

Variation of Oxygen-to-Carbon Ratio in Oxyacetylene Flame

L.V. Saraf¹, K. J. Bunch², M.H. Engelhard¹ and P.L. Gassman¹

1. Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA

2. National Security Division, Pacific Northwest National Laboratory, Richland WA

Abstract – We present micro-structural and surface analysis of carbon soot using variation in C_2H_2 to O_2 ratio in oxyacetylene flame torch. Preliminary analysis indicate that at higher oxygen content, formation of SiO_2 nanotubes and amorphous-SiC like structure take place while at higher C_2H_2 flame content, we observe majority of amorphous carbon with an evidence of some amorphous sp^3 hybridization.

INTRODUCTION

Effective and affordable approaches to synthesize uniform diamond coatings are essential for their utilization in commercial devices. Majority of the efforts in this direction are based upon usage of chemical vapor deposition (CVD) methods [1-3]. For commercialization purposes, CVD based methods are costly and time consuming. One of the possible solutions to tackle these challenges is usage of oxyacetylene open flame torch to coat carbon based materials. Hansen et al; have indicated that diamonds can be synthesized by using oxyacetylene flame torch technique. [4] Other than its cost effectiveness, this technique provides unique flexibility to coat carbon based phases on a large area. The technique also is potentially less dependent on the size and shape of the coating surface. In this report, we explore the usefulness of oxyacetylene open torch flame experiments and provide some preliminary results towards formation of sp^3 hybridization.

Carbon based materials are commonly analyzed using techniques like x-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Techniques like XRD and SEM are useful for overall structure and morphological analysis whereas XPS and Raman are useful to get supporting confirmation of the data. Raman spectroscopy is useful technique to identify the difference between various carbon phases whereas XPS is highly sensitive to any Si-C reaction products, when coatings are carried out on silicon substrates. In this report, we have utilized these techniques for carbon phase and morphology analysis.

EXPERIMENT

The schematic of a simple experimental set-up is shown in Figure 1. The set-up consist of a water cooled substrate holder, oxyacetylene flame torch, xyz measurement scale and two gas mass flow meters for oxygen and acetylene each. The coatings were carried out for 5 min. and flame tip to silicon distance was maintained at half inch. The flow rates were varied by keeping the total flow rate at 1 SCFH.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. A focused monochromatic Al $K\alpha$ X-ray 1486.7 eV source with 16-element multichannel detection was used in the experiment. The X-ray beam was 101 W, 107 μ m in diameter, and rastered over an area of 1.4 0.2 mm. High-energy resolution spectra were collected using a pass energy of 23.5 eV. The binding energy scale was calibrated using the Cu $2p_{3/2}$ peak at 932.6 eV and the Au $4f_{7/2}$ peak at 83.9 eV.

Raman spectroscopy measurements were carried out using FT-Raman Bruker FRA 106 module and IFS66/V microscope. The Bruker R 590-D Raman microscope was directly connected to FTIR and Raman module. A 1.5-W, 1064-nm YAG laser was used to the input optics of the microscope as an excitation source. Use of the dedicated 1064-nm YAG laser for excitation essentially eliminates fluorescence interferences which is an advantage over dispersive Raman methods.

XRD measurements were carried out using a Phillips X'pert θ - 2θ diffractometer. Slow scanning was used to enhance the signal quality. X-ray profile fitting of the scans were carried out using JADE program.

SEM measurements were carried out using FEI Helios dual-beam microscope and a LEO 982 field emission microscope with resolution of 1 nm at 30 KV and 4 nm at 1.0 KV using multiple detectors.

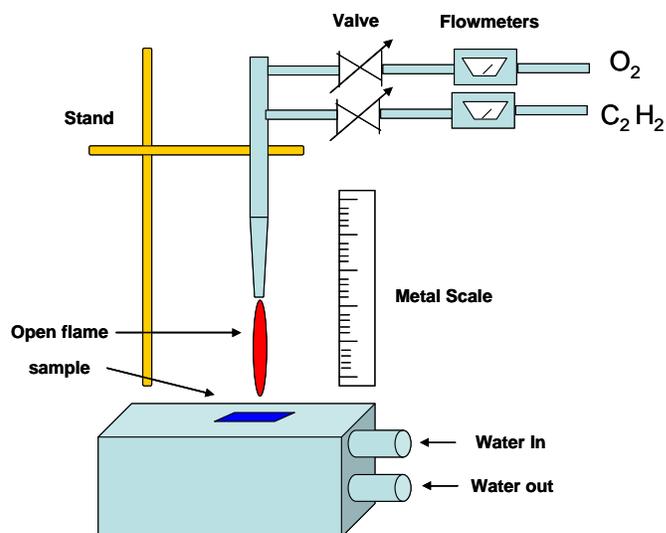


Figure 1: Schematics of oxyacetylene open flame deposition technique to study carbon phases.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 2008		2. REPORT TYPE		3. DATES COVERED 00-00-2008 to 00-00-2008	
4. TITLE AND SUBTITLE Variation of Oxygen-to-Carbon Ratio in Oxyacetylene Flame				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002137. Proceedings of the 2008 IEEE International Conference on Nanotechnology (8th) Held in Arlington, TX on August 18-21, 2008. U.S. Government or Federal Rights License					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

RESULTS AND DISCUSSION

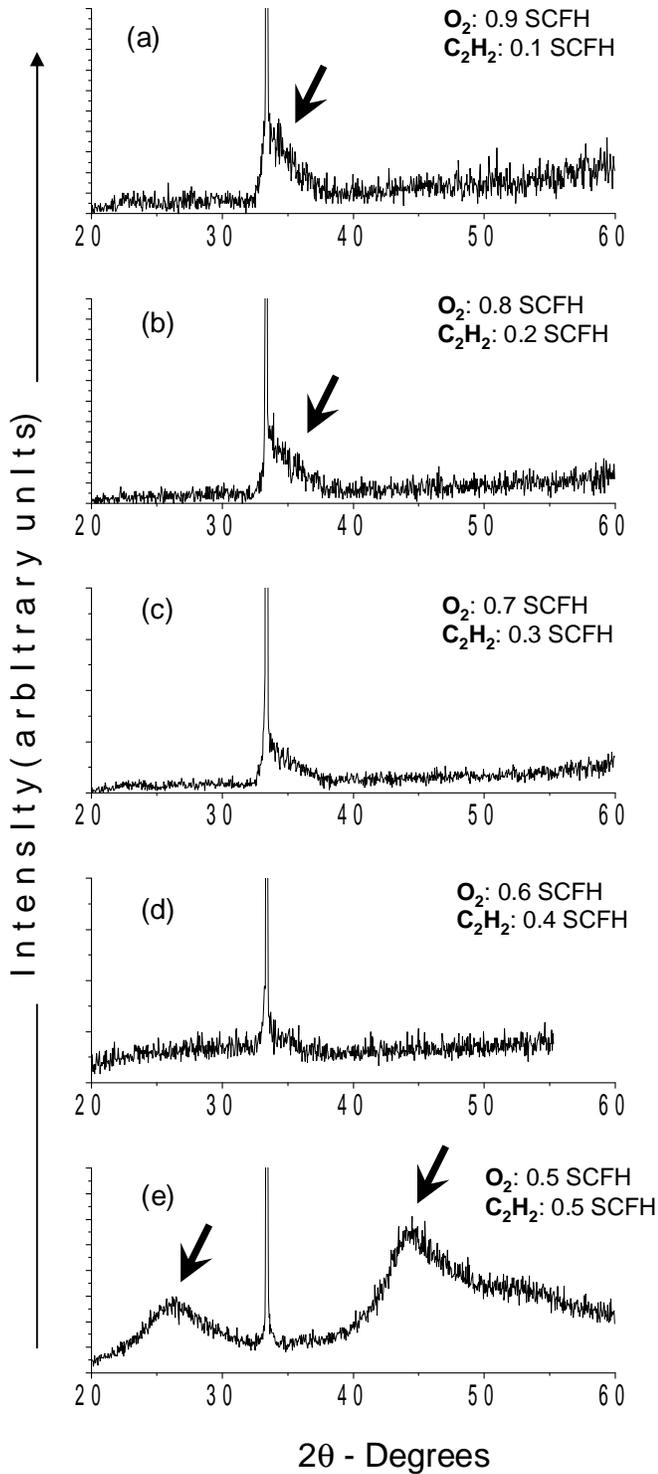


Figure 2: (a-e) indicate XRD scans of samples grown with different oxygen to acetylene ratio. Early indications are high oxygen flame tend to create SiC like structures whereas high carbon flame produces more amorphous graphite like structures. The interested region related to Si-C reactions is indicated by arrows in (a) and (b). The arrows in (e) represent amorphous graphite regions with some indication of amorphous sp^3 type bonding. The sharp peak at the center represents silicon substrate position.

Figure 2 (a-e) represents XRD scans for the samples deposited with various O_2 and C_2H_2 flow rate mixtures. As indicated, the total flow rate was maintained at 1 SCFH and ratio of carbon to oxygen was varied. The sharp peak around 33° represents substrate silicon position. As seen from the XRD scans in Figure 2, two major differences were noticed. At higher oxygen, shoulder of silicon peak at 33° increased significantly and at higher carbon amount broad peaks centered at 27° and 43° increased significantly. Silicon peak shoulder enhancement in Figure 2 (a, b) and broad peaks in Figure 2 (e) are shown by arrows. The 2θ region from $33-40$ deg. is related to Si-C reaction. A slow scan around this 2θ region for the case of flow mixture C_2H_2 : 0.2 SCFH and O_2 : 0.8 SCFH and a typical SEM micrograph of the surface is shown in Figure 3 (a, b). The results clearly indicate an overlapped combination of broad peaks at 34.7° , 35.8° and 36.7° . From these results, it is reasonable to predict formation of amorphous SiC.

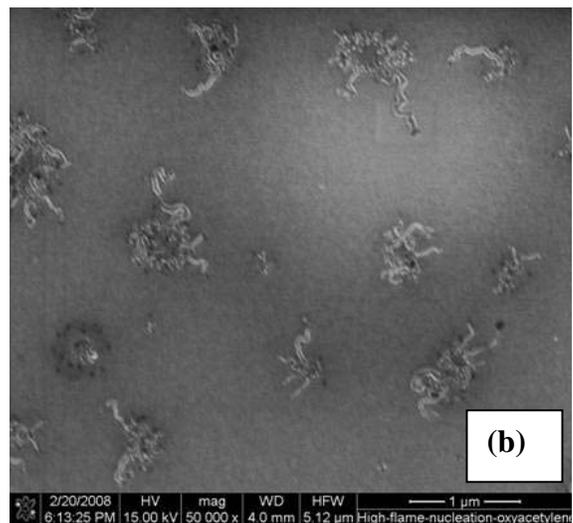
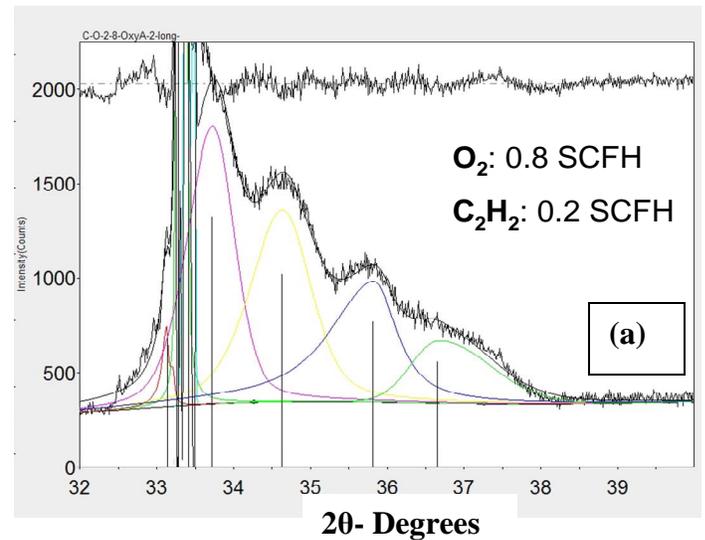


Figure 3: (a) XRD slow scan of sample grown with $C_2H_2:O_2$ ratio of 0.2:0.8 SCFH. (b) SEM micrograph of typical sample surface at high oxygen conditions where nano-wire structures were observed.

SEM micrograph at high oxygen condition indicates formation of nano-wires randomly nucleating on the sample surface. High flame temperature due to enhanced oxygen seems to contribute nanowire formation. Since surface properties measured by XPS (not shown) indicate thick silicon oxide layer, it is reasonable to predict that at least surface of these nano-wires contain silicon oxide. More analysis need to be carried out to examine the core of these nano-wires.

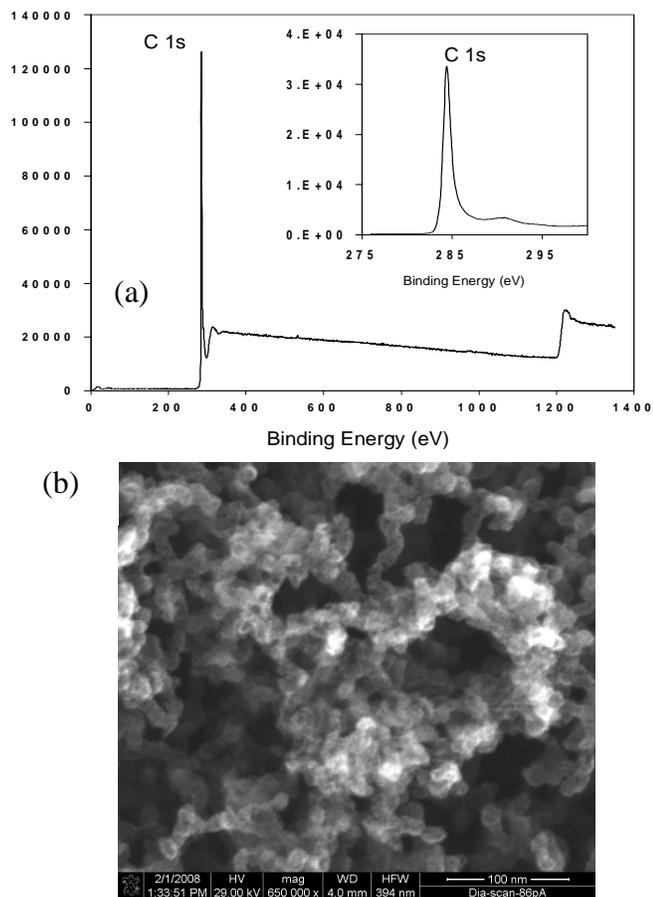


Figure 4: (a) Typical XPS survey scan of carbon films grown at high carbon conditions. Inset: High resolution XPS scan around C 1s position. (b) Typical high resolution SEM image of samples deposited at high carbon conditions.

The broad peaks at 27⁰ and 43⁰ in Figure 2 (e) indicate formation of amorphous graphite. However additional analysis including slow XRD scan is necessary to interpret the data in details. Figure 4 (a) indicate XPS surface properties of sample deposited at high carbon conditions. As seen in the spectrum, high amount of carbon is evident with a strong C 1s position. High resolution SEM image in Figure 4 (b) indicate amorphous graphitic structure with embedded nanocrystals. The analysis also confirms that there is no significant shift in the C 1s position indicating most of the carbon is in sp² type bonding i.e. in the form of graphite like structure. To better interpret our results, we have also carried out additional analysis on these samples by Raman spectroscopy and slow XRD scan.

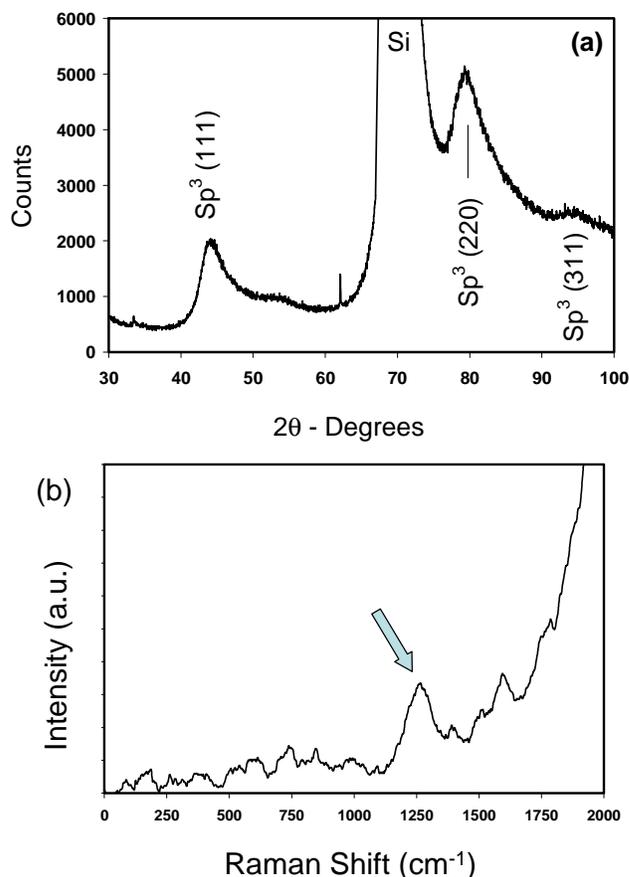


Figure 5: (a) Slow XRD scan of the samples deposited at high carbon conditions. (b) Raman spectroscopy measurement on a typical sample coated with high carbon conditions.

Figure 5 (a, b) indicate slow XRD scan and Raman spectroscopy measurements on samples coated at high carbon conditions. As indicated in Figure 5 (a), the positions representing amorphous graphite also overlap on positions representing sp³ hybridization. Thus, Raman spectroscopy becomes useful technique to distinguish between sp² and sp³ type bonding. As seen in Figure 5 (b), we have seen a weak peak at 1250 cm⁻¹ quite possibly representing small content of amorphous sp³ hybridization. It was shown by Prawer et.al; [5] that a peak at 1250 cm⁻¹ arises from amorphous sp³ type of hybridization. Earlier ab initio calculations [6] of Raman spectra of nanocrystalline diamond indicates that, for calculated molecules of ~1 nm in diameter, a broad peak around 1250 cm⁻¹ should represent nanocrystalline diamond. Another report by Yushin et.al; [7] also indicates that the Raman signal at 1250 cm⁻¹ should rise from amorphous diamond or sp³ type hybridization. A previous study also observed that an amorphous network, generated by quenching high density high temperature carbon, contain a large fraction of tetrahedral bonding sites. [8] Based upon these studies and highly sensitive nature of Raman spectroscopy technique to detect molecular vibrations, it can be interpreted that small fraction of amorphous sp³ type hybridization is present in our samples. However the challenging task will be to enhance the

quantity and degree of crystallization to take an additional step towards depositing uniform coating with sp^3 type carbon bonds.

CONCLUSIONS

We present preliminary results related to micro-structural and surface analysis of carbon coated samples by using variation in C_2H_2 to O_2 ratio in oxyacetylene flame torch. Our analysis indicate that at higher oxygen content, formation of SiO_2 nanotubes and amorphous-SiC like structure take place while at higher C_2H_2 flame content, we observe majority of amorphous carbon with an evidence of trace amorphous sp^3 type carbon bonding.

ACKNOWLEDGEMENTS

The authors would like to sincerely thank Randy Odd for his help during set-up of oxyacetylene experiments. The study is partly supported by Laboratory Directed Research and Development (LDRD) efforts under the grant #DE-AC05-76RL01830. This study is also supported by user process at Environmental Molecular Science Laboratory (EMSL). The work was conducted in EMSL at Pacific Northwest National Laboratory (PNNL). EMSL is a national scientific user facility for Office of Biological and Environmental Research (BER) under the contract DE-AC06-76RL01830.

REFERENCES

- [1] Z. Remes, Y. Avigal, R. Kalish, C. Uzan-Saguy, A. Chack, and M. Nesládek, "Structural, optical and electrical properties of nano-diamond films deposited by HFCVD on borosilicate glass, fused silica and silicon at low temperature", *phys. stat. sol. (a)*, vol. 201, 2499–2502 (2004)
- [2] Y. Lifshitz, C. H. Lee, Y. Wu, W. J. Zhang, I. Bello, and S. T. Lee, "Role of nucleation in nanodiamond film growth", *Appl. Phys. Lett.* Vol.88, 243114 (2006)
- [3] S.G. Wang, Q. Zhang, S.F. Yoon, J. Ahn, Q. Wang, D.J. Yang, Q. Zhou, Q.F. Huang, "Preparation and electron field emission properties of nano-diamond films", *Materials Letters*, vol.56, 948-951 (2002).
- [4] L.M. Hanssen, W.A. Carrington, J.E. Butler and K.A. Snail, "Diamond synthesis using an oxygen-acetylene torch", *Materials Letters*, vol.61, 2847-2850 (2007).
- [5] S. Praver, K.W. Nugent, D.N. Jamieson, J.O. Orwa, L.A. Bursill, J.L. Peng, "The Raman spectrum of nanocrystalline diamond", *Chemical Physics Letters*, vol.332, 93-97 (2000).
- [6] J. Filik, J. N. Harvey, N. L. Allan, P. W. May, J. E. P. Dahl, S. Liu, and R. M. K. Carlson, "Raman spectroscopy of nanocrystalline diamond: An ab initio approach", *Phys. Rev. B* vol.74, 035423 (2006).
- [7] G.N. Yushin, S. Osswald, V.I. Padalko, G.P. Bogatyreva, Y. Gogotsi, "Effect of sintering on structure of nanodiamond", *Diamond & Related Materials* vol. 14, 1721-1729 (2005).
- [8] C.Z. Wang, K.M. Ho, "Structure, dynamics and electronic properties of diamondlike amorphous carbon" *Phys. Rev. Lett.* Vol. 71, 1184-1187 (1993).