

Growth of high quality carbon nanotubes on free standing diamond substrates

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Abstract

Carbon nanotubes (CNTs) were grown on diamond-coated Si substrates and free-standing diamond wafers to develop efficient thermal interface materials for thermal management applications. High quality, translucent, free-standing diamond substrates were processed in a 5 kW microwave plasma chemical vapor deposition (CVD) system using CH₄ as precursor. Ni and Ni-9%W-1.5% Fe catalyst islands were deposited to nucleate CNTs directly onto the diamond substrates. Randomly-oriented multi-walled CNTs forming a mat of ~5 μm thickness and consisting of ~20 nm diameter tubes were observed to grow in a thermal CVD system using C₂H₂ as precursor. Transmission electron microscopy and Raman analyses confirmed the presence of high quality CNTs on diamond showing a D/G peak ratio of 0.2-0.3 in Raman spectra.

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1. Introduction

Three carbon-based materials have demonstrated the potential for high thermal conductivity: graphite, diamonds and carbon nanotubes (CNTs). Due to the high thermal conductivity (~ 1800 W/Km) of diamond, heat spreaders made of diamond plates are useful for thermal management in high power electronic devices [1] such as laser diodes, RF power transistors, etc. Diamond heat spreaders help to quickly transfer heat from the devices to heat sinks and thus improve the reliability and device performance [2]. Diamond coatings deposited by chemical vapor deposition (CVD) were also investigated to serve as heat spreading films for thermally limited high-power high-frequency devices [3]. In addition to diamond films, discrete CNTs also were found to have very high thermal conductivity (~ 3000 W/Km) along with high mechanical compliance and thus offer a potential for the development of the next generation thermal interface materials [4-6]. CNTs can make excellent thermal interface materials if the proper quality can be maintained along with a robust attachment to the desired devices. For example, chip cooling with CNT microfin architectures have been recently proposed by Kordas et al. [5]. CNT films as thermal interface materials were also discussed by Zhu et al. [6]. Initial results by this group showed that an assembly with CNTs has a thermal conductivity of 81 W/m·K and a thermal resistance of 0.43 cm²/K/W.

As an interface material, CNTs have been demonstrated to grow on a variety of materials/substrates. Cola et al. studied the performance of a thermal interface material consisting of Cu foil and CNT arrays and reported that thermal interface resistances of less than 10 mm² K/W are possible [7]. Xu and Fisher [8] reported enhancements in thermal conductance using CNT arrays grown on Si wafers by plasma enhanced CVD and reported a thermal interface resistance of 19.8 mm² K/W. Cola et al. [9] investigated CNT arrays grown on SiC to serve as

thermal interface materials for high temperature SiC devices and achieved thermal resistances less than $10 \text{ mm}^2 \text{ K/W}$. CNTs were grown by Wang et al. on both sides of metallic substrates to fabricate thermal interface materials [10]. Samples fabricated in this study were measured to have thermal interface resistance of $12 \text{ mm}^2 \text{ K/W}$. CNTs were also grown on constantan substrates for similar applications without the use of catalysts [11]. Carbon nanofiber-Cu composite films have been reported by Ngo et al. to have very low thermal resistances ($0.25 \text{ cm}^2 \text{ K/W}$) to serve as thermal interface materials for microelectronic packaging [12].

It is therefore reasonable to consider the growth of CNTs on diamond, since both can have superior thermal conductance. A structure containing a composite of diamond substrates for heat spreading and CNTs for heat radiation on top of them could provide a useful combination to efficiently conduct away the heat. Enhancement of thermal diffusivity properties of the diamond spreaders can be expected by combining CNTs grown on diamond substrates. In the present work, initial results of growth and characterization of CNTs grown on diamond substrates are presented.

2. Experimental

Diamond substrates were grown in a 5 kW microwave plasma CVD system on 2 inch diameter silicon wafers. Prior to the diamond growth, the Si wafers were thoroughly cleaned and scratched with diamond crystals (pre-seeding) in an ultrasonic bath to initiate nucleation [13]. Diamond growth was carried out in a low concentration of CH_4 (1.5-2%) as the carbon source gas in a carrier gas of hydrogen. Diamond films were grown using microwave powers between 2500-4000 W at temperatures of 850-900°C for 6 to 7 days to obtain films of ~100 micron thickness. Free-standing diamond substrates were subsequently obtained by dissolving away the

silicon wafer using chemical etchants. A catalyst layer (Ni or Ni-9%W-1.5% Fe) was then deposited by sputtering directly onto the diamond substrates without using any intermediate layers. In addition to pure Ni, alloy catalysts were also used to encourage base growth. [14]. All the depositions were done at room temperature and the metal catalyst layers from 210 nm thickness were deposited by varying the deposition time. While some samples were treated in Ar/5 % H₂ atmosphere for 30 min to create catalyst islands prior to CNT growth, other samples were directly used for CNT growth without a prior heat treatment.

CNT growth was done in a lab-constructed thermal CVD system using a 1 inch diameter quartz tube in a horizontal furnace. Initially, the tube furnace was evacuated by using a rough pump and then purged with Ar/5%H₂ for 20 min. The furnace with the samples was heated in an Ar/5 % H₂ atmosphere to 750-800^oC. A precursor gas of 10 vol% C₂H₂ in an argon carrier gas was introduced as the carbon source at a flow rate of 50-400 sccm. The CNTs were grown for different lengths of time varying from 30 to 120 min. The samples were then cooled in an Ar/ 5% H₂ mixture to room temperature. Some samples were also grown at a total pressure of 90 torr to observe the effect of low pressure growth.

Both diamond and CNT/diamond samples were analyzed by using a high resolution FEI Sirion scanning electron microscope (SEM) and a Delta Nu Raman microscope using a 532 nm diode laser. A Rigaku powder x-ray diffractometer (XRD) was used to obtain theta-two theta scans from the samples. CNTs from the diamond substrate were separated and then transferred to a copper grid and analyzed in a FEI Tecnai F20 analytical transmission electron microscope (TEM) with a point-to-point resolution of 0.21 nm to determine the crystalline quality.

3. Results and Discussion

Using microwave plasma CVD, diamond coatings up to 100 μm thick were processed. Figure 1 shows a SEM image of a diamond substrate processed in the present study. It can be seen that these substrates have large crystals of diamonds with sharp facets and as a result have rough surfaces. Figure 2 shows a theta-two theta XRD patterns taken from a diamond substrate. Peaks corresponding to different orientations of the diamond were noted, indicating the polycrystalline nature of the diamond substrates. Figure 3 shows Raman spectra taken from one of the large crystal diamond substrates. A sharp peak at 1332 cm^{-1} at room temperature is observed with a very low G peak at 1550 cm^{-1} , indicating a high degree of sp^3 bonding in the carbon and that the samples are of high quality. Similar sharp peaks were also noted in high-quality diamond substrates in the literature [15, 16].

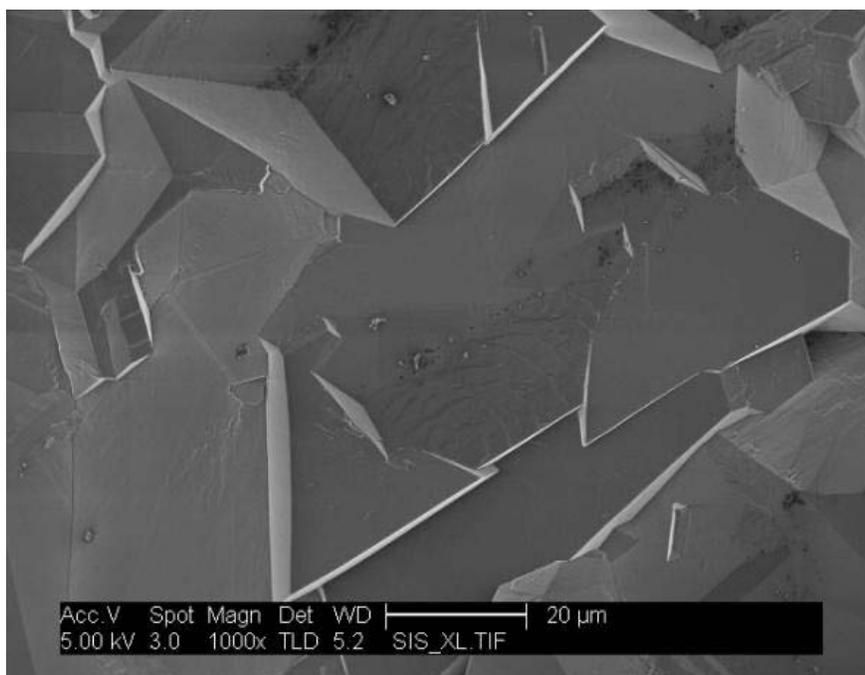


Figure 1 SEM micrograph of as-grown diamond sample showing facets of crystals

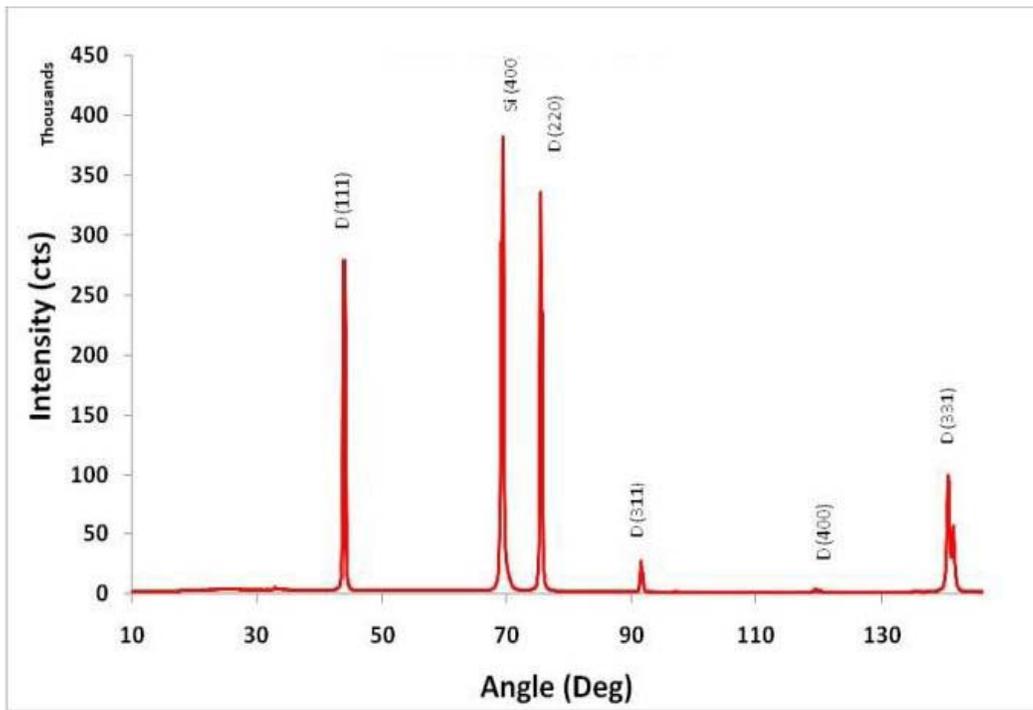


Figure 2. X-ray diffraction pattern taken from a diamond substrate

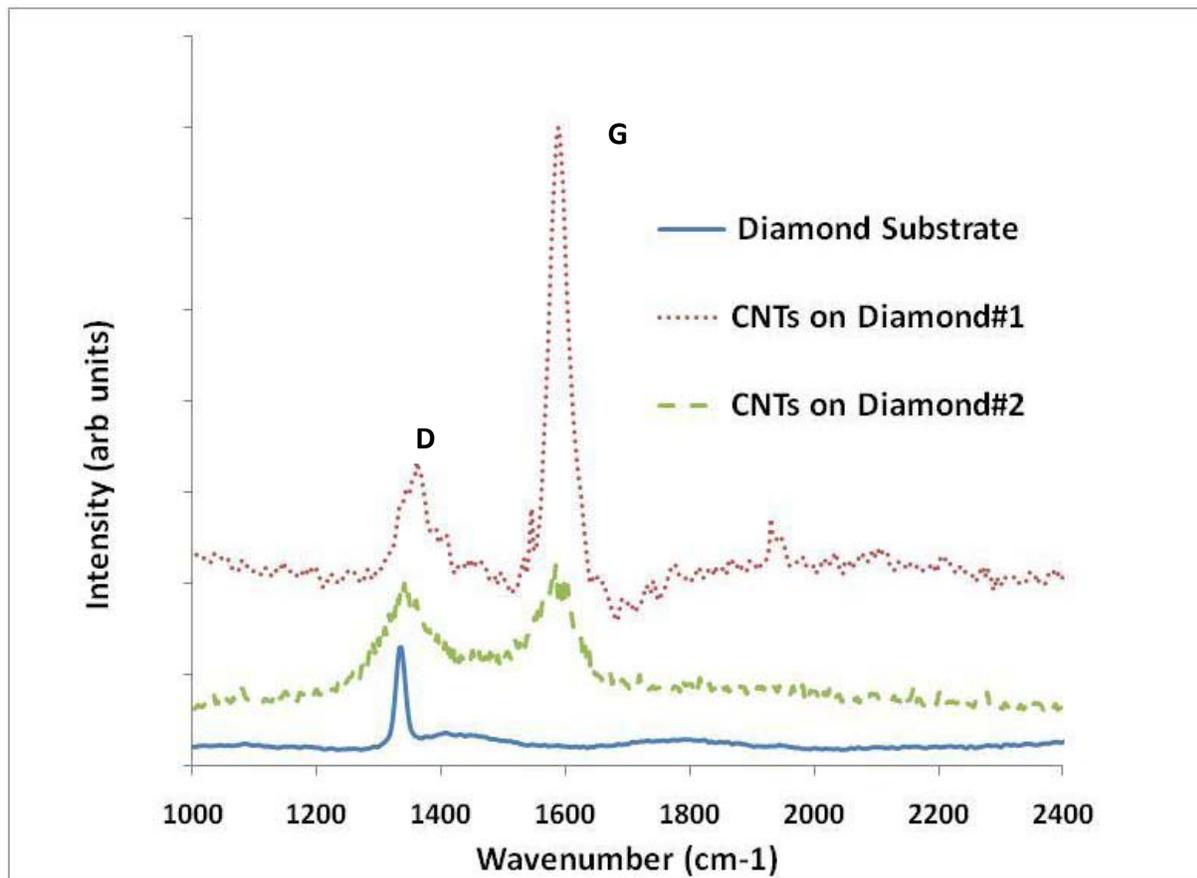


Figure 3. Raman spectra taken from a diamond substrate as compared to CNT/diamond samples grown at two different processing conditions (#1 in low pressure of 90 torr, #2 atmospheric pressure)

The free-standing diamond substrates obtained by dissolving the Si substrate were found to be fairly translucent, providing an additional indication of very low impurity levels (sp^2 carbon etc.) in these substrates. The lower impurity levels in the diamond films are desirable due to their better thermal conductivities [1]. In addition, the microstructure of polycrystalline diamond films with grain boundaries also influences thermal conductivity [17, 18]. Since the large crystal diamond substrates have a reduced grain boundary area, the in-plane thermal conductivity is expected to be better in large crystal diamond substrates as compared to small crystal diamond substrates. The quality of the diamond substrates just described under the conditions in this study appears to be most suitable for growing CNTs for thermal management studies.

Complete CNT coverage of rough diamond substrates is very important for improved thermal contact. Experiments were conducted with several samples of different metal layer thicknesses and sputtering parameters to determine the effect on catalyst coverage, as coverage of the catalyst particles will determine the final CNT coverage. Since intermediate layers were not used, catalyst particle coarsening was likely to occur during annealing. In addition, the facets present in the diamond could assist in the rapid coarsening of the catalyst particles due to the presence of the valleys between grains. Figure 4 shows a CNT grown on a diamond sample deposited with a 2-5 nm thick Ni-9%W-1.5%Fe catalyst using initial set of sputtering conditions (30 mA, 0.44 KV, 200 mtorr Ar, 10 min). After the CNT growth on these samples, it can be seen that only certain facets were found to be covered with a high density of CNTs (bright areas), whereas other areas appear to have a very low density (dark areas). Although the whole area of the substrate was exposed to CNT growth, only certain areas had the appropriate metal catalysts necessary for the growth and this resulted in partial coverage of the surface.

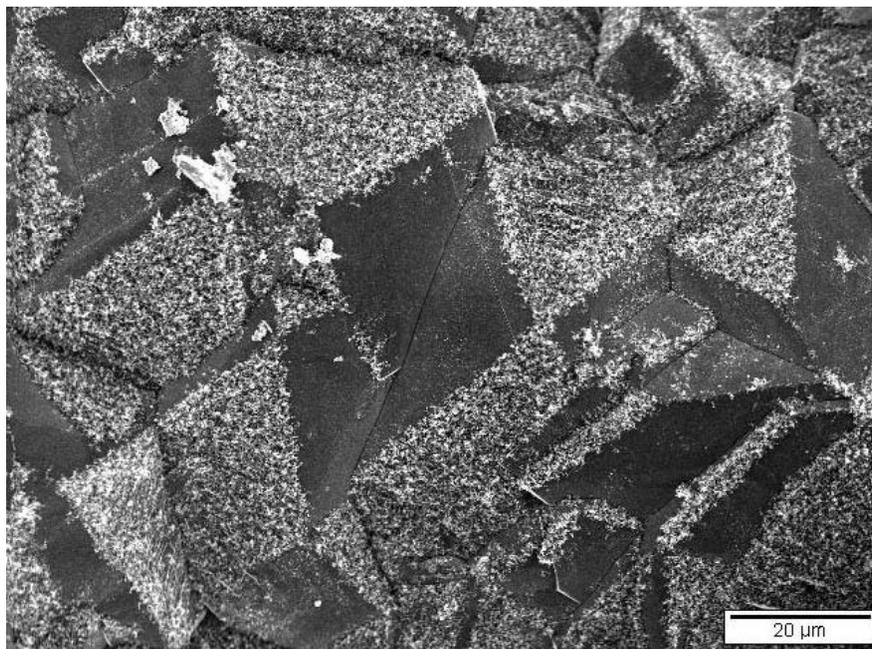


Figure 4. Partial coverage of CNTs grown on diamond substrate partially covered with Ni-W-Fe deposited by using initial sputtering conditions.

Proper coverage of the surface was obtained using optimized sputtering conditions (190 mA, 0.32 KV, 200 mtorr Ar, 2 min) and around 5-9 nm thick Ni was deposited to create the catalyst nanoparticles. As shown in Figure 5, complete coverage of the substrate with CNT growth is possible with a catalyst layer. Although the initial diamond substrate surface was rough due to the faceting, the surface is completely covered with a thin layer of CNT carpet. A higher magnification photomicrograph of the samples is shown in Figure 6, where randomly-oriented CNTs can be clearly seen. A cross-sectional SEM micrograph of the sample shown in Figure 7 demonstrates that 3-5 micron thick CNT carpet is present on the samples. Samples processed with the optimized sputtering conditions for Ni-9%W-1.5% Fe also provided similar CNT coverage.

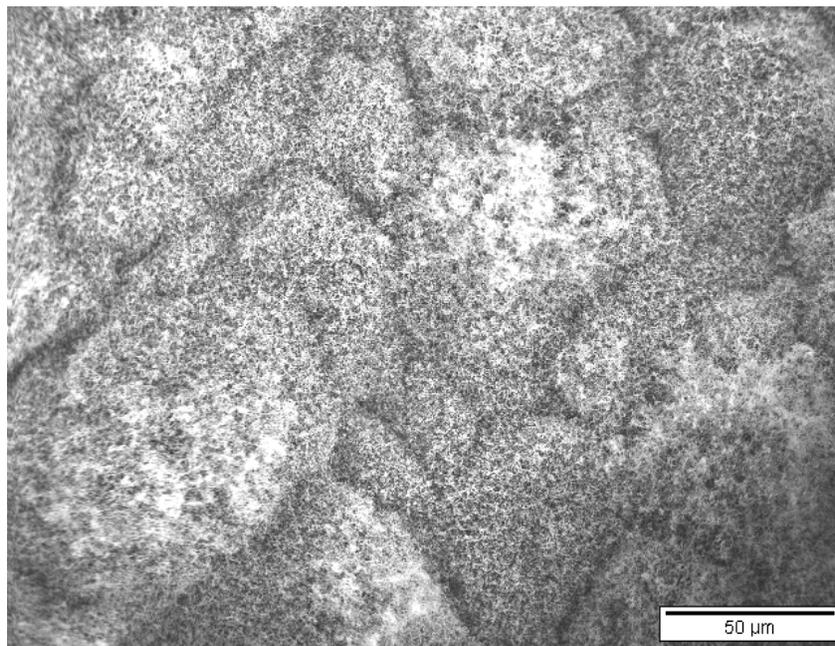


Figure 5. Complete coverage of CNTs on diamond substrates with Ni catalysts deposited by sputtering using optimized conditions

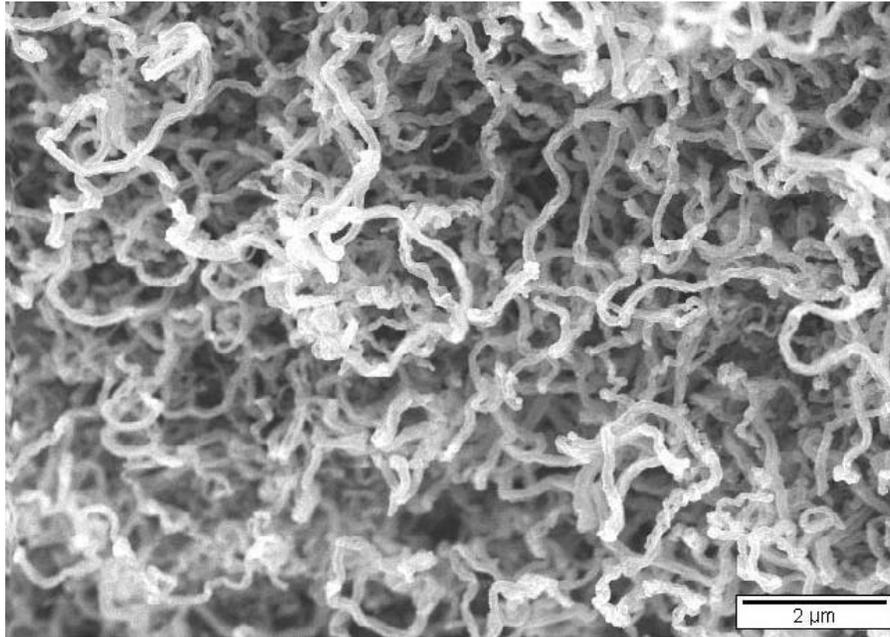


Figure 6. Higher magnification photomicrograph showing the CNTs grown on a diamond substrate

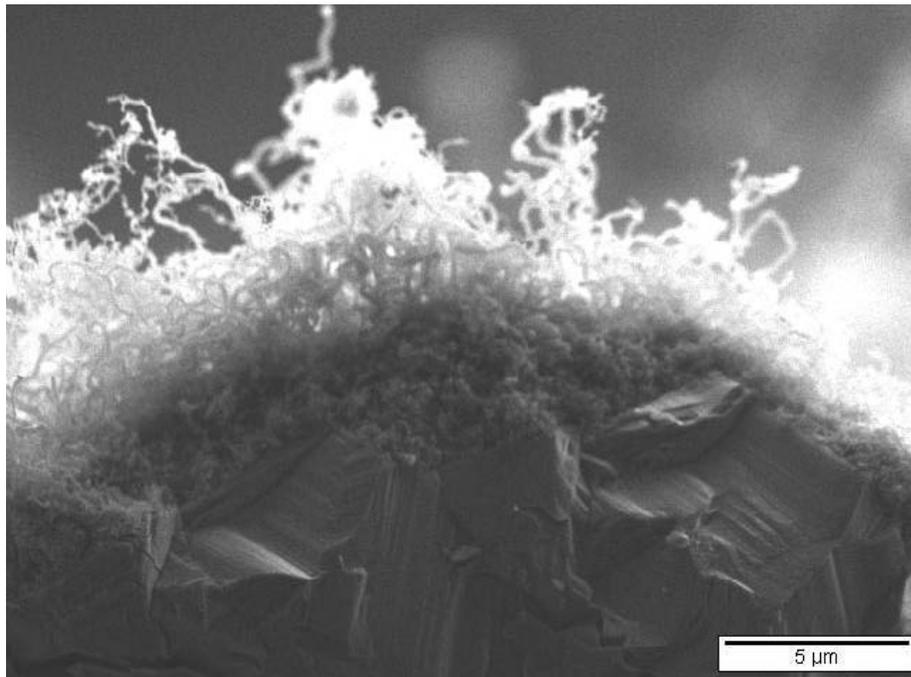
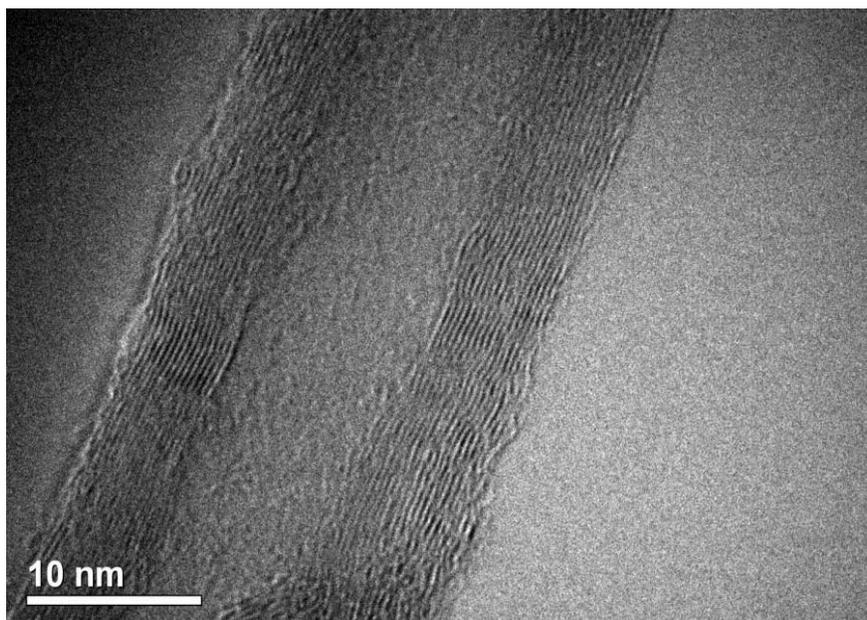


Figure 7. Cross-sectional SEM image showing CNTs grown on a diamond substrate

CNTs observed by TEM (image show in Figure 8a) indicate that the diameter of the samples is around 20 nm. High resolution TEM of the samples show that growth of high crystalline-quality CNTs on diamond substrates is possible. This particular image is of a MWCNT where 16 walls are present as shown in Figure 8b. In order to further confirm the quality of these CNTs, Raman spectra were taken on different samples. Figure 3 shows a D/G peak ratio of 0.89 for the sample grown in atmospheric pressures (CNT/diamond #2). However, in other samples (CNT/diamond#1) grown with Ni islands and 400 sccm of C_2H_2 flow rate in 90 torr of pressure, a D/G ratio as low as 0.3 was obtained as shown in Figure 3 indicating the possibility of growing high-quality MWCNTs on diamonds. It is shown in the literature that smaller the D/G ratio, the better the structural purity of the graphitic materials [19] and in the present study samples showed D/G ratios of 0.2-0.3 when grown in low pressure.



(a)



(b)

Figure 8(a). TEM micrograph showing 20 nm diameter CNTs grown on diamond substrates
(b) High resolution TEM micrograph showing 16 walls of highly crystalline MWCNT

The lower pressure growth seems to improve the D/G ratio of CNTs grown on diamond as opposed to atmospheric pressure growth. While increasing the growth times resulted in longer tubes, the growth temperature variations between 750 – 800°C did not show much noticeable changes in CNTs. Also, prior heat treatment of the catalyst islands did not appear to influence the growth of CNTs, as the samples heated in Ar/H₂ environment prior to CVD or the samples treated in the CNT furnace yielded similar quality CNTs. With the growth of CNT on diamond substrates demonstrated as possible for thermal applications, thermal resistance measurements of these substrates are underway.

4. Conclusions

It is shown that high-quality multi-wall CNTs can be grown on diamond substrates without using intermediate oxide buffer layers. Both Ni and Ni-9%W-1.5%Fe catalysts deposited by optimized sputtering conditions were found to produce CNTs on rough diamond substrates. Proof of the good CNT crystallinity was provided by TEM and Raman spectroscopy, with a D/G ratio of 0.2-0.3 in Raman spectra being observed on such samples.

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