

# Variation of Oxygen-to-Carbon Ratio in Oxyacetylene Flame

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**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  $\mu$ 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  $\theta$ -2 $\theta$  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.

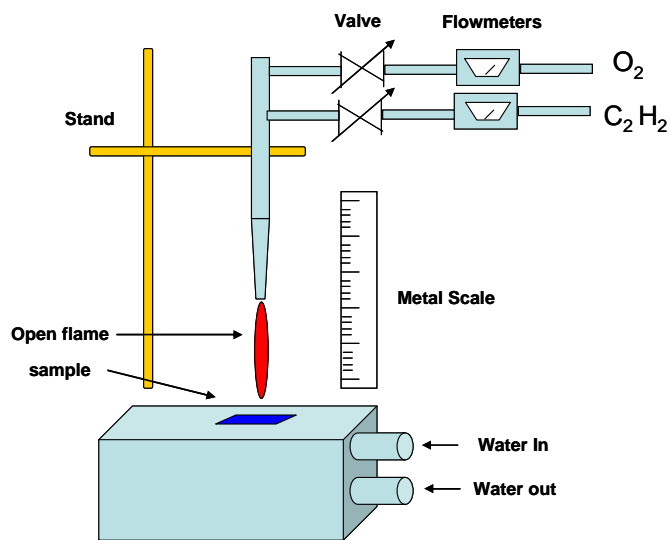


Figure 1: Schematics of oxyacetylene open flame deposition technique to study carbon phases.

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## RESULTS AND DISCUSSION

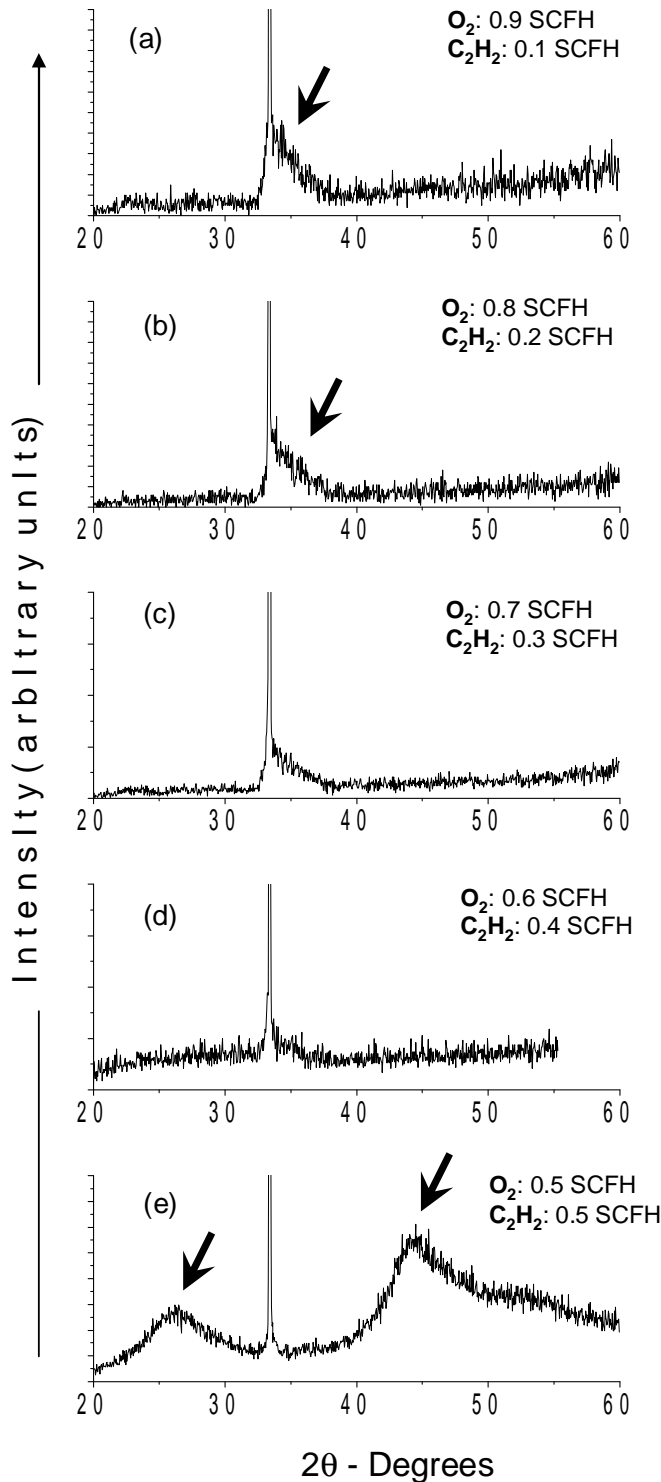


Figure 2: (a-e) indicate XRD scans of samples grown with different oxygen to acetylene ratio. Early indications are high oxygen flame tend to create SiC like structures whereas high carbon flame produces more amorphous graphite like structures. The interested region related to Si-C reactions is indicated 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  $33^\circ$  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  $33^\circ$  increased significantly and at higher carbon amount broad peaks centered at  $27^\circ$  and  $43^\circ$  increased significantly. Silicon peak shoulder enhancement in Figure 2 (a, b) and broad peaks in Figure 2 (e) are shown by arrows. The  $2\theta$  region from  $33$ - $40$  deg. is related to Si-C reaction. A slow scan around this  $2\theta$  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  $34.7^\circ$ ,  $35.8^\circ$  and  $36.7^\circ$ . From these results, it is reasonable to predict formation of amorphous SiC.

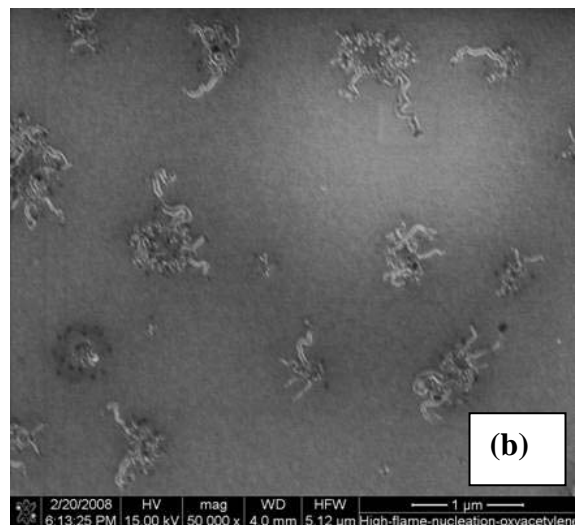
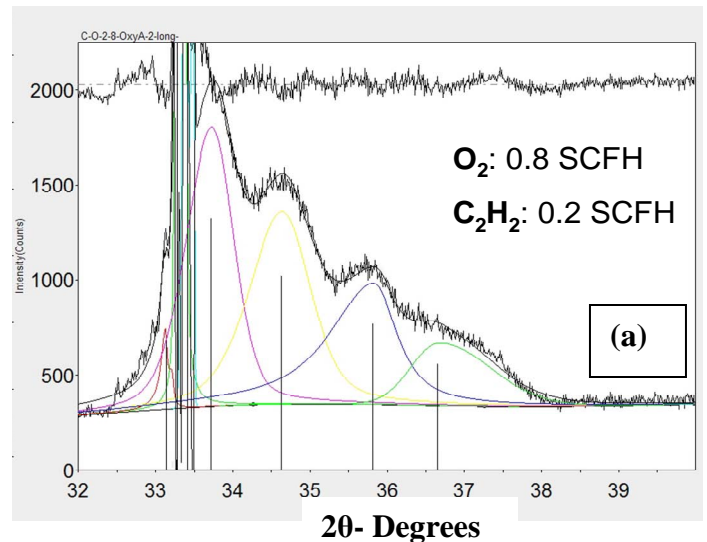


Figure 3: (a) XRD slow scan of sample grown with  $C_2H_2:O_2$  ratio of 0.2:0.8 SCFH. (b) SEM micrograph of typical sample surface at high oxygen conditions where nano-wire structures were observed.

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.

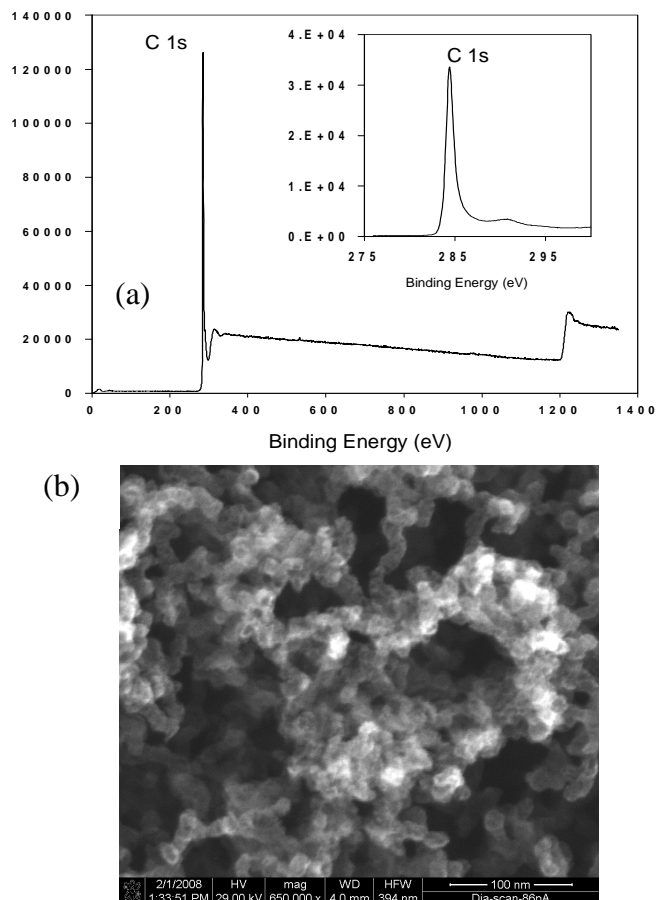


Figure 4: (a) Typical XPS survey scan of carbon films grown at high carbon conditions. Inset: High resolution XPS scan around C 1s position. (b) Typical high resolution SEM image of samples deposited at high carbon conditions.

The broad peaks at  $27^0$  and  $43^0$  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  $sp^2$  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.

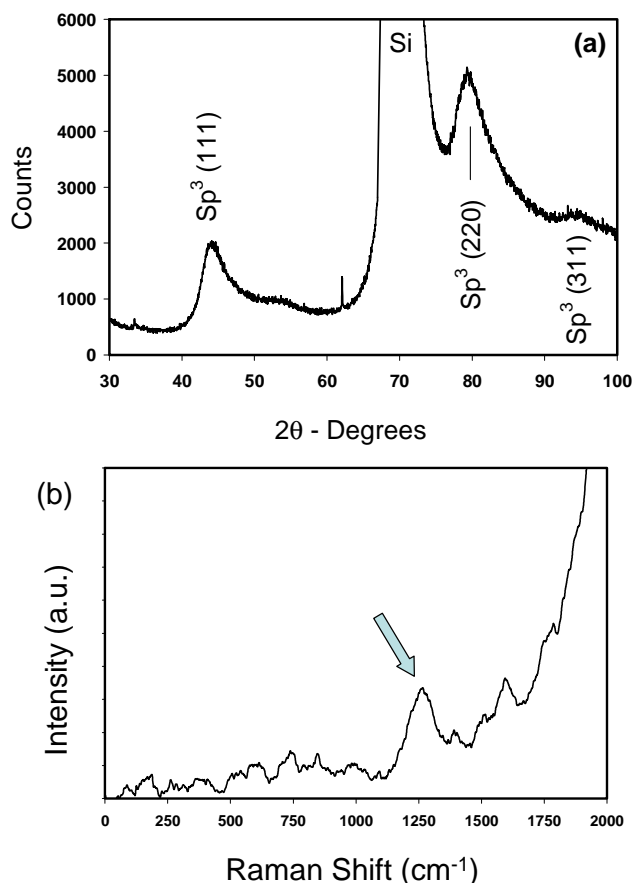


Figure 5: (a) Slow XRD scan of the samples deposited at high carbon conditions. (b) Raman spectroscopy measurement on a typical sample coated with high carbon conditions.

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  $sp^3$  hybridization. Thus, Raman spectroscopy becomes useful technique to distinguish between  $sp^2$  and  $sp^3$  type bonding. As seen in Figure 5 (b), we have seen a weak peak at  $1250\text{ cm}^{-1}$  quite possibly representing small content of amorphous  $sp^3$  hybridization. It was shown by Prawer et.al; [5] that a peak at  $1250\text{ cm}^{-1}$  arises from amorphous  $sp^3$  type of hybridization. Earlier ab initio calculations [6] of Raman spectra of nanocrystalline diamond indicates that, for calculated molecules of  $\sim 1\text{ nm}$  in diameter, a broad peak around  $1250\text{ cm}^{-1}$  should represent nanocrystalline diamond. Another report by Yushin et.al; [7] also indicates that the Raman signal at  $1250\text{ cm}^{-1}$  should rise from amorphous diamond or  $sp^3$  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  $sp^3$  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.

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