

Characterization of Nitrogen-doped a-C:H Films Deposited by Cathodic-arc Activated Deposition Process

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Abstract

Nitrogen-doped Cr-C:H/N films containing chromium were synthesized by using cathodic-arc activated deposition (CAAD) process. Metal plasma with intensive ion energies catalyzes the decomposition of hydrocarbon gas (C₂H₂), and results in the deposition of amorphous carbon films. Nitrogen was introduced to form nitrogen-containing Cr-C:H/N films, which contained a mixture of sp² and sp³ carbon bonds. The deposited carbon films consist of nanocomposite Cr-C:H/N films on top of a graded chromium nitride interlayer. The wear properties were correlated with the nitrogen doping. Cr-C:H/N films exhibit a steady state friction coefficient lower than 0.11 when deposited at low N₂/C₂H₂ flow rate ratio (<15%). Cr-C:H/N possesses improved wear properties, resulting from its adhered dense microstructure and the nature of the transferred layer induced by the friction condition between the Cr-C:H/N coatings and the sliding counterpart.

Keywords: Amorphous carbon films; Cathodic-arc activated deposition; Wear; Carbon nitride

1. Introduction

The amorphous carbon film with diamond-like (a-C:H) properties is a meta-stable, amorphous phase of carbon having sp^3 and sp^2 bonds with various amounts of hydrogen. These hydrogen-containing diamond-like carbon (DLC) films have received considerable interest over the past two decades because of their high hardness, wear resistance, as well as attractive optical and electrical properties [1,2]. Arora et al. [3] addressed the problem of high compressive stress of DLC and its relaxation mechanism. They demonstrated that nitrogen incorporation in DLC films could lower the compressive stress. In addition, Jun Qi [4] revealed the effects of film thickness on mechanical and tribological properties of nitrogenated DLC films. Traditional approaches to obtain carbon nitride (CN_x) films involve reactive sputtering, filtered arc deposition (FAD), and plasma enhanced chemical vapor deposition (PECVD) [5-9]. Some efforts [10-17] have been directed toward improving the adhesion of DLC films by depositing an interlayer or graded interlayers between the DLC film and its substrate. The interlayer of Ti, Zr, W, Nb, Si, Cr or WC demonstrated its potential in improving film adhesion and wear properties. Among various PVD processes, cathodic arc plasma possesses the highest ionization ratio, which ensures the deposition of an amorphous carbon film with a higher hardness value and compact film microstructure. In the cathodic-arc activated deposition

(CAAD) process [18], high-energy metal plasma assists the cracking and decomposing of hydrocarbon feed gases, such as CH_4 and C_2H_2 . As a result, a DLC film doped with the cathode metal is deposited on the substrate [18,19].

In the present work, metal plasma with high ion energies induces the decomposition of nitrogen and hydrocarbon gas (C_2H_2), and facilitates the formation of a metal-doped and nitrogen-containing a-C:H (a-C:H/N) films. Because nitrogen is a weak dopant in carbon [16], techniques include XPS, and FTIR are utilized to obtain information on bonding and electronic structure in this study.

2. Experimental details

Nitrogen-containing a-C:H films were deposited on M2 tool steel and Si substrates using a cathodic arc system, MASC-2226 manufactured by Multi-Arc Inc. Details of the experimental parameters are shown in Table 1. Chromium was selected as the cathode material for depositing nitrogen-containing a-C:H films. A graded chromium nitride interlayer was deposited to reduce the internal stress of the composite a-C:H/N coating. The transition layer from metal nitride to a-C:H and a-C:H/N was formed by switching the reactive gas gradually from N_2 to mixed $\text{N}_2/\text{C}_2\text{H}_2$.

The film adhesion was evaluated by Rockwell indentation test [20]. Structural and

morphological characterizations were performed using a JOEL JSM-6300F field emission scanning electron microscope, an atomic force microscope, a MAC MXP18 X-ray diffractometer (XRD), and a high-resolution transmission electron microscope (HRTEM). The characteristics of a-C:H and a-C:H/N bonding were identified by a Fourier transform infrared spectroscope and a X-ray photoelectron spectroscope with monochromatized Mg K α radiation. The compositional analysis was performed using an Auger electron spectroscope (AES) combined with sputtering by an Ar⁺ beam. The mechanical properties of DLC films were analyzed by using a microhardness tester, operated at 10 g load. Tribological properties such as friction coefficient were evaluated by using a ball-on-disk wear tester with a 6-mm diameter WC ball as a counter material at a normal load of 10N. The wear test was performed at a speed of 30cm/sec in a controlled air (28 °C and 80% relative humidity).

3. Experimental Results

3.1 Microstructure analysis

As shown in Fig. 1, the cross- section SEM micrographs reveal the microstructure of the a-C:H and a-CN:H films. The film thickness was controlled at 2 μ m. The deposition rate was about 0.05 μ m/min. The Cr-doped DLC (Cr-C:H) and Cr-C:H/N with N₂/C₂H₂ flow rate ratio of 15% depict a dense and compact microstructure with

well-attached interface. In comparison, nodular microstructure was observed in Cr-C:H/N ($N_2/C_2H_2=25\%$). AFM examination reveals that all the Cr-C:H and Cr-C:H/N films possess smooth surface morphology at average roughness Ra 4.8 - Ra 9.2 nm.

By measuring and analyzing the XPS spectra of all carbon films, the N/C atomic ratio increases proportionally with increasing N_2/C_2H_2 flow rate ratio. As the N_2/C_2H_2 flow rate ratio is maintained at 15%, the N/C atomic ratio in the film is 4.5%, which possesses the best wear properties and will be explained later.

Figure 2 shows an Auger depth profile of a Cr-C:H/N film with a nitrogen concentration of 4.5% (N_2/C_2H_2 flow rate ratio = 15%). The concentration ratio of Cr to N is about 1.3:1 in the metal nitride layer. In the transition layer, the concentration of carbon increases from 0 at% to 60 at%, and the concentration of chromium decreases from 44 at% to 20 at%. In the Cr-C:H/N layer, the concentration of carbon is 60 at%, and that of chromium is 20 at%. The average composition of the top Cr-C:H/N layer remains stable throughout the thickness. Fluctuation in the concentration of carbon, nitrogen, and chromium is found in the depth profile, especially in the region of Cr-C:H/N layer.

Strong metal nitride peaks are observed in XRD analysis on the film deposited with N_2/C_2H_2 flow rate ratio below 25% (N/C atomic ratio in the film is in the range

of 1.7% - 4.5%), CrN(111) and CrN(200) show up as the preferred orientation. When the N_2/C_2H_2 flow rate ratio is higher than 90%, additional metal carbide peaks $Cr_3C_2(060)$, $Cr_3C_2(310)$ are observed. The cross-sectional TEM micrograph and selected area diffraction (SAD) of a Cr-C:H/N film with nitrogen content of 4.5% (N_2/C_2H_2 flow rate ratio = 15%) are shown in Fig. 3. The Cr-C:H/N film has an interlaminar structure with the darker lamellae being Cr-rich and C-deficient. Fig. 3(a) is the SAD pattern of the underlying CrN interlayer, which was found to possess a columnar structure. The SAD pattern has d-spaces of 2.39, 2.06, 1.47, and 1.254 Å corresponding to CrN(111), CrN(200), CrN(220), and CrN(311), respectively. When C_2H_2 reactive gas was introduced, the film structure changed abruptly with decreasing crystalline morphology. Figure 3(b) shows the SAD ring pattern from the lower area of the transition layer. CrN remains the primary phase. As C_2H_2 was further increased, the film turned into a disordered phase containing fine polycrystalline grains of Cr_3C_2 (230) and Cr_3C_2 (370), as shown in Figure 3(c). When the N_2/C_2H_2 flow rate ratio was decreased less than 15%, the film changed into amorphous phase, showing only diffuse ring pattern in SAD (Figure 3(d)).

3.2 Chemical analysis of C-N bonding

FTIR measurements were employed to reveal the structure of the a- C:H/N films.

The IR spectra exhibited characteristic bands of the CAAD-induced a-C:H and a-C:H/N films at around 1370 cm^{-1} (deformation vibration of $\text{sp}^3\text{-CH}_3$), 1430 cm^{-1} (scissor vibration of $\text{sp}^3\text{-CH}_2$), 1600 cm^{-1} (double bond stretching of C=C or C=N), and 2910 cm^{-1} (stretching vibration CH_n group). As the nitrogen content increases, the peak associated with nitrogen bonding (at around 1600 cm^{-1}) increases and the peaks of CH stretching decrease compared to that of nitrogen bonding, as shown in Figure 4. In addition, $\text{C}\equiv\text{N}$ bond at 2200 cm^{-1} was identified at high flow rate ratio.

Figure 5 reveals the N1s core level XPS spectra of Cr-C:H/N films under various $\text{N}_2/\text{C}_2\text{H}_2$ flow rate ratio. In this study, the peaks at about 398.5 eV and 400.5 eV are related to sp^3 C-N bonds and sp^2 C=N bonds, respectively. The result shows that there is a higher concentration of C=N bonds corresponding to lower $\text{N}_2/\text{C}_2\text{H}_2$ flow rate ratio. At higher $\text{N}_2/\text{C}_2\text{H}_2$ flow rate ratio, the Cr-C:H/N film exhibits an increase of sp^3 C-N bonds.

3.3 Tribological evaluation

The Rockwell indentation tests on all Cr-C:H/N coatings showed a criteria HF1 fracture mode, indicating favorable adhesion properties of those coatings. As measured by microhardness tester, the hardness value of the Cr-C:H/N film ranges from 28 Gpa to 35 Gpa. The higher nitrogen content in the film, the lower

microhardness was measured.

As shown in Fig. 6, the initial friction coefficient of Cr-C:H films is 0.15, which is lower than that of the other Cr-C:H/N films. The steady state friction coefficient of Cr-C:H/N films with a lower N_2/C_2H_2 flow rate ratio of 7% is 0.08, which is lower than that of Cr-C:H films. At higher N_2/C_2H_2 flow rate ratio of 25%, the steady state friction coefficient of Cr-C:H/N films increases to 0.13.

4. Discussion

In our previous studies [18, 19], diamond-like carbon films were synthesized by using a cathodic-arc activated deposition process. Energetic Cr plasma with intensive plasma activates the decomposition of hydrocarbon gas and deposits an amorphous carbon film containing a mixture of sp^2 and sp^3 carbon bonded structures with high hardness of 35 Gpa. In this study, properly doped chromium and small fraction of nitrogen inclusions aid in stress release, which result in improved tribological properties and good adhesion between the a-C:H/N film and substrate.

From the cross-sectional TEM micrograph and SAD pattern, an amorphous nanocomposite structure was observed in the Cr-C:H/N layer. Fluctuation in the AES depth profile agrees with the interval of the film structure. The thickness of each Cr-rich and Cr-deficient lamellae in the Cr-C:H/N layer is about 13 nm and 24 nm,

respectively. The formation of the nanocomposite structure is associated with the positioning of individual Cr cathodes, which deposits Cr-rich Cr-C:H/N layer only when the substrate is within the line-of-sight range of the Cr plasma. When the substrate is moved away from the primary Cr plasma, Cr-deficient Cr-C:H/N layer is deposited. However, since the concentration fluctuation is only 5%, limit influence on the mechanical properties of Cr-C:H/N is anticipated. Better film uniformity can be achieved via appropriate cathode configuration.

The FTIR study indicates the domination of CH_n stretching modes in the Cr-C:H coating, resulting from the application of C_2H_2 . New features emerge when the nitrogen content is increased. There are N-H stretching modes located at around 3300cm^{-1} , a $\text{C}\equiv\text{N}$ triple bond stretching located at 2200 cm^{-1} , and a $\text{C}=\text{N}$ double bond stretching located at around 1600 cm^{-1} [5-7, 22]. It is suggested that when a small amount of nitrogen is incorporated in a sp^2 rich a-C:H structure, the N atoms take substitutional positions in the graphitic layers without changing the shape or properties of the basal planes. For higher concentration of nitrogen, there must be more than one nitrogen atom in some graphitic rings and this high local concentration of nitrogen can promote the formation of pentagons and facilitate the cross linking between the planes through sp^3 -coordinated carbon atoms [5]. In this study, when higher $\text{N}_2/\text{C}_2\text{H}_2$ flow rate ratio was introduced for synthesizing Cr-C:H/N films, an

increase of sp^3 C-N bonds was observed (Figure 5). The result is in agreement with the previous studies [5-6, 23]. the N_2/C_2H_2 flow rate ratio is directly proportional to nitrogen incorporation, which affects the distribution of C=N bonds and sp^3 C-N bonded sites, as shown in the N1s spectra of the Cr-C:H/N films.

As determined by Rockwell-C indentation test, the Cr-C:H/N film, with N_2/C_2H_2 flow rate ratio lower than 15%, demonstrated better adhesion (a criteria of HF1) and conformed well to the plastic deformation around the indents. The graded design of the coating structure with metal nitride interlayer improved adhesion and reduced the residual stress, which is desirable for industrial applications [10-17].

Wear performance of a-C:H coatings is controlled by friction and adhesion. The friction coefficient of a-C:H coatings depends on the test environment and the film chemistry. From the ball-on-disk wear test in this study, the friction coefficient of Cr-C:H/N is characterized by a typical two stage behavior. During the initial 100 m sliding distance, the development of friction is controlled by surface roughness of Cr-C:H/N films. In the second stage, the wear and mass transfer reached a steady state. The reduction of friction coefficient is controlled by the nature of the transferred layer induced by the friction condition between the Cr-C:H/N coatings and the sliding counterpart, which is similar to other results of DLC coatings [14]. When the Cr-C:H/N films were deposited with lower N_2/C_2H_2 flow rate ratio (<15%), the steady

state friction coefficient is lower than 0.11, which is due to its dense structure and the nature of the transferred layer induced by the friction condition between the Cr-C:H/N coatings and sliding counterpart. When the Cr-C:H/N films were deposited with higher N_2/C_2H_2 flow rate ratio (>25%), the friction coefficient increased due to the nodular structure in the film and the formation of C_xN phase, which might obstruct the friction mechanism of amorphous carbon films. This is consistent with the results reported by T. Ohana et al.[25].

5. Conclusions

1. Composite Cr-C:H/N films with nitrogen doping were synthesized by using a cathodic-arc activated deposition (CAAD) process. When deposited with flow rate ratio of N_2/C_2H_2 less than 15%, a dense film structure was observed. The structure became nodular when the N_2/C_2H_2 flow rate ratio was higher than 25%.
2. XRD, AES and HRTEM analyses reveal the amorphous nature of the CAAD-deposited Cr-C:H/N films deposited with lower N_2/C_2H_2 flow rate ratio. An amorphous nanocomposite structure was found in the Cr-C:H/N layer. The N_2/C_2H_2 flow rate ratio is directly proportional to the nitrogen incorporation, which affects the distribution of C=N bonds and sp^3 C-N bonds. When a small amount of nitrogen is incorporated in a sp^2 rich a-C:H structure, the N atoms take

substitutional positions in the graphitic layers without changing the shape or properties of the basal planes. For higher concentration of nitrogen, there must be more than one nitrogen atom in some graphitic rings and this high local concentration of nitrogen can promote the formation sp^3 C-N bonds.

3. Cr-C:H/N films exhibit a steady state friction coefficient lower than 0.11 when deposited at low N_2/C_2H_2 flow rate ratio (<15%). Cr-C:H/N possesses excellent wear properties, which is due to dense film structure and the nature of the transfer layer induced by the friction condition between the Cr-C:H/N coatings and the sliding counterpart. In conjunction with the improved film adhesion, the nitrogen-containing Cr-C:H/N film demonstrate potential for tribological applications requiring higher fracture toughness.

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Table 1

Deposition parameters of CAE synthesized nitrogen-containing a-C:H films

Parameters	Values
Base pressure (Pa)	5×10^{-3}
Reactive gas pressure (Pa)	1.5
Deposition time of metal nitride layer, transition layer, and a-C:H/N layer (min)	10,15, and 20
Distance of cathode to substrate (mm)	180
CAE target	Cr (100 mm in diameter)
Cathode current (A)	60
Bias voltage at ion cleaning stage (V)	-1000
Bias voltage at coating stage (V)	-100 (100 kHz pulsed)
Substrate temperature ($^{\circ}$ C)	120-160
N ₂ /C ₂ H ₂ ratio during a-C:H/N coating stage (%)	0, 3.5, 7, 15, 20, 25, 90, 170

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Fig. 1. Cross-section SEM micrographs of DLC films deposited by CAAD process with various nitrogen doping: (a) Cr-C:H; (b) Cr-C:H/N ($N_2/C_2H_2=15\%$), and (c) Cr-C:H/N ($N_2/C_2H_2=25\%$).

Fig. 2. AES depth profiles of elements in the CAAD-deposited Cr-C:H/N film.

Fig. 3. Cross-sectional TEM micrograph of a Cr-C:H/N film with N/C atomic ratio of 4.5%.

Figure 4. The FTIR spectra of the Cr-C:H and Cr-C:H/N ($N_2/C_2H_2=170\%$) films.

Figure. 5. N1s XPS spectra of Cr-C:H/N films with various N_2/C_2H_2 flow rate ratio.

Figure 6. The friction properties of Cr-C:H/N films sliding against WC counterparts at a normal load of 10N in air with 80% relative humidity.

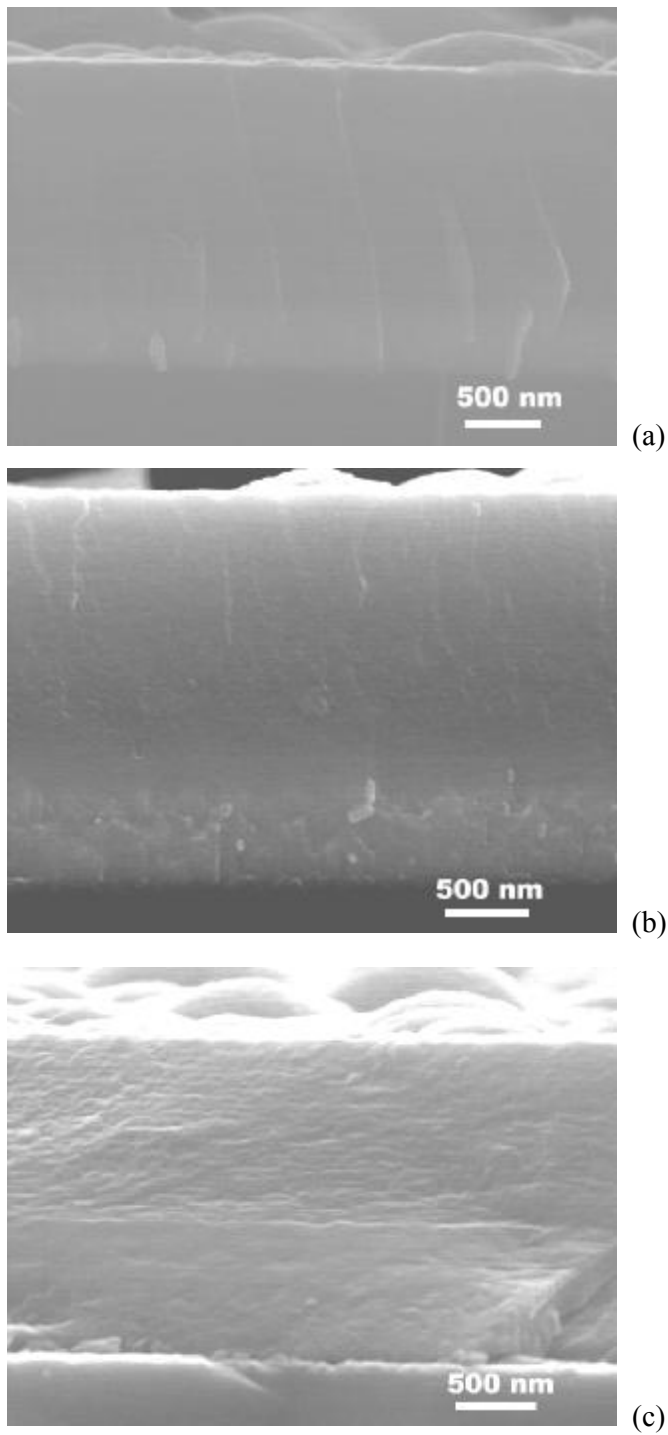


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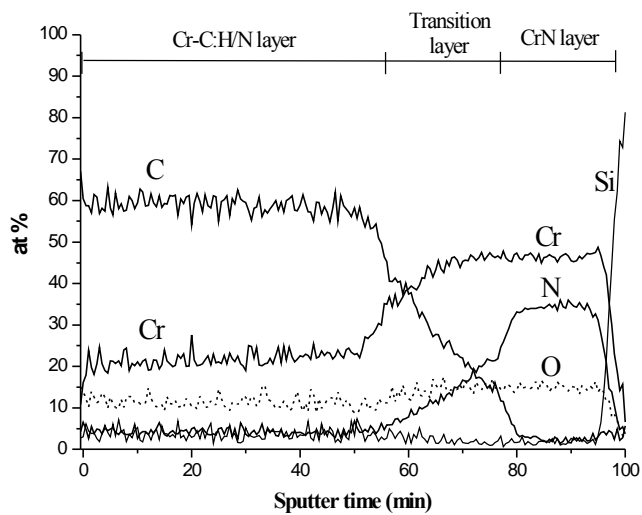


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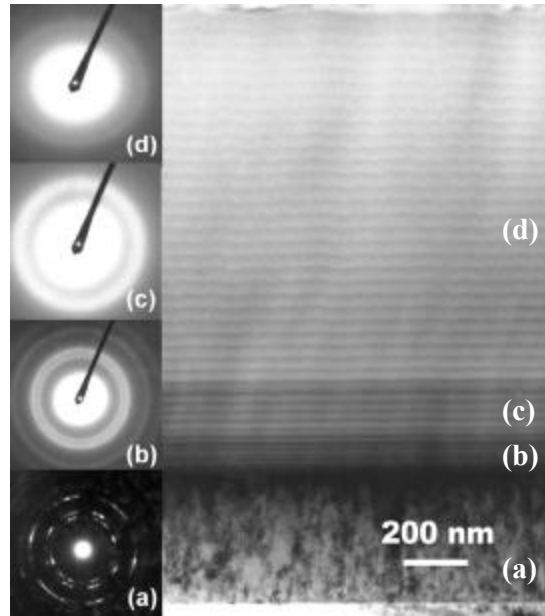


Fig. 3. Cross-sectional TEM micrograph of a Cr-C:H/N film with N/C atomic ratio of 4.5%.

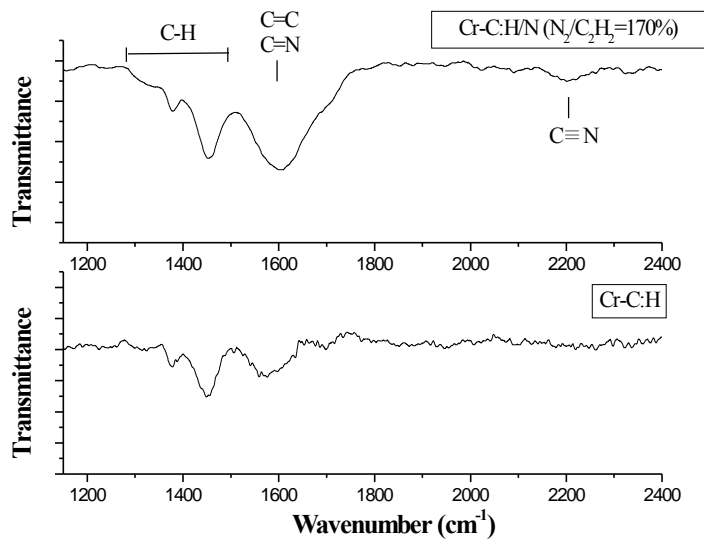


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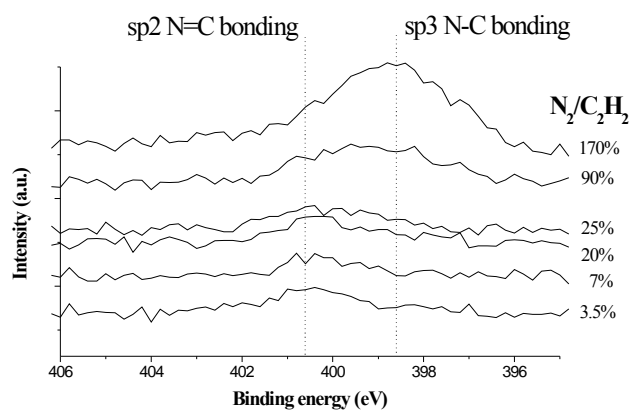


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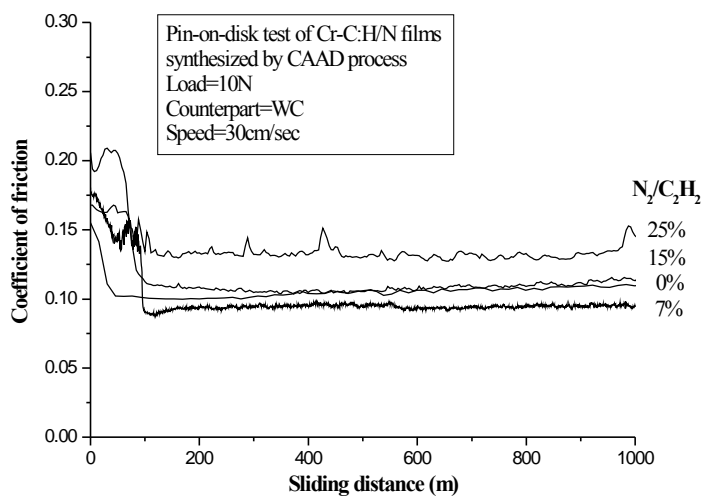


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