

Ultraviolet temporal spectrum analysis of laser induced GaAs plasma

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Time-resolved optical emission spectroscopy in ultraviolet was used to characterize a ablation plasma on a GaAs target, produced by 1064nm, 10ns pulsed laser. The evolution and the character of the spectra were analyzed. Under the assumption of local thermodynamic equilibrium, the electron temperature was obtained in the early stages of the plasma using blackbody approximation for the emitted radiation and in the later stages of the plasma by a Boltzmann plot for the lines intensities. The line broadenings of the N II (399.50 nm) and the Ga I (294.36 nm) were used to estimate the evolution of the electron density. The time evolution of the electron temperature and the electron density were obtained. In addition, the line width and shift of Ga I 287.40 nm and As I 278.02 nm lines were detected and analyzed.

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1. Introduction

Laser ablation of materials has been an interesting subject of many experimental and theoretical study since the high-power laser became available. When the high-power laser is focused on the surface of the material, the material would undergo melting, evaporation, ionization and thus the plasma forms. It is very useful for the basic understanding of laser-material interaction and some practical application such as PLD [1] for thin film growth. Detailed investigation of the optical emission of the plasma can give important information of the plasma. Emission spectroscopy is a powerful tool for rapid, multielement material analysis. Numerous examples of these kinds of measurements have been reported [2, 3].

GaAs (gallium arsenide) is an important semiconductor material and has some electronic properties which are superior to those of silicon. It has a higher saturated electron velocity and higher electron mobility, allowing transistors made from it to function at frequencies in excess of 250 GHz. Those properties recommend GaAs circuitry in mobile phones, satellite communications, microwave point-to-point links, and some radar systems. At our knowledge, only few studies by emission spectroscopy of this material exist [4, 5]. PLD is a very effective method for producing GaAs film. The investigation on the laser-induced GaAs plasma can provide helpful parameters to improve the PLD technology.

The objective of the present work is to explore the character of GaAs plasma by detecting its time-resolved emission spectra and obtain the evolution of plasma parameters at different laser irradiances. Meanwhile the spectral lines broadening and shift are analyzed.

2. Experimental setup

Details of the experimental setup have been illustrated in [3]. The Q-switched Nd: YAG laser device (Quanta Ray DCR-3) is used to produce the laser plasma. The Nd: YAG laser maximum output is about 1J in a Gaussian pulse of 10ns. The laser beam is focused onto a spot about 0.6 mm in diameter by a lens (L1) of focal length 6.3 cm. A GaAs slice is used as target. The sample is positioned on a sample holder. The sample holder must permit a two-dimensional movement to allow fresh target areas to be irradiated by the laser. In the direction perpendicular to the incident laser beam, two cylindrical lenses (L2 and L3) are used to image the plasma optical emission onto the entrance slit of the spectrometer with a 1:1 magnification. The spectrometer is equipped with a 1200 groove/mm grating. The emission spectrum is subsequently detected by using a time and space resolved detecting system with an ICCD matrix of 1024*1024 pixels. The spectral range goes from UV (190nm) to NIR (900nm) with dispersion for the entire system of about 0.03 nm/pixel. With an entrance slit width of the spectrometer of 12 μ m, the system resolution is about 0.01 nm. The emission spectrum is then stored on a personal computer.

3. Results and discussion

3.1. Plasma emission

The plasma spectra are obtained at two different ultraviolet wavelength ranges, the first one between 215 nm and 245 nm and the second one between 265 nm and 295 nm, at an observation distance $d=2$ mm above the target surface. In addition the spectra of the range between

380 nm and 410nm is also detected. Emission spectra at different delays after the laser pulse are presented in the Fig.1. As it can be seen, in the very early stage the ablation plasma emit a very strong continuum. The intensity reaches its maximum at about 20 ns after the laser pulse. Then it decreases slowly with the plasma expanding, which comes from the cooperation of the bremsstrahlung and recombination processes of the plasma. With increase of the time, the spectral line emission of neutral atoms As and Ga can be observed, as shown in Fig.1 (b).

After a rough analysis of the spectra, the time evolution of the lines emitted by As I at 278.0 nm and Ga I at 287.4 and 294.4 nm are obtained for different laser energies, as presented in Fig. 2. The intensities of the spectral lines increase as the laser energy is varied from 10 mJ to 30 mJ. Three main features can be easily identified. The first is that the spectrum line of As atom emerge earlier but last for shorter time than those of Ga atom. recombination of Ga ions.

The reason for this is that the transition upper energy levels of the As lines are higher than those of the Ga lines, as shown in Fig. 3. At the early stage of plasma formation [6], the density and the temperature of the plasma is high, so the atom can be excited to the high states. But with expansion of the plasma, the decrease of the density and temperature lead to a reduction in the number of atom in the high states and the intensity of the corresponding lines.

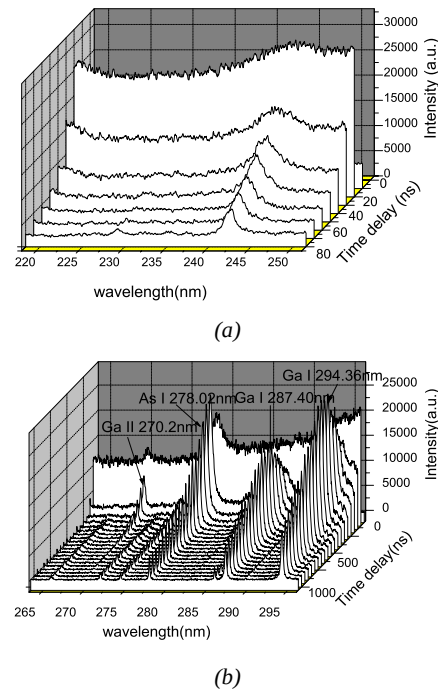


Fig. 1. Emission spectrum in ultraviolet generated by the 1064 nm, 10 ns laser (A) continuum emission (B) spectral line emission.

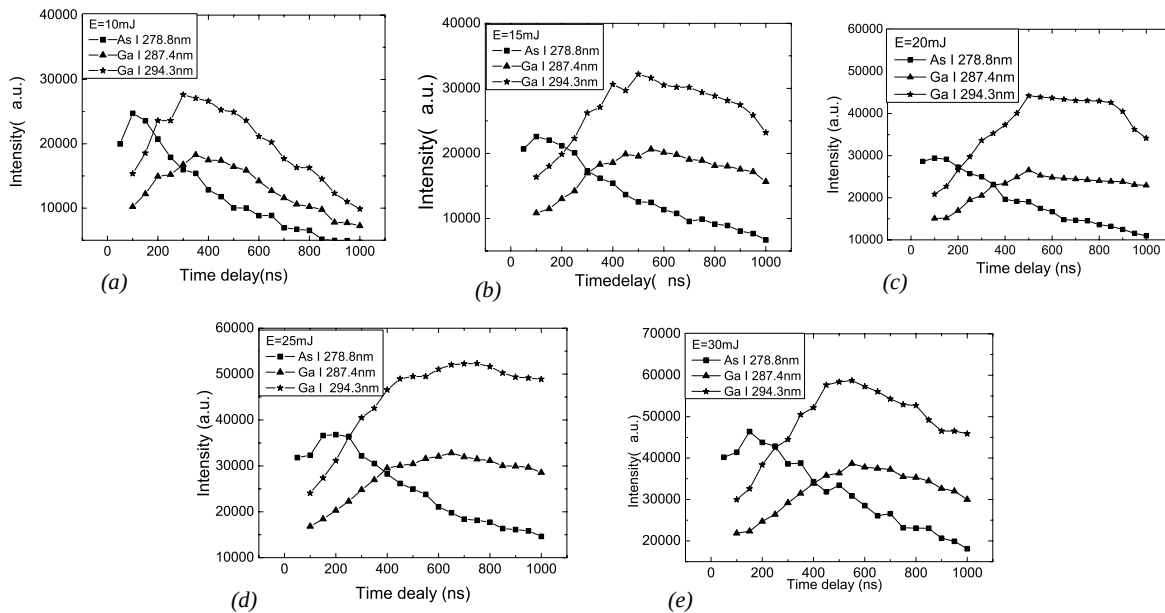


Fig. 2. The relative intensity of the spectral line emission of neutral gallium and arsenic induced by five different energy values as function of time delay (A)10mJ (B)15mJ (C)20mJ (D)25mJ (E)30mJ.

The second fact is that the atomic line intensities of the both species, Ga and As, begin with a increasing dependence in time followed by a decrease. This behavior is especially evidenced for the Ga atomic lines. We can explain this phenomenon as follows: the intensity of light emitted at particular wavelengths from an excited state is

proportional to the density of atoms in that excited state .so the recorded changes of the intensity of the spectral line at different time delays give information on the excited atoms.there are some transition from some high excited state to the upper energy levels of the Ga or As atom lines. For example as shown in Fig. 3 (a), the

lower energy level of Ga I 425 nm corresponding to transitions between the np^2P ($70 \geq n \geq 28$), nd^2D ($34 \geq n \geq 27$) and $5s^2S_{1/2}$ of Ga I is the upper energy level of Ga I 403.30 nm and 417.20 nm. The atoms transit from the upper energy level of 425nm to the lower energy level $5s^2S_{1/2}$, so the density of the atoms in the $5s^2S_{1/2}$ is increased. The same condition of Ga 287.40nm and 294.36 nm are exited which upper energy levels are the lower energy levels of lines transited from nf^2F ($8 \geq n \geq 4$) That is the chief reason of the phenomenon of increase at first and then decrease in the neutral atom lines. The third feature is that the intensities of emission lines increase as the laser

irradiance increases. Meanwhile the time of the Ga I lines reaching maximum postponed and the decrease trend becomes inconspicuous. This fact can be explained as follows: the increase in the intensity is due to the absorption of the laser energy by the plasma. The incident energy absorbed by the plasma is used to increase the internal energy of the plasma, so more energy can maintain the raise stage of the Ga lines for a longer time. The intensities descending trend of the Ga I spectral lines become very slow, which is mostly attributed to the ionization limited 48380 cm^{-1} .

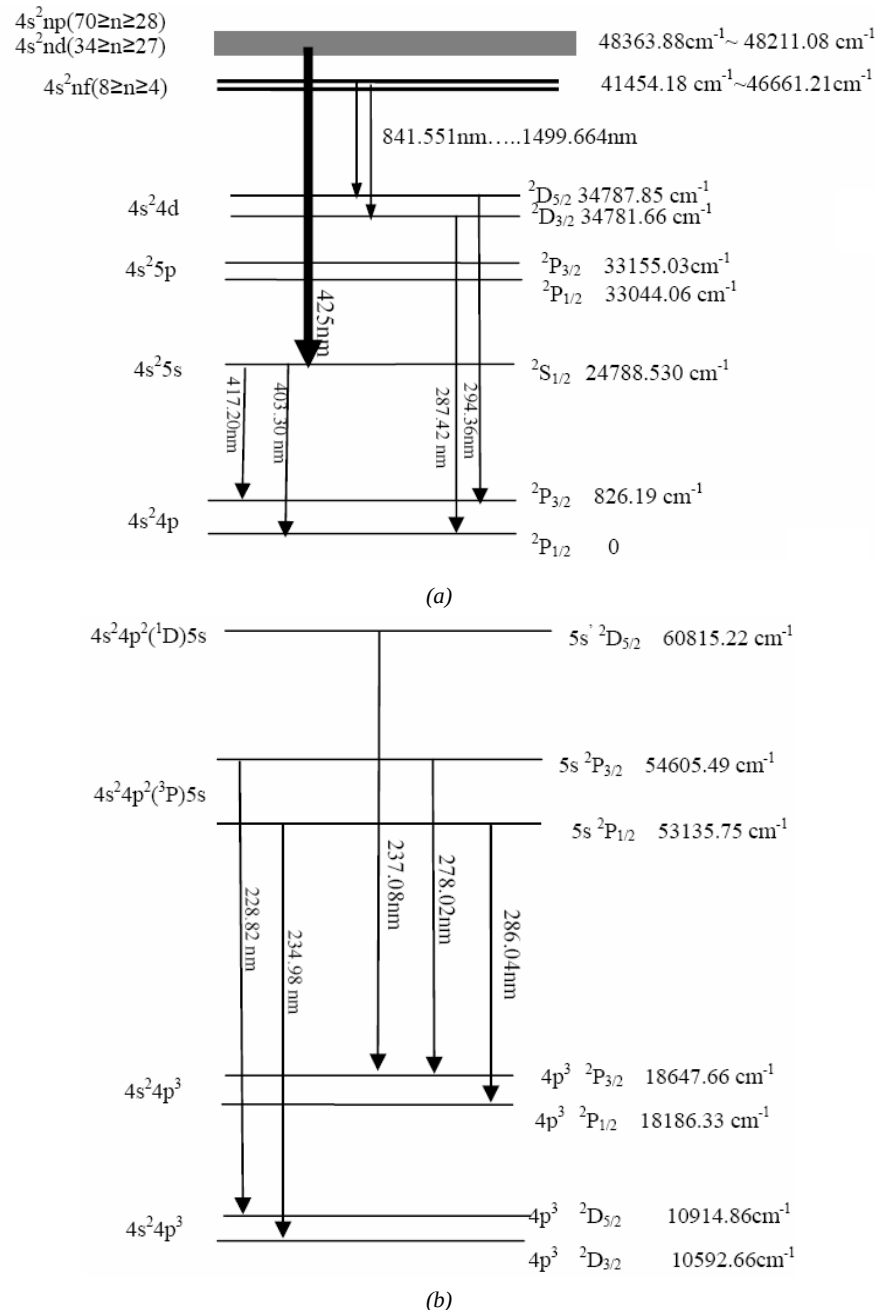


Fig. 3. Partial energy level diagrams of (a) neutral gallium (b) neutral arsenic.

3.2 Electron temperature measurement

The electron temperature is a very important parameter for laser induced plasma. It can reflect the highly transitory behavior of plasma. Many works have been carried out to determine this parameter in a time-resolved manner [7].

Under the assumption of LTE, the Boltzmann plot method is the most widely used method to calculate the electron temperature using the equation:

$$\ln \frac{I_{mn} \lambda_{mn}}{A_{mn} g_m} = -\left(\frac{1}{kT_e}\right) E_m + \ln\left(\frac{hcN_0}{U}\right) \quad (1)$$

Table 1. Details of the chosen transition with their emission wavelength, upper state energy, statistical weights of upper (g_m) and lower (g_n) state, and transition probably (A_{mn}).

Species	Wavelength (nm)	E_m (cm ⁻¹)	E_n (cm ⁻¹)	g_m	g_n	A_{mn} (10 ⁸ s ⁻¹)
AsI	228.81	54605.491	10914.866	4	6	3.827
AsI	234.98	53135.750	10592.666	2	4	12.90
AsI	236.97	60834.954	18647.663	4	4	2.900
AsI	274.50	54605.491	18186.328	4	2	4.621
AsI	278.02	54605.491	18647.663	4	4	14.92

In the initial stage of the plasma, there is no isolated line emerged. The Boltzmann plot method cannot be used to get the temperature. But the radiation of the plasma is similar to the radiation of the blackbody. So the radiation intensity can be described by the equation of the blackbody radiation:

$$I = \frac{2hc^2}{\lambda^5} \times \frac{1}{e^{hc/k\lambda T} - 1} \quad (2)$$

The temperature can be determined by the relative intensity measurements at different wavelengths:

$$\frac{I_1}{I_2} = \left(\frac{\lambda_2}{\lambda_1}\right)^5 \times \frac{e^{hc/k\lambda_2 T} - 1}{e^{hc/k\lambda_1 T} - 1} \quad (3)$$

So the whole process can be divided to two parts. (1) The early stage of the plasma: equation (3) is used to estimate the electron temperature. (2) The expansion stage: as the lines of As I emerge, five of them are used to estimate the electron temperature by using equation (1). Fig. 4 shows the time evolution of the electron temperature for different laser energies. The electron temperature peak rises from about 18000 K to about 25500 K as the laser energy increases from 10 mJ to 30 mJ. The temperature in the early stage is very high and decreases quickly with the expansion of the plasma. But in the later stage the change of the temperature becomes very slowly. Fig.4 also suggests that the black body radiation approximation is not the most appropriate way. This method is just as a rough

estimation. where I_{mn} , λ_{mn} , A_{mn} , g_m , and E_m are the line intensity, wavelength, transition probability, statistical weight and energy for the upper level, respectively. T_e , c and k are the electron temperature, velocity of light and Boltzmann constant, respectively. The total number density N_0 and the partition function U are not required in this method. Many works have used this method to estimate the electron temperature [8,9]. Five lines of neutral As (228.81 nm, 234.98 nm, 236.97nm, 274.50nm, 278.02 nm) are used to estimate the electron temperature. The spectroscopic details of the transition lines are listed in Table 1.

estimation.

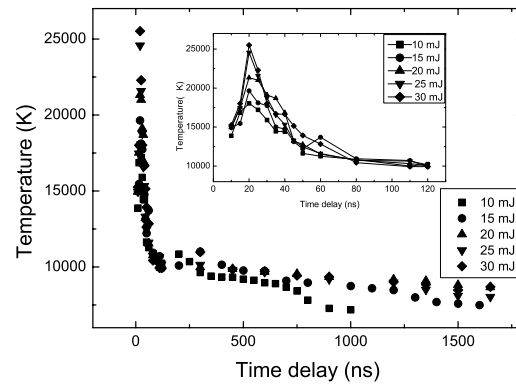


Fig. 4. Variation of the temperature with the time delay by five different laser energy values. The inset gives the variation of the temperature as function of time delay in the early stage.

3.3. Electron density measurement

As was known, the line profiles are determined by the collisions of the emitting atoms with ions and electrons (Stark broadening), and also by the movement of the emitting species (Doppler broadening). Stark broadening has been proved to be the dominating mechanism of line broadening in laser plasma [6]. In fact, for our conditions, the Doppler broadening for Ga and As species is about 0.01nm.

The full width at half maximum (FWHM) of the line profile obtained by Stark broadening, $\Delta\lambda_{1/2}$ is related to the electron density N_e and the electron temperature T (by means of number particles in the Debye sphere) by [10]:

$$\Delta\lambda_{1/2} = 2w \left(\frac{N_e}{10^{16}} \right) + 3.5A \left(\frac{N_e}{10^{16}} \right)^{1/4} \times \left(1 - \frac{3}{4} N_D^{-1/3} \right) w \left(\frac{N_e}{10^{16}} \right) \quad (4)$$

$$N_D = 1.72 \times 10^9 \frac{[T_e(\text{eV})]^{3/2}}{[N_e(\text{cm}^{-3})]^{1/2}} \quad (5)$$

Here, the first term is contribution due to electron impact and the second one is the ion broadening correction. w , A , and N_D are the electron impact parameter, ion broadening parameter, the number of particles in the Debye sphere, respectively. In most cases, the ion contribution to line broadening is much smaller than that due to the electron impact. So in practice the second term in equation (4) would be neglected, so that the equation (4) is simplified as follows:

$$\Delta\lambda_{1/2} = 2w \left(\frac{N_e}{10^{16}} \right) \quad (6)$$

This equation is usually used to obtain the electron density. We must remind that besides the real broadening produced into the plasma, the line profile observed by the spectrum detecting system includes also the instrumental broadening. To insure the accuracy of the result, the instrumental broadening was also considered and a deconvolution procedure was carried out. In our measurement, the NII 399.5 nm line is used to estimate the electron density. Value of $w=0.028$ nm given in [11] in the temperature region between 5000K and 8000 K near to our conditions are used in this paper. This is because w and A are weak function of temperature. The trend of electron number density is shown in Fig. 5.

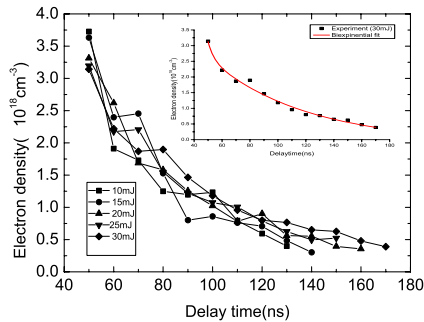


Fig. 5. Electron density of plasma at 2.0 mm from the target surface with five laser energy values. The inset gives the evolution of the density ablated by 30 mJ approximated by a biexponential function.

The Fig. 5 shows that the electron density evolution can be approximated by a decreasing biexponential

function. The biexponential function can be expressed in the following formation:

$$Y = Y_0 + A_1 e^{-\frac{(x-x_0)}{t_1}} + A_2 e^{-\frac{(x-x_0)}{t_2}} \quad (7)$$

A physical rationale for approximating evolution by a biexponential function can be provided as follows: when the particle density is non-uniform, the plasma can be conditionally divided into two compartments: one of the compartment located far from the edges of the plasma and the evolution of particle density can be considered as unrestricted. Evolution of particle density from the second compartment located near the boundaries, is more restricted due to encountering the boundaries. With the increase of the time delay, the electron density decreases about from $3.5 \times 10^{18} \text{ cm}^{-3}$ to $0.5 \times 10^{18} \text{ cm}^{-3}$. But by contrast with the lines intensities, which change with the laser energy, as it is shown in fig.2, the electron density seems to do not depend on the laser energy obviously.

On the basis of equation (6), the electron density is approximately proportional to the FWHM of Stark broadening. So the evolution of the electron density can be estimated indirectly. Fig. 6 shows the measured FWHM of the Ga I emission line at 294.4 nm. The evolution of the FWHM can also be approximated by a decreasing biexponential function. So the evolution of the electron density is a decreasing biexponential function which decrease rapidly within 400 ns and the slowly after 600 ns.

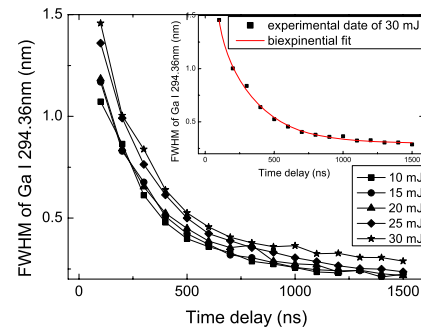


Fig. 6. Measured FWHM of the emission line at 294.36 nm of neutral Ga. The inset gives the experimental data of 30 mJ and the biexponential fit lines. Dashed lines are the experimental data points, solid lines is the biexponential fit lines.

3.4 Line broadening and shift

Although the Stark effect is the main mechanism of line-broadening, it is distinguishing for different elements. In our work we measure the line widths and shifts of As I 278.02 nm and Ga I 287.40 nm respectively and also compare them and analyze the differences. First, the Stark width of the Ga I 287.40 nm is larger than that of As I

278.02 nm, as shown in Fig. 7. This result is acquired at the laser energy of 10 mJ. The similar situations can also be detected in other laser energies. It can be explained by the relation of the stark width and the effective ionization potential [12]. The stark width's dependence on lower-level ionization potential is

$$w = \sum_k A_k I^{-k} \quad (8)$$

where A_k is coefficient independent of the lower level ionization potential I . As shown in the Fig. 3 (b), As I 278.02 nm line is attributed to $5s^2P_{3/2} \rightarrow 4p^3^2P_{3/2}$ transition, the corresponding lower-level ionization potential is 7.74 eV. While Ga I 287.40 nm line corresponds to $4s^24d^2D_{3/2} \rightarrow 4s^24p^2P_{1/2}$ and the lower-level ionization potential is 6.0 eV, so the corresponding width should be larger than that of As I line.

Unlike the line width, the line shift have different trend for two spectral lines. The shift of As I 278.02 nm is distinct but the line shift of Ga I 287.40 nm is too small to be considered. It is mostly attributed to their level states and the quadratic stark effect [13]. The shift of level is more significant for the higher excited state. As shown in the Fig.3, the upper and lower states of Ga I 287.40 nm line are both lower than that of the As I 278.02 nm line. So quadratic stark effect is more effective in transition of the As I 278.02 nm line.

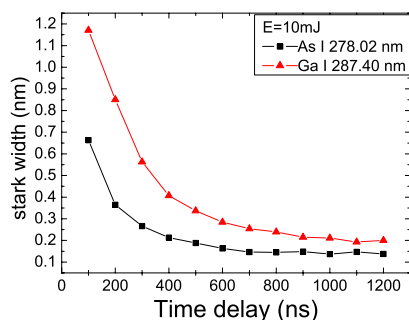


Fig. 7. The stark widths of the Ga I 287.40 nm and the As I 278.02 nm as function of time delay.

4. Conclusions

We have presented a study of the GaAs plasma induced by a Nd:YAG laser in air for five different energies and investigated the time-resolved emission spectra. The evolution and the character of the spectral lines were analyzed. Under the assumption of LTE, the plasma parameter such as the electron temperature and the density were extracted. Boltzmann plot method and black body radiation approximation were used to calculate the electron temperature. The result indicates that the electron temperature reaches the maximum at 20 ns which corresponds the time of the intensity of the continuous

spectra reaching the maximum. The line width of the N II (399.50 nm) and the Ga I (294.36 nm) were used to estimate the evolution of the electron density. The electron density at the initial stage is very high and decreases rapidly at first but becomes tardo with the time delay. The evolution of the electron density can be fitted by a decreasing biexponential function. In addition, we detected and analyzed the line width and shift of the Ga I 287.40 nm and As I 278.02 nm line. The line width of Ga I 287.40 nm is larger than that of As I 278.02 nm. While the line shift of As I 278.02 nm line is more significant than that of Ga I 287.40 nm line.

Acknowledgments

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References

- [1] M. Liu, X. Q. Wei, Z. G. Zhang, G. Sun, C. S. Chen, C. S. Xue, H. Z. Zhuang, B. Y. Man, *Appl. Surf. Sci.* **252**, 4321 (2006).
- [2] L. Gui-Yun, B. Xia, Z. Gang, *Chin. Phys.* **13**, 4 (2004).
- [3] B. Y. Man, *Appl. Phys. B* **67**, 241 (1998).
- [4] G. H. Lv, B. Y. Man, Y. H. Zhang, A. H. Liu, Q. G. Zhang, *Optik* **115**, 347 (2004).
- [5] B. Y. Man, X. T. Wang, X. R. Hu, X. X. Guo, Y. Miao, *N. S. T.* **8**, 98 (1997).
- [6] B. Y. Man, Q. L. Dong, A. H. Liu, X. Q. Wei, Q. G. Zhang, J. L. He, X. T. Wang, *J. Opt. A-Pure Appl. Opt.* **6**, 17 (2004).
- [7] N. Tian-Ye, C. Jin-Xiang, L. Lei, L. Jin-Ying, W. Yan, W. Liang, L. You, *Chin. Phys.* **16**, 9 (2007).
- [8] M. J. Ying, Y. Y. Xia, Y. M. Sun, Y. Ch. Ma, M. W. Zhao, X. T. Hao, X. D. Liu, *Opt. Laser. Techno.* **35**, 475 (2003).
- [9] H. L. Xu, J. Bernhardt, P. Mathieu, G. Roy, S. L. Chin, *J. Appl. Phys.* **101**, 033124 (2007).
- [10] G. Bekefi, *Principle of laser plasma*, Wiley, New York, 593, 1976.
- [11] H. R. Griem, *Plasma spectroscopy*, McGraw-Hill, New York, 463, 1964.
- [12] I. S. Lakicevic, *Astron. Astrophys.* **127**, 37 (1983).
- [13] B. H. Bransder, C. J. Joachaen, *Physics of atoms and molecules*, Longman, London, New York, 378, 1983.

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