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Gas Discharge Source of Synchronous Flows of UV Radiation and Silver Sulphide Microstructures

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The results of the study of the characteristics of a pulsed source of time-synchronous UV radiation streams of silver atoms and ions and micro-nanostructures of silver sulfide are given. An overvoltage nanosecond discharge was ignited in nitrogen between electrodes made of silver sulfide (Ag_2S) at a distance between electrodes of 2 mm. Silver sulfide vapors were introduced into the gas-vapor mixture "Nitrogen - Ag_2S" due to the ectonic mechanism. The voltage and current pulses, the pulsed power of the discharge, the energy contribution to the plasma for one pulse at pulse repetition frequencies of 40 - 1000 Hz were studied. The spectral characteristics of the discharge and the spatial characteristics of the microstructures deposited from the discharge plasma on a quartz substrate installed near the electrode system were studied.

The discharge can be used as a source of bactericidal radiation and a source of microstructures based on silver sulfide, as well as a plasma chemical reactor for the synthesis of thin microstructured films of silver sulfide.

Key words: silver sulphide, overvoltage nanosecond discharge, radiation spectrum, plasma, pulsed source.

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Introduction

Gas-discharge sources of bactericidal UV radiation at transitions of atoms and ions of transition metals (Cu, Zn, Fe) were successfully developed by pumping an overvoltage nanosecond discharge in atmospheric pressure air between electrodes with Cu, Zn, Fe [1]. To increase the bactericidal effect, they also used a flow of transition metal oxide nanostructures. During the deposition of such a flow on a solid substrate installed near the electrode system, the synthesis of thin nanostructured films of transition metal oxides was carried out. Introduction of vapors of the electrode material occurred due to microexplosions of inhomogeneities of the electrode surface in the form of nanopoints in a strong electric field (formation of ectons [2]). The plasma of the overvoltage nanosecond discharge was quite homogeneous even without preliminary ionization of the interelectrode gap, since the role of preliminary ionization here was performed by a beam of runaway electrons and accompanying X-ray radiation [3, 4].

In addition to transition metals, silver and sulfur atoms also have a strong bactericidal effect, so it is promising to obtain a plasma flow based on silver and sulfur, which is synchronized with the UV flow of silver plasma. On the basis of a vapor-gas mixture of "air - silver sulfide (Ag_2S)", a similar source was implemented on the basis of an overvoltage nanosecond discharge between electrodes made of a polycrystalline Ag_2S compound in air at atmospheric pressure [5-7]. In this work, the possibility of synthesizing thin films of the superionic conductor - silver sulfide [8], which is promising for their use in completely solid-state lithium - ion batteries [9,10] was also established by the method of micro-Raman spectroscopy.

Since the buffer gas - air in [7] contained a significant amount of oxygen, oxygen atoms and ions were present in the plasma flow, and impurities of oxygen-containing compounds were detected in the synthesized thin films. Therefore, it is also important to conduct similar studies with a buffer gas that does not contain oxygen. Such a buffer gas can be nitrogen at atmospheric pressure, which

is inexpensive, allowing nitrogen to flow through the discharge gap at subsonic speeds. Currently, there are no characteristics of an overvoltage nanosecond discharge between silver sulfide electrodes in nitrogen, which prevents the use of such a source in electrical engineering, microelectronics, and medicine.

The article presents the results of the study of the electrical and optical characteristics of the source of UV radiation flows and microstructures of silver sulfide, which was excited with the help of an overvoltage nanosecond discharge between silver sulfide electrodes in nitrogen.

I. Conditions of the experiment

A high-voltage discharge with a duration of 100 – 450 ns was ignited between two electrodes, which were made of a polycrystalline Ag_2S compound. The distance between the electrodes was 2 mm. The radius of rounding of the end parts of the cylindrical electrodes is 10 mm. The diameter of the electrodes is 5 mm.

The scheme of the installation, the structure of the discharge device and other conditions for studying the characteristics of an overvoltage nanosecond discharge are given in [1].

The discharge was ignited by overvoltage of the discharge gap, when a beam of runaway electrons is formed in it [3]. Under the action of such a beam, the discharge in Nitrogen at a pressure of p = 101 kPa was uniform and had an aperture area of 4 mm^2. In a strong electric field on the working surface of an electrode made of a superionic conductor (Ag_2S), micro-explosions of inhomogeneities occur on the surface of the electrodes [2], which contributed to the introduction of vapors of the polycrystalline compound Ag_2S into the plasma and the formation of a flow of UV radiation and a synchronous flow of microparticles based on the compound Ag_2S, which were deposited on a quartz substrate.

II. Characteristics of discharge and synthesized microstructures

In Fig. 1. oscillograms of voltage and current pulses, pulsed power of the discharge and energy contribution to the plasma of the gas-vapor mixture "Nitrogen - silver sulfide" for one discharge pulse are given.

The total duration of voltage pulses reached 450 ns. The voltage pulse was characterized by the presence of oscillations lasting 40 - 50 ns, which were caused by the mismatch between the output resistance of the high-voltage voltage pulse modulator and the plasma resistance. The largest values of voltage drop and discharge current were obtained at $p(N_2)$ = 101 kPa. The maximum pulsed power of the overvoltage nanosecond discharge was observed at $p(N_2)$ = 101 kPa in the first 125 ns from the moment of its ignition and reached 1.0 MW.

When the nitrogen pressure was reduced to 13.3 kPa,

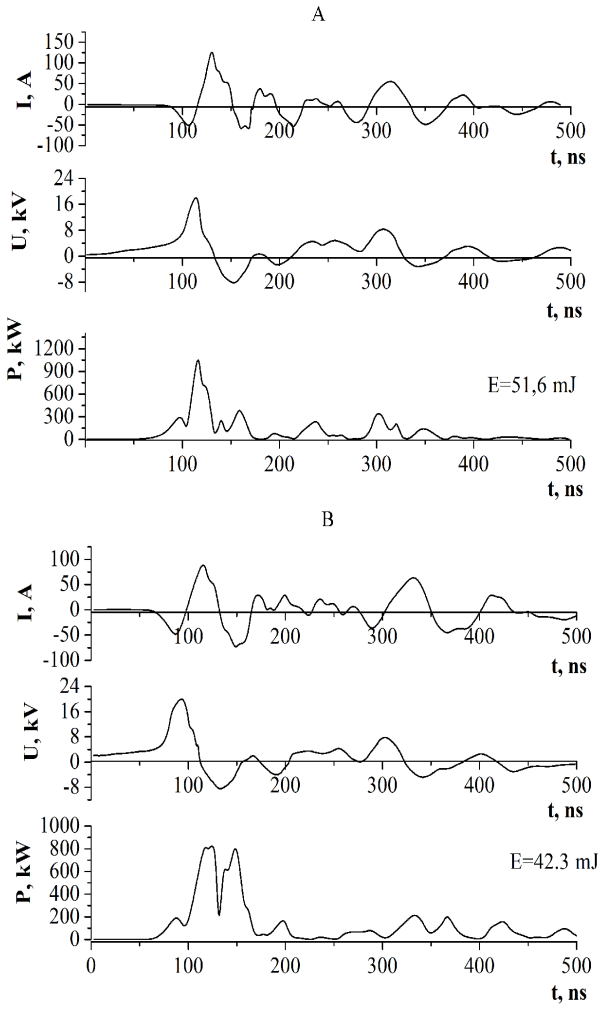

Fig. 1. Oscillograms of current pulses, voltages, pulsed power, and energy contribution to the plasma of an overvoltage nanosecond discharge for one discharge pulse ($p(N_2)$ = 101 kPa, (A); 13.3 kPa (B)).

two pulse power maxima were observed in the time range of 120 – 150 ns. The energy of a single electric pulse at nitrogen atmospheric pressure reached 51.6 mJ, and at $p(N_2)$ = 13.3 kPa it was equal to 42.3 mJ.

Dependencies of the discharge radiation density in nitrogen-silver sulfide gas-vapor mixtures on the pressure of nitrogen and the main parameters of its excitation system: the frequency of pulse tracking and the value of the charging voltage of the working capacitor of the high-voltage modulator of nanosecond pulses was carried out at a distance of 15 cm from the center of the interelectrode gap at an angle of 4π steradians. They are shown in Fig. 2 - 4.

The discharge emitted most effectively in the UV-C (bactericidal ultraviolet) and UV-A ranges. The maximum value of the average power of UV - plasma radiation at the atmospheric pressure of Nitrogen was obtained at the frequency f = 1000 Hz and the charging voltage of 20 kV (Fig. 2.-3). It reached 1 W in the wavelength range of 200 - 400 nm in the region of the installed substrate, on which a thin film of plasma was deposited.

The radiation spectrum of a nanosecond discharge in the gas-vapor mixture "N_2 - Ag_2S" at the atmospheric pressure of Nitrogen and the repetition frequency of

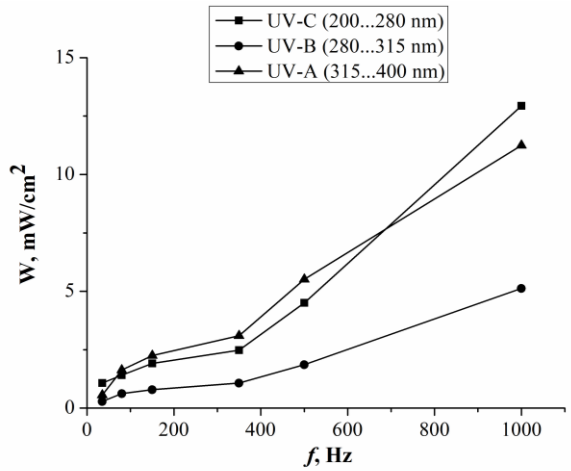

Fig. 2. Dependencies of UV power density – radiation in the UV-C, UV-B, UV-A ranges for the discharge plasma on the frequency of repetition of voltage pulses at a charging voltage of U = 13 kV in Nitrogen between electrodes with Ag_2S at a pressure of $p(N_2)$ = 101 kPa.

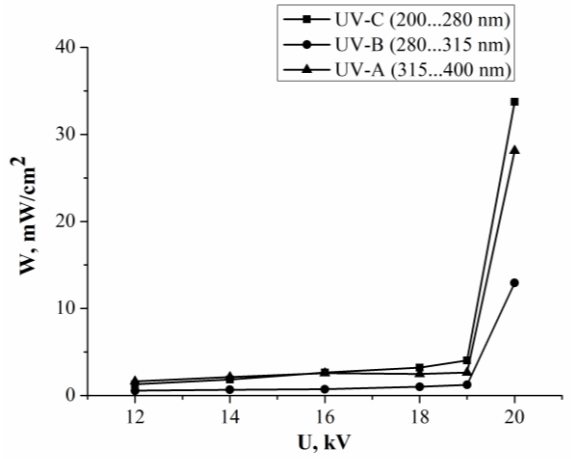

Fig. 3. Dependencies of UV power density - UV-C, UV-B, UV-A radiation - discharge ranges on the voltage on the electrodes at f = 80 Hz in atmospheric pressure nitrogen between Ag_2S electrodes.

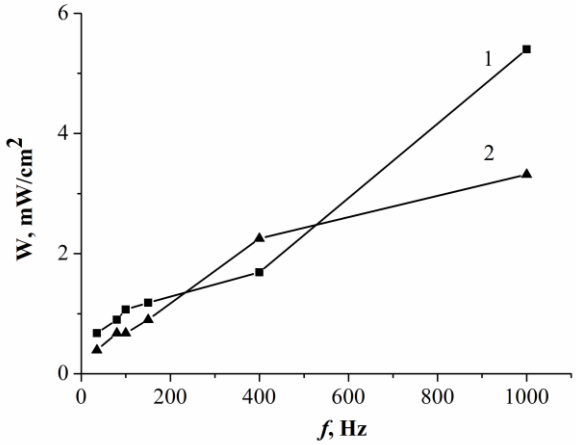

Fig. 4. Dependencies of UV power density – UV-A radiation – discharge range on the frequency of repetition of current pulses at a charging voltage of U = 13 kV in atmospheric pressure nitrogen between electrodes with Ag_2S at pressures: 1 – 101 kPa and 2 – 13.3 kPa.

Table 1

Maximum values of the power density of nanosecond UV radiation in vapor-gas mixtures "Nitrogen - silver sulfide" at different pressures of Nitrogen ($U_{ch.}$ = 20 kV, f=1000 Hz).

Spectral range	p(Nitrogen)= 13.3 kPa	p(Nitrogen) = 101 kPa
	W, mJ/cm^2	W, mJ/cm^2
UV-C (200 - 280 nm)	7.9	33.6
UV-B (280 - 315 nm)	2.5	12.9
UV-A (315 - 400 nm)	7.3	28.1

voltage pulses - 1000 Hz is shown in Fig. 5. The results of the identification of spectral lines are shown in Table 2 for the spectrum from Fig. 5. The reference book [11] was used to decode the spectrum.

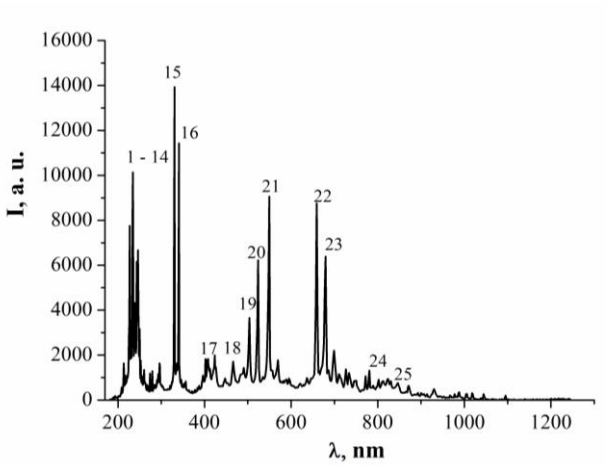

Fig. 5. The radiation spectrum of a nanosecond discharge between the electrodes of the Ag_2S compound at the atmospheric pressure of Nitrogen and the frequency f = 1000 Hz.

As can be seen from Table 2, the ultraviolet part of the spectrum was dominated by radiation at the transitions of an atom and a singly charged silver ion. The most intense were the resonance spectral lines of the silver atom at 328.06 nm Ag I and 338.28 nm Ag I. The 224.64 spectral lines stood out from the ion spectral lines by intensity; 232.02 nm. No signs of the presence of characteristic molecular bands of the nitrogen molecule in the spectral range of 280 - 390 nm were found, which is characteristic of a spark discharge in air at atmospheric pressure, which is characterized by large values of the E/N parameter.

When reducing the frequency to 80 Hz and the nitrogen pressure to 13.3 kPa, a decrease in the intensity of all spectral lines was observed, which is due to a decrease in the energy contribution to the plasma and a decrease in the concentration of the electrode material in the plasma.

The formation of excited silver atoms and ions can occur during the excitation of a silver atom by electrons, in the processes of excitation of a singly charged silver ion by electrons with subsequent recombination of silver ions (Ag II).

Table 2

The results of the identification of the spectra of nanosecond discharge plasma radiation between the electrodes from the Ag_2S compound at atmospheric pressure of Nitrogen (d = 2 mm; f = 1000 Hz).

№	λ_{tab}, nm	I_{exp} a. u.	Object	$E_{low.}$, eV	$E_{up.}$, eV	$Lower_{term}$	$Upper_{term}$
1	211.38	1630	Ag II	4.85	10.71	$4d^9(^2D_{5/2})5s\ ^2[^5/_2]_3$	$4d^9(^2D_{5/2})5p\ ^2[^5/_2]^\circ_3$
2	224.64	7753	Ag II	4.85	10.37	$4d^9(^2D_{5/2})5s\ ^2[^5/_2]_3$	$4d^9(^2D_{5/2})5p\ ^2[^7/_2]^\circ_4$
3	227.99	3538	Ag II	5.70	11.05	$4d^9(^2D_{3/2})5s\ ^2[^3/_2]_2$	$4d^9(^2D_{3/2})5p\ ^2[^5/_2]^\circ_3$
4	232.02	10134	Ag II	5.05	10.36	$4d9(^2D_{5/2})\ 5s^2[^5/_2]_2$	$4d^9(^2D_{5/2})\ 5p\ ^2[^3/_2]^\circ_1$
5	238.62	4326	Ag II	11.14	16.34	$4d^9(^2D_{3/2})5p\ \ ^2[3/2]^\circ_1$	$4d^9(^2D_{3/2})5d\ \ ^2[3/2]_2$
6	241.13	6153	Ag II	5.42	10.56	$4d^9(^2D_{3/2})5s\ ^2[3/2]_1$	$4d^9(^2D_{5/2})5p\ ^2[5/2]^\circ_2$
7	243.77	3941	Ag II	4.85	9.94	$4d^9(^2D_{5/2})5s\ ^2[^5/_2]_3$	$4d^9(^2D_{5/2})\ 5p\ ^2[^3/_2]^\circ_2$
8	244.78	6661	Ag II	5.70	10.77	$4d^9(^2D_{3/2})5s\ ^2[3/2]_2$	$4d^9(^2D_{3/2})5p\ \ ^2[5/2]^\circ_2$
9	260.59	1342	Ag II	10.18	14.94	$4d^9(^2D_{5/2})\ 5p\ \ ^2[^7/_2]^\circ_3$	$4d^9(^2D_{5/2})6s\ ^2[^5/_2]_3$
12	271.17	1178	Ag II	10.37	14.94	$4d^9(^2D_{5/2})\ 5p\ ^2[^7/_2]^\circ_4$	$4d^9(^2D_{5/2})\ 6s\ 2[^5/_2]\ 3$
13	276.75	1281	Ag II	5.70	10.18	$4d^9(^2D_{3/2})5s\ ^2[3/2]_2$	$4d^9(^2D_{5/2})5p\ ^2[7/2]^\circ_3$
14	293.83	1631	Ag II	10.77	14.99	$4d^9(^2D_{3/2})5p\ ^2[5/2]^\circ_2$	$4d_9(^2D_{5/2})6s\ ^2[5/2]_2$
15	328.06	13923	Ag I	0.00	3.77	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P^\circ_{3/2}$
16	338.28	11421	Ag I	0.00	3.66	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P^\circ_{1/2}$
17	405.54	1807	Ag I	3.66	6.72	$4d^{10}5p\ ^2P^\circ_{1/2}$	$4d^{10}6d\ ^2D_{3/2}$
18	464.30	1706	N II	18.47	21.15	$3s\ ^3P^0$	$3p\ ^3P$
19	500.515	3651	N II	20.66	23.14	$2s^22p^3p\ \ ^3D_3$	$2s^22p^3d\ ^3F^\circ_4$
20	520.90	6217	Ag I	3.66	6.04	$4d^{10}5p\ ^2P^\circ_{1/2}$	$4d^{10}5d\ ^2D_{3/2}$
21	546.54	9052	Ag I	3.77	6.04	$4d^{10}5p\ ^2P^\circ_{3/2}$	$4d^{10}5d\ ^2D_{5/2}$
22	657.07 - 328.06 (2)	8748	Ag I	0.00	3.77	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P^\circ_{3/2}$
23	679.2 - 338.28 (2)	6384	Ag I	0.00	3.66	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P^\circ_{1/2}$
24	800.51	904	Ag II	14.94	16.49	$4d^9(^2D_{5/2})6s\ ^2[5/2]_3$	$4d^9(^2D_{5/2})\ 6p\ ^2[5/2]^\circ_3$
25	869.47	631	S I	7.86	9.29	$3s^23p^3\ (^4S^\circ)\ 4p\ ^5P_3$	$3s^23p^3(^4S^\circ)4d\ ^5D^\circ_4$

When the quartz substrate was installed at a distance of 2 – 3 cm from the center of the discharge gap and the discharge burning time was 30-40 minutes, the deposition of microstructures from the products of sputtering of the electrode material in nitrogen of atmospheric pressure was recorded on the substrate. The characteristic sizes of surface microstructures are 10 - 20 μm.

Conclusions

The study of the characteristics of the source of synchronous streams of UV radiation and silver sulfide nanostructures with pumping by an overvoltage nanosecond discharge between the electrodes from the polycrystalline compound Ag_2S in nitrogen revealed the following:

- with the total duration of the voltage pulses up to 450 ns, the largest value of the impulse electric power of the discharge reached - 1.0 MW with the energy in a separate pulse - 51.6 mJ; a decrease in nitrogen pressure to 13.3 kPa led to a decrease in the amplitudes of voltage, current, and pulse power, and the energy in the pulse decreased to 42.3 mJ;

- discharge plasma in the UV range of wavelengths radiated at the transitions of an atom and a singly charged silver ion; resonance spectral lines of the silver atom (328.06; and 338.28 nm Ag I) were distinguished by intensity; the discharge plasma is the source of the flow of UV radiation and the flow of silver sulfide nanostructures, which is promising for applications in micro-nanotechnology, medicine, and microbiology; the highest power density of ultraviolet radiation at the transitions of atoms and singly charged silver ions was obtained at the atmospheric pressure of Nitrogen at the repetition frequency of voltage pulses f = 1000 Hz;

- surface microstructures with dimensions of 10 - 20 μm were synthesized during deposition of electrode erosion products on a quartz substrate installed near the electrode system.

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Газорозрядне джерело синхронних потоків УФ-випромінювання і мікроструктур сульфіду срібла

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Приводяться результати дослідження характеристик імпульсного джерела синхронних в часі потоків УФ-випромінювання атомів та іонів срібла і мікро-наноструктур сульфіду срібла. Перенапружений наносекундний розряд запалювався в азоті між електродами з сульфіду срібла (Ag_2S) при віддалі між електродами – 2 мм. Пари сульфіду срібла вносились в газопарову суміш «Азот - Ag_2S» за рахунок ектонного механізму. Досліджено імпульси напруги, струму, імпульсна потужність розряду, енергетичний внесок в плазму за один імпульс при частотах повторення імпульсів 40 - 1000 Гц. Вивчались спектральні характеристики розряду та просторові характеристики мікроструктур, осаджених з плазми розряду на кварцову підкладку, встановлену біля системи електродів.

Розряд може бути використаний як джерело бактерицидного випромінювання і джерело мікроструктур на основі сульфіду срібла, а також як плазмохімічний реактор з синтезу тонких мікроструктурованих плівок сульфіду срібла.

Ключові слова: сульфід срібла, перенапружений наносекундний розряд, спектр випромінювання, плазма, імпульсне джерело.