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Nitrogen Rich Carbon Nitride Thin Films Deposited by Hybrid PLD Technique

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Highly nitrogenated CN_x films were created by pulsed laser deposition (PLD), combined with radiofrequency (RF) and hollow cathode (HC) discharges. The N/C ratio higher than 1 was measured. Deposition set-up and results of optical measurement are discussed.

Keywords: laser deposition; carbon nitride; radiofrequency discharge; hollow cathode discharge

I. INTRODUCTION

Liu and Cohen predicted superhard β -C₃N₄ structure that should be harder than diamond [1]. For PLD creation of carbon nitride thin films, a graphite target ablated in nitrogen ambient is most often used. In laser deposition the N/C reached is always lower than the required one for β -C₃N₄ stoichiometry. The CN_x films created by PLD usually exhibit N/C ~ 0.4. In this work a new concept of additional RF and HC discharges was applied in order to produce an enhanced nitrogen content.

II. EXPERIMENTAL

The CN_x films were deposited by a KrF excimer laser ablation of a graphite target. For nitrogen excitation a RF generator (13.56 MHz, square wave modulation with adjustable pulse duration in the region 0 – 5 kHz) was used. 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 flat aluminium electrodes, with electrode distance of 20 mm, the discharge was concentrated mainly between two electrodes for nitrogen pressure region of 5- 100 Pa of nitrogen.. The laser beam was focused onto the target by quartz lens to reach a fluency of $F=10\text{-}12\text{ J/cm}^2$. In the experiments with HC discharges one of the RF electrodes was fabricated (from aluminum or carbon) as a cylinder with a hole inside and N_2 flew through the hole. In the first experiments the stream of excited nitrogen gas, ejected from the hole, was directed onto the substrate – Fig. 1b. Due to the high tensions in the deposited DLC films, the direction of stream was then changed as shown in Fig. 1c. The film composition was studied by electron microprobe using wavelength dispersive X- ray analysis (WDX). For comparison of the optical properties, nitrogen-rich films ($\text{N/C} \sim 1$) were prepared also by inductively coupled plasma CVD utilizing chemical transport reactions (ICP-CTR) and by ICP-CVD with gas precursors ($\text{Ar/CCl}_4/\text{HN}_3$)(ICP- GP) [2].

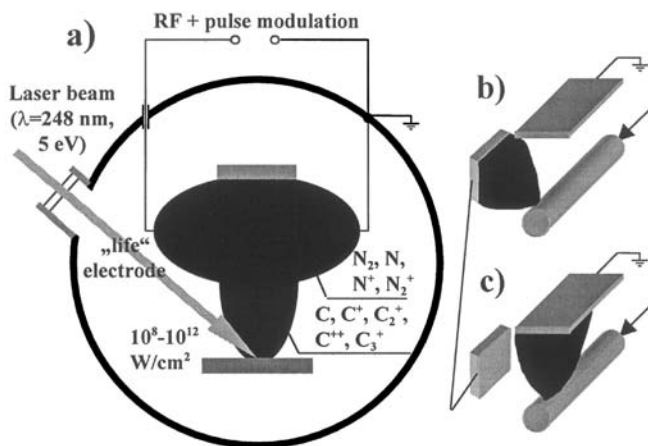


FIGURE 1. Experimental scheme of the combined laser deposition and RF discharge (a) and with HC alignment sideward (b) and upward (c).

III. RESULTS AND DISCUSSION

The deposition conditions and results of WDX measurement for PLD + RF discharge are summarised in Table 1. It can be seen that using PLD without discharge leads to $\text{N/C} \sim 0.4$ (sample T23). Applying additional RF discharge, the reached N/C ratios were higher than 1 (E7, A6). For PLD combined with RF and HC (with aluminum “life” electrode), N/C ratio higher than 3.0 was achieved; however there was also a lot of aluminum in the layers - see Table 2. To avoid the aluminum contamination of the layers

the 'life' HC electrode was fabricated from graphite. Using graphite HC electrode N/C ~ 1 was measured for both nitrogen jet directions.

Sample	P (N ₂) [Pa]	RF peak [W]	Thickness h [nm]	O [at%]	C [at%]	N [at%]	N/C [at%]
E7	5	50	500	7.79	45.11	46.93	1.04
A6	20	50	200 - 700	3.61	47.04	49.34	1.05
T23	20	-	1400	4.45	69.32	26.23	0.38

TABLE 1. Deposition conditions and WDX composition of CN_x films created by PLD and PLD + RF discharge

Sample	P (N ₂) [Pa]	RF peak [W]	RF aver. [W]	Modul. [RF on:off]	Thickn. h [nm]	C [at%]	N [at%]	Al [at%]	N/C [at%]
MA1	10	-	25	-	420	36.7	40.1	11.6	1.09
ZA1	10	35	25	3:1	420	41.3	43.8	4.5	1.06
Z35	10	46	25	2:1	360	42.7	43.1	5.5	1.01
N26	10	150	50	1:1	100-300	8.5	27.6	37.8	3.24
U30	20	-	50	-	200-210	7.8	17.5	40.8	2.24
M150	10	-	150	-	180-250	14.0	39.4	20.9	2.81

TABLE 2. Deposition conditions and composition of CN_x films created by PLD and PLD + RF + HC (Al) discharges (modulation frequency 3.5 kHz).

It was proposed that β -C₃N₄ could find applications as a transparent material [8]. The superhard materials in general, should possess a high transmittance in wide spectral regions [3] and the calculations predict a minimum gap for β -C₃N₄ of about 6.4 eV [4]. The transmission of our nitrogen-rich CN_x films is shown in Fig. 2; the corresponding gaps are in the range of 1.3 – 2.4 eV (see also [5]) which indicates that the films are not suitable for UV applications.

IV. CONCLUSION

Thin CN_x films were prepared by PLD and by a combination of PLD with RF and HC discharges. The application of discharges leads to a drastic increase of the N/C ratio in the films; however they can be contaminated by material from the HC electrode. The direction of the activated nitrogen stream from the HC electrode has impact on the tensions in the CN_x layers. These highly nitrogenated films exhibited rather poor optical properties.

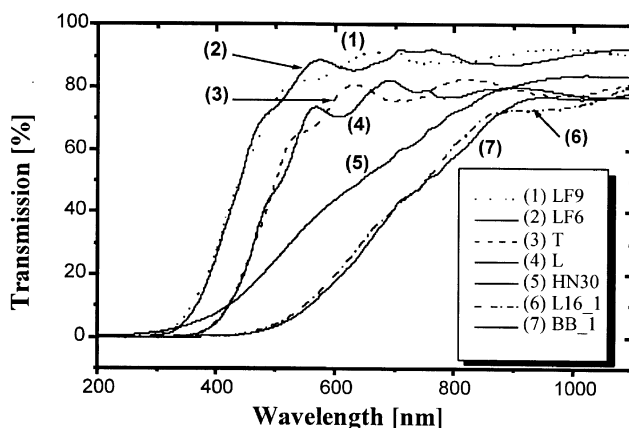


Fig.2. Transmission of CN_x films (LF6, LF9 created by ICP-GP; T, L by ICP- GTR; L16_1, BB_1 by PLD + RF; HN30 by PLD + HC).

V. ACKNOWLEDGEMENT

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