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Surface Modification of Carbon Nanotubes Using Poly (Vinyl Alcohol) For Sensor Applications

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Abstract

Surface modification of the carbon nanotubes plays an important role for their utilization in various applications. In this study, single-wall and multiwall nanotubes were grown on a 1 cm^2 silicon dioxide substrate using chemical vapor deposition. The surface of grown nanotubes was modified by polyvinyl alcohol and the wettability on nanotubes was investigated. This functionalisation tends to change the surface of nanotubes into hydrophilic thus increasing its sensitivity. The electrical characterization of these modified nanotubes was performed since it is expected that by adapting analytes onto the polyvinyl alcohol modified nanotubes, the electric transport property of CNT may be changed. Sensor applications of these modified nanotubes are also suggested.

Keywords

Carbon Nanotubes, Surface Modification, PVOH, Sensors, Nanosensors

1. Introduction

The excellent mechanical and electrical properties of carbon nanotubes make them attractive to various device applications including sensor applications. Single wall nanotubes have been synthesized into different shapes for various electronic applications (Choi and Choi, 2004).Single wall nanotubes have also been grown selectively to make nanoscale transistors (Choi et al., 2003). Carbon nanotubes based sensors have been shown to have detection capability for gas molecules such as NO_2 and other organic vapors (Li et al., 2003). This sensing mechanism is attributed to the changes in the electrical conductivity of these nanotubes caused by the charge transfer from the gas molecule. Moreover due to their large surface area, carbon nanotubes have high sensitivity for gas and chemical vapors at room

temperature as compared to conventional metal oxides sensors which operate at high temperatures. The gas sensing capability of the intrinsic nanotubes can be greatly enhanced by functionalisation with different molecules and functional groups. Polymer coated carbon nanotubes have shown high sensitivity and selectivity for gases like NH_3 and NO_2 (Qi, et al., 2003). While other studies have shown that nanotube based polymer composites can be used for strain sensing (Dharap, et al., 2004). Since carbon nanotubes are hydrophobic in nature they cannot be directly used for applications like relative humidity sensing. Polyvinyl alcohol (PVOH) is well known for its hydrophilic properties. It is atactic yet semicrystalline in nature which becomes surface-active at hydrophobic surface/water interfaces and concentrates at these sites allowing crystallization to occur. It is a water soluble polymer which is used in various industries such as textiles, adhesives, ceramics and paper. Recently its application as a polymer coating on a SAW device for improving the chemical sensing capability was shown (Kozlov et al., 2003), (Penza, et al., 1999). Earlier studies in which PVOH was used for functionalisation of carbon nanotubes mainly focused on improving the mechanical properties of nanotubes (Zhang et al., 2003). Here we present initial results of the effect of functionalisation by PVOH. The wettability behavior of nanotubes is studied as it plays a crucial role in adsorption and sensing of the analytes. These PVOH functionalised nanotubes may be used for sensing gases like CO and biomolecules which are not detected by pristine nanotubes.

2. Experimental Details

Carbon nanotubes were grown on $1cm^2$ SiO_2/Si substrates using CVD process. Single wall tubes were grown on iron thin film at 900°C by using methane and ethylene as precursors, while multiwall carbon nanotubes were grown on the similar substrate at 700°C by using ethylene as precursor. The catalyst for all the samples were deposited by using spin coating method with speeds ranging from 500-1000 rpm. The functionalisation of the nanotubes was down by submersion of the substrate into aqueous solution of PVOH (99% hydrolyzed, MW-89-98K, obtained from Alfa Aesar), which was prepared by mixing PVOH with deionized water at the ratio 1:10000 (w/v) and heating at 90°C for 1 hour with constant stirring. The substrate was kept in the solution overnight, since the functionalisation of PVOH occurs while cooling. The substrates were then removed by rinsing with copious amount of deionized water and drying under vacuum.

To study the effect on the wettability of the carbon nanotubes by PVOH functionalisation, dynamic contact angles were measured by using contact angle analyzer. The contact angles of the functionalized CNTs were compared with that of the pristine carbon nanotubes. The electrical characterization was carried out by using probe station (Desert Cryogenics) coupled with semiconductor parameter analyzer (Agilent, 8146C). The IV characterization was conducted in vacuum conditions.

3. Results and Discussion

Figure 1 illustrates the SEM micrographs of multiwall carbon nanotubes before and after functionalisation with PVOH. It can be clearly seen that even a small amount (0.001 % w/v) of PVOH can significantly change the surface morphology of the nanotubes. In Figure 2 the effect on the water droplet deposited on the multiwall nanotubes before and after functionalisation is shown. The dynamic contact angles (advancing and receding) were measured for both single wall and multiwall carbon nanotubes. In Table 1 it can be seen that there is change in contact angle from 148 to 24 (advancing angle) corresponding to an average of 84% decrease when carbon nanotubes are functionalized. This clearly suggests that PVOH can be used for modifying the hydrophobic behavior of nanotubes to highly hydrophilic. The basic mechanism of interaction between the PVOH and nanotubes can be attributed to the lowering of interfacial free energy which is evident from the change in the contact angles of the functionalized nanotubes. PVOH tends to crystallize and introduce an alcohol functional group on the surface of the nanotubes. These functional groups can further act as intermediate for linking with various molecules which are to be sensed.

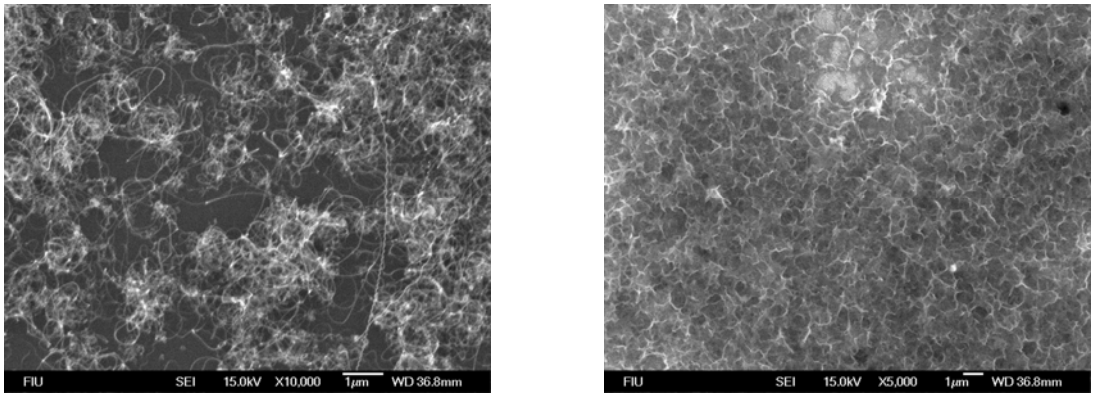


Figure 1: Multiwall carbon nanotubes without functionalisation (Left) and with PVOH functionalisation (Right)

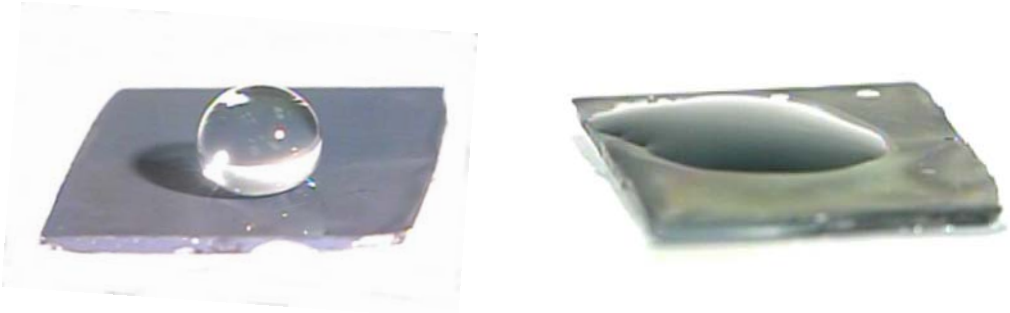


Figure 2: Effect on the water droplet deposited on the multiwall carbon nanotubes before (left) and after (right). (Size of each sample: 1 cm^2)

Table 1: Effect of PVOH functionalisation on single wall and multiwall carbon nanotubes

	Advancing Angle	Receding Angle
SWNT (Before Functionalisation)	139.8	121
SWNT (After Functionalisation)	25.6	18.2
MWNT 1 (Before Functionalisation)	147.8	133.8
MWNT 1 (After Functionalisation)	23.6	19
MWNT 2 (Before Functionalisation)	148.2	139.8
MWNT 2 (After Functionalisation)	34	25.2

SWNT: Single Wall NanoTube

MWNT: Multi Wall NanoTube

0.001% w/v of PVOH in distilled water

4. Conclusion

In this study single wall and multiwall carbon nanotubes were functionalized by using PVOH. It was shown that PVOH is able to modify the surface behavior of single or multiwall carbon nanotube from hydrophobic to highly hydrophilic. These findings are being further studied for possible use of functionalized carbon nanotubes for humidity, gas and bimolecular sensing. The IV characterization is also being studied to understand the charge transport mechanism in these modified carbon nanotubes.

5. References

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