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Investigation of conditions of synthesis of thin films of silver nitride ($AgNO_3$) in a high-frequency low-pressure discharge

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The results of studying the characteristics of a low-pressure high-frequency discharge in air (p = 10 Pa) for the synthesis of thin films from silver nitride, due to the electron sputtering mechanism of a polycrystalline electrode from the compound Ag_2S, are presented. For the synthesis of thin films based on the $AgNO_3$ compound, the phenomenon of explosive emission of natural inhomogeneities on the surface of a polycrystalline electrode was used, in which, as a result of the destruction of electrodes from the Ag_2S superionic conductor, a silver vapor flow was formed, which, after interaction with a low-density air plasma, condensed in the form of silver nitride on placed near a dielectric substrate. The resulting films can be used in medicine, biotechnology, biomedical engineering, and agriculture.

Keywords: high-frequency discharge, thin films, silver nitride, radiation spectrum, plasma.

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Introduction

The results of studying the synthesis of carbon nanotubes during the deposition of HF plasma products are given in [1]. It was found that the optimal discharge power was W=10-12 W. At W > 12 W, the surface of the synthesized product with nanotubes was etched, nanotube nuclei were agglomerated, and carbon nanoclusters and multilayer graphene structures were formed.

In [2], the results of the formation of polyethylene and silver nitride from the active gas phase formed during electron beam dispersion are presented; nanocomposite coatings of polyethylene and silver were formed, their structure and morphology were studied, as well as the effect of laser assistance on the processes of film synthesis. It has been shown that under laser assistance, silver nanoparticles formed during dispersion have an autocatalytic effect on the processes of salt decomposition, and heating of the coating leads to the formation of a more uniform structure with a lower protrusion height.

The results of magnetron synthesis of thin nanostructured zinc oxide films using UV irradiation of a substrate with a film in the process of its synthesis by radiation of a mercury lamp are given in [3]. Here it was found that UV-assisted growth of transparent ZnO layers improves their electrical characteristics by creating additional donor centers and reducing the scattering of electric charge carriers at grain boundaries. Therefore, when optimizing the process of synthesizing thin films based on silver using a high-frequency discharge in low-pressure air, it will be important to study the optical characteristics of the plasma of this discharge. When using microexplosions on the surface of a polycrystalline electrode made of Ag_2S compound at an air pressure of 10 Pa.

The emission spectra of a silver-based plasma under fore-vacuum conditions, using the example of a low-energy laser plasma, both when using a pure silver target and from an $AgGaS_2$ compound, are given in [4, 5].

For laser silver plasma in the spectral range of 270-550 nm, where the spectral characteristics were studied, the most intense were the spectral lines of the silver atom with wavelengths: 546.5; 520.9; 421.1; 405.5; 338.3; 328.1 nm [4]. The excited component of the laser plasma based on the $AgGaS_2$ compound was predominantly represented by S II and Ag II ions, as well as the Rydberg states of Ag I and Ga I [5].

In [6, 7], the results of the study and application of silver nanoparticles, which were obtained by the erosion of silver electrodes as a result of the ignition of high-current short-duration discharges in water, are presented.

The spectral characteristics of a gas-discharge plasma based on the Ag_2S superionic conductor, the conditions for the destruction of polycrystalline electrodes from this compound under conditions of a high-frequency low-pressure discharge, and the products of air destruction in such a plasma are currently absent. The possibility of synthesizing thin films of silver nitride based on the degradation products of the Ag_2S compound and air in a low-pressure HF plasma has also not been studied.

The article presents the results of a study of the spatial, electrical and spectral characteristics of a high-frequency low-pressure air discharge between an electrode based on a polycrystalline Ag_2S compound and a stainless steel electrode, as well as the results of a study of the optical characteristics of thin films synthesized on the basis of sputtering products of the Ag_2S compound and RF-discharge products in low pressure air.

I. Methods and experimental technique

A low-pressure high-frequency discharge in air (p = 10 Pa) between an electrode made of a superionic conductor based on an Ag_2S compound and a stainless steel electrode was ignited in a discharge chamber made of Plexiglas (Fig. 1). Massive samples of polycrystals based on the Ag_2S superionic conductor were synthesized in the technological laboratory of the chemical faculty of the Uzhhorod National University.

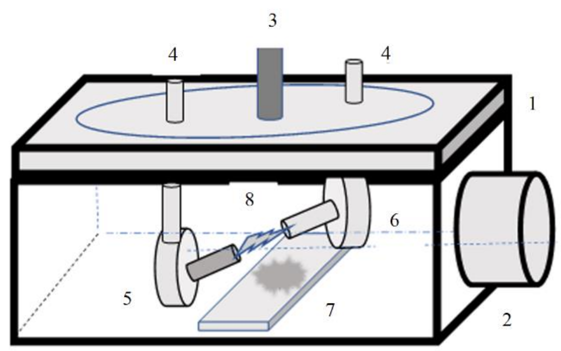

Fig. 1. Scheme of a gas-discharge reactor: a body of a discharge chamber made of plexiglass (1), an output quartz window (2), a fitting connected to a vacuum-gas-mixing system (3), high-voltage inputs (4), an electrode from the studied material - Ag_2S (5), stainless steel electrode (6), glass substrate for deposition of thin films of silver nitride (7), discharge area (8).

HF discharge was ignited using an EN57M high-frequency electrosurgery device with the following initial characteristics: power consumption from the power supply did not exceed 1.8 kW, voltage amplitude - 1 kV, maximum average output power 300-350 W, operating frequency - 1.7, output shape voltage, sinusoidal, modulated by power supply voltage. The discharge was ignited at a distance between the electrodes of 8 mm between their end parts with a rounding radius of 10 mm. The electrode diameter was 5 mm. Voltage was applied to an electrode made of a polycrystalline sample of a superionic conductor, Ag_2S, and a stainless steel electrode was grounded.

Oscillograms of voltage pulses across the discharge gap and oscillograms of current pulses were recorded using a broadband capacitive voltage divider, a Rogowski coil, and a 6LOR-04 broadband oscilloscope. The time separation of this system for measuring the characteristics of electrical impulses was 2–3 ns.

To record the emission spectra of high-frequency discharge plasma, a digital two-channel spectrometer with astigmatism compensation "SL-40-2-1024USB" was used. Working spectrum of the spectrometer: 200-1200 nm.

More details on the methods and technique of the experiment are given in [8].

The scheme of the plasma-chemical reactor for gas-discharge synthesis of thin films based on the Ag_2S superionic conductor is shown in Fig.1. The distance between the electrodes was 8 mm. The HF discharge was ignited when the discharge gap was overvoltaged, when a beam of runaway electrons was formed in it. Under the action of this beam and the accompanying X-ray radiation, the discharge in air at a pressure of 10 Pa, even with a rather inhomogeneous distribution of the electric field strength between electrodes with radii of curvature of hemispherical working surfaces (~10 mm), was quite uniform. In a strong electric field on the working surface of an electrode based on the Ag_2S compound, nanowister microexplosions occur on the electrode surface, which contributed to the introduction of vapors of the superionic conductor Ag_2S products and their decay (Ag, ...) into low-pressure air plasma and their deposition on a glass substrate in the form of thin films.

When a glass substrate was installed at a distance of 8 mm from the center of the discharge gap (Fig. 1) and the discharge burning time was 10–30 minutes, the deposition of a thin film from the products of sputtering of the electrode material and the products of air destruction in the discharge was recorded on the substrate. The obtained samples of thin films were studied using an XploRA PLUS Raman spectrometer.

HF photographs were obtained using a digital camera (exposure time ≈ 1 s), photographs of the thin film surface were obtained using an optical microscope and a camera, with a system magnification of 1500.

When conducting experimental studies, a digital two-channel spectrometer with astigmatism compensation "SL-40-2-1024USB" and a Raman spectrometer "XploRA PLUS" of the center for the collective use of scientific equipment "Laboratory of Experimental and Applied Physics" at the Far Eastern Higher Educational Institution were used.

II. Spatial, electrical and spectral characteristics

When a high-frequency voltage is applied to the electrode from the Ag_2S superionic conductor in a low-pressure air media (p = 10 Pa), a diffuse, spatially homogeneous high-frequency discharge ignites. In a strong electric field in the vicinity of nanowisters located on the working surface of an unpolished polycrystalline electrode, an intense field emission of electrons begins, which ends with a microexplosion of the wister and the introduction of vapors of the Ag_2S compound into the interelectrode gap of the HF discharge, which, when destroyed in plasma, serve as a source of an atom. See also sulfur. The plasma simultaneously acts as a source of UV radiation and clusters and nanostructures based on the Ag_2S compound and its degradation products entering the surrounding space, where a glass substrate is placed, on which a thin film is formed based on the degradation products of the Ag_2S compound and low-pressure air plasma. We also observed a similar picture for an overvoltage nanosecond atmospheric pressure discharge in air between copper electrodes [9].

Fig.2. presents the image of the system of HF electrodes and the discharge between them at an air pressure in the discharge chamber of 10 Pa.

Fig. 2. View of a high-frequency discharge in air at a pressure of p - 10 Pa and an average electrical power of the HF discharge- 300 W.

The HF discharge between the electrode made of a polycrystalline compound (Ag_2S) and the stainless steel electrode ignited in a diffuse form, which is due to the presence of preliminary ionization of the discharge gap in the form of a flow of runaway electrons, X-ray and ultraviolet radiation, as well as low air pressure. This type of HF discharge is a prerequisite for obtaining uniform flows of the Ag_2S compound sputtered from the electrode surface and its degradation products in plasma, as well as for the flow of UV radiation from the discharge and the deposition of electrode material products on a glass substrate in the form of a thin film.

Fig.3 presents an oscillogram of high-frequency voltage pulses, which was applied to a polycrystalline electrode and a discharge current. In this experiment, the highest voltage amplitude reached 1 kV, and the average power at the output of the power supply was 300 W.

The radiation spectrum of plasma based on a superionic conductor and the results of identification of the most intense spectral lines of an atom, a singly charged silver ion, as well as the spectral bands of a sulfur molecule in a high-frequency discharge are shown in Fig. 4 and in the Table 1.

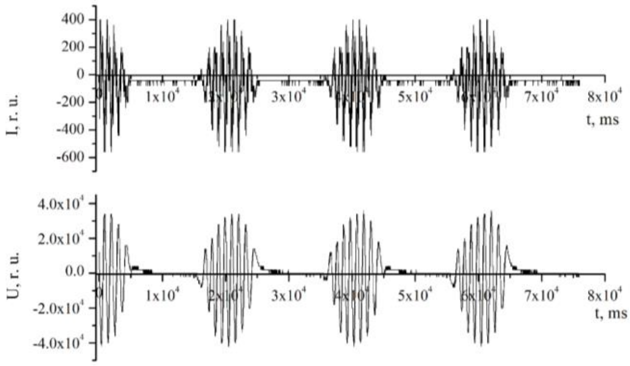

Fig. 3. Oscillograms of the voltage between the explosive electrodes and the discharge current at an air pressure of 10 Pa and a distance between the electrodes of 8 mm.

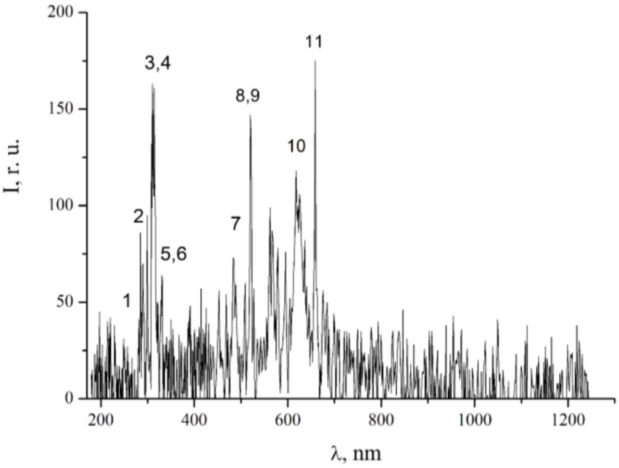

Fig. 4. HF discharge radiation spectrum between a superionic conductor electrode and a stainless steel electrode in air at a pressure of p=10 Pa (W=300 W).

In [10], the results of studying the electronic structure of the silver chalcogenide compound Ag_2S both experimentally using photoelectron spectroscopy and theoretically are presented. When an Ag_2S compound is injected from the surface of a polycrystalline electrode into an HF-discharge plasma, it is easily destroyed by electrons with the release of silver atoms, which are excited by the HF electrons (Table 1). The investigated plasma radiates in the spectral range of 230-340 nm. The main sources of radiation in the UV - spectral range were atoms and singly charged silver ions, as well as bands of a diatomic sulfur molecule. In the visible region of the plasma radiation spectrum, there were transitions of the silver atom and ion, and individual bands of the nitrogen molecule were also observed [11].

Figure 5 shows photographs of a thin film synthesized from the sputtering products of a polycrystalline electrode in an overvoltage nanosecond discharge of atmospheric pressure in air on the surface of a glass plate. The plate was installed at a distance of 8 mm from the center of the interelectrode gap. The photographs of the surface of the synthesized thin films shown in Figures 5 and 6 were obtained using an optical microscope with a magnification of 1500 times.

Table 1.

The results of identification of the most intense spectral emission lines of an atom and a singly charged silver ion, as well as the spectral bands of a sulfur molecule at an air pressure of p = 10 Pa in a HF discharge ignited at a distance between the electrodes from the Ag_2S compound d = 8 mm and a frequency f = 1.76 MHz

№	**λ_{tab}, nm**	**I_{exp} a.u.**	**Object**	**$E_{low.}$, eV**	**$E_{up.}$, eV**	**$Lower_{term}$**	**$Upper_{term}$**
1	232.02	29	Ag II	5.70	11.05	$4d^9(^2D_{3/2})5s\ ^2[^3/_2]_2$	$4d^9(^2D_{3/2})5p\ ^2[^5/_2]°_3$
2	298.95	95	S_2	$^3\Sigma$-$^3\Sigma$ (6;1)			
3	309.15	163	S_2	$^3\Sigma$-$^3\Sigma$ (5;2)			
4	313.22	161	S_2	$^3\Sigma$-$^3\Sigma$ (4;2)			
5	328.06	64	Ag I	0.00	3.77	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P°_{3/2}$
6	338.28	28	Ag I	0.00	3.66	$4d^{10}5s^2S_{1/2}$	$4d^{10}5p^2P°_{1/2}$
7	484.782	72	Ag I	0.71	9.84	$4d^95s(^3D)5p\ ^4F°_{7/2}$	$4d^95s(^3D)6s\ ^4D_{7/2}$
8	520.90	147	Ag I	3.66	6.04	$4d^{10}5p\ ^2P°_{1/2}$	$4d^{10}5d\ ^2D_{3/2}$
9	562.24	99	Ag II	15.82	18.02	$4d^9(^2D_{5/2})5d\ ^2[7/2]_4$	$4d^9(^2D_{5/2})4f^2[9/2]°_5$
10	616.58	118	S_2	$^3\Sigma$-$^3\Sigma$ (9;30)			
11	657.07 - second order 328.06	175	Ag I	0.00	3.77	$4d^{10}5s\ ^2S_{1/2}$	$4d^{10}5p\ ^2P°_{3/2}$

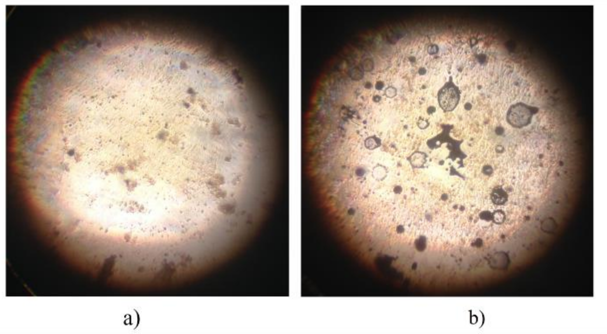

Fig. 5. Photographs of different parts of the surface of a thin film synthesized from the degradation products of polycrystalline electrodes based on the Ag_2S superionic conductor in an overvoltage nanosecond discharge in air (p = 103 kPa; f = 1 kHz; d = 2 mm).

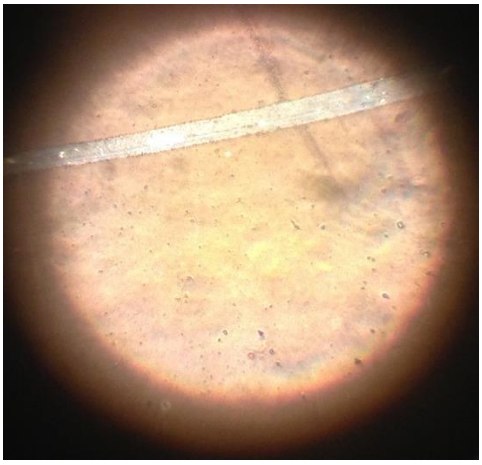

Fig. 6. Photograph of the surface of a thin film synthesized from the degradation products of a polycrystalline electrode based on the Ag_2S superionic conductor in a low-pressure high-frequency discharge in air (p = 10 Pa; f = 1.76 MHz; d = 8 mm).

As follows from Fig. 5, the surface of the films synthesized from the degradation products of the Ag_2S compound in an overvoltage nanosecond discharge in air at atmospheric pressure was quite uniform. The horizontal width of the photograph was 15 μm. However, against the background of a uniform film surface, slices of a sputtered polycrystalline electrode of micron size were observed.

On Fig.6 an image of the surface of a film obtained using the degradation products of a polycrystalline electrode in HF discharge in low-pressure air is shown. As follows from Fig. 6 the surface of the synthesized film is much more uniform than in Fig.5 and there are no separate fragments of the polycrystalline electrode on it.

Raman spectra of a thin film synthesized from HF discharge products in air at a pressure of p=10 Pa are shown in Fig.7. The Raman spectrum of scattering by a thin film of the compound $AgNO_3$ is also shown there [12].

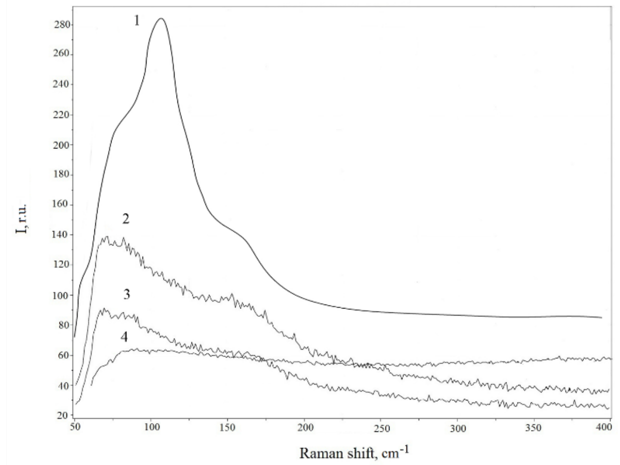

Fig. 7. Raman scattering spectra of a silver nitride compound and a thin film of a sputtered polycrystalline electrode in our studies:
1 – Raman spectrum of the $AgNO_3$ compound [12], 2, 3 – Raman light scattering spectra obtained from different parts of the film synthesized on the basis of the Ag_2S compound sputtered in HF plasma in low-pressure air, 4 – Raman spectrum of the glass substrate.

It follows from Fig. 7 that the Raman scattering spectrum of the films synthesized by us is identical to the control spectrum of the $AgNO_3$ compound. Since the silver nitride film was synthesized with automatic assistance of plasma UV radiation, it should have a lower resistance compared to the typical synthesis of such films by magnetron sputtering [2].

Conclusions

Thus, it has been found that when an electrode made of a polycrystalline Ag_2S compound is sputtered in a low-pressure high-frequency discharge in air, a thin film based on the $AgNO_3$ compound is synthesized on a dielectric substrate installed near the electrode system.

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Дослідження умов синтезу тонких плівок нітриду срібла ($AgNO_3$) у високочастотному розряді низького тиску

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Наведено результати дослідження характеристик високочастотного розряду низького тиску в повітрі (p = 10 Па) для синтезу тонких плівок з нітриду срібла, за рахунок ектонного механізму розпорошення полікристалічного електрода з сполуки Ag_2S. Для синтезу тонких плівок на основі сполуки $AgNO_3$ використано явище вибухової емісії природних неоднорідностей на поверхні полікристалічного електрода, при якому в результаті руйнування електродів з суперіонного провідника Ag_2S формувався потік парів срібла, який, після взаємодії з плазмою повітря низької густини, конденсувався у формі тонкої плівки з нітриду срібла на встановленій поблизу діелектричній підкладці. Одержані плівки можуть бути використані в медицині, біотехнологіях, біомедичній інженерії, а також у сільському господарстві.

Ключові слова: високочастотний розряд, тонкі плівки, нітрид срібла, спектр випромінювання, плазма.