DIAMOND-LIKE CARBON DEPOSITION BY A TRIODE PECVD

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Abstract. We studied the tribological behavior of diamond-like carbon (DLC) films produced from acetylene in a plasma enhanced chemical vapor deposition (PECVD) system. Films were deposited on AISI 304 stainless steel samples prepared by the deposition of acetylene at different distances from the plasma. Measurements of ball–cratering (Calotest) and scratching resistance were done to evaluate the wear resistance and the adhesion of the films. FTIR, AFM and RAMAN spectroscopy technics were used to elucidate the structural chemistry of each film and correlate it to the tribological properties.

Keywords: DLC, PECVD, distance effect, tribology

1. Introduction

The continuous search for better hard layers of amorphous hydrogenated carbon (a-C:H is due to its wide spectrum of properties and consequent wide applicability in metal-mechanic, biomedicine and semiconductor industry. Its potential high mechanic hardness, sometimes above 20 GPa, and low friction coefficient enhances abrasion resistance (Robertson, 1999, Huang, 2002). The deposition technique, Plasma Enhanced Chemical Vapor Deposition (PECVD) is

largely studied used in industrial application, because of the possibilities of uniform coating of large areas at temperatures near room values. Grill (1999) stated that the most important limiting factors of the process is the low adhesion to some metallic substrates, which is caused by high residual stress, which limits the maximum useful layer thickness.

In the last decade, a great deal of understanding has been obtained about the structure of DLC films deposited by PECVD and their relationship with the processing parameters, for which the atmosphere composition and pressure, as well as the substrate bias voltage and plasma density outstand (Grill, 1999). These factors set for example the most important structural characteristic of a-C:H films, the sp^3/sp^2 bond ratio of the carbon atoms (Robertson, 2002), which determines the optical, electrical and tribological properties (Silva *et al*, 1998).

In the last 10 years there has been a great interest in alloying a-C:H films with nitrogen (Freire, 1997) and different metals (C.W. Moura. Dissertação de Mestrado. REDEMAT. 2005.). The interest in N is aimed to the search of solids with structure analogous to the hypothetic compound β-C_3N_4, proposed by Liu and Cohen (1989) that, in theory, would be harder than diamond, and for structural as well as electrical, optical, mechanical and tribological properties modifications. The nitrogen incorporation on the films can reduce the inner compressive tension associated with low mechanical hardness variations (Franceschini, Achete and Freire, 1992).

In this paper a study of a triode CVD processing for the deposition of DLC films is investigated, as a contribution for the development of potential hybrid coatings.

2. Experimental procedures

The films studied in this paper were obtained by triode CVD deposition of DLC using acetylene as a precursor, in a chamber with a total volume of 640 l, at temperatures of 300°C, pressure of 2.3x10^{-3}mbar. The samples were previously nitretated by a 90 sccm nitrogen flow and the process gas (acetylene) was supplied to the deposition chamber with a 80 sccm acetylene flow during a deposition time of 60 min. A plasma torch was formed by a argon source operated at 720W. The samples were heated and etched by the plasma for 15 min. before the coating and held in a rotary apparatus in 3 positions (Fig. 1), being placed in the distances showed in the Tab. 1.
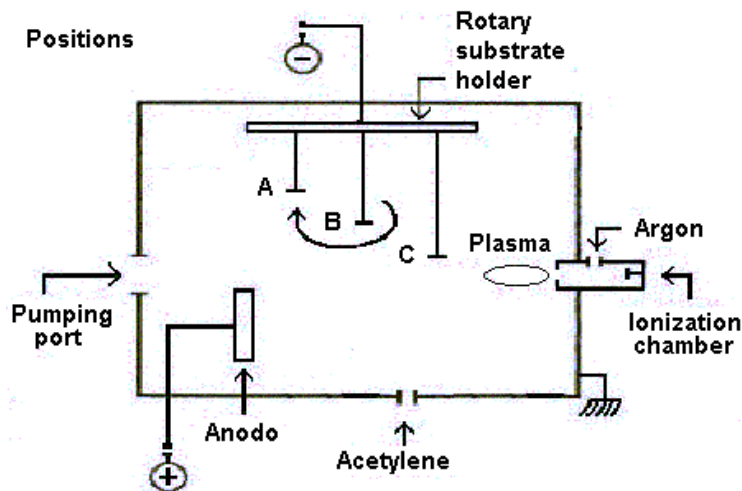

Figure 1. Schematic diagram of deposition chamber

Table 1. Vertical distances from the plasma for sample positions (cm)

Position	Dist. from the plasma (cm)
A	30
B	14
C	6

Reflection – absorption infrared (FTIR) measurements were made with a BOMEN DA8 machine, 500 scans were done for each spectrum and the resolution was 4 cm^{-1}. Atomic Force Microscopy (AFM) fom Digital Instruments, model Dimension 3000, operating on tapping mode, was used to verify the topography three-dimensional of thin films. The surface scanning of the films was done with a commercial silicon probe.

The ball–cratering (Calotest) tests were carried out using a ball-cratering tribometer developed by the Laboratory of Engineering and Surface Modifications (LEMS) of CETEC, and shown in Fig. 2. The apparatus consists of a bearing

steel ball rotating against a metallic wear plate with abrasive paste (diamond paste, medium diameter of 1 µm) passing between the contact points. The steel ball is a standard 41.3 mm bearing ball and it is rotated by means of an engine fitted with a spin–counter device. The scratching resistance tests were done in a CSM REVETEST equipment, with a loading between 0 and 20 N, with a vertical velocity of 60 N.min^{-1} and a horizontal velocity of 30 mm.min^{-1}. Two scratches were done in each sample.
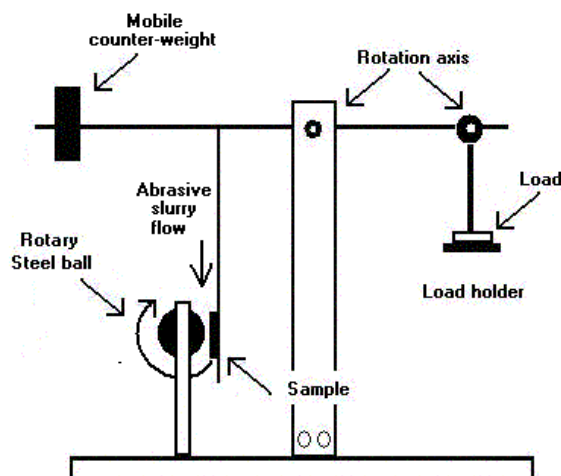

Figure 2. Schematic diagram of the ball-cratering tribometer

3. Results and Discussion

Table 2 shows the areas under the curve (I) of the absorption bands associated with sp^3 and sp^2 structures in DLC films deposited at different distances from the plasma for the conditions described above (acetylene ratio of 80 sccm, deposition time of 60 min.).

Table 2. Areas of the absorption bands due to stretching modes of sp^3 and sp^2 structures for DLC deposited at different distances from the plasma

Position	Dist. Plasma (cm)	I_{sp3} (cm^{-1})	I_{sp2} (cm^{-1})
A	30	3.7	5.9
B	14	79.3	5.3
C	6	52.8	2.1

The FTIR spectra of the samples show a CH_n stretching band which can be divided in two areas, one from 2800 up to 2960 cm^{-1}, created by the absorption modes of CH_2 and CH_3 stretching in sp^3 (diamond like) configurations (Demichelis, 1995; Giorgis, 1997; Prado, 1997; Robertson, 1999; Robertson, 2002; Saw, Idrus e Ibrahim, 2000; Zhang et al., 1998) and the other, from 2960 up to 3085 cm^{-1} (Robertson, 1999; Giorgis, 1997), due to the stretching of these compounds in sp^2 configurations.

It is known that, while essentially all sp^3 sites in a-C are hydrogenated, many sp^2 sites are not (Robertson, 1999). So, it is not possible to use the relation between the area of the absorption band in the FTIR due to sp^3 C-H stretching modes and the area of the band due to sp^2 C-H stretching modes to get an exact value of the relation between the amount of sp^2 and sp^3 carbon atoms in the sample. But, by the same argument, the area of the sp^2 C-H stretching band can be used as a way to measure the minimum value of sp^2. Logically, we can't compare the area of the sp^2 band directly with the area of the sp^3 one since they have different absorption strengths associated with them. But, if normalization is done to eliminate the effect of different thickness (or different optical paths) it is logical to compare the area of the sp^3 band in one sample with the area in another the same being valid for the sp^2 one.

From Tab. 2 it is possible to see that the sp^3 (diamond) content is larger for a distance of 14 cm, with substantial reduction for both extreme positions.

The end of the scratchs for each one of the coating conditions are shown in Fig. 3. The horizontal and vertical double–sided arrows indicate that, in positions B and C, scratches larger than that in position A were done. Position B presented a major loss of adhesion, as can be seen due to the film chips present around the scrath.
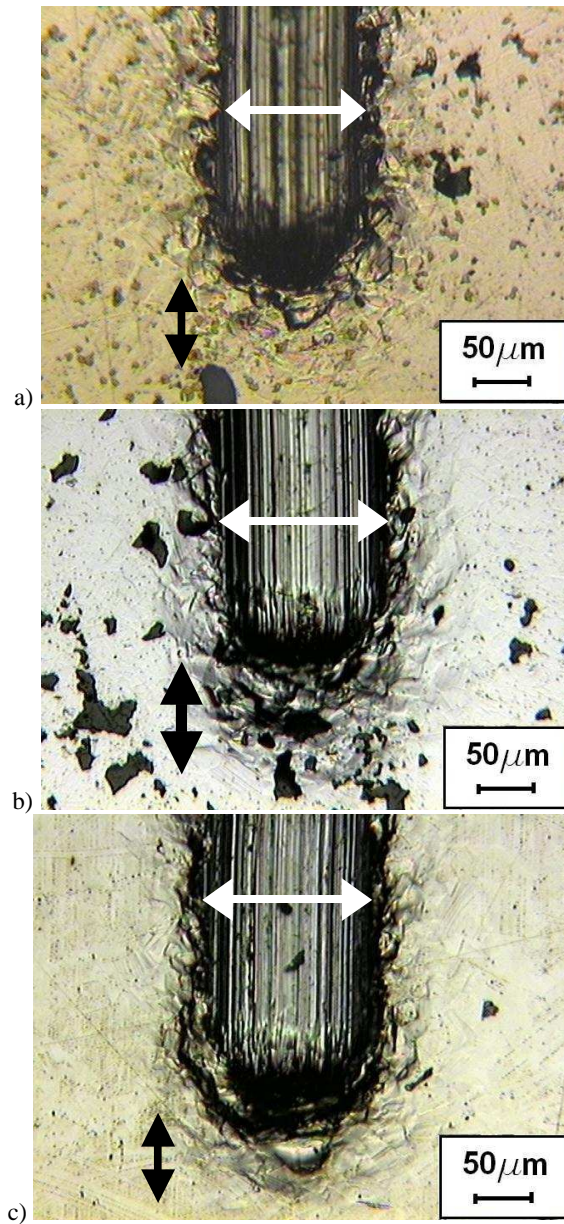
Figure 3. Optical image of scratch damage to samples at a) position A, b) position B and c) position C

The results showed that a high distance from the plasma results in a more resistant film, with high adhesion. Further testing should be done to evaluate the reasons for this finding.

Table 3 shows the wear rate measured by the ball–cratering test for samples obtained at distances described above. According to these data, we found a lower wear rate for the DLC sample in position A. Table 3 shows as well that for distances B and C, there is no difference between the obtained data, and a rise of wear rate of about 34% if compared with A position. This is probably due to the sp^2 (graphite) content in sample placed in position A, which is higher than in the other samples. Unfortunately, this alternative cannot be reasonably supported by the FTIR findings, once the sp^2 content didn't reflect the C=C due to the graphite structures by the reasons mentioned above.

Table 3. Wear rate measured by the ball–cratering test.

Position	Wear rate (m^2/N)
A	7.28×10^{-16}
B	1.1×10^{-15}
C	1.1×10^{-15}

Figure 4 compares the AFM topological analysis of samples obtained at all positions by three-dimensional images of 2 μm sided square areas.
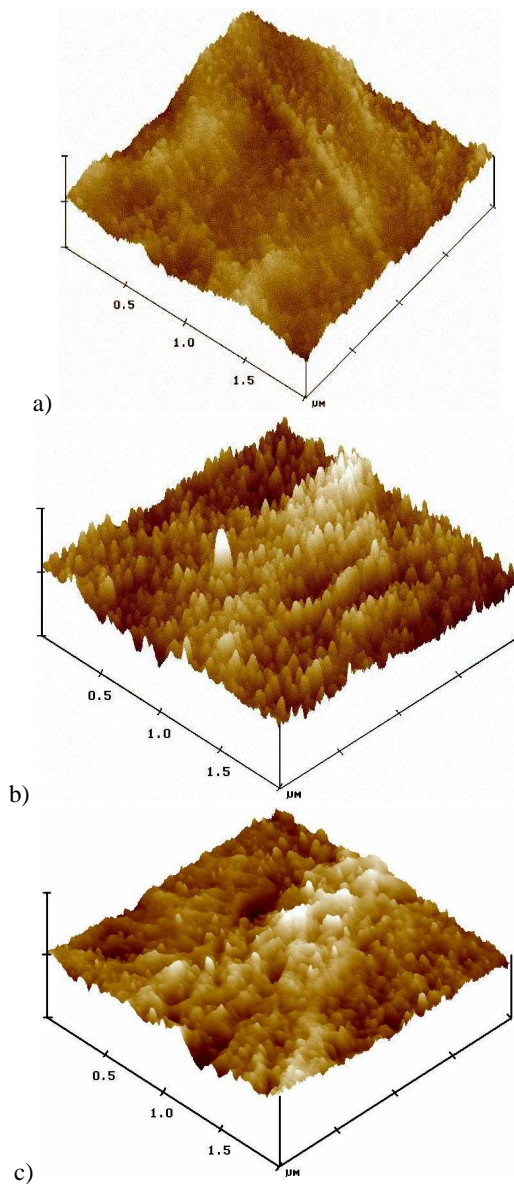

Figure 5. AFM three-dimensional images of samples at a) position A, b) position B and c) position C

Is possible to see more acute spikes on the sample obtained at position B, suggesting that this phenomenon was caused by the acetylene ionized molecules availability in this position of the chamber. The roughness evaluated by AFM techniques for the positions A, B and C were respectively 2.062 nm, 3.278 nm and 2.975 nm, in spite of the film features mentioned above, which indicates the lower roughness for the highest distance from the plasma. The subsequent thickness evaluation could also confirm the lower substrate influence.

4. Conclusions

In this study, we compare some conditions for DLC production in a specific triode CVD deposition of DLC and a position effect with respect to a plasma source was verified, based on IR measurements of sp^3 content, Raman shift, wear and scratch resistances.

5. Acknowledgements

6. References

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