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Amorphous carbon nitrogenated films prepared by plasma immersion ion implantation and deposition

Elidiane C. Rangel [a,*], Steven F. Durrant [a], Rita C.C. Rangel [b], Milton E. Kayama [b], Richard Landers [c], Nilson C. da Cruz [a]

[a] *Laboratório de Plasmas Tecnológicos, UNESP, Unidade Diferenciada Sorocaba/Iperó, Av. Três de Março, 511 Alto da Boa Vista, 18087-180 Sorocaba, SP, Brazil*
[b] *Laboratório de Plasmas, Departamento de Física e Química, UNESP, Av. Dr. Ariberto Pereira da Cunha, 333, 12410 516 Guaratinguetá, SP, Brazil*
[c] *Grupo de Física de Superfícies, Departamento de Física Aplicada, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, 13083-970 Campinas, SP, Brazil*

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Abstract

In this work, an investigation was conducted on amorphous hydrogenated–nitrogenated carbon films prepared by plasma immersion ion implantation and deposition. Glow discharge was excited by radiofrequency power (13.56 MHz, 40 W) whereas the substrate-holder was biased with 25 kV negative pulses. The films were deposited from benzene, nitrogen and argon mixtures. The proportion of nitrogen in the chamber feed (R_N) was varied against that of argon, while keeping the total pressure constant (1.3 Pa). From infrared reflectance-absorbance spectroscopy it was observed that the molecular structure of the benzene is not preserved in the film. Nitrogen was incorporated from the plasma while oxygen arose as a contaminant. X-ray photoelectron spectroscopy revealed that N/C and O/C atomic ratios change slightly with R_N. Water wettability decreased as the proportion of N in the gas phase increased while surface roughness underwent just small changes. Nanoindentation measurements showed that film deposition by means of ion bombardment was beneficial to the mechanical properties of the film–substrate interface. The intensity of the modifications correlates well with the degree of ion bombardment.

Keywords: Plasma immersion ion implantation and deposition; Mechanical properties; Wettability; Roughness

1. Introduction

Recent scientific and technological developments have generated great demand for the production of nano-scale materials and devices. An example is the requirement for ultra-thin protective coatings on the computer hard drives. In such devices, the shorter the distance between the writing head and the disk, the greater the density of information that can be stored. Thus, protective layers with reduced dimensions are of great technological importance. In addition to the physical dimensions, properties such as hardness, scratch- and wear-resistance should be appropriate to the application.

A very promising way of obtaining films of specified thickness and physical properties is via plasma immersion ion implantation and deposition (*PIIID*) [1]. This technique enables deposition of films under ion bombardment. Substrates are immersed in plasmas containing organic or metallic compounds while biased with negative high voltage pulses [2]. Low energy species are deposited onto all the surfaces exposed to the plasma. During the on-time of the pulses, however, ions are attracted and implanted into the sample. The alternation of film deposition and ion bombardment permits *in situ* modification of the growing layer [3]. The degree of modification is determined by the process parameters which include plasma (composition, density and energy) and pulse (magnitude, frequency and duty cycle) characteristics.

PIIID has been successfully employed to improve the mechanical and tribological surface properties of steels, through carbon implantation [4,5], for the deposition of metallic, amorphous and diamond-like carbon films [6–8], and for the formation of silicon carbide by silicon immersion

* Corresponding author.
E-mail address: elidiane@sorocaba.unesp.br (E.C. Rangel).

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in methane plasmas [9,10]. In the present paper, we concentrate on the fabrication of ultra thin films by *PIIID* using benzene–nitrogen–argon mixtures. The production of amorphous nitrogenated–hydrogenated carbon films with improved mechanical properties was the main goal of this work. Mechanical resistance is directly related to durability and then needed even in applications where hardness itself is not important (as in optical, biological and electronic devices).

2. Experimental details

Films investigated in this work were deposited in the apparatus depicted in Fig. 1. The complete description of the system can be found elsewhere [11]. Briefly, it is composed by a stainless steel reactor, a vacuum system and a radiofrequency power supply. Prior each deposition, the reactor is evacuated from atmospheric down to 10^{-1} Pa by a rotary pump and afterwards to 10^{-3} Pa using a turbo molecular pump connected to a second rotary pump. Gases and organic compounds are injected in the reactor passing through needle valves and the plasma is generated by the application of radiofrequency (rf) power (13.56 MHz, 0 to 300 W) to a stainless steel electrode within the reactor. An impedance matching circuit maximizes the power delivered to the glow. The chamber walls are grounded and the sample holder (lowermost electrode) is biased with negative pulses (saw-like tooth signals) with frequencies in the range 2 to 125 Hz.

In this work microscope glass plates and stainless steel pieces of about 1×2 cm^2 were used as substrates. They were cleaned through ultrasonic baths of 20 min using first a commercial detergent for organic removal, water and finally isopropyl alcohol. The substrates were then dried in a muffle furnace at 70 °C for 30 min.

Cleaned substrates were placed in the holder and radio-frequency (13.56 MHz, 40 W) glow discharges were excited from argon–nitrogen–benzene mixtures. To enable film deposition upon ion bombardment, 25 kV–60 Hz negative pulses were supplied to the samples simultaneously to the plasma ignition. The partial pressure of benzene was maintained at 0.26 Pa for all the experiments. The proportion of nitrogen in the gas feed was increased from 0% to 80%, whereas that of argon was correspondingly decreased, maintaining the total pressure at 1.3 Pa. After each deposition (of 30 min), the chamber was purged with nitrogen.

X-ray photoelectron spectroscopy (*XPS*) was employed to analyze the chemical composition of the films prepared onto stainless steel plates. The spectra were collected using a VSW HA100 spectrometer using the procedures previously given in the literature [12]. The molecular structure of the films was investigated by InfraRed Reflectance-Absorbance Spectroscopy (*IRRAS*), in a Bomen MB-101 spectrometer. Aluminum coated glass plates were used as substrates in this case. In the samples prepared for thickness measurements, a glass mask was used to prevent film deposition in part of the glass substrate, generating a step between protected and exposed areas. Average film thickness was evaluated from at least three measurements of the step height, performed in different points of the sample. A Tencor Alfa-Step 200 instrument was employed for that.

Film wettability was evaluated by contact angle measurements, using the sessile drop technique. In such approach, a liquid drop is deposited onto the sample surface and the angle (θ) at the intercept of the tangent plane to the drop and surface, is determined. As the contact angle depends on the interaction of species from the droplet and the solid, it gives insights into surface wettability. A Ramé-Hart 100-00 automated goniometer was employed for the measurements using deionized water droplets of 0.2 μl. Measurements were performed in three

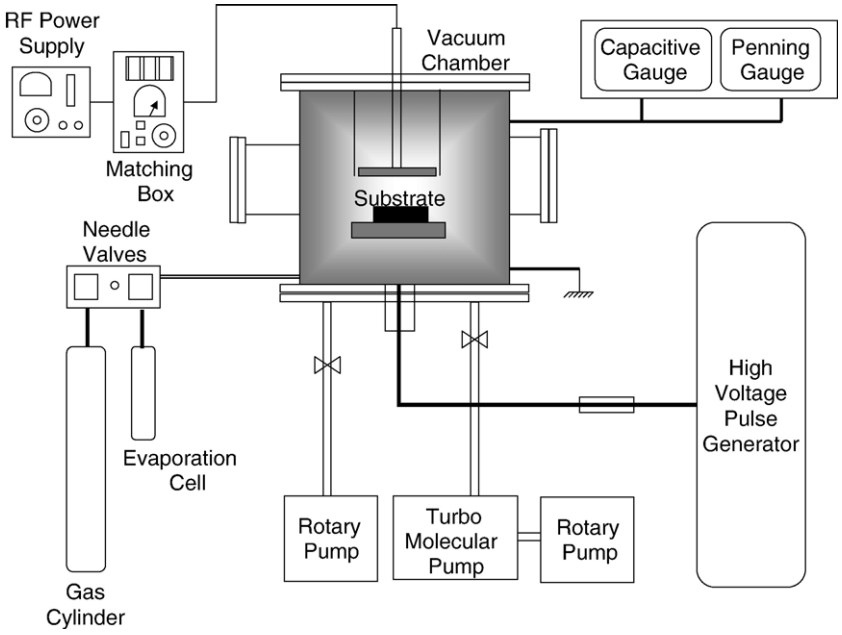

Fig. 1. Experimental apparatus employed for film deposition by *PIIID* and conventional *PECVD* processes.