FORMATION OF EXCITED STATES OF SILVER AND COPPER ATOMS IN LASER PLASMA

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The temporal dependences of the populations of excited atomic states in the laser erosive plasma of silver and copper are investigated at the 1-mm and 7-mm distances from targets. The presence of the inverse population of the excited states of copper (silver) with the 4*d*, 5*d*, 5*p* (5*d*, 6*d*) electron configurations with respect to the 4*p* (5*p*) states is discovered in various spatial regions of the plasma moving through the extraction zone of radiation. The long-term observation of the inversion of the population of CuI and AgI excited states (about 1 μs) is explained by the formation of autoionization atomic states in the laser plasma. It is proposed to use the discovered phenomenon in short-wave radiation sources.

1. Introduction

Effective lasers on self-contained transitions of copper atoms were created due to the excitation with a pulse-periodic longitudinal discharge. The oscillation wavelengths of such lasers are equal to 510.6 and 578.2 nm, whereas the pulse durations amount to several tens of nanoseconds [1, 2]. In [3], it was discovered that the addition of silver atoms to the active medium of a copper vapor laser results in the 10-% increase of its lasing power. Certain physical interest is attracted to the clarification of the conditions allowing one to increase the efficiency of operation of such lasers and the possibility to create the inversion for atomic transitions in metals (CuI, AgI) by other mechanisms, as well as the introduction of various admixtures in the working medium for the purpose of obtaining the quasi-stationary generation in the ultraviolet spectral region. Experiments of such a kind can be performed in the laser torch plasma formed with the use of a high-power short-pulse solid-state laser. In this case, the principal distinction is the recombination mechanism of the creation of the inverse population in contrast to the one conditioned by inelastic collisions in plasma, as well as the use of a plasmodynamic flow as the active medium.

Due to their large electroconductivity, copper and silver are also widely used as conductors in order to connect different elements in microelectronics [4]. The fabrication of nanocomposite materials,, as well as those with injected nanoparticles of copper and silver, allows one to considerably expand the possibilities to control the properties of a substance [5]. Compounds based on these materials are used as gas sensors [6]. The given materials find a still wider use in optical and electronic devices as components of multicomponent compounds, for example YBaCuO, $AgGaS_2$, $CuGaO_2$, $AgSbS_2$, and others [7–9]. An essential role in the creation, reduction in price, processing, and synthesis of the listed substances and devices on their basis is played by various laser microtechnologies. One ever more uses the laser deposition of films and the laser synthesis of nanoparticles of single- and many-component composition [5, 7, 8]. That is why it is important to study the laser erosive torch on the basis of copper and silver in order to optimize the properties of films deposited from the laser plasma containing these substances, control the synthesis of nanoparticles from the laser plasma, and detect the peculiarities of the time-space evolution of the laser torch plasma.

One of the peculiarities that we discovered in the silver- and copper-based laser plasma is the formation of Rydberg and autoionization two-electron excited states in it, which results in the complication of the energy balance in the plasma, decrease of the number of ions in it, and accumulation of the plasma energy in the form of highly excited atoms [10, 11]. The given phenomenon can find a wide use in quantum electronics opening up additional possibilities of the extension of recombination and relaxation processes in plasma. But systematic investigations of the time-space evolution of the copper-silver laser plasma are scanty and of integral character, the temporal dynamics of the radiation and parameters of the laser torch plasma is little investigated, and the mechanisms of formation of many-electron excited states in the laser plasma are not studied [12, 13].

In the given work, the method of emission spectroscopy of the laser erosive plasma of silver and copper is used for the investigation of the dynamics of formation of excited atomic states at small distances from the target and the energy distribution of the population of excited atomic states.

2. Investigation Technique and Procedure

Based on the emission characteristics of the laser plasma, it is possible to calculate the temperature and the concentration of particles in it [10]. The most effective method is that of emission spectroscopy at a high space-time resolution of the radiation intensity of the laser plasma [14]. Thus, one can obtain data on the evolution of the concentration profile of the erosive plasma moving from the laser target and study the properties of such a plasma. The understanding of the influence of the parameters of the laser torch plasma on its space-time dynamics and the dependence of the parameters, radiation, and composition of the laser plasma on the specific peculiarities of its expansion gives a possibility to control both the plasma properties and the quality of final products and devices that can be created on its basis. The determination of the temporal dependences of the laser plasma parameters requires to overcome certain difficulties; they are mainly a high accuracy and, as a consequence, the determination of the correlation and the mutual influence between various characteristics, mechanisms, processes, and external factors. These questions can be answered only after a systematical complex study of the laser torch plasma.

As we clarified from the investigation of the time-averaged spectra, the principal specific feature of the laser erosive plasma of copper and silver is the presence of autoionization atomic states in it. It is been discovered that this plasma is characterized with a considerable influence of the recombination instability on the generation of excited atomic states and a comparatively high temperature (several electron-volts) [10, 11].

The procedure and the technique of investigations of the laser plasma radiation with a high temporal resolution are described in our works [10, 11]. The investigation of the temporal dependences of the population of excited states is performed on the basis of the known oscillograms of the radiation intensity of spectral lines from the laser plasma [10, 11, 14, 15] and the spectroscopic constants for these spectral lines [16, 17]. With their help, the population N_m of the m-th excited level can be presented as

$$N_m = \sum_i I_{mi}/(A_{mi}h\nu_{mi}), \tag{1}$$

where I_{mi} denotes the radiation intensity in the case of the transition from the m-th level to the i-th one, A_{mi} is the transition probability, and $h\nu_{mi}$ is the energy of a radiation quantum.

At the beginning, we drew an averaged straight line over the whole energy distribution of the population of excited states presented in the logarithmic scale, at which two points were chosen arbitrarily. After that, it is easy to calculate the electron temperature according to the formula

$$kT_e = E_2 - E_1/\ln(N_1 g_2/N_2 g_1), \tag{2}$$

where k is the Boltzmann constant, and g is the statistical weight of the level.

3. Results and Their Discussion

The evolution of the plasma depends on its initial parameters, the concentration profile formed under the influence of the interaction of the laser radiation with the target and its vapors. These peculiarities are best observed at small distances from the target. The largest number of atoms in autoionization states is concentrated just at the leading edge of the plasma, which indicates the importance of the interaction of the laser radiation with the plasma for their formation. Later on, due to the motion of the laser plasma through the residual gas atmosphere, its initial concentration profile deforms in the process of expansion, formation of a shock wave, mixing of plasma particles with one another and the external gas, whose pressure lies, in our case, within the limits 3–12 Pa. A certain role is also played by the sensitivity of the mechanisms of formation of excited atoms to the nonuniformity of the plasma parameters in different spatial regions. The superposition of all these factors determines the form of the oscillograms of radiation of the spectral lines used for the determination of the population of an excited atomic state. The temporal dependence of the population of the silver and copper atomic excited states in the laser plasma is presented in Fig. 1. Table contains the initial data used for the calculation of the relative value of the population of excited states based on the temporal dependences of the plasma radiation intensity at various wavelengths. Due to a high rate of the plasma motion (for the leading edge of the silver-copper laser plasma, it amounts to 20–35 km/s), we can investigate the efficiency of the formation of excited atoms, that pass through the extraction zone of radiation, in various spatial regions from the leading to the trailing edge of the plasma, by orienting themselves according to the time of

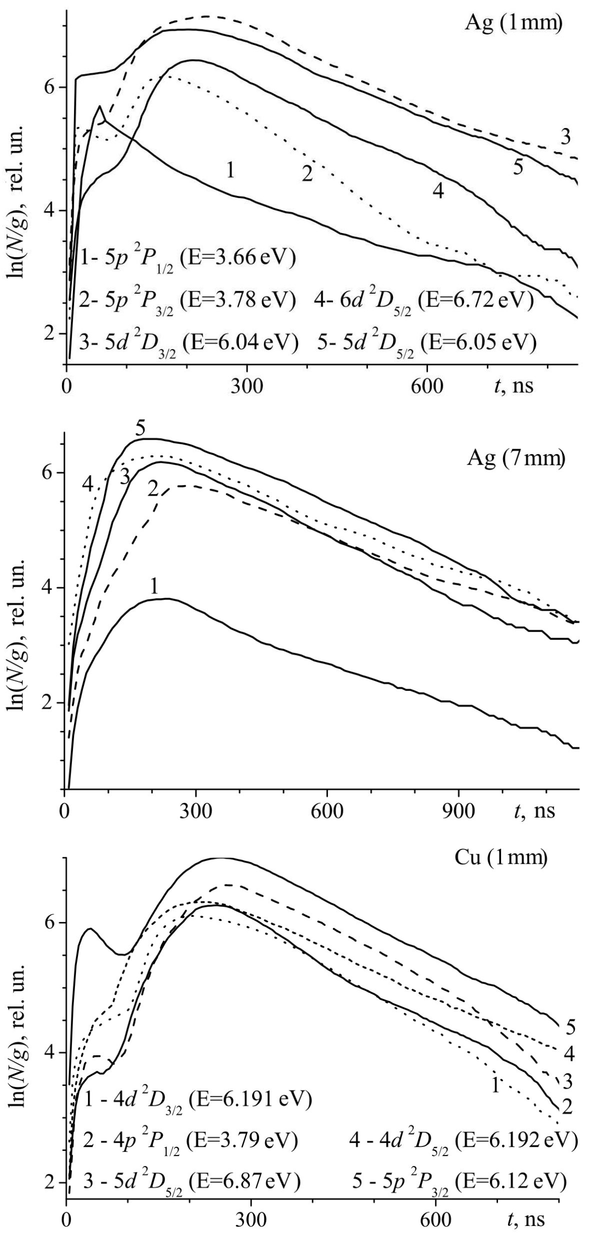

Fig. 1. Temporal dependence of the population of various excited states of Ag and Cu atoms. The notations for excited states of Ag atoms are the same at different distances from the target

observation of a certain region of the radiation oscillogram. From Fig. 1, one can see that, in the process of motion of the laser torch plasma of silver at the region from 1 to 7 mm from the target, the first maximum disappears, while the expansion of the plasma during its motion is inessential. One can also notice that, at a distance of 1 mm from the target, the first maximum in the case of silver is observed later and the second one – earlier than that in the case of copper.

Due to the fact that one observes no ion radiation from the copper-silver laser plasma despite its high temperature, the mainly inverse form of the temporal dependence of the population of excited states is most probably determined by the radiative and thermal relaxation of the autoionization states, as well as by the recombination of one-charged ions in the ground state. Such a relaxation is very slow as one can see from the increase of the energy distribution inversion for the investigated excited states in the case of the motion of the laser plasma from the target. This testifies to the fact that the lower excited states of silver and copper ions, as well as the autoionization states of their atoms, have rather large lifetimes. This effect is supplemented by an increase of the ionization degree of the plasma due to a high rate of expansion, as well as the deceleration of the recombination because of a high temperature. The motion of the silver-copper laser plasma at a distance of 1 to 7 mm from the target lasts for 200–300 ns like the experimentally determined time of the recombination [11].

The detailed consideration of the dynamics of variation of the population of excited states (Fig. 1) testifies to the more intense formation of the lower excited states of silver atoms at the leading edge in the corresponding plasma at a distance of 1 mm from the target. Moreover, this intensification lasts almost up to the leading edge of the second maximum. Under the same conditions, one almost cannot observe the formation of the lower excited states of copper atoms. In the both cases, the leading edge of the laser plasma mainly consists of highly excited atoms and ions, while, in the case of the silver laser plasma, it is also characterized by a high temperature. In the central

Characteristics of the spectral transitions used for the determination of the temporal dependences of the populations of excited states of Cu and Ag atoms

λ, nm	Lower level		Upper level		A, 10^8 s^{-1}	
	Energy, eV	Term	Energy, eV	Term	Source	
					[17]	[16]
338.3 AgI	0.000	$5s\ ^2S_{1/2}$	3.664	$5p\ ^2P_{1/2}$	1.30	1.22
421.1 AgI	3.778	$5p\ ^2P_{3/2}$	6.722	$6d\ ^2D_{5/2}$	–	0.26
520.9 AgI	3.664	$5p\ ^2P_{1/2}$	6.044	$5d\ ^2D_{3/2}$	0.75	0.69
328.1 AgI	0.000	$5s\ ^2S_{1/2}$	3.778	$5p\ ^2P_{3/2}$	1.40	1.38
546.5 AgI	3.778	$5p\ ^2P_{3/2}$	6.047	$5d\ ^2D_{5/2}$	0.86	0.79
261.8 CuI	1.389	$4s^2\ ^2D_{5/2}$	6.123	$5p\ ^2P_{3/2}$	0.307	0.307
276.6 CuI	1.642	$4s^2\ ^2D_{3/2}$	6.123	$5p\ ^2P_{3/2}$	0.096	0.096
521.8 CuI	3.817	$4p\ ^2P_{3/2}$	6.192	$4d\ ^2D_{5/2}$	0.75	1.22
406.3 CuI	3.817	$4p\ ^2P_{3/2}$	6.868	$5d\ ^2D_{5/2}$	0.21	0.21
327.4 CuI	0.000	$4s\ ^2S_{1/2}$	3.786	$4p\ ^2P_{1/2}$	1.37	1.36
515.3 CuI	3.786	$4p\ ^2P_{1/2}$	6.192	$4d\ ^2D_{3/2}$	0.6	1.03

regions of the plasma, the variation of the populations is rather monotonous in all the cases up to the trailing edge and the time of the order of 700–900 ns.

The dynamics of the distribution of the population of excited states is given in Fig. 2. For the sake of comparison, this figure presents the distributions of the population of excited states at the moments corresponding to the leading edge of the plasma, the plasma region at once behind the leading edge, in the central part, and at the trailing edge. In the case of the silver laser plasma, there exists a region at a distance of 1 mm from the target, at once at the leading edge, where the distribution can be considered as a thermal one within the error of determination of the populations. In this approximation, the electron temperature at the leading edge can reach 10 eV, and then it rapidly decreases. In order to simplify Fig. 2, we averaged the populations of the energy levels, whose energies differed by less than 0.1 eV.

In 200 ns, there already starts the prevailing motion of atoms down over the energy levels that manifests itself in the energy distribution of the population of excited states as the appearance of the inversion of the populations of the excited states of silver atoms. The influence of the recombination instability gradually increases in the direction of the trailing plasma edge.

In the silver laser plasma, the energy distribution of the populations at a distance of 7 mm from the target at the leading and trailing edges of the laser torch corresponds to a complete inversion without any influence of the recombination instability that manifests itself only in the central regions of the plasma.

For the copper laser plasma, the energy distribution of the populations at a distance of 1 mm from the target indicates a complete inversion at the center of the laser torch and the inversion with the appearance of the recombination instability at the leading and trailing edges of the laser plasma.

Such a form of the energy distribution of the population of excited states in the silver-copper laser plasma results in large errors in the determination of the temporal dependence of the electron temperature based on the chosen technique. The least error corresponds to the case of the pronounced recombination instability and approximately amounts to 60 % both for copper and silver. The parameters of the given plasma can be also judged from the form of the energy distribution of the population of excited states. Moreover, one should remember that the manifestation of the recombination instability is promoted by the high plasma density and temperature in the case where the recombination

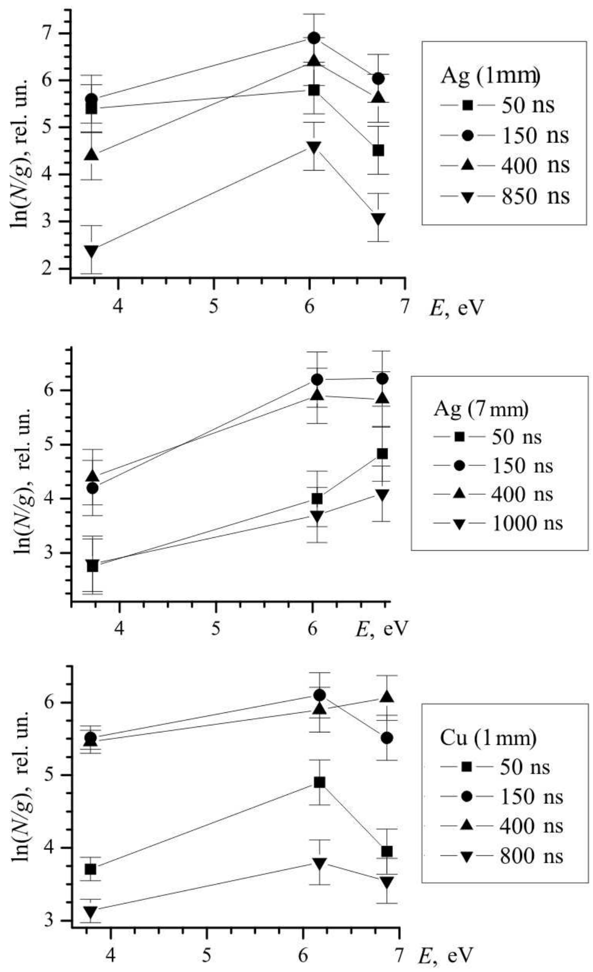

Fig. 2. Characteristic form of the energy distributions of the population of excited states of Cu and Ag atoms at various time moments

processes make a considerable contribution to the formation of highly excited atomic states.

In such a way, one can obtain satisfactory results, but, in order to increase the accuracy of the obtained values of the electron temperature, it is necessary to use additional measuring techniques for the determination of the parameters of the laser torch copper-silver plasma. For this purpose, one can use the Langmuir probe method [13] that is appropriate in the case of a silver laser plasma and can provide a certain information for the analysis of the peculiarities of the laser plasma as compared to the spectroscopic investigation methods.

Our measurements testify to the fact that the electron temperature at the central regions of the copper-silver laser torch plasma is almost constant. Here, one can mark out the regions of the laser plasma that exist

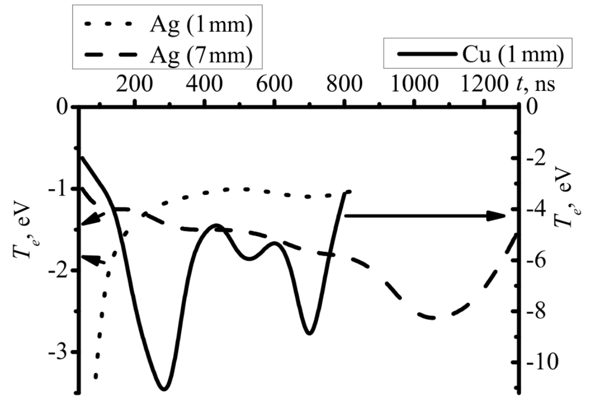

Fig. 3. Manifestation of the inversion in the energy distribution of the population of excited states presented in the Table at various time moments for the Cu-Ag laser plasma. The values of the populations of excited states, whose energies differ by ∼0.1 eV, are averaged to improve the obviousness

during the time interval of up to 300 ns and have the same temperature approximately equal to 1 eV. As the error amounts to 60 %, these data are of estimating character.

An advantage of the emission spectroscopy is the possibility to investigate the specific character of the formation of excited states of atoms and ions, as well as the energy distribution of the population of excited states. Using this method, one can trace the appearance of the inversion within the investigated excited states for various spatial regions of the plasma. The inversion of the population of excited atomic states in the copper-silver laser plasma depending on time is presented in Fig. 3.

From Fig. 3, it follows that, in the case of copper, the character of the flow of atoms from the upper energy levels to the lower ones differs from that in the case of silver. The minima on the graphs in Fig. 3 correspond to the least inversion of the distribution of the population of excited states. The dynamics of the inversion in the silver laser plasma at a distance of 1 mm from the target testifies to very low values of this quantity at the leading edge, while, at 300 ns, one observes a plateau with an almost constant value of the inversion up to the trailing plasma edge. At a distance of 7 mm from the target in the silver laser plasma, there appears a sharp minimum of the inversion at the trailing plasma edge and, after that, one observes again its increase. But, from the leading edge, the inversion monotonously decreases during 800 ns. The minimum of the inversion in the range 600–800 ns is also observed at the trailing edge of the silver laser plasma at a distance of 1 mm from the target, but it is not pronounced. The principal distinction in the manifestation of the inversion of the population of atomic excited states for the silver laser plasma in the process of its motion from 1 to 7 mm from the target lies in an increase of the inversion at the leading edge and its decrease at the trailing one.

At a distance of 1 mm from the target, the inversion of the distribution of the chosen excited states of copper atoms evolves with time in sharp discrete steps in contrast to the case of the silver plasma at the same distance, whereas the forms of the dependences become similar only in 300 ns. For the copper plasma at the leading and trailing edges, the inversion sharply increases, by reaching its maximal values. While, closer to the center of the plasma, the inversion already reaches its minimal values both from the leading and trailing edges. In the central regions of the plasma observed in the time interval of 400–600 ns, the inversion again increases and changes weakly.

In the region of the minimal inversion, the influence of thermal processes on the formation of the excited atomic states becomes stronger. It is accompanied by anincrease in the electron temperature, as well as in the relative population of lower excited atomic states. The intensification of thermal processes can occur at the leading edge due to the formation of a shock wave and at the trailing one due to a change in the character of the motion from the expansion and the rectilinear motion to the contraction and the mixing. The temperature can vary in the self-oscillation mode at the expense of the energy released in the process of recombination. This increases the temperature and decreases the efficiency of the recombination processes in the laser plasma.

A considerable role in the prevalent motion of atoms down over the energy levels is played by the concentration profile of the plasma. This testifies to the dominance of highly excited, ionized atoms and atoms in the autoionization states in the plasma at a low temperature, which imposes certain limitations on the the charge composition of the plasma depending on the specific power of the laser radiation. At an insufficient power of the laser radiation, ionized particles will concentrate at the leading edge of the plasma torch but only till the moment when the concentration profile and the composition of the plasma in various spatial parts start to change due to the motion of the plasma from the target. We did not observe a total inversion for the laser plasma of other elements, though the inversion was observed in the excited states of one-charged ions [18]. But, in these cases, the evolution of the laser torch plasma rapidly converts the population distribution of ions (for which it is even more difficult to achieve a large concentration than for atoms) to the thermal form. That is why the inversion can be observed only during short time intervals and at very small distances from the target. In the cases of copper and silver, the inversion observed for a long time and at large distances from the target is conditioned to our mind, first of all, by the formation of autoionization atomic states, which prevents energy losses for the formation of ions. In such a way, the motion of particles up over the energy levels is impeded. This phenomenon can be promising for the creation of sources of radiation with shorter waves in the case of the transfer to 10-nm technologies in electronic engineering. Unfortunately, the generation is theoretically possible in this case at the maximal wavelength that is tenfold larger. That is why the explanation of the reasons and the mechanisms of formation of the autoionization states of copper and silver atoms can give keys for the obtaining of such states of ions, whose excitation energy would allow one to obtain the lasing in the soft X-ray spectral region and also to considerably decrease the energy losses for radiation sources of such a kind.

4. Conclusions

Based on the most intense spectral lines of the laser plasma radiation, we have investigated the space-time variation of the populations of excited states of copper and silver atoms, whose energies lie in the range 3–7 eV.

It is shown that the temporal dependences of the populations of excited atomic states of silver ($5p\ ^2P_{1/2}$, $6d\ ^2D_{5/2}$, $5d\ ^2D_{3/2}$, $5p\ ^2P_{3/2}$, $5d\ ^2D_{5/2}$) and those of copper ($5p\ ^2P_{3/2}$, $5p\ ^2P_{3/2}$, $4d\ ^2D_{5/2}$, $5d\ ^2D_{5/2}$, $4p\ ^2P_{1/2}$, $4d\ ^2D_{3/2}$) at a distance of 1 mm from the target are characterized by two maxima, one of which is observed only during 100 ns and disappears as the distance from the target increases (judging by the same dependence for silver at the 7-mm distance from the target).

It is discovered that the energy distribution for the population of the investigated excited states of copper and silver atoms in a laser torch is inverse during all the time, and its form is considerably influenced by the recombination instability.

The estimates of the electron temperature in the central regions of the laser torch plasma of copper and silver demonstrate that the temperature is not practically changed during the whole time of observations (≈300 ns) and approximately amounts to 1 eV both at the 1-mm and 7-mm distances from the target. At the leading edge of the silver laser plasma, the electron temperature can reach 10 eV at a distance of 1 mm from the target.

As the plasma propagates 1 to 7 mm from the target, the inversion increases at the leading edge of the silver laser plasma and decreases at its trailing edge. In the case of the copper laser plasma, the inversion at a distance of 1 mm from the target is changed step-wise along the plasma torch. The minimum of the inversion is observed at once behind the leading edge of the plasma and before its trailing edge. For the silver laser plasma, the inversion appears to be more pronounced than that for the copper laser plasma at a distance of 1 mm from the target.

The inversion of the population of excited states in the copper-silver laser plasma is observed during the time interval of about 1 μs. To our mind, such a long-term observation of the inversion is conditioned by the formation of autoionization atomic states in the plasma that accumulate a large quantity of the energy supplied for the formation of the plasma. We propose to use the given phenomenon for the development of short-wave radiation sources, which will considerably decrease the energy losses for the formation of the active medium of a radiator.

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УТВОРЕННЯ ЗБУДЖЕНИХ АТОМІВ МІДІ ТА СРІБЛА В ЛАЗЕРНІЙ ПЛАЗМІ

М.П. Чучман, О.К. Шуаібов

Р е з ю м е

Досліджено часові залежності заселеності збуджених станів атомів у лазерній ерозійній плазмі срібла й міді на відстанях 1 і 7 мм від мішеней. Виявлено наявність інверсної заселеності збуджених станів міді (срібла) з електронною конфігурацією $4d$, $5d$, $5p$ ($5d$, $6d$) відносно станів з електронною конфігурацією $4p$ ($5p$) у різних просторових областях плазми, яка рухається через зону відбору випромінювання. Тривале спостереження інверсії заселеності збуджених станів CuI та AgI (близько 1 мкс) пояснено утворенням в лазерній плазмі автоіонізаційних станів атомів. Запропоновано використання виявленого явища у короткохвильових джерелах випромінювання.