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Carbon nitride films by RF plasma assisted PLD: Spectroscopic and electronic analysis

E. Cappelli[a,*], S. Orlando[b], D.M. Trucchi[a], A. Bellucci[a], V. Valentini[a], A. Mezzi[c], S. Kaciulis[c]

[a] CNR-ISC, Montelibretti, via Salaria Km 29.3, P.O.B. 10, 00016 Rome, Italy
[b] CNR-IMIP sez. Potenza, 85050 Tito Scalo, Potenza, Italy
[c] CNR-ISMN, Montelibretti, via Salaria Km 29.3, P.O.B. 10, 00016 Rome, Italy

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ABSTRACT

Carbon nitride (CN*x*) thin films have been grown on Si ⟨1 0 0⟩ by 193 nm ArF ns pulsed laser ablation of a pure graphite target in a low pressure atmosphere of a RF generated N_2 plasma and compared with samples grown by PLD in pure nitrogen atmosphere. Composition, structure and bonding of the deposited materials have been evaluated by X-ray photoelectron spectroscopy (XPS), and Raman scattering. Significant chemical and micro-structural changes have been registered, associated to different nitrogen incorporation in the two types of films analyzed. The intensity of the reactive activated species is, indeed, increased by the presence of the bias confined RF plasma, as compared to the bare nitrogen atmosphere, thus resulting in a different nitrogen uptake in the growing films. The process has been also investigated by some preliminary optical emission studies of the carbon plume expanding in the nitrogen atmosphere. Optical emission spectroscopy reveals the presence of many excited species like C^+ ions, C atoms, C_2, N_2; and CN radicals, and N_2^+ molecular ions, whose relative intensity appears to be increased in the presence of the RF plasma. The films were also characterised for electrical properties by the "four-probe-test method" determining sheet resistivity and correlating surface conductivity with chemical composition.

1. Introduction

Many research works have been published on deposition and characterisation of a new form of amorphous carbon, containing different amounts of nitrogen, defined as carbon nitride (*a*-CN*x*). Most of these films have been produced by reactive pulsed laser depositon (PLD), on a suitable substrate, made by a nanosecond, ultraviolet (UV) laser irradiation of a polycrystalline graphite target in a low-pressure nitrogen gas atmosphere [1–3].

The resulting film seem to offer some benefits compared with pure carbon films, like increased resilience to mechanical wear [4] and reduced surface roughness [5] because of its excellent physical properties, such as high hardness, low coefficient of friction and high thermal conductivity. The deposited CN*x* films have been subjected to many different analysis techniques, in an attempt to understand the film properties and correlate them with the characteristics and composition of the activated species in the ablation plume, from which the films are formed, e.g., the densities, velocity, and energy distribution [6–12].

Many authors found that more nitrogen could be incorporated in the films with a proper negative DC bias voltage, the negative voltage playing a predominant role in the nitrogen incorporation, formation of tetrahedral CN bonds and suppression of a graphite-like CN state [13–20].

In the present work, we introduced a DC (direct current) biased and ring confined plasma configuration, radio frequency (RF) generated, and investigated, by optical emission spectroscopy, its effect on activated molecular species and ions, generated by the carbon plume expanding in a nitrogen plasma. We tried to identify any possible change in structure or relevant effects on macroscopic properties of the films, like composition, physical–chemical properties, film stability and adhesion to Si substrate. Adhesion and stability have been reported to be critical parameters for the reliability and application of *a*-CN films; spontaneous delamination and spalling have been observed in ambient environment for magnetron sputtered films [21]. Our experimental procedure was properly optimized to improve film quality, stability and adhesion.

2. Experimental

2.1. Preparation of films

Carbon nitride thin films were prepared by a pulsed ArF excimer laser (Lambda Physik COMPex 102) with 193 nm wavelength, 30 ns duration, repetition rate 10 Hz and pulse energy in the range 55–60 mJ, with a corresponding fluence of ~2.5 J/cm^2 on the tar-

* Corresponding author. Tel.: +39 0690672 230; fax: +39 0690672 227.
E-mail address: emilia.cappelli@isc.cnr.it (E. Cappelli).

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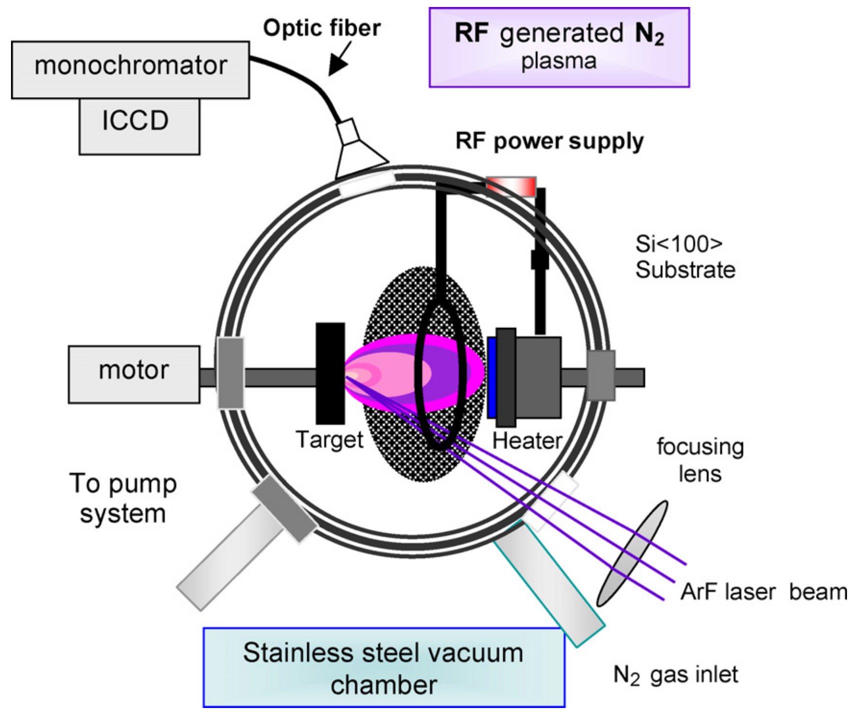

Fig. 1. The RF plasma assisted PLD apparatus: (i) the N_2 plasma, generated between the ring (− pole) and the grounded substrate, crossing the plume and (ii) the experimental set-up for optical emission spectroscopy measurements.

get. The laser beam was focused at an angle of 45° on a pyrolytic graphite target (99.999% purity). High-purity N_2 (99.999%) was used as reactance gas. During the deposition, the target was rotated to ensure uniform erosion over the target surface. Facing the target at a distance of ∼5 cm from it, the substrates were mounted on a heated holder. A RF 13.56-MHz Huttinger PFG 300 system (maximum power output 300 W) was used to generate plasma of nitrogen in the chamber. The schematic picture and diagram of the experimental set-up are shown in Fig. 1. In order to generate plasma localized near the substrate, a ring-shaped electrode was placed between the target and the substrate at a distance from the substrate ∼1.5 cm, shorter than the distance between the ring and the target.

Since there is a sensible increase of kinetic energy of incoming positive ions bombarding the growing film, when the negative electrode is connected to the substrate holder, we used an alternative configuration, with inverted DC polarization, to decrease the etching effects of positive ions. Before depositions the chamber was evacuated to $\sim 5.0 \times 10^{-5}$ Pa. The substrates were *p*-type Si ⟨1 0 0⟩ wafers cleaned ultrasonically in n-hexane. During the deposition, N_2 flux was regulated by a mass flow controller (MKS 0-200).

2.2. Chemical characterization (XPS and Raman spectroscopy)

XPS experiments were carried out by an ESCALAB MKII (VG Scientific Ltd., U.K.) spectrometer, equipped with a standard Al Kα excitation source and a 5-channeltron detection system. Photoelectron spectra were collected at 20 eV constant pass energy of the analyser and a base pressure in analysis chamber of 10^{-8} Pa. The binding energy (BE) scale was calibrated by measuring Au 4f spectrum from sputter-cleaned Au 99.99% foil and setting Au $4f_{7/2}$ peak to BE = 84.0 eV. The accuracy of experimental BE scale was ±0.1 eV. The curve fitting is carried out with a mixture of Gaussian and Lorentzian functions.

Raman spectra were collected on samples at room temperature in the back-scattering geometry with an in Via Renishaw spectrometer equipped with an air-cooled CCD detector and a super-Notch filter. The emission line at 488.0 nm from an Ar^+ ion laser was focused on the sample under a Leica DLML microscope using a 5× objective. Spectra were acquired for each sample with a power of the incident beam on the sample of about 5 mW. The spectral resolution was 2 cm^{-1} and the spectra were calibrated using the 520.5 cm^{-1} line of silicon.

2.3. Electronic properties

The electrical characterization has been performed in a vacuum chamber by the “four-contact-in-line-points probe” method. This method allows the measurement of the sheet resistance under dark conditions. The sheet resistance is a measure of resistance of thin films with almost uniform thickness, commonly used to characterize thin film materials. The utility of the method, as opposed to *resistance or resistivity*, is that it is directly measured using a four-terminal sensing measurement. The set-up scheme and details of the method are reported elsewhere [22].

2.4. Optical emission spectroscopy (OES)

Plume emission images were spectrally investigated from a direction perpendicular to its axis and recorded by imaging the side-on view of the luminescent plume onto a fast gated intensified CCD system (ORIEL Instruments INSTASPEC V, 1024 pixels × 256 pixels, 25–mm image intensifier, P43 Phosphor, and sensitivity from approximately 180 nm to 850 nm). Oriel InstaSpec Basic software controlled the camera and collection of the ICCD image data.

The ICCD camera was coupled to a Jobin Yvon compact monochromator model CP-140-1605 covering the 380–780 nm spectral range, equipped with a 405 grooves/mm grating blazed at 450 nm wavelength. A glass fiber transfers the emission of the plume onto the entrance slit of the monochromator. The ICCD camera is connected to a host computer via a general purpose interface bus (GPIB) (Fig. 1).