R&D of Gas-Based Laser Plasmas toward Material Processing

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Research and developments of gas-based laser plasmas toward material processing are reported. Transmission of plasmas, ultraviolet spectra, photo-excitation on glass material, and sterilization performance of gas-based laser plasmas using a gas-puff and a gas cell targets are evaluated. A co-axial gas-puff target as a intense VUV source and an evaluating method of refractive index changes of glass surface during the photo-excitation are developed toward LPAD.

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1 Introduction

Laser plasmas [1] have been studied had been studied in extreme ultraviolet lithography (EUVL) [2,3] and laser-induced breakdown spectroscopy (LIBS) [4] in vacuum ultraviolet (VUV) wavelength region by using a focused pulsed-laser beam onto solid materials or gas medium. Gas-based laser plasmas caused by laser-induced gas breakdown [5-7] can generate VUV emission easily with less debris compared with laser plasmas with solid materials. We have studied that characteristics of gas breakdown changes with wavelengths, gas media and pressure as well as controlling energies[8], indicating that, combination of shorter wavelength of laser, shorter focal length of lens can reduce the required laser input energy. Since gas medium surrounding the gas-based laser plasma can absorb generated VUV emission, gas-puff targets [9-11] were suggested to avoid this absorption.

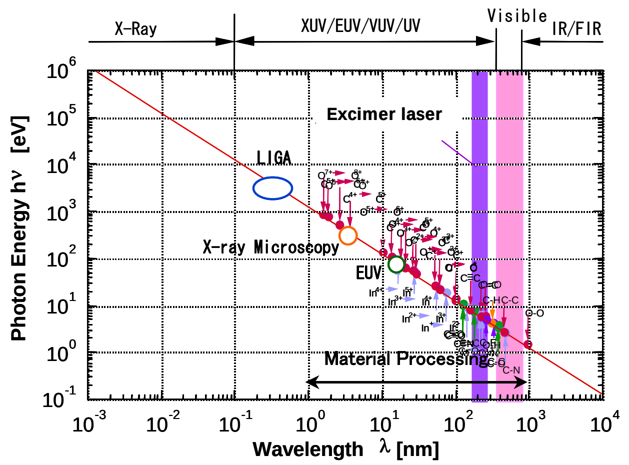


Fig.1 Interesting wavelengths and photon energies with excitation energies of several ions.

Figure 1 shows interesting wavelengths and photon energies at the wavelength range between UV and x-ray regions. lithographie galvanoformung abformung (LIGA) [12, 13], X-ray microscopy [14], EUVL [2,3] as well as material processing have been requested from view of industry. However, material processing using ultraviolet emission from laser plasmas had not been studied well except EUVL (~13.5 nm), soft-x-ray microscopy (2.8~4.4 nm) and LIGA (0.2~0.6 nm).

Figure 2 shows calculated attenuation lengths for quartz, silicon, parylene-N and PMMA as a function of photon energy. These materials have small attenuation lengths at the wavelength between 10nm and 100nm where many excitation energies of several ions exist as shown in Fig. 1.

As mentioned above, gas-based laser plasmas can generate intense VUV emission with low debris easily. Intense VUV emission requires certain gas medium with suitable gas-puff target when one wants to irradiate sample surface even inside the processing chamber.

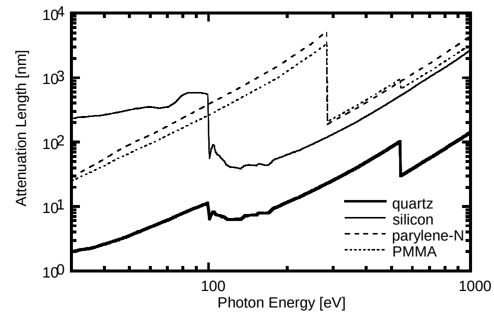


Fig.2 Calculated attenuation lengths for quartz (SiO_2, 2.2 g/cm^3), silicon (Si, 2.33 g/cm^3), parylene-N(C_8H_8, 1.11 g/cm^3) and PMMA($C_{16}H_{14}O_3$, 1.2 g/cm^3) as a function of photon energy.

2 Experimental studies of gas-based laser plasmas toward laser plasma assisted deposition (LPAD)[16]

Figure 3 shows a schematic view of laser plasma assisted deposition (LPAD). The substrate surface would be excited by photons from gas-based laser plasma before or during deposition from the evaporator in order to achieve higher adhesion. A gas-puff target can be used to generate intense pulsed VUV photons. The pulsed VUV photons would excite the surface of the glass substrate as shown in Fig.3.

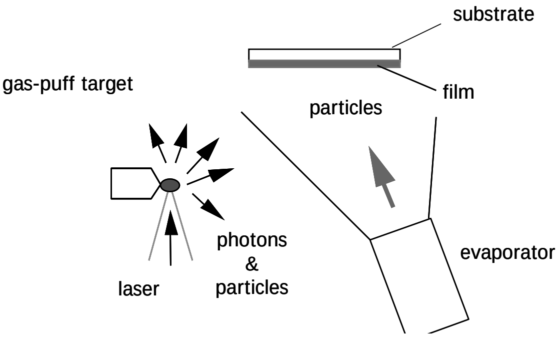


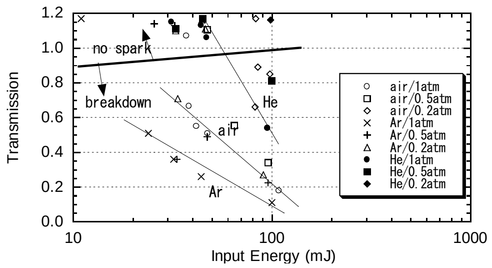
Fig.3 Schematic of Laser Plasma Assisted Deposition (LPAD).

2.1 Properties of transmission and UV emission of laser-induced gas breakdown [8]

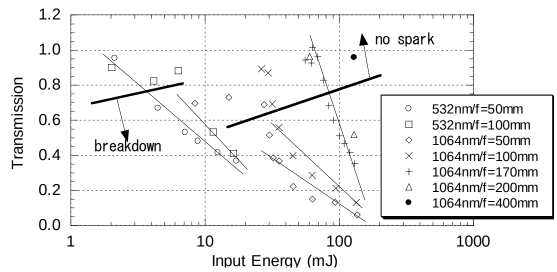
Figure 4 shows typical CCD images for various gas medium. As seen in this figure, Ar is most intense compared with other gas media, i.e. air and He. It is indicated that laser plasma due to laser-induced gas breakdown would grow toward the direction of focusing lens. The transmission through laser plasmas would decrease as the plasma extended its length.

Figure 5 shows the transmission through the gas when the YAG laser beam was focused by changing gas media, wavelengths and focusing lenses. According to Fig. 5, the breakdown in the Ar gas medium shows the lowest breakdown threshold compared with the air and He gas media. Breakdowns were judged by visible emissions at the focusing position. Transmission is not unity because of the accuracies of powermeters. Measured breakdown thresholds were >30 mJ, 23-25 mJ, 25-27 mJ, 7-14 mJ, and 3-4 mJ for He, the air, N_2, Ar, and Xe gases, respectively. The experimental result with the 532 nm laser (SHG) shows lower breakdown threshold compared that with the 1064 nm one. Shorter focusing shows lower breakdown threshold. Considering to the damage of the lens with exposure to the plasma, the shortest focusing lens is 20 mm with the conventional YAG laser system.

Kr plasma in the gas cell shows uniform spectrum below 300 nm in the wavelength range reaching as short as 120 nm when the purity of Kr is high, while the wavelength range between 120 and 180 nm was disappeared when the purity was lower because of impurity gas media, especially oxygen. When the shorter wavelength below 120 nm is required, a gas-puff target is necessary to reduce the absorption of VUV photon due to the ambient gas.

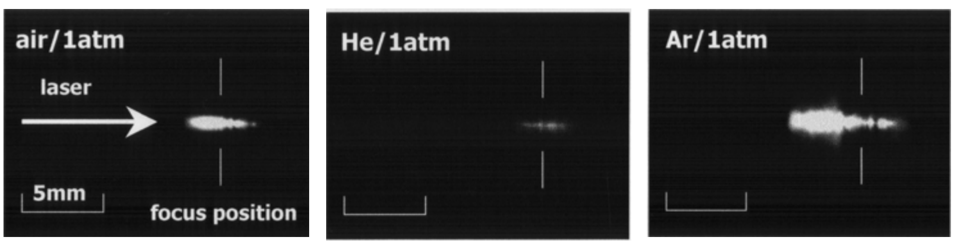


(a)



(b)

Fig. 5 Transmission properties through laser plasma by laser-induced gas breakdown as a function of input energy with (a) gas media and (b) laser wavelengths and focusing lengths.



(a) (b) (c)

Fig. 4 Transverse CCD images of laser plasmas by gas breakdown in (a) the air, (b) He and (c) Ar gas media with the YAG laser (1064 nm/ 7 ns) and a fo-

2.2 Photo-excitation due to VUV emissions from gas-based laser plasmas [16, 17]

Figure 6 shows the schematic view of sample configuration to observe interaction between laser-induced gas breakdown and glass samples. Samples were located at the distance of 130 mm from the gas-puff target. The gas-puff target was a double-stream type with gas condition of inside (Ar) and outside (He) gases and was operated under the condition shown in Fig. 7. The signals shown in Fig. 8 were sensitive with vacuum condition. Unstable excitation signal were observed on the glass surface just after the laser irradiation to the gas-puff target located in the vacuum chamber. Considering transmission of ambient gas from gas-puff target, the observed signal would be originated from photoelectron excited due to VUV emissions of photon energies from 15 to 40 eV, i.e. wavelengths from 80 to 30 nm. (see Fig. 9)

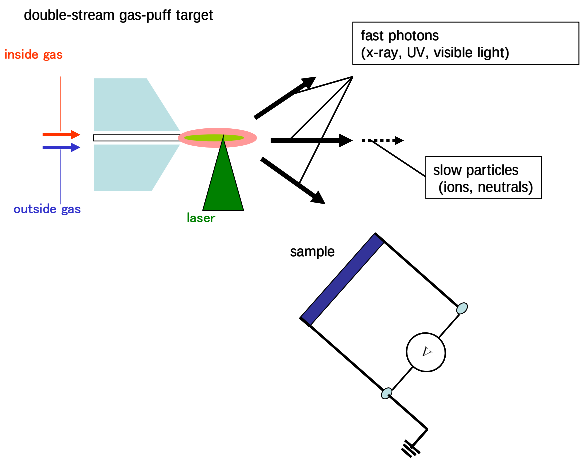


Fig. 6 Schematic of sample configuration to study interaction between laser-induced gas breakdown and glass samples. Samples were located at the distance of 130 mm from the gas-puff target.

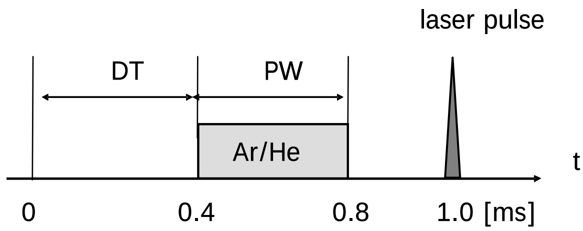


Fig. 7 Temporal diagram of the delay time (DT) and the pulse width (PW) for triggering the gas-puff target and the laser pulse.

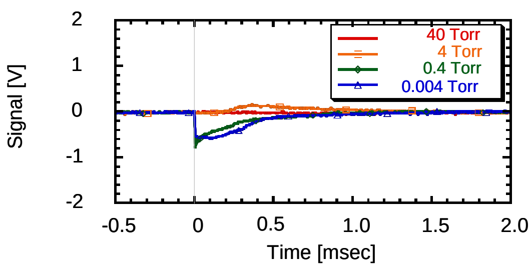


Fig. 8 Measured unstable signals between both ends of a glass sample as a function of pressure.

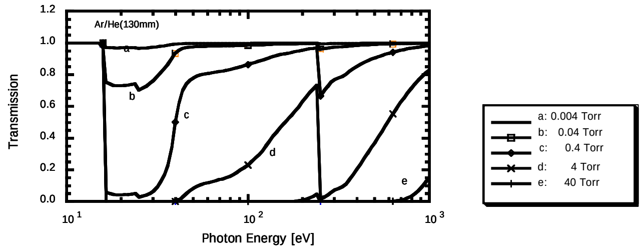


Fig. 9 Calculated transmission thorough 130mm-long Ar/He mixture gas as a function of pressure.

2.3 Development of co-axial gas-puff laser plasma VUV source [17]

In order to generate more intense VUV photons, larger laser plasma is required rather than highly ionized plasma. Therefore the focusing volume should be increased, for example, using a line-focusing lens.

Figure 10 shows a developed co-axial gas-puff target in order to generate intense VUV emissions by increasing their volume using an axicon lens and a single nozzle gas-puff target system GP-08. An axicon lens with a hole was located at the extended nozzle of the gas-puff target, which can generate a line-focus along gas stream injected from the nozzle. In order to separate gas-puff apparatus and laser beam, the 45-deg total reflection of the prism is used. Laser pulse was operated with gas injection time. Ar laser plasma with which approximately 1 cm-long gas plasma was successfully created in vacuum. (see Fig. 11)

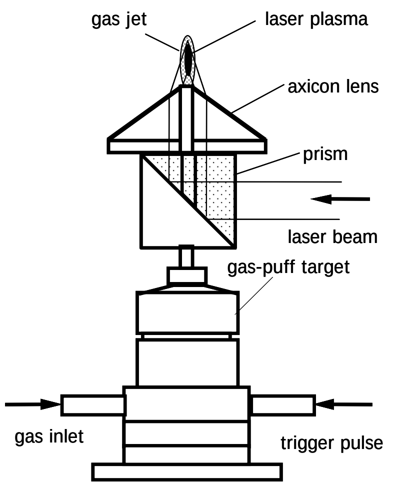


Fig. 10 Schematic of a co-axial gas-puff laser plasma source with an axicon lens. The gas-puff target is a single nozzle type, GP-08.

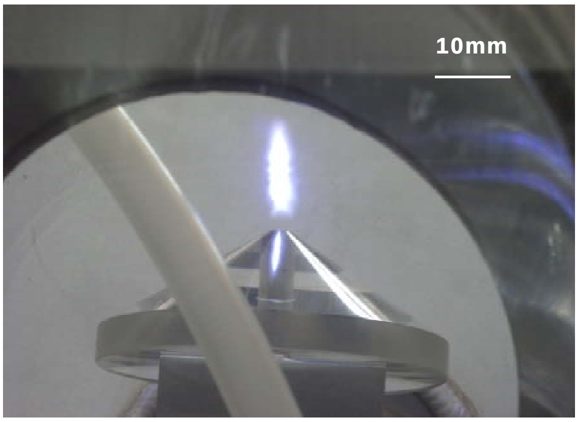


Fig. 11 1 cm-long Ar laser plasma generated in vacuum using a co-axial gas-puff target.

2.4 Evaluation method of refractive index changes using surface plasmon resonance.

When the surface is excited by VUV photons from laser plasma, photo-electron would change the refractive index of glass substrate. Evaluation method using surface plasmon resonance (SPR) is one of solutions for measuring refractive index changes optically.

Figure 12 shows the schematic of the measuring system to detect SPR between metal and glass surfaces. If the photo-excited glass film has refraction index change, it would be observed as a fingerprint of SPR which has wavelength and angle dependences on CCD detectors.[18] The SPR signal is very sensitive to the thickness and the refractive index of glass film. When the thickness is fixed, the resonance condition is explained for the change in the refractive index.

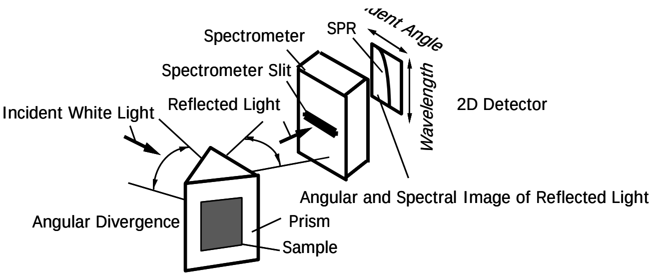
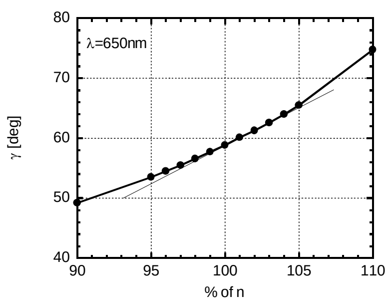
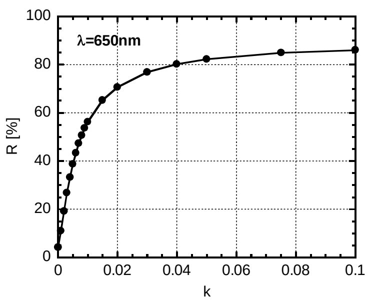


Fig. 12 Schematic view of spectroscopic attenuated total reflection (S-ATR) system diagnosing SPR fingerprints.



(a)



(b)

Figure 13 shows a schematic of experimental setup to detect refractive index change on glass surface. The sample was prepared to detect the SPR fingerprint with the S-ATR system. Figure 14 shows the calculated SPR fingerprints as a function of the real part and imaginary part of refractive index of glass material, respectively. Figure 15 shows behaviors of resonance angle and transmission derived from the data shown Fig. 14.

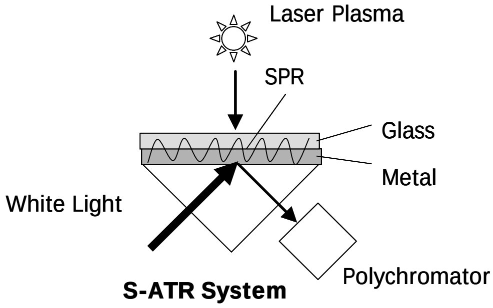


Fig. 13 Schematic of the spectroscopic attenuated total reflection (S-ATR) system diagnosing refractive index changes due to photo-excitation by laser plasma.

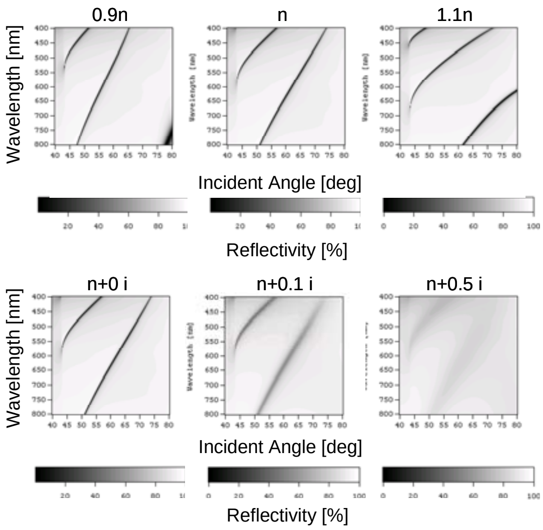


Fig. 14 Calculated SPR fingerprints by changing the real part (upper) and the imaginary part (lower) of refractive index of a 500 nm-thick quartz film coated on a 50 nm-thick silver film on a 60 deg-quartz prism.

3 Sterilization performance of UV emission from gas-based laser plasmas [19]

We have also reported their UV sterilization performances on microorganisms toward biotechnological application as a intese UV source which is alternative to a low-pressure mercury lamp.

Figure 16 shows the experimental setup to sterilize microorganisms by UV radiation. Sterilization performance between radiation at the wavelength of 254 nm from a low-pressure mercury lamp and UV emission gas-based laser plasmas in a gas cell are evaluated. Samples containing microorganisms were prepared in petri dishes with a quartz window on the bottom. The UV emission form laser-induced gas breakdown was irradiated through both this quartz window and the quartz window on the gas cell filled with various kinds of gas media.

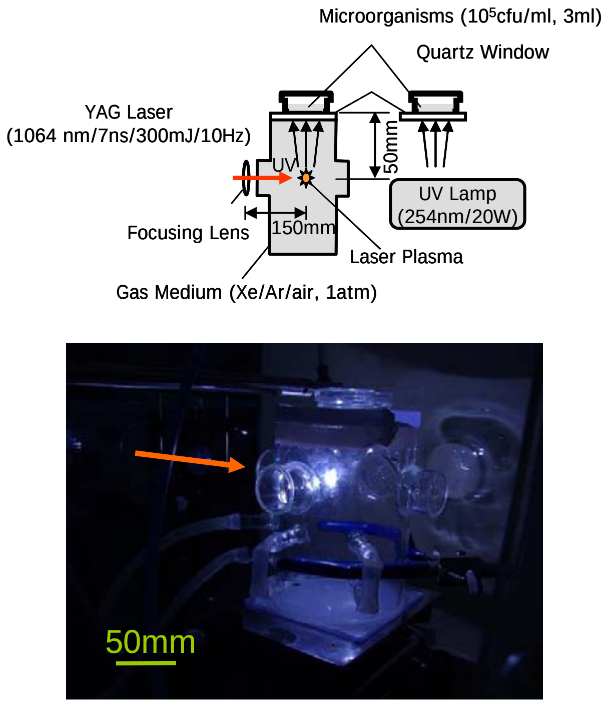


Fig. 16 Experimental setup and picture of laser-induced gas breakdown in a gas cell.

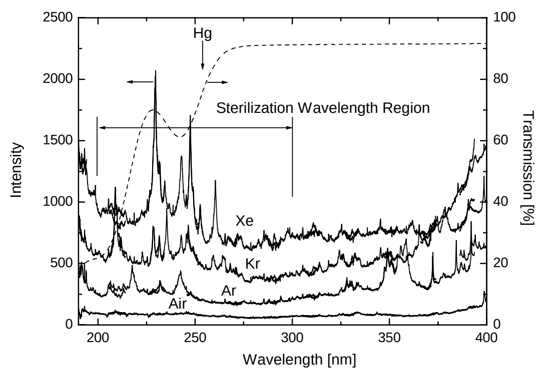


Fig. 17 UV spectra from various gas-based laser plasmas with YAG laser (100 mJ/ 532 nm/ 7 ns) with a f=30 mm focusing lens with the transmission of the quartz window.

Figure 17 shows typical spectra of UV emissions from various gas-based laser plasmas generated with f=30 mm lens. An UV spectrometer (KV-201, Bunkoukeiki Co., Ltd.) equipped a back-illuminated CCD (model DV434BN, Andor Technology Co., Ltd.) was used. The UV emissions from laser plasmas exist below and above 254 nm from the low-pressure mercury lamp. Unfortunately the UV emissions below 200 nm cannot reach microorganism through the quarts window. Considering that sterilization occurs below 300 nm, the Xe gas breakdown generated the most intense UV emission between 200 and 300 nm.

In the sterilization experiment, an energy of 300 mJ from the YAG laser system (Surelite, HOYA continuum Co., Ltd.) was focused with an f=150 mm lens. Microorganisms were illuminated by the laser plasma through a quartz window.

Figure 18 shows sterilization performance of the UV emissions on *Escherichia coli*. As seen in this figure, Xe gas breakdown showed the best sterilization performance. It can sterilize more than 99% of microorganisms within 2 h, while a 20-W low-pressure mercury lamp can sterilize them completely within 10 min. This means that laser plasma by laser-induced gas breakdown needs more sterilization performance in place of the low-pressure mercury lamp.

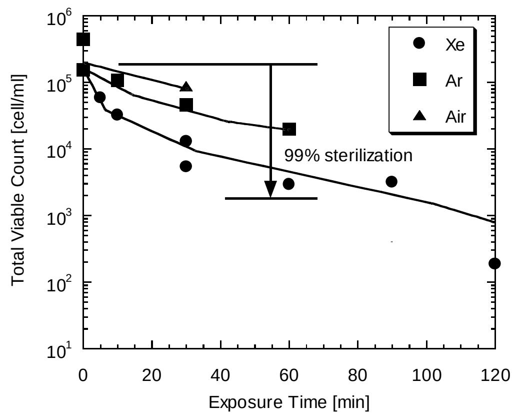


Fig. 18 Sterilization performance of laser plasmas on *E coli* with various gas media as a function of exposure time.

4 Summary

In this paper, research and developments of gas-based laser plasma toward material processing are reported with experimental findings and numerical estimations. Experimentally, Xe plasma by laser-induced gas breakdown generated in the gas cell emits most intense UV emission between 200 and 300 nm in wavelength in a gas cell and showed the best sterilization performance compared with those by other gas breakdowns. It is found that the purity of the gas medium in the gas cell is very important to generate VUV photons in the wavelength shorter than 180 nm. It is also indicated that the surface of glass material can be excited by VUV emission from a double–stream gas-puff target between 30 and 80 nm in wavelength. A co-axial gas-puff target with large plasma would be more intense in VUV wavelength range compared to the double-stream gas-puff target. SPR fingerprints by S-ATR method were estimated in order to detect refractive index change due to photo-excited glass surface optically.

It is found that gas-based laser plasma generate enough VUV emission to excite glass surface. Further research is necessary for applying gas-based laser plasmas toward various types of material processing.

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