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Atomic force microscopy investigation on the effects of annealing on amorphous carbon nitride films deposited by rf-magnetron sputtering

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Atomic Force Microscopy was used to study the effects of thermal annealing on the surface topography and the tribological properties of amorphous carbon nitride thin films deposited by rf-magnetron sputtering. The results show that the surface roughness decreases with the increase of the annealing temperature. The friction coefficients at the interface between a Si_3N_4 tip and the amorphous carbon nitride films surface decrease with increasing smoothness of the surface.

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Since the beginning of the seventies, amorphous carbon films (a-C) have been the focus of intensive research due to their interesting physical and chemical properties[1]. Despite their high internal stress, which limits their adhesion to the substrates, a-C films have interesting mechanical and tribological properties, such as, high hardness, low friction coefficient and low wear rates, properties that make these materials suitable for several applications as protective coatings[2]. Since Cohen and Liu[3] proposed that the bulk modulus of a hypothetical material, β-C_3N_4, structurally analogous to β-silicon nitride, may be greater than diamond, the study of nitrogen incorporation into carbon films has received special attention[4]. In which concerns films deposited by sputtering, it was shown that amorphous carbon nitride films (a-CN) deposited without any bias applied to the substrates are soft polymeric materials (paracyanogen-like films)[5]. On the other hand, a-CN films deposited by dc-sputtering with negatively biased substrates can be as hard as a-C films, with improved tribological properties: lower friction coefficients and wear rates[6]. One of the most current applications of a-C and a-CN films is overcoating on magnetic recording disks. In this case, the knowledge of the tribological and topological properties of the coating films is largely required because the durability of the disk depends on them.

In spite of the large efforts made to optimize the deposition conditions, there are few results regarding the structural and compositional modifications induced in a-CN films by thermal treatment[7-9]. In this work, we present an analysis of the annealing effects on paracyanogen-like films by measuring the rms roughness and the friction coefficient between the surface of an unlubricated amorphous carbon nitride film and an AFM tip. It is shown that the decrease in the value of the friction coefficient is correlated to the decrease in the surface roughness when the annealing temperature increases.

The a-CN films were deposited by rf-magnetron sputtering onto n-doped <100>-Si substrates mounted over a water-cooled sample holder. A high purity (99.95%) graphite target of 8-cm diameter was sputtered in N_2 atmosphere. The base pressure of the vacuum system was better than 10^{-4} Pa and the deposition pressure was 1 Pa. The rf power was kept constant and equal to 150 W. No bias was applied to the substrates. The N/C atomic ratio was determined by Rutherford backscattering spectrometry (RBS). The film density was obtained by combining the film thickness measured using a stylus profilometer and the areal density obtained by RBS. The samples were annealed at fixed temperatures into a quartz tube furnace at pressure lower than 10^{-4} Pa. The annealing time was 30 min and the temperature varied from 300 to 700 ºC. No kind of sequential annealing was applied to the samples. Besides the nitrogen losses (the N/C atomic ratio is reduced from 0.71 to 0.52, as determined by RBS), the film density increases from 0.8 to 1.2 x 10^{23} atoms/cm^3, in the temperature range here studied[10]. Details of the chemical and structural characterization of the films were published elsewhere[10-12]. After annealing, no efforts were made to avoid contact of the films with ambient air so that aging might have occurred on the a-CN surfaces under investigation.

The AFM studies were performed using a TopoMetrix Microscope in an environment of controlled ambient conditions[13]. Bingelli and Mate[14] have shown that the influence of the humidity on the friction coefficients determined by AFM is extremely reduced for amorphous carbon surfaces, even for relative humidities up to 95%. This behavior was explained by the low hidrophilicity of amorphous carbon surfaces. Despite of that, the relative air humidity (35%) and room temperature (21 ^oC) were kept constant during the measurements. The data acquisitions were performed in lateral force mode for friction studies and in constant force mode for topography imaging and roughness analysis. The samples were cleaned with an ultrasonic cleaner in an acetone bath before being analyzed. Prior to any AFM measurement the samples were imaged on a 2x2 μm^2 area making sure that no defects or contamination were present. The rms roughness was obtained over a 1 μm^2 area, with a scan rate of 2 Hz and normal force of 20 nN. In the friction force regime, both images (lateral force forward and reverse) were acquired. During image acquisition by friction mode, the normal force was varied by increasing the loading force, moving the sample upward to the tip by the z-piezoelectric. The slope of the best linear fitting of lateral *vs*. normal force curves is the friction coefficient of the interface of the tip and the sample surface. The absolute values of friction coefficients were obtained calibrating the AFM set up by measuring the mica and glass friction coefficients reported by Putman et al.[15,16].

In Fig. 1 we show the AFM images obtained from an as-deposited a-CN film (a) and from a sample annealed 700 ^oC (b). Several samples were analyzed for each annealing temperature and for every one of them 10 different regions of the film were studied with similar results. The rms surface roughness, defined as the measurement of the variation in height of the surface[17], was studied. Before the roughness analysis, the plane fit (first order) was removed by using a least-square algorithm to fit the image to a plane and then subtracting the plane from the image. It has to be noted that, the plane fit procedure was used to remove the sample tilt artifact. The decrease in roughness with increasing annealing temperature can be seen in Table I. The value of the rms roughness decreases by a factor of 2 as the temperature of annealing increases up to 700 ^oC. Raman and infrared analyses suggest that the thermal treatment of these films induces important structural modifications, progressively changing from a polymer-like material to a more graphitic one in the temperature range here studied[12]. The surface roughness in someway reflects this structural modification.

The friction coefficients presented in Table I are the average values from the friction coefficients obtained at 10 different regions on each film surface and the error bars represent the standard deviation of the friction coefficients values for each sample. The data show that the friction coefficient decreases by almost 40 % with the increase of the annealing temperature.

It is known that any change on the surface topography can lead to modifications in the friction forces[18]. Changes in the contact area and, consequently, variations in the attractive forces between the sample and the tip during the scanning explain the correlation between the topography and friction force data. The AFM tip is rough on a nanometer scale, so that many microasperities of the tip touch the film surface while in contact. Then, as the tip approaches the surface, the microasperities undergo deformations which increase the contact area and therefore modify the attractive forces between the tip and the sample. Mate[19] has reported that, on hard carbon films, topography and friction are correlated in the sense that lateral forces vary when attractive van der Waals forces change while scanning.

In our experiment it is observed that the lateral force on a valley is higher than on a top of a corrugation. This can be explained by the fact that as the tip scans from a top to a valley the contact area between tip and sample increases, due to lateral contact. In this case the attractive forces between sample and tip increase and, as a consequence, the lateral force increases as well. Fixing the normal force at 40 nN during scanning, for a film surface with a roughness of 4.4 nm the difference between the lateral forces measured at a top and a valley is 0.08 nN, while for a roughness of 2.7 nm this difference is only 0.02 nN. As a consequence, when the a-CN film surfaces become smoother, smaller changes on the tip contact area occur resulting in smaller friction coefficients.

In conclusion, in this letter it is reported a systematic AFM analysis of the annealing effects on a-CN films. The surface roughness decreases with increasing annealing temperature as a consequence of a rearrangement of the film microstructure. This means that, there is an improvement of the tribological properties of soft a-CN films: a reduction of both surface roughness and friction coefficients. Finally, the correlation between the decrease in friction coefficients with the decrease in rms roughness can be attributed to variations of the attractive forces between the tip and the surface while scanning.

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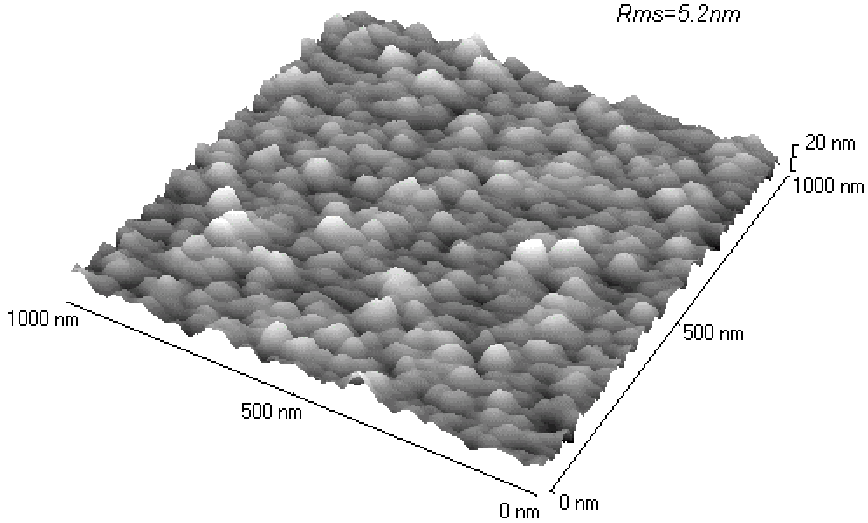
Table I: Rms roughness and friction coefficients as functions of the annealing temperature.

Annealing Temp.(ºC)	Rms roughness (nm)	Friction Coefficients
as-deposited film	5.2 ± 0.2	0.20 ± 0.04
300	4.4 ± 0.4	0.18 ± 0.04
500	2.9 ± 0.2	0.15 ± 0.03
700	2.7 ± 0.3	0.13 ± 0.02

Figure 1: AFM pictures obtained from:(a) as-deposited sample;(b) sample annealed at 700 ^{o}C.

(a)



(b)