SPECTROSCOPIC STUDY OF LASER-PRODUCED SILVER PLASMA

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Time-averaged spectra of a laser plume and the time dynamics of the most intense spectral lines are studied under neodymium laser irradiation (1.06 μm; $(1 \div 3) \times 10^8$ W/cm^2; 20 ns; 12 Hz) in vacuum (3—5 Pa) at distances of 1 and 7 mm from a silver target. The obtained results are used to construct a time-averaged energy distribution of excited states of silver atoms and to estimate the relaxation time and electron temperature.

Introduction

In recent years, a considerable attention is devoted to investigations of the laser-produced plasma for the following reasons: the possibility to create film materials for micro- and optoelectronics demands, development of nanotechnology, improvement of the quantitative spectral analysis [1—4]. The emission spectroscopy allows one to investigate the main regularities of the evolution of a laser-produced plasma with a strong spatio-temporal separation. The obtained results are important to optimize the above-mentioned processes.

We failed to find papers with the detailed spectroscopic diagnostics of the ablation silver plasma. Therefore, in the present paper, we investigate the characteristic emission spectra of such a plasma and their space-time development. The obtained results give an idea of the main ways of the creation of excited particles, enable the more detailed analysis of multicomponent samples containing silver, and reveal the most intense lines which are adequate to estimate plasma parameters.

It is necessary to mention such particular applications of the obtained results as the control over the energy balance, localization of the influence when silver contacts are deposited and adjusted, and optimization of the processes of laser deposition of complex silver-containing chalcogenide compounds of the $\mathrm{A^{I}B^{III(V)}C^{VI}}$ type which are used as working elements of nonlinear radiation converters for photovoltaic cells.

1. Experimental Devices and Approach

Time-averaged emission spectra and oscillograms of the spectral line intensity of the laser-produced plasma are investigated in a wavelength range of 200—600 nm, taking into account the spectral response of the setup. For the time-averaged measuring, a monochromator MDR-2, a photomultiplier FEU-106, and a recorder KSP-4 were used. For the time measuring, the signal was supplied to a photomultiplier "Foton" and an oscillograph S1-99. Measurement errors of the intensity did not exceed 10%, the time resolution was 30 ns. The plasma was created due to the effect of the laser irradiation (1.06 μm; $(1 \div 3) \cdot 10^8$ W/cm^2; 20 ns; 12 Hz) on the silver target in a vacuum chamber at a pressure of $3 \div 5$ Pa. The spectrum identification was carried out using works [5—8], from which spectroscopic constants were taken to evaluate the energy level populations and electron temperature. The experimental devices and approach are described in more details in the previous works [9, 10].

The distribution of the higher level populations of silver atoms in the plasma was calculated by the formula [11]

$$\frac{N_i}{g_i} = \sum_k \frac{\lambda_{ik} I_{ik}}{A_{ik} g_i}, \tag{1}$$

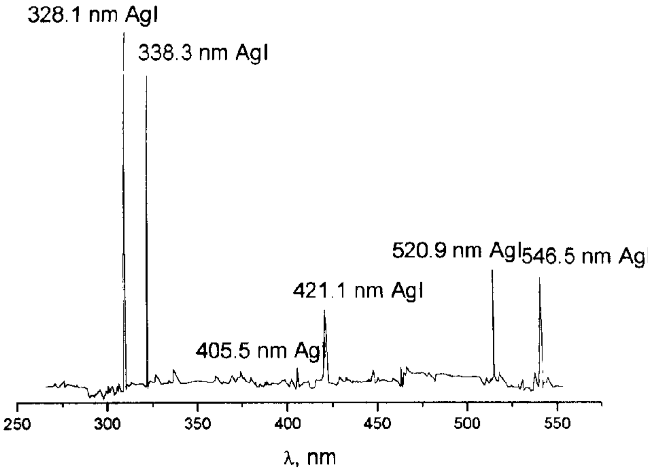


Fig.1. Characteristic time-averaged spectrum of radiation of the laser-produced silver plasma at a distance of 7 mm from the target

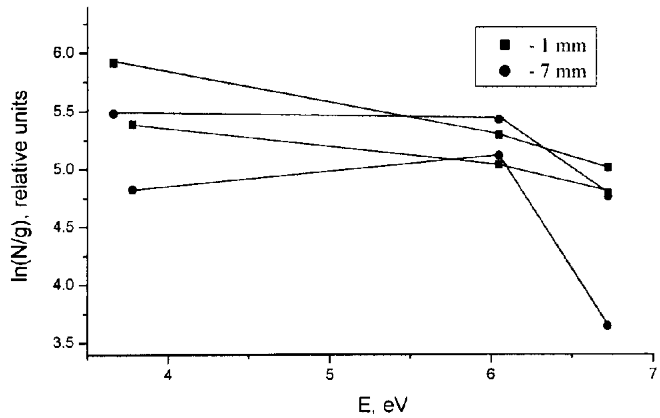


Fig.2. Energy distribution of the excited states of silver atoms in the laser plume at distances of 1 and 7 mm

where N_i the level population with statistical weight g_i, A_{ik} is the probability of a spectral transition to a lower level k, and I_{ik} is the radiation intensity with a wavelength λ_{ik}. The slope of a line passing through the obtained points on the plot of $\ln(N_i/g_i)$ vs energy E_i enables the electron temperature to be evaluated. The recombination time t_{r} was evaluated using the line slope of the natural logarithm of the intensity that was determined on the trailing edge of the oscillogram of radiative transitions from higher excited states. These states are populated mainly by the electron recombination with silver atoms [12].

2. Results and Discussions

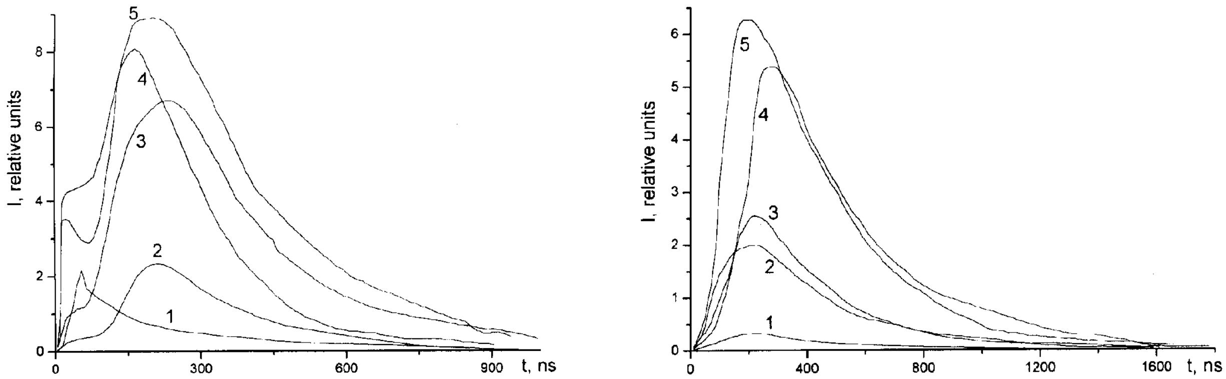
A typical form of the emission spectrum is presented in Fig. 1 and its interpretation is given in the Table, taking into account the instrument sensitivity. In particular, in the Table, the percentage contributions of each line to the line spectrum of the plasma are presented. The main lines evident in this spectrum are 546.5; 520.9; 421.1; 405.5; 338.3; 328.1 nm. In the laser-produced plasma, the radiation of silver atoms was not found, but transitions from shifted terms were observed.

The contributions of the separate spectral lines to the total intensity of the time-averaged spectrum at the distances of 1 and 7 mm from the target

λ, nm	$\Delta I/k_\lambda$, %		E, eV	Term
	1 nm	7 mm		
546.5	16.9	19.3	6.05	$5d\,^2D_{5/2}$
520.9	7.9	16.0	6.04	$5d\,^2D_{3/2}$
467.7	—	1.4	9.94	—
466.8	1.4	0.8	6.43	$7s^2S_{1/2}$
461.6	1.3	0.9	10.49	—
447.6	0.5	1.4	6.43	$7s^2S_{1/2}$
421.1	5.5	5.8	6.72	$6d\,^2D_{5/2}$
405.5	2.7	1.1	6.72	$6d\,^2D_{3/2}$
381.1	0.9	0.6	7.02	—
370.9	0.7	0.9	7.12	—
338.3	26.1	23.2	3.66	$5p^2P_{1/2}$
328.1	36.0	28.1	3.78	$5p^2P_{3/2}$

When increasing the distance from the target, the percentage contribution of higher states $5d\,^2D_{5/2,3/2}$ to the radiation intensity increases and the contribution of lower states $5p\,^2P_{3/2,1/2}$ decreases. But the intensity of transitions from these levels remains high at all distances. Using intensities of the more strong spectral lines, we constructed the energy distribution of time-averaged level populations (Fig.2). In Fig. 2, one can see that the Boltzmann equilibrium distribution is realized in the plasma near the target (at the distance of 1 mm). In this case, small dimensions of the laser plume promote the plasma thermalization upon collisions of heavy particles with electrons, and the electron temperature is 4.1 eV. The distribution form indicates that there are recombination instabilities [13] in the plasma and that, at a distance of 7 mm from the target, the plasma expands and cools.

The given conclusions are in accordance with increasing the radiation intensity, which corresponds to transitions from the higher excited states of silver atoms and to decreasing the intensity of transitions from the lower levels as well. The absence of the radiation of ions in the laser plume indicates that they are mainly in the ground state. The presence of charged particles in the laser plume, under similar conditions of irradiation, is confirmed with the use of a Langmuir probe at larger distances from the target [14]. High temperature may be one of the reasons of a slowness of the recombination processes because of the power dependence of the



a **b**

Fig.3. Oscillograms of the most intense spectral lines in the laser-produced silver plasma at distances 1 (*a*) and 7 mm (*b*) from the target. *1* — 338.3 nm AgI; *2* — 421.1; *3* — 520.9; *4* — 328.1; *5* — 546.5

recombination time on the electron temperature: $t_{\rm r} \sim T^{9/2}$ [12].

Due to the laser irradiation, the creation of silver ions and Rydberg states of Ag atoms are the most energetically favorable processes on the target surface. Therefore, their subsequent relaxation will be determined by conditions in the ablation plume, affecting, to the certain extent, spatio-temporal variations of the intensity along with the influence of the recession dynamics on the signal. Such a situation extends the capabilities of the laser-produced plasma diagnostics.

Understanding both the processes of creation of excited particles in the laser plume and their recession dynamics is most important for the quantitative spectral analysis and for the thin film deposition. The film quality strongly depends on the energy which is brought by particles into the substrate. In this regard, the kinetic energy and excitation energy play an important role. The incoming particles with moderate kinetic energies is most important to prevent the fracture of layers which already have been created and to introduce a considerable energy by excited particles, which allows one to carry out the deposition under room temperatures.

Time dependences of the radiation intensity of the strongest lines are shown in Fig. 3, where the intensity scales are matched. As follows from this figure, the intensities of the almost all spectral lines decrease when the distance from the target is increased from 1 to 7 mm. Also the form of oscillograms changes appreciably. Two maxima for the higher excited states are discovered at the distance of 1 mm, while only one maximum is revealed at the distance of 7 mm and the radiation duration is longer approximately by a factor of 1.5. This indicates that the plasma cloud expands during the recession. Also, having compared the energies of the higher levels, the time dependence of intensity and the probabilities of radiative transitions, we may say that, though there is an inessential difference in the transition probabilities of the higher levels which are close in energy, their radiation decay reveals a selectivity. This is probably caused by the photogeneration of excited particles or ions and their recombination, since correlations of the intensity with the cross section of the electron-impact excitation are not discovered [15]. As the recession velocity is high, the time variation of the intensity is defined mainly by the recession dynamics [10]. This can be broken only for the lower excited states which are sensitive to temperature. For these reasons, the high temperature accompanies the first maximum of the radiation and especially manifests itself between the first and second peaks, which is confirmed by the time dependence of the spectral line intensity at 338.3 nm. Transitions with wavelengths of 328.1 and 546.5 nm, whose higher levels have the largest section of the electron-impact excitation among the observed ones, are the most intense on the leading edge of the first and second maxima. The energy of the higher level of the transition with a wavelength of 328.1 nm is below the mean electron temperature, but greater than the energy of the higher level for the transition with a wavelength of 338.3 nm. At the distance of 7 mm from the target, a rapid increase of the intensity is observed for transitions from the levels of high energies, and the intensities of the radiation at 328.1 and 546.5 nm are stand out considerably only on the trailing edge. This means that the velocities of ions and neutral silver particles are different, which may be one of the reasons for the variation of the dynamics of the laser plume moving and also points out on the considerable role of the Coulomb interaction of charges when the plume is forming. Also the adiabatic nature of the expansion can influence the plasma recession dynamics [14], when increasing the plasma temperature results in decreasing the velocity.

The investigation of the recombination time by the declining of the radiation intensity of the spectral line of 421.1 nm reveals that, when the distance from the target is increased from 1 to 7 mm, the recombination time increases from 212 to 328 ns. At the distance of 1 mm, the logarithm of the intensity changes the slope. This indicates that the recombination time decreases in the tail ($t_{\mathrm{r}} = 131$ ns at $t > 700$ ns).

In the laser-produced silver plasma, the mean electron concentration changes with time and in space at short distances within an order of magnitude only [14], and the recombination time t_r depends on the electron concentration N_e as N_e^{-2}. From this, we can conclude that t_r also depends on temperature. In turn, this indicates that a conversion of the essential part of the energy of an ordered motion and of the energy which liberates at the recombination into heat is realized, i.e. the transition from the collisionless mode of the expansion to that where kinetic reactions dominate. Therefore, the greater the distance from the target, the better the conditions for film deposition.

Conclusions

The spectroscopic diagnostics of the laser-produced silver plasma allows us to reveal intense spectral lines which correspond to single-electron transitions of silver atoms and also weak spectral lines which correspond to the relaxation of the shifted levels. Lines with wavelengths of 546.5, 520.9, 421.5, 405.5, 338.3, 328.1 nm give the greatest percentage contribution to the intensity of the time-averaged spectrum. Their total intensity, at the distances of 1 and 7 mm, is 95.1 and 93.5% of the total spectrum intensity, respectively. With increasing the distance to the target, the intensity contribution rises for the radiative transition from levels of $5d\,^2D_{5/2,3/2}$ and decreases for the states of $5p\,^2P_{3/2,1/2}$.

The time-averaged distribution of the population of excited states over energy indicates that the plasma is thermalized at $r = 1$ mm, the electron temperature being 4.1 eV. At the distance of 7 mm, this distribution is nonequilibrium. We attribute the last fact to the silver ion recombination in the expanding plasma plume. The recombination times at the distances of 1 and 7 mm are 212 and 328 ns. The time dependence of the emission is the evidence for changing the laser plume structure under the recession from a split plasma blob to a continuous one.

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СПЕКТРОСКОПІЧНЕ ДОСЛІДЖЕННЯ
ХАРАКТЕРИСТИК ЛАЗЕРНОЇ ПЛАЗМИ СРІБЛА

О.К. Шуаібов, М.П. Чучман, Л.Л. Шимон

Р е з ю м е

Досліджено усереднені за часом спектри випромінювання лазерного факела та часову динаміку найінтенсивніших спектральних ліній на відстанях $r = 1$ та 7 мм від мішені із срібла при дії на неї в вакуумі (3—5 Па) випромінювання неодимового лазера (1,06 мкм; $(1 \div 3) \cdot 10^8$ Вт/см^2; 20 нс; 12 Гц). Одержані дані використано для побудови усередненого в часі розподілу за енергіями збуджених станів атомів срібла, оцінки часу рекомбінації та температури електронів.