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Determination of parameters of the laser-induced silicon plasma by laser-induced breakdown spectroscopy

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С использованием методики лазерной спектроскопии исследованы свойства лазерной плазмы при нормальном атмосферном давлении, формирующейся на поверхности кремния под действием лазерного пучка Nd:YAG с длиной волны 1064 нм и длительностью импульса 10 нс. Рассмотрены спектральные профили и механизмы расширения спектра лазерной плазмы, сформированной на поверхности кремния. Плотность электронов в плазме на определяли методом Штарка для расширения спектральных линий лазерной плазмы. Температуру электронов рассчитывали в зависимости от плотности мощности лазерного излучения и соотношения интенсивностей двух спектральных линий, образованных одним и тем же ионным переходом, а также с использованием уравнения Больцмана.

Ключевые слова: LIBS, спектроскопия, лазерная плазма, электронная плотность, метод расширения Штарка, профиль линии Гаусса, профиль линии Лоренца.

We study the properties of laser plasma at normal atmospheric pressure, which is induced on the surface of silicon under the action of an Nd:YAG laser beam with a wavelength of 1064 nm and a pulse duration of 10 ns using the method of laser spectroscopy. The spectral profiles and mechanisms of the spectrum expansion of laser plasma induced on the surface of the silicon substrate are considered. The different fitting functions were used for the analysis of plasma parameters of the Si target. The Gaussian fitting function of the spectral lines was more suitable for accurate calculations of the electron density by the Stark expansion method. The electron temperature was calculated depending on the power density of the laser light and the ratio of the intensity of two spectral lines formed by the same ionic transition, as well as using the Boltzmann equation.

Keywords: LIBS, spectroscopy, laser plasma, electron density, Stark expansion method, Gaussian line profile, Lorentzian line profile.

I. Introduction

Laser-induced breakdown spectroscopy (LIBS) remains to be one of the main methods due to its simplicity and express analysis of the plasma parameters. This technique allows the qualitatively and quantitatively composition analysis of unknown elements (like metals, polymers, semiconductors etc.) by their plasma emission excited in the field of ultrashort laser pulses [1-2]. Usually, the process analyzing the composition of elements consists of three steps. First, the plasma emission should be induced on the material's surface using ultrashort laser pulses, the second

step is recording plasma spectrum in the spectrophotometer, and the last step is analyzing the collected plasma spectrum using certain mathematical procedures. In this work, we studied laser-induced plasma (LIP) parameters of the silicon target in normal conditions. Nowadays, the silicon element is one of the semiconductor and unique materials, and it forms a major part of high-tech electronic, photocell and display devices. There is a great need to recycle and restore this element [3]. However, the above mentioned application requires a high-quality and low-impurity Si wafer. The composition analysis based on the LIBS technique can provide an express analysis of the composition of the silicon substrates.

II. Materials and methods

The study of the parameters of the plasma-induced on the surface of silicon target by the LIBS method is described. The LIP on the surface of the Si target was excited with an Nd:YAG laser at the wavelength of 1064 nm and a pulse duration of 10 ns under normal conditions. The fibre spectrophotometer (HR4000, Ocean Optics) was used as a detector of the plasma emission (Fig. 1). The spectrophotometer is a high-precision optical fibre spectrometer that provides optical accuracy up to 0.025 nm full width of the half maximum (FWHM) and allows to analyze plasma spectra in the wavelength range of 200 nm to 1100 nm.

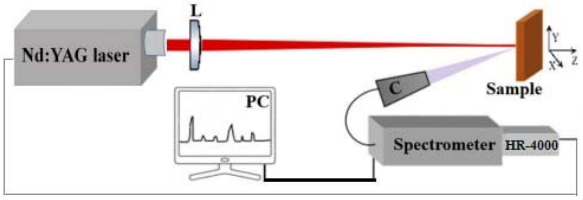


Figure 1. Optical scheme of the experimental setup on LIBS.

The plasma excited on the surface of the Si target consists of spectral lines of a transition of neutral atoms (I) and single-charged ions (II) (Fig. 2).

LIP on the surface of Si, excluding the effect of expansion mechanisms, the transition of an electron from a high energy level to a low energy level in stationary atom results in its thin line spectral intensity due to natural expansion. However, when working with plasma, the expansion mechanisms help form a spectral line with a larger width. Natural expansion occurs due to the Heisenberg uncertainty principle

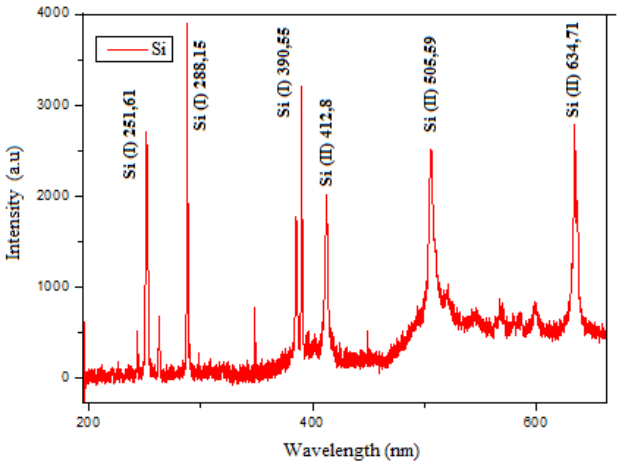


Figure 2. Plasma emission spectrum induced on the silicon surface by 1064 nm laser pulse.

which is significant in plasma spectroscopy [4, 5] because spectral lines expand only naturally. The Doppler effect is one of the main plasma expansion mechanisms [6-9]. The Doppler width depends on the system's temperature and the element's atomic mass [5, 6].

$$\Delta\lambda_D = \left(7.2\times10^{-7}\right)\left(\frac{T}{M}\right)^{1/2}\lambda_0\,, \qquad (1)$$

where M is the atomic mass of the element and λ_0 is the central wavelength of the spectral line.

Collision or pressure expansion is another major mechanism of line expansion in plasma, which occurs when atoms or radiating ions collide with neutral or charged particles [5, 7]. The colliding of the excited ions with different neutral atoms leads to the Van der Vaals expansion of the spectral line of the LIP. The collision between the excited atom and the same neutral atom in the ground state leads to resonance expansion [5, 7, 8]. Van der Vaals' expansion results from the dipole interaction between the excited atom, the induced dipole, and the other neutral atom in the ground state [10, 11]. The resonance expansion occurs between the same neutral atoms with high and low energy levels that transition the electric dipole to the ground state [11, 12]. This effect contributes not only to the expansion of the spectrum but also to the shift of the emitted wavelength [6, 7, 13]. Stark expansion occurs when charged particles collide with ions or electrons [6, 13]. The electric field of an ion or electron also causes the atom's energy levels to split into lower levels, which contributes to their emission. The variation of the spectral lines occurs

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due to the transition of excited electrons between the lower excited and ground state level [6, 13].

The spectral line can widen due to the instrumental perturbations rather than combining Doppler and collision or pressure expansion [8], and this may be possible when using a low-precision spectrometer for spectral analysis. However, a high-precision spectrometer does not entirely eliminate the broadening of the spectral line. Instrumental resolution may be as high as possible, but plasma expansion is still a significant contributor to the spectral lines. Here the magnitudes of Natural, Doppler, Stark, Resonance, Van der Waals and Instrumental expansion are shown in Table 1 [14].

Table 1. The magnitudes of the expansion mechanisms in the laser-indused plasma.

Expansion mechanisms	Size (nm)
Natural	10^{-4}
Doppler	10^{-3}
Stark	10^{-2}–10
Resonance	10^{-3}
Van der Vals	10^{-3}
Instrumental	10^{-1}–10^{-3}

Usually, Doppler expansion leads to the Gaussian line profile, and collision expansion gives the Lorentz profile [6, 15]. A compromise must be made between the Lorentz and Gauss profiles because the spectral line obtained from LIBS plasma includes the line width developed from Doppler and collision magnification. Combining the two profiles gives the Voigt profile, but it is not easy to apply in the analysis [15]. While computer programs can still perform Voigt fitting, the computation time is much longer, especially if the spectral lines are asymmetric.

We compared three fitting models, Gaussian, Lorentzian and Voigt (Fig. 3). In the case of Gaussian fitting was better due to the determination coefficient (R^2) being closer to one, the corresponding function represents the data set well. In this case, the Gaussian fitting has a detection coefficient close to 1 compared to Lorentzian and Voigt.

III. Determination of electron density

The wavelengths for silicon ions corresponding to the plasma spectra and the widths of these transition lines were determined, which made it possible to determine the concentrations of free electrons in the plasma using the Stark expansion method.

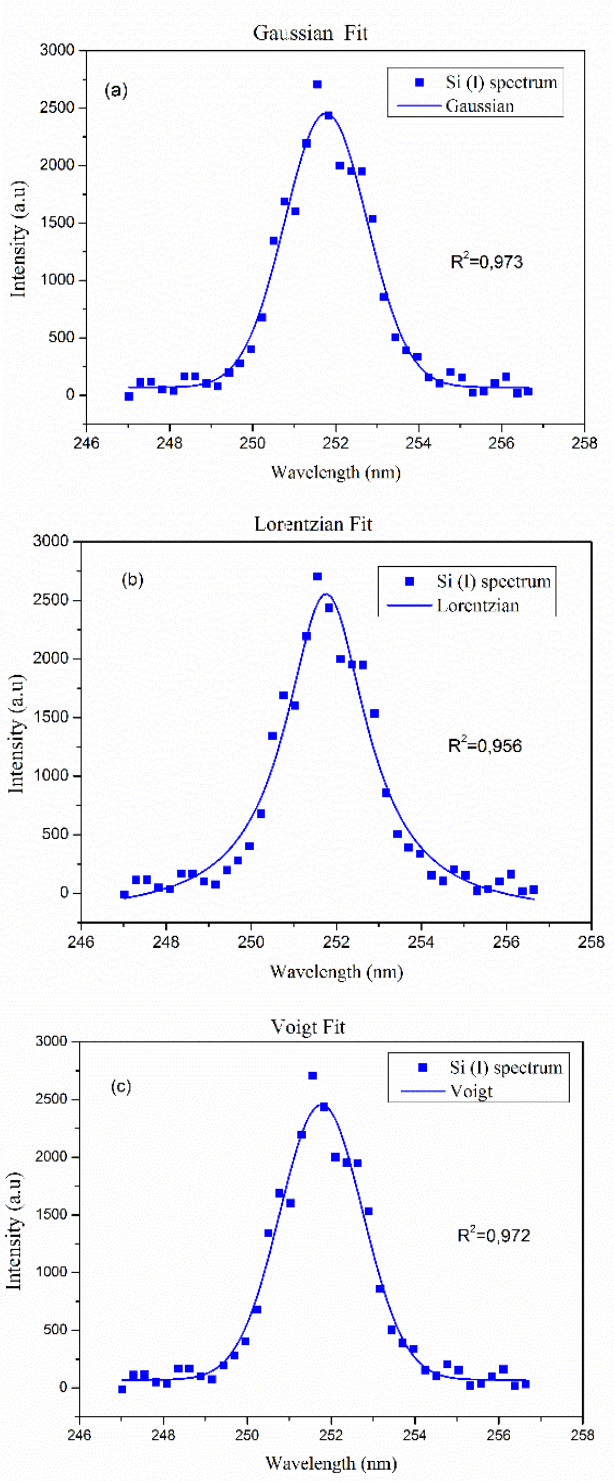


Figure 3. Spectral line of the neutral atoms of Si (I) in the plasma: Gaussian (a), Lorentzian (b), Voigt (c) fits.

The Stark effect is the displacement and division of the spectral lines of atoms and molecules due to the presence of this external field. The Stark effect can also be observed for emission and absorption lines.

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The abrupt expansion of the spectrum results from the collision of charged particles by lines in the plasma spectrum. As shown by the difference between the electron density and the FWHM, the Stark extended line is as follows:

$$\Delta\lambda_{1/2} = \left[2W\left(\frac{n_e}{10^{16}}\right) + 3.5A\left(\frac{n_e}{10^{16}}\right)^{1/4}\left(1-\frac{3}{4}N_D^{-1/3}\right)W\left(\frac{n_e}{10^{16}}\right)\right]\text{Å}, \quad (2)$$

where N_D is the number of particles in the Debye sphere, A is the interaction parameter of ions, and W is the electron interaction parameter. First and second terms on the right side of the equation express expansions due to the interaction of electrons and ions. For non-hydrogen ions, Stark expansion is dominated by electron interaction and thus ion interaction, and the coefficient of ion interaction is negligible [16]. The resulting Stark expansion is as follows.

$$\Delta\lambda_{1/2} = 2W\left(\frac{n_e}{10^{16}}\right)\text{Å}. \quad (3)$$

$\Delta\lambda_{1/2}$ = FWHM is the full width of the half maximum for the corresponding spectral line, n_e – electron density.

The electron densities were determined using the Stark expansion method on a scale corresponding to the wavelength values of the spectrum formed by the neutral atoms and charged ion transitions of the Si element (I) and (II) (Table 2). In this case, half of the spectral band width (FWHM) was determined by Gauss fitting with a high detection coefficient R^2 for the silicon spectrum line (Fig. 3). Here, ionic transitions with very close scales were separated and calculated separately.

The numerical value of electron interaction parameter W was taken from tabled data [17]. The Mc Whirter criterion gives the lower limit of the electron density to check the condition for the validity of the local thermodynamic equilibrium (LTE) [18]:

$$n_e \geq 1.6\times10^{12}T^{1/2}(\Delta E)^3 \quad (4)$$

where T (in K) is the plasma temperature and E (in eV) is the energy difference between the states, which are expected to be in LTE. The electron density from the Eq. 3 was equal to be $n_e \approx 10^{16}$ cm^{-3} at the 0.8 eV of the LIP. The electron densities determined in our experiments are higher than this required number density to satisfy the LTE conditions.

Table 2. The parameters of the Si plasma undused by the laser ablation.

Element	Si (I)		Si (I)
λ (nm)	251.61		288.15
FWHM (nm)	2.33		0.85
W (Å)	0.70		0.54
n (10^{17} cm^{-3})	1.66		0.78
Element	Si (II)	Si (II)	Si (II)
λ (nm)	412.8	505.59	634.71
FWHM (nm)	1.9	3.51	1.28
W (Å)	1.29	1.8	1,2
n (10^{17} cm^{-3})	0.73	0.97	0.54

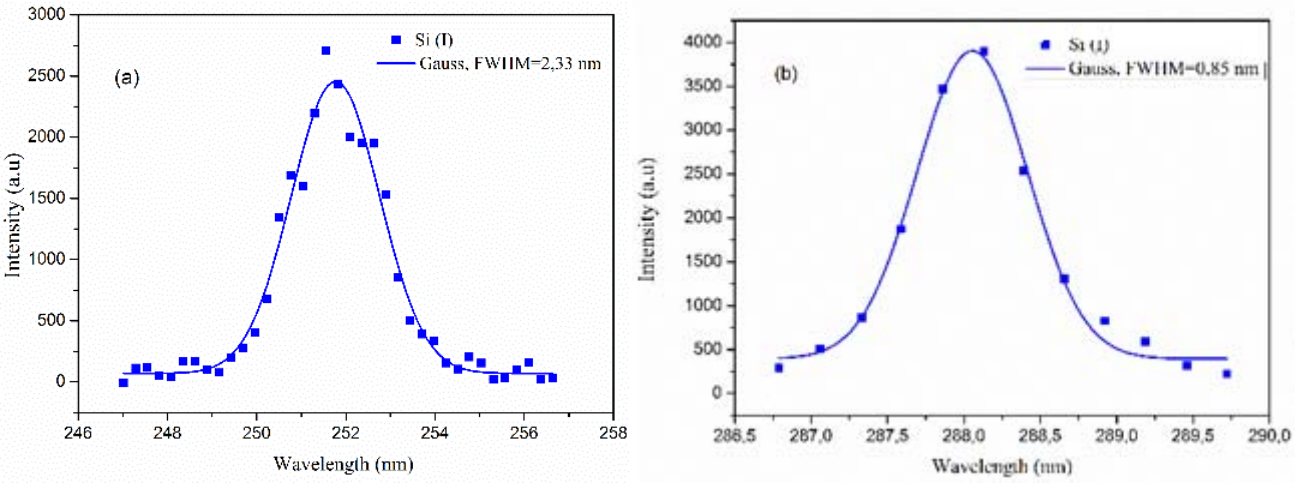


Figure 4 (a,b). Intensity dependence of the spectral line of the plasma emission on the Si target surface: (a) Si (I) λ = 251.61 nm; (b) Si (I)λ= 288.15 nm.

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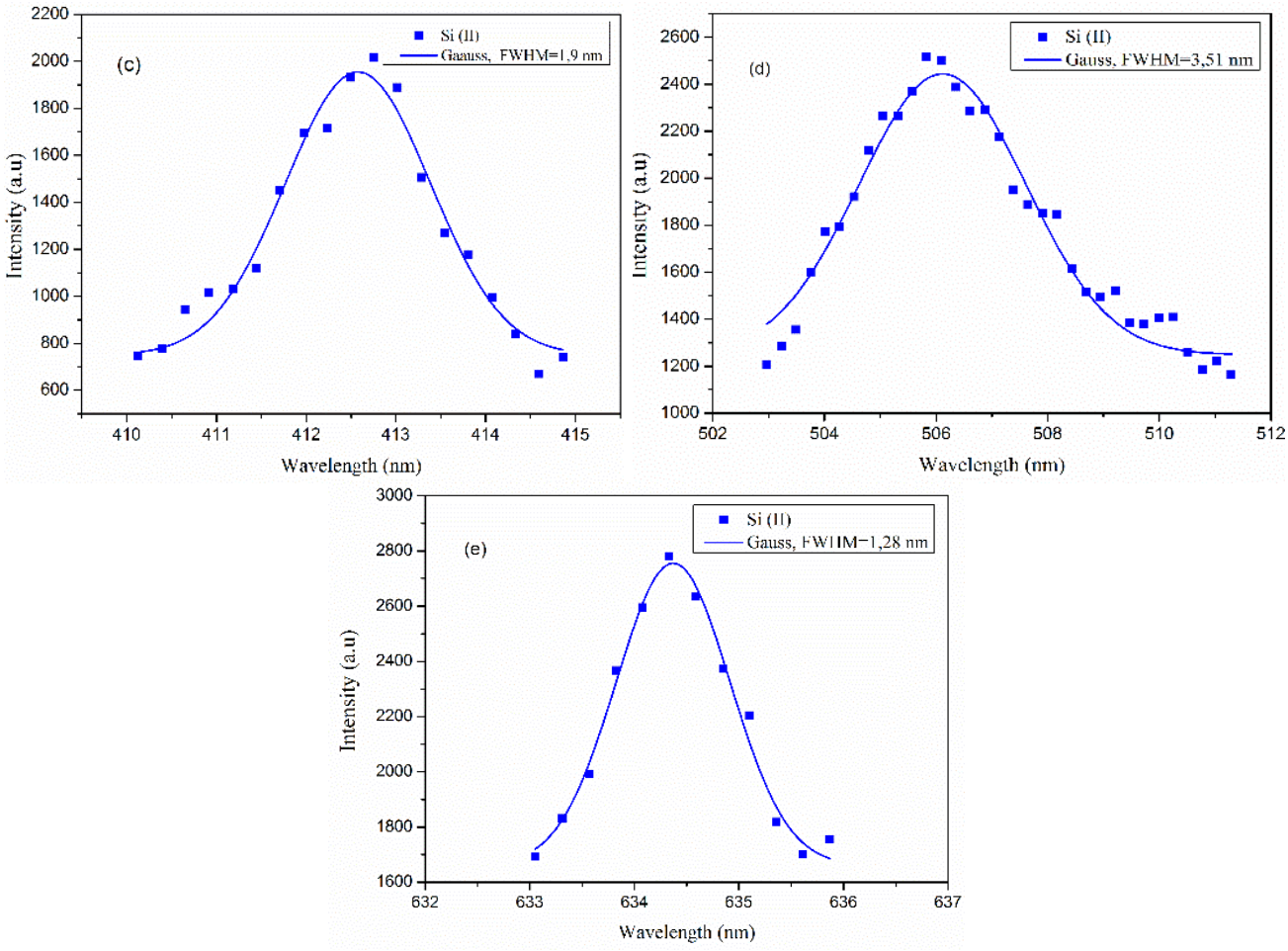


Figure 4 (c,d,e). Intensity dependence of the spectral line of the plasma emission on Si target surface: (c) Si (II) λ = 412.8 nm; (d) Si (II) λ = 505.59 nm; (e) Alignment of the spectra on the scales Si (II) λ= 634.71 nm with the Gaussian impulse.

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IV. Determination of electron temperature

In the first approach, the temperature of the Si plasma is determined by the laser power density [19, 23]. The expression for determining the temperature is as follows:

$$T = q^{4/9} A_z^{2/9} \left(\frac{Z}{Z+1} \right)^{2/3}, \qquad (5)$$

where q is the power density of the focused laser radiation, A is the atomic mass, and Z is the number of multicharged ions in the plasma. The power density of the Nd:YAG laser selected in the experiment is 10^{11} W/cm^2. The atomic mass of Si is 28.08 g/mol and Z is equal to (I) and (II).The given values were set to (5) and the plasma temperature was determined Z=1, T=1.89 eV and Z=2, T=2.3 eV.

Second, the plasma temperature is determined using the well-known Boltzmann plot method via the relative line intensities of the emission spectrum of the laser-induced Si plasma plume. Considering the plasma in the local thermodynamic equilibrium (LTE), the populations of different excited levels at a specific temperature obey the Boltzmann distribution law [13, 20]

$$N_i = g_i \frac{N_0}{U(T)} \exp\left(-\frac{E_i}{kT_e} \right), \qquad (6)$$

where g_i is the statistical weight of the upper level, N_0 (cm^{-3}) is the total number density, $U(T)$ is the partition function, E_i (J) is the energy of the excited level, k (J/K) is the Boltzmann constant and $T_e(K)$ is the excitation temperature. The line intensity of a

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transition from an upper level to a lower level is expressed as:

$$h\nu_{ik} A_{ik} N_i = \frac{hc}{\lambda_{ik}} A_{ik} g_i \frac{N_0}{U(T)} \exp\left(-\frac{E_i}{kT_e}\right), \qquad (7)$$

where the subscripts i and k represent the upper and lower atomic levels, λ_{ik} (nm) is the wavelength of the spectral line, A_{ik} (s^{-1}) is the transition probability for the spontaneous emission.

Considering plasma as an optically thin, where the matter is not in thermodynamical equilibrium with the radiation, because collisions between particles and photons are very rare, the simplest method for the intensity ratio of the two emission lines is used and excitation temperature is reformulated:

$$T_e = \frac{(E_2 - E_1)}{k \ln\left(\frac{I_1}{I_2}\frac{\lambda_1}{\lambda_2}\frac{A_2}{A_1}\frac{g_2}{g_1}\right)}. \qquad (8)$$

Taking the two lead lines at 251.61 nm (g_1=5, A_1= 1.68×10^8 s^{-1}) and 288.15 nm (g_2=3, A_2=2.17×10^8 s^{-1}), and substituting the observed line intensities and the other constants in this equation we calculated the excitation temperature as 6.01 eV.

A more accurate value of the excitation temperature can be calculated using the Boltzmann plot method in which several spectral lines and their relative line intensities are considered [20]:

$$\ln\left(\frac{I_{ik}\lambda_{ik}}{hcA_{ik}g_i}\right) = -\frac{E_i}{kT_e} + \ln\left(\frac{N_0}{U(T)}\right). \qquad (9)$$

A plot of the left side of this equation versus the energies of the upper levels yields a straight line with a slope of $1/kT_e$. In Table 3, the transition wavelengths (nm), upper level energies, statistical weights (g) and transition probabilities (s^{-1}) of the six lines used to construct the Boltzmann plot are listed.

Table 3. The parameters of the Si-neutral atoms, and ions induced by laser ablation.

Atom/ ion	Wavelength, λ_{ki}, (nm)	Upper level energy, E_k, (sm^{-1})	Statistical weight g_k	Transition probabilities $A_{ki}\times10^8$, (s^{-1})
Si (I)	251.61	39955.053	5	1.68
Si (I)	288.15	40991.884	3	2.17
Si (I)	390.55	40991.884	3	0.133
Si (II)	412.57	103556.16	6	1.49
Si (II)	505.59	101024.35	6	1.45
Si (II)	634.37	81251.32	2	0.68

The Boltzmann plot is shown in Fig. 5. The plot's linearity is evident, reflecting that the plasma may be considered optically thin.

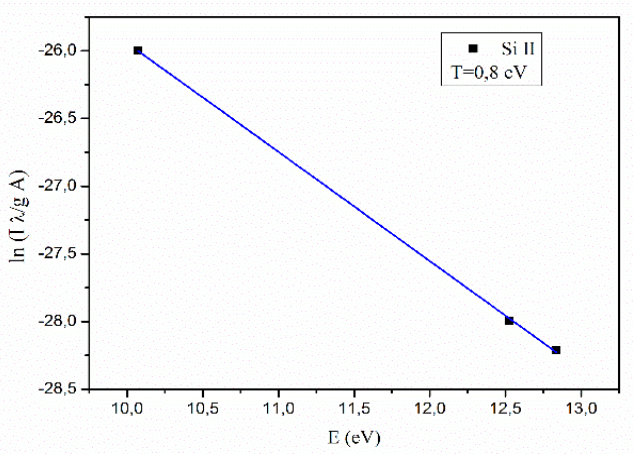


Figure 5. Boltzmann plot based on three Si II spectral lines.

It was found that the value of Si (II) forsingle-chargedion transitions is T=0.8 eV, where the graph's slope indicates the plasma temperature.

The plasma frequency is given by [21, 23]:

$$\nu_p = 8.9\times10^3 \, n_e^{1/2}$$

where n_e is the electron density. For our case, the plasma frequency is estimated as 3.44×10^{12} Hz, less than the laser frequency. Hence, energy loss due to laser reflection from the plasma is insignificant.

The comparative results of the optical study of dependence of Si plasma temperature on the distance from the sample surface demonstrated the variation of the electron temperature in the range from 7500 to 4000 K. The electron density which changes from 3.2×10^{17} to 1.8×10^{17} cm^{-3} seems to be in local thermodynamic equilibrium (LTE) condition [22]. In particular, the electron temperature in the distance 0.05 mm and 2 mm from the target surface was estimated as 13980 K, and 12110 K, respectively.

V. Conclusions

We studied the laser-induced plasma on the Si surface by using 10 ns pulse duration and wavelength of 1064 nm laser pulses. The parameters of the laser-induced plasma plumes were estimated. The electron concentration and plasma temperatures were estimated and their values were equal to $n_e \approx 10^{17}$ cm^{-3} and $T_e \approx 0.8$ eV. The calculation of the plasma parameters was based on the Stark expansion method. Using obtained results for Si, it is possible to conduct qualitative and quantitative analysis of Si-mixed substances in the solid state.

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Кремний юзасида ҳосил бўлган плазмани параметрларини LIBS спектроскопияси ёрдамида аниқлаш

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Ушбу ишда нормал атмосфера босимида кремний юзасига тўлқин узунлиги 1064 нм, импульс давомийлиги 10 нс бўлган Nd:YAG лазер нурланиши таъсирида ҳосил бўлган плазма спектроскопик усули ёрдамида ўрганилди. Кремний сиртида ҳосил қилинган лазер плазмаси спектрини кенгайтириш механизмлари ва спектр профиллари кўриб чиқилди. Кремний плазмасини асосий хусусияти бўлган электрон зичлиги Штарк кенгайиш усули ёрдамида аниқланди. Электрон температураси лазер нури қувват зичлигига боғлиқ равишда ва бир хил ион ўтишдан ҳосил бўлган иккита спектрал чизиқнинг интенсивлиги нисбати билан ҳамда Больцман тенгламасидан фойдаланиб ҳисобланди.

Калит сўзлар: LIBS, спектроскопия, лазер плазмаси, электрон зичлиги, Штарк кенгайиш усули, Гаусс профили, Лоренц профили.

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