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Spectroscopic Investigation of Laser-Induced Graphene Plasma

Madyan Ahmed Khalaf
Department of Physics, College of Sciences, Mustansiriyah University, Baghdad, Iraq

التحقق الطيفي لبلازما الجرافين المحتثة بالليزر

مدين احمد خلف
قسم علوم الفيزياء، كلية العلوم، الجامعة المستنصرية، بغداد، العراق

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ABSTRACT

In this paper, graphene plasma was obtained through the interaction of the fundamental radiation from a pulsed Nd:YAG laser at the fundamental wavelength of 1064 nm focused onto a solid plane of graphene material. This reaction was carried out under conditions of an atmospheric status. The resulting plasma was tested using an optical emission spectroscopy technique. The temperature of the electrons is calculated by the tow line ratio of C I and C II emission lines singly ionised, and the density of the plasma electron is calculated with Saha-Boltzmann equation. The upper limit of the electron temperature was approximately 1.544 eV. The corresponding electron density was 11.5×10^{15} cm^{-3}. Then the electron temperature decreased when the energy was 300 mJ and it was near 1.462 eV, corresponding to the density of those electrons 8.7×10^{15} cm^{-3}.

الملخص

في هذا البحث، تم الحصول على بلازما الجرافين من خلال تفاعل إشعاع ليزر Nd:YAG النبضي عند الطول الموجي الأساسي البالغ 1064 نانومتر المركز على السطح المستوي الصلب لمادة الجرافين في الغلاف الجوي الاعتيادي. تم تشخيص البلازما الناتجة عن طريق تقنية طيف الانبعاث الضوئي. وتم حساب درجة حرارة الإلكترونات باستخدام طريقة النسبة بين خطين طيفيين من خطوط انبعاث C I و C II للتأين الفردي، وتم حساب كثافة إلكترون البلازما باستخدام معادلة Saha- Boltzmann. وكان الحد الأعلى لدرجة حرارة الإلكترون حوالي 1.544 إلكترون فولت تقابلها كثافة إلكترونات 11.5 × 10^{15} سم$^{-3}$. ثم انخفضت درجة حرارة الإلكترون عند وصول الطاقة إلى 300 مللي جول ، لتكون حوالي 1.462 إلكترون فولت، في المقابل أصبحت كثافة تلك الإلكترونات 8.7 × 10^{15} سم$^{-3}$.

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1. Introduction

Laser-induced plasma spectroscopy (LIPS) has gained great popularity in recent years as a strong spectrochemical analysis technique. With LIPS, a pulsed laser is used to vaporise and ionise a material sample producing a luminous plasma when the laser irradiance reaches the material's breakdown threshold (Luo et al. 2010). Plasma production begins shortly after the laser photon hits the target surface. The optical detection of atomic and molecular species is accomplished by the examination of their laser-induced plasma emission spectra. LIPS is an atomic emission spectroscopy analytical technique that can be used to evaluate any type of matter, whether the form is solid, liquid or gaseous (Safeen et al. 2019). LIPS is also a spectroscopic technique used to determine electron density, the temperature of the electron and the number densities of the plasma plume. Varying conditions, such as ambient environment, laser energy and laser pulse duration, affect laser-induced plasma temperatures. Most LIPS temperature studies report that with increased laser energy, pulse duration, laser wavelength and ambient pressure, the plasma temperature tends to increase (Asamoah and Hongbing 2017). Laser-induced plasma's existence and dynamics depend on various parameters, such as laser wavelength, spot size, pulse duration, ambient environment, etc. Experiments may be conducted either at atmospheric pressure or in the presence of any ambient gas using this technique (Hanif and Salik 2014). The width, shape and shift properties of the emission line may provide information on plasma temperature and density of the electron. Plasma temperature is an important thermodynamic property due to its ability to explain and forecast other plasma properties, for instance, relative energy level populations and particle speed distribution (Hassan and Aswad 2019). The LIPS technology can be used in geological surveys, biopharmaceuticals, environmental detection and other fields. Increasing plasma spectral intensity will effectively increase the sensitivity and accuracy of the technique of laser-induced breakdown spectroscopy (Ren et al. 2019). Optical emission spectroscopy has recently received a great deal of consideration for representation based on LIPS (Khalaf et al. 2020).

Graphene is an atomically thin layer of carbon atoms densely compacted with a hexagonal lattice structure in a two-dimensional honeycomb. Graphene is a zero-gap semiconductor and the structure allows ultrafast extraction of photo-generated carriers, leading to the operation of variable bandwidth (Al-khattib et al. 2019). Graphene has thus shown many special characteristics, such as high room temperature mobility, the carrier quantum Hall effect, good optical clarity, a large theoretical specific surface area and outstanding thermal conductivity (Liu et al. 2012). In this paper, we study the parameters of the laser-induced graphene plasma as a function of the laser energies under conditions of normal atmospheric pressure at fixed distances from the target surface to the laser crystal. For the characterisation of graphene plasma, we used the electron temperature for neutral and ionised species and the electron number density. Furthermore, to increase the sensitivity and selectivity of the emission spectra, the pulse LIPS was introduced, and the plasma parameters were investigated as a function of laser energy.

Corresponding Author: Madyan Ahmed Khalaf madyan.a@uomustansiriyah.edu.iq ,009647906813456 المؤلف المراسل: مدين احمد خلف

2. Experimental Details

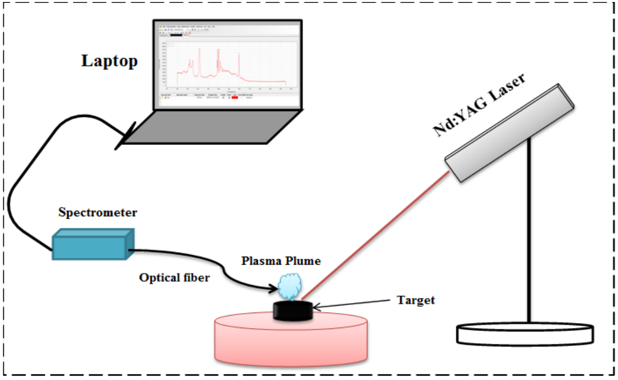
2.1. The Sample Preparation:

3 grams of pure graphene, approximately 99.999% pure, were placed in an iron mould and pressed at 7 bar for 15 minutes, resulting in a disc of 1 cm in diameter and 3 mm thick.

2.2. The Experimental Set-up:

The experimental LIPS arrangement is shown in Figure 1. The system consists of a Nd:YAG laser source, a monochromatic time-resolved detector for plasma formation and target vaporisation. A 1064 nm beam with 9 ns pulse width and 6 Hz pulse repetition rate from a Q-switched Nd:YAG laser was used, emitting a laser pulse with 300–700 mJ energy. A 10 cm focal length convex lens was used to focus the laser beam on the target. The spectral dependence of the radiation emitted by the ablated plasma was detected and analysed with time resolution, using a Surwit spectrometer (S3000-UV-NIR) made by Surwit Technology Inc. This spectrometer is designed for spectrum analysis in food, chemistry, biology and many other fields. It has a wavelength range (190nm–1100nm), Detector (TCD1305 UV enhanced CCD) and grating rate of 600 grooves/mm at 250nm and 750nm. Over a wavelength range of (200-600) nm, each spectrum was obtained.

Figure 1: The scheme of the experimental set-up used in LIPS



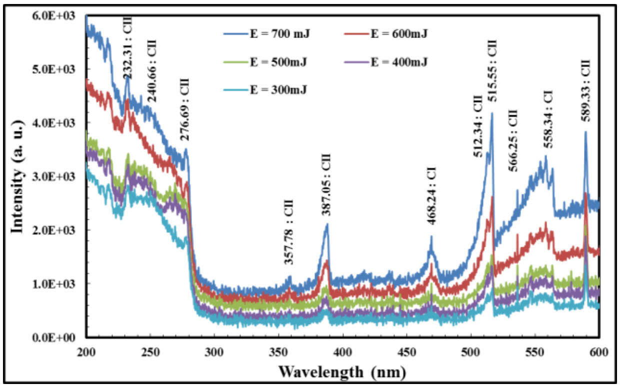
3. Result and Discussion

3.1. Optical Emission Spectra of Graphene Plasma in Air:

We calculated the fundamental parameters of the plasma T_e and N_e using the ratio between two spectral lines and the Saha-Boltzmann method from the spectroscopic study of many transition lines. Two spectral lines, C(I) and C(II), were used under the presumption of local thermodynamic equilibrium (LTE) at 468.24 nm and 515.55 nm. The spectroscopic parameters of the lines used to measure electron temperature are mentioned by Kramida et al. (2020) (National Institute of Standards and Technology (NIST) Atomic spectra database. 2019). The plasma electron number density was estimated at 468.24 nm, and 515.55 nm from the Saha-Boltzmann method of the C(I) and C(II) transition. This spectrum was acquired when the laser pulse arrived on the sample surface at 9 s gate delay and was analysed using the NIST database.

Figure 2 displays the portion of the graphene emission spectra obtained using the Nd:YAG laser's specific wavelength (1064 nm). At approximately 8×10^{12} W/cm^2 laser irradiance, these spectra range between 200 nm to 600 nm. The analysis reveals that most of the neutral graphene emission lines lie in visible regions and are near infrared, while single graphene ionised lines are observed in the UV field of the spectrum. The analysed spectra were used in the calculation of electron temperature and electron number density.

Figure 2: The single pulse emission spectra of graphene emitted by the 1064 nm laser at different laser energies.



3.2. Electron Temperature (T_e) and Electron Number Density (N_e) Diagnostics:

Electron temperature and electron number density are the basic parameters used in studying the complex phenomena found in plasma. These parameters are determined when the plasma is in an LTE state. The collisional excitations in LTE are more dominant than the radiative transitions and the Boltzmann distribution is followed by the population of the excited states. Therefore, the ratio between two spectral lines (Khalaf and Hmood 2020) can be used to calculate the plasma temperature.

$$T_e = \frac{-(E_1 - E_2)}{k \ln\left(\frac{I_1 \lambda_1 A_2 g_2}{I_2 \lambda_2 A_1 g_1}\right)} \qquad (1)$$

where I_1 and I_2 is the intensity, g is the statistical weight, (A_1 and A_2) is the transition probability, λ is the wavelength, (E_1 and E_2) is the energy of excited state in eV and k is Boltzmann constant.

To understand the dissociation of ionisation and excitation processes taking place in plasma, electron temperature determination is important. Most of the outer electrons of the atoms get excited as the laser light interacts with the target surface. Bond splitting occurs and evaporation of the target material takes place as the energy is greater than the binding energy of the target material. Thus, without the knowledge of the total number density or the partition function, the electron temperature can be calculated. The electron temperature of the plasma reached about 1.544 eV at the surface of the material 10 cm away, then it decreased and became 1.462 eV. These are shown in Figure 3 in the case of the first wavelength (1064 nm). This higher temperature value is due to the absorption by the electrons of the laser radiation by the reverse absorption mechanism of bremsstrahlung. Also, this activity was due to the transfer of laser thermal energy to electron kinetic energy because of the rising forward peak of laser energy with a steady laser spot duration. The Saha-Boltzmann equation of the emitted species (Khalaf and Hmood 2020)The expression used for electron density calculation is:

$$n_e = \frac{I_1}{I_2^*} 6.04 \times 10^{21} (T)^{3/2} e^{\frac{(E_1 - E_2 - X_Z)}{kT}} \qquad (2)$$

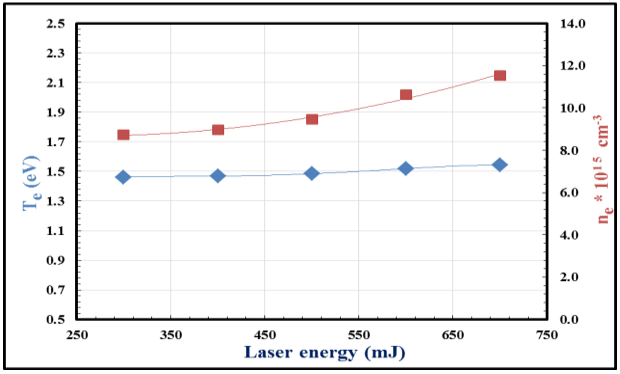
X_z : is the ionisation energy in eV

A significant parameter used to characterise a plasma environment is electron density, which is also critical for maintaining thermodynamic equilibrium. Using the Saha- Boltzmann equation, the electron density (n_e) in the plasma can be calculated from the emission coefficient and strength of spectral lines. The density of the electron number varied by approximately 11.5×10^{15} cm^{-3} at the energy of 700 eV, and then decreased to reach 8.7×10^{15} cm^{-3} at the energy of 300 eV, as shown in Figure 3. The absorption of laser photons in plasma by electron-neutral inverse bremsstrahlung (IB) can be due to this rise in electron density as laser energy increases. The excitation and ionisation temperatures increase as the energy consumed increases, as does the plasma's electron density (Abbas 2019). The parameters of graphene spectral lines plasma are tabulated in Table 1 by using equations 1 and 2.

Table 1: The variation of electron temperature and electron number density at different laser energies of graphene plasma

Laser Energy (mJ)	T_e (eV)	$n_e \times 10^{15}$ (cm^{-3})
700	1.544	11.5
600	1.518	10.6
500	1.484	9.4
400	1.469	9.0
300	1.462	8.7

Figure 3: The alternating temperature of the electrons and the density of the electrons relative to the change of the laser energies.



3.3. Effect of Laser Energy on the Other Plasma Parameters:

The effect of laser energy on Debye length and the plasma parameter determined using equations 3 , 4 and 5, respectively are described in this section (Ahmed et al. 2020).

$$f_p = \sqrt{\frac{e^2\, n_e}{m_e\, \varepsilon_o}} \tag{3}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_o\, k\, T_e}{n_e\, q_e^2}} \cong 7430 * \left(\frac{T_e}{n_e}\right)^{1/2} \tag{4}$$

$$N_D = \frac{4}{3}\, \pi\, \lambda_D{}^3 n_e \tag{5}$$

Where n_e is the density of the electron, T_e is the electron temperature, ε_o is permittivity of free space, k is Boltzmann constant and e is the electro$_n$ charge.

Table 2 shows the measured plasma frequency (f_p), Debye duration (λ_D) and Debye number (N_D) for the graphe$_{ne}$ target at various laser pulse energies.

Figures 4 and 5 illustrate the variation of the graphene plasma parameters referred to in paragraph 3 above in relation to the change in laser energies. It is evident from the above that these parameters have a close and solid relationship with both the temperature of the electron and the density of the electron. This is evidenced by the above equations as the frequency depends entirely on the density of electrons and is directly proportional to it, so it increases while the other parameters decrease, resulting in the fact that the spectrum developing from the interaction of the laser with the material of graphene was the spectrum of the plasma.

Table 2: The variation of plasma frequency (f_p), Debye duration (λ_D), and Debye number (N_D) at different laser energies of graphene plasma

Laser energy (mJ)	$f_p \times 10^{11}$ (Hz)	$\lambda_D \times 10^{-3}$ (cm)	$N_D \times 10^7$
700	9.646	0.798	2.457
600	9.254	0.825	2.499
500	8.729	0.865	2.559
400	8.497	0.884	2.589
300	8.394	0.892	2.602

Figure 4: The influence of Laser energies on plasma frequency (f_p) and Debye length (λ_D) of graphene plasma

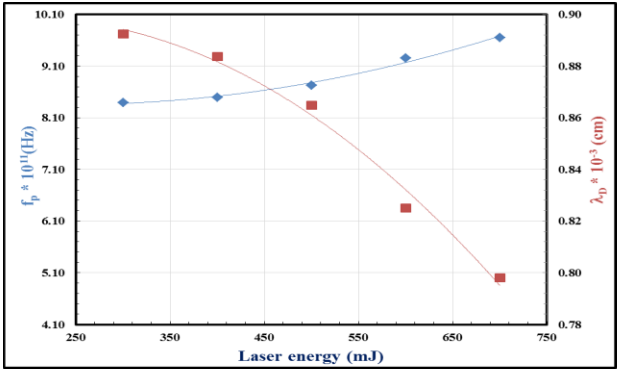
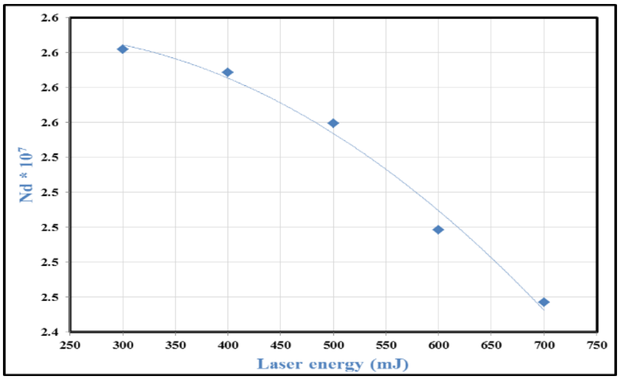


Figure 5: The influence of Laser energies Debye number (N_D) of graphene plasma



4. Conclusions

The improvement made by experimenting with laser-induced plasma properties has been critically assessed in this article. The emission has been recorded using a wavelength range of 200 nm–600 nm. Determining plasma physical parameters was accomplished using optical emission spectroscopy. Also, the Nd:YAG laser strength effects of graphene plasma T_e and n_e were analysed in this paper. The present findings show that the increase in laser energy indicates an increase in the intensity of the emission line for the target. Using1064 nm, the electron temperature was determined in the case of the laser-induced plasma in air, the values of T_e, ne and f_p were increased while the values of λ_D and N_D were decreased in laser-induced plasma in air.

Biography

Madyan Ahmed Khalaf

Department of Physics, College of Science, Mustansiriyah University, Baghdad, Iraq, 009647906813456, madyan.a@uomustansiriyah.edu.iq

Mr. Khalaf is an assistant lecturer in the Department of Physics, College of Sciences, Al-Mustansiriyah University and is a university faculty member. He obtained his master's degree from the College of Science, Al-Mustansiriyah University, with a degree of distinction. He obtained a bachelor's degree, with honours, and has many papers published in Scopus-indexed journals. He specialises in plasma physics. He also has experience in the field of nanotechnology and has published a research paper on this subject in an important Iraqi scientific journal.

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