Study of Hydrogen and Deuterium Emission Characteristics in Laser-Induced Low-Pressure Helium Plasma for the Suppression of Surface Water Contamination

12 AUTHORS, INCLUDING:

Munadi Muna
Universitas Diponegoro
7 PUBLICATIONS **16** CITATIONS

SEE PROFILE

Rinda Hedwig
Binus University
52 PUBLICATIONS **304** CITATIONS

SEE PROFILE

Maria Margaretha Suliyanti
Research Center for Physics -Indonesian Insti…
37 PUBLICATIONS **252** CITATIONS

SEE PROFILE

Zener Sukra Lie
University of Fukui
36 PUBLICATIONS **148** CITATIONS

SEE PROFILE

Study of Hydrogen and Deuterium Emission Characteristics in Laser-Induced Low-Pressure Helium Plasma for the Suppression of Surface Water Contamination

Munadi

Department of Mechanical Engineering, Faculty of Engineering, Diponegoro University, Tembalang Campus, Semarang 50275, Indonesia

Marincan Pardede, Rinda Hedwig, Maria Margaretha Suliyanti, Tjung Jie Lie, Zener Sukra Lie, and Koo Hendrik Kurniawan*

Research Center of Maju Makmur Mandiri Foundation, 40 Srengseng Raya, Kembangan, Jakarta Barat 11630, Indonesia

Kiichiro Kagawa

Department of Physics, Faculty of Education and Regional Studies, Fukui University, 9-1 Bunkyo 3-Chome, Fukui 910-8507, Japan

Muliadi Ramli and Kenichi Fukumoto

Program of Nuclear Power and Energy Safety Engineering, Graduate School of Engineering, Fukui University, Fukui 910-8507, Japan

Tadashi Maruyama

Integrated Research Institute, Tokyo Institute of Technology, 4259 Nagatsuda-cho, Midori-ku, Yokohama 226-8503, Japan

May On Tjia

Physics of Magnetism and Photonics Group, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, 10 Ganesha, Bandung 40132, Indonesia

An experimental study was conducted in search of the experimental condition required for the much needed suppression of spectral interference caused by surface water in hydrogen analysis using laser-induced low-pressure helium plasma spectroscopy. The problem arising from the difficulty in distinguishing hydrogen emission from hydrogen impurity inside the sample and that coming from the water molecules was overcome by taking advantage of similar emission characteristics shared by hydrogen and deuterium demonstrated in this experiment by the distinct time-dependent and pressure-dependent variations of the D and H emission intensities from the D-doped zircaloy-4 samples. This similarity allows the study of H impurity emission in terms of D emission from the D-doped samples and thereby separating it from the H emission originating from the water molecules. Employing this strategy has allowed us to achieve the large suppression of water induced spectral interference from the previous minimum of 400 μg/g to the current value of 30 μg/g when a laser beam of 34 mJ under tight focusing condition was employed. Along with this favorable result, this experimental condition has also provided a much better (about 6-fold higher) spatial resolution, although these results were achieved at the expense of reducing the linear calibration range from the previous 4 300 μg/g to the present 200 μg/g.

Laser-induced plasma spectroscopy (LIPS), first introduced in 1962,[1] has since undergone continuous and rapid development as a viable analytical method. In particular, the laser-induced breakdown spectroscopy (LIBS), which was first published in the 1982,[2] has recently become one of the most widely adopted

---

* Author to whom correspondence should be addressed. Koo H. Kurniawan, Research Center of Maju Makmur Mandiri Foundation, 40 Srengseng Raya, Kembangan, Jakarta Barat 11630, Indonesia. Phone: 62–21-5867663, 62–21-5867660. Fax: 62–21-5867670 or 62–21-5809144. E-mail: kurnia18@cbn.net.id. Homepage: http://www.mmmfoundation.org

(1) Brech, F.; Cross, L. *Appl. Spectrosc.* **1962**, *16*, 59.
(2) Loree, T. R.; Radziemski, L. J. *Plasma Chem. Plasma Proc.* **1981**, *1*, 271–280.

spectrochemical methods in a wide ranging fields of research and application.[3-7] Unfortunately, its application to hydrogen analysis has so far remained less than satisfactory due to the spectral broadening and intensity diminution effects found in the hydrogen emission line.[8]

It was recently shown, however,[9] that a strong and sharp hydrogen emission promising for spectrochemical application could be detected from a zircaloy-4 sample using laser-induced shockwave plasma spectroscopy (LISPS). This was made possible by the employment of a low-pressure surrounding gas which is crucial for overcoming the aforementioned unfavorable effects found in LIBS. It was also shown that the spectral interference by surface water on the zircaloy sample could be reduced by means of appropriate adjustment of both the energy of the pulsed laser and its focused/defocused position. Specifically, the unwanted hydrogen emission was found to decrease with increasing shift of the focusing lens position toward the target. This unwanted spectral interference was shown to be largely suppressed at a 45 mm shift of the lens position without significantly compromising the impurity hydrogen emission intensity when the laser energy was raised to around 140 mJ, which was the maximum allowed by the optical damage threshold of the optical system. Further shift of the lens position was found to result in deterioration of the signal intensity. While an excellent linear calibration curve was obtained in this case, it was nevertheless plagued by its large nonzero intercept, indicating a residual surface water content of around 400 ppm.

For further suppression of this recalcitrant contamination effect, one needs to resolve the difficult problem of distinguishing between the emission from the impurity hydrogen inside the sample and that contributed by the surface water. Overcoming this problem will allow us to ascertain the dominant experimental factors affecting each of the two emission lines. In turn, this will enable us to determine the optimal experimental condition for maximum suppression of the contaminating hydrogen emission without compromising the desired signal quality. In dealing with this problem, we have the following line of thought. First, having roughly twice the hydrogen mass, the deuterium remains much lighter than the host elements in the sample. It is therefore expected to undergo similar time-mismatch effect in the shock wave excitation process observed on hydrogen emission in a low-pressure ambient gas.[10] It was suggested that the much higher speed acquired by the ablated H atoms of much smaller mass will lead to a time mismatch between the rapid and premature passage of the H atom cluster and the shock wave formation by the much heavier major host elements from the sample. This

asynchronous effect was responsible for the distinct time-dependent and pressure-dependent intensity variation of H emission observed in low-pressure ambient helium gas. Given the similar relative mass differences from those of the major host elements, the H and D impurity emission can be expected to share the same basic characteristics. This implies that experimental factors affecting the H emission can be investigated via the D emission which has been shown to be completely resolvable from the hydrogen emission.[11,12] Second, since the water molecules are expected to be relatively free from the deuterium, one may hope to exclude the contribution from the water molecules to the deuterium emission spectrum, thereby allowing the separate detection of the contaminating emission from the intended signal as represented in this case by the D emission.

For the implementation of those ideas, the time-dependent and pressure-dependent emission of both the D and H impurities in the D-doped zircaloy-4 samples will be examined and compared with the emission characteristics from the major host element Zr. Having verified the validity of our working assumption, we will proceed with the subsequent experiment for the search of appropriate experimental conditions for the maximum suppression of water molecules' interference. It will be shown that the desired result can be achieved with 34 mJ laser pulses under a tight focusing condition.

EXPERIMENTAL PROCEDURES

The experimental setup used in this study is basically the same as the one used in the previous work.[9] In this experiment, a special cylindrical chamber with an inner side diameter of 115 mm was designed with several entry ports to allow the control and monitoring of the specific conditions inside the chamber. The laser employed (Nd:YAG, Quanta Ray LAB SERIES, 1064 nm, 8 ns, maximum energy of 450 mJ) was operated in the Q-sw mode at 10 Hz repetition rate with the laser output energy varied by means of a set of filters. The laser beam was focused by a moveable lens of 200 mm focal length and directed onto the sample surface perpendicularly through a quartz window. The He−Ne laser diode is a position marker used to align the invisible Nd:YAG laser with the laser diode illuminated spot on the sample surface. The shot-to-shot fluctuation of the laser was estimated to be approximately 3%.

The main targets employed in this experiment consist of a set of zircaloy-4 samples which are composed of 98.23 wt % zirconium with 1.45% tin, 0.21% iron, 0.1% chromium, and 0.01% hafnium doped with various concentrations of hydrogen impurity (0, 50, 100, 200, 400, 600, 800, and 4 300 μg/g) and those doped with 100 and 1 000 μg/g deuterium impurities. All the samples measure 10 mm × 10 mm in cross sectional area and 1 mm in thickness. After placing the sample in the chamber, the chamber was evacuated using a vacuum pump to a pressure of 0.01 Pa. Subsequently the chamber was heated up until 150 °C for 30 min to remove most of the surface water, before the high purity helium gas (Air Liquid, 5N) was introduced into the chamber until a

(3) Russo, R. E.; Mao, X.; Lu, H.; Gonzales, J.; Mao, S. S. *Talanta* **2002**, *57*, 425−451.

(4) Sdorra, W.; Niemax, K. *Mikrochim. Acta* **1992**, *107*, 319−327.

(5) Cremers, D. A.; Radziemski, L. J. *Handbook of Laser Induced Breakdown Spectroscopy*; John Wiley & Sons, Ltd: Chichester, U.K., 2006.

(6) Miziolek, A. W.; Palleschi, V.; Schechter, I.; *Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications*; Cambridge University Press: Cambridge, U.K., 2006.

(7) Winefordner, J. D.; Gornushkin, I. B.; Correl, T.; Gibb, E.; Smith, B. W.; Omenetto, N. *J. Anal. At. Spectrom.* **2004**, *19*, 1061−1083.

(8) Konjevic, N. *Phys. Rep.* **1999**, *316*, 399−401.

(9) Kurniawan, K. H.; Pardede, M.; Hedwig, R.; Lie, Z. S.; Lie, T. J.; Kurniawan, P. D.; Ramli, M.; Fukumoto, K.; Niki, H.; Abdulmadjid, S. N.; Maruyama, T.; Idris, N.; Kagawa, K.; Tjia, M. O. *Anal. Chem.* **2007**, *79* (7), 2703−2707.

(10) Kurniawan, K. H.; Kagawa, K. *Appl. Spectrosc. Rev.* **2006**, *41* (2), 99−130.

(11) Kurniawan, K. H.; Lie, T. J.; Suliyanti, M. M.; Hedwig, R.; Abdulmadjid, S. N.; Pardede, M.; Idris, N.; Kobayashi, T.; Kusumoto, Y.; Kagawa, K.; Tjia, M. O. *J. Appl. Phys.* **2005**, *98* (9), 093302 1−3.

(12) Kurniawan, K. H.; Lie, T. J.; Suliyanti, M. M.; Hedwig, R.; Pardede, M.; Kurniawan, D. P.; Kusumoto, Y.; Kagawa, K. *Anal. Chem.* **2006**, *78* (16), 5768−5773.

pressure of 650 Pa was reached at a constant flow of 2 L/min. The chamber temperature chosen for this experiment was lower compared to that used previously (200 °C),[9] since the deuterium became completely evaporated when the temperature was increased to 200 °C due to the weaker bonding energy of Zr−D as compared to Zr−H. The gas pressure of helium (650 Pa) and the above-mentioned chamber temperature (150 °C) were henceforth kept constant during the experiment.

The plasma emission was detected by an optical multichannel analyzer (OMA system, Andor I*Star intensified CCD 1 024 × 256 pixels) attached on one side to a spectrograph (McPherson model 2061 with 1 000 mm focal length f/8.6 Czerny−Turner configuration) and connected to an optical fiber on the other side. The entrance end of the fiber was inserted through a cylindrical quartz tube well into the chamber and kept at a position 6 mm above the sample surface and at a distance of 80 mm from the center of the plasma. At this position, the fiber was expected to collect the emitted radiation entering within 27° of the solid angle. The spectral window, covered by the detector, has a width of 20 nm at 500 nm wavelength. The accumulated data of 100 detected spectra from each irradiated spot were monitored on a screen and recorded to yield the averaged results presented here. During the experiment, the gate delay and gate width of the OMA system were set at 1 and 50 μs, respectively, unless otherwise stated. The spectral resolution of the OMA system is 0.009 nm at 500 nm.

The intensity-versus-time curves of the spatially resolved emission intensity were measured by means of an oscilloscopic technique with a time resolution of 1 ns. In this measurement, the monochromator (Spex M-750, Czerny−Turner configuration, f = 750 mm with 1 200 grooves/mm, resolution of 0.01 nm) was fixed at the wavelengths corresponding to Zr I 650.6 nm and D I 656.1 nm separately. The plasma at a certain position was imaged using a quartz lens of focal length 10 cm onto the entrance slit of the monochromator. The slit height and slit width of the monochromator were set at 15 mm and 100 μm, respectively. The electric signal output from the photomultiplier (Hamamatsu IP-28) was fed through a fast preamplifier (Stanford Research SRS 240) to a digital sampling storage scope (Tektronix TDS 2012). The trigger signal of the oscilloscope was connected directly to the synchronized output trigger of the laser system. The data collection was carried out using a printer.

The sample surface condition was constantly monitored during the repeated laser irradiation and data acquisition process, using a stereomicroscope (Mini Dia Stereo MDS-40, Nissho Optical Co. Ltd.) through a 50 mm quartz window installed parallel to the sample surface. The working distance between the objective lens and the sample surface was kept at 135 mm.

RESULTS AND DISCUSSION

As mentioned earlier, one of the expected distinct characteristics of the deuterium excitation process can be investigated from its time-resolved emission spectra in conjunction with those of the hydrogen and the host element (Zr). The results presented in Figure 1 were obtained from the high D concentration (1 000 μg/g) zircaloy-4 sample with 34 mJ laser irradiation and 650 Pa surrounding helium gas at gate delays of (a) 500 ns, (b) 1 μs, and (c) 5 μs. Figure 1a displays strong ionic emission lines together with the much weaker atomic emission lines of D I 656.1 nm and Zr I 650.6 nm. These ionic lines weaken drastically in
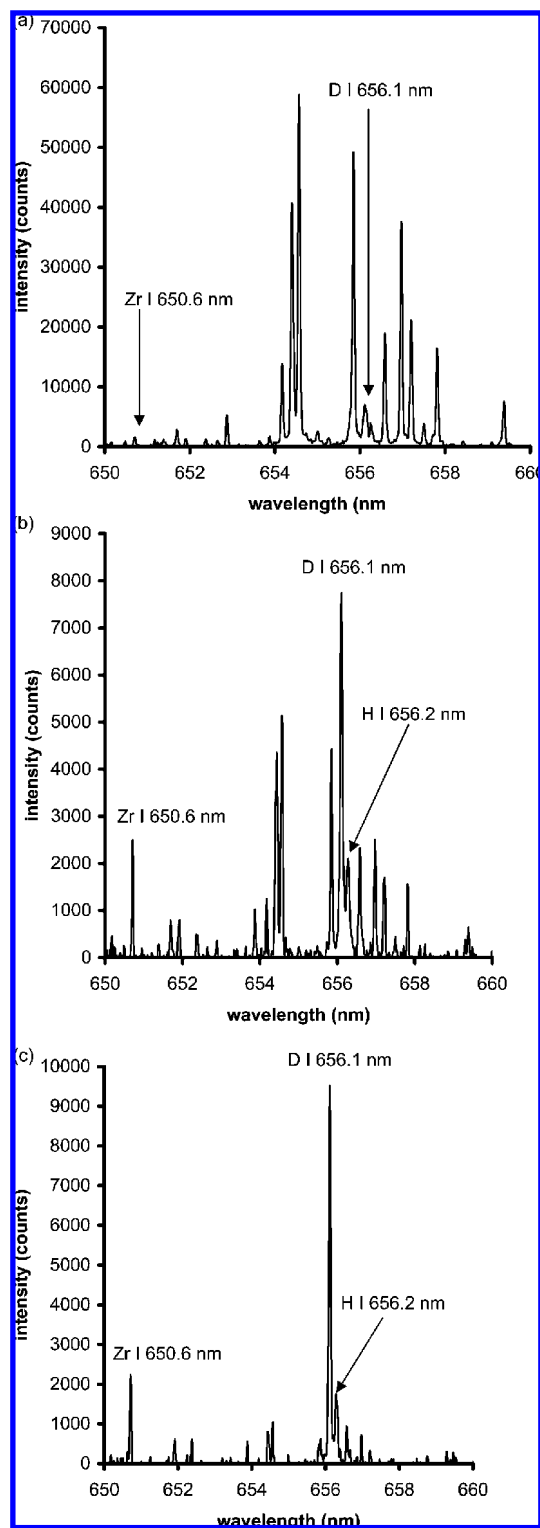

Figure 1. The time-resolved emission spectra taken using a zircaloy-4 sample containing 1 000 ppm of deuterium for gate delays of (a) 500 ns, (b) 1 μs, and (c) 5 μs. The laser energy was fixed at 34 mJ. The surrounding helium gas pressure was kept at 650 Pa.

Figure 1b, in concurrence with perceptible increases of the D and Zr emission intensities. Finally at 5 μs, as observed in Figure 1c, the ionic lines have largely disappeared. These intensity variations nicely fit the general pattern of time-dependent variation of H emission intensity observed from the H-doped zircaloy sample in the laser-induced shock-wave plasma spectroscopy.[10]
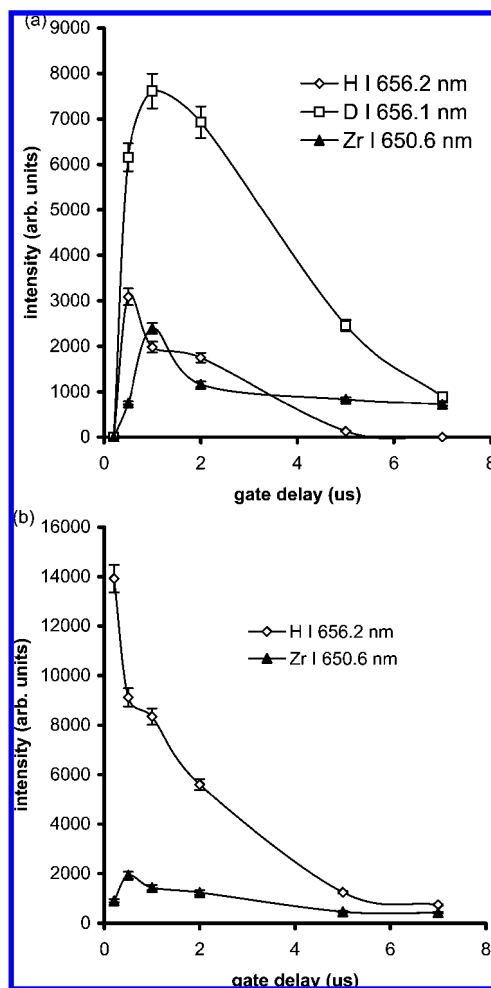
Figure 2. The intensity-versus-time curves of D I 656.1 nm, H I 656.2 nm, and Zr I 650.6 nm from samples of zircaloy-4 containing (a) 1 000 μg/g deuterium and (b) 4 300 μg/g hydrogen. The laser energy was fixed at 34 mJ. The surrounding helium pressure was kept at 650 Pa.

Figure 3. The intensity-versus-time curves of (a) D I 656.1 nm and (b) Zr I 650.6 nm from a zircaloy-4 sample containing 1 000 μg/g of deuterium, measured at 4 mm above sample surface by the lens imaging technique, with 34 mJ laser energy and 650 Pa surrounding helium pressure.

The detailed comparisons of the intensity-versus-time curves of D, H, and Zr are described by Figure 2 for zircaloy samples with (a) 1 000 μg/g deuterium and (b) 4 300 μg/g hydrogen, measured with tightly focused 34 mJ laser pulses. Apart from the considerably higher D emission intensity associated with the high D concentration, the intensity-versus-time curves of all three emission lines in Figure 2a display the same rapid initial rise up to 1 μs, the following fast decline, and the final slower decay, each associated with the initial collision excitation, the subsequent shock excitation, and finally the long cooling-off process. Each of these processes has been extensively discussed in our previous work.[10] However, one notes upon a further look at the figure, that in contrast to the Zr emission time profile which features the typical very slow decay, the time profiles of both the D and H emission lines share basically the same and relatively much faster decay with time. More or less the same basic features are exhibited in Figure 2b except that the rapid initial rises which were not observable in this case for the following reason. The excessively high H-concentration in zircaloy-4 is known to cause severe cracking of the sample. This will inevitably lead to a weakening of the sample mechanical property and thereby reduces the ablated speeds of the atoms. This is in turn
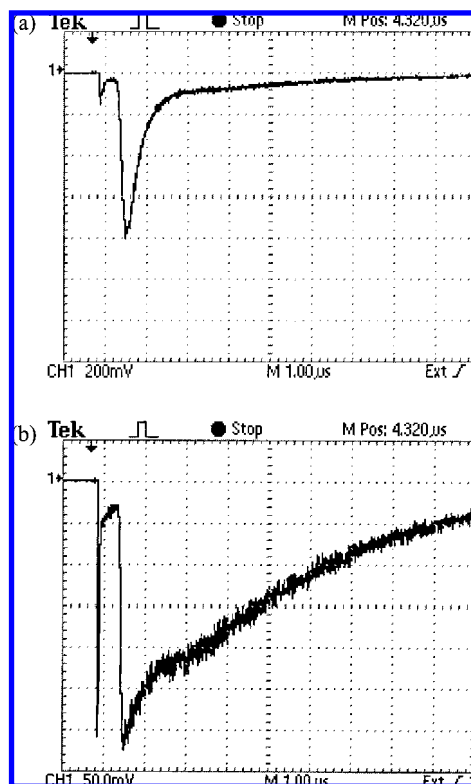
expected to result in a less effective collision excitation process.

Further evidence of the shock-wave excitation process taking place during the plasma formation was provided by the intensity-versus-time curve of the spatially resolved emission intensities of Zr I 650.6 nm and D I 656.1 nm from the high D concentration sample measured with the same laser energy and helium pressure. The result is presented in Figure 3 for (a) D I 656.1 nm and (b) Zr I 650.6 nm emission detected at 4 mm from the sample surface. We note that both D and Zr emission intensities share exactly the same rise time of 500 ns. The same common rise time of 1 000 ns was found when the emission was detected at a position 7 mm from the sample surface. This implies the effective and simultaneous operation of the shock-wave excitation process for D and Zr emission alike. Further, the relatively short emission period of D shown in Figure 3a is also in good agreement with our explanation based on the mismatching effect which is associated with the early passage of the fast moving D atoms during the formation of the shock front, around which the excitation is supposed to takes place most effectively. Therefore this signifies that only a small part of D atom clusters caught by the shock-front in the limited region just behind the shock-front were excited, yielding the narrow emission period shown in the figure. On the other hand for Zr atoms, the shock front was mainly formed by the Zr atoms themselves and moved together with the ablated Zr atoms, yielding a much more persistent excitation process as manifested by the wide emission time-interval seen in Figure 3b.
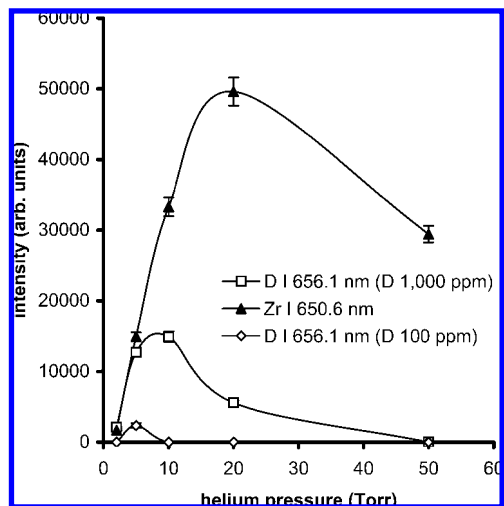
Figure 4. Relationship of emission intensities of D I 656.1 nm and Zr I 650.6 nm with surrounding helium pressures for zircaloy-4 samples containing 100 μg/g and 1 000 μg/g deuterium impurities. The spectra were obtained by averaging data accumulated by 100 laser shots of 34 mJ laser energy and detected with a gate delay and gate width of 1 and 50 μs, respectively.

In addition to the study on the time-dependent behavior, it is also important to examine and compare the pressure-dependent characteristics of the emission intensities of D, H, and Zr. Figure 4 shows the pressure-dependent behaviors of the D and Zr emission intensities from the high- and low-D concentration samples. In both cases, the D and Zr emission intensities show the general trend of initial increase with increasing helium pressure up to a certain maximum value before reversing the trend beyond that. However, the behaviors of the two emission lines clearly differ in their overall characteristics. The much stronger Zr emission intensity displays the typical slow decline with gas pressure beyond its value at maximum intensity and remain clearly observable even at 101 kPa in agreement with that reported previously from the zinc sample.[13] On the other hand, the D emission intensity reduces rather abruptly to 0 at 6.5 kPa for the high-D concentration sample and at 1.3 kPa for the low-D concentration sample, in proportion with the different concentrations. This resembles exactly the behavior of H emission, which was explained as mainly ascribable to the mismatching effect.[10]

Having demonstrated the similarity in the basic characteristics of D and H emission, we now proceed with the investigation of spectral interference by surface water molecules. The result of measurement from the sample of high deuterium concentration is shown in Figure 5. The spectrum was obtained from averaging the accumulated spectra produced by 100 laser shots with 34 mJ laser energy in 650 Pa helium surrounding gas. It is seen that a strong and sharp D I 656.1 nm (D_α) emission is accompanied by a relatively weak H I 656.2 nm (H_α) emission. It was found that replacing the helium surrounding gas with nitrogen gas at 260 Pa led to greatly reduced D emission along with the appearance of a number of adjacent and even overlapping unknown emission lines. This simply reaffirms the obvious advantage of ambient helium gas over ambient nitrogen gas for
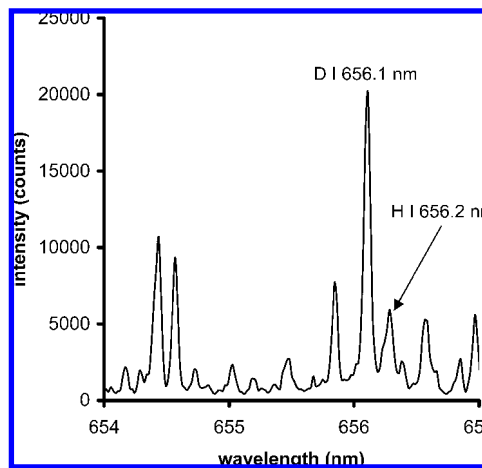
(13) Kurniawan, K. H.; Ishikawa, Y.; Nakajima, S.; Kagawa, K. *Appl. Spectrosc.* **1997**, *51* (12), 1769−1780.

Figure 5. The hydrogen and deuterium emission spectra measured from a zircaloy-4 sample containing 1 000 μg/g of deuterium impurity with a laser energy of 34 mJ, gate delay and gate width of 1 and 50 μs, respectively, and ambient helium gas at 650 Pa. The spectra were obtained by averaging data accumulated by 100 laser shots.

deuterium analysis using laser-induced plasma, just as demonstrated previously for hydrogen analysis.[14]

Returning to the problem over the origin of the weak H emission in Figure 5, it is worthwhile to recall that the adverse effect of increasing the laser energy on the surface water induced spectral interference was already pointed out in a previous study.[9] This effect is examined in more details here by measuring the energy-dependent emission intensities from the zircaloy samples. The results are presented in Figure 6a for a hydrogen free sample and in Figure 6b for sample of high D concentration. We note first of all, the conspicuous absence of H emission in Figure 6a for laser energy below 35 mJ, which necessarily implies the negligible contribution from water molecules in this energy regime. Therefore, the appearance of weak H emission at laser energy $\leq$20 mJ in Figure 6b is not to be attributed to water molecules. We are thus left with no other choice but identifying the origin of the low-energy H emission with a hydrogen impurity inside the sample. It is indeed reasonable to envisage the simultaneous introduction of a minute amount of H atoms during the preparation of the zircaloy sample with a high concentration of deuterium of 99.6% purity. We may therefore conclude that operating the laser at an energy of 34 mJ will allow a clear detection of D emission with negligible spectral interference from the surface water.

Further, we must address the significant increase in H emission intensity from water molecules at higher laser energy as shown in Figure 6b. Again, it is useful to refer to our previous works on the shock-wave plasma,[14] which described the growth of the hemispherical plasma size with increasing laser energy, resulting in enlarged contact area between the plasma and sample surface. As a result, additional surface water molecules engulfed by this extended plasma may be dissociated and excited, leading to enhanced H emission. Meanwhile the possible contribution from the water vapor in the surrounding gas can be excluded on

(14) Pardede, M.; Hedwig, R.; Suliyanti, M. M.; Lie, Z. S.; Lie, T. J.; Kurniawan, D. P.; Kurniawan, K. H.; Ramli, M.; Fukumoto, K.; Niki, H.; Abdulmadjid, S. N.; Idris, N.; Maruyama, T.; Kagawa, K.; Tjia, M. O. *Appl. Phys. B* **2007**, *89* (2−3), 291−298.
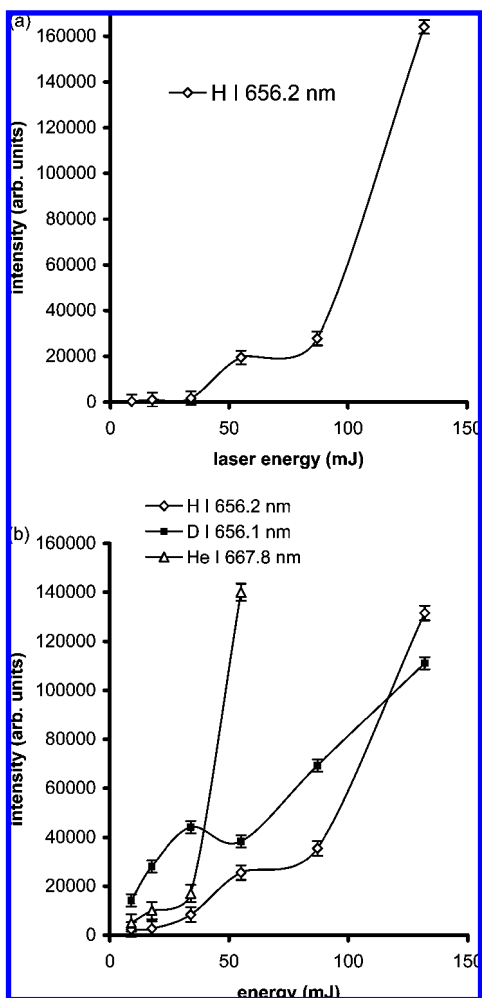
Figure 6. Laser energy-dependent emission intensities of H I 656.2 nm, D I 656.1 nm, He I 667.8 nm obtained with ambient helium at 650 Pa and a gate delay and gate width of 1 and 50 μs, respectively. The spectra were obtained after averaging data accumulated by 100 laser shots from zircaloy-4 samples containing (a) 0 μg/g hydrogen and (b) 1 000 μg/g deuterium.

Figure 7. Calibration curve obtained from zircaloy-4 samples containing different concentrations of hydrogen impurity with a laser energy of 34 mJ and a gate delay and gate width of 1 and 50 μs, respectively. The spectra were obtained by averaging the data accumulated from 120 laser shots.

the basis of the observed reduction in H emission when laser cleaning was applied to the sample surface prior to the measurement.[15] It is also important to note that in addition to the large suppression of surface water emission without compromising the emission intensity of hydrogen impurity, the adopted experimental condition was also found to yield an excellent spatial resolution (crater diameter of 0.5 mm) as compared to our previous work (crater diameter of 3 mm).[9] Apparently, this is the result of employing a tightly focused laser beam in this experiment.

The favorable condition described above was then employed for the intensity–concentration correlation measurement on the zircaloy-4 samples prepared with different concentrations of hydrogen. Each data point in the presented result is the average of 120 data points produced by 120 successive laser shots on the same spot. This measurement was then repeated on five different spots on the surface of the same sample, which were found to yield highly reproducible results implying the uniformity of the impurity hydrogen distribution in the sample. The averages of
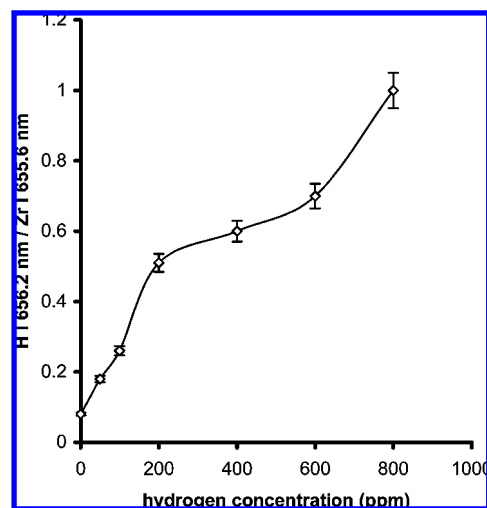
(15) Kurniawan, K. H.; Lie, T. J.; Idris, N.; Kobayashi, T.; Suyanto, H.; Maruyama, T.; Kagawa, K.; Tjia, M. O. *J. Appl. Phys.* **2004**, *96* (3), 1301–1309.

such five measurement results for samples with different impurity hydrogen concentrations were then plotted in Figure 7 to display the relation between the H impurity concentration and its associated emission intensity. Unfortunately, the relation over the entire range considered exhibits a nonlinear behavior. While it is interesting in its own right, its adequate explanation is simply beyond the scope of this study. However, it is important to note that a reasonably linear relationship does exist in the limited range from 0 to 200 μg/g H concentration. More importantly, as far as this study is concerned, the presence of the surface water is greatly reduced to around 30 μg/g as indicated by the intercept at zero impurity H. For a comparison, our previous result from a similar study,[9] which produced a linear calibration curve for a more extended range, has nonetheless a much larger intercept of roughly 400 μg/g hydrogen concentration. We suppose that the large suppression of water interference achieved in the present study was largely made possible by the use of relatively low laser energy (34 mJ) as explained earlier, as well as the tight focusing condition employed in the experiment, which resulted in a much smaller size plasma and hence much smaller contact area with the sample surface.

CONCLUSION

We have shown in this work that the hydrogen and deuterium emission from hydrogen doped and deuterium doped zircaloy-4 samples share similar pressure-dependent and time-dependent characteristics in a laser-induced low-pressure helium plasma. Taking advantage of this similarity and the relative rarity of deuterium in surface water, we have succeeded to ascertain the experimental conditions which greatly suppress the spectral interference from water molecules down to 30 μg/g at laser energy of 34 mJ under tight focusing conditions, without scarifying the signal intensity of H. This value of the zero intercept is much lower than the 400 μg/g intercept obtained previously with higher laser energy under a largely

defocused condition. Further, the experimental condition also admits an excellent spatial resolution as indicated by the crater size of 0.5 mm diameter. As a tradeoff however, the linear calibration obtained in this case is limited to a maximum H concentration of 200 μg/g. Finally, this study also demonstrates that the use of high-purity helium surrounding gas of around 650 Pa is crucial to the high emission efficiency attained in this experiment.