Laser-Induced Graphene Formation Enhanced by Dielectric Barrier Discharge Plasma on Polyamide Film

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https://doi.org/10.29072/basjs.20260116

ARTICLE INFO

Received: 10 September 2025

Accepted: 05 February 2026

Published: 30 April 2026

Keywords:

Cold plasma, Carbonization, Graphene, Polyamide, Plasma, LIBS

ABSTRACT

This research work, demonstrates the surface modification of polyamide films by two processes, cold plasma treatment combined with laser irradiation through laser induced breakdown spectroscopy technique (LIBS). A nanosecond pulsed Nd:YAG laser was employed with various pulse energy of (500, 550, 600) mJ to induce surface carbonization after plasma treatment with various duration of (1,3,5) minutes. The influence of plasma treatment time on the laser-induced carbonization was studied. The results showed that plasma pre-treatment is significantly enhancing the laser interaction with the polyamide surface among the examined durations, 3 minutes of plasma exposure time produced the most intense LIBS spectra. This is leading to optimal surface activation for carbon formation. The obtained results are offering availability of tuning the polyamide surface properties for applications in the field of photonics, sensing, and flexible electronic technologies.

1. Introduction

In recent years, Kapton tape, which is based on polyimide, has attracted increasing attention in engineering, optoelectronic, and energy-related applications due to its high thermal stability as well as its excellent mechanical and chemical resistance, making it suitable for use under extreme operating conditions. Recent studies have also highlighted the thermal carbonization of polyimide surfaces as an effective approach to support such applications and to obtain graphene-like materials with high purity. However, activation processes based on nanosecond pulsed laser irradiation still face significant technical challenges. The main restrictions include inefficient coupling of laser energy with the surface and undesired surface ablation. Hence, it is reducing the effectiveness of carbon layer formation and limit the controllability over the resulting surface morphology. Additionally, the low surface energy and chemical stability of polyamide limit its effectiveness in applications that demand strong surface adhesion, compatibility with coatings, or certain functional attributes. Therefore, it is essential to develop surface modification techniques that improve the physical and chemical properties of polyimide while maintaining its bulk characteristics.

One of these techniques are physical surface treatments, including cold plasma treatment before laser irradiation. Exposure to cold plasma plays an important role for activating the polymer surface by breaking the bonds of C–C and C–N , thereby increasing surface reactivity and enhancing subsequent chemical interactions during laser irradiation**[1,2].** Activated carbon on the surface stimulated rapid surface changes, resulting in the creation of functional groups like carbonyl and carboxyl groups. This treatment improves substantially the surface properties of the polymer, including wettability, wetting rate, and surface energy. In contrast to conventional thermal modification in ovens, plasma treatment enables accurate surface structuring while maintaining the essential bulk characteristics of the polymer**[3-5].**

Laser treatment is subsequently performed using sources such as Excimer or Nd:YAG lasers under various environments, including O_2 or CO_2. This technique generates localized photothermal and photochemical alterations, leading to enhanced adhesion, the elimination of contaminants, and the formation of new functional surface layers. These effects have demonstrated a significant improvement in the adhesion properties of polyamide surfaces for engineering applications. Consequently, cold plasma treatment is an effective and modern method for preparing polymer surfaces before laser modification**[4-7].**

This research is based on the hypothesis that pre-activation DBD plasma, which can significantly enhance the effectiveness of laser-induced carbonization (LIC) on polyimide films using a 1064 nm nanosecond Nd:YAG laser. Furthermore, it suggests that the combined plasma-laser method offers a more controlled means of achieving surface carbonization, thereby reducing significant thermal damage, which is often associated with only laser treatments .

This study explores the usage of atmospheric DBD plasma pre-treatment combined with nanosecond Nd:YAG laser irradiation, contrasting with conventional techniques that predominantly depend on thermal processes for generating graphene like carbon using CO_2 lasers. The plasma step improves laser interaction with the surface, leading to more efficient and controlled carbonization. The novelty of this work lies in systematically applying this synergistic approach and monitoring the process in real time, an aspect that has not been investigated in the existing literature**[8,9].**

Laser-induced breakdown spectroscopy (LIBS) is utilized as an in-situ diagnostic method to observe plasma emissions and carbon formation during laser irradiation, while the Nd:YAG laser behaves simultaneously as the surface modification source. This approach enables a systematic assessment of process parameters and determination of optimal conditions for carbon layer development**[10].**

The aims of this study are:

a) To assess how the duration of DBD plasma pre-treatment affects the activation of polyamide surface .
b) To optimize laser pulse energy for precise surface carbonization.
c) To employ LIBS as an in-situ method for observing plasma emissions and carbon formation;
d) To analyse the structural characteristics of the generated carbon layer through Raman spectroscopy.

The carbon layer produced by this plasma–laser synergistic treatment holds promise for numerous applications, including flexible electronics and printed sensors that offer both high conductivity and mechanical flexibility, gas and biosensing devices with improved sensitivity, energy storage elements like supercapacitors and batteries, as well as optoelectronic, photonic devices and thermal management systems in microelectronic **[11, 12].**

This research integrates plasma pre-treatment, nanosecond laser irradiation, and real-time spectroscopic diagnostics to thoroughly explore the mechanisms of polyamide surface carbonization mechanisms. As a result, it provides a new possibilities for designing precisely engineered carbon surfaces for advanced material applications.

2. Materials and Methods

2.1 Synthesis of Samples

2.1.1 Polyamide

Commercial polyamide(Kapton, DuPont^{TM}, 99.9 % purity) was used in this work. The film of polyamide has a thickness of 100 µm. The samples were cut into 2×2 cm^2 pieces and placed on a piece of glass for handling, then cleaned by ethanol to be ready for the measurements.

2.1.2 Laser induced breakdown spectroscopy

Given the growing demand for accurate elemental and isotopic analysis, laser-induced breakdown spectroscopy (LIBS) stands out as an effective and versatile technique. It operates by directing a high-energy laser pulse onto the surface of a material, which leads to rapid heating ablation, and ionization of surface atoms. Ones the laser intensity exceeds the breakdown threshold of the material, a highly energetic plasma is formed. This plasma contains a mix of excited species release energy in the form of light as they transition to lower energy levels. The emitted light is composed of distinct spectral lines that can be used to determine the elemental of the materials **[10].** LIBS system utilized a passively Q-switched Nd:YAG laser (HF-302A, China) operating at a wavelength of 1064 nm, with a pulse duration of 10 ns and a repetition rate of 6 Hz. The laser beam was focused onto the polyamide film by using convex lens with a focal length of 100 mm. The laser spot diameter on the sample surface was about 1 mm, due to slight defocusing to ensure stable plasma formation and controlled surface carbonization. The pulse energy was adjusted at (500, 550, 600) mJ with multiple shots on the same area. This laser configuration is widely adopted in LIBS applications due to its capability to produce high-energy pulse over very short timescales, enabling efficient plasma generation on the samples. To analyse the emitted light from the plasma, the laser system was integrated with a spectrometer (OPTOSKY ATP2400), covering a spectral range from 190 to 1110 nm. The spectrometer resolution included a minimum wavelength of 190 ± 10 nm, and a maximum of 1110 ± 10 nm with a signal-to-noise ratio (SNR) exceeding 500:1. The system was calibrated to approach saturation intensity for optimal detection sensitivity. The resolution was verified using the full width at half maximum (FWHM) of the mercury-argon lamp at 546.088 nm, which should not exceed 1 nm.

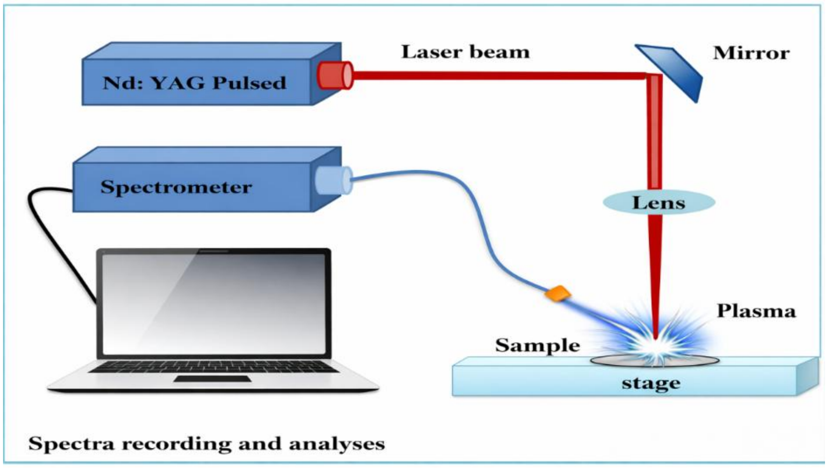


Figure 1. The setup of laser induced breakdown spectroscopy **[12].**

This spectrometer function by dispersing the light emitted from the plasma into its constituent wavelengths enabling elemental identification based on unique emission lines. Data acquisition and analysis were carried out using a computer linked to the spectrometer as shown in Fig.1.

2.1.3 DBD plasma system

Cold plasma treatment was carried out by using DBD plasma system see Fig. 2. It was generated in ambient air using a parallel-plate electrode (with 10 cm diameter) configuration with an inter-electrode gap of approximately 2.0 mm. The applied voltage ranged from 5 to 25 kV, providing stable and uniform plasma exposure across the treated area. The treatment time was adjusted to be (1, 3, 5) min.

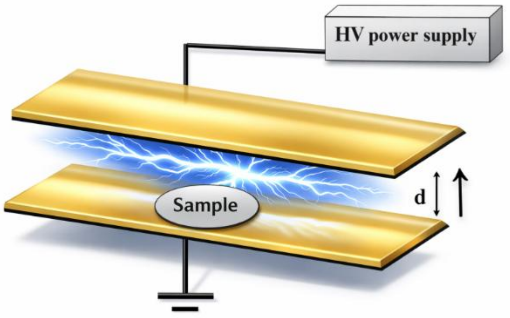


Figure 2. Open air DBD plasma system.

3. Results

3.1 Cold plasma treatment and LIBS

Cold plasma treatment and laser modification have become staple techniques for enhancing the surface properties of polymeric materials, especially polyamides. Figure 3 shows the polyamide film after plasma exposure(Time: 3 Min.) and LIBS measurements, laser pulse energy is 500 mJ.

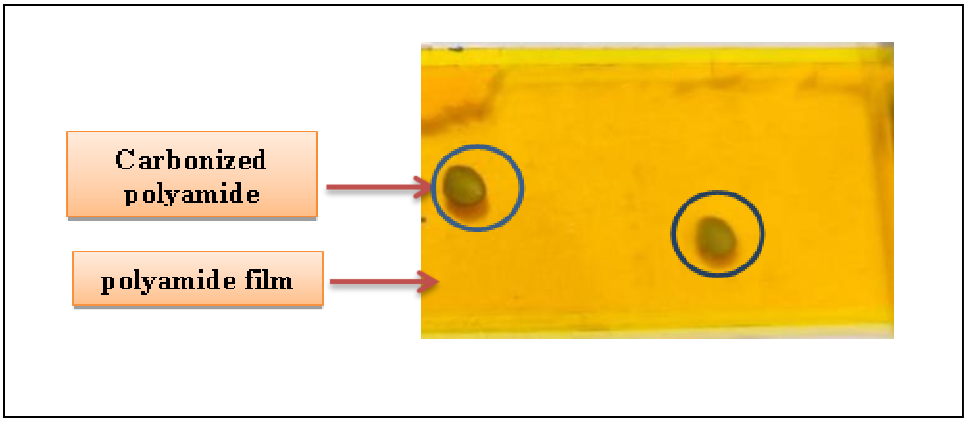


Figure 3. Polyamide film after plasma treatment and LIBS measurement.

After exposure to atmospheric DBD plasma, the surface of the polyamide film undergoes significant chemical activation due to interactions with reactive species generated from ambient air. These species include nitrogen-, oxygen-, and hydrogen-containing radicals, ions, and excited molecules, which are formed during plasma discharge.

The interaction of these reactive air species with the polyamide surface leads to the breaking of weak surface bonds and the rearrangement of polymer chains, followed by the formation of new surface functionalities. This process promotes surface cleaning by removing weak boundary layers, organic contaminants, and adsorbed hydrocarbons.

Since DBD plasma primarily affects only the top few nanometers of the polyamide surface, the bulk mechanical and thermal properties of the material remain unchanged. However, the plasma-induced surface restructuring results in increased surface roughness and surface energy, which enhances surface reactivity and facilitates subsequent laser-induced carbonization **[13].**

Based on the above discussion, laser irradiation alone, particularly with nanosecond pulse duration, does not provide sufficient energy density to induce controlled carbonization, as rapid heat dissipation leads to surface ablation before carbon formation can occur.

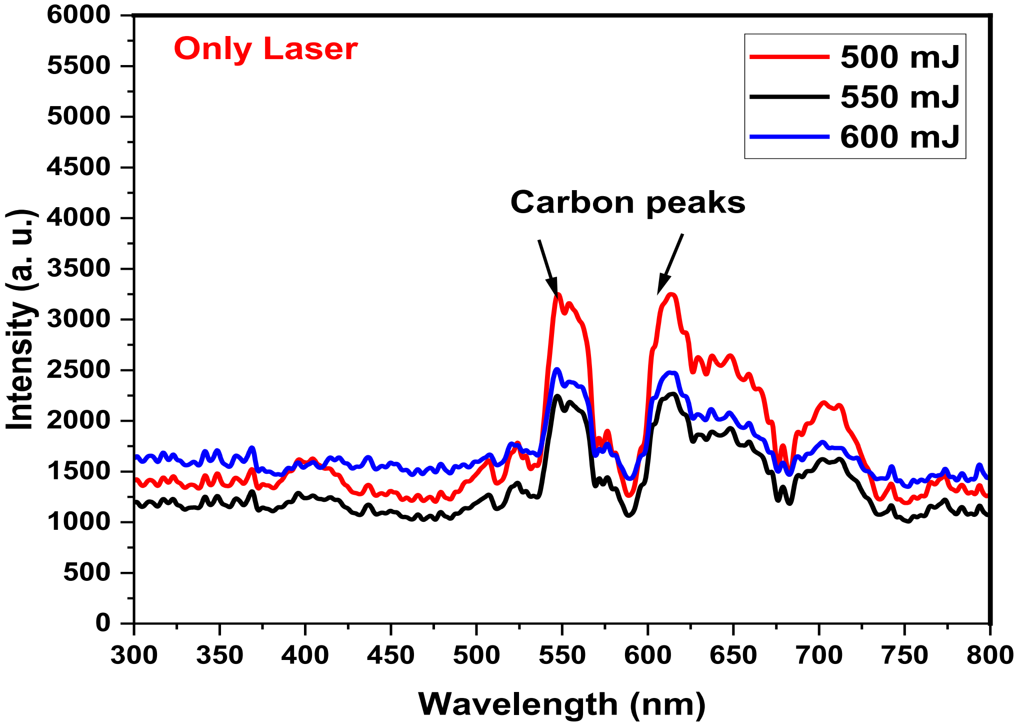
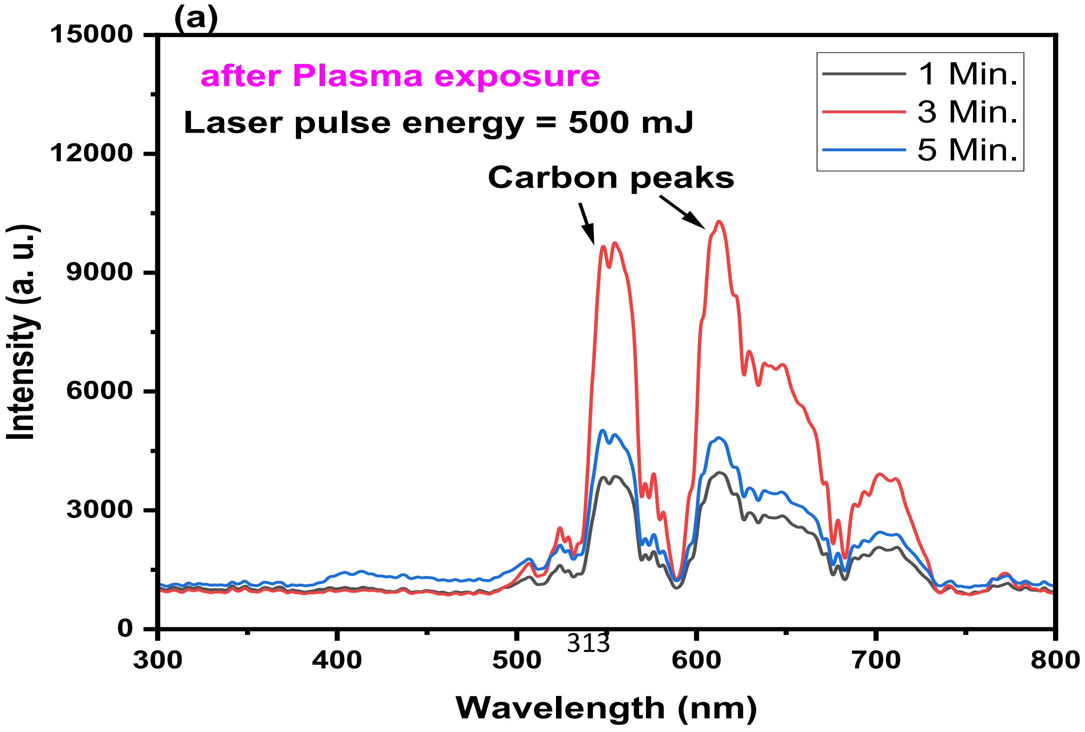


Figure 4. LIBS spectra of polyamide at various laser pulse energy.

In contrast, the combination of atmospheric DBD plasma pre-treatment and subsequent laser irradiation enhances surface activation and energy absorption, enabling effective carbonization of the polyamide surface. The resulting laser-induced carbon structures exhibit characteristics that make them suitable for applications such as chemical and optical sensing, flexible electronics, and photonic devices **[14].**



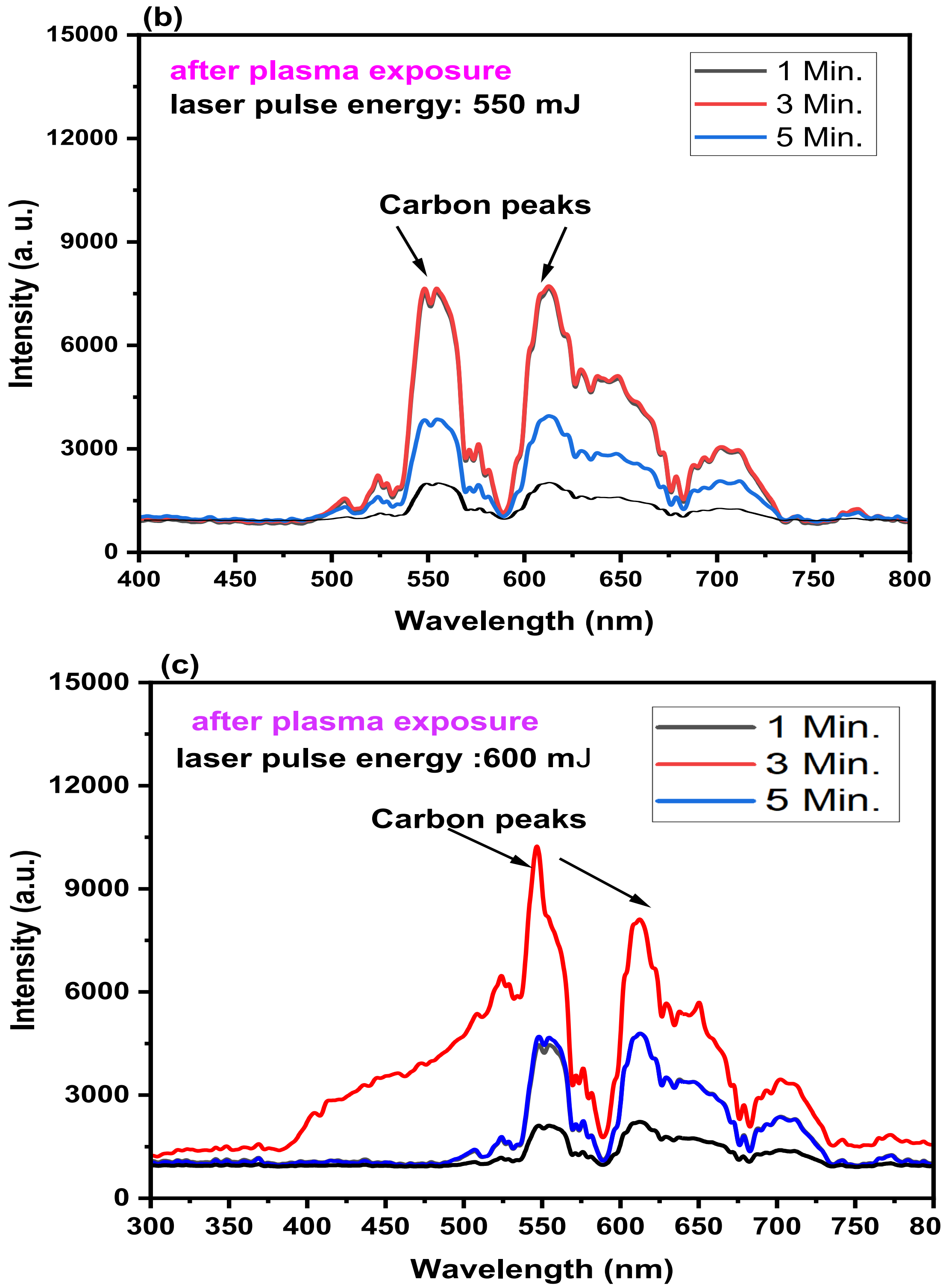


Figure 5. LIBS spectra of polyamide after plasma exposure at various laser pulse energy, a) 500 mJ, b) 550 mJ, c) 600 mJ.

Raman spectroscopy was selected as the primary structural characterization technique due to its high sensitivity to carbon bonding and graphitic ordering. Raman spectroscopy was selectively applied to the sample processed at a laser pulse energy of 500 mJ, as this condition showed the most pronounced carbonization behavior based on the LIBS results. Among all investigated laser energies, the 500 mJ condition exhibited the highest carbon peak intensity and the most stable emission features, indicating effective carbon formation. In contrast, higher laser energies led to plasma shielding and self-absorption effects, while lower energies resulted in insufficient carbon-related signals. Therefore, Raman analysis was employed for this optimal condition to confirm the structural characteristics of the laser-induced carbon layer. Therefore, Raman shift for polyamide film that treated with 3 minutes plasma exposure time and laser pulse energy of 500 mJ as shown in Fig. 6.

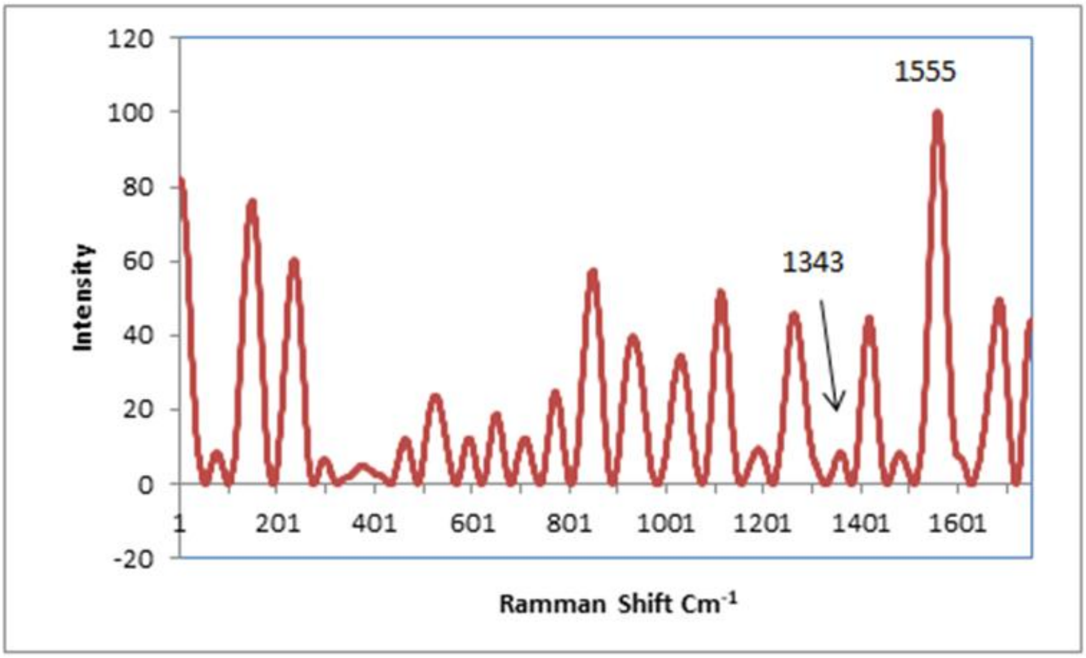


Figure 6. Raman shift for polyamide treated with 3 minutes plasma and 500 mJ laser pulse energy.

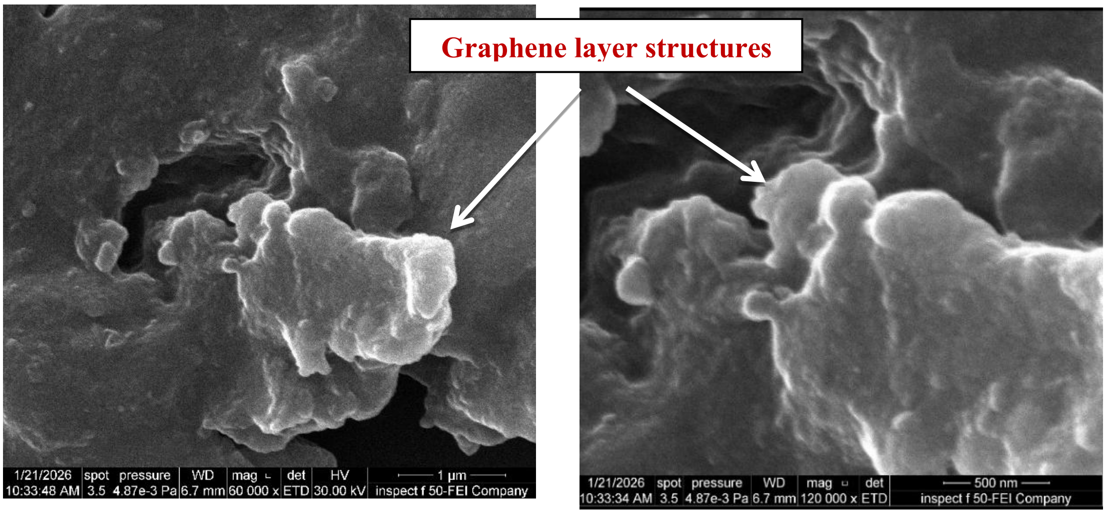


Figure 7. SEM micrograph of the treated polyamide by DBD plasma and Nd:YAG laser, the observed morphological changes indicate roughness surface increasing and activation.

4. Discussion

Figure 4 shows the LIBS spectra of polyamide at various laser pulse energy, the maximum intensity was at 500 mJ pulse energy, this is due to more excited states atoms\ions leading to stronger emission than with 500 mJ laser pulse energy (above the breakdown threshold). While, 600 mJ laser pulse energy cause plasma shielding and self-absorption, then the plasma becomes more dense results dropping in the emission intensity. Also, higher energy may be causing deep craters, which leading to optical scattering and low signal intensity.

Figure 5 shows the LIBS spectra of polyamide after plasma exposure. It is clear that 3 Min. exposure time was efficient for polyamide carbonization. The surface activation by plasma is time dependent, therefore, 1 Min. is mostly short to modify the surface of polyamide causing low carbonization.

Sufficient chemical activation can be achieved with 3 minutes plasma exposure time, which introducing weak bonds that lower the wanted energy for carbon formation results effective laser energy absorption. This proses is leading to localized carbonization without deep damage. At 5 minutes exposure time, the formation of oxides or by-products could prevent carbon formation, as well as laser induced carbonization **[15, 16].** Moreover, Figures 4 and 5 exhibit a consistent trend, where the strongest carbon peak intensity is recorded at a laser pulse energy of 500 mJ, while the weakest response appears at 550 mJ.

Raman spectroscopy can detect the molecular vibrations, as well as the changes in the chemical bonding and material structure. In laser carbonized polyamide, the formation of carbon structure implies as D-band (~ 1343 nm) from defects, amorphous carbon, as shown in Fig.6. On the other hand, G-band (~ 1555 nm) due to graphitic carbon (sp2 bonds) is presented. These two introduced peaks indicates that the plasma pre-treatment enhancing the surface reactivity, which promises laser carbonization **[17, 18].** The intensity ratio of the D to G band is approximately 0.1, reflecting a high degree of structural order in the resulting carbon layer and confirming the efficiency of the carbonization process. In addition to the D and G bands, several weaker Raman features appear in the spectrum, which can be attributed to residual polyamide structures, surface functional groups, and amorphous carbon species generated during laser processing **[19].** Since the focus of this study is on graphene-like carbon formation, detailed analysis of these minor peaks is beyond the scope of the present work.

SEM micrographs reveal significant morphological transformation of the Kapton surface after DBD plasma and Nd:YAG laser treatment as shown in Fig.7.The initially smooth polymer surface evolved into a rough, fractured, and flake-like structure, indicating effective polymer decomposition and carbon reorganization. At higher magnifications, wrinkled sheet-like features and porous domains were clearly observed, which are characteristic of graphene-like carbon materials **[20].** The formation of micro- and meso-scale voids is attributed to the rapid release of gaseous species during laser-induced carbonization. These morphological features strongly suggest the successful generation of laser-induced graphene or few-layer graphene structures on the Kapton substrate.

5. Conclusions

This research demonstrates that the combination approaches of cold plasma pre-treatment followed by laser irradiation can modify effectively the surface properties of polyamide films. This modification is enhancing the potential for graphitization. The results showed that plasma exposure time plays an essential condition for chemical activation and structural changing. Which gives better absorption of laser energy and carbonization effect. Short plasma exposure time (1 Min) is insufficient surface modification, while (5 Min) makes the surface in the case of over oxidation leading to reduce the resulted carbon. 3 minutes plasma exposure time and 500 mJ laser pulse energy are the optimal parameters to achieve controlled surface of polyamide for advanced applications in electronics, sensors, and other devices.

Future studies will focus on extending the surface chemical analysis of plasma–laser treated polyamide films using X-ray Photoelectron Spectroscopy (XPS) to provide deeper insight into the evolution of surface functional groups and carbon bonding states. Such analysis will enable a more detailed correlation between plasma pre-treatment conditions and laser-induced carbonization mechanisms. Additionally, advanced surface-sensitive techniques may be employed to further refine the understanding of structure–property relationships for optimized laser-induced carbon materials.

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تكوين الجرافين المحفز بالليزر والمعزز ببلازما التفريغ الحاجزي على غشاء البولي أمايد

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المستخلص

يعرض هذا البحث تعديل سطح أفلام البولي-أمايد باستخدام عمليتين متكاملتين، وهما: المعالجة بالبلازما الباردة مترافقة مع تشعيع ليزري من خلال تقنية التحليل الطيفي للانهيار الليزري (LIBS). تم استخدام ليزر Nd:YAG نبضي يعمل في نطاق النانوثانية بطاقة نبضية مختلفة (500، 550، 600 ميلي جول) لتحفيز كربنة السطح بعد معالجة مسبقة بالبلازما لمدة زمنية متغيرة (1، 3، 5 دقائق).تمت دراسة تأثير زمن المعالجة بالبلازما على عملية الكربنة المحفزة بالليزر، وأظهرت النتائج أن المعالجة المسبقة بالبلازما تعزز بشكل ملحوظ تفاعل الليزر مع سطح البولي-أمايد، حيث أن زمن المعالجة بالبلازما لمدة 3 دقائق أنتج أكثر كثافة لاطياف البلازما المتولدة بالليزر LIBS ، مما يشير إلى تحقيق تنشيط سطحي مثالي لتكوين الكربون. توفر النتائج المتحصل عليها إمكانية ضبط خصائص سطح البولي-أمايد بما يتناسب مع تطبيقات متعددة في مجالات الفوتونيك، والتحسس، والتقنيات الإلكترونية المرنة.

الكلمات المفتاحية: البلازما الباردة، الكربنة، الجرافين، البولي أميد، البلازما، التحليل الطيفي بالانهيار المستحث بالليزر..