

Laser deposition of CN_x films combined with RF and hollow cathode discharges

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Pulsed laser deposition (PLD) combined with additional RF and hollow cathode (HC) discharges for deposition of CN_x films are studied. The RF discharge was held between two electrodes situated parallel to plasma plume from a graphite target. Influence of RF power, nitrogen pressure, modulation frequency and modulation pulse rate on nitrogen content was observed. The production of nitrogen species in the RF discharge was observed by optical emission spectroscopy (OES). In PLD combined with RF and HC discharges one of the RF electrodes was used to supply nitrogen gas on the substrate. Films were characterized by WDX, XRD and by scratch and microhardness testers. The nitrogen content in CN_x films sharply increased with additional discharges. An N/C ratio higher than 1.1 was measured.

Keywords : laser deposition, carbon nitride films, radiofrequency discharge, hollow cathode discharge, optical emission spectroscopy

1. Introduction

Liu and Cohen predicted β-C_3N_4 structure which should be harder than diamond [1]. For PLD creation of carbon nitride (CN_x) thin films, a graphite target ablated in nitrogen ambient is most often used. The Kinetic energy of ablated species depends mainly on laser power density, target properties and nitrogen pressure. The properties and kinetics of plasma are, to a considerable degree, determined by the concentration of excited atoms. To reach high concentration of nitrogen in CN_x layers, the bonds of N_2 molecules have to be broken and activated to obtain chemically active nitrogen. Nitrogen molecules can be broken by the plasma plume from graphite target, or by additional discharge. To break N_2 molecule the kinetic energy of species in the plume has to be ~9.7 eV (or 7.3 eV, 8.5 eV, 11.8 eV [2]). Nitrogen molecules in both the upper state, A $^3\Sigma_u^+$, and lower (ground) state, X $^1\Sigma_g^+$, of the transition, dissociate into two ^4S atoms [2]. It is generally agreed that although all discharges through nitrogen produce predominantly ^4S atomic species, there is an interesting difference in the propagation of these excited molecules in relation with various types of discharges. The chemical reactivity of active nitrogen is mainly due to the ground state and excited atoms. It is interesting that the activation of pure nitrogen may require electron energy as high as 20 eV, which considerably exceeds the energy needed for dissociation, excitation, or even ionization of nitrogen [2].

In laser deposition, the concentration of nitrogen in CN_x films increases with nitrogen ambient pressure [3]. For high pressures, the film growth rate and the mean free path of active species are low and nitrogen activated in the plasma plume can hardly reach the substrate. This can be one reason why highly nitrogenated and very hard films were not, till now, successfully formed using only a simple laser deposition method [3]. The superhard β-C_3N_4 phase of carbon nitride was locally identified only in hybrid laser deposition systems, where additional discharge like microwave and RF discharges were used to produce fragments of N_2 molecules.[3-7].

In this work, the additional RF and HC discharges were produced to enhance nitrogen content in PLD created CN_x layers. The RF discharge was produced between two flat electrodes placed along the plasma plume. Production of atomic and molecular nitrogen was checked by an OES also.

2. Experimental

The C-N films were deposited by a KrF excimer laser (LUMONICS laser, type PM 842, pulse energy up to 450 mJ, λ= 248 nm, τ_{FWHM}= 20ns) ablation of graphite target. The deposition stainless-steel chamber was equipped with completely oil- free vacuum system (Balzers Diaphragm Vacuum Pump type MD 4TC and Balzers Turbomolecular Drag Pump with Holzwecker stage type TMH 260). Sputtered carbon fragments were deposited on the substrate, and combined with active nitrogen species generated in the vicinity of substrate by RF or RF + HC discharges. The RF discharge was sustained by two flat rectangular electrodes situated between the target and the substrate, parallel to the plasma plume (see Fig.1a). For nitrogen excitation the RF Huttinger generator (type PFG 300, 13.56 MHz, 300 W, square wave modulation with adjustable pulse duration in region 0 – 5000 Hz), with tuning network PFM 1500A, was used. Various stainless steel and aluminium RF electrodes were constructed and tested. Stainless steel and aluminium water-cooled electrode holders were finally used. The ablated material was collected on the (100) silicon, or on the stainless steel substrates. The films were deposited at substrate temperature T_s = 25 ^oC. The substrate was placed at a distance d_{t-s}= 40 mm from the target. The reaction chamber was evacuated down to p < $2x10^{-4}$ Pa before each deposition. The nitrogen gas pressure was varied in the 1-40 Pa range. The laser beam was focused onto a target by means of quartz lens to give a fluence of F=10-12 J/cm^2.

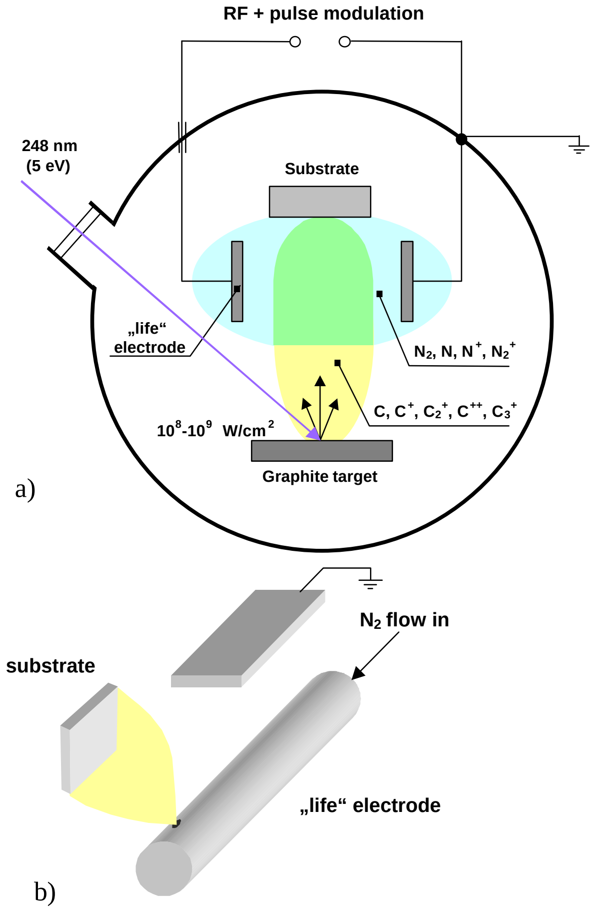

Fig. 1*. Scheme of PLD combined with pulse modulated RF (a) and hollow cathode discharges (b)*

For this energy density the C, C^+, C_2^+, C^{++} and C_3^+ spices were found in plasma plume by time of flight mass spectroscopy and Resonant ionisation spectroscopy [8].

One of the RF electrodes was fabricated as cylinder with a hole inside for additional HC discharge. The N_2 gas flew through the hole and was directed onto the substrate – see Fig.1b. For HC discharge aluminium and carbon electrodes were fabricated.

The film composition was studied by electron microprobe using wavelength dispersive X- ray analysis (WDX) with a X-ray microanalyser JXA 733 of JEOL. Energy of primary electrons was kept at 5 keV. The plastic microhardness H of the deposited CN_x thin films was tested by Fischerscope-HCU-100V. The adhesion of the films to the substrate was measured by a scratch test. The scratch tip was a standard Rockwell diamond cone (radius 0.2 mm and angle 120^o). The crystalline structure of the films was investigated by XRD analysis in a Bragg-Brentano alignment, using CuK_α radiation.

The OES was taken with a grating monochromator (Applied Photophysics), lock-in nanovoltmeter type 232B (Unipan) and a photomultiplier R928 (Hamamatsu). The recovered signal was recorded by a Le Croy 9400 storage oscilloscope. The emission signals from N_2, N_2^+ and atomic N, N^+ species were studied in the wavelength regions of 330nm - 368 nm, 360nm - 400 nm, 396nm - 420 nm, 460 nm - 503 nm and 560 nm – 570 nm. For the OES measurement the RF power was adjusted up to 200 W and RF modulation frequency was changed from 250 Hz to 5000 Hz (modulation ratio was 1:1, 2:1 or 1:2; RF power on:off).

3. Results and discussion

To hold the discharge between the two RF electrodes various shapes of electrodes were tested. The best results were reached with two identical shape electrodes, rectangular preferable. For the electrode distance of 15 mm, the discharge was concentrated mainly between the electrodes for nitrogen pressure between 1 Pa and 100 Pa.

From OES it was found that the yield of the signal from atomic nitrogen N_{at}, molecular nitrogen N_2 and ionised molecular nitrogen N_2^+ depends on RF power, modulation frequency, RF modulation rate and nitrogen pressure [9]. An example of emission signals from N_{at}, N_2 and their ratio, as function of the modulation frequency is shown in Fig.2. We see that for the mentioned parameters both signals increase with the RF modulation frequency and the maximum in N_{at}/N_2 ratio can be easily identified.

For PLD combined with RF discharge it was found that N/C ratio in the CN_x films depends on RF discharge power, nitrogen pressure, modulation frequency and modulation ratio. Film created only by PLD exhibited N/C ~ 0.4 (H ~ 6-7 GPa), but with additional RF discharge the N/C ~ 1.2 (H ~ 3-4 GPa) was possible to reach (for 50 W, 20 Pa of N_2, without modulation). We see that plastic microhardness H was lower for higher N/C. The adhesion of films created without RF discharge was in the region 10N – 20N, the adhesion with additional RF was in the region 5N – 15N. The content of oxygen in layers created on Si substrates was up to 10 at.%. On stainless steel substrates the content was found to be lower (to about 5 %). With higher RF power the N/C was usually higher, but there was overheating of the RF electrodes for RF power over 150 W.

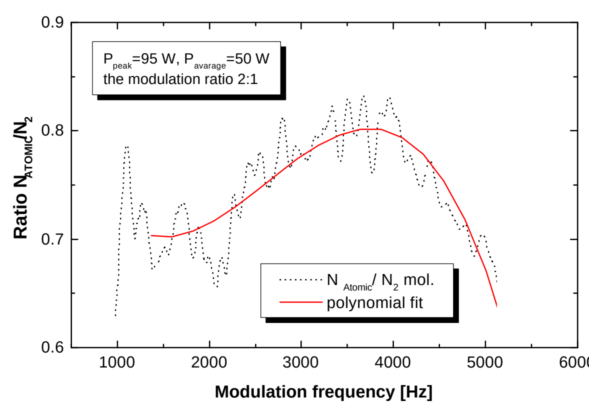

Fig.2. *The ratio of N_{at}/N_2 lines as a function of RF discharge modulation frequency (average power P_{av} = 50 W, peak power P_{peak} = 95 W, modulation ratio 2:1 (pulse on/off)*

For PLD combined with RF and HC discharges, using aluminium HC electrode, the N/C as high as 1.2 was found (30W, without RF modulation, 30 Pa of N_2, N_2 flow rate ~ 65 sccm). But Al was also present in the layers. For carbon HC electrode, the N/C ~ 1.1 was measured. For lower N_2 pressures (10 Pa, 15 Pa) the layers peeled off from the substrate within one week. For pressures of 20 Pa the tension in the film was lower and films were stable.

No XRD peaks were found in CN_x layers, even on the special cut Si substrates (4.5^o from 100 axis).

4. Conclusions

CNx films were produced by PLD, and by a combination of PLD with additional RF and HC discharges. With additional discharges a sharp increase of N/C ratio in CN_x films was found. Positive influence of RF discharge on the yield of excited nitrogen was checked by OES. The maximum N/C reached was in the region 1.1 – 1.2. For higher N/C the film microhardnes was lower. No distinct changes in N/C ratio was found between the case of PLD + RF discharge only **-** compared to PLD + RF + HC discharges. No XRD peaks from CN_x films were observed. A lot of parameters influence the nitrogen content and N/C ratio: nitrogen pressure, RF power, RF modulation frequency and modulation rate. Then, there is a need to carry out a detailed study of CNx films produced by the employed method.

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