduced coercive field with increasing temperatures. The monolayer thick coating of an ultra high temperature multifunctional ceramic SiCN makes these composite nanotubes very promising for sensing applications in harsh environments.

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1. Introduction

Polymer derived silicon carbo-nitride (SiCN) ceramics have been shown to possess interesting multifunctional properties including high thermal conductivity, high temperature physical and chemical stability (> 1100 °C), high temperature oxidation resistance, and giant piezoresistive and magnetic properties [1–5]. Carbon nanotubes (CNTs) on the other hand are extraordinarily flexible and unlike other 1-D nanomaterials, CNTs can be bent repeatedly up to as much as 18% strain value [6,7]. The flexibility of CNTs makes them easy to manipulate in a 3-D space and arrange them in a specific configuration. Recently there have been attempts to use CNTs as template material for synthesis of composite nanotubes. Both SiCN and CNTs have been shown to possess large piezoresistive properties and finite magnetic behavior due to the presence of a small concentration of metallic catalyst particles during synthesis [4,8]. Thus a composite in a core–shell configuration with SiCN forming the shell and CNTs as core will lead to flexible ceramic nanotubes with high temperature piezoresistivity, magnetic and electrical behavior.

2. Experimental

SiCN coated CNTs were synthesized through the polymer precursor route. Commercially available silazane-based precursor Polyurea-methylvinylsilazane—Cerasert™-SN (Kion Specialty Polymers, PA) was used as the precursor for SiCN [9]. As-synthesized multiwalled carbon nanotubes (MWCNTs, obtained from a commercial source) were dispersed in a solution containing 10 vol.% of Ceraset in acetone. The mixture was sonicated for 30 min and later dried in an oven at 80 °C. Next, the dried Ceraset-NT powder was pyrolyzed to convert the polymer into the ceramic by heating in an alumina tube furnace at 1100 °C under nitrogen atmosphere for a period of 4 h. Fig. 1(a) shows the scanning electron microscope (SEM) images of the nanotubes coated with SiCN which are in the form of a forest and appear bright compared to pure CNTs. Since we did not conduct cross-section TEM of the coated CNTs, it is difficult to assess if the SiCN coating was preferentially on the external surface. The thickness of SiCN coating is in the vicinity of one monolayer based upon a recent study by Shah and Raj who have shown that after monolayer formation the wetting attachment ruptures before the SiCN–CNT due to the amorphous nature of the structure and excellent wetting characteristics of the CNTs by polymer precursor [10].

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3. Results and discussion

Transmission electron microscopy (TEM) on synthesized composite nanotubes was performed using Philips EM 420 and Titan 300 X-Twin S-TEM (FEI Company). Fig. 1(b) shows the low magnification image of a single nanotube reflecting flexible geometry and uniformity of coating. Fig. 1(c) and (d) confirm the presence of a very thin layer comprising of Si and C elements. We can very clearly see SiCN coating on the nanotube using the Si-Energy window (or Slit) in the electron energy loss spectroscopy (EELS) map using Energy Filtering TEM. Further, EDS analysis of the outer layers of a nanotube specimen showed a high surface oxygen with the following composition SiC(0.2)N(0.13)O(1.2) particularly for thick nanotubes.

Focused ion beam (FIB, FEI Helios 600 Nanolab) SEM fitted with Omniprobe™ micromanipulator was used for separation and mounting of individual NTs on the platinum electrodes for electrical characterization (ABTECH Scientific, Inc.). Sample preparation involved drying of nanotubes from a chloroform solution in the form of a mat and mounting on a SEM stub. This makes the nanotubes easily accessible for selection and separation by a micromanipulator probe [7]. An individual nanotube was separated on the tungsten microscopy probe attached to the Omniprobe manipulator. The nanotube was welded to the probe tip using Pt which was deposited by injecting a metal organic precursor into the chamber and the scanning area of contact with a high current electron beam operated at 5 kV and >40 nA. Unlike other FIB processes, the Ga ion beam was not used for deposition to avoid beam damage. The nanotube was then transferred from the probe to the test structure where it was welded to the Pt electrodes as shown in Fig. 2(a) [7].

The electrical I–V characterization of the nanotube was performed by using the Semiconductor Parameter Analyzer (HP 4145v). For comparison, the tests were carried out with and without the presence of a nanotube. The I–V behavior was measured in the case of the SiCN–CNT nanotube as well as MWCNT, indicating a decent electrical contact between the nanotube and platinum electrodes as shown in Fig. 2(b).

![Fig. 1. (a) SEM image showing the SiCN coated carbon nanotube forest. (b) Low magnification TEM image showing SiCN–NTs. (c) EELS map using Energy Filtering TEM. (d) Elemental mapping for Si and C.](image-url)
Open (or bare glass substrate) circuit measurement showed non-ohmic behavior which suggests that the measured $I-V$ characteristics were from the nanotube although contribution from the Pt-Carbon welds is not completely ruled out. A resistivity magnitude of $2.5 \times 10^3 \, \Omega\,\text{cm}$ was observed for the composite nanotube with a diameter of 140 nm and a length of ~15 µm. Studies indicate [11,12] that nanotube resistance varies from 1–1000 kΩ. The value of resistivity observed in our composite NW specimen is close to that of SiCN nanorods ($1.0698 \times 10^3 \, \Omega\,\text{cm}$) synthesized by a chemical vapor deposition (CVD) process [13] and higher than that of crystalline SiC nanorods ($2.2 \times 10^{-2} \, \Omega\,\text{cm}$) [14]. The increased resistivity of the SiCN–NT nanotubes can be partially attributed to the finite amount of surface oxygen observed in these NTs while annealing at 1100 °C. Other factors such as compositional and structural factors including substitution of N on the C sites, the amorphous nature of SiCN, interfacial defects between the CNT and SiCN also contribute to enhanced contact resistance.

The linear $I-V$ behavior of composite nanotubes could be associated to the phase and structure of SiCN and a good contact between the tubes and electrodes. Ceramics synthesized by a polymer precursor route are considered as pseudo-amorphous compounds and specifically in the case of SiCN the composition can vary from SiC$_{0.68}$N$_{0.32}$ to SiC$_{1.58}$N$_{1}$. The varying compositional profile and tube-morphology have been shown
to improve the emission current characteristics of the SiCN material, with a low threshold and high current density [15]. A dense monolayer of SiCN on CNT reduces the presence of dangling bond provides an adequate conduction path while a varying compositional profile results in changes in molecule size to accommodate the misfit. Self-assembly along the 1D structure such as CNT has a low barrier energy as compared to planar surfaces due to an availability of more bonding sites. Thus, compared to a CNT paper [9], CNT tubes will have a denser and uniform coating of SiCN.

In order to further confirm the uniformity and study the effect of SiCN coating on the magnetic properties of CNTs, we investigated the temperature dependence of magnetization. Since the MWCNTs were synthesized using Fe as catalyst particle, they could have small traces of magnetic ions attached during the synthesis process, which can be used as the signature for detecting the SiCN coating. Recent magnetic studies on bulk SiCN–Fe2O3 (Ceraset/Fe) composites have shown that during pyrolysis of Ceraset, the reactivity of the metallic ions such as of Fe with Si and C leads to the formation of Fe3Si and Fe3SiC phases [16]. This modifies the magnetic moment of SiCN–CNT from MWCNT. Taking this into consideration, we studied the magnetic properties of both bare and SiCN coated MWCNTs using a superconducting quantum interference device (SQUID) magnetometer in a temperature range of 5 K to 300 K. Fig. 2(c)–(f) shows the M–H loops at specific temperatures of 5 K, 100 K, 200 K, and 300 K respectively. The magnetic measurements shown in Fig. 2 were normalized with respect to the amount of materials used. The following can be noted in this figure: 1) the coercive field in the hysteresis loops for the MWCNT decreases with increasing temperature. 2) The shape of the hysteresis loop for MWCNTs shows constriction in the middle which could be due to shape anisotropy. 3) Magnitude of coercive field for core–shell nanotubes reduces with increasing temperature and 4) magnetization for core–shell nanotubes reduces to around 0.8 emu/g compared with MWCNT of the order of 2.5 emu/g. These characteristics can be explained by taking into account the existence of a mixture of single domain and superparamagnetic nanostructures at low temperatures. With decreasing temperature the superparamagnetic behavior changes into a ferromagnetic state. The interesting aspect of this result is a dramatic reduction in the saturation magnetization and coercive field of the SiCN–CNT nanotubes. We believe this occurs due to the reaction at the interface between the Si and metallic iron present in the CNTs during pyrolysis. The SEM-EDS analysis on bulk CNTs showed very low quantities of Fe (<6 wt.%) and hence it is difficult to confirm the exact chemical nature of this reaction. However, such reactions will reduce the magnetic moment of Fe3Si and Fe3SiC as compared with pure Fe. These results clearly demonstrate that our SiCN coating on CNT was formed with good adhesion.

4. Summary

In summary, we demonstrate the synthesis of a pseudo-amorphous SiCN monolayer coating on surfaces of multiwalled CNTs through a polymer precursor route. Electrical characterization was conducted on individual composite nanotubes (SiCN coated CNT with large aspect ratio) using an FIB and 3-D manipulation system. A resistivity magnitude of 2.55 × 103 Ω cm was measured for the nanotubes at room temperature. Magnetic measurements on the core–shell nanotubes show a decrease in coercivity and narrow hysteresis loops with increasing temperatures.

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