AFRL-RZ-WP-TP-2011-2049

GROWTH OF HIGH QUALITY CARBON NANOTUBES ON FREE-STANDING DIAMOND SUBSTRATES (POSTPRINT)

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MARCH 2010

AIR FORCE RESEARCH LABORATORY
PROPULSION DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7251
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
March 2010	Journal Article	March 2008 – March 2010

4. TITLE AND SUBTITLE
GROWTH OF HIGH QUALITY CARBON NANOTUBES ON FREE-STANDING DIAMOND SUBSTRATES (POSTPRINT)

5a. CONTRACT NUMBER In-House
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER 62203F

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5d. PROJECT NUMBER 3145
5e. TASK NUMBER 32
5f. WORK UNIT NUMBER 314532ZE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RZPG
11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RZ-WP-TP-2011-2049

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES
This paper contains color. PA Case Number: 88ABW-2010-1418; Clearance Date: 23 Mar 2010. Post print published in: Carbon, V48, pp 2442-2446 (2010)

14. ABSTRACT
Carbon nanotubes (C"JTs) 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. "Ji and Ni-9%W-l.5% Fe catalyst islands were deposited to nucleate CNTs directly onto the diamond substrates. Randomly-oriented multi-walled CNTs forming a mat of 5 1m 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 DIG peak ratio of 0,2-0.3 in Raman spectra.

15. SUBJECT TERMS
Carbon nanotubes, diamond, plasma. microscopy, translucent. substrates, thelmaL microwave, spectra, catalyst, chemical. wafer

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Kevin Yost
Unclassified	Unclassified	Unclassified	SAR	7	19b. TELEPHONE NUMBER *(Include Area Code)* 937-255-6246

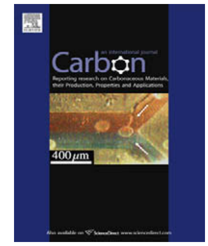
Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

carbon 48 (2010) 2442 2446

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon



Growth of high-quality carbon nanotubes on free-standing diamond substrates

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ARTICLE INFO

Article history:
Received 7 October 2009
Accepted 9 March 2010
Available online 15 March 2010

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 CH_4 as precur sor. 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 C_2H_2 as precursor. Transmission electron microscopy and Raman anal yses 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 poten tial for high thermal conductivity: graphite, diamonds and carbon nanotubes (CNTs). Due to the high thermal conductiv ity (~1800 W/km) of diamond, heat spreaders made of dia mond 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 materi als [4 6]. CNTs can make excellent thermal interface materi als 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 ther mal conductivity of 81 W/m K and a thermal resistance of 0.43 cm^2 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

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0008 6223/$ see front matter Published by Elsevier Ltd.
doi:10.1016/j.carbon.2010.03.013

of Cu foil and CNT arrays and reported that thermal interface resistances of less than 10 mm^2 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 mm^2 K/W. Cola et al. [9] investigated CNT arrays grown on SiC to serve as thermal interface materials for high tem perature SiC devices and achieved thermal resistances less than 10 mm^2 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 mea sured to have thermal interface resistance of 12 mm^2 K/W. CNTs were also grown on constantan substrates for similar applications without the use of catalysts [11]. Carbon nanofi ber Cu composite films have been reported by Ngo et al. to have very low thermal resistances (0.25 cm^2 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 conduc tance. A structure containing a composite of diamond sub strates 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 com bining 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 in. diameter silicon wafers. Prior to the dia mond growth, the Si wafers were thoroughly cleaned and scratched with diamond crystals (pre seeding) in an ultra sonic bath to initiate nucleation [13]. Diamond growth was carried out in a low concentration of CH_4 (1.5 2%) as the car bon source gas in a carrier gas of hydrogen. Diamond films were grown using microwave powers between 2500 and 4000 W at temperatures of 850 900 °C for 6 7 days to obtain films of $\sim$100 μm thickness. Free standing diamond sub strates 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 2 to 10 nm thickness were deposited by varying the deposition time. While some samples were treated in Ar/5% H_2 atmo sphere 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 in. diameter quartz tube in a horizontal fur nace. Initially, the tube furnace was evacuated by using a rough pump and then purged with Ar/5% H_2 for 20 min. The furnace with the samples was heated in an Ar/5% H_2 atmo sphere to 750 800 °C. A precursor gas of 10 vol.% C_2H_2 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% H_2 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 micro scope (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 sam ples. 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 crystal line quality.

3. Results and discussion

Using microwave plasma CVD, diamond coatings up to 100 μm thick were processed. Fig. 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. Fig. 2 shows a theta two theta XRD pattern taken from a diamond substrate. Peaks corresponding to different orientations of the diamond were noted, indicating the polycrystalline nature of the diamond substrates. Fig. 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].

The free standing diamond substrates obtained by dis solving 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 polycrys talline diamond films with grain boundaries also influences

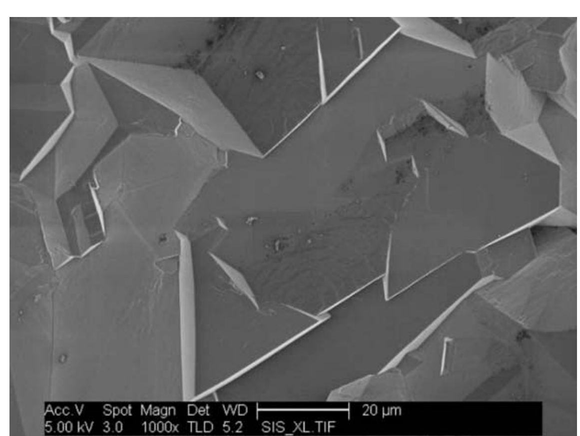

Fig. 1 – SEM micrograph of as-grown diamond sample showing facets of crystals.

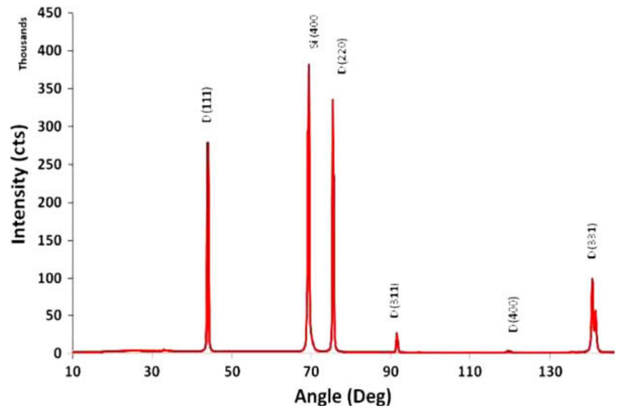

Fig. 2 – X-ray diffraction pattern taken from a diamond substrate.

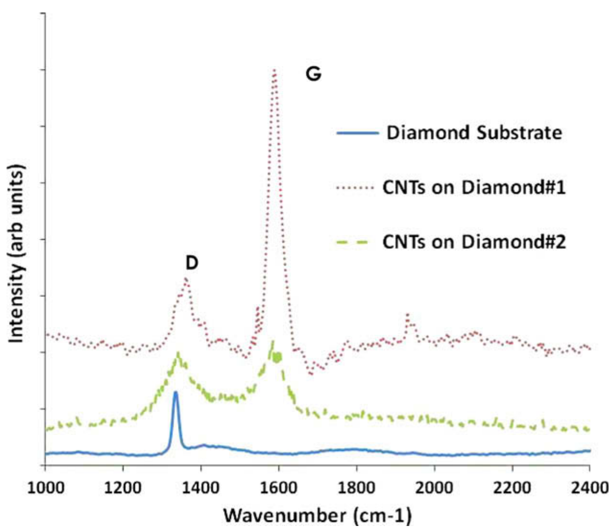

Fig. 3 – Raman spectra taken from a diamond substrate as compared to CNT/diamond samples grown at two different processing conditions (#1 in low pressure of 90 torr, #2 atmospheric pressure).

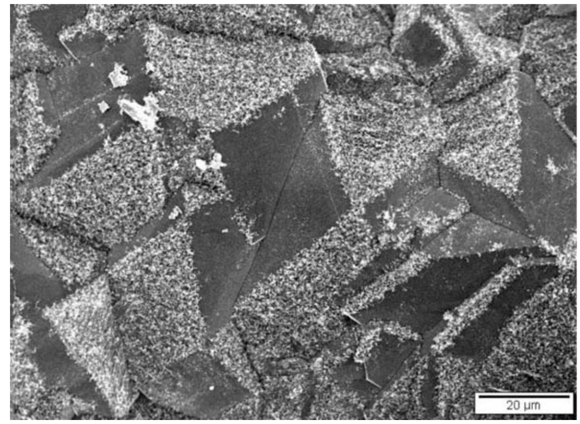

Fig. 4 – Partial coverage of CNTs grown on diamond substrate partially covered with Ni–W–Fe deposited by using initial sputtering conditions.

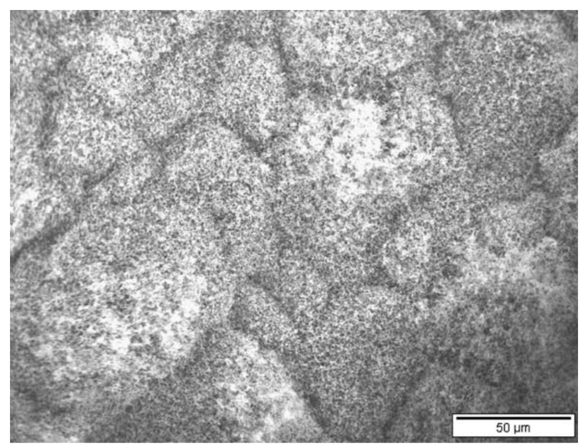

Fig. 5 – Complete coverage of CNTs on diamond substrates with Ni catalysts deposited by sputtering using optimized conditions.

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. Fig. 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.

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 Fig. 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 Fig. 6, where randomly oriented CNTs can be clearly seen. A cross sectional SEM micrograph of the sample shown in Fig. 7 demonstrates that 3 5 µm thick CNT carpet is present on the

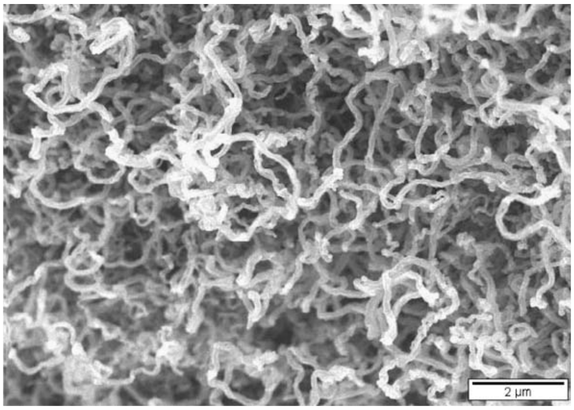

Fig. 6 – Higher magnification photomicrograph showing the CNTs grown on a diamond substrate.

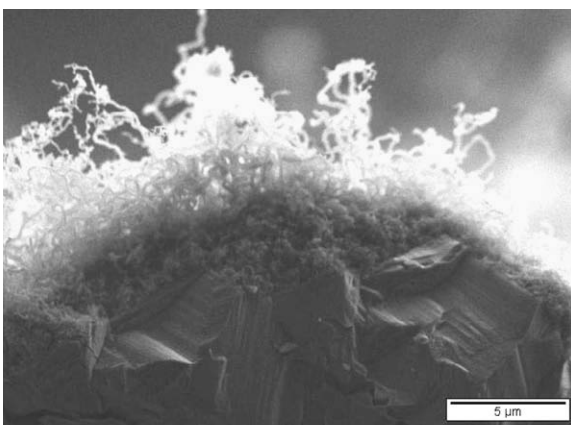

Fig. 7 – Cross-sectional SEM image showing CNTs grown on a diamond substrate.

samples. Samples processed with the optimized sputtering conditions for Ni 9%W 1.5%Fe also provided similar CNT coverage.

CNTs observed by TEM (image show in Fig. 8a) indicate that the diameter of the samples is around 20 nm. High reso lution TEM of the samples show that growth of high crystal line quality CNTs on diamond substrates is possible. This particular image is of a MWCNT where 16 walls are present as shown in Fig. 8b. In order to further confirm the quality of these CNTs, Raman spectra were taken on different sam ples. Fig. 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* ra tio as low as 0.3 was obtained as shown in Fig. 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.

The lower pressure growth seems to improve the *D*/*G* ratio of CNTs grown on diamond as opposed to atmospheric pres sure growth. While increasing the growth times resulted in longer tubes, the growth temperature variations between

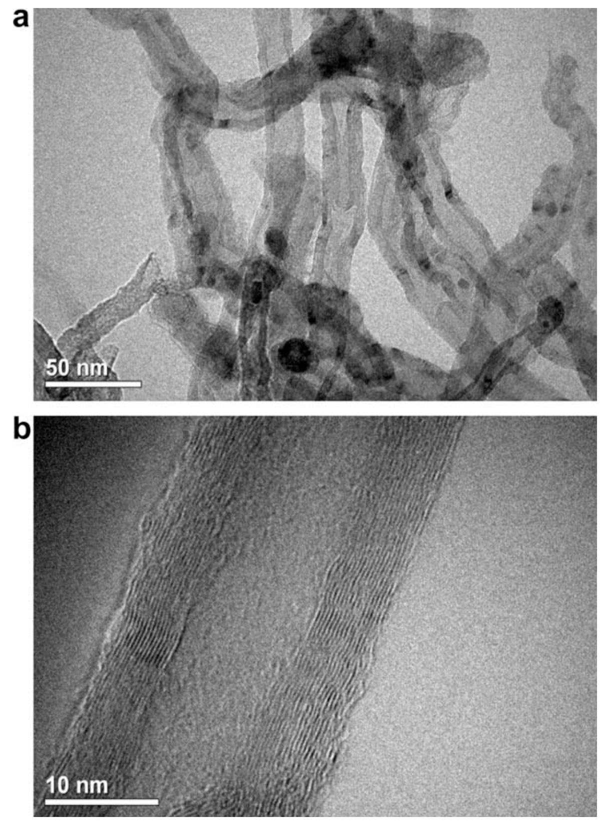

Fig. 8 – (a) TEM micrograph showing 20 nm diameter CNTs grown on diamond substrates and (b) high resolution TEM micrograph showing 16 walls of highly crystalline MWCNT.

750 and 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/H_2 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 mea surements 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 buf fer 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 crystal linity 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.

Acknowledgements

The authors thank Larry Christy for his assistance in process ing some of the samples. The Air Force Office of Scientific Re search and the Propulsion Directorate of AFRL provided the financial support of this work.

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