

# XPS and XAS preliminary studies of diamond-like carbon films prepared by HiPIMS technique

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**Abstract.** X-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) were employed for the investigations of diamond-like carbon (DLC) films prepared by high-power impulse magnetron sputtering technique (HiPIMS). The measurements were done ex-situ, i.e. the prepared DLC samples were exposed to air during transferring from the deposition to analysis chambers. It is inevitable that the surface of the samples was contaminated by absorbed air molecules. XPS analyses revealed that the main surface contaminants are carbon and oxygen, which introduce the difficulties for the determination of carbon species in the DLC films. In this work, a complementary XAS technique was used for analyzing carbon species in the DLC films. It was found that the DLC film contain more  $sp^2$  than  $sp^3$  carbon. The discrepancy in the  $sp^2/sp^3$  ratio from the two techniques is different as a result of the difference in depth/surface sensitivity.

## 1. Introduction

The DLC is a disordered mixture of C atoms with  $sp^2$  and  $sp^3$  hybridizations. The  $sp^3$  bonding of DLC confers many beneficial properties of the diamond itself, such as high mechanical hardness and chemical and electrochemical inertness. While the  $sp^2$  bonding controls the electronic and optical properties [1]. Thus, one of the essential factors governing the quality of DLC films is the ratio of  $sp^2/sp^3$  carbon atoms. In the past few decades, DLC has attracted increasing interests because of its outstanding properties such as high mechanical hardness, good wear resistance, low friction coefficient, optical transparency, high chemical inertness and biocompatibility [2]. Due to these exceptional properties, DLC films have been widely used in industrial applications such as protective coating for magnetic recording disks, optical windows, cutting tools and micro-electromechanical devices.

Magnetron sputtering is an extremely versatile technique that has been widely used for the preparation of both hydrogenated and hydrogen-free DLC films. One of the interesting magnetron sputtering techniques is high-power impulse magnetron sputtering (HiPIMS). HiPIMS is an advanced sputtering technique used for thin film coatings. The technique is based on magnetron sputter

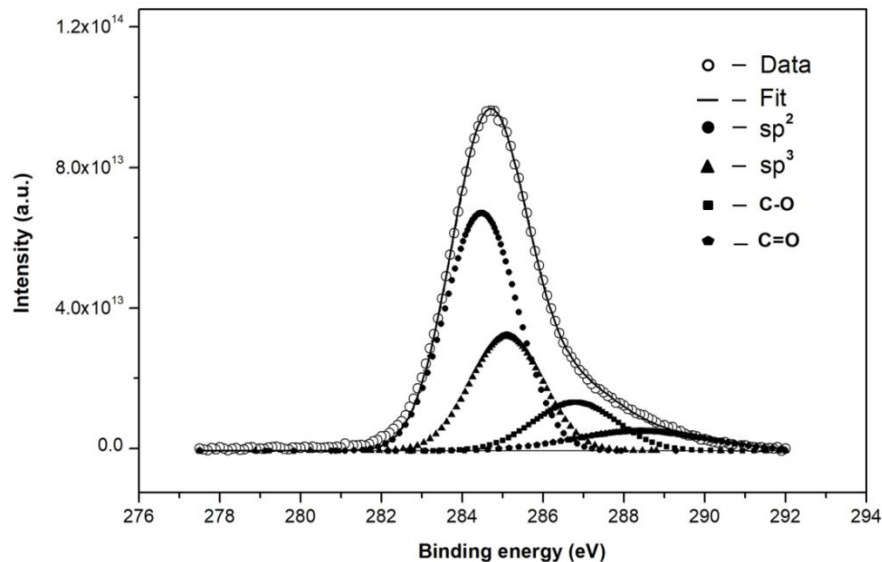
deposition. It employs high power impulse for the magnetron head. The peak power density of HiPIMS technique is normally higher than  $1 \text{ kW/cm}^2$ , which is more than a factor of 100 greater than those obtained by conventional direct-current magnetron sputtering systems. The current density of HiPIMS is over  $1 \text{ A/cm}^2$  [3,4].

In this work, the DLC film preparation experimented with HiPIMS technique. The hybridizations and contaminations on the surface of DLC films were examined by X-ray photoelectron spectroscopy (XPS). However, a common problem in analyzing the results with this technique is contaminated with gas molecules absorbed on films surfaces. Due to XPS is a surface-sensitive quantitative spectroscopic technique. If there is a contamination on the film surface, the measurement results may lead to wrong interpretations. Therefore, the DLC films were also analyzed by X-ray absorption spectroscopy (XAS).

## 2. Experimental

Glass substrates were cleaned with a mixed solution of ethanol and DI water in an ultrasonic cleaner for 20 min. The substrates were dried by  $\text{N}_2$  gas before being loading into the chamber. DLC film was deposited for 60 minutes on the substrate using the average power of 157 watts HiPIMS. The target is pure graphite with 3 inches in diameter. The distance between the target to the substrate was 11 cm. The flow rate of Ar gas was 10 sccm. The base pressure and operating pressures were  $2.7 \times 10^{-5}$  and  $2.2 \times 10^{-2}$  mbar, respectively. XPS and XAS measurements were carried out to characterize the quantitative results of a composition of the films. XPS measurements were performed by using monochromatized  $\text{Al K}\alpha$  (1486.7 eV) for the excitation. XAS measurements were carried out at the beamline 3.2a of the Synchrotron Light Research Institute of Thailand [5].

## 3. Results and Discussion



**Figure 1.** Deconvolution of the C1s XPS spectrum of the DLC film prepared by HiPIMS

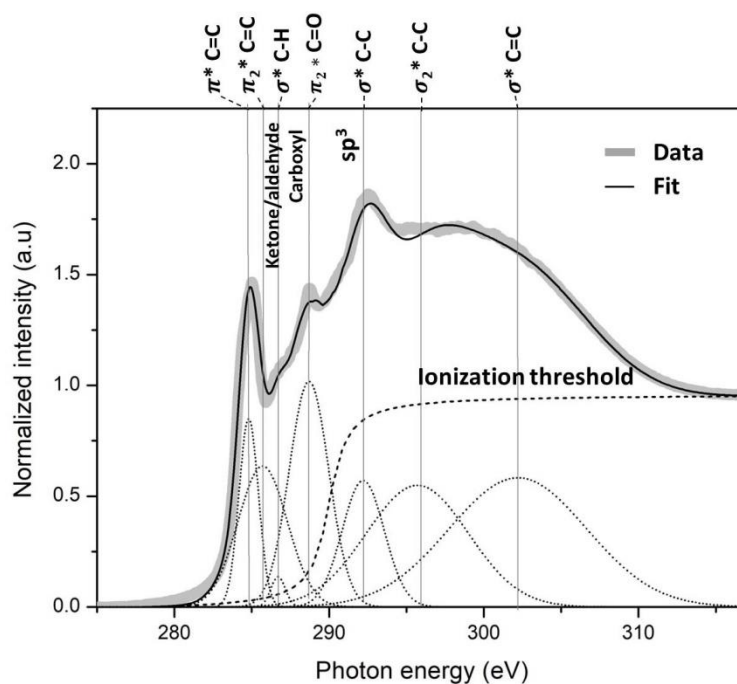
Figure 1 shows the C1s XPS peak taken from the DLC film. The XPS spectrum was background-subtracted and then deconvoluted by Voigt function fitting. C1s peaks in the XPS spectrum are commonly used to identify chemical states of the amorphous carbon films. The C1s spectrum of the DLC film was deconvoluted into four sub-peaks with the positions at 284.5, 285.1, 286.8 and 288.4 eV, respectively [6]. The assignments of the C1s peaks are given in table 1. The C1s peaks around 284.5 and 285.1 eV corresponds to the graphitic structure (the  $\text{sp}^2$  carbon ( $\text{C}=\text{C}$ )) and the diamond structure (the  $\text{sp}^3$  carbon ( $\text{C}-\text{C}$ )), respectively [7]. From the figure, it is obvious that the fraction of the  $\text{sp}^3$  configuration is less than the  $\text{sp}^2$  configuration. Two more C species existing in the C1s XPS

spectrum are attributed to C-O, C=O and O-C=O bonds due to film contamination from exposure to the atmosphere [8].

**Table 1.** Assignment of C1s XPS peaks taken from a DLC film.

Binding energy (eV)	Peak Area ( % )	Assignment
284.5	53.5	C=C ( $sp^2$ )
285.1	25.8	C-C ( $sp^3$ )
286.8	12.5	C-O
288.4	8.1	C=O

Figure 2 shows the normalized C K-edge XANES spectra of the DLC film and curve fitting. The measured spectrum was deconvoluted by curve fitting, giving the Gaussian transition peaks (from 1s to the allowed orbitals) and the ionization step function [9]. The assignments of the obtained fitted peaks are given in table 2. The peaks corresponding to the  $\pi^*$  and  $\sigma^*$  bands at 284.8 eV and 292.2 eV are typical for the C=C bond ( $sp^2$ ) and the tetrahedral C-C bond ( $sp^3$ ), respectively [10]. Other peaks are originated from different carbon species: Ketone/Aldehyde ( $\sigma^*$  C - H) at 286.7eV, carboxyl carbon (C=O(OH)) at 288.7 eV, Cls  $\sigma^*$  of C-C at 293.5 eV, Cls  $\sigma^*$  of C=C at 300eV and Cls  $\sigma_1^*$  of O=C-OH at 296.6 and Cls  $\sigma_2^*$  of O=C-OH at 303.5 eV [11,12].



**Figure 2.** Normalized C K-edge XANES spectrum of DLC films with curve fitting

The results from both techniques confirm that carbon in the DLC film exists in the  $sp^2$  configuration more than the  $sp^3$  configuration. XPS analysis of DLC found that the  $sp^2/sp^3$  ratio is about 1.7. This value is slightly lower than that obtained from XAS analysis, which is 2.0. The discrepancy in the  $sp^2$  to  $sp^3$  ratio may be due to the differences in the probed depth. XPS is more surface sensitive than XAS and, thus, XPS spectra may include information of surface contaminations, leading to inaccurate data reduction. This might be a subject for further investigations where removing surface contaminations might be necessary.

**Table 2.** Peak assignment of the transitions from the 1s to different orbitals and the ionization energy.

Photon energy (eV)	Peak Area ( % )	Assignment
284.8	6.58	$\pi^* \text{C}=\text{C}$
285.7	12.57	$\pi_2^* \text{C}=\text{C}$
286.7	0.79	$\sigma^* \text{C}-\text{H}$
288.7	16.16	$\pi_2^* \text{C}=\text{O}(\text{OH})$
290.0	-	Ionization threshold
292.2	9.58	$\sigma^* \text{C}-\text{C}$
295.7	22.35	$\sigma^* \text{C}-\text{C}$
302.2	31.96	$\sigma^* \text{C}=\text{C}$

#### 4. Conclusion

The DLC films prepared by HiPIMS were studying by XPS and XAS techniques. The results from the two techniques reveal that the DLC films contain  $\text{sp}^2$  carbon than  $\text{sp}^3$  carbon. However, the discrepancy of the  $\text{sp}^2/\text{sp}^3$  ratio was found when comparing the results from the two techniques. This may be due to the fact that the techniques probe two samples at different depth regions and, thus, the surface contaminations contribute to obtained results with different magnitudes.

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