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Effect of hexane precursor diluted with argon on the adherent diamond-like properties of carbon films on steel surfaces

G. Capote [a,*], G.F. Silva [b], V.J. Trava-Airoldi [b]

[a] Universidad Nacional de Colombia, Facultad de Ciencias, Departamento de Física, Carrera 45, N. 26–85 - Edificio Uriel Gutiérrez, Bogotá D.C., Colombia
[b] Instituto Nacional de Pesquisas Espaciais (INPE), Laboratório Associado de Sensores e Materiais (LAS), Av. dos Astronautas, 1758 - São José dos Campos, 12227–010 SP, Brazil

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ABSTRACT

Various precursors of diamond-like carbon (DLC) growth have been studied in order to find the best set of mechanical and tribological proprieties. Gaseous hexane (C_6H_{14}) stands out as an option because of its high vapor pressure and the fact that it accepts dilution with other hydrocarbons or even nanoparticles, forming convenient colloidal substances. Therefore, in the present paper, hexane will be studied using argon as an inert additional gas, in order to determine the mechanical and tribological properties and microstructure of DLC films deposited via a modified and asymmetrical bipolar pulsed-DC plasma enhanced chemical vapor deposition system. The addition of argon to the hexane precursor atmosphere is expected to increase the ratio of ion to neutral radicals on the surface of the growing film without changing the H/C ratio of the gas mixture. The film's microstructure and the hydrogen contents were probed by means of Raman spectroscopy. The internal stress was determined through measurement of the change in the substrate curvature by means of a profilometer, while nanoindentation experiments showed the hardness of the film. The adhesion of the films was evaluated via the scratch test. In order to overcome the low adhesion of these films on AISI 304 stainless steel surfaces, a silicon interlayer, obtained by using low-energy ion implantation and silane as a precursor gas, was used. The results show that the precursor hexane atmosphere diluted with argon induces modifications in the properties of the films when a high quantity of argon is used. The importance of the effect of ion bombardment during film growth on the properties of the films was confirmed.

1. Introduction

Development of nanostructured materials with improved, tailor-designed properties is a fundamental need for the growth and advancement of many important industries. Plasma synthesis of coatings is a powerful and versatile way to obtain such materials. Among them, the family of diamond-like carbon (DLC) coatings stands out due to its properties: high elastic modulus and hardness, chemical inertness, low friction and high wear resistance, high thermal conductivity, biocompatibility, and the possibility of tuning these properties through specific settings of the plasma conditions and the deposition technique [1]. Amorphous hydrogenated carbon films (a-C:H) are usually obtained via plasma decomposition of a hydrocarbon-containing precursor atmosphere.

In DLC films deposited via hydrocarbon plasma decomposition, the structure is composed of sp^2 hybridized clusters interconnected by sp^3 hybridized carbon atoms. It is accepted theory that surface chemisorption of carbon carrying neutral radicals is the main channel for film growth [2]. The addition of noble gases to the hydrocarbon precursor atmosphere is expected to increase the ratio of ion to neutral radicals on the surface of the growing film without changing the H/C ratio of the gas mixture. This is in fact a powerful way to investigate the effect of ion bombardment on the structural arrangement and properties of DLC films. Hexane (C_6H_{14}) has been studied in order to obtain a high deposition rate and also for use as a nanoparticle colloid bed [3–6].

A comparison between the effects of atmospheres of methane (CH_4) diluted with various noble gases has been carried out [7,8]. This research investigated the structural, mechanical, and optical properties of the films. The effects of dilution with argon (Ar), up to 98%, have also been investigated [9–11]. Nevertheless, in spite of intense experimental and theoretical research, it is not yet fully understood which mechanisms and plasma species are responsible for the film deposition process [2,12].

The influence of radio frequency plasma enhanced chemical vapor deposition (PECVD) parameters on DLC films was investigated by Caschera et al. [13]. Thin DLC films were deposited in a CH_4/H_2 plasma using Ar as a gas carrier, with various ratios of gas flow as a variable parameter. The effect of cathodic ion bombardment also was investigated. The obtained results allowed determining the chemical composition of the films, as well as the sp^2/sp^3 ratio of the carbon bonds and their dependence on the hydrogen flow. These studies demonstrated that

* Corresponding author. Tel.: +57 1 316 5000; fax: +57 1 316 5165.
E-mail address: gcapoter@unal.edu.co (G. Capote).

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the optimal conditions for DLC deposition at room temperature were an anodic configuration with CH_4 and H_2 flow rates of approximately 2 sccm.

Despite the many advantages of the DLC coatings, the major disadvantage of hard film deposition is that there is often a relatively low adhesion on steel substrates, caused by very high total compressive stress on these coatings [14–17]. In order to overcome the high residual stress and low adherence of DLC films, a thin amorphous silicon interlayer has been deposited as an interface, using PECVD techniques and silane (SiH_4) as precursor gases [6,18–23].

In the present paper, in order to improve the DLC films' adhesion to AISI 304 stainless steel substrates, a thin amorphous silicon interlayer was used. Interlayer and DLC films were grown employing a modified asymmetrical bipolar pulsed-DC PECVD system, using a mixture of silane and argon gas as precursor and gaseous hexane and argon gas mixtures, respectively. Hexane was used in order to obtain a high deposition rate and also by the fact that it accepts dilution with other hydrocarbons or even nanoparticles. The films were analyzed according to their microstructural, mechanical, and tribological properties as a function of the amount of argon diluted in the hexane. The result showed that the atmosphere of argon diluted in hexane induced modifications in the properties of the DLC films when a high quantity of argon was used.

2. Experimental procedures

DLC films and silicon interlayers were deposited using a modified pulsed-DC PECVD system, employing an asymmetrical bipolar pulsed-DC power supply [6,23]. The voltage waveform consisted of a fixed positive pulse amplitude of 40 V, followed by a variable negative pulse between −500 and −1000 V. A pulse frequency of 25 kHz was used, resulting in duty cycles of 50%. Interlayers were grown using 50–50% mass flow rate of silane (SiH_4) and argon gas mixture as precursor, while DLC films were deposited employing gaseous hexane and different concentrations of argon gas mixtures, respectively.

The polished AISI 304 stainless steel (C ≤0.08%; Cr = 18–20%; Ni = 8–10.5%; Mn ≤2%; Si ≤1%; P ≤0.045%; S ≤0.03%; Fe-balanced) were used as substrates (dimensions 1.5 × 1.5 cm^2).

The measured hardness value for AISI 304 stainless steel was about 3.5 GPa. The substrates were ultrasonically cleaned in an acetone bath for 10 min, followed by an acid dip to remove the native oxide layer before being loaded into the vacuum chamber. The substrates were fixed on the cathode electrode powered by a DC power supply, while the chamber wall was grounded. Before deposition, steel substrates were cleaned with argon ions for 30 min.

An amorphous silicon interlayer was obtained using a silane–argon plasma at a pressure of 6.7 Pa, at room temperature (300 K), and applying a bias voltage of −800 V. The interlayer thickness was about 300 nm. DLC films were deposited with a total gas pressure of 9.3 Pa up to a thickness of approximately 2 μm. The applied self-bias voltage was kept constant at −800 V. The films were deposited using Ar/(Ar + C_6H_{14}) flow ratios from 0 to 65%, using a constant gaseous hexane input flow of 10 sccm, and varying the Ar gas flow in the range of 0.5 to 20 sccm. Deposition temperatures were controlled through a thermocouple, and they were never higher than 360 K. In a previous work [6], the DLC films deposited using the same technique and hexane as precursor gas were analyzed according to their microstructure, mechanical, and tribological properties as a function of applied self-bias voltage for film deposition.

The film's atomic arrangements were analyzed via 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 approximately 0.6 mW, and the laser spot was 2.5 μm in 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 in the visible Raman spectra were used to estimate the hydrogen content in the DLC films, not detailed in this paper, following the methodology described by Casiraghi et al. [24]. The determination of the hydrogen through Raman spectroscopy was verified via the elastic recoil detection analysis (ERDA) method, explained in a previous paper [22].

Total compressive stress was determined by measuring the substrate curvature before and after the DLC film deposition with a stylus profilometer and by analyzing the results with the well-known Stoney's equation [25]. Nanohardness was measured with the instrumented hardness test, which was carried out using Hysitron TI 750™ equipment with a Vickers indenter. The maximum load applied was 10 mN, and at least 10 valid measurements were made for each sample. The depth achieved was less than 10% of total film thickness in order to avoid influence of the substrate during the measurements. The load–unload cycles and hardness values were performed according to the Oliver–Pharr method [26]. The films' surface roughness was analyzed through confocal laser scanning microscopy. An LSM 700 microscope was used, operating with a stable solid-state laser with a wavelength of 405 nm. The surface area analyzed was 120 × 120 μm.

The friction coefficients and wear rates were determined using a CETR UMT-2M-110 pin-on-disk tribometer in rotative mode, under ambient conditions (20 °C, 40% RH). A hard 420b stainless steel ball with a radius of 6 mm and AISI 304 stainless steel substrates coated with a minimum 2 μm-thick DLC film was used as a friction pair. The measurements were carried out using a sliding speed of 10 mm/s, while keeping the applied load constant at 4 N for 1000 cycles. The wear rate was determined following the Archard wear law [27], where the volume of the crater in the coating was divided by the applied load and the track length of the sliding steel ball. Under these experimental measurement conditions, the temperature at the films' surface was below 330 K, and no thermal degradation of the DLC films occurred.

The adherence of the DLC films to steel substrates was measured via a conventional scratch test. Critical loads, Lc1, were determined using classical scratch test with a diamond tip, in which the applied load varied from 1 to 20 N, with a sliding speed of 0.1 mm/s. The critical load value was determined by the load at which the coating was stripped from the substrate.

3. Results and discussion

3.1. Structure of the films

The deposition rate as a function of the amount of argon in the hexane atmosphere (Ar/(Ar + C_6H_{14})) is shown in Fig. 1. High deposition rates were obtained for all films (between 3 and 4.5 μm/h). The use of hexane as a hydrocarbon precursor gas, as well as the high value of applied negative self-bias voltage (−800 V), considerably increased the deposition rates in comparison with the previous papers, when methane and lower values of the self-bias voltages were employed [21,22]. In Fig. 1 it was observed that the deposition rate of DLC films firstly increased with the amount of argon in the hexane atmosphere. It reached a maximum at about 30% of Ar/(Ar + C_6H_{14}) ratio, and then it drops as Ar percentage continued increasing. This behavior may be explained because with the hexane–argon mixture the ion assisted radical reaction increased. For lower densities of argon the sputtering effect may be offset to aid in growth rate due to the expected increase in the density of electrons in the discharge. The density of the plasma becomes more intense. The deposition rates measured for films deposited with highly diluted hexane atmospheres (55 and 65%) are lower than those obtained for films deposited in less diluted atmospheres (about 30%). This behavior may be due to a more energetic ion bombardment, leading to a higher quantity of argon ions, and consequently a preferential surface sputtering. For that reason, in these films the surface roughness also increased (see Fig. 5). The interaction of the impinging argon ions with the atoms at the growing surface can produce an elastic recoil process, and it can cause sputtering