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High N-content a-C:N films elaborated by femtosecond PLD with plasma assistance

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ABSTRACT

Amorphous carbon nitride (a-C:N) thin films are a interesting class of carbon-based electrode materials. Therefore, synthesis and characterization of these materials have found lot of interest in environmental analytical microsystems. Herein, we report the nitrogen-doped amorphous carbon thin film elaboration by femtosecond pulsed laser deposition (fs-PLD) both with and without a plasma assistance. The chemical composition and atomic bonding configuration of the films were investigated by multi-wavelength (MW) Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and electron energy-loss spectroscopy (EELS). The highest nitrogen content, 28 at.%, was obtained with plasma assistance. The $I(D)/I(G)$ ratio and the G peak position increased as a function of nitrogen concentration, whereas the dispersion and full width at half maximum (FWHM) of G peak decreased. This indicates more ordered graphitic like structures in the films both in terms of topological and structural, depending on the nitrogen content. EELS investigations were correlated with MW Raman results. The interpretation of XPS spectra of carbon nitride films remains a challenge. Plasma assisted PLD in the femtosecond regime led to a significant high nitrogen concentration, which is highlighted on the basis of collisional processes in the carbon plasma plume interacting with the nitrogen plasma.

1. Introduction

In the last decade, the deposition of higher nitrogen content amorphous carbon films received specific attention following the theoretical prediction of a hypothetical C_3N_4 phase isostructural to β-Si_3N_4 whose hardness might be equal or superior to that of diamond [1,2]. Although the synthesis of such crystalline C_3N_4 compound was not successful the resulting amorphous CN (a-C:N) materials found applications in optical and magnetic storage technology as protective coatings [3,4]. In particular, it is found that a higher nitrogen incorporation has a beneficial effect on electronic properties and its use as electrode material [5–10] as well as many other potential applications [11].

The properties of amorphous carbon nitride coatings strongly depend on the deposition methods [4,12–14], since various types of chemical and physical vapor deposition techniques have been used (including hybrid coating processes), such as radio frequency plasma enhanced chemical vapor deposition (RF PECVD) eventually carried with direct current (DC) magnetron sputtering [4,13], ion beam assisted cathodic arc deposition [15], filtered pulsed cathodic arc deposition [16,17], pulsed laser deposition (PLD) [10,12,18], DC magnetron sputtering [19] and electrochemical deposition [20]. Among the above mentioned techniques, the PLD is a promising way to deposit carbon nitride films with enhanced physical, chemical and electrochemical properties because it can be easily carried out even on non-conductive substrates and at low substrate temperatures during film growth. Up to now, most of the works deal with the deposition of a-C:N films by nanosecond pulsed laser deposition [12,21,22]. Recent studies have shown the ability to dope amorphous carbon (a-C) materials by femtosecond pulsed laser deposition (fs-PLD) [18,23] but nitrogen doped a-C films deposited by femtosecond PLD, in particular with plasma assistance, is still largely unexplored. Such investigation may be paramount for the synthesis of a-C:N films with significantly higher

Abbreviations: a-C, amorphous carbon; a-C:N, amorphous carbon nitride; Biased a-C:N, DC plasma assistance deposited amorphous carbon nitride.

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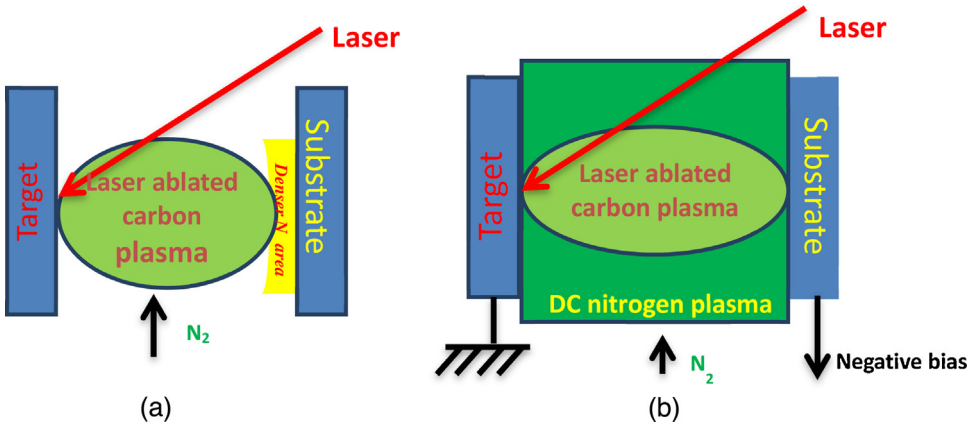

Fig. 1. Schematic view of the deposition configuration (a) without bias assistance, (b) with bias assistance.

nitrogen contents, typically in the 20–50 at.% range. Muhl et al. [24] reviewed the deposition methods for carbon nitride films and pointed out that to overcome this limitation, atomic or ionic nitrogen should be used to bombard the film surface during the deposition process. Reactive plasma is an effective way to enhance the ionization of the gas molecules. DC glow discharge with proper bias voltage improve the N content in films [25–28]. Moreover this method is easier to operate compared to other atomic and ion sources. Thus the coupling of direct current plasma assistance with femtosecond laser ablation is of prime interest and will be developed in the present paper.

Many researchers characterized the a-C:N materials by different techniques. X-ray photoelectron spectroscopy (XPS) has been used extensively to study the chemical bonding configurations [4,12,13,15,16,18,29,30,32,41–45] with however a still controversial identification of carbon and nitrogen bonding configurations. Therefore, it is obvious that complementary additional techniques are important to obtain a more complete knowledge of a-C:N films. On the one hand, the electron energy-loss spectroscopy (EELS) provides useful information regarding the bonding character of the films [29,30], on the other hand, Raman spectroscopy is a standard and non-destructive technique widely used for the characterization of all kinds of carbon-based materials.

In this paper, we emphasize the advantages of using reactive PLD over the conventional PLD in terms of N content and CN bonds formation. The effect of deposition conditions on the chemical composition and atomic bonding structure of the carbon nitride films is studied by X-ray photoelectron spectroscopy (XPS) combined with EELS and MW Raman spectroscopy in order to obtain consistent conclusions on the bonding structure of carbon and nitrogen in a-C:N films with various nitrogen contents tailored by plasma assistance of the femtosecond PLD process.

2. Experimental

Amorphous carbon nitride thin films were prepared by femtosecond pulsed laser deposition (fs-PLD) with and without the assistance of DC discharge plasma. Deposition of films is performed at room temperature by ablating a graphite target onto silicon (Si) substrates. A femtosecond laser system working at 800 nm wavelength, with pulse duration of 60 fs and a repetition rate of 1 kHz was used. The laser beam was focused at an angle of 45° onto a high purity graphite target (99.9995% purity). The substrates were mounted on sample holder at a distance of 36 mm from the target. High purity (99.9995%) N_2 gas was used as the reactant gas. A DC source was used to generate a plasma of nitrogen into the chamber. The negative electrode of the DC power supply was connected to the sample holder to increase the incoming ion energy and the positive electrode was grounded. The scheme of the two experimental configurations is shown in Fig. 1. The deposition has been carried out with or without the DC power supply in order to study the effect of plasma assistance on the composition and properties of growing films especially in terms of nitrogen content and carbon hybridization. Before the deposition, the chamber was pumped until a base pressure of 10^{-4} Pa. The substrates were also carefully cleaned before introduction into the deposition chamber using successive ultrasonic baths of acetone and ethanol. A mass flow controller regulates the static pressure of N_2 flux at 10 Pa pressure for the films deposited by fs PLD and 5 Pa for fs-PLD films deposited with plasma using 250 V applied DC discharge voltage. For all the deposition conditions the laser fluence was kept constant to 5 J/cm^2. The experimental parameters are shown in Table 1. The thickness of the films, measured by a profilometer (Vecco Dektak), is controlled by the deposition time.

Table 1
Experimental conditions for femtosecond PLD of films.

	a-C	a-C:N	Biased a-C:N
Laser source	Ti: sapphire 800 nm		
Pulse width	60 fs		
Pulse energy	1 mJ		
Repetition rate	1 kHz		
Fluence	5 J/cm^2		
Deposition rate	10 nm/min	2.5 nm/min	8 nm/min
N_2 pressure	–	10 Pa	5 Pa
DC biased voltage	–	–	250 V

Chemical surface analyses were carried out using X-ray Photoelectron Spectroscopy. The analyses were performed with a Thermo VG Thetaprobe spectrometer instrument with a focused monochromatic AlKα source ($h\nu$ = 1486.68 eV, 400 μm spot size). Photoelectrons were analyzed using a concentric hemispherical analyzer operating in the constant ΔE mode. The energy scale was calibrated with sputter-cleaned pure reference samples of Au, Ag and Cu in order that Au4f$_{7/2}$, Ag3d$_{5/2}$ and Cu3p$_{3/2}$ were positioned at binding energies of respectively 83.98, 386.26 and 932.67 eV. For all the samples analyzed, narrow scans were recorded for C1s, O1s and N1s with step size of 0.1 eV and pass energy of 50 eV. This pass energy gives a width of the Ag3d$_{5/2}$ peak measured on a sputter clean pure Ag sample of 0.55 eV. Components in C1s and N1s peaks were adjusted using lineshapes consisting of a convolution product of a Gaussian function (75%) and Lorentzian function (25%). Multi-wavelength (MW) unpolarized Raman spectroscopy has been performed using an Aramis Jobin Yvon spectrometer at four different laser excitation wavelengths, namely, 325 nm, 442 nm, 488 nm and 633 nm. The spectral resolution was 2 cm^{-1}.