OPTICAL CHARACTERISTICS OF EROSION GALLIUM, INDIUM AND COPPER LASER PLASMA

A.K.Shuaibov, L.L.Shimon, A.J.Dashchenko, M.P.Chuchman

Uzhhorod National University, Pidhirna str., 46, Uzhhorod, 88000, Ukraine,
e-mail: ishev@univ.uzhgorod.ua

The results of the studies of the emission from an erosion gallium, indium and copper laser plasma at a moderate intensity (W=(0.5-2)×10^9 W/cm^2) of a 1.06 μm laser radiation are presented. It is shown that, under these conditions, the lower excited states of gallium, indium and copper atoms are populated most efficiently. Among the ions, only the most intense GaII and InII lines are observed in the emission spectrum. The populations of the excited states of the atoms and ions are not related to direct electron excitation, but are determined by the recombination of ions with slow electrons. The bottlenecks of the recombination fluxes in the system of energy levels GaII, GaI, InII, InI and CuI are determined. The results obtained are of interest for spectroscopic diagnostics of erosion plasma produced from gallium-containing layered crystals during the laser deposition of thin films.

Introduction

Ga, In and Cu are the individual constituents of layered crystals $CuInS_2$, $PbGa_2S_4$ and others, which are widely used for deposition of thin films in the working element of the solar batteries [1] and other equipment on the basis of microelectronics. Optical characteristics of laser plasma of crystals are not investigated sufficiently, since its emission spectra are rather complicated and consists of 5 or 6 different excited components. Therefore, it is important to investigate the distribution of emission intensity on the transitions of separate crystal components. The majority of such experiments were carried out earlier with YAG: Nd^{3+}-lasers and photographic monitoring of laser jet plasma emission. The quantitative data on the emission intensity of Ga, In and Cu laser plasma in typical conditions of deposition of the crystal substance in vacuum, are absent.

In this paper we present the results of studying the emission from excited atoms and ions of gallium, indium and copper in different spatial regions of a plasma jet produced under irradiation by a YAG: Nd^{3+}-laser at a moderate pulse energy.

Experimental

The experiments were carried out with a repetitive neodymium Q-switched laser. The pulse duration was 20 ns and the repetition rate was 12 Hz. The laser beam was focused to a spot 0.4–0.5 mm in diameter, which allowed us to obtain the intensity of (0.5–2)×10^9 W/cm^2 on the target surface. A plate of especially pure gallium, indium or copper was positioned inside a vacuum chamber. The emission in the 200 to 600 nm spectral region was analyzed with the help of an MDR-2 monochromator. A lens collected radiation emitted from different spatial regions of the plasma jet. Most study was given to the emission from the core of the plasma jet, whose center was located 1 mm away from the metal surface, and from the jet region located 7 mm away from the surface. Time averaged spectra were detected by a FEU-106 photomultiplier and recorded by a KSP-4 recorder. The FEU-106+MDR-2 system was calibrated with hydrogen and tungsten band lamps, which allowed us to measure the relative intensities of emission lines [2]. The measurements of pulsed radiation were performed with an ELU-14FS electron linear multiplier and a 6LOR-04 oscillograph. Longer radiation pulses were recorded with a FOTON pulsed photomultiplier connected to a C1-99 oscilloscope [3].

Optical characteristics

The emission spectrum of the erosion gallium, indium and copper plasma jet consists of atoms and singly charged ions (GaII and InII) spectral lines against the continuum background extended over the entire wavelength range under investigation. The emission from higher ionization states of ions was not detected. The identified emission lines, relative intensities of InI and InII lines, and the distribution of radiation fluxes ($\Delta I/k_\lambda$) over InI and InII transitions in the 200- to 600-nm spectral range are given in Table 1.

Table 1. Intensity distribution in the emission spectrum of the indium plasma jet.

N	λ, nm	Atom (ion)	Transition	E_{up}, eV	J/k_λ, a.u.	$\Delta J/k_\lambda$, %
1	511.7	InII	-	-	<0.05	(<1)
2	468.5	InII	-	15.32	0.05	<5
3	465.8	InII	$5^3D_{1,2,3}$-$4^3F_{2,3,4}$	21.12	0.05	<5
4	451.1	InI	$5^2P_{3/2}$-$6^2S_{1/2}$	3.02	1.00	20
5	410.2	InI	$5^2P_{1/2}$-$6^2S_{1/2}$	3.02	0.75	15
6	383.5	InII	-	15.33	<0.05	(<1)
7	325.8 (6)	InI	$5^2P_{3/2}$-$5^2D_{5/2,3/2}$	4.08	0.85	20
8	303.9	InI	$5^2P_{1/2}$-$5^2D_{3/2}$	4.08	0.50	10
9	295.7	InI	$5^2P_{3/2}$-$5^4P_{3/2}$	4.47	0.20	<5
10	293.2	InI	$5^2P_{3/2}$-$7^2S_{1/2}$	4.50	0.20	<5
11	289.1	InII	5^1P_1-$4d^{10}5p^2\,{}^1D_1$	17.88	<0.05	(<1)
12	283.7	InI	$5^2P_{3/2}$-$5^4P_{5/2}$	4.64	0.05	<5
13	275.3	InI	$5^2P_{1/2}$-$7^2S_{1/2}$	4.50	0.10	<5
14	271.0 (4)	InI	$5^2P_{3/2}$-$6^2D_{5/2,3/2}$	4.84	0.35	10
15	260.1	InI	$5^2P_{3/2}$-$8^2S_{1/2}$	5.05	<0.05	(<1)
16	256.0	InI	$5^2P_{1/2}$-$6^2P_{3/2}$	4.84	0.10	<5
17	249.6	InII	-	-	0.05	(<1)

The value ($\Delta I/k_\lambda$) is expressed in percent and presents the ratio of the intensity of each line to the total emission intensity of all lines (without the continuum intensity) over the entire wavelength range under investigation. The most efficiently populated levels are the lower states of GaI, namely, $5^2S_{1/2}$ and $4^2D_{5/2,\,3/2}$ states [4]. Four most intense lines of gallium atoms comprise 90% of the total line-emission intensity of the plasma jet in the 200 to 600 nm wavelength range. Like in aluminum laser plasmas [5], the main mechanism for populating GaI and GaII excited states is associated with the recombination of slow electrons with gallium ions. In this case, electrons are more efficiently captured into the upper GaI and GaII states. Further, due to collisions between GaI and GaII with thermal electrons, the energy of the populated levels of GaI atoms lowers to a certain excited state corresponding to the bottleneck of the recombination flux; then, the emission of spectral lines occurs from this state. In our case, the bottleneck of the recombination flux is the GaI $5^2D_{5/2,\,3/2}$ state with the energy of 5.01 eV. For the GaII ions, the bottleneck is the 4^1D_5 level with the energy E_{up}=23.0 eV. To study the mechanism for populating the excited states of gallium atoms in more detail, we investigated the time behavior of the radiation emitted via GaI and GaII transitions. The waveforms of the intensity of the most intense GaI and GaII lines from the core of the plasma jet are shown in Fig. 1.

The radiation lifetimes of GaI and GaII excited states were less than 7 ns. Therefore, the duration of emission via an individual

GaI transition is determined by the recombination time of GaII ions, and the duration of line emission of the excited singly charged ions is determined by the recombination time of GaIII ions.

In [5], the expression $\ln[I(t)/I(0)] = -t/\tau_r$ was deduced for the decay of the intensity of spectral lines *I(t)* for ions with charge z as a function of time *(t)*, which allows one to determine the recombination time (τ_r) for ions with the charge $z+1$ (for atoms, we have $z=0$). In the core of the laser plasma (d=1 mm), the value of τ_r for GaIII ions is 10 ns and it is τ_r= 140 ns for GaII ions. The average propagation velocity of the gallium plasma jet (for d=1-7 mm) estimated from the waveforms of the GaI emission line (Fig. 1(3)) is 12.6 km/s.

The most intense lines of InI are 451.1; 410.2 and 325.8 nm. The bottlenecks of the recombination fluxes of the indium laser plasma are the levels InII ($4^3F_{2,3,4}$; E_{up}=21.12 eV) and InI ($8^2S_{1/2}$; E_{up}=5.04 eV). Dynamics of indium laser plasma emission was the same as the results, given in Fig. 1. Optical characteristics of copper laser plasma jet are presented in Table 2.

Table 2. Intensity distribution in the emission spectrum of the copper plasma jet.

N	λ, nm ,CuI	Transition	*j*	E_{up} , eV	$I/k\lambda$, a.u.	$\Delta I/k\lambda$, %
1.	521.8	$4p\ ^2P^0$-$4d\ ^2D$	3/2 - 5/2	6.19	0.80	10
2.	515.3	$4p\ ^2P^0$-$4d\ ^2D$	1/2-3/2	6.19	0.25	3
3.	510.6	$4s^2\ ^2D$-$4p\ ^2P^0$	5/2-3/2	3.82	0.05	0.6
4.	427.5	$4p'\ ^4P^0$-$5s'\ ^4D$	5/2 - 7/2	7.74	0.05	0.6
5.	406.3(2)	$4p\ ^2P^0$-$5d\ ^2D$	3/2-3/2,5/2	6.87	0.25	3.0
6.	402.3	$4p\ ^2P^0$-$5d\ ^2D$	1/2-3/2	6.87	0.15	1.8
7.	368.7	$4p\ ^2P^0$-$6d\ ^2D$	3/2-5/2	7.18	0.10	1.2
8.	365.6	$4p'\ ^4D^0$-$4d'\ ^2G$	7/2-5/2	8.78	0.05	0.6
9.	351.2	$4p'\ ^4D^0$-$4d'\ ^4G$	7/2-9/2	8.92	0.05	0.6
10.	348.4	$4p'\ ^4D^0$-$4d'\ ^4G$	5/2-7/2	9.06	0.05	0.6
11.	341.5 +341.3	$4p'\ ^2D^0$-$4d''\ ^2D$ $4p'\ ^2P^0$-$4d''\ ^2P$	3/2-3/2 1/2-1/2	9.35 9.31	0.05	0.6
12.	330.8	$4p'\ ^4F^0$-$4d'\ ^4G$	9/2-1/2	8.82	0.05	0.6
13.	327.4	$4s\ ^2S$-$4p\ ^2P^0$	1/2-1/2	3.79	1.00	12.0
14.	324.8	$4s\ ^2S$-$4p\ ^2P^0$	1/2-3/2	3.82	1.00	12.0
15.	276.6	$4s^2\ ^2D$-$5p\ ^2P^0$	3/2-3/2,1/2	6.12	0.05	0.6
16.	261.8	$4s^2\ ^2D$-$5p\ ^2P^0$	5/2-3/2	6.12	0.15	1.8
17.	254.7	$4p'\ ^4P^0$-$7s'\ ^4D$	5/2-7/2	9.70	0.05	0.6
18.	249.2	$4s\ ^2S$-$4p'\ ^4P^0$	1/2-3/2	4.97	0.10	1.1
19.	239.3	$4s\ ^2D$-$6p\ ^2P^0$	3/2-3/2	6.82	0.10	1.1
20.	229.4	$4s\ ^2D$-$6p\ ^2P^0$	5/2-3/2	6.79	0.55	6.3
21.	226.4 +226.1	$4s\ ^2D$-$7p\ ^2P^0$ $4s\ ^2D$-$4f\ ^2F^0$	3/2-1/2 5/2-7/2	7.12 6.87	0.45	5.1
22.	224.4	$4s\ ^2S$-$4p'\ D^0$	1/2-3/2	5.52	0.45	5.1
23.	223.0	$4s^2\ ^2D$-$4p''\ ^2F^0$	5/2-7/2	6.95	0.90	11.0
24.	221.5	$4s^2\ ^2D$-$4p''\ ^2P^0$	5/2-3/2	6.98	0.90	11.0
25.	219.9(8) +219.9(6)	$4s\ ^2D$-$4p''\ ^2D^0$ $4s\ ^2D$-$4p''\ ^2D^0$	3/2-3/2 5/2-5/2	7.28 7,02	0.70	9.0

The most intense were the emission lines from resonance levels. The second group of intense CuI lines was in UV range of spectrum ($\Delta\lambda$=210-230 nm) and belonged to transitions from shifted CuI levels, including those with energy exceeding the *ionization potential of CuI* (E_i =7.73 eV). The bottleneck of the recombination flux of copper laser plasma is above one-fold ionization potential of Cu atoms. Waveforms of the emission on Cu I transitions had two maxima which were determined by two phases of surface evaporation of the target. On the emission waveforms for λ=521.8 nm *CuI and resonance line of copper the second* maximum was the main.

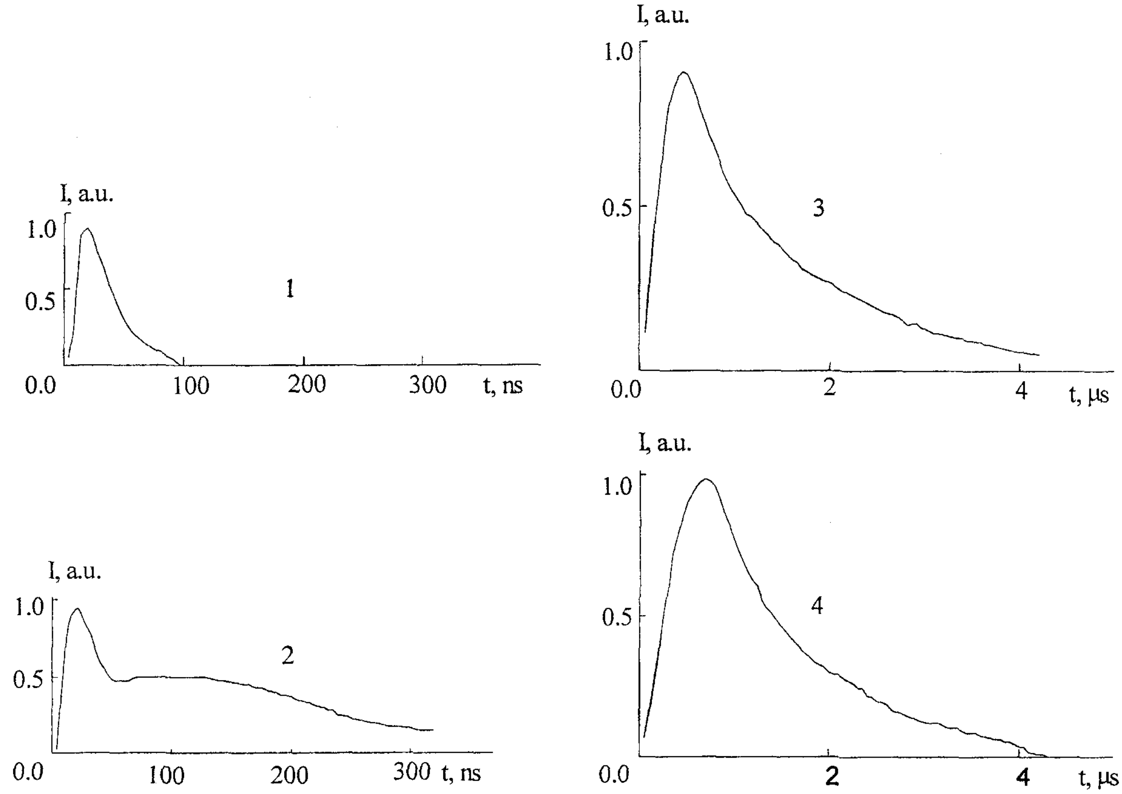

Fig.1. Waveforms of the intensity of radiation emitted via the transitions of gallium atoms and ions from the core of the laser plasma (1-2, r=1 mm) and from the laser plasma jet (3-4, r=7 mm):278.0 nm GaII (1); 417.3 nm GaI (2, 3); 425.6 nm Ga II (4).

The presented results could be used for measuring of n_e, T_e and other parameters of laser plasma of layered crystals ($CuInS_2$, $PbGa_2S_4$ and others).

References

1. M.L.Fearheiley, H.J.Lewerenz, M.Fyetes, *Solar Energy Materials*, **19**, 167 (1989).
2. A.K.Shuaibov *et al.*, *Journal of Physical Studies* **3**, 47 (1999).
3. A.K.Shuaibov, *High Temperature* **36**, 484 (1998).
4. A.K.Shuaibov, L.L.Shimon, A.I.Dashchenko, Y.M.Semenyuk, *Problems of economic and social development of the region and the practice of scientific experimen*, **16,** 192 (2000).
5. L.T.Sukhov, *Laser Spectral Analysis* (Nauka, Novosibirsk. 1990) [in Russian].

ОПТИЧНІ ХАРАКТЕРИСТИКИ ЛАЗЕРНОЇ ЕРОЗІЙНОЇ ПЛАЗМИ ГАЛІЮ, ІНДІЮ ТА МІДІ

О.К.Шуаібов, Л.Л.Шимон, А.Й.Дащенко, М.П.Чучман

Ужгородський національний університет, вул. Підгірна, 46, Ужгород, 88000
e-mail: ishev@univ.uzhgorod.ua

Наводяться результати досліджень випромінювання лазерної плазми галію, індію та міді. Плазма формувалась за допомогою неодимового лазера потужністю випромінювання в області фокусування $(0.5\text{-}2.0)\times10^9$ Вт×см$^{-2}$. Показано, що найбільш ефективно заселяються низькорозташовані збуджені стани GaI, InI та CuI. Для іонної складової випромінювання плазми спостерігались лише найбільш інтенсивні спектральні лінії GaII та InII. Заселення збуджених станів атомів та іонів у лазерній плазмі відбувається в результаті реакції діелектронної рекомбінації. За випромінюванням плазми визначено вузькі місця рекомбінаційних потоків у системі енергетичних рівнів GaII, GaI, InII, InI та CuI. Отримані результати використовуються для спектроскопічної діагностики ерозійної плазми кристалів, що в свою чергу застосовуються при лазерному напиленні тонких плівок.