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# Characterization of hydrogen-free diamond-like carbon film deposited on cyclic olefin copolymer

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#### Abstract

In this study, the feasibility of the diamond-like carbon (DLC) film as a viable component for cyclic olefin copolymer (COC) substrate overcoat was assessed. Featured by its advanced physical and chemical properties such as high hardness, chemical stability, and wide band-gap optical transparency, the hydrogen-free DLC exhibits promising characteristics as the overcoat for flexible substrates or other TFT components. Ultra smooth, DLC thin films were synthesized by using a filter arc deposition (FAD) system and a cathodic arc evaporation (CAE) system. Raman spectroscopy, ESCA, Nano-Indentation, and electron microscopy were used to characterize the electronic, morphological, and microstructure properties of the DLC coatings. Results indicate that the device-quality DLC needs to be synthesized at lower substrate bias potential to retain high  $sp^3/sp^2$  ratio. The bending tests demonstrated a 30-fold improvement of the DLC-protected COC over that of the unprotected COC. Water vapor permeability tests demonstrated a 25-fold improvement of the DLC-protected COC over that of unprotected COC. © 2008 Elsevier B.V. All rights reserved.

Keywords: FAD, filter are deposition; CAE, cathodic are evaporation; COC, cyclic olefin copolymer; DLC, diamond-like carbon

## 1. Introduction

The amorphous carbon films with diamond-like properties, containing a significant fraction of sp<sup>3</sup> bonds is well known for its excellent tribological properties, high mechanical hardness and chemical inertness [1–3]. These diamond-like carbon (DLC) films support many applications such as protective coatings for cutting tools, precision molds, car parts, biomedical materials and optical windows [4–7]. With its high smoothness, high sp<sup>3</sup>/sp<sup>2</sup> ratio, hydrogen-free DLC could be suitable for applications in metal insulator opto-electronic devices.

In this research, DLC thin films were deposited by using both conventional cathodic arc evaporation (CAE) and filter arc deposition (FAD) processes. The CAE process utilized metallic Cr as the cathode, following a cathodic arc activated deposition (CAAD) procedure, which has been described elsewhere [8–10].

\* Corresponding author. E-mail address: brain1166@yahoo.com.tw (F.-K. Chen). The FAD, based on graphite cathodes has been successfully utilized in preparing DLC thin films [11–14]. FAD can effectively filter out undesirable particles by control of the magnetic field in the plasma tube. FAD is also a low temperature deposition method with a better ion ratio and higher ion energy. By FAD deposition, films with strong sp<sup>3</sup> bonding are easily produced.

A new amorphous engineering thermoplastic, cyclic olefin copolymer (COC) has been used for many types of optical, electrical and mechanical applications [15–20] due to its outstanding properties of higher transparence, lower birefringence, lower dispersion and lower water absorption [21]. Purpose of this research is to study the material issues upon depositing high sp<sup>3</sup>/sp<sup>2</sup> DLC thin films on top of COC flexible substrates.

#### 2. Experiment details

DLC thin films were deposited on Si wafer by CAE (chromium cathode) and FAD (graphite cathode) deposition systems, as shown in Table 1. Details of the system schematics were shown elsewhere [8,11].

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Table 1 Experimental parameters graphite and chromium target

Parameter	Value	Value
Target	Graphite	Chromium
Bias (V)	-25, -75, -100, -125, -150	-25, -75, -100, -125, -150
Reaction gas	Ar, N <sub>2</sub>	Ar, N <sub>2</sub> , C <sub>2</sub> H <sub>2</sub>
Chamber press (Pa)	1.5	1.5
Current (A)	40	40
Temperature (°C)	200-250	200–250
Time (min)	10-30	10-30

Scanning electron microscopy (JOEL JSM-7000F) is utilized to observe the surface morphology and cross-sectional images. Raman spectroscopy (3D Nanometer Scale Raman PL Microspectrometer) and X-ray photoelectron spectrometry (XPS, PHI 1600), using Mg K $\alpha$  radiation (hv=1253.6 eV), were employed to identify the binding state, the species of the compounds and the sp<sup>3</sup>/sp<sup>2</sup> ratio of the film. Chemical structure analyses of DLC thin films were conducted by micro-FTIR spectroscopy (FTIR, JASCO 6100). The adhesion and water vapor permeability were examined by the bending test (Bending instrument, JUSTICE JIA-802) and water transmission test.

## 3. Results and discussion

### 3.1. Chemical states and bonding analyses of DLC

The quantitative  $sp^3/sp^2$  ratios can be extracted from the ESAC data as shown in Fig. 1. The ESCA spectra of the DLC thin films, including Cls (284.5 eV), O1s (531.0 eV), and Cr2p2/3 (576.9 eV). The O1s peak is attributed to the excessive oxygen in the deposition chamber. The calculated  $sp^3/sp^2$  ratios are in the range 1.0–1.9. The intensity ratio  $I_D/I_G$ , as an indicator to  $sp^3/sp^2$ , showing the preference of DLC with higher



Fig. 2. Calculated  $sp^3/sp^2$  ratios of DLC at various bias potentials (a) FAD (graphite cathode) and (b) CAE (chromium cathode).

sp<sup>3</sup>/sp<sup>2</sup>, thus lower  $I_D/I_G$ , at lower bias potentials, as show in Fig. 2. The ESCA analyses depicted the advantage of FAD, which produced DLC with higher sp<sup>3</sup>/sp<sup>2</sup> ratio, resulting from the higher plasma density of FAD [11]. When DLC was



Fig. 1. ESCA spectra of C target and Cr target films at various bias.

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