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Structural and Mechanical Properties of CN_x and CP_x Thin Solid Films

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Abstract. The inherent resiliency, hardness and relatively low friction coefficient of the fullerene-like (FL) allotrope of carbon nitride (CN_x) thin solid films give them potential in numerous tribological applications. In this work, we study the substitution of N with P to grow FL- CP_x to achieve better cross- and inter-linking of the graphene planes, improving thus the material's mechanical and tribological properties. The CN_x and CP_x films have been synthesized by DC magnetron sputtering. HRTEM have shown the CP_x films exhibit a short range ordered structure with FL characteristics for substrate temperature of 300 °C and for a phosphorus content of 10-15 at.%. These films show better mechanical properties in terms of hardness and resiliency compared to those of the FL- CN_x films. The low water adsorption of the films is correlated to the theoretical prediction for low density of dangling bonds in both, CN_x and CP_x . First-principles calculations based on Density Functional Theory (DFT) were performed to provide additional insight on the structure and bonding in CN_x , CP_x , and a-C compounds.

Introduction

Amorphous carbon-based coatings have found many applications as protective coatings and solid lubricants. By tuning the C sp^3 -to- sp^2 bonding ratio and by alloying the carbon with other elements, the properties of the coatings can be tailored. Recently, we have shown that it is possible to incorporate fullerene-like features to a solid matrix of C and N. The resulting so called fullerene-like (FL) compound consists of sp^2 -coordinated graphitic basal planes that are buckled due to the presence of pentagons and cross-linked at sp^3 -hybridized C sites, both of which are caused by structural incorporation of nitrogen. This fullerene-like carbon nitride (FL- CN_x), which possess a superior resiliency to mechanical deformation due to its unique superelasticity, show potential as protective top coat on computer hard disks and biocompatible coatings on orthopedic implants [1].

While the relatively weak adhesion of FL- CN_x films to ferrous substrates has been solved by the application intermediate layers of, e.g. CrN_x [1], we have proposed that the P substitution may improve their mechanical properties [2]. In this work we compare the structural and mechanical properties of CP_x and CN_x films deposited by DC magnetron sputtering. The film microstructure was characterized by high resolution transmission electron microscopy (TEM) and the mechanical characteristics were examined by nanoindentation testing. A quartz crystal microbalance (QCM) placed in a vacuum chamber was used to measure their water adsorption. To provide additional insight into the structural features of CP_x compounds, we performed first-principles calculations within the framework of Density Functional Theory (DFT).

Experimental Procedure and Modeling Details

CP_x and CN_x thin solid films have been deposited onto highly-doped Si(001) and NaCl(001) substrates by magnetron sputtering, as described previously [2]. For CP_x , we have used a compound target containing 12 at% of phosphorus prepared by statically pressing the mixture of graphite and red phosphorus. The high vacuum (HV) system applied for growth had a base pressure of $\sim 5 \times 10^{-7}$ Torr. The magnetron was operated in an Ar discharge with gas pressure (P_{Ar}) in the range of 3–9 mTorr. The substrate temperature (T_s) ranged between 150 °C and 600 °C and a bias voltage (U_b) between –20 V and –70 V was applied. The thickness of the as-deposited films was ~ 1.2 μm for the nanoindentation testing and ~ 50 nm for TEM characterization, with a deposition rate of ~ 0.4 Å/s.

The microstructure of the films deposited onto NaCl substrates was examined in a Technai G2 electron microscope (EM) for high resolution transmission electron microscopy (HRTEM) imaging and a Philips CM20 for selected area electron diffraction (SAED) pattern analysis, both operated at 200 kV.

The mechanical properties of the CP_x films were investigated by nano-indentation experiments using a 90° three-sided cube corner diamond tip in a Triboscope® (Hysitron Inc). Hardness and reduced modulus were calculated from the stiffness obtained by area function fitting to the unload part of the curve in the length 20% to 95% of penetration. Recovery was defined as $(h_{max} - h_r)/h_{max}$, where h_{max} is the maximum penetration depth and h_r is the residual depth of indent. Hardness was defined as $H = P_{max}/A$ where A is the area of contact at the peak load P_{max} . A was calculated from the area function obtained by indenting fused silica as reference material.

The water adsorption of the films was measured by a QCM placed inside a vacuum chamber operating in the range 10^{-8} – 10^3 Torr. The mass of water adsorbed on the surface of the quartz crystal was calculated using the Sauerbrey equation [3].

In what concerns the modeling, finite model systems simulating a-C, a- CP_x , as well as systems in which P is incorporated in strongly interlocked graphene sheets (to represent FL- CP_x) were considered. The study involved both geometry optimizations and cohesive energy (E_{coh}) calculations performed within the DFT framework in its Generalized Gradient Approximation (GGA). Differences in cohesive energies $|\Delta E_{coh}|$ for the possible structures were determined by an optimization strategy presented elsewhere [4], making use of the Gaussian 03 program.

Results and Discussion

Figure 1 displays a HRTEM image and the corresponding SAED pattern from a $CP_{0.1}$ film deposited at $T_s = 300$ °C, $U_b = -25$ V, and $P_{Ar} = 3$ mTorr. The film is essentially amorphous, but

Figure 1: HRTEM image and corresponding SAED pattern and its intensity distribution from a $CP_{0.1}$ thin film.

exhibits short-range ordering with fragments of curved graphene sheets. Although the presence of any larger packages of the FL structure similar to FL- CN_x cannot be ruled out from such HRTEM images due to the possible superposition of nanoscale features, it is not expected for CP_x since the calculations show a strong tendency for P-induced inter-linking of the graphene which breaks the continuity of the planes [2]. The SAED pattern shows that the $CP_{0.1}$ film has broad rings at ~ 1.6 Å, ~ 2.6 Å, and ~ 5.9 Å. These rings differ from those of other C allotropes, as well as from FL structures like FL- CN_x . This shows that incorporation of P in graphene has a unique influence on the film structure formation. In contrast, CP_x films

deposited at $T_s = 300$ °C and working gas pressure of 6 mTorr and 9 mTorr show amorphous

structure with close to graphitic short-range ordering. These samples exhibit SAED peaks at ~ 1.2 Å, ~ 2.15 Å, and ~ 4 Å. The first two peaks coincide with those also found in FL-CN_x [5], and some other amorphous C allotropes. The position of the third peak at ~ 4 Å, however, differs slightly from the ~ 3.5 Å peak typical for the FL structure known from FL-CN_x [5].

Figure 2 shows nanoindentation load–unload curves for CP_{0.1} films deposited at $T_S = 300$ °C and CP_{0.025} films deposited at 600 °C. Both CP_x thin films are harder to indent than a characteristic FL-CN_x film. The CP_{0.025} films had a hardness of 18.2 GPa at 2 mN indentation load. For comparison, the FL-CN_{0.16} film has a hardness of 15.4 GPa for the same load. The work of plastic deformation, represented by the surface enclosed by load–unload curves, shows a more pronounced plastic deformation for CP_{0.025} films compared to FL-CN_{0.16}. Specifically, the elastic recovery ratio of the CP_{0.025} film is 0.63 compared to 0.74 for FL-CN_{0.16}. CP_{0.1}, on the other hand, displays a significantly reduced work of plastic deformation compared to CP_{0.025}, improved recovery to the value of 72%, and hardness of 24.4 GPa. Thus, the CP_x films exhibit a similar recovery to FL-CN_x, but are harder to indent. Mean surface roughness of the films, as determined by AFM, is ~ 0.5 nm for films deposited at $T_S = 300$ °C and ~ 0.9 nm for films deposited at $T_S = 600$ °C. Thus, the influence of the substrate roughness on the indentation results can be neglected for the used penetration depths.

Figure 3 shows the adsorption of water versus the water vapor pressure for films deposited under different conditions. All carbon-based films have a characteristic dependence of water coverage on the H₂O vapor pressure. There are, however, differences in the amounts of the adsorbed water:

- i) Pure carbon films adsorb more water than phosphorous-carbide films;
- ii) Fullerene films adsorb less water than amorphous films.

It has been shown the surface roughness could play an important role on the water adsorption. However, surface roughness differences are small in our case, and only play a role in the adsorption of water at high levels of RH, where capillary condensation can occur in the valleys giving thicker water films [3,6].

The surface of the sputtered carbon-based films is heterogeneous and is composed of different hybridized carbon atoms (sp , sp^2 , and sp^3) and dangling bonds. As soon as the surface is exposed to air, its dangling bonds react with oxygen and form oxygen containing polar groups such as C-O-C, C-OH, and C=O. Because of the hydrogen bonding tendency of water, the adsorption of water is sensitive to the polarity of the adsorbent surface and is enhanced by the presence of oxidized carbon. We should expect that, because of the fullerene structure, FL-CP_x films have the lowest number of dangling bonds and, in consequence, low water adsorption. Electron spin resonance measurements confirmed this assumption for carbon nitride coatings. In a previous work,

Figure 2 Nanoindentation curves from CP_x thin films deposited at 300 °C (CP_{0.1}) and 600 °C (CP_{0.025}). The FL-CN_{0.16} film was deposited at 450 °C.

Fig. 3. The water surface density adsorbed on the surface of carbon overcoats at 50 °C versus water vapor pressure.

we reported that FL-CN_x shows the lower adsorption rate, and that a-C adsorbs more than 14 times the amount adsorbed by the fullerene coatings [6]. The differences in adsorption on our films must be understood in the context of their microstructural differences, as explained below by a theoretical model.

Figure 4: Correlation of energy cost versus experimental water adsorption on amorphous and FL carbon-based compounds. Both dashed lines are only for guiding the eyes.

bond formation. The error bars, displayed for FL compounds only, indicate the variation of the energy values due to the diversity of defects in these systems. The decrease of water adsorption on different FL and amorphous films correlates very well with the theoretically predicted reduction of dangling bonds on the film surfaces.

In conclusion, CP_x thin films deposited at 300 °C presents a unique microstructure with highly curved and interlinked FL features. In term of mechanical properties, CP_{0.1} thin films are harder than FL-CN_{0.16} counterparts, and can be considered as resilient with a hardness of 24 GPa and an elastic recovery of 72%. The CP_{0.1} films present low water adsorption, which can be linked with a low amount of dangling bonds, as confirmed by our theoretical calculations.

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