INFLUENCE OF THE SILICON INTERLAYER ON DIAMOND-LIKE CARBON FILMS DEPOSITED ON GLASS SUBSTRATES

INFLUÊNCIA DA INTERCAMADA DE SILÍCIO NOS FILMES FINOS DE CARBONO-TIPO DIAMANTE DEPOSITADOS SOBRE SUBSTRATOS DE VIDRO

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ABSTRACT: *Diamond-like carbon (DLC) films as a hard protective coating have achieved great success in a diversity of technological applications. However, adhesion of DLC films to substrates can restrict their applications. The influence of a silicon interlayer in order to improve DLC adhesion on glass substrates was investigated. Amorphous silicon interlayer and DLC films were deposited using plasma enhanced chemical vapor deposition from silane and methane, respectively. The bonding structure, transmittance, refraction index, and adherence of the films were also evaluated regarding the thickness of the silicon interlayer. Raman scattering spectroscopy did not show any substantial difference in DLC structure due to the interlayer thickness of the silicon. Optical measurements showed a sharp decrease of transmittance in the ultra-violet region caused by the fundamental absorption of the light. In addition, the absorption edge of transmittance shifted toward longer wavelength side in the ultra-violet region as the thickness of the silicon interlayer increased. The tribological results showed an increase of DLC adherence as the silicon interlayer increased, which was characterized by less cracks around the grooves.*

Keywords: diamond-like carbon; silicon interlayer; adhesion; optical properties.

RESUMO: *A utilização de filmes finos de carbono-tipo diamante (DLC) como revestimento protetor de alta dureza alcançou grande sucesso em uma diversidade de aplicações tecnológicas. Entretanto, a adesão desse filme pode restringir suas aplicações. A influência de uma intercamada de silício para aumentar a adesão do filme de DLC à substratos de vidro foi investigada. A intercamada de silício e os filmes de DLC foram depositados utilizando a técnica de deposição química da fase vapor assistida por plasma, a partir dos gases silano e metano, respectivamente. A estrutura da ligação, transmitância, índice de refração e aderência dos filmes foram avaliados de acordo com a espessura da intercamada de silício. A espectroscopia de espalhamento Raman não mostrou nenhuma diferença substancial na estrutura do DLC devido às mudanças na espessura da intercamada de silício. Mas medidas ópticas mostram uma diminuição acentuada da transmitância na região ultra-violeta provocada pela absorção fundamental da luz. Além disso, as extremidades de absorção nas medidas de transmitância deslocaram-se para comprimentos de onda maiores, na região de ultra-violeta, com o aumento da espessura da intercamada de silício. Os resultados tribológicos mostram um aumento na aderência do filme de DLC com o aumento da intercamada de silício, caracterizada por menos fendas ao redor das ranhuras.*

Palavras-chave: carbono-tipo diamante; intercamada de silício; adesão; propriedades ópticas.

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1. INTRODUCTION

Diamond-like carbon (DLC) films have been actively studied over the last decade in the field of material engineering. Consisting of dense amorphous carbon or hydrocarbon, DLC mechanical properties fall between those of graphite and diamond (ROBERTSON, 2002; DONNET *et al.*, 1999; DONNET; GRILL, 1997). As a hard protective coating, DLC films achieve great success in a diversity of technological applications such as coatings for magnetic and optical disks, optical devices, bar-code scanners, sunglasses, poly (ethylene terephthalate) bottles and others (ROBERTSON, 2002; DONNET *et al.*, 1999; DONNET; GRILL, 1997; DAMASCENO; CAMARGO JR.; CREMONA, 2002; DAMASCENO; CAMARGO JR., 2008).

However, the adhesion of DLC films to substrate materials can restrict their applications (YATSUZUKA *et al.*, 2008). Funada *et al.* (2000) studied the adhesion strength of DLC films on glass with mixing layer prepared by ion beam assisted deposition. Damasceno and Camargo Jr. (2008) produced DLC-Si films as a protective coating for polycarbonate substrates with high adherence. Other authors have been studied the use of a silicon interlayer in order to improve DLC adhesion on metallic substrates (BONETTI *et al.*, 2006; CAPOTE *et al.*, 2008). In this paper, it was investigated the influence of silicon interlayer on DLC films deposited on glass substrates.

2. EXPERIMENTAL PROCEDURES

The amorphous silicon interlayer and DLC films were deposited using plasma enhanced chemical vapor deposition (PECVD) from silane and methane on glass microscope slides. The glass substrates were cleaned ultrasonically in an acetone bath for 15 min, and then dried in nitrogen atmosphere. The clean samples were mounted on a water-cooled, 4.8 cm diameter cathode into the plasma chamber. The cathode was fed by a pulsed DC power supply, with variable pulse voltage from 0 to -1000 V.

Into the chamber (vacuum base pressure of 1.3 mPa) the substrates were additionally sputter cleaned by argon discharge with 1 sccm gas flow at 11.3 Pa working pressure and a discharge voltage of -700 V for 20 min prior to deposition. In order to enhance the DLC film adhesion to the substrates (BONETTI *et al.*, 2006; CAPOTE *et al.*, 2008), a thin amorphous silicon interlayer was deposited using silane as the precursor gas (1 sccm gas flow at 11.3 Pa and a discharge voltage of -700 V). The silicon interlayer thickness was varied according to the deposition time.

The DLC films were deposited at room temperature under controlled conditions (1 sccm gas flow at 11.3 Pa and a discharge voltage of -700 V) to obtain maximum hardness, minimum stress, and a maximum deposition rate (MARCIANO *et al.*, 2008; MARCIANO *et al.*, 2009).

During the deposition process, part of the samples was covered with a mechanical mask to produce a step between the deposited and non-deposited regions. This step was measured by the prophilometer (Tencor, Alpha Step 500), and the deposition rates were determined.

The atomic arrangement of the films was analyzed by Raman scattering spectroscopy using a Renishaw 2000 system with an Ar^+-ion laser (λ = 514 nm) in backscattering geometry. The laser power on

the sample was ~0.6 mW and the laser spot had 2.5 µm diameter. The Raman shift was calibrated in relation to the diamond peak at 1332 cm^{-1}. All measurements were carried out in air at room temperature. The slopes of the photoluminescence background (PLB) in visible Raman spectra were used to estimate the hydrogen content in the DLC films (CASIRAGHI; FERRARI; ROBERTSON, 2005).

The optical properties of the samples were evaluated with the UV-Vis-NIR scanning spectrophotometer U-3501 Hitachi. The refractive index (n) of the films was determined from transmittance values corresponding to first-order transmission minima positions.

According to Sreemany and Sen (2004), consider a transparent homogeneous film of uniform thickness, d, and refractive index, n, is bounded on either side by two semi-infinite non-absorbing layers of refractive indices n_0 and n_2.

Then, at normal incidence, transmittance (T) and reflectance (R) of the film (for a parallel beam of light of unit amplitude and of wavelength (λ) are given by Heavens (1955):

$$T = \frac{n_2}{n_0}\left[\frac{t_1^2 t_2^2}{1 + 2r_1 r_2 \cos 2\delta_1 + r_1^2 r_2^2}\right] \qquad (1)$$

$$R = \left(\frac{r_1^2 + 2r_1 r_2 \cos 2\delta_1 + r_2^2}{1 + 2r_1 r_2 \cos 2\delta_1 + r_1^2 r_2^2}\right) \qquad (2)$$

where

$$\delta_1 = \left(nd\frac{2\pi}{\lambda}\right) \qquad (3)$$

and t_1, t_2, r_1 and r_2 are the Fresnel coefficients given by

$$t_1 = \left(\frac{2n_0}{n_0 + n}\right) \qquad (4a)$$

$$t_2 = \left(\frac{2n}{n + n_2}\right) \qquad (4b)$$

$$r_1 = \left(\frac{n_0 - n}{n_0 + n}\right) \qquad (4c)$$

$$r_2 = \left(\frac{n - n_2}{n + n_2}\right) \qquad (4d)$$

When $n_0 < n > n_2$ or $n_0 > n < n_2$ (e.g., DLC film on glass substrate; $n_0 = 1$ (air), $n \sim 2$ (film), $n_2 = 1.515$ (glass)). At normal incidence, minima (T_{min} and R_{min}) and maxima (T_{max} and R_{max}) of the transmittance and reflectance curves occur at

For T_{min}: $\quad nd = \left[\frac{1}{4}(2m+1)\lambda\right] \qquad (5a)$

For T_{max}: $\quad nd = \left[\frac{1}{4}(2m+2)\lambda\right] \qquad (5b)$

For R_{min}: $\quad nd = \left[\frac{1}{4}(2m+2)\lambda\right] \qquad (5c)$

For R_{max}: $\quad nd = \left[\frac{1}{4}(2m+1)\lambda\right] \qquad (5d)$

where m (= 0, 1, 2, 3, . . .) is the order of the minima and maxima.

At normal incidence, values of T_{min} and T_{max} are obtained from Eq. (1) as

$$T_{min} = \left[\frac{4n_0 n^2 n_2}{(n_0 n_2 + n^2)^2}\right] \qquad (6a)$$

$$T_{max} = \left[\frac{4n_0 n_2}{(n_0 + n_2)^2}\right] \qquad (6b)$$

Eqs. (6a) and (6b) show that at normal incidence, transmittance values at minima

positions (T_{min}) are dependent on film refractive index, whereas transmittance values at maxima positions (T_{max}) are not.

Therefore, refractive index, $n(\lambda)$, of the film corresponding to the wavelength λ at transmittance minima position could be determined from measured absolute T_{min} value provided n_0 and n_2 are known.

There is still no recognized method for evaluating high adhesion strengths, although some indirect methods have been developed (OLLENDORF; SCHNEIDER, 1999). In this study, the micro-scratch test was conducted on test samples using a conical tip 200 μm radius diamond stylus (Rockwell C 120°) to evaluate the adherence between the film and the substrate (BURNETT; RICKERBY, 1997). According to standard methodology, the load at which the coating was stripped from the substrate was deemed the critical load, which can also be detected by an acoustic detector to visualize the nucleation and propagation of cracks. If the coating peeled off the substrate surface while the stylus tip passed over it, the adherence was considered weak. On the other hand, if the coating only cracked in a roughly semicircular arc along the scratch without peeling off, the adherence was considered good. The normal force was increased up to 40 N. This test had already been used by a number of groups to study hard, thin, well-adhering coatings (MARCIANO *et al.*, 2008; BURNETT; RICKERBY, 1997; BLEES *et al.*, 2000).

3. RESULTS AND DISCUSSION

The deposition rate of DLC films on glass substrates was approximately 5 nm/min (almost a third part of DLC deposition rate on metallic surfaces (BONETTI *et al.*, 2006; CAPOTE *et al.*, 2008)). This behavior was expected since metals are generally very good electrical conductors, better than glass.

Raman scattering spectroscopy was used to evaluate the chemical structure of the DLC films. Typical DLC spectra, as show in Fig. 1, exhibit two distribution bands in the 1000-1800 cm^{-1} range. These two bands are defined as the graphite (*G*) and disorder (*D*) bands that originate from sp^2 sites, because the 514 nm (2.4 eV) excitation resonates with $\pi \to \pi^*$ transitions at sp^2 sites, so that the disorder band will overshadow the contribution of sp^3 sites (ROBERTSON, 2002). The spectra of all the samples were deconvoluted into *D* and *G* bands, respectively using two Gaussian curves (CASIRAGHI; FERRARI; ROBERTSON, 2005). Table 1 summarizes the main characteristics of the Raman spectra of DLC films according to the silicon interlayer thickness. The main factor affecting band position, width and intensity is the clustering of sp^2 phase (CASIRAGHI *et al.*, 2005). The full width at half maximum of the *G* band, FWHM (*G*) and *G* band position both measure disorder, however, FWHM (*G*) is mainly sensitive to structural disorder, while *G* position is mainly sensitive to topological disorder (CASIRAGHI; FERRARI; ROBERTSON, 2005). From our results, Raman spectra could not provide any substantial difference in DLC structure due to the increase of silicon interlayer thickness.
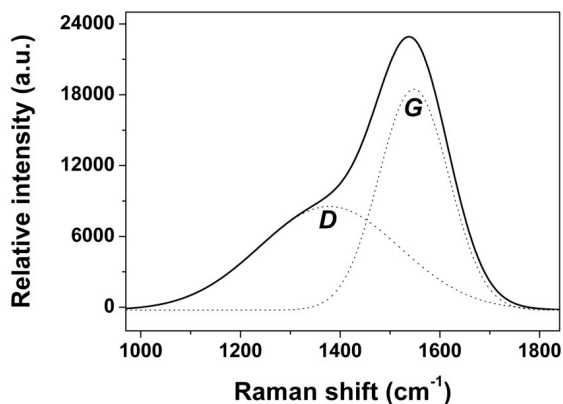
Fig. 1 - Typical Raman scattering spectrum from DLC film with a 5 nm thickness silicon interlayer.

Table 1 - Gaussian fitting results of Raman spectra from DLC films according to the silicon interlayer thickness

Silicon interlayer	*D* Band Position	*G* Band Position	FWHM (*G*)	I_D/I_G	[H] (%)
5	1359.5	1545.4	164.8	1.19	29.4
10	1370.4	1544.9	170.1	0.91	25.7
25	1367.8	1544.1	171.0	0.73	26.3
50	1376.6	1547.5	165.1	0.94	25.3

Study on optical properties of a thin film is fundamentally based on reflectance (*R*) and transmittance (*T*) data. Fig. 2 shows the transmittance spectra of DLC films according to the silicon interlayer thickness (constant DLC thickness), where it is possible to see some transmittance maxima and minima of different orders (*m* = 1, 2,…). As the silicon interlayer thickness increases, location of a particular transmittance extrema (T_{min} or T_{max}) shifts towards longer wavelength side. The films also show a sharp decrease of transmittance in the ultra-violet region (Fig. 2b) and this is caused by the fundamental absorption of the light. It is also noticed that the absorption edge of transmittance shifts towards longer wavelength side in the ultra-violet region as the silicon interlayer thickness increases.
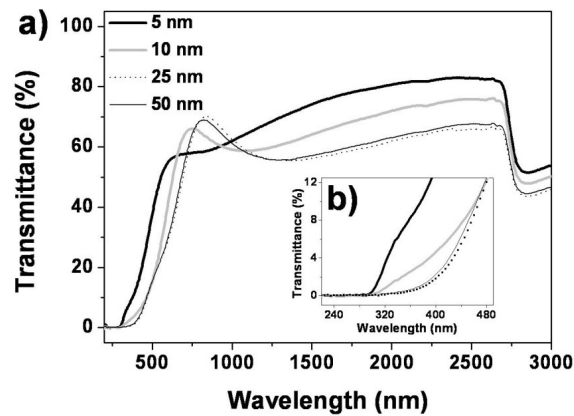
Fig. 2 - Transmittance spectra of DLC films according to the silicon interlayer thickness.

Fig. 3 shows the transmittance spectra of DLC films in two different thickness and different silicon interlayer thickness. The DLC films had good transparency in the visible region; however, the transparency was degraded in the UV region. In the visible region, the whole transmittance decreased as the film thickness increased; the number of sp^2 bonds in the films also increased. The change in bonding structure increased the density of π electrons, and thus, absorbance of the DLC films in the visible range increased (GUO, 2008).
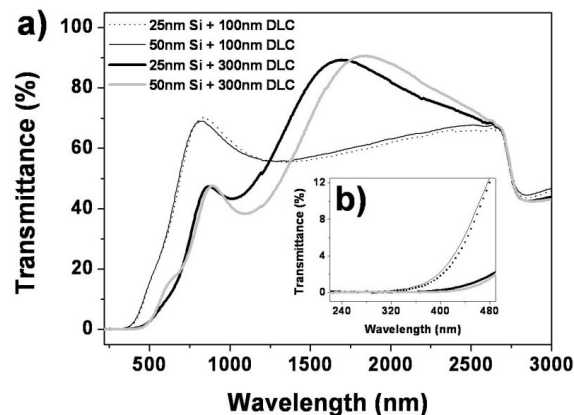

Fig. 3 - Transmittance spectra of DLC films in two different thickness and different silicon interlayer thickness.

Estimated values of n from first-order transmission minima of DLC films according to the silicon interlayer and DLC thickness are given in Table 2. For this, measured value of transmittance (T) corresponding to first-order (m = 1) minima was used. Considering n_0 = 1 and n_2 = 1.515, film refractive index (DLC + silicon interlayer), n, was determined from equation 6a. From Table 2 data, it is possible to see that the main factor affecting the increase in refractive index is the increase of DLC thickness.

A typical experimental result relating to the scratching on DLC film deposited on glass substrate is shown in Fig. 4. Curve 4a shows the derivative of the tangential force and the applied normal load during the scratching, and curve 4b corresponds to the acoustic emission and the applied normal load during scratching.

Table 2 - Estimated values of refractive index according to the silicon interlayer and DLC thickness

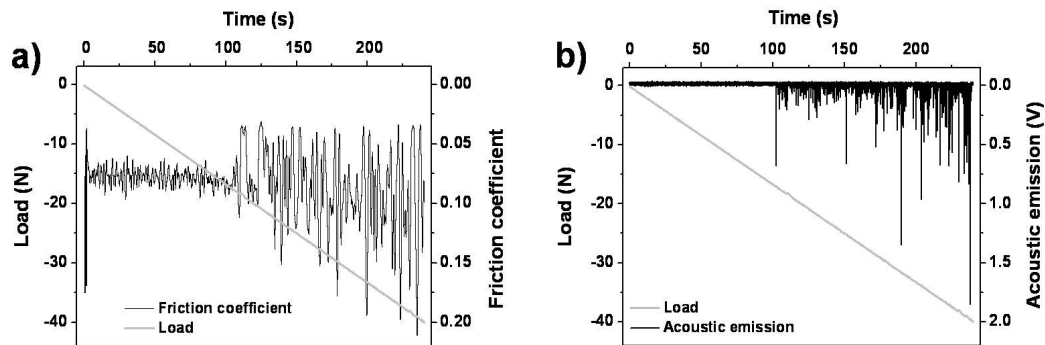| Silicon interlayer	DLC thickness	Total film	Refractive index, *n*
5	100	105	2.7
5	300	305	3.3
10	100	110	2.7
10	300	310	2.8
25	100	125	2.7
25	300	325	3.3
50	100	150	2.7
50	300	350	3.5

Fig. 4 - Typical scratch test using an indenter Rockwell C 120° on DLC films deposited on glass substrate with a silicon interlayer. (a) Derivative of the tangential force and applied normal load versus time. (b) Acoustic emission intensity and applied normal load versus time.

The rupture or flaking of the film (on the surface) leads to a discrete acoustic emission with high amplitude produced by brutal release of elastic energy stored (ZAIDI *et al.*, 2006). This process is followed recording of the associated acoustic emission, which allows determination of the points corresponding to failure (ZAIDI *et al.*, 2006). Fig. 4b shows the abrupt increase of acoustic emission signal, which suggests the beginning of the film deterioration.

At the critical load, the indenter vertical depth abruptly increases and the coefficient of friction suddenly changes (HUANG; XU; LU, 2002). Fig. 5 shows the critical load evolution and friction coefficient at the critical load for DLC films according to the silicon interlayer thickness (constant DLC thickness). The critical load of crack initiation was calculated for an average of 3 tests. Similar that in the case of metallic substrates (CAPOTE *et al.*, 2008), until a thickness of

10 nm, silicon interlayer thickness could not increase the coating adhesion. On the other hand, the friction coefficient slightly increases with the increase of silicon interlayer thickness. This increase can be a result of the increase of peeled material during the tests due to the increase of silicon interlayer thickness.
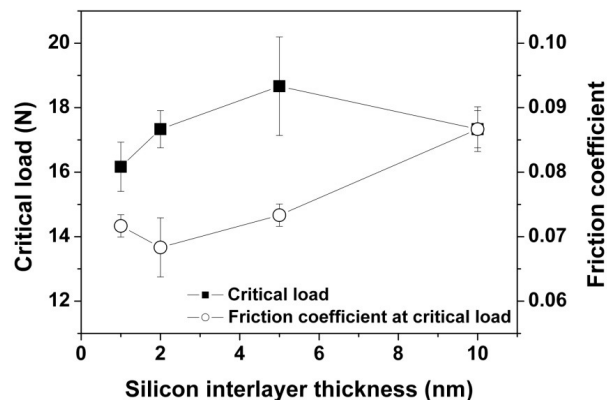

Fig. 5 - Average critical load and its corresponding friction coefficient for DLC films according to the silicon interlayer thickness. Each value was calculated for an average of 3 tests.

Optical observations reveal the real appearance of the samples after the scratching tests. In the initiation of the process, a small area of the film began to be detached in front of the indenter and optical observations of the DLC films according to the silicon interlayer thickness in the ending of scratch (40 N of load). As expanded by the traveling of the indenter. Finally, cracks were generated around the detachment area, and the area was removed from the substrate. Fig. 6 shows

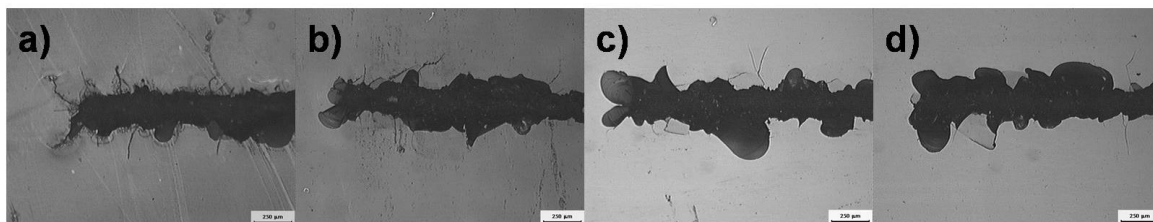the silicon interlayer increases, less cracks appeared around the groove.

Fig. 6 - Optical observations of the DLC films in the ending of scratch (40 N of load) according to the silicon interlayer thickness: a) 5 nm, b) 10 nm, c) 25 nm and d) 50 nm.

4. CONCLUSION

The use of DLC films on glass substrates, as a hard protective coating, is very important in a diversity of technological applications. Its use is highly dependent on the adherence to the substrate and its optical properties.

In the current paper, it was investigated the use of a thin amorphous silicon interlayer in order to increase the deposition of DLC

films on glass substrates. Raman scattering spectroscopy does not show any substantial difference in DLC structure due to the silicon interlayer thickness. Optical measurements show a sharp decrease of transmittance in the ultra-violet region caused by the fundamental absorption of the light. In addition, the absorption edge of transmittance shifts toward longer wavelength side in the ultra-violet region as the silicon interlayer thickness increased. The tribological results show an increase of DLC adherence as the silicon interlayer increases, which is characterized by less cracks around the grooves.

5. ACKNOWLEDGEMENTS

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