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# Cr-diamondlike carbon nanocomposite films: Synthesis, characterization and properties

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**Abstract**

Diamondlike carbon (DLC) films, known for exhibiting attractive combination of properties, have been extensively studied in the recent past. The inherent, internal compressive stresses affecting their adhesion and their relatively low thermal stability above 400 °C are two major drawbacks preventing wide usage of these films. Carbide formers incorporated into the carbon network have the potential to stabilize the film structure, relax internal stresses and improve their performance. The present work focuses on the synthesis, structure and mechanical and tribological property characterization of Cr-containing nanocomposite DLC films. The films were synthesized using a plasma-enhanced hybrid chemical vapor and physical vapor deposition process in a discharge composed of a mixture of $CH_4$ and Ar gases. The Cr content in the films varied up to 18 at.%. The film morphology and composition were characterized by scanning and transmission electron microscopy, X-ray photoelectron spectroscopy and nuclear reaction analysis. The mechanical and tribological behavior of the films was studied as a function of Cr concentration by conducting nanoindentation and pin-on-disc experiments, respectively. The results showed that the films can be either amorphous with dispersed metallic-like Cr (at low Cr content) or nanocomposite consisting of face-centered cubic metastable CrC nanoparticles dispersed in the DLC matrix. Films with low Cr content (<5 at.%) were found to possess similar tribological characteristics with those of pure DLC films. Incorporation of more Cr (>12 at.%) results in larger chromium carbide particles that have an adverse effect on wear resistance. The films with the low Cr content offer the opportunity to combine the excellent tribological behavior with other desirable properties deriving from the presence of the second phase.


*Keywords:* Tribology; Plasma processing and deposition; Diamondlike carbon; Chromium

## 1. Introduction

Diamondlike carbon (DLC) films have been extensively studied for more than a decade, due to their unique combination of chemical inertness, mechanical, tribological and optical properties. The inherent compressive stresses that develop during synthesis from their diamondlike content ($sp^3$ carbon bonding) that affects adhesion and their thermal stability are two major drawbacks with DLC films. It is well known that DLC films are thermally unstable beyond 350 °C [1,2]. Above 400 °C the changes are more profound and graphitization of the film occurs by conversion of C bonds from $sp^3$ to $sp^2$. Such temperatures can very well be reached at hot spots during wear, as has been shown by Liu and Meletis [3]. The graphitization process and its kinetics are the controlling parameters of the tribological behavior of these films as has been proposed by the latter authors in their wear-induced graphitization mechanism [3].

Thereby, for more than a decade, most of the scientific studies in the area of DLC films have been concentrated in the area of metal-containing DLC (Me-DLC) films in an effort to improve wear resistance, adhesion, thermal stability and toughness. A number of studies on synthesis and characterization of Me-DLC films have been conducted [4–20]. Among these the main emphasis had been

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on Si [4–7], Ti [8–17], Ta [10,12], W [8,10–13,16–19] and Nb [9,12,16,20] containing DLC. Even though Cr is a carbide former and possesses an attractive combination of other properties (corrosion resistance, wear resistance, etc.) very little work has been performed in this area. Su and Kao [9] reported an increase in microhardness and decrease in wear by increasing Cr content but no microstructural details were reported for the Cr-DLC coatings. Sunkara and co-workers [21,22] discussed structural and electrochemical characterization of Cr-DLC. Fan et al. [23] performed z-contrast imaging and electron energy loss spectroscopy on Cr-doped DLC and reported uniform Cr distribution in the C matrix at lower levels (~6 at.%) and Cr-rich cluster formation at high doping levels (~12 at.%).

The purpose of the present work was to initiate a systematic study of the processing–structure–property relationship in Cr-DLC films as a function of Cr content. The overall objective is to develop a better understanding of these systems and identify microstructures/compositional ranges where tribological performance, thermal stability and mechanical properties can be optimized.

## 2. Experimental details

### 2.1. Processing

Silicon (100) wafers, 50 mm in diameter, were used as the substrate material. The substrate was first cleaned ultrasonically in acetone, dried in air and mounted on a stainless steel holder (diameter 55 mm) in the chamber. All films were synthesized using a surface modification system designed and constructed in our laboratory [24]. The system allows three different modes of operation: conventional (diode) and intensified (triode) plasma-enhanced (PE) processing, ion beam assisted deposition/ treatment and magnetron sputter deposition. A combination of two or more processes (hybrid process) can be utilized for synthesizing nanocomposite films.

Before the hybrid physical vapor deposition (PVD) and PE chemical vapor deposition (CVD), the chamber was first evacuated down to $1.33 \times 10^{-4}$ Pa and purged with Ar several times. Then, the Si wafer was sputter-cleaned for 20 min using $Ar^+$ at 3.3 Pa chamber pressure and −1500 V bias voltage. The Cr-DLC films were synthesized by sputtering of a Cr target (99.5% Cr) in a $CH_4$ and Ar discharge (ratio of 1:5.33 and total flow rate 47.5 sccm). The substrate was biased at −1000 V and placed at a distance of 16 cm from the magnetron target. The Cr content in the Cr-DLC films was varied by running the magnetron under current control and modulating the current between 100 and 350 mA. The chamber pressure was maintained at 2.66 Pa. After processing, the substrate was cooled inside the chamber in an argon atmosphere. The substrate temperature during deposition remained below 100 °C.

Two small areas at diametrically opposite sides were masked on each specimen surface, preventing deposition and allowing thickness measurement using a Veeco optical profilometer (WYKO NT1100).

### 2.2. Composition and structural characterization

Carbon and chromium content in the films was determined by wavelength-dispersive spectroscopy (WDS) utilizing a JEOL JXA 733 super electron probe microscope at 15 keV accelerating voltage and 10 nA beam current. Appropriate standards were used for instrument calibration. Hydrogen content in the films was measured by nuclear reaction analysis (NRA) using a nitrogen-15 ion ($^{15}N$) beam from an accelerator to react with protons [25]. The depth profile of hydrogen content in the a-C:H films was obtained by increasing the $^{15}N$ beam energy from 6.38 to 7 MeV in steps of 100 keV. Penetration depth was calibrated by taking the density of graphite as a standard.

X-ray diffraction (XRD) experiments were performed using a Rigaku Miniflex $2\theta$ diffractometer with a Cu-$K_\alpha$ ($\lambda = 1.5418$ Å) source over the $2\theta$ range from 20° to 80° at a scanning rate 0.5°/min. Also, low angle (LA) XRD experiments were conducted using Philips x'pert diffractometer in thin film mode with a Cu-$K_\alpha$ source over the $2\theta$ range from 25° to 115° with a step size of 0.05° and scanning rate of 0.15°/min. XRD patterns were obtained to determine if any crystalline phases were present.

High-resolution transmission electron microscopy (HRTEM) of Cr-DLC specimens was performed on a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å. Cross-sectional slices were obtained by cutting the specimens along a direction normal to the coating surface and then gluing, face to face, the two coating surfaces. Cross-sectional specimens for TEM observation were prepared by mechanical grinding, polishing, and dimpling followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691) at 4.5 keV at an angle of 5°.

The synchrotron facility at the LSU Center of Advanced Microstructures and Devices was utilized to conduct X-ray absorption spectroscopy (XAS) analysis from Cr-DLC specimens with various levels of Cr content. Measurements at the K edge of Cr (5989.2 eV) were performed using a double crystal monochromator, operating with Si (111) crystals. Two ion chambers were used to detect the intensities before and after beam interaction with the specimen. The monochromatized X-ray beam with a fixed exit DCM was utilized for the experiments. The experiments were conducted in total electron yield mode.

The chemical state of Cr and C was analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS 165 high-performance multi-technique electron spectrometer. The top contaminated surface layer was removed using $Ar^+$ sputtering at 5 kV and 10 mA for 60 s. Subsequently, a monochromatic Al $K_\alpha$ excitation source was used to obtain