Nanotribological performance of fullerene-like carbon nitride films

Francisco Javier Flores-Ruiz
Christian Ivan Enriquez-Flores
Fernando Chiñas-Castillo
Francisco Javier Espinoza-Beltrán

Available at: https://works.bepress.com/oaxaca_mexico_tribologia/21/
Nanotribological performance of fullerene-like carbon nitride films

Francisco Javier Flores-Ruiz a, Christian Ivan Enriquez-Flores a, Fernando Chiñas-Castillo b,*, Francisco Javier Espinoza-Beltrán a

a Centro de Investigación y Estudios Avanzados (CINVESTAV) IPN, Unidad Querétaro, Lib. Norponiente 2000, Real de Juriquilla, C.P. 76230, Querétaro, Qro., México
b Department of Mechanical Engineering, Instituto Tecnológico de Oaxaca, Oaxaca, Oax. Col. Tecnológico No. 125, C.P. 68030, Oaxaca, Oax., Mexico

A R T I C L E   I N F O
Article history:
Received 6 March 2014
Received in revised form 25 June 2014
Accepted 29 June 2014
Available online 5 July 2014

Keywords:
AFM
Fullerene-like carbon nitride
Coatings
Nanotribological
Nanoindentation

A B S T R A C T
Fullerene-like carbon nitride films exhibit high elastic modulus and low friction coefficient. In this study, thin CNx films were deposited on silicon substrate by DC magnetron sputtering and the tribological behavior at nanoscale was evaluated using an atomic force microscope. Results show that CNx films with fullerene-like structure have a friction coefficient (CoF ~ 0.009–0.022) that is lower than amorphous CNx films (CoF ~ 0.028–0.032). Analysis of specimens characterized by X-ray photoelectron spectroscopy shows that films with fullerene-like structure have a higher number of sp2 CN bonds and exhibit the best mechanical properties with high values of elastic modulus (E > 180 GPa) and hardness (H > 20 GPa). The elastic recovery determined on specimens with a fullerene-like CNx structure was 95% while specimens of amorphous CNx structure had only 75% elastic recovery.

1. Introduction

Low friction coefficient, high elastic recovery, high modulus and very good wear resistance when subjected to non-lubricated contact conditions [1,2] are well known characteristics of carbon nitride films that have been used in industry from magnetic storage devices [3,4] to biomedical applications [5]. However widespread use of CNx films in full scale industrial applications has been limited mainly by low adherence and high compressive stresses when films are deposited over steel substrate [6]. Recently, Broitman et al. [7,8] grew CNx films on steel substrates using a thin chromium sublayer in order to improve the adhesion of coatings to the steel surface and using a high-power impulse magnetron sputtering (HIPIMS) in master-slave configuration.

From the wide variety of carbon nitride (CNx) films, a material called fullerene-like CNx has been the most attractive to study. This film is formed by bend and cross-linking of nitrogen substituted graphene planes [1]. In the past CNx films have been deposited via magnetron sputtering under high substrate temperature (100–550 °C) and nitrogen-rich atmosphere (0–35%), resulting in high elastic modulus films compared to regular carbon films [9,10]. The most common tribological test used to evaluate friction and wear characteristics of CNx films is a ball on disk configuration [11–13], considered a macro-scale test while at nanoscale characterization involves mainly the use of atomic force microscopy (AFM) [14]. Since carbon and carbon nitride films are starting to be used in MEMS and NEMS devices, nanotribological performance of non-lubricated CNx coated surfaces is necessary. Schwarz et al. [15] investigated the tribological behavior of diamond and amorphous carbon films using an AFM probe coated with amorphous carbon, registering coefficients of friction (CoF) of 0.26 and 0.45 in air, respectively. Riedo et al. [16] use V-shaped silicon nitride cantilevers to measure the friction force of diamond-like carbon, carbon nitride and graphite films finding that friction forces \( F_T \) (DLC) > \( F_T \) (amorphous CNx) > \( F_T \) (Graphite). Absolute values of friction force are not provided since there was a relatively large uncertainty on the calibration method. Recently, Mo et al. [17] showed that the relation \( F_T = (\text{CoF}) (F_N) \) is valid and can be applied at nanoscale, however, the limitations at nanoscale studies arise from the accurate characterization of the spring constant for the AFM probe. The AFM probe is usually considered as a cantilever beam with rectangular geometry, where the spring constant is calculated from the equations used for isotropic solids [18]. In determining the precise dimensions of the AFM cantilever to apply these equations usually involves scanning electron microscopy measurements and is not always easy.

In the present work a comparative study on the chemical bonding structure of CNx films, mechanical properties and their tribological performance at nanoscale, using the procedure developed...
by Enriquez-Flores et al. to determine reliable spring constants, to evaluate the friction force [19].

2. Experimental

2.1. Deposition of carbon nitride films

Carbon nitride (CNx) thin films were deposited on mirror-polished single-crystal (1 0 0) silicon wafers by direct current magnetron sputtering technique with a MDX500 source and a carbon target as cathode with 50.8 mm diameter, located 50 mm from the substrate. A turbomolecular pump evacuated the evaporation chamber to a base pressure lower than 1 × 10⁻⁶ mbar. Nitrogen and argon of ultrahigh purity grade was introduced into the processing chamber while mass flow and total pressure of the evaporation process was computer controlled. Wafer substrates were immersed in a 1:1:1 mixture of ethanol, acetone and xylene in an ultrasonic bath for 10 min, rinsed in acetone and finally rinsed in ethanol for 10 further min and finally sputter-cleaned for 10 min before film deposition. The deposition parameters selected were work pressure 2 × 10⁻⁴ mbar, substrate temperature 200 °C, sputtering target power density (ρ) 10.8 W/cm², substrate bias voltage –250 V and evaporation time 20 min for a thicknesses of about 60 nm. Nitrogen portion in the Ar–N₂ mixture was varied from 13% to 19% in steps of 1% to form CNx film specimens labeled 1CNx, 2CNx, 3CNx . . . and 7CNx, controlling the nitrogen flow respect to total Ar/N₂ flow. The gas mixture was computer controlled to keep a constant working pressure.

2.2. Structure and composition of CNx films

Structure of CNx films was characterized by Raman spectroscopy on a micro-Dilor Labram spectrometer with a 50× objective and a 512 nm wavelength He–Ne laser line of 30 mW and the spot size was 2 μm. All measurements were taken at room temperature with no special sample preparation.

Chemical composition of deposited films was determined using SEM-EDS Philips XL30 energy dispersive X-ray spectroscopy at an electron beam energy of 2 keV, beam current 2.0 nA and detector take-off angle of 35°.

XPS analysis gives rise to useful information such as composition, chemical state, and thickness etc. of thin films. XPS chemical structure of CNx film prepared was performed on a Thermo Inter-

covamex XPS system equipped with a hemispherical electron analyzer and a monochromatic Al Kα X-ray source. A pass-energy of 15 eV in the analyzer allowed high-resolution XPS binding energy studies at a take-off angle of 85°. Photoelectron spectra were analyzed via software AAnalyzer®, Shirley-type background and Gauss-type functions were used to adjust data.

2.3. Nanomechanical characterization of CNx films

Nanoindentation tests on CNx films were carried out using a computer controlled Hysitron Ubi nanoindentor with displacement resolution better than 0.04 nm and high-resolution load of 1 μN. The films were tested using a Berkovich diamond indenter in the load range of 500–1250 μN. Before the experiments, the nanoindentor was fully calibrated by performing indentations on fused silica (E = 72.5 GPa, H = 9.5 GPa) samples at different loads. All nanoindentation tests were achieved at room conditions of 23 °C and 35% relative humidity. A total of 25 indentations were performed for each film.

A qualitative elastic recovery of the carbon nitride films under study can be determined using the indentation load–unload curve and performing the ratio of the final indentation depth. The recorded data taken from these curves for each CNx specimen was used to determine elastic modulus (Er) and elastic recovery (%R) from equation (1).

This elastic recovery is defined as

\[
R(\%) = \frac{d_{\text{max}} - d_{\text{res}}}{d_{\text{max}}} \times 100
\]

where \( d_{\text{max}} \) is the displacement at maximum load and \( d_{\text{res}} \) is the residual or plastic displacement after load removal. A lower value means more elastic recovery, while a higher value means that plastic effects take over.

2.4. Nanotribological performance of CNx films

Nanotribological evaluations of CNx films under study were carried out on a Bruker/Veco/Digital Instrument Nanoscope IV Dimension 3100 Atomic Force Microscope (AFM). The AFM was operated in contact mode using probes of rectangular silicon beams (Budget Sensors 75DLC) coated with a thin diamond layer with thickness of 15 nm on tip side and aluminum layer of 30 nm on detector side of the cantilever. These probes have a spring constant in the range from 1 to 7 N/m, length 225 ± 25 μm, width 28 ± 5 μm, thickness 3 ± 1 μm, tip height 15 ± 5 μm and tip radius <15 nm.

For a more accurate measurement of friction force, a spring constant value of the AFM cantilever probe was determined from spectra resonance frequencies from 50 kHz to 2.5 MHz and free vibration FEA modeling according to reference [20]. Starting from the cantilever dimensions provided by the manufacturer and taking into account relevant geometric parameters such as length, upper width, lower width and thickness, it is possible to obtain the effective dimensions of the probe. In the FEA analysis the cantilever is considered that the AFM probe was fabricated with orthotropic crystalline silicon, trapezoidal geometry, triangular end and inclination of probe-to-sample surface and an iterative procedure to minimize error of calculated to experimental frequencies. Using the calculated data for the AFM cantilever and the methodology given by Ruan and Bhushan was used in this section [21].

3. Results and discussion

3.1. Raman spectra of carbon nitride films

Fig. 1 shows Raman spectra of the seven specimens CNx films prepared. Characteristic bands D and G are identified in the range between 800 cm⁻¹ and 2000 cm⁻¹, fitted with a Voigt and Breign–Wigner–Fano (BWF) linear profile. While some authors suggest the use of a Lorentzian linear shape for D band [22–24], it was realized that Lorentzian line did not fit well below 1000 cm⁻¹ and for this reason Voig line was necessary. In order to reduce the number of fitting variables in Fig. 1, a simultaneous fitting for all Raman spectra was carried out. Asymmetry for G band is ~11.5 and position is 1584 cm⁻¹ while D band position appears at 1391 cm⁻¹. The \( I_D/I_G \) ratio values were 1.124, 1.1, 1 for films labeled as 1CNx, 2CNx, 3CNx, 4CNx films, respectively. Films labeled as 5CNx, 6CNx and 7CNx had an \( I_D/I_G \) ratio of 1. These values of \( I_D/I_G \) ratios and G band position correspond to a a-CNx films according to the model reported by Ferrari and Robertson [24]. These films are comprised of sp³ CN bonds, about ~20% nitrogen and some sp² bonds that may be due to molecular vibration of CC or CN bonds, however this is not possible to discern properly in the spectra because these vibrations are too close [25]. Atomic percentages of carbon, nitrogen and oxygen for each film are shown in Table 1.

3.2. XPS analysis of carbon nitride films

After XPS analysis of the CNx samples prepared, just oxygen, carbon and nitrogen were detected. Presence of oxygen may be due
to the prolonged exposure of samples to laboratory atmosphere. High-resolution XPS (HR-XPS) data for C 1s and N 1s are shown in Figs. 2 and 3 respectively.

Deconvolution of photoelectron spectra through peak-fitting of experimental data was carried out to observe the chemical bond configuration. Bonds of sp² C present at a binding energy (BE) of 248.8 eV were taken as reference to align the HR-XPS C 1s spectra [28]. Best fits to core levels of C 1s and N 1s resulted in four and three deconvoluted Gaussian peaks, respectively. Peaks for C 1s were located at binding energies of 284.8 eV, 285.6 ± 0.07 eV, 287 ± 0.3 eV and 288.9 ± 0.2 eV, assigned to links of carbon–carbon in sp² configuration (sp² C), nitrogen–carbon in sp² configuration (sp² CN), nitrogen–carbon in sp³ configuration (sp³ CN) and finally, oxygen–carbon, respectively. These results are in agreement with recent XPS studies [4,11,27]. Neidhardt and Hultman [28] assigned the sp³ CN peak at 287 eV to carbon nitride bonds in crystalline clusters (β-CN₃N₄) but the β-CN₃N₄ phase requires a nitrogen content of 57 at.%. Deconvoluted peaks for N 1s were located at binding energies BE of 398.9 ± 0.1 eV, 400.8 ± 0.1 eV and 403 ± 0.1 eV. These BE are assigned to links of carbon–nitrogen with configuration sp³ (sp³ CN), carbon–nitrogen with configuration sp² (sp² CN) and oxygen–nitrogen, respectively. These results are in agreement with previous carbon nitride results [11]. The peak positions and contributions of bonding types from XPS curve fitting are summarized in Table 2. It is shown that for 4CNx specimen, for C 1s and N 1s area fractions of sp³ CN bond increased while area fractions of sp² CN and sp² C decreased.

### 3.3. Nanoindentation analysis of carbon nitride films

Nanoindentation results at a maximum load of 1250 µN for all CNx films prepared are shown in Fig. 4. Elastic recovery R(%) of CNx films is shown in Fig. 5. It can be observed that prepared films with fullerene-like structure exhibit high elastic recovery when subjected to nanoindentation. Films from 1CNx to 3CNx present a rapid increase in elastic recovery from ~70% to ~94%, respectively. CNx films with elastic recovery values around R(%) ~70% are characteristic of carbon nitrides with amorphous structure [10]. However 3CNx and 4CNx that show elastic recovery values of R(%) ~ 94% and R(%) ~ 92% are typical of carbon nitrides with fullerene-like structure. Fullerene-like CNx films have structure that is a combination of hexagonal and pentagonal rings, where their planes are curved and have intersections. These types of films usually have elastic recovery values higher than 85% and high mechanical properties [10,28]. From 5CNx

### Table 1

Atomic percentage of elements in CNx films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C  at.%</th>
<th>N  at.%</th>
<th>O  at.%</th>
<th>(at.%N × 100)/(at.%N + at.%C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1CNx</td>
<td>86.095</td>
<td>9.68</td>
<td>4.225</td>
<td>10.1</td>
</tr>
<tr>
<td>2CNx</td>
<td>87.09</td>
<td>9.86</td>
<td>3.04</td>
<td>10.2</td>
</tr>
<tr>
<td>3CNx</td>
<td>86.43</td>
<td>11.15</td>
<td>2.42</td>
<td>11.4</td>
</tr>
<tr>
<td>4CNx</td>
<td>85.69</td>
<td>11.585</td>
<td>2.725</td>
<td>11.9</td>
</tr>
<tr>
<td>5CNx</td>
<td>82.355</td>
<td>12.67</td>
<td>4.97</td>
<td>13.3</td>
</tr>
<tr>
<td>6CNx</td>
<td>85.38</td>
<td>12.395</td>
<td>2.23</td>
<td>12.7</td>
</tr>
<tr>
<td>7CNx</td>
<td>86.365</td>
<td>10.98</td>
<td>2.655</td>
<td>11.3</td>
</tr>
</tbody>
</table>

### Table 2

Binding energies of bonding types contributing to XPS C 1s and N 1s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s</th>
<th>N 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sp²C</td>
<td>sp³CN</td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>284.8</td>
<td>285.6</td>
</tr>
<tr>
<td>1CNx</td>
<td>23.77</td>
<td>55.82</td>
</tr>
<tr>
<td>4CNx</td>
<td>20.11</td>
<td>40.49</td>
</tr>
<tr>
<td>7CNx</td>
<td>22.27</td>
<td>57.91</td>
</tr>
</tbody>
</table>
film to 7CNx film the elastic recovery gradually decreases to 80% showing again typical behavior of amorphous carbon films. The highest value of elastic recovery was found for 3CNx and 4CNx films that have a nitrogen content of 11.4 at.% and 11.9 at.%, respectively. The elastic modulus (E) of the CNx films prepared was calculated using the Oliver and Pharr method [29] and their values are shown in Fig. 5. The highest values of E are around 185 GPa for 3CNx and 4CNx films. The indentation hardness was 9.6 GPa, 12 GPa, 21 GPa, 20.6 GPa, 13 GPa, 16.3 GPa and 11 GPa for 1CNx, 2CNx, ..., 7CNx, respectively. Because the curvature radius of the Berkovich indenter (>200 nm) is blunt relative to coating thickness (~200 nm) then, the indentation hardness calculated from the load–displacement curve using the Oliver–Pharr method cannot be considered quantitative. The fullerene-like structure of the CNx films prepared in this study is related to their elastic modulus, high elastic recovery values and dominating effect of sp^3 CN bonds only, since no nitrogen–oxygen bonds are detected.

3.4. Nanotribological performance of carbon nitride films

Fig. 6 shows results of friction force vs. load from 1CNx, 3CNx, 4CNx and 7CNx films. Experimental data is fitted linearly and the slope gives the friction coefficient (CoF). Friction coefficient results for all samples tested are shown in Fig. 7. By exciting the cantilever probe by means of a piezoelectric transducer located at the probe holder it was possible to find three experimental free resonance frequencies: \( f_1 = 71.05 \text{kHz}, \) \( f_2 = 444.40 \text{kHz} \) and \( f_3 = 1245.0 \text{kHz} \). A
finite element analysis of the cantilever probe resulted in three calculated resonance frequencies: $f_1 = 70.59$ kHz, $f_2 = 444.27$ kHz and $f_3 = 1245.70$ kHz, and effective geometrical parameters of the probe such as length $248.04$ μm, upper width $38.05$ μm and lower width $23.56$ μm, thickness $3.07$ μm and spring constant $2.47$ N/m.

Carbon nitride films samples of fullerene-like structure 3CNx and 4CNx show a decrease in friction coefficient (CoF). It is observed that this friction coefficient reduction in samples 3CNx and 4CNx is related to an increase of $sp^3$ bonds CN hybridization, an increase in elastic modulus and elastic recovery. The indentation hardness, even tough is not quantititative, shows this increase tendency on samples 3CNx and 4CNx. On the other hand, samples 5CNx, 6CNx and 7CNx show a gradual increase in the CoF combined with a decrease in elastic modulus and elastic recovery, probably related to a reduction in atomic percentage of nitrogen, as indicated in Table 2. Previous research on carbon nitride films reports that the exceptional mechanical properties and performance of fullerene-like films are conditioned to its graphene structure. Neidhardt and Hultman [28] reported that the most probable cause for graphene planes deformation in carbon nitride with fullerene-like structure is due to pentagonal defects and in minor influence to stone-Wales (SW) defects. Formation of pentagonal defects and graphene plane curvature is linked to precursor species that do not only grow the film structure and make it more complicated, but also affects the final film structure [30, 31]. Chemical interaction of nitrogen with carbon target forms a mixture of C$_N$$_x$ species on the surface during the sputtering process. These formed species are eventually ejected from the target surface to the substrate specimen by the Ar–N$_2$ ion flux and then the majority of the species depositing on the substrate specimen are C atoms, C and N ions and CN species, which are the precursors of CNx films. Such precursors act as building blocks of fullerene-like carbon nitride structure evolution [32]. Based on XPS results and previously mentioned statements, the decrease of $sp^2$ C and $sp^3$ CN and the increase of $sp^3$ CN fractions for film samples 3CNx and 4CNx are strongly dependent on nitrogen ratio, atomic position rearrangements of precursor species and redistribution of nitrogen atoms. The increase in $sp^3$ CN bonds may be due to double pentagon defects that are energetically more favorable than single pentagon defects, leading to structures more resistant to deformation and with outstanding mechanical properties [30, 31].

4. Conclusions

Fullerene-like structure films with elastic recovery values of 94.5% and 92.5% were obtained on samples 3CNx and 4CNx. The mechanical properties of fullerene-like CNx films 3CNx and 4CNx were $E = 187.2$ GPa, $H = 21$ GPa and $E = 184.5$ GPa, $H = 20.6$ GPa respectively. It was determined on these fullerene-like films an increment of 34.86% and 50.57% in fractions of C 1s and N 1s. Quantitative values of friction coefficient were determined using DLC covered AFM probes for all CNx films. From the samples prepared, specimens 3CNx and 4CNx showed a fullerene-like structure and a friction coefficient of $0.010 \pm 0.006$ and $0.020 \pm 0.002$. In general, fullerene-like samples 3CNx and 4CNx exhibit a friction reduction compared to the rest of the specimens with an amorphous structure. This observed improvement is strongly related to the increase of $sp^3$ CN bonds.

Acknowledgments

The authors wish to express their sincere thanks to the National Council for Science and Technology (CONACyT) and the Secretary of Public Education (SEP) for the financial support under projects 079901 to carry out the present work.

References


