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Iyer, Ajai; Kaskela, Antti; Johansson, Leena-Sisko; Liu, Xuwen; Kauppinen, Esko I.; Koskinen, Jari Single Walled Carbon Nanotube network - Tetrahedral Amorphous Carbon composite film

Published in: Journal of Applied Physics

DOI: 10.1063/1.4922242

Published: 01/01/2015

Document Version Publisher's PDF, also known as Version of record

Please cite the original version:

Iver, A., Kaskela, A., Johansson, L.-S., Liu, X., Kauppinen, E. I., & Koskinen, J. (2015). Single Walled Carbon Nanotube network - Tetrahedral Amorphous Carbon composite film. *Journal of Applied Physics*, *117*(22), 1-10. Article 225302. https://doi.org/10.1063/1.4922242

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Citation: Journal of Applied Physics **117**, 225302 (2015); doi: 10.1063/1.4922242 View online: http://dx.doi.org/10.1063/1.4922242 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/22?ver=pdfcov Published by the AIP Publishing

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Single walled carbon nanotube network—Tetrahedral amorphous carbon composite film

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(Received 19 February 2015; accepted 26 May 2015; published online 10 June 2015)

Single walled carbon nanotube network (SWCNTN) was coated by tetrahedral amorphous carbon (ta-C) using a pulsed Filtered Cathodic Vacuum Arc system to form a SWCNTN—ta-C composite film. The effects of SWCNTN areal coverage density and ta-C coating thickness on the composite film properties were investigated. X-Ray photoelectron spectroscopy measurements prove the presence of high quality sp³ bonded ta-C coating on the SWCNTN. Raman spectroscopy suggests that the single wall carbon nanotubes (SWCNTs) forming the network survived encapsulation in the ta-C coating. Nano-mechanical testing suggests that the ta-C coated SWCNTN has superior wear performance compared to uncoated SWCNTN. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4922242]

I. INTRODUCTION

Due to their unique electrical, mechanical, and optical properties, carbon nanotubes (CNTs) have been widely researched for multiple application areas since their discovery in 1991.¹ CNT and CNT networks (CNTNs) have been used to fabricate transistors,²⁻⁴ optically transparent conductors for flexible electronics and solar cells,^{5–7} bio-sensors,^{8,9} thermo-acoustic emitters,¹⁰ quantum electronic devices,^{11,12} and field emission electron sources.¹³ However, in most applications, these CNTs and CNTNs are prone to mechanical damage and environmental contamination (such as adsorption of chemical species) which can degrade their properties. It would be desirable to have a protective thin film coating on top of the CNT/CNTN with good mechanical properties, chemical inertness, optical transparency, and large band-gap, to improve the durability of the CNT/CNTN based components. A strong candidate for this protective thin film is sp³ bonded carbon such as Diamond like Amorphous Carbon (DLC) films.¹⁴

The term DLC is used for amorphous carbon films with varying fraction of sp³ and sp² bonded carbon and tetrahedral amorphous carbon (ta-C) is non-hydrogenated DLC film with sp³ fraction above 70%.¹⁴ Traditionally, DLC films have been used as protective coatings to improve the mechanical properties of bulk materials.^{15–17} There are very few papers which have evaluated the nanoscale structure and chemical bonding configuration of DLC-CNT composites. Chemical Vapor Deposition (CVD) process has been used to deposit 1 μ m thick DLC on dense vertical CNT forest with increased toughness of the composite.¹⁸ CVD process has

been used to deposit 25–30 nm thick DLC on dense vertical CNT forest, to improve the field emission and lifetime of CNT.¹⁹ Filtered Cathodic Vacuum Arc (FCVA) process has been used to deposit 5 μ m thick DLC on top of dense vertical CNT to form a visco-elastic composite.²⁰ Pulsed laser deposition (PLD) has been used to deposit 50 nm thick DLC on Single walled carbon nanotube (SWCNT) bundles with increased scratch resistance while maintaining conduction properties.²¹ FCVA process has been used to deposit 25 nm thick DLC on dense SWCNT networks for increased elasticity and better nano-wear resistance.²² However, no surface sensitive test has been reported in literature, to validate the presence of sp³ bonded carbon coating on the surface of sp² carbon nanostructure, especially for coating thickness comparable to nanostructure height.

In this work, we report synthesis and characterization of carbon nanomaterial composite, consisting of ta-C coating on SWCNT networks (SWCNTN). X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface of the composite and obtain direct evidence of sp³ bonded carbon (ta-C) on the SWCNTN. The composite was also characterized by Scanning Electron Microscope (SEM) and Raman Spectroscopy. Additionally, nano-indentation and nano-wear tests were performed to characterize the hardness of carbon coating and mechanical wear resistance of the composite. The effect of, changes in SWCNTN areal coverage density, on the quality of carbon coating and mechanical wear resistance have also been studied.

II. EXPERIMENTAL DETAILS

SWCNTs were synthesized by high temperature floating catalyst CVD process, based on thermal decomposition of ferrocene to form iron nanoparticles.^{6,10,23} This was followed

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by catalytic decomposition of carbon monoxide via Bouduard reaction on the iron nanoparticle surfaces, leading to nucleation and growth of SWCNT in gas phase, inside a quartz walled laminar flow reactor, maintained at 880 °C based on previous optimization.⁶ The SWCNTs can aggregate in gas phase forming bundles, consisting of several parallel SWCNTs due to surface energy minimization.²⁴ SWCNTs were collected on nitrocellulose membrane filters (Millipore Ltd. HAWP, 0.45 μ m pore size) at the outlet of the reactor to form randomly oriented SWCNT networks (Fig. 1(a)).

Silicon (100) with 100 nm of thermal oxide, cut into $1 \text{ cm} \times 1 \text{ cm}$ pieces was used as substrate material (Fig. 1(a)). The substrates were cleaned by ultra-sonication for 3 minutes in HPLC grade acetone (Sigma-Aldrich) followed by 3 min of ultra-sonication in ethanol. The substrates were



FIG. 1. Sample preparation process (not drawn to scale); (a) SWCNTN on membrane filter and the substrate, (b) press transfer of SWCNTN onto the substrate, (c) SWCNTN densification step, (d) as prepared sample showing areas covered by SWCNTN, and (e) Carbon coating by p-FCVA process.

TABLE I. Sample details.

Sample name	SWCNTN areal coverage density	Carbon coating thickness (nm)	OPT performed (Y/N)	OPT time/calculate detch thickness	Final carbon coating thickness (nm)	Total composite film thickness (nm)
S-100-20	100%	20	Ν	_	20	75 ± 3
S-40-20	40%	20	Ν	_	20	32 ± 1
S-40-OPT	40%	10	Y	30 s/3 nm	7	17 ± 2

blow dried using nitrogen gas and dried on a hot plate at $120 \,^{\circ}$ C for a few minutes to evaporate adsorbed water vapor. The substrates were then plasma cleaned (Fishione Instruments Model 1020 plasma cleaner) for 1 min with a mix of 75% argon and 25% oxygen.

The SWCNTN were transferred onto the substrates by a room temperature press transfer process.⁶ The membrane filters with SWCNTN were cut into strips of $0.5 \text{ cm} \times 0.8 \text{ cm}$, placed on substrates (SWCNTN side down) and pressed between clean glass slides with a pressure of around 3×10^5 Pa to ensure conformal contact (Fig. 1(b)). The filter was subsequently peeled off leaving the SWCNTN adhered to the surface. The press transfer process was followed by solvent based densification step where the SWCNTN is wetted with ethanol (Fig. 1(c)). The surface tension of the evaporating ethanol layer leads to densification of the SWCNTN in the -z direction.⁶ Post densification the samples are dried on a hot plate at $120 \,^{\circ}$ C for a few minutes to evaporate adsorbed water vapor following which they are ready for carbon coating process (Fig. 1(d)).

Carbon coating was deposited onto the press transferred SWCNTN using a pulsed Filtered Cathodic Vacuum Arc (p-FCVA) deposition system (Fig. 1(e)). The cathodes were 6.35 mm diameter Graphite rods of 99.997% purity (Goodfellow) in a dual cathode configuration with a knee filter (45° bend) to filter out macro-particles and guide the plasma.²⁵ A pulse forming network, charged to 400 V (pulse current 650 A) was used to strike the triggerless arc²⁶ with a frequency of 1 Hz. The depositions were performed at working pressures of 2×10^{-6} Torr and room temperature, for a target to substrate distance of 110 mm. The substrates were at floating potential and were rotated to ensure homogenous

film deposition. The deposition rate of carbon coating was around 0.1 nm/pulse (on silicon), for target to substrate distance of 110 mm, as measured by contact profilometer. The p-FCVA process and the deposition parameters used here results in ta-C coatings on flat surfaces and are well documented in literature.^{14–16,25–28} However, in this work, it is not yet proven that the coating on the SWCNTN is ta-C and the term carbon coating shall be used, till proved otherwise. With each sample, a clean reference Silicon substrate with resist marking was also deposited with carbon coating under the same conditions to check coating quality.

The samples analyzed in this work are described in Table I. The thickness of carbon coated SWCNTN samples and reference Silicon with carbon coating was checked using Dektak 6 M (Veeco) contact profilometer. Samples were imaged by S-4700 (Hitachi) SEM. SWCNTN areal coverage density was defined as the percentage of substrate area covered by the SWCNTN, inside the strip area. As checked by SEM imaging (Fig. 2) two different SWCNTN areal coverage densities were analyzed, namely, low density (40% areal coverage) and high density (100% areal coverage). It must be pointed out that the measured thickness of uncoated 100% areal coverage SWCNTN is around 5 times higher than the uncoated 40% areal coverage SWCNTN. Sample S-40-OPT (Table I) was subjected to Oxygen Plasma treatment (OPT) for 30 s under mild conditions and compared to a sample similar to S-40-OPT with no coating. The OPT was performed in Fishione Instruments system (Model 1020) with gas mix of 75% argon and 25% O2 and 12-15 eV ion energy on target. It has been shown that at such low ion energies there is no sputtering component due to Argon and all



FIG. 2. SEM images of uncoated SWCNTN's; (a) SWCNTN with average 40% areal coverage density; (b) SWCNTN with 100% areal coverage density.

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the etching is due to chemical reaction between carbon and oxygen.²⁹ Calibration with reference carbon coatings of different thickness deposited on Silicon (100) showed OPT etch rates to be around 0.124 nm/s. The calibrated etch rate was used to calculate the thickness of carbon coating etched for S-40-OPT, and final coating thickness is confirmed by contact profilometer.

Raman spectroscopy was performed using LabRAM HR (Jobin Yvon Horiba) system. Argon laser with $\lambda = 488 \text{ nm}$ (power = 10 mW) with a BX41 (Olympus) microscope and $100 \times$ objective lens with spot size less than 1 μ m was used for all the samples. XPS was performed by an Axis Ultra electron spectrometer (Kratos Analytical) using monochromatic Aluminium K α (E = 1487 eV) irradiation. Experiments were performed in ultra-high vacuum on as-received specimen after an overnight evacuation, in order to preserve the surface chemistry intact. Low resolution survey scans were recorded in hybrid mode, together with high resolution C1s regional spectra using 5 eV pass energy and 50 meV energy step with X-Ray power of 150 W; in all XPS measurements the area of analysis was 700 μ m \times 300 μ m. The XPS data were analyzed with CasaXPS (elemental composition) and Origin (high resolution C 1s peak fits). Nano-mechanical tests were performed by TI-900 TriboIndentor (Hysitron, Inc.) using a Berkowitz tip (nominal diameter 200 nm) for nano-indentation and nano-wear tests. Nano-indentation tests, to check the hardness of ta-C film were performed on two samples, namely, reference ta-C film (50 nm thickness) and reference ta-C film post OPT (45 nm thickness). The nano-indentation tests were performed in load controlled mode, for four points per sample with loads from $100 \,\mu\text{N}$ to 400 μ N and increment of 100 μ N per point. Nano-wear testing of all the samples was performed with three different forces of $10 \,\mu\text{N}$, $20 \,\mu\text{N}$, and $60 \,\mu\text{N}$. The scan area for each force was $1 \,\mu\text{m} \times 1 \,\mu\text{m}$ and single pass scan was performed for all the samples. Pre and post wear scan imaging of an area of $10\,\mu\text{m}$ \times $10\,\mu\text{m}$ was performed using small force of $0.5 \,\mu\text{N}$ to avoid any changes to the samples. The average volume for each wear crater was calculated as the product of average crater dimensions $(X_{avg}*Y_{avg}*D_{avg})$ as found from line profiles. Maximum crater volume for each crater was calculated by the product of scan area and measured composite film thickness.

III. RESULTS AND DISCUSSION

A. SEM

SEM imaging of samples was performed both pre (Fig. 2) and post deposition (Fig. 3). Image analysis, using ImageJ software shows areal coverage density is average



FIG. 3. SEM images post deposition (a) and (b) and post deposition followed by OPT (c) and (d). (a) Sample S-100-20, (b) sample S-40-20, (c) sample S-40-OPT pre oxygen plasma treatment, and (d) sample S-40-OPT post 30 s oxygen plasma treatment.

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40% in case of samples S-40–20 and S-40-OPT (Fig. 2(a)) and 100% for S-100–20 (Fig. 2(b)). The SWCNTN consists of SWCNT bundles and by image analysis the bundle diameters are in the range of 6–20 nm.

The SEM images of samples post deposition (Figs. 3(a)-3(c)) when compared to pre-deposition images (Figs. 2(a) and 2(b)) show presence of a coating due to thickening of individual SWCNT bundles and morphology different from uncoated bundles. Additionally, sample S-40-OPT was subjected to OPT in mild conditions for 30 s with a reference sample similar to S-40-OPT but without carbon coating. Post OPT, SEM analysis reveals absence of SWCNTN for the reference sample (not shown) but sample S-40-OPT still shows the presence of SWCNTN (Fig. 3(d)) indicating that the coating protected the SWCNTN bundles during OPT.

B. Raman spectroscopy

Fig. 4 shows the Raman spectrum for the uncoated SWCNTN sample with all the prominent peaks marked.^{30,31} Radial Breathing Mode (RBM) peaks have been fitted with Lorentzian peaks (inset of Fig. 4), and Eq. $(1)^{30}$ was used to calculate SWCNT diameters, which are in the range of 1.0–1.6 nm

$$\omega_{\text{RBM}} = (A/d_t) + B \text{ where } A = 234 \text{ nm/cm}$$

and $B = 10 \text{ cm}^{-1}$. (1)

The Raman spectroscopy for carbon coated SWCNTs is challenging, as visible wavelength Raman does not directly indicate presence of sp^3 bonded carbon, especially when coated over sp^2 carbon.^{14,32}

Since the SWCNTN does not cover all the area of the substrate (Fig. 1(d)), so after carbon coating there are two distinct areas in every sample, namely, area with SWCNTN + carbon coating and areas with only carbon coating (Fig. 1(e)). The Raman data from only carbon coated areas were plotted and could be fitted by two Gaussian peaks with I(D)/I(G) values in the range of 0.28–0.33 for the coated



FIG. 4. Raman data with prominent peaks labeled, for uncoated SWCNTN after room temperature press transfer process and ethanol densification. * indicates peaks due to silicon substrate. Inset shows RBM peaks of uncoated SWCNTN fitted by Lorentian peaks for SWCNT diameter estimations.

samples (refer supplemental Fig. $S1^{33}$). These I(D)/I(G) values and fitting trend are characteristic of ta-C^{14,32} proving that for non-SWCNTN areas the carbon coating is ta-C. The Raman plots shown in Fig. 5 are Si peak self normalized and representative of the situation for samples S-40-20, S-100-20 and S-40-OPT. Each Raman spectrum in Fig. 5 is individually normalized such that the Silicon peak intensity is 1.

From Figs. 5(a), 5(c), and 5(e), it can be seen that the Raman signal for the coated SWCNTN rides on the ta-C signal and this indicates that SWCNT bundles are encapsulated by ta-C coating.²¹ It is observed from Figs. 5(b), 5(d), and 5(f) that for coated SWCNTN there is broadening of D, G, and G' peaks when compared to uncoated SWCNTN, which is not well understood. This effect could be caused by the damage of SWCNTs at the top (1-2 nm) of the bundles for the first few nanometers of coating deposi $tion^{21,22,34}$ due to C+ ions generated in the p-FCVA process.^{14–16,32} However, similar effects are observed when SWCNTs are subjected to pressure^{35,36} and ta-C is known to have high compressive stress.^{14–16} The narrowing of D, G, and G' peaks and better peak separation of G- and G+ peaks for S-40-OPT (Figs. 5(e) and 5(f)) compared to the other samples (Figs. 5(a)-5(d)) is attributed to the thinner ta-C coating and OPT process performed on the sample. As an integral part of its formation, the ta-C coating has few atomic layer thick, sp² rich surface layer^{14,29} which might lead to reduction of Raman intensity. This surface layer is removed as part of the OPT process²⁹ leading to change of the Raman spectra of S-40-OPT compared to the non-OPT samples.

Raman spectral data (Fig. 5) indicate that the SWCNTs survive encapsulation in the carbon coating. From the data, hypothesis can be formed that the carbon coating being deposited is ta-C.

C. XPS

XPS is an ideal tool for identification of the nature of the carbon coating on the SWCNTN compared to visible wavelength Raman spectroscopy which has problems arising from large Raman cross-section of sp² hybridized carbon compared to sp³ hybridized carbon and no direct evidence of sp³ hybridized carbon.³² XPS has no biasing between sp² and sp³ hybridized carbon¹⁴ and it probes the surface of the sample (typically 5 nm) and gives direct evidence of sp³ hybridized carbon on the sample surface.

Fig. 6 shows the curve fitted XPS high resolution C1s spectra for the samples, while the XPS survey spectra and elemental analysis are given in supplementary. Apart from one sample (see below), the C1s regions were fit with Gaussian-Lorenzian components after the removal of Shirley background. The C1s spectrum for uncoated SWCNTN only (Fig. 6(a)) was fitted with an asymmetric Doniach-Sunjic³⁷ profile, to fit conductive sp² bonded carbon due to its semi-metallic behavior³⁸ and a Gaussian component. The Doniach-Sunjic fit peak at 284.4 eV is identified as sp² bonded carbon $^{39-42}$ and the uncoated SWCNTN has dominant sp² carbon bonding fraction (around 82% of C1s spectrum area). The Gaussian

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FIG. 5. Silicon peak normalized Raman Spectra; (a) S-40-20 carbon coated SWCNTN (black) and ta-C on S-40-20 (red). (b) Comparison of uncoated SWCNTN (blue) and carbon coated SWCNTN of S-40-20 (black). (c) S-100-20 carbon coated SWCNTN (black) and ta-C on S-100-20 (red). (d) Comparison of uncoated SWCNTN (blue) and carbon coated SWCNTN of S-100-20 (black). (e) Post OPT S-40-OPT carbon coated SWCNTN (black) and ta-C of S-40-OPT (red). (f) Comparison of uncoated SWCNTN (blue) and carbon coated SWCNTN of S-40-OPT post OPT (black). * indicates peaks due to Silicon from substrate.

component at 285.5 eV is attributed to defects in the nanotube structure as shown in literature 43,44 and minor surface contamination.

Fig. 6(b) shows the C1s spectra for 20 nm ta-C film deposited on Silicon substrate under the same deposition conditions as samples S-100-20 and S-40-20 as a reference for XPS testing. It must be noted that the sp^2 component in ta-C is fitted with Gaussian-Lorentian component too, because the sp^2 phase is disordered and the ta-C is insulating in nature.³⁹ The reference ta-C spectrum (Fig. 6(b)) has primary peaks at

284.4 eV and 285.3 eV corresponding to sp^2 and sp^3 bonded carbon, respectively. There is a secondary peak at 286.5 eV, attributed to C-O contamination, due to air exposure. The peak fits match well with similar studies in literature^{39–42} and show significant sp^3 bonding fraction (around 75% of C1s spectrum area).

Comparing the C1s spectra for coated samples (Figs. 6(c)-6(e)) with the reference ta-C spectrum (Fig. 6(b)), it is observed that the spectral shape for the plots is similar. For comparison (not shown), the sp² peak for the coated samples



FIG. 6. XPS C1s spectra for different samples with peak de-convolution. (a) Uncoated SWCNTN shows 82% sp² bonding fraction, (b) 20 nm reference ta-C on Si shows 75% sp³ bonding fraction, (c) sample S-40-20 shows 74.5% sp³ bonding fraction, (d) sample S-100-20 shows 75% sp³ bonding fraction, (e) sample S-40-OPT post OPT for 30 s shows 83% sp³ bonding fraction.

was also fitted using a Doniach-Sunjic profile and there was no significant change in the sp³ bonding fraction due to the different sp² fit shapes. Hence, the sp² peaks for coated samples were fitted using Gaussian-Lorentian component, for ease of comparison with reference ta-C sample.

The C1s spectra for S-40-20 (Fig. 6(c)) and S-100-20 (Fig. 6(d)) have primary peaks at 284.4 eV and 285.3 eV and show sp³ bonding fraction similar to ta-C reference sample (Fig. 6(b)). These results indicate clearly that the carbon coating on top of the SWCNTN is ta-C. From Figs. 6(c) and 6(d), it is also evident that the ta-C coating quality on the

SWCNTN is not affected by differences in areal coverage density of the SWCNTN. The C1s spectrum of sample S-40-OPT post OPT (Fig. 6(e)) shows much higher sp³ bonding fraction than the other samples (Figs. 6(b)–6(d)) as the oxygen plasma etches sp² bonded carbon faster than sp³ bonded carbon.²⁹ The OPT process removes the few atom thick layer of sp² carbon which forms at the top of ta-C coating as part of deposition process^{41,45,46} and also reduces sp² bonded carbon content in the ta-C coating itself, making it richer in sp³ bonded carbon.^{29,46,47} From the XPS elemental analysis (Refer supplemental Fig. S2³³) around 2%, excess oxygen is present on S-40-OPT sample when compared to the other ta-C coated samples due to the OPT process.

D. Nano-mechanical testing

From the load-displacement curves of each point (refer supplemental Figs. S3 and S4³³) the film hardness was calculated by Oliver-Pharr method⁴⁸ using commercial software provided by Hysitron Inc. The average value of hardness (H) for the ta-C film is 16 GPa, which matches literature.⁴⁹ The average value of hardness (H) for the OPT ta-C film is 17.5 GPa indicating that post OPT the ta-C film becomes harder.

Nano-wear tests were performed to estimate the volume of displaced material as a function of applied force. Fig. 7 shows the images acquired by the TI-900 TriboIndentor (refer Sec. II) of the samples post wear testing by forces $10 \,\mu$ N, $20 \,\mu$ N, and $60 \,\mu$ N. Wear tests on reference ta-C film

of 50 nm thickness with the maximum force of $60 \,\mu\text{N}$ showed insignificant wear of the films, matching literature, ^{17,49,50} hence ta-C wear for lower forces is not considered relevant. In case of uncoated SWCNTN sample (Figs. 7(a) and 7(b)), it was seen that for applied force 20 μ N or more the material was displaced till substrate. From Figs. 7(c)–7(e), the pile-up on one end of the crater indicates significant amount of material displacement for ta-C coated SWCNTN in case of 60 μ N applied force compared to lower forces.

Fig. 8(a) shows plot of the ratio of wear volume to maximum crater volume as a function of applied force for all samples. Fig. 8(b) shows plot of the ratio of average crater depth to measured film thickness as a function of applied force for all samples. Fig. 8(a) indicates that ta-C coated SWCNTN have significantly smaller wear volume ratio when compared to uncoated SWCNTN, for applied forces lower than 60 μ N. Similar trend is observed from Fig. 8(b),



FIG. 7. SPM images of wear craters after nano-wear tests. (a) Uncoated SWCNTN with applied force $10 \,\mu$ N and $20 \,\mu$ N, (b) uncoated SWCNTN with applied force $60 \,\mu$ N, (c) S-100-20, (d) S-40-20, and (e) S-40-OPT.

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FIG. 8. (a) Plot of Ratio of wear volume to maximum crater volume as a function of applied force. (b) Plot of Ratio of average wear depth to measured film thickness as a function of applied force. For both plots uncoated SWCNTN (diamonds-blue), S-100-20 (squares-red), S-40-20 (triangles-green) and S-40-OPT (circles-magenta). Dotted lines are drawn for guidance of the eye only.

where ta-C coated SWCNTN show lower average wear depth w.r.t film thickness when compared with uncoated SWCNTN. These results indicate that the 60 μ N force is an extreme case for these samples and nano-wear performance of ta-C coated SWCNTN is better than uncoated SWCNTN for applied forces below 60 μ N. Also from Fig. 8, the wear performance of S-40-OPT (around 7 nm thick ta-C coating) is observed to be similar to S-40-20 (20 nm thick ta-C coating). This indicates that, wear performance of ta-C coated SWCNTN can be improved if OPT process is performed, which increases the sp^3 content (Fig. 6(e)) and makes the ta-C film harder (shown by increased hardness values for OPT sample by nano-indentation). Sample S-100-20 shows the lowest ratio of wear volume (Fig. 8(a)) and lowest ratio of average depth (Fig. 8(b)) compared to the other samples. To the best understanding of the authors, this effect could be attributed to the fact that S-100-20 has thicker SWCNTN layer and post ta-C deposition the composite might have visco-elastic recovery properties.²²

IV. CONCLUSIONS

In this work SWCNTN - ta-C composite films were successfully fabricated and characterized. The XPS data showed without ambiguity that the carbon coating on the SWCNTN is sp^3 bonded tetrahedral amorphous carbon (ta-C) with similar quality as pure ta-C films. It was shown by Raman spectroscopy that the SWCNTs in the network survive encapsulation in a matrix of sp^3 bonded tetrahedral amorphous carbon. Nano-wear testing of the composite films showed that the ta-C coating improved the wear resistance of the SWCNTN. Wear resistance is further improved by oxygen plasma treatment of ta-C coated SWCNTN composite which etches the sp^2 component of ta-C and enhances the sp^3 component.

ACKNOWLEDGMENTS

The sponsorship of Academy of Finland through research project HISCON (No. 259595) is acknowledged.

Antti Kaskela and Esko I. Kauppinen also acknowledge financial support from TEKES via CARLA-project, Aalto Energy Efficiency (AEF) program via MOPPI-project and JST-EC DG RTD Coordinated Research Project "IRENA" within the Strategic International Collaborative Research Program (SICORP).

Help with XPS data collection by Dr. Joseph Campbell from Department of Forest Products Technology, Aalto University is acknowledged.

Special thanks to Mr. Oskari Elomaa for his fruitful discussions and proof reading of this manuscript.

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