

STUDY OF CARBON FILMS DEPOSITION BY PECVD WITH Si INCORPORATION BY VACUUM EVAPORATION

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Abstract. A doping method was developed for diamond-like carbon (DLC) films production. An electron beam device was used as silicon source in a plasma enhanced chemical vapor deposition (PECVD) system. Two AISI 304 stainless steel samples, one made by DLC doped with silicon and the other with pure DLC were obtained. Measurements of ball-cratering (Calotest), scratching resistance, infrared and raman spectroscopies were used to elucidate the structural chemistry of each film and correlate it to the tribological properties.

Keywords: DLC, PECVD, electron beam, silicon doping, tribology

1. Introduction

The hard layers of amorphous hydrogenated carbon (a-C:H) generated by Plasma Enhanced Chemical Vapor Deposition (PECVD) are being largely studied because of their wide applicability in mechanic resistance, biomedicine and semiconductor materials. Its high mechanic hardness, sometimes above 20 GPa, with low friction coefficient gives a great mechanic abrasion resistance (Robertson, 1999). The deposition technique, PECVD, has a large industrial application, because of the possibilities of uniform coating of large areas at temperatures near ambient. Grill (1999) stated that the most important limiting factors are the high residual inner tension which limits the maximum useful layer thickness and the low adhesion to some metallic substrates, which is caused by the lack of occurrence of stable interfaces, in opposition of films deposited over Si substrates, in which a thin SiC layer is formed.

In the last two decades there has been growing interest on the C-Si system. On the C rich side there has been a great deal of understanding about the structure X properties relationship of DLC films deposited by PECVD and their relationship with processing parameters (Grill, 1999, Robertson, 2002), mainly based on the outstanding tribological properties possible. On the Si rich side the interest is due to its photovoltaics applications.

The continuous search for better and less expensive high performance layers makes vacuum evaporation based processes attractive. In the last 10 years there has been, a great interest in alloying C and C-N systems (C.W. Moura. Dissertação de Mestrado. REDEMAT. 2005.). Their interest in incorporating N is aimed to the search of solids with structure analogous to the hypothetic compound $\beta\text{-C}_3\text{N}_4$, 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 incorporation of C in Si is attractive due to its effect in the band gap the resulting semiconductors.

In this paper, we investigate the feasibility of incorporation Si on ion plated DLC by a triode e-beam reactive activated physical deposition process

2. Experimental procedures

The films studied in this paper were obtained by deposition of acetylene in a chamber with a total volume of 640 l (Fig. 1), at temperatures of 300°C, pressure of 2.3×10^{-3} mbar. the plasma source was operated at 720W. The samples were heated and etched by the plasma for 15 min. before the coating. A "p" doped silicon target was used as a Si source for the doped sample, being excited by an e-beam with an emission current of 0.2 A. The process gas (acetylene) was supplied to the processing chamber at flow rates of 80 sccm for the pure DLC and of 40 sccm for silicon doped DLC. The samples were held in a rotary apparatus negatively charged, at a minimum distance of 14 cm from the plasma, as showed in the Fig. 1.

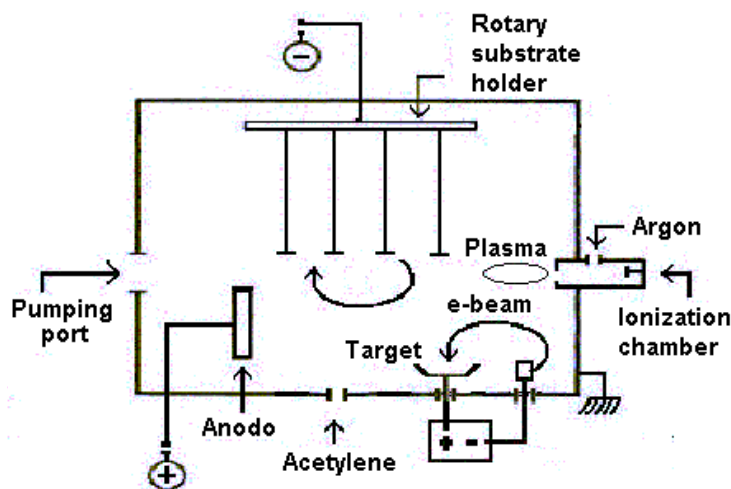


Figure 1. Schematic diagram of deposition chamber

The ball-cratering (Calotest) tests were carried out using a ball-cratering tribometer developed by the Laboratory of Engineering and Modifications of Surface (LEMS) of CETEC, 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 point. 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 CSAM REVETEST equipment, with a loading between 0 and 20 N, with a vertical velocity of 60 $\text{N} \cdot \text{min}^{-1}$ and a horizontal velocity of 30 $\text{mm} \cdot \text{min}^{-1}$. Two scratches were done in each sample.

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} . Raman spectra were measured using a JOBIN YVON HORIBA equipment, model LABRAN 800 with visible laser excitation ($\lambda = 632 \text{ nm}$ and 10 mW over the sample) with a 2 cm^{-1} precision in Raman shift, from the Metallurgical Engineering Dept. of UFMG.

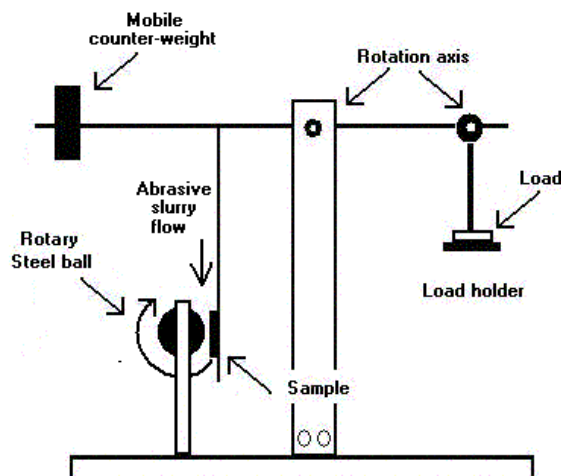


Figure 2. Schematic diagram of the ball-cratering tribometer

3. Results and Discussion

Table 1 shows the areas under the curve (I) of the absorption bands associated with sp^3 and sp^2 structures in DLC films with and without silicon and wear rate obtained from the ball-cratering tests.

Table 1. Comparison between optical (FTIR) and tribological data obtained for DLC samples deposited with and without silicon.

Sample	$I_{sp^3} (cm^{-1})$	$I_{sp^2} (cm^{-1})$	Wear rate (m^2/N)
DLC	79.3	5.3	$1.11 \cdot 10^{-15}$
DLC + silicon	19.5	14.3	$7.49 \cdot 10^{-15}$

The FTIR spectra of the samples showed 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 a sp^3 (diamond like) configuration (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.

Therefore, from Tab. 1, it is possible to see that there is evidence of more sp^3 structures (diamond) and less sp^2 (graphite) in pure DLC than in DLC films with silicon.

According to the data in Tab. 1, we found a wear rate larger for the DLC sample doped with silicon than for the pure DLC one. This was expected due to the higher content of sp^3 structures found in the pure DLC sample by FTIR analysis. If the silicon is introduced with the aim of lower the residual stress in DLC films, it is clear its consequent wear resistance reduction.

The scratch testing caused little cracking on the first scratch done in all extension of the pure DLC sample; on the second scratch, the cracking began at a normal load of 6,86 N. Both scratches done on the silicon doped DLC sample showed cracks in all its extension. Fig. 3 shows the scratch tests results of samples of pure DLC (a) and silicon doped DLC (b). The double-sided arrows in the pictures delimit the damage showed by the great film lifting at the exiting extremity of the indenter tip. It can be noted that the scratch done in the silicon doped DLC caused a lower damage, probably because the gain of adhesion, in spite of wear resistance loss verified above.

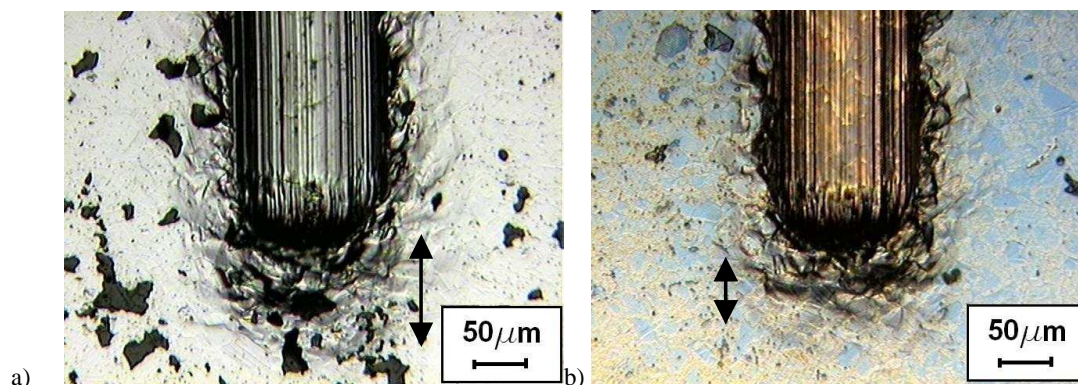


Figure 3. Optical image of scratch damage to samples of a) pure DLC and b) silicon doped DLC

Raman spectroscopy gives important details about bonding structures of DLC films. The C–C diamond bonds show a well-defined Raman active mode around 1332 cm^{-1} , whereas single crystal graphite (C=C vibration mode on the hexagonal chain plane) has a single Raman active mode at 1580 cm^{-1} labeled “G” (for ‘graphite’). At 1350 cm^{-1} appears the disordered graphite second mode (named “D” for ‘disordered’) (Robertson, 2002).

The Raman spectra of DLC films, pure and doped with silicon, are compared in Fig. 4 where it is observable the occurrence of an active mode in 1327 cm^{-1} , a graphite active mode at 1599 cm^{-1} and amorphous silicon modes below 500 cm^{-1} . According to Robertson (2002), the G and D modes dominate the Raman spectra of a-C by scattering of the sp^2 sites. The π states have lower energy than the σ states and so they are much more polarisable, giving to the sp^2 sites 50–230 times larger Raman cross-section than sp^3 sites. The observed modes, on the other hand, show a strong peak on 1327 cm^{-1} , which could be attributed to left shifted ‘disordered’ graphite peak.

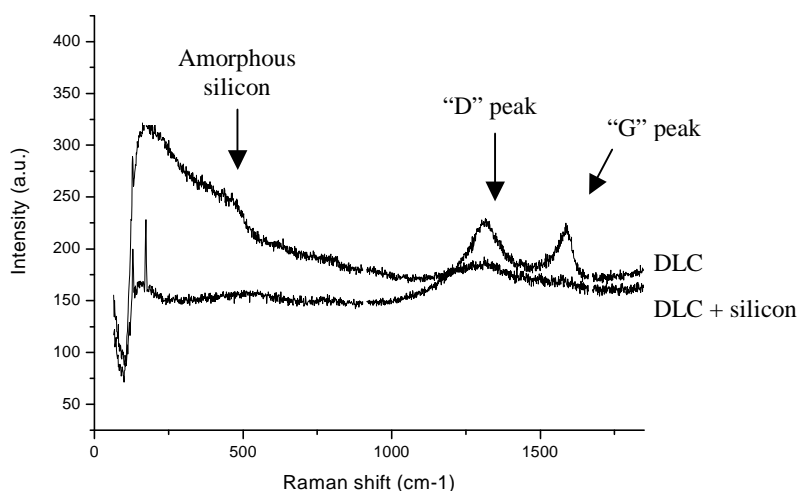


Figure 4. Raman spectra of deposited films at different doping conditions

It is interesting to notice that the Raman spectrum of the film of DLC plus silicon have a small peak that can be attributed to diamond-like carbon (sp^3) structures, this peak is small if compared with the peak for pure DLC, as expected from the IR. The peak due to graphite is practically non-existent in the Raman spectrum of DLC + silicon though, while the IR predicts a larger amount of graphite than in the pure DLC. The difference may indicate a difference in graphite content from one part of the sample to the other, since the regions where IR and Raman were measured were not the same.

4. Conclusions

The DLC films present diamond-like features and it is shown that the incorporation of silicon in the deposited films caused a significant reduction of the sp^3 (diamond) content and a consequent loss of wear resistance. The silicon atoms play the role of reducing the residual stress of thin DLC films, which was confirmed by scratching resistance tests.

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6. References

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7. Responsibility notice

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