Introduction

Laser-induced breakdown spectroscopy (LIBS), in which emission spectra of sample species are observed and evaluated for elemental analysis, has been applied to a variety of analytical applications.\textsuperscript{1,2} Applications now spread over a wide range of different industrial and scientific fields, such as for the analysis of process control in metallurgical and ceramic industries, investigations on soils and rocks in geochemistry, detection of explosives, examinations on cultural heritage and archeology, forensic studies, and development of biological materials in the field of biomedicine.\textsuperscript{3–7} These applications are realized by several features of LIBS; namely, it can provide an analytical result rapidly with little sample pretreatments and under open air atmosphere during the measurement. LIBS also can be conducted with easily-handled and inexpensive devices, which can be integrated in portable or even handheld devices.\textsuperscript{1,6,8} In practice, LIBS becomes a powerful tool to carry out field investigations and on-site/in-line analyses, such as the determination of ore grade in a mining place and element-based sorting of scrapped metallic materials.\textsuperscript{9,10}

Along with the application fields to be widespread, a variety of academic studies on LIBS have been conducted. However, in relation to the fundamental mechanisms of this technique, several facets remain largely unclear, because the resultant plasma is too complicated to be explained by a simplified physical model. Typically, the plasma is repeatedly produced for a plasma duration period of several \( \mu \text{s} \), for which the excitation process would be varied dynamically. In fact, the behavior of the plasma, its evolution and the properties of the involved species (including their excitation and de-excitation paths) have very complex aspects. They are dependent on several internal and external conditions, such as the properties of the specimen, the laser source (e.g. energy, pulse duration, and wavelength), and the plasma atmosphere (e.g. composition of the plasma gas and pressure). As a matter of course, all these factors have an influence on the emission behavior of the laser-induced plasma (LIP) and thus determine the outcome of the LIBS experiment. Therefore, we should optimize these parameters in order to take advantage of the full potential of the LIBS technique. Naturally, this requires a deeper insight into the physical nature of the LIP, especially regarding the time-dependent characteristics with the progress of a pulsed plasma. Therefore, the demands of research for this viewpoint is exceptionally high.

Since a LIP varies spatially as well as temporally with the progress of plasma expansion after the laser shot, emission imaging may provide useful information in fundamental and application studies of LIBS. Several studies on the plasma images of LIP were reported using an emission spectrometer...
equipped with collimator optics.11–17 Bulatov et al. reported spectroscopic imaging of laser-produced plasmas for the first time, to investigate the characteristics of the spectral image at particular wavelengths.11 Vogt et al. reported time-resolved spectral images of a LIP in several pressure conditions to apply the LIBS measurement to field analysis, such as planetary surveys.12,13 Dawood et al. obtained two-dimensional (2D) emission images of an aluminum ionic line when a 308-nm nanosecond excimer laser was irradiated on an aluminum target.14 This research indicated that the plume of LIP was varied temporally and spatially by both plasma gas composition and their gas pressures. Zhu et al. suggested a simultaneous and multispot laser irradiation system combined with a 2D emission imaging which was detected with an ICCD detector in LIBS.15 Our previous papers reported 2D emission images of copper which were excited by LIP on a copper surface.16,17 A spatially resolved analysis of a selected Cu emission line was performed to give a wavelength dispersed 2D visualization of the plasma, indicating that the plasma expansion was strongly influenced by both the plasma gas type and the gas pressure.16,17 In this measurement, the experimental results were based on average emission intensities that were recorded over the whole lifetime of the plasma; therefore, no time resolution could be extracted from the data. The temporal emission images of LIP could provide important information on the excitation phenomenon occurring in the pulse-like laser plasma and also on the optimization of the experimental parameters. However, few scientific papers have been published with respect to a direct comparison of the temporal and spatial emission images between different plasma gases and pressures.

The aim of the present study is to obtain insights into the LIP through temporally and spatially measurements of a copper emission line. For this purpose, we employed a LIBS apparatus equipped with an intensified charge coupled detector (ICCD) having higher detection sensitivity as well as faster gating, as an alternative to normal CCD. We focused upon how the kind of plasma gases and their pressure levels affected the transient characteristics of the plasma after laser irradiation. With the temporally resolved measurements, intensity-time profiles were systematically obtained for the different plasma regimes, and provided significant information on the excitation/de-excitation phenomena occurring in the LIP.

**Experimental**

A schematic diagram of the setup applied in the LIBS experiments is depicted in Fig. 1. The laser source consisted of a Q-switched pulsed Nd:YAG laser (Minilite I, Continuum, UK) featuring a pulse width of 3 – 5 ns and an output wavelength of 532 nm (SHG mode). A repetition rate of 15 Hz was applied with a laser power of about 12 mJ/pulse. The energy of the pulsed laser was measured using a power meter for lasers, consisting of a thermal sensor (3A-P, Ophir, Israel) and the measuring unit (Nova, Ophir, Israel). The laser beam was bent on a reflective mirror (TFMH-25.4C05-532, Sigma Koki, Japan) and focused on the sample surface with a plano-convex lens (SLB-20-100P, Sigma Koki, Japan). A single shot of the laser left a crater having a diameter of about 150 μm.

A laboratory-made plasma chamber had a gas inlet, a vacuum port, a borosilicate glass window (OPB-50C05-1-5, Sigma Koki, Japan) at the entry of the laser beam, and a quartz glass window (OPSQ-40C02-1-5, Sigma Koki, Japan) at the exit pointing towards an imaging spectrometer. A specimen plate was placed on a sample stage inside the plasma chamber. Ahead of the experiment, the chamber was evacuated using a rotary vacuum pump (GLD-136A, ULVAC, Japan). The pressure in the chamber was monitored with a Pirani gauge (detection unit: GP-H, ULVAC, Japan; power supply and readout: GP-1000G, ULVAC, Japan) or a capacitance manometer (manometer: Baratron Type 626, MKS, USA; power supply and readout: Type 113, MKS, USA) which were placed between the vacuum port of the sample chamber and the vacuum pump. After evacuating down to a constant pressure of less than 20 Pa, high purity argon (>99.999% purity), krypton (>99.999% purity), helium (>99.99995% purity) or nitrogen (>99.9995% purity) was introduced into the chamber as the plasma gas, and the chamber pressure was adjusted with each leak valve. The experiments were conducted in a continuous flow of plasma gas at a constant pressure of 100, 300, 600, or 900 Pa.

All experiments were conducted with high purity copper plates (>99.99%, Nilaco, Japan) as the sample. As-received surfaces were irradiated by the laser beam. The plasma emission was collected and imaged through a collimator optics, dispersed by an imaging spectrometer (IMS-250TKW, Bunkou Keiki, Japan), which had a grating of 2400 lines/mm with an actual resolution of ca. 0.1 nm, and detected by an intensified charge-coupled device (ICCD) camera (DH734-18F-03, Andor, UK). In that way, a 2D emission image...
could be obtained for a particular emission line. The spatial range of the recorded 2D images amounted to an overall dimension of 300 × 300 pixels with an approximate pixel length of 21 pixels/mm. Additionally, the ICCD camera was coupled with the laser source via an external trigger to allow for a time-gated detection, as illustrated in Fig. 2. The standard emission measurements were conducted with a gate width (duration time of recording) of 100 ns and delay times of 100, 300, 500, and 1000 ns after the onset of the initial laser pulse. For all experiments, an exposure time of 2 s was applied and the intensities for the 30 repetitive laser pulses (at the laser frequency of 15 Hz) were integrated on the chip of the ICCD camera. The maximum gain of the detector was selected for the majority of the measurements; however, the gain was appropriately reduced in case of saturation of the ICCD camera for certain measurement conditions.

Optical transitions between the 3d^4p and 3d^4s electron configurations of singly-ionized copper give rise to many emission lines of Cu II in a wavelength range of 195 – 250 nm. 18 The Cu II 224.700-nm line, which is assigned to an optical transition from the 3d^4p ^3P_2 (8.2347 eV) to 3d^4s^2 ^1D_2 (2.7187 eV), is the most sensitive in these emission lines. 19 Because of the high excitation energy of the corresponding upper level (8.23 + 7.73 eV), the population would be determined mainly by initial energy transfer from the laser beam and any recombination processes during the decay period would be ignored. Further, the Cu II 224.700 nm is free from self-absorption due to a non-resonance transition of ionic copper species. From these straightforward characteristics, this Cu II line was selected for the spectral imaging of the LIP.

A series of ten replicates was conducted for each measurement condition. Prior to each series, background intensities were determined by blocking the path of the laser beam, so that no light of the plasma could reach the detector. The 2D background images were directly subtracted from the 2D data of plasma emission using the built-in calculation program (Solis, Andor, UK). The raw data were obtained in the form of (300 × 300) matrices representing the relative emission intensity for each distinct pixel of the ICCD device. The data evaluation was performed using analysis software (OriginPro 2019b, OriginLab Corporation, USA).

For every data point, an average matrix was calculated out of the ten replicates. Thereafter, normalization was performed within each series of delay times (from 100 to 1000 ns). The data points of the average matrices for a delay series were normalized to a range from zero to unity by using Eq. (1). For that, a matrix with the highest distinct maximum intensity was first determined (usually the 100-ns matrix). Then, this maximal matrix intensity was set to 1 and the minimal matrix intensity of the same matrix to 0 (negative matrix values were not considered).

\[ I_{\text{norm}} = \frac{(I - I_{\text{min}})}{(I_{\text{max}} - I_{\text{min}})} \quad \text{SD}(I_{\text{norm}}) = \text{SD}(I)/(I_{\text{max}} - I_{\text{min}}), \]  

where \( I_{\text{min}} \) and \( I_{\text{max}} \) denote the minimum and maximum average intensities within the series of four delay times, in estimation of the normalized intensity, \( I_{\text{norm}} \), and the corresponding standard deviations, SD.

Subsequently, the normalized data were visualized in the form of intensity contour plots (spatial intensity profiles). For that, a natural logarithmic intensity scale comprising 15 partitions was applied. A cut-off level of 10% of the maximal intensity in the scale was utilized. The intensity increments were roughly represented using different colors from blue to red. Furthermore, overall intensities of the 2D images were calculated by summation of the distinct average matrix values. For comparison reasons, the integrated intensities of the four delay times regarded for each measurement condition were normalized to a range between 0 and 1 using Eq. (1).

Results and Discussion

Emission profiles of the Cu II 224.700 nm line in different plasma gas atmospheres

We observed 2D plasma images for the normalized emission intensities of the Cu II 224.700-nm line, for different plasma gases of argon, krypton, nitrogen, and helium, when the measurements were conducted at delay times of 100, 300, 500, and 1000 ns. In this case, the gas pressure in the chamber was fixed at 300 Pa. Figure 3 shows the contour plots for the single delay times at a constant intensity scale over time (which is based on the delay of 100 ns), and in Fig. 4, their intensity scales are adjusted for every time delay to make it easy to see weaker intensity profiles. These emission profiles represent a temporal decay of the emission intensity and an expansion of the resultant plasma. This effect can be easily related to the general behavior of the LIP, as previous research already mentioned that the excitation conditions decay rapidly and monotonically along with the plasma expansion. 24 Unnikrishnan et al. reported the temperature and electron density of a LIP produced by a 355-nm pulsed Nd:YAG laser when it was irradiated onto a copper solid sample in air at atmospheric pressure. 20 Atomic and ionic lines of copper were measured with delay times of 300 – 2000 ns, indicating that the excitation temperature decreased in delay times of 700 – 1000 ns. However, it should be noted that our emission profiles, shown in Figs. 3 and 4, exhibit a large difference between the four atmosphere gases.

In terms of the emission intensity decay, a clear distinction can be made between on the one hand argon and krypton and on the other hand helium and nitrogen. As visualized in Fig. 3, the intensity quenching in argon and krypton is significantly less pronounced than in helium and nitrogen atmosphere. In fact, as compared to the starting intensities at 100 ns, the emission intensities at 1000 ns lay in the region of 20% for argon and krypton while large decays to less than 3% are observed for helium and nitrogen (cf. the adjusted intensity scales in Fig. 4). In order to validate this behavior systematically, the distinct intensities for each contour plot were estimated by normalizing.
Fig. 3 Normalized intensity profiles of the Cu II 224.700 nm emission line at four delay times for different plasma gases at 300 Pa (from the left column: Ar, Kr, N₂, He) when a constant intensity scale is set for each plasma gas.

Fig. 4 Normalized intensity profiles of the Cu II 224.700 nm emission line at four delay times for different plasma gases at 300 Pa (from the left column: Ar, Kr, N₂, He), when their intensity scales are adjusted to the maximum intensity for each delay. The white supporting lines refer to the height of the Ar profiles.
Fig. 5 Plot of the normalized integrated emission intensities of the Cu II 224.700 nm emission line against the delay time for different plasma gases: argon (square), krypton (circle), helium (triangle), and nitrogen (inverted triangle), when the gas pressure is fixed at 300 Pa. Error bars represent the single standard deviation ($n = 10$).

and then integrating the signal intensity of all the pixels in the detector. Figure 5 shows plots of the overall intensity of the Cu II line against the delay time for different plasma gases. The error bars in Fig. 5 were estimated from the standard deviation of the intensity in ten individual measurements. The plots clearly indicate that the emission intensity quenching in helium and nitrogen follows an exponential decay, whereas such simple decays cannot be observed for the plasma gases of argon and krypton. Assuming that the population of copper in the plasma linearly relates to the emission intensity, the number density of the excited species decreases down to less than 10% during a duration from 100 to 500 ns in the helium and nitrogen plasmas, while ca. 50% of the excited species remains in the krypton and argon plasmas.

Apart from the differing behavior in emission quenching, Fig. 4 reveals a discrepancy in the spatial distribution of the emission intensity in the four atmosphere gases. For a delay of 100 ns, only slight differences can be observed in the shape and spatial expansion of these emission profiles. Contrarily, for longer delay times, a highly dispersed emission shape evolves under helium atmosphere while the profiles stay rather compact in argon, krypton and nitrogen. Among the latter, the most compacted plasma emission is observed in krypton where only a slight expansion occurs between 100 and 1000 ns. The profiles under nitrogen atmosphere are similar in dimension to krypton while the emission shape in argon is more dispersed (see white lines in Fig. 4).

In order to explain these emission behaviors, we should consider several fundamental processes involved in the excitation/de-excitation of copper species as well as gas species. Initially, the focused irradiation of a laser pulse, having an incident energy of $E$, produces highly energetic particles at a localized hot breakdown zone just above the irradiated surface, due to inverse bremsstrahlung and thermal excitation: $^{10}$

$$\text{Cu} + \text{E (laser incident energy) } \rightarrow \text{Cu}^+ + e^- \quad \text{(high kinetic energy)} .$$  

$$\text{Cu}^+ + e^- \rightarrow \text{Cu}^{++} + z^+ , \quad \text{(2)}$$

$$\text{G} + \text{E (laser incident energy) } \rightarrow \text{G}^+ + e^- \quad \text{(high kinetic energy)} .$$  

$$\text{G}^+ + e^- \rightarrow \text{G}^{++} + z^+ , \quad \text{(2')}$

where $G$ is an atom/molecule of gas species, and $z^+$ means highly-ionized species of copper and plasma gas.

At the same time, collisional recombination occurs leading to emission of an unspecified background continuum (mainly caused by bremsstrahlung) and finally to neutral excited species of copper and plasma gas, indicated with an asterisk (*):

$$\text{Cu}^{++} + e^- \rightarrow \text{Cu}^{++} + \text{hv(continuum)} \ldots \rightarrow \text{Cu}^+ + e^- \rightarrow \text{Cu}^*, \quad \text{(3)}$$

$$\text{G}^{++} + e^- \rightarrow \text{G}^{++} + \text{hv(continuum)} \ldots \rightarrow \text{G}^+ + e^- \rightarrow \text{G}^*. \quad \text{(3')}$

Since these processes occur within or shortly after the laser pulse, they considerably contribute only to the plasma profiles of 100 ns. In fact, as shown in Fig. 5, the intensity profiles at the initial stage show a high similarity in their shapes, regardless of the plasma gas type. Therefore, it can be assumed that the nature of the mechanisms in Eqs. (2) and (3) is commonly preserved in all surrounding atmosphere gases.

Parallel to the excitation mechanism of Eqs. (1) and (2), excited atomic and ionic copper species are also formed by collisions with high energy particles. Besides free electrons, excited species of the plasma gas can act as the energy donor. Apart from direct collisional impact, where kinetic energy of the donor (free electron or gas particle with high kinetic energy) is transferred (Eq. (4)), an internal energy transfer from excited gas particles can occur as well, such as a Penning-type collision (Eq. (5)) and a charge-transfer collision (Eq. (6)): $^{21,22}$

$$\text{Cu} + e^- \rightarrow \text{Cu}^+ + 2e^- \quad \text{(low kinetic energy)} .$$  

$$\text{Cu} + \text{G} \rightarrow \text{Cu}^+ + \text{G} \quad \text{(low kinetic energy)} + e^- . \quad \text{(4)}$$

$$\text{Cu} + \text{G}^+ \rightarrow \text{Cu}^+ + \text{G}^+ + e^- . \quad \text{(5)}$$

$$\text{Cu} + \text{G}^+ \rightarrow \text{Cu}^+ + \text{G} . \quad \text{(6)}$$

Finally, a de-excitation process between the excited levels results in emission of Cu II 224.700 nm as in the following equation:

$$\text{Cu}^+ \rightarrow \text{Cu}^{++} + \text{hv(continuum)} \ldots \rightarrow \text{Cu}^{++} + \text{hv(continuum)} \ldots \rightarrow \text{Cu}^{++} + \text{hv(continuum)} .$$  

With increasing delay time after the laser pulse, the plasma expands and gradually cools down. At that time, the processes involved in Eqs. (2) and (3) are no longer present and excitation mechanisms based on Eqs. (4) - (6) are the main source for excited atomic and ionic copper species. On the other hand, the number density of high energy particles drastically decreases with the progress of the spatial expansion. This is especially the case for free electrons that exhibit high cross sections for recombination with charged particles. In contrast, particular excited states of gas species, called metastable states, should possess longer lifetimes. Hence, they can provide their internal energy for the reactions in Eqs. (5) and (6) even after comparatively long delays times.

Due to that relationship, it can be assumed that the interactions between the highly excited particles, which are created during the plasma breakdown (i.e. at the beginning of the LIP), and the surrounding gas have a major influence on the shape and the intensity of the copper emission for late delay times.$^{16,17}$ In fact,
these interactions are highly dependent on the physical and spectrochemical properties of the supporting gas for the plasma. The so-called stopping power of the gases, i.e. the amount of kinetic energy that a highly energetic particle loses during expansion per distance, differs drastically between the four applied gases in the present study. Table 1 lists several physical properties of these gases.23–26 The thermal conductivity is a macroscopic physical quantity to indicate the extent to which gas species interact with each other, and is dependent on temperature: higher temperatures gradually increase the thermal conductivities.23 However, the temperature dependence is similar between argon, nitrogen and helium;26 namely, helium always has much higher thermal conductivity than argon and nitrogen. Therefore, the thermal conductivity at room temperature can be effective for discussions on LIP.

In a LIP under helium atmosphere, the high energy particles experience low interactions with the helium atoms and can expand mostly without loss of their kinetic energy to the gas. This is due to the low stopping power of helium which derives from its narrow collision profile, large mean free path length and high thermal conductivity (cf. Table 1). With regard to the emission of the Cu I 224.700 nm line, this leads to a widely spread emission profile for later delay times due to the low confinement of the plasma by helium, as seen in Fig. 4. Furthermore, a fast temporal decay of the emission intensity can be observed (cf. Fig. 5). This is because the excitation of copper species almost solely occurs through the very short-lived, highly energetic free electrons formed during plasma breakdown in the early stage of the LIP. The other gases, argon, krypton and nitrogen, have significantly higher stopping powers resulting in very confined emission profiles compared to helium. The gases with the highest stopping powers, which can receive kinetic energy more effectively, are krypton and nitrogen due to their large collisional profile, short mean free path length and rather easily accessible excitation levels (cf. Table 1). In these gases, high energy particles transfer their energy at an early stage of their expansion in near proximity to the breakdown zone. This results in the most compact emission profiles among all investigated gases, as shown in Fig. 4. For argon gas, more dispersed shapes of the copper emission are observed. This matches with the lower stopping power of argon compared to krypton and nitrogen, due to the longer mean free path and less easily accessible energy levels, as shown in Table 1.

The temporal behavior of the copper emission intensity in the argon, krypton and nitrogen plasmas may be explained by the effects of stopping power as well. In addition, considerable amounts of excited, relatively long-lived gas species are present even in the expanded plasma (formed through direct collisional excitation by high energy particles like free electrons). For argon and krypton, this results in a significantly slower decay of the ionic copper emission lines, as found in Fig. 5. This can be explained by the assumption that the excited gas species can act as an energy reservoir with comparably long lifetime, where they can have internal energy in their particular excited levels.16,22 Subsequently, collisional energy transfer to copper species occurs, leading to the intensity of the copper ionic line observable for late delay times. The situation in nitrogen gas, however, represents an exception. Due to its high stopping power, condensed emission profiles are observed, indicating a large interaction between nitrogen molecules and expanding high energy particles. Therefore, high number densities of excited nitrogen species can be expected. However, the temporal intensity decay proceeds in an exponential way comparable with helium gas, as indicated in Fig. 5. This leads to the conclusion that, although present in considerable amounts, the excited nitrogen species would perform less significant energy transfer to copper. A reasonable explanation for this behavior might be found in the molecular, diatomic character of nitrogen. In contrast to the monoatomic gases, argon and krypton, nitrogen molecule possesses rotational and vibrational degrees of freedom, resulting in a large number of vibrational/rotational energy levels. Therefore, paths of non-radiative thermal deexcitation become available that are not accessible for the noble gases. This effect contributes to a rapid self-quenching of the nitrogen LIP, which would produce the excited species for collisional energy impact to copper less sufficiently. This can explain the strong temporal decay of the ionic copper line in nitrogen since excited copper species are mainly formed by direct impact of free electrons shortly after the laser pulse. The impact of the excited nitrogen molecules on the formation of excited copper species at the expansion stage of the LIP is comparably low.

**Pressure dependence of the emission profiles of the Cu II 224.700 nm in different gas atmospheres**

Besides the type of the plasma gas, another important parameter is the pressure level of the supporting gas surrounding the plasma. For example, it was found in our previous work that the gas pressure of the plasma atmosphere gas has a strong influence on the spatial evolution and the emission of the LIP.

In order to find out more about this relationship, experiments were conducted at different pressure levels of the four plasma gases. Figures 6 and 7 show 2D maps of the normalized emission intensity of the Cu II 224.700 nm line at different pressure levels of krypton and helium atmosphere. Different delay times and atmosphere pressures between 100 and 900 Pa (600 Pa for helium, respectively) were applied. Figures 8 and 9 show variations in the integrated and normalized emission intensities as a function of the delay time in the krypton and helium plasmas.

The emission profiles of krypton as well as of helium clearly indicate high discrepancies between the different pressure levels. In general, low pressure results in larger dispersion of the emission profiles while more compact shapes can be observed for higher gas pressure levels. Analogous trends were also found for experiments with argon and nitrogen atmosphere (data not shown). This can easily be explained by the stronger confinement of the plasma for more compressed gas atmospheres. In gases with higher pressure, the mean free path length decreases and therefore more collisions between high energy particles and copper occur close to the breakdown zone. At lower pressure levels, the energy carriers, such as free electrons

|                      | Argon          | Krypton        | Helium         | Nitrogen (N₂)  |
|----------------------|----------------|----------------|----------------|----------------|
| Mean free path (m) at 273 K and 300 Pa | 2.13 × 10⁻⁵ | 1.63 × 10⁻⁵ | 5.83 × 10⁻⁵ | 1.97 × 10⁻⁵ |
| Thermal conductivity (W/m K) at 298 K | 0.0176²² | 0.0093²² | 0.155²² | 0.0257²² |
| Ionization energy (eV) | 15.76²³ | 14.00²³ | 24.59²³ | 15.58²⁴ |
Fig. 6  Normalized intensity profiles of the Cu II 224.700 nm line for Kr atmosphere at different pressure levels (from left: 100, 300, 600, 900 Pa) and delay times, when a constant intensity scale is set for each pressure condition.

Fig. 7  Normalized intensity profiles of the Cu II 224.700 nm line for He atmosphere at different pressure levels (from left: 100, 300, 600 Pa) and delay times, when a constant intensity scale is set for each pressure condition.
and excited gas particles with high kinetic energy, can travel longer distances before collisional energy transfer occurs. Therefore, the emission profile becomes more dispersed with decreasing pressure of the plasma gas.

An interesting facet of the pressure dependency is the difference in the course of the intensity decay. In helium atmosphere, a lower pressure level leads to faster decay of the Cu II line reaching lower maximal intensities after 1000 ns, as found in Figs. 7 and 9. This can be explained with the very low confinement of the LIP for low pressure levels, which causes a fast dispersion of the plasma energy through less interactions with fast electrons and therefore rapid cooldown. Hence, shorter lifetimes of the high energy particles involved in the copper excitation can be expected. In krypton atmosphere, however, the trend was contrary (similar trends were also observed in argon atmosphere). The fastest decay of emission intensity could be observed at 900 Pa, as found in Fig. 8. The condition of 900 Pa also featured the lowest remaining maximal intensity at 1000 ns. According to the emission profiles, in krypton, all investigated pressure levels showed a considerably high amount of plasma confinement. Assuming that the population of copper in the plasma linearly relates to the emission intensity, 25 - 45% of the copper excited species still remains at a delay time of 500 ns in the krypton LIP, whereas they almost disappear in the helium LIP regardless of the helium pressure. This implies that a relatively long-lived plasma is maintained for all pressure conditions of krypton, in contrast to the drastic decay in helium for 100 Pa. One possible explanation for these observations might be that the mean free path length for collisions actually decreases during the plasma expansion at higher pressure levels; however, in the krypton plasma, the collision partners for the excitation of the Cu II line would be still populated at the higher pressure levels. Therefore, the collisional energy transfer leading to copper excitation occurs closer to the breakdown zone and at an earlier stage of the plasma expansion. This might result in a shift of the copper emission to earlier delay.

![Fig. 8](image_url) Plot of the normalized integrated emission intensities of the Cu II 224.700-nm emission line against the delay time in Kr atmosphere at different pressure levels of 100 Pa (square), 300 Pa (circle), 600 Pa (triangle) and 900 Pa (inverted triangle). Error bars represent the single standard deviation ($n = 10$).

![Fig. 9](image_url) Plot of the normalized integrated emission intensities of the Cu II 224.700-nm emission line against the delay time in He atmosphere at different pressure levels of 100 Pa (square), 300 Pa (circle), and 600 Pa (triangle). Error bars represent the single standard deviation ($n = 10$).

![Fig. 10](image_url) Schematic drawing of the laser-induced plasma in Kr (a) and He (b) atmospheres to illustrate the degree of collisional interactions with copper atom.
times with increasing atmosphere pressure, regardless of the type of plasma gas. Figure 10 illustrates a schematic drawing of the excitation phenomena of a copper atom, in comparison between krypton and helium atmospheric gas. An important factor for determining the excitation of the Cu II line is that the excited helium species causes weak collisional interactions with copper atoms in addition to the electrons leaving from the plasma region without any energy loss, compared to the strong interaction in the case of krypton.

Conclusions

This study confirmed that the temporal behavior of a laser-induced plasma on copper surfaces was strongly influenced by the type of plasma gases and their pressure levels. These 2D emission images indicated the course of plasma extensions after a single laser shot on the copper surface was significantly dependent on these experimental factors. Namely, very compact shapes were found in krypton and nitrogen while high dispersion of the emission profile occurred in helium, and the intensity decay in a pulsed plasma appeared less prominently in argon and krypton, compared to helium and nitrogen. These results could be principally explained by a difference in the stopping power between these plasma gases; however, it was affected also by the spectrochemical properties of the gases, such as the structure of their excited energy levels. This could explain the discrepancies for the LIP in argon and krypton atmospheres compared to nitrogen. Although having similar stopping powers, a significantly less rapid emission decay was observed in argon and krypton, most likely originating from internal energy transfer of copper with excited metastable gas atoms at late delays. In contrast, radiation-less thermal deexcitation among a large number of vibrational/rotational excited levels might be significant in molecular nitrogen, preventing energy transfer for the excitation of copper and therefore leading to a rapid decay of the copper emission. Regarding the pressure dependency of the LIP, rather compact emission profiles were observed for high pressure levels while lower pressure led to high dispersion of the emitting copper species.

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