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Signal enhancement of neutral He emission lines by fast electron bombardment of laser-induced He plasma

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A time-resolved spectroscopic study is performed on the enhancement signals of He gas plasma emission using nanosecond (ns) and picosecond (ps) lasers in an orthogonal configuration. The ns laser is used for the He gas plasma generation and the ps laser is employed for the ejection of fast electrons from a metal target, which serves to excite subsequently the He atoms in the plasma. The study is focused on the most dominant He I 587.6 nm and He I 667.8 nm emission lines suggested to be responsible for the He-assisted excitation (HAE) mechanism. The time-dependent intensity enhancements induced by the fast electrons generated with a series of delayed ps laser ablations are deduced from the intensity time profiles of both He emission lines. The results clearly lead to the conclusion that the metastable excited triplet He atoms are actually the species overwhelmingly produced during the recombination process in the ns laser-induced He gas plasma. These metastable He atoms are believed to serve as the major energy source for the delayed excitation of analyte atoms in ns laser-induced breakdown spectroscopy (LIBS) using He ambient gas. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4960991]

INTRODUCTION

The advantages of using helium ambient gas for improving the analytical performance in LIBS have been widely reported in the published literature dating back to early 1990s.1–4 In the more recently reported studies, the uses of helium ambient gas in a variety of experimental arrangements and applications have been further demonstrated. In particular, favorable results have been reported for the analyses of halogens.5–8 Besides, the highly sensitive hydrogen analysis of Zr and Ti using...
He ambient gas have also been reported previously. Those favorable effects of He ambient gas have been elucidated to be closely related to the crucial role of a He metastable excited state (He*) which serves as a temporary energy reservoir for the subsequent excitation of the ablated analyte atoms. Further, the triplet He* was suggested to play the major role since the He I 587.6 nm emission associated with transition from the triplet excited state has much stronger intensity than that of He I 667.8 nm emission from the singlet excited state. However, no report has so far been published on the explicit identification of the specific major He* species produced in the laser-induced plasma. What is known in the literature until now is the report of Horiguchi et al. on their observation of the transient variation of He* population in the He gas plasma generated by pulsed electric discharge. Using the Hook method, they were able to indicate that the population of triplet He* measured in the period after the cessation of the discharge current is nearly two orders of magnitude larger than the singlet He* population. The aim of this study is on the other hand devoted to reveal a more direct evidence for the dominant production of triplet He* over its singlet species in laser induced He plasma.

For this purpose, the time-dependent emission intensities of He I 587.6 nm and He I 667.8 nm are measured using the orthogonal double pulse LIBS set-up similar to the one adopted previously, but using the two lasers to serve different functions in the present experiments as explained in the following section.

**EXPERIMENTAL PROCEDURE**

A schematic description of the experimental set-up is reproduced in Fig. 1 for easy reference. The set-up features two orthogonally configured Nd-YAG laser systems. The ns laser (Quanta Ray, LAB 130-10, 1,064 nm, max energy of 450 mJ, FWHM 8 ns) is operated in the Q-switched mode at a fixed energy of 80 mJ (after attenuated by using a series of neutral density attenuator). It is positioned above the target and focused by a lens of focal length of 120 mm to deliver a power density of 25 GW/cm² for the generation of He gas plasma in the chamber at a spot 5 mm in front of the metal target. The chamber used in this experiment was specially designed and constructed as described...
The pressure of the high purity He gas (Air Liquid, 6N) inside the chamber is maintained at 760 Torr with a constant He flow rate of 3.5 l/min. The mode locked ps laser (EKSPLA, PL 2143, 1,064 nm, max energy of 30 mJ, FWHM 20 ps) which is also operated in the Q-switched mode at a fixed energy of 25 mJ is focused by a quartz lens of 120 mm focal length on the target with a spot size of 160 µm yielding an effective power density of 100 GW/cm². This ps laser pulses are employed to produce the fast electron from the laser ablated zircaloy target for further excitation of He by the fast electron bombardment. This two-laser arrangement is different from the conventional double pulse experiments\textsuperscript{20–30} where the two lasers are employed for direct ablation and further excitation of the ablated atoms. Although the ps laser is employed to serve the specific role of producing fast electrons from the target, its irradiation on the target will inevitably generate emission from the ablated atoms and the He atoms in the ambient gas near the target surface. In order to prevent the unwanted interference from those emission processes near the target surface, a mask is used as shown in Fig. 1 and the effectiveness of its blocking function is experimentally verified. While both lasers are simultaneously operated in all measurements performed in this experiment, they are selectively block according to the specific mode of each measurements as specified later. The emission spectra of the He plasma are collected by an optical fiber of 10 µm diameter with its entrance end fixed inside the chamber at a position about 2 cm sidewise from the He plasma. The other end of the optical fiber is connected to a spectrograph (McPherson, model 209, Czerny Turner configuration, f = 100 cm, slit width 10 µm). One of its dual output ports is connected to a photomultiplier tube (Hamamatsu model IP-28 with 2 ns response time) for time-dependent intensity measurement of the specific He emission line. The other output port is connected to an intensified charge coupled device (ICCD) (Andor i*Star intensified CCD 1,024x256 pixels) for the detection of emission spectra with a high spectral resolution of better than 0.018 nm.

RESULTS AND DISCUSSION

In connection with the use of fast electrons ejected with the ps laser pulse for the excitation of He atoms in the He gas plasma, it is worthwhile to show that the process is indeed physically reasonable. This is related to the ionization processes of the ablated target atoms, which are roughly classified by the dimensionless Keldysh parameter $\gamma$ determined by the following formula\textsuperscript{31,32}

$$\gamma = \sqrt{\frac{4\pi^2 m_e e^3}{e^2}} \sqrt{\frac{E_I}{\lambda^2 I}}$$

where $E_I$ is the ionization energy of Zr (7 eV), $I$ is power density of the laser irradiation on the target surface (100 GW/cm²), $\lambda$ is the central wavelength of the laser (1,064 nm). The numerical value of the prefactor in the Keldysh formula can be calculated from the self evident physical constants. The calculation yields the result of $\gamma = 21$ is much larger than 1. It implies that the ionization is induced by a multiphoton process and can be regarded as above-threshold ionization (ATI) process which produces the energetic electrons needed for the Helium excitations observed in the experiment.

As mentioned in the previous papers,\textsuperscript{18,33,34} the He I 587.6 nm emission line was consistently found to dominate over the accompanying He I 667.8 nm signal in the experiments. The spectrum measured without activating the ps laser is presented in Fig. 2 by using low resolution OMA system (spectrograph of focal length 150 mm) in order to capture the wide spectral range of He emission. It is clearly seen that the most dominant triplet He emission line is He I 587.6 nm (T) and the most dominant singlet He emission line is He I 667.8 nm (S). The time-dependent characteristics of these two emission lines and the comparison between them are therefore the focuses of this study. The time variations of the He I 587.6 nm emission intensity are measured with an oscilloscope under the irradiations of either the ns laser alone, ps laser alone, or both lasers with certain time delays in between as specified later. Fig. 3(a) shows the oscilloscope trace of the time-dependent He I 587.6 nm emission intensity associated with the transition from the 3D triplet state of He atoms under the sole irradiation of the ns laser. Fig. 3(b) displays the time profile of the same He emission intensity recorded with the ps laser irradiation started 3 µs after generation of the He gas plasma by
FIG. 2. Emission spectrum of He gas plasma obtained by operating ns laser only, and using low resolution spectrograph of focal length 150 mm together with an OMA system operated at 200 ns gate delay and 50 µs gate width.

the ns laser, while Fig. 3(c) shows the intensity time profile of the same emission line under the irradiation of ps laser alone. The considerably shorter emission duration of less than 1 µs as indicated in Fig. 3(c) is due to the larger scale unit (four times the unit used in Figs. 3(a) and 3(b)) use in this figure such that the long emission tail is largely swamped by the background. It is important to add that comparison between the photos presented below the intensity profiles in Figs. 3(a) and 3(b) also indicated the signal enhancement effect of the ps laser irradiation. It is worthwhile to recall that upon the ps laser irradiation on the target, an orange emission of He I 587.6 nm does appear from a small plasma just in front of the target surface as mentioned earlier. This is shown by the plasma photo below the intensity profile in Fig. 3(c), which is taken near the target surface.

A comparison between Fig. 3(a) and Fig. 3(b) clearly shows perceptible intensity gain of He I 587.6 nm emission line starting with a little delay of several tens of ns which is just about the time
needed by the fast electrons to arrive at the He plasma. By subtracting the signal of Fig. 3(b) from that of Fig. 3(a), the resultant difference (shaded area in Fig. 3(b)) represents the gain due to electron excitation of the He atoms in the relatively long lived excited state (2^3P state in this case). It should be stressed in this connection that the possibility of direct excitation of He atoms in the gas plasma by the ps laser is very small, as the ps laser is tightly focused on the surface of the metal target and hence the ns laser generated He gas plasma is really out of the focus from the ps laser beam in its passage to the target. Besides, if the enhancement were the result of ionization or excitation by the ps laser irradiation, the signal enhancement signal would have occurred right after the initiation of ps laser irradiation, instead of being delayed by a few tens of nanoseconds as recorded in the present experiment.

It is understood that the gain shown in Fig. 3(b) is the result of re-excitation of the lower energy end state 2^1P in the triplet 3^1D – 2^3P transition. The key to this gain is clearly the presence of He* in the 2^3P state which implies the availability of 3^1D He* in the He gas plasma. In other words, the intensity gain is proportional to the available amount of excited 3^1D He atoms produced in the plasma. The same process should also work for the singlet transition. Namely, an intensity gain of He I 667.8 nm emission line would also be observed if the He* atoms in singlet 2^1P excited state were also available in the He gas plasma, although this would occur at a different delay time due to different lifetimes of the excited states.

For the purpose of comparing those two processes, it is necessary to extend the experiment by repeating the same intensity measurement of both emission lines over a range of various time delays of the ps laser irradiation. The He emission enhancement signal induced by the fast electrons for each delay time is obtained by subtracting the results from the two modes of measurement displayed in Figs. 3(a) and 3(b). The difference in intensity counts at each delay time is then time integrated to give the intensity enhancement curves plotted in Fig. 4 for both He I 587.6 nm and He I 667.8 nm emission lines. As explained above, these two curves provide the useful information on the time-dependent population variations of the corresponding He* atoms produced in the ns laser-induced He gas plasma.

One readily observes from this figure the initial rapid rise of intensity enhancement of the He I 587.6 nm emission at shorter delay times of the ps laser irradiation. It reaches its maximum at 5 µs delay, followed by a rapid decay before flatten off at 10 µs delay of the ps laser irradiation. This implies that the initial increase of He* (He in 3^1D metastable excited state) population takes place right after the recombination process between He ions and electrons following the ionization of He

FIG. 4. Enhancement signals of He I 587.6 nm and He I 667.8 nm emission intensities versus time delay of ps laser irradiation with respect to initiation of the ns laser irradiation, which are deduced from emission peaks of the corresponding emission lines measured with the use of ICCD.
atoms by the ns laser. It is interesting to add that this is consistent with our previous experimental result showing the rapid decrease of He ions and electrons within 5µs after the laser irradiation. The following rapid decline of the He I 587.6 nm emission intensity within the short period of 5 µs -10 µs is likely due to the combined effect of decreased availability of the 2P state and Penning-like collision induced energy transfer between the newly excited 3D He* and the earlier de-excited He* in the gas plasma. In contrary, the enhancement of the He I 667.8 nm emission is seen to be much lower with relatively minor variation over the entire time span covered by the experiment.

CONCLUSION

Based on those experimental results presented above, we are led to conclude that the triplet metastable excited He atoms associated with the He I 587.6 nm emission are the most dominant product in the laser induced He plasma as previously found in the case of He gas plasma excited by pulsed electric discharge. This result has thus confirmed the previously suggested role of the metastable triplet excited state of He atoms as the major source for the subsequent energy transfer activated HAE process responsible for the delayed emission process yielding the sharp atomic emission lines practically free from continuum emission background as reported previously.

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