

STRUCTURAL PROPERTY COMPARISON OF NEW AND USED DIAMOND-LIKE CARBON/TITANIUM DOUBLE-LAYER FILMS

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Abstract

Diamond-like carbon (DLC) based films are usually applied to devices as protective coating in devices demanding excellent mechanical properties in order to improve tribological performances. In this work, DLC/Ti double-layer thin films were deposited on a moving part of Heads Gimbal Assembly (HGA) tester and were put in the operation for 1000 h. Comparison of structural properties of the newly deposited and after full operation samples was investigated. Surface morphology was examined by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used for examining chemical composition of films. Moreover, the structural properties were studied by near edge X-ray absorption fine structure (NEXAFS) spectroscopy and Raman spectroscopy. The results show a good tribological performance of the film as there was no significant difference between the new and used sample.

Keywords: DLC films, NEXAFS, XPS, Raman spectroscopy

Introduction

Diamond-like carbon (DLC) coating is a surface modification in order to enhance the performance because of its excellent properties such as high hardness, low friction, wear resistance coefficients, chemical inertness and biocompatibility. Therefore, DLC films have been used in several industrial applications for example anti-reflection protective layer for solar cells and IR windows, protective

layer for tool materials and magnetic disks, micro-electronic and photonic devices, and coating for biomedical purposes (Robertson, 2002; Bewilogua and Hofmann, 2014). Chemical and physical depositions are possibly used to fabricate DLC films on many substrate materials. For tribological purpose, the internal stress is an important issue. The effective solution to reduce the internal stress

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and improve the adhesion in DLC films are metal doping and introducing interlayer between the substrate and film. Titanium is a famous material used as the interlayers or doping elements in DLC films to solve the adhesion problem (Wang *et al.*, 2007; Segura *et al.*, 2009; Park *et al.*, 2015).

In this work, comparative of structural properties of the newly coated DLC/Ti double-layer thin films on a moving part of Heads Gimbal Assembly (HGA) tester and after been in real operation for 1000 h was examined. Surface morphology of DLC films was studied by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was performed for chemical composition. Moreover, the structural properties were studied by near edge X-ray absorption fine structure (NEXAFS) spectroscopy and Raman spectroscopy.

Materials and Methods

DLC/Ti double-layer thin films were coated on a stainless grade 303 as a real working part of a Heads Gimbal Assembly (HGA) tester. Sample A and C are the newly deposited but sample B and D was used in real operation. There are two kinds of substrates, the thick substrates were found in A and B samples, the thinner one were found in C and D. All samples were characterized by several techniques. The high resolution scanning electron microscope combined with focused ion beam (FIB) and energy dispersive x-ray spectroscopy (EDX) (AURIGA, Zeiss) were used to examine the thickness and prove of the structure of DLC/Ti double-layer thin films.

Chemical composition of DLC/Ti double-layer thin films were examined by XPS at Beamline 3.2Ub, Synchrotron Light Research Institute (SLRI), Thailand. The XPS survey scan spectrum were collected from 0 to 580 eV with energy step 1.0 eV. The narrow-scan C1s and O1s XPS spectra with binding energy in range from 276 to 294 and 526-540 eV respectively with energy step of 0.1 eV were performed for quantitative analysis. The XPS spectra with Shirley background subtraction were deconvoluted using combinations of Gaussian-Lorentzian function.

The NEXAFS experiment was carried out at Beamline 3.2Ub Synchrotron Light Research Institute (SLRI), Thailand. The carbon K-edge and O K-edge NEXAFS spectra were collected in the photon energy range of 275-325 eV with scanning step of 0.1 eV. The position of carbon K-edge was calibrated by aligning the π^* resonance peak of highly oriented graphite (HOPG) to 284.8 eV.

The structural properties of the DLC films were investigated by Raman spectroscopy (SENTERRA, Bruker). Raman spectra were collected at room temperature by a wavelength dispersive Raman microscope with an excitation light of 532 nm, a laser power of 40 mW, and 25 $\mu\text{m} \times 1000 \mu\text{m}$ slit. The spectra were measured in 50-2700 cm^{-1} range with Raman shift resolution of 0.5 cm^{-1} . The characteristic peaks were fitted with Gaussian functions.

Results and Discussion

Figure 1 shows the cross-section SEM micrographs of DLC films on the metal substrate with an intermediate Ti layer. The thickness of DLC and Ti layer depending on the samples are in the range of about 400-650 and 150-320 nm respectively. EDX result (Figure 2.) confirms that the structure of the samples is double layer thin films.

XPS spectrum of sample B containing the main peaks of C1s and O1s. The deconvoluted XPS C1s spectra of DLC films with peak positions

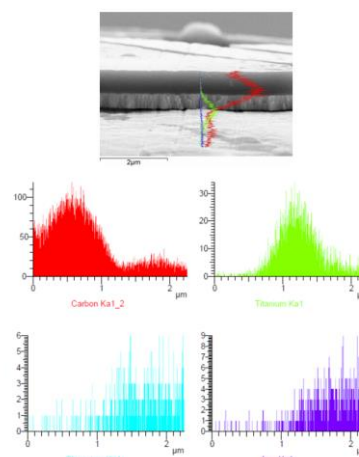


Figure 1. The cross-section SEM micrographs of DLC films on the metal substrate with an intermediate Ti layer.

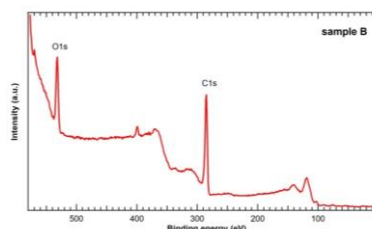


Figure 2. EDX result of sample D shows the DLC film on metal substrate with an intermediate Ti layer.

corresponding to C-sp² (284.0 eV), C-sp³ (285.5 eV) C-O (287.1 eV) and C = O (289.0 eV) respectively are shown in Figure 3(b). The O1s XPS spectra in Figure 3(b) can be fitted into three main peaks indicating the presence of some oxygen atoms bonded to carbon (O = C or O = C) which are located at the binding energy ranging from 532 to 536 eV (Thanun *et al.*, 2020).

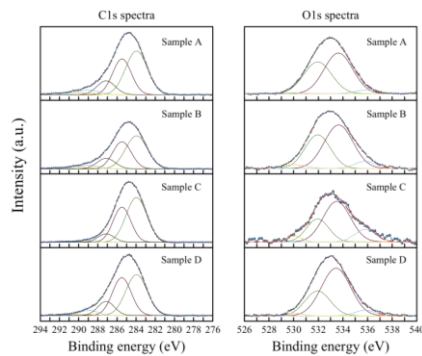


Figure 3. (a) XPS survey scan of sample B. (b) C1s and O1s XPS spectra and fitting of sample A, B, C and D.

Figure 4 demonstrates the Carbon K-edge NEXAFS spectra of samples A, B, C and D respectively. The first peak at the photon energy of approximately 284.8 eV was identified as the transition of the C 1s core level electrons to the unoccupied π^* orbitals ($1s \rightarrow \pi^*$, C = C). The transition of the overlapping C 1s to the unoccupied σ^* at the energy of 288.3 eV shows the presence of C = O bonding (Watts *et al.*, 2006; Zhou *et al.*, 2017; Chunjaemsri *et al.*, 2020). Figure 4, also shows indifferent features in the local bonding configuration for the spectra of all samples. No obvious difference of all spectral features of the C K-edge NEXAFS spectra reveals that there was no detectable change in the carbon network structure between the new and the used samples.

The deconvolution of the D and G bands is presented in the Figure 5. The DLC films were deconvoluted in their Raman spectra region into three Gaussian functions located at approximately 1141, 1367 and 1556 cm^{-1} , corresponding to D', D and G band respectively (Ferrari and Robertson, 2000). The Raman parameters such as Position (G), FWHM and I_D/I_G ratio of sample A, B, C and D acquired by the fitting the Raman spectra are listed in Table 1. The Positions (G) for all samples are almost the same. In addition I_D/I_G ratio for the same type of sample exhibits similar value. These results imply that the carbon bonding content of all film samples has not been are not significantly altered after a 1,000 h in real operation.

Conclusions

The DLC/Ti double layer thin films were characterized by several methods including SEM, EDX, XPS, NEXAFS and Raman spectroscopy. SEM and EDX results confirm that the structure of the samples is DLC film with an intermediate titanium layer. The comparison of structural properties of the newly deposited DLC/Ti double layer thin films samples and the samples that has been put in real operation for 1,000 h was studied. The results showed that there was no detectable in the structural properties of the new and used samples

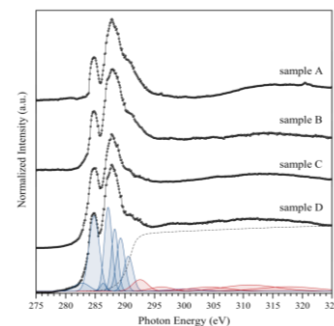


Figure 4. NEXAFS carbon K-edge spectra of sample A, B, C and D. The example of the curve-fitting is shown by the blue lines in sample D.

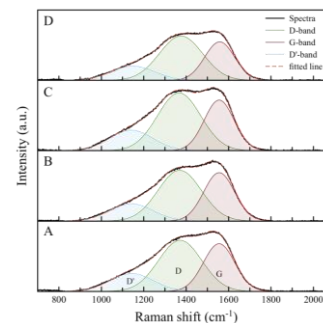


Figure 5. Raman spectra and fitting of sample A, B, C and D with triple Gaussian peaks.

Table 1. The results of Raman curve-fitting from Figure 5. Raman parameters: Position (G), FWHM and I_D/I_G ratio of sample A, B, C and D.

Sample	Positions (G) (cm^{-1})	FWHM	I_D/I_G ratio
A	1555.12	174.01	1.48
B	1555.47	170.90	1.47
C	1555.53	166.02	1.65
D	1555.87	166.10	1.66

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