Effect of nitrogen surrounding gas and plasma assistance on nitrogen incorporation in a-C:N films by femtosecond pulsed laser deposition

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In the context of nitrogen-rich amorphous carbon thin films ultrafast pulsed laser deposition from graphite targets in inert nitrogen or nitrogen plasma ambient, this study assesses the correlation between the ablation plume composition and dynamics and the thin films contents and structures. The use of both optical emission spectroscopy and spectrally resolved 2D imaging, coupled with intensified CCD tempo-ral resolution, allows to precisely follow such species of the plume as CN and C_2 molecules, from their apparition to their deposition on the substrate. The results show that carbon–nitrogen bonding arises at the early time of expansion with little changes in quantity thereafter. The key role of the DC-bias is in lowering the molecular weight of the ambient gas, thus easing molecules way toward the target and interfering with the chemical reaction for CN generation. Depending on the ambient pressure, these pro-cesses will have drastically different effects on the thin films properties and contents. This work thus explains the origin of high nitrogen contents in a-C:N thin films obtained using DC-bias, and proposes an easy *in situ* optical observation-based way to predict and look for the best conditions to maximize those contents in future work.

1. Introduction

Nitrogen doped amorphous carbon (a-C:N) thin films attract a lot of attention in research and industry since the first theoretical calculation by Liu and Cohen [1,2], owing to a wide range of potential applications [3]. Pulsed laser deposition (PLD) has proved to be a very relevant process to grow such amorphous carbon nitride thin films [4]. Amongst this technique's advantages are low temperature deposition, low level of contamination, stoichiometry and reproducibility of thin films characteristics. Various PLD experiments have shown the potential benefits of nitrogen activation by using external plasma generated by RF and DC discharges. This can lead to an increase of the N/C atomic ratio as well as to the formation of more sp^2 rich graphitic like structures [5–7]. Until now, most studies have dealt with deposition of high N content amorphous carbon (a-C:N) films by nanosecond pulsed laser deposition (ns-PLD). In a recent study, we have demonstrated the possibility to incorporate high N contents in DLC by using DC bias assisted femtosecond pulsed laser deposition (fs-PLD) with low nitrogen pressure and low DC bias values [7].

The properties of films obtained by PLD are mostly affected by the characteristics of the laser-induced plasma plume. The dynamics and quantities of the various laser-ablated plume species strongly affect the deposition process, which in turn determines the properties of the deposited thin films. When the deposition is performed in a reactive atmosphere, the chemical reactions of the ablated species with the ambient gas are a key factor for the thin film composition and structure. Hence, the characteristics of the plume produced by pulsed laser ablation and their influence on the process involved in thin film deposition are of great interest. There are several techniques for the characterization of the laser-ablated plume, such as optical emission spectroscopy (OES) [8–10], spectrally resolved direct ultrafast imaging [11–13], time of flight mass spectroscopy [14], and laser induced fluorescence spectroscopy [15]. Those allow finding out the correlation between plasma parameters and deposited film properties. Among them, OES is effective for *in situ* studies of the plume dynamics and its interaction with a reactive gas, particularly to observe when and where chemical bonding take place and how the generated species carry on their path to the deposition substrate [10,14–16].

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However, the mechanisms of the DC bias fs-PLD process have not yet been fully understood, especially in the case of a-C:N films deposition. It is desirable to diagnose carbon to nitrogen bonding in the plasma during fs-PLD or DC bias fs-PLD. In particular, this may explain DC-bias fs-PLD's interests for generating high nitrogen contents.

This work presents a study of plumes produced from graphite target by ultrafast laser ablation in vacuum, nitrogen atmosphere and DC bias nitrogen plasma analyzed *via* ultrafast OES technique and spectrally-resolved ultrafast imaging, in order to address and better understand C—N bonding formation and high N content incorporation into the films produced by DC bias assisted fs-PLD.

2. Experimental setup

The femtosecond interaction takes place in an ultra-vacuum chamber ($\sim 10^{-5}$ Pa). A 99.98% pure graphite disk is set on a rotating target holder, facing a fixed substrate 3.6 cm away. The laser beam is focused on the graphite target at 45° incidence, using a 500 mm focal lens, producing a 10^4 μm^2 ellipsoidal Gaussian spot. The laser (Ti:Sapphire COHERENT LEGEND) pulse duration at full-width half maximum is 50 fs, with a pulse energy 0.5 mJ, yielding a fluence of 5 J/cm^2. To produce a-C:N thin films, the ablation of graphite is performed in nitrogen atmosphere. Inert N_2 is introduced in the chamber post vacuum. Two nitrogen pressures are used in this work: 1 and 10 Pa. In order to favor nitrogen incorporation in the thin films, a negative direct current (DC) bias is induced between the target and the substrate to generate a nitrogen plasma for the plume to expand in. This system has already been presented in detail in preceding work [7] where thin films deposited at various pressures and DC biases were studied. The electric potential between the target and the substrate is either 0 or −250 V.

To understand the process of CN bonding during the ablation plume generation, expansion and deposition on the substrate, as well as the plume interaction with the ambient gas, two ICCD based technique are used to record the optical emission of the ablation plume. The first one is optical emission spectroscopy (OES): the emission from the first 7 mm of the plume along the ejection axis is collected in an UV–vis optical fiber through a 35 mm focal lens. The signal from the fiber is then sent into a Princeton Acton spectrometer coupled with a Princeton PIMAX-3 intensified charge-coupled device (ICCD) camera, giving it a spectral resolution less than 0.25 nm and a temporal resolution of 10 ns. In parallel, the plume is studied by direct ICCD imaging using a Hamamatsu Orca 12 ER with a UV–vis objective. Optical band pass filters with a 10 nm bandwidth are set in front of the camera to isolate the spectral range of emission from selected species from the plume, specifically CN and C_2. In both cases, the use of ICCD allows for a precise record of the temporal evolution of both the plume dynamics and plume composition, with a resolution better than 10 ns in both cases. All delays given in the following sections are counted from the laser pulse interaction with the target. The scheme of the fs-PLD setup with DC-plasma assistance and the two optical ICCD *in situ* characterization setup is represented in Fig. 1.

In order to link *in situ* observations of the ablation plume with the contents of elaborated thin films, samples are deposited on silicon by PLD in the four selected conditions for which ablation plumes are studied here (two pressures and two DC bias conditions). The nitrogen content and C—N bonding states are determined by X-ray photoelectron spectroscopy (XPS). The analysis is performed with Thermos VG theta probe spectrometer instrument with focused monochromatic AlKα (1486.68 eV) radiation using a hemispherical analyzer of 50 eV pass energy under ultra-high vacuum conditions.

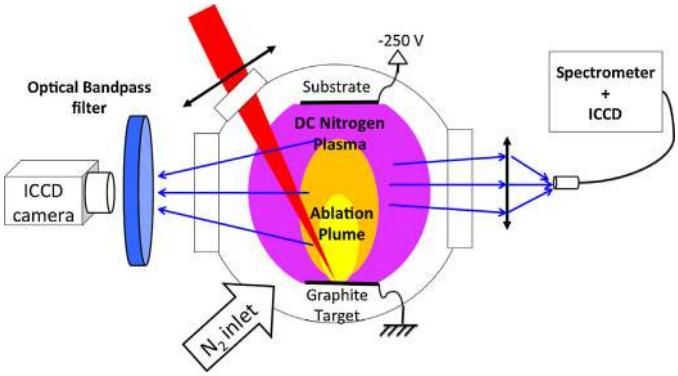


Fig. 1. Experimental setup used for OES and spectrally-resolved 2D imaging of the plasma.

This setup is used to precisely observe the different plume species evolution and dynamics, in particular, the formation of CN molecules and their behavior compared to the rest of the plume, in order to understand the variations in N content in nitrogenated amorphous carbon thin films and how plasma assistance can increase N content.

3. Results

3.1. Optical emission spectroscopy

First, we compare the optical emission spectra of plumes expanding in vacuum or nitrogen atmosphere, with or without the DC bias. Fig. 2 shows spectra obtained at a pressure of 10 Pa and with vacuum. by integrating all the emitted light from 20 ns up to 50 μs after interaction. These delays are chosen to avoid the initial bremsstrahlung before 20 ns and because no notable emission can be recorded past 50 μs.

Numerous emission lines and bands can be observed. All emission lines correspond to either C II or C I spectroscopic lines, indicating the emission of C^+ ions and neutral C atoms, respectively. None can be attributed to pure nitrogen species. In vacuum, C II lines are visible during few hundred nanoseconds after interaction, and C I during 1 μs. In nitrogen, these emissions almost disappear after 200 ns. The observation of C II and C I in vacuum is in agreement with previous detailed studies of femtosecond ablation of graphite [17,18].

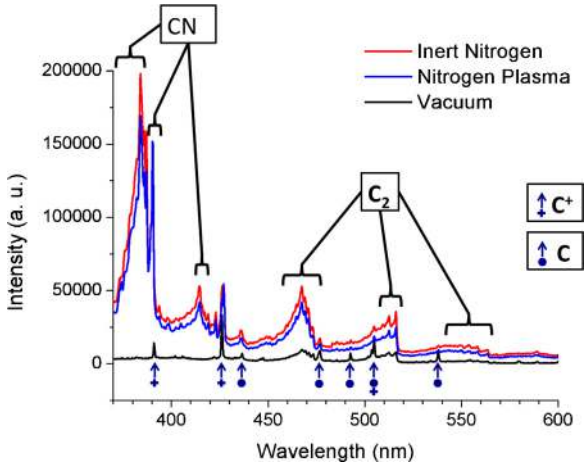


Fig. 2. Optical emission spectra of graphite ablation plumes expanding in vacuum and various gas conditions at 10 Pa recorded from 20 ns to 15 μs after interaction.

The emission bands observed in vacuum correspond accurately to the well-known Swan Bands [19] emitted by C_2 molecules, with main heads at 466.8, 516.5, and 554.0 nm (visible only when zoomed). These relatively large bands appear in all recorded spectra, with different intensities. They have already been well observed and detailed in vacuum [17,18]. They can be observed up to few μs after interaction in vacuum, few tens of μs after interaction in inert nitrogen and nitrogen plasma.

The most notable feature of these spectra is the three huge bands in the short wavelength region, which appear only in nitrogen ambient. All of them can be associated to the Violet System [19] emitted by CN molecules vibrational transition. The widest one belongs to the main system, and consists of three heads at 385.1, 385.5 and 386.2 nm. The thinner ones belong to the tail bands, with heads at 391.0 and 407.9 nm. The former can be distinguished over time from the C II line appearing in vacuum and centered at 391.9 nm [20]. This emission is clearly visible after initial bremsstrahlung (20 ns after interaction), and is maximal in the first 100 ns after interaction. The emission from CN behaves quite similarly to C_2 in nitrogen ambient, existing during 30 μs after interaction.

Similar species are observed at similar times when using a pressure of 1 Pa. These observations only concern a section of the plume close to the target, and give no idea of the species dynamics. The spectral position and bandwidths of the different species emission allow using spectral band pass optical filters in order to select species for 2-D imaging of the plume, so as to locate the species, and to determine their quantity when they reach the substrate during PLD.

3.2. Spectrally resolved 2-D imaging

Several optical band pass filters are used to select the emission of the different species. Filters going from 375 to 385 nm and 387 to 397 nm allow assessing CN emissions. A filter going from 425 to 435 nm allows recording C II emission. C_2 bands are observed through filters going from 455 to 465 and 515 to 525 nm. C I emission is recorded in the range of 535–545 nm. Ambiguities can only appear for the recorded lines, which emission can be convoluted with broader molecular bands, but are minored by two facts. First, C I and C II emissions only exist for less than 200 ns in nitrogen. Second, spatial segregation between ions, atoms and molecules has been evidenced in vacuum [18], and might be expected here.

The images recorded with the C I and C II filters always contain a component ahead of the main plume, which is not recorded using the filters selected for CN and C_2. This indicates that the spatial segregation still exist in nitrogen ambient. Additionally, the observations confirm the fast disappearing of these components. They have the same behavior, quantity and speed whether or not DC bias is used, and cannot be observed more than a centimeter away from the target.

In the interest of this work, the most striking feature is the behavior of the CN and C_2 components because of the predominance of C_2 for amorphous carbon films growth [18] and the incorporation of nitrogen in the films through plasma reactions and CN bonding. Here, the study will be separated between the 1 and 10 Pa pressure conditions.

Fig. 3 presents CN and C_2 emissions in 1 Pa of either inert nitrogen or nitrogen plasma, recorded at (a) 1000–1200 ns after laser interaction and (b) 2500–3000 ns after laser interaction. The emission is normalized to the maximum of the four images in each case.

The plume expands while its center of mass progresses normally along the ejection axis, with the major part of the plume making contact with the substrate in any case. Indeed, as can be seen at delay 2500–3000 ns after interaction, the substrate (at 3.6 cm from target) is "showered" by the C_2 and CN molecules. The use of DC bias to induce nitrogen plasma does not modify the quantity of emission due to C_2 molecules. However, the emission due to CN is considerably higher in the case of inert nitrogen ambient rather than plasma.

This is confirmed by Fig. 4, which features a summation of the emission shown in Fig. 3 along the ejection axis. Here, the quantity of C_2 emission is always quite comparable, while CN emission is much stronger in the case of plasma ambient nitrogen.

An important fact to notice is that, however limited the effect, in every case, the CN emission always appears slightly further from the target compared to C_2 emission, even if the two components are mixed. Finally, it should be observed that when using nitrogen plasma, both CN and C_2 molecules seem to progress faster and further than their respective counterpart in inert nitrogen.

The same observations are then carried with 10 Pa of ambient gas, as presented in Fig. 5. The same delays and filters from Fig. 3 are used, in order to observe C_2 and CN between 1000 and 1200 ns and 2500 and 3000 ns after laser interaction. The first important difference with preceding observations is that the quantities of the various species are not dramatically changed by the use of DC bias. In particular during 1000–1200 ns, the plume emissions look quantitatively similar.

In contrast to what happens at 1 Pa, the plume center of mass presents a very weak evolution between the two different delays. This is confirmed by Fig. 6, which sums the emission recorded in Fig. 5 along the ejection axis. Even when studied at longer delays, until the plume no longer emits, the bulk of the emitting plasma plume under 10 Pa never makes contact with the substrate. Only the front of the plume expands enough to reach the substrate.

Despite these differences, the CN emission still can be observed, in all cases globally further than C_2, even though the various components are still much intermixed. Similarly to the 1 Pa pressure case, CN and C_2 plume components progress slightly further when expanding in plasma rather than inert ambient gas. It means that more species from the plume front can make contact with the substrate in the plasma ambient case.

These two different pressures with or without DC bias induce very different plasma plumes, with the DC bias inducing quite different effects depending on N_2 pressure. In particular, CN and C_2 species impinging on the substrate may authorize different growth conditions during deposition. This should lead to different N contents in deposited a-C:N films.

Table 1
Nitrogen contents from a-C:N thin films deposited by femtosecond laser deposition with various bias and pressure conditions.

Pressure (Pa)	Bias (V)	N contents (%)
1	0	13
1	−250	10
10	0	16
10	−250	25

3.3. Thin films quantification of nitrogen content

a-C:N thin films are deposited on silicon substrate, and are studied by XPS, as was done in our previous work [7]. The details of fitting procedure permitting to obtain N contents from XPS spectra can be found in [7]. The results obtained here for the different pressures and biases are presented in Table 1.

In inert nitrogen surrounding gas, at the highest pressure, the N content of the films increases with pressure from 13 to 16%. At low pressure, the DC bias induces a decrease of the N contents from 13 to 10%, while at high pressure, it induces an increase of the N content, from 16% up to 25%. The pressure related differences in

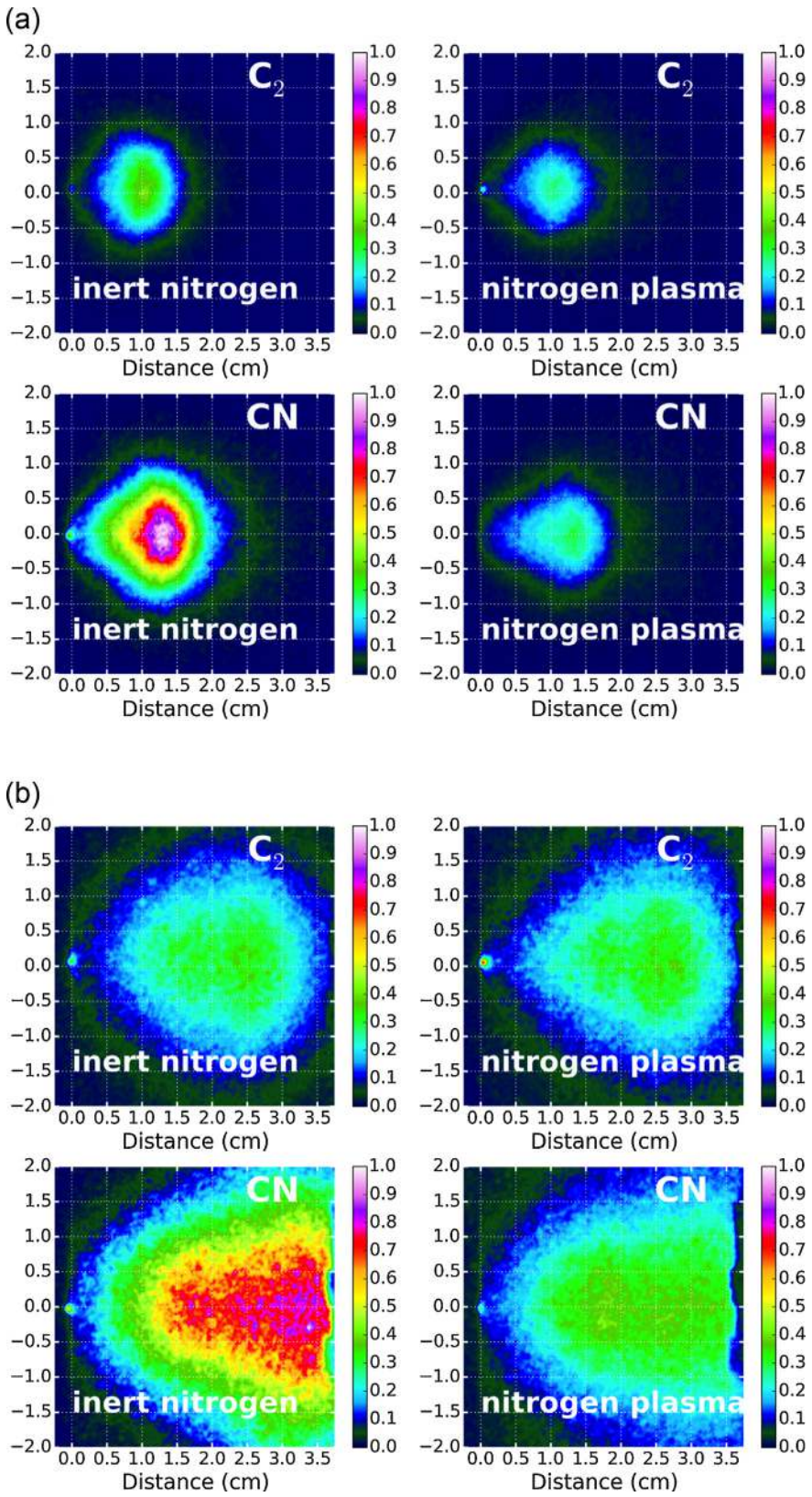


Fig. 3. Spectrally resolved emission from CN (375–385 nm) and C_2 (455–475 nm) of fs laser-induced carbon plasma plume expansion in 1 Pa of inert N_2 gas or of nitrogen plasma between (a) 1000–1200 ns and (b) 2500–3000 ns after laser interaction.

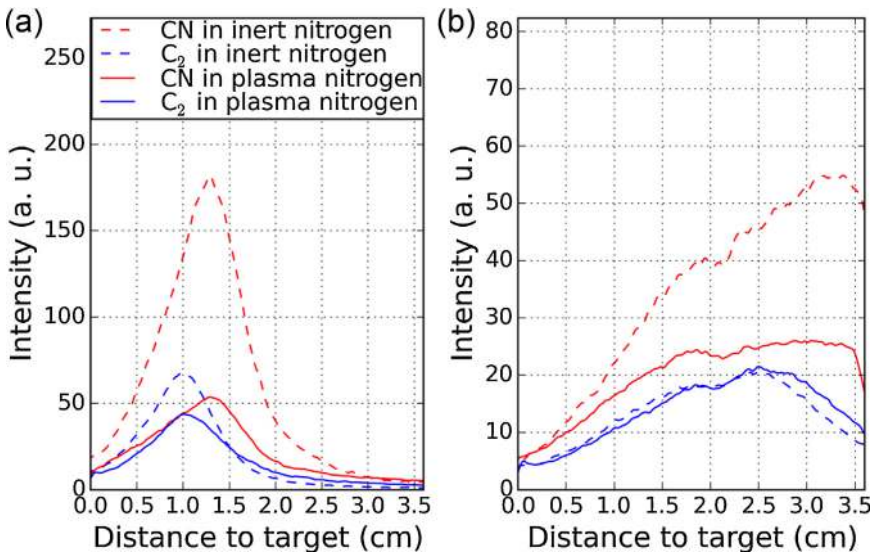


Fig. 4. Emission from CN and C_2 molecules summed along the ejection axis in 1 Pa of N_2 inert gas or nitrogen plasma from (a) 1000–1200 ns and (b) 2500–3000 ns after laser interaction.

the behaviors induced by the DC bias on the laser-induced ablation plume induce a difference in the thin films nitrogen content.

4. Discussion

Contrary to the rest of the plume, ions and neutrals seem to be relatively unaffected by the use of DC-bias. Their quantity remains constant, and within the few hundred nanoseconds during which they are visible, they always appear to progress faster in the plume. It is possible that they reach the substrate in a non-radiative state. Anyway, they disappear at centimetric distance from the target and ahead of the main CN/C_2 plume, that is to say that any recombination process between C^+, C and the nitrogen ambient, with or without DC bias, will be excluded here. This is different to what has been observed previously in [13], where higher pressure was used (more than 40 Pa). Thus, it can be expected that at higher pressure, the C + and C components are squeezed between expanding C_2 and ambient gas.

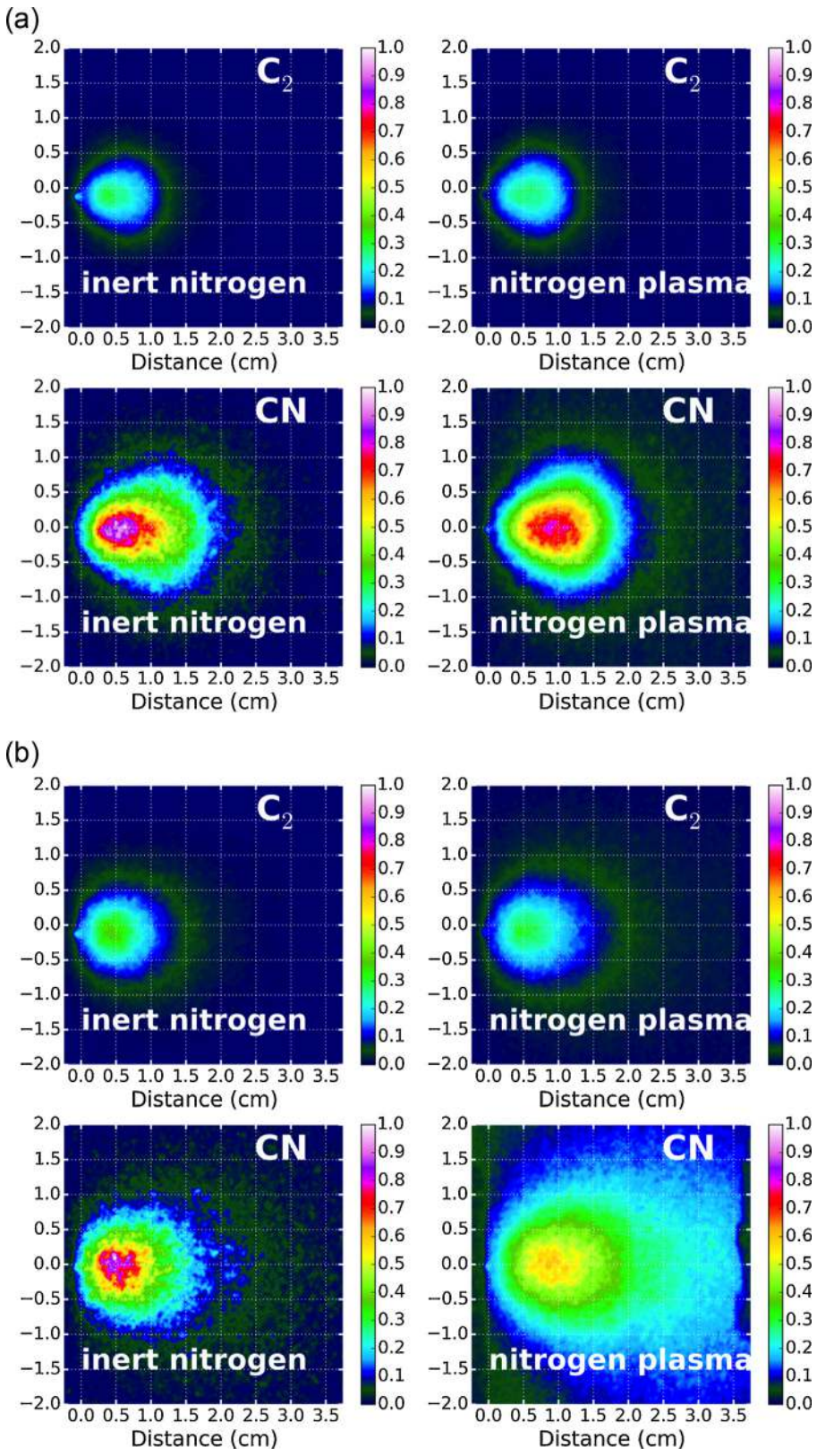
The CN emission appearing after only a few tens of nanosecond after plume interaction indicates that the CN bonding takes place during the very first few nanosecond of plume expansion, when the plume is a hot optically thick plasma [21,22]. Molecular dynamics studies have shown that a huge part of the ablated matter, in the case of graphite ablation, remain in the form of molecules from the first picoseconds after interaction [23,24]. This should mean that CN are expected to form from the interaction between N_2 and C_2 at high temperature *via* $C_2 + N_2 \rightarrow 2CN$, as has been suggested for nanosecond interaction [12]. Note that from the end of bremsstrahlung to the disappearance of most species or their collection on the substrate, the ratio of CN emission over C_2 emission remains almost constant. That is to say that the chemical reaction leading to CN bonding does not occur after the first few tens of nanoseconds after interaction. Then, at the pressures and laser fluence used, the formation of CN is due only to interaction between the hot plume and the ambient gas or plasma at the beginning of the expansion. As expected, in all cases, the CN and C_2 components appear really intermixed, with the CN center of mass slightly ahead of the C_2 one.

At the lower pressure (1 Pa), the use of a DC bias strongly reduces CN component quantity, while affecting weakly C_2 formation. A key factor in the ablation plume dynamics in ambient gas is the atomic weight of gas molecules [25]. The dissociation of molecules in the nitrogen plasma should reduce the average atomic weight of surrounding gas encountered by the expanding plume. Thus, C_2 molecules will have an easier way to flow toward the substrate through the plasma. This will reduce the number of C_2/N_2 interactions necessary to trigger the $C_2 + N_2 \rightarrow 2CN$ reactions. From a hydrodynamic viewpoint, the faster expansion of the plume reduces the duration for which it is hot and dense enough to trigger the chemical reaction. Another explanation could be the lack of N_2 in the nitrogen plasma, but this seems unlikely, since the same should be true in the 10 Pa pressure condition, where no decrease of CN component is observed when using a DC bias. The easier penetration of the plume in the nitrogen plasma is confirmed by the observation of the CN and C_2 center of mass being slightly further at the same acquisition times in plasma than in inert nitrogen surrounding atmosphere.

The laser-induced plasma plume then propagates to the substrate where it is deposited as a-C:N layer. It appears only logical that with a lower proportion of CN in the plume using a DC bias, one obtains a lower N content in the deposited thin films. The observed plume contents and dynamics correlate then very well to the thin films properties at low pressure.

With increasing pressure, the emitted plume center of mass does not reach the substrate any more; only its front makes contact with it. Moreover, the plume front is richer in CN, due to their formation location, the center of mass of the CN component being slightly ahead of the C_2. Despite almost the same overall ratio between CN and C_2 emission in inert gas at both pressures, a higher N content is obtained in the thin films at the higher pressure. This happens by limiting substrate contact to the CN richer part of the plume, yielding an increase in nitrogen ratio from 13 to 16%.

Contrary to lower pressure condition, DC bias increases the CN component emission at 10 Pa. This is related to the fact that at this pressure, the N^+ rich nitrogen plasma remains strong enough to prevent expansion and favor the temperature and pressure become high enough to trigger CN formation in the first tens of nanosecond after interaction. Moreover, the nitrogen plasma lets CN and C_2 flowing more easily than the inert nitrogen surrounding gas. It ensures an even better, in particular faster, contact between the substrate and plume front. This is especially clear in Fig. 6, where one can observe a contact with the CN plume as early as at 1 μs after interaction when using DC bias. Note that the C_2 contact with the plume is favored too, but only later, when the CN emission on the substrate is half its maximum along the ejection axis. Thus, a



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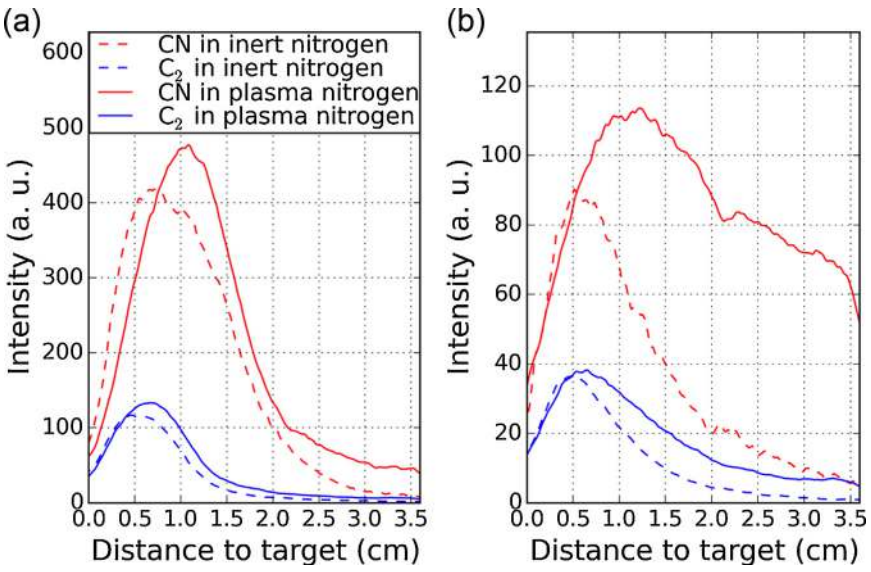

Fig. 6. Emission from CN and C_2 molecules summed along the ejection axis in 1 Pa of N_2 inert gas or nitrogen plasma from (a) 1000–1200 ns and (b) 2500–3000 ns after laser interaction.

higher contact with the CN rich part of the plume is ensured when using the DC bias, as confirmed by the very high N contents of the thin films deposited in these conditions.

5. Conclusion

The graphite ultrafast ablation plume expanding in nitrogen at various pressures (1 and 10 Pa) with only a nitrogen-surrounding atmosphere or in presence of nitrogen plasma between target and PLD substrate is studied through optical emission spectroscopy and spectrally resolved ultrafast imaging. Results are correlated to a-C:N deposited thin films through their N contents evaluated with XPS spectroscopy.

The DC bias assistance has been found to have a detrimental or enhancing effect on the N contents of the a-C:N thin films depending on the pressure used. This is related to an easier flow of laser-ablated molecules in a N^+ rich ambient gas rather than inert N_2. At low pressure, this reduces CN contents in the plume due to less interaction between C_2 and N_2, with the whole plume contacting the substrate, inducing lower N contents in the film. On the opposite, a high pressure was sufficient to trigger a strong CN formation reaction, while limiting the plume/substrate interaction to the CN rich plume front only. The DC bias thus could enhance N contents of a-C:N thin films from 16 to 25% at 10 Pa.

Considering the high potential of N-rich a-C:N alloyed thin films as active sensors for biopollutants or heavy metals detectors, this study shows how very high N contents of such films can be obtained. Indeed by studying the optical emission from the plume, one can optimize pressure and bias conditions for which strong CN formation is triggered, and ablation plume front and substrate interaction is favored

Both qualitative and quantitative study of optical emission at higher pressure and DC-bias will be conducted in the future in order to find the best working point for enhancing CN molecules interaction with the deposition substrate. Deposition will be made in these conditions in order to confirm the expectation of higher N-contents. This should permit to reach even higher N contents in thin films than presented here.

Acknowledgement

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