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Characterization of Diamond-like Carbon (DLC) Films Deposited by Filtered Cathodic Vacuum arc Technique

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Abstract

Diamond-like carbon (DLC) films were prepared on AISI H13 hot-work tool steel substrates by filtered cathodic vacuum arc (FCVA) technique under variable substrate DC biasing. The atomic structures of the films were investigated by Raman spectroscopy, X-ray photoelectron spectroscopy, and near edge x-ray absorption fine structure spectroscopy. The Raman spectra revealed that when the magnitude of the bias voltage increased, the G peak was shifted toward lower wave numbers, and indicated that the sp^3 content in the DLC films increased. The ratios between the sp^3 and sp^2 bonds in the films were verified by X-ray photoelectron spectroscopy, and the analyses from near-edge x-ray absorption fine structure measurements demonstrated the mixture of the sp^3, sp^2 bonds together with C-O, C-H bonds, and the amorphous structure in the DLC films.

Key words : Filtered cathodic vacuum arc, Diamond-like carbon, Amorphous carbon film, Bias voltage

Introduction

AISI H13 hot-work tool steel is the most popular materials for hot working of industries in Thailand. It has been utilized as parts of hot molds, punches, extrusion dies, and forging because of its high toughness, wear and abrasion resistance and red hardness. However, applications of AISI H13 under an exposure to lubricant and high temperature may result in the corrosion of surface, leading to severe degradation of the properties. A possible way to solve this problem is to use surface modification methods such as carburizing, carbonitriding, nitriding, chemical vapor deposition, and physical vapor deposition to help improve the corrosion resistance. In the past, hard Cr-plating has been the most widely used technique for this purpose. However, despite the excellent wear and corrosion resistance properties, the negative health impact and environmental in hazards in the form of chromic-acid by-products have led to the reduction of hard Cr-plating usage worldwide.(1) In recent years, diamond-like carbon (DLC) coating becomes a more environmental-friendly alternative to Cr-plating. DLC possesses excellent physical and chemical properties similar to those of diamond film(2,3), having extreme characteristics of not only high hardness and wear resistance, and low friction coefficient, but also high chemical inertness. As a result, the DLC coatings have been extensively used to prevent corrosion in molds, sliding parts, auto mobile parts, magnetic storage disks, cutting tools, high precision gears, micro electro-mechanical devices and biomedical equipment.(4) The properties of DLC films are strongly dependent on the fraction of sp^3/sp^2 C bonding as the mixed bonds provide combined characteristics of diamond and graphite. In many applications of DLC, the sp^3 C bonding is desirable as it provides higher hardness, Yong's modulus, and wear resistance. There are several deposition methods which have been successfully used to synthesize the DLC films: plasma-enhanced chemical vapor deposition(5) , ion-beam deposition(6) , DC and RF magnetron sputtering depositions(7) , ion plating(8) , laser ablation, mass selected ion beam deposition, plasma-immersion ion implantation and deposition(9-11) , and filtered cathodic vacuum arc (FCVA) deposition.(12) Among these, FCVA has been proved as one of the most successful to synthesize high quality DLC films, typically having sp^3-bonded C close to 90% of the total mass.(13,14) However, in metallurgical applications, one of the main problems of DLC films prepared on steel substrates is the poor adhesion due to the diffusion of C from the films into the steel substrates, after which delaminating of the DLC films takes place.(15) This problem can

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be solved by depositing a barrier layer prior to the DLC coatings to hinder the C diffusion.(16) Many effective barrier layers have been applied such as Si(16), Nb(17), TiN(17), Ti(17), W(17), Cr(18), and Mo.(19)

The objective of this work is to investigate compositions and structures of DLC films prepared on AISI H13 hot work tool steel substrates by FCVA using a variety of the substrate negative bias voltages in order to improve the sp^3/sp^2 bonding ratio. The DLC films were examined by Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and near edge x-ray absorption fine structure (NEXAFS) spectroscopy.

Materials and Experimental procedures

DLC films were deposited on AISI H13 hot work tool steel substrates (the chemical composition of the steel is shown in Table 1) at room temperature using FCVA under variable negative DC biasing on the substrates. To prepare the substrates, first, the steel was cut into rectangular pieces of 10 mm × 10 mm × 2.5 mm. Then, the samples were heat-treated at 1075°C followed by oil quenching and tempering. Their hardness at this stage was measured as about 50 HRC, which was within the standard range of this material. Subsequently, the samples were polished with SiC sand paper in order to smoothen the surface, and then successively cleaned by ultra-sonication in acetone, isopropyl alcohol, and de-ionized water for 5 minutes each. The samples were pre-coated with ~100 nm Ti interlayer by DC magnetron sputtering to improve the adhesion and to prevent the C inter-diffusion. For DLC deposition, the samples were introduced to the FCVA chamber which was later pumped down to ~3.0 × 10–5 Torr by a turbo-molecular pump. The C deposition is supplied by a graphite rod with a diameter of 6.25 mm and purity of 99.99%. During the deposition, a negative DC bias was applied to the samples. For each set of samples, we selected the bias voltage ($-V_b$) from 100 to 1000 V. The film thickness was controlled by the deposition time.

Table 1. Chemical composition of AISI H13 hot work tool steel.

Elements	**C**	**Si**	**Cr**	**Mo**	**V**	**Fe**
Wt. %	0.40	1.00	5.30	1.40	1.00	Bal.

The bonding structure of the deposited DLC films was characterized by Raman spectroscopy with the source λ of 514.5 nm produced by a 20 mW Ar-ion laser. The chemical states and the electronic structures of the films were determined by XPS at Beamline 3.2a: PES and NEXAFS at Beamline 3.2b: PEEM at the Synchrotron Light Research Institute (Public Organization), Thailand. The Raman and XPS spectra were curve-fitted by ORIGIN and ADVANTAGE softwares to evaluate the I_D/I_G ratio, the G peak position, the sp^3/sp^2 contents in the DLC films for comparison with other references.

Results and Discussions

Raman spectroscopy in the 800–2300 cm^{-1} spectral range is extensively used to identify the sp^3 and sp^2 sites in the DLC film.(20) For pure diamond, the Raman peak is located at 1332 cm^{-1}, while for graphite the peaks are located at 1350 and 1580 cm^{-1}(21-23)

The Raman spectrum of disordered graphite shows two sharp peaks. The peak around 1580–1600 cm^{-1} is designated as the "G" peak attributed to graphite-like layers of sp^2 microdomains, and the other peak around 1350 cm^{-1} is designated as the "D" peak representing bond-angle disorder in the sp^2 graphite-like microdomains.(24-27) In comparison, the Raman spectrum of amorphous C contains two broad peaks, a G peak centered around 1500-1700 cm^{-1} and a D peak centered around 1200-1450 cm^{-1}.

Figure 1, shows the Raman spectra of DLC films deposited with different substrate bias voltages. The spectra from all samples in this study have similar shape, with a broad skewed peak centered at approximately 1560 cm^{-1}, which is the characteristic of the diamond-like structure.(28) Each spectrum can be decomposed into two Gaussian line curves, one at the lower wave numbers between 1350 and 1370 cm^{-1} (D peak) and the other at the higher wave numbers between 1545 and 1565 cm^{-1} (G peak). The structure of the different C films can be specified by analyzing features in the Raman spectra, such as the relative position of G and D peaks, the intensity ratio of the fitted Gaussian curves representing each peak (I_D/I_G), or the full width half maximum of each.(29) From Figure 2, when the magnitude of the bias voltage increase from –100 to –200 V, the G peak shifted toward lower wave numbers from 1564 to 1557 cm^{-1}. For the bias voltage from -600 to -1000 V, the G peak shifted to lower wave numbers from 1560 to 1546 cm^{-1}. In the same way, the D peak also shifted toward lower wave numbers. The shift of G peak position toward the lower wave numbers has been related to the increase of the sp^3 fraction of the DLC films.(30) In our results, the G peak position tends to decrease as the negative bias voltage increases, which suggests that more sp^3 content can be achieved by applying higher sample bias. The increase of the sp^3 bonding is mainly owing to the higher acceleration of bombarding ion species during the FVCA deposition, leading to implantation and local densification under the surface of the DLC films.(31)

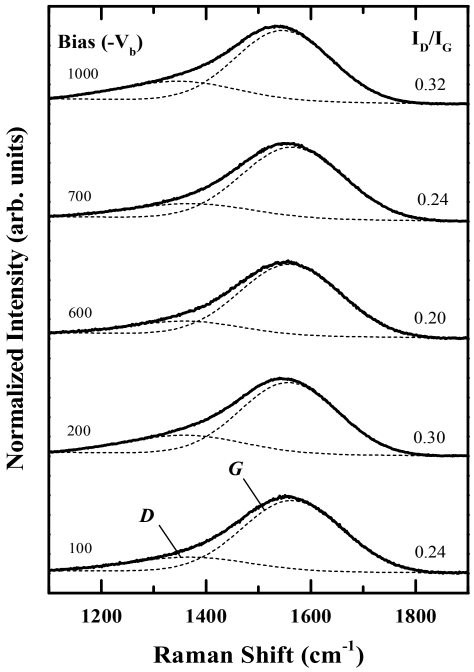

Figure 1. Raman spectra of DLC films prepared by FCVA at different negative bias voltages.

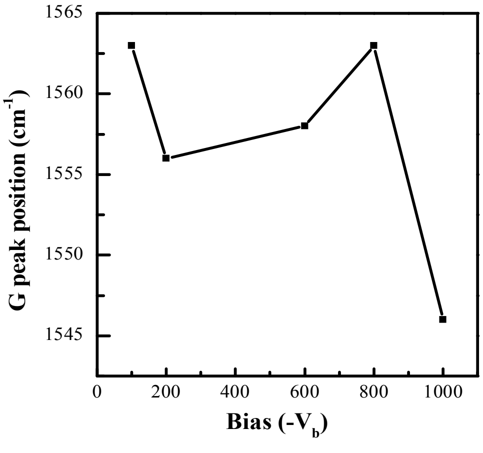

Figure 2. Position of the G peak as a function of the negative bias voltage.

XPS is used to study the chemical states of the prepared DLC films. In Figure 3, the C1s XPS spectra of the -100 V and -1000 V DLC films were deconvoluted into three peaks at around 287.5, 285.0, and 284.0 eV. The background is subtracted by Shirley method. The first peak at 287.5 eV is corresponded to C–O bonding from contamination which may have been deposited during the sample preparation and from moisture in the atmosphere while the peaks at 285.0 and 284.0 eV are corresponded to sp^3 bonding (diamond), and sp^2 bonding (graphite), respectively. Our XPS measurement is consistent with reference(5) , thus confirming the diamond-like structure in the films. From Gaussian fitting, the calculated percentages of sp^3, sp^2 C-C, and C-O bonds are shown in Table 2.

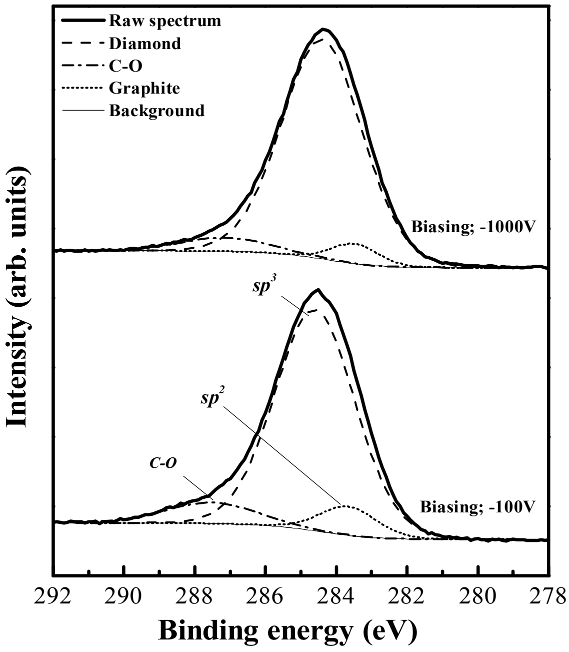

Figure 3. C1s XPS spectra of DLC films prepared by FCVA with negative bias voltages of 100 and 1000 V.

Table 2. Peak positions in the XPS spectra of DLC films analyzed using Gaussian-curve fitting procedure

Bias (-V$_b$)	Structure	Center (eV)	Area	At. %
1000	C-sp^3	284.9	382.8	89.1
	C-sp^2	284.0	26.2	4.7
	C-O	287.7	20.2	6.2
100	C-sp^3	285.0	229.5	83.3
	C-sp^2	284.2	21.2	7.6
	C-O	288.0	24.5	9.1

The NEXAFS technique is performed in the electron-yield mode to determine electronic structure of the sp^3 and sp^2 bond mixture. Figure 4, shows the C K-edge absorption spectra of the DLC films deposited under the sample bias of -100, -600, and -1000 V. The spectra of all samples show three main peaks. The peak located at 285.2 eV is corresponded to the transition from C (1s) $\rightarrow \pi^*$ state in graphite (sp^2 hybridization), the small shoulder near 287.8 eV is due to the C (1s) $\rightarrow \sigma^*$ transition of carbon atoms bonded to H and O [sp^3 (C–H) or sp^2 (C=O)]. The peak located at 289.5 eV is due to the transition of C (1s) $\rightarrow \sigma^*$ state, the characteristics for diamond's sp^3 hybridization. The broadened absorption feature behind 291 eV reveals the amorphous structure of the films.(32) Taking the NEXAFS measurements with longer acquisition time to improve the quality of the spectra are required in order to further analyze the difference in the electronic structures between DLC films deposited in the different conditions.

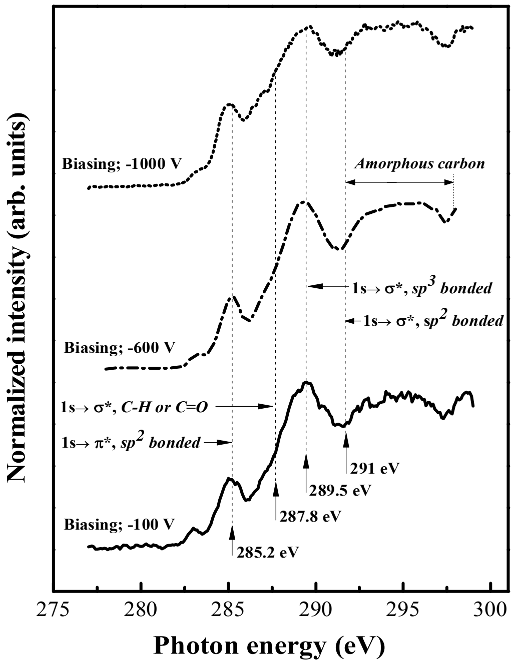

Figure 4. Carbon K-edge spectra of DLC films synthesized using FCVA with a substrate negative bias voltage at 100, 600, and 1000 V.

Conclusions

The DLC films were successfully synthesized by FCVA using substrate negative DC biasing as a variable to control the sp3 content. The bonding ratio and the atomic structure of the DLC films were investigated with Raman spectroscopy, XPS, and NEXAFS techniques. The measurement results can be summarized as follows.

a. The Raman spectra of the DLC films reveal that an increase in the negative bias voltage improves the sp^3 content of the DLC films.
b. XPS demonstrates that the DLC films mainly contain a mixture of sp^3 and sp^2 bonds along with C-O bonding. The peak-fitting results from DLC deposited under -100 and -1000 V bias are in agreement with the Raman measurement.
c. NEXAFS spectra illustrate the amorphous structure of the films, and the C-O and C-H bonds mixing among the sp^3 and sp^2 bonds.

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