Synthesis of Thin Films Based on Silver Sulfide in Air at Atmospheric Pressure in a Gas Discharge


Uzhhorod National University, Narodna Sq. 3, 88000 Uzhhorod, Ukraine

(Received 11 January 2023; revised manuscript received 17 February 2023; published online 24 February 2023)

The characteristics of an overvoltage high-voltage nanosecond discharge in air at atmospheric pressure between polycrystalline electrodes made of a superionic conductor, silver sulfide (Ag$_2$S), are given. In the process of microexplosions of inhomogeneities on the working surfaces of the electrodes in a strong electric field, vapors of the Ag$_2$S compound and its dissociation products in the plasma are introduced into the interelectrode space due to the formation of etons. This creates prerequisites for the synthesis of thin films from this material, which have the properties of superionic conductors and photovoltaic compounds and can be deposited on a dielectric substrate installed in a discharge gap. Spatial and electrical properties of nanosecond overvoltage discharges and Raman scattering spectra of synthesized thin films and their surfaces were investigated. Discharge plasma parameters were modeled in a mixture of Ag$_2$S superionic conductor vapor and air. Numerical calculations were performed using a program that solves the Boltzmann equation for the electron energy distribution function. The transport characteristics of discharge electrons and rate constants of electronic processes were calculated depending on the values of the $E/N$ parameter in the experimental range of 1-1000 Td of the study of discharge properties. Raman light scattering spectra of thin films synthesized from electrode erosion products in air plasma are presented.

Keywords: Overvoltage nanosecond discharge, Superionic conductor, Thin films, Radiation spectrum, Plasma.

DOI: 10.21272/jnep.15(1).01010

1. INTRODUCTION

For the synthesis of nanostructures of superionic conductors, which are intended for various applications in micro-nanotechnology, mainly chemical methods are used, methods of exploding thin wires or plates when a current pulse of hundreds to thousands of amperes is passed through them. Therefore, the application of synthesis technologies of these nanostructures based on more technological and less expensive gas discharge technologies is promising. At the same time, it is possible to carry out the synthesis of nanostructures without the use of vacuum technology in low-cost gases such as nitrogen, argon or air, both in gasostatic conditions and in low-speed gas flows.

The results of the synthesis of thin films based on zinc oxide using UV illumination of the substrate with the film in the process of its growth with the help of radiation from a mercury lamp are given in [1]. Here it was found that UV-assisted growth of transparent ZnO layers improves their electrical characteristics due to the creation of additional donor centers and reduction of the scattering of electric charge carriers at grain boundaries. The disadvantage of this method of synthesizing thin films from zinc oxide is the use of a separate source of UV radiation in the film synthesis process.

The restoration of the superionic superconductor – Ag$_2$S on silver objects of antiquity to metallic silver in a vacuum in the form of powder during the deposition of a coating based on the Ag$_2$S compound from the gas phase, which was formed by an electron beam with an energy of 800-1600 eV, are presented. The disadvantage of this method of synthesizing films based on silver sulfate is the need to maintain a high vacuum in the reactor and use an expensive UV laser with nanosecond generation pulses.

In [4, 5] chemical methods of synthesis of superionic conductor – Ag$_2$S were used. The results of the hydrochemical deposition of Ag$_2$S/Ag heteronanostructures and the study of the phase transformation "acanthite – Ag$_2$S – argentite – Ag$_2$S" were reported in [4]. It was established that the concentration of vacant sites in the metal sublattice of argentite exceeded 92 %, and the "acanthite argentite" transformation in the Ag$_2$S/Ag heteronanostructure was reversible upon application of an external bias voltage. At the same time, the appearance of argentite – Ag$_2$S, which conducts current well, was observed instead of acanthite – Ag$_2$S, which does not conduct current; the channel with high conductivity was formed from argentite – Ag$_2$S and silver (Ag).

In [5], the results of the synthesis of nanoparticles of the superionic conductor Ag$_2$S by the method of chemical condensation in an aqueous solution are given. Thin films were synthesized on the basis of a colloidal solution; the stability range of colloidal solutions of silver sulfide and the size and size distribution of Ag$_2$S nanoparticles in the films at different concentrations of the starting reagents were established.

* alexsander.shuaibov@uzhnu.edu ua
In [6], the results of the synthesis of CdO, Ag2S, Ag nanostructures (with a diameter of ~5-30 nm) in a nanosecond discharge in liquid nitrogen between cadmium and silver electrodes are presented. Cubic nanoparticles based on cadmium were formed at a voltage of ~4 kV, and at a voltage of 7-10 kV they were elongated and had thread-like ends. Cadmium nanowires were formed by collecting individual cadmium nanoparticles in liquid nitrogen, while silver nanoparticles were spherical and assembled into two-dimensional dendritic structures when the voltage was increased.

Therefore, the search for a new method of synthesizing thin films based on a superionic conductor – Ag2S, improving the conditions and reducing the cost of the synthesis process due to the use of an overvoltage nanosecond discharge of atmospheric pressure between electrodes from a compound based on superionic conductors with an eutectic mechanism of their dispersion in air is currently relevant for us. Thus, there is no need to use a separate source of UV radiation to illuminate the substrate with the film during its synthesis, vacuum technology and expensive buffer gases.

The practical application of this research consists in the use of the cheapest buffer gas – air at atmospheric pressure, which does not need to be used in plasma chemical reactors of open type of vacuum technology, and the flow of clusters and nanoparticles of the superionic conductor is automatically accompanied by the flow of UV-plasma radiation, which can improve the properties of the synthesized surface microstructures. Since the stream of nanoparticles is formed on the basis of a silver compound, which is characterized by significant antibacterial properties, the synthesized coatings can be used in micro-nanoelectronics as well as in microbiology, medicine and biomedical engineering.

2. TECHNIQUE AND CONDITIONS OF THE EXPERIMENT

A nanosecond discharge between the electrodes from a superionic conductor made from a polycrystalline compound – silver sulfide (Ag2S) was ignited in a dielectric discharge chamber (Fig. 1). The diameter of the cylindrical electrodes is 6 mm, and the distance is 2 mm. The radii of rounding of the working end surfaces of the electrodes are the same and are R = 10-12 mm.

The overvoltage nanosecond discharge was ignited using a bipolar high-voltage modulator of voltage pulses with a total duration of 50-150 ns and a total amplitude of positive and negative components of ± 20-60 kV. The high-voltage bipolar nanosecond pulse generator is built according to the scheme with resonant recharging of the storage low-inductance capacitor with a capacity of 1540 pF. The TGP-1000-25 hydrogen pulse thyatron served as the commutator in the modulator. The frequency of repetition of voltage pulses could vary between 40-1000 Hz.

A digital two-channel spectrometer with astigmatism compensation was used to record the plasma radiation spectra of an overvoltage nanosecond discharge.

The technique and method of the experiment are given in detail in [7].

3. CHARACTERISTICS OF AN OVERVOLTAGE NANOSECOND DISCHARGE

In Fig. 2, an image of an overvoltage nanosecond discharge in air of atmospheric pressure between the electrodes of the Ag2S compound is presented, which ignited and burned in a diffuse form.

At a distance between the electrodes of d = 2 mm, a high-voltage nanosecond discharge was ignited at a significant overvoltage of the discharge gap, when a beam of "runaway" electrons was formed in it. Therefore, for this type of discharges, the role of the preionization system is performed by a beam of electrons – "runaways" and accompanying X-ray radiation [8].

In Fig. 3, oscillograms of current pulses, voltage and pulsed power of an overvoltage nanosecond discharge between electrodes made of the Ag2S compound are shown. In this experiment, the total duration of the voltage pulses reached 400-450 ns, and the voltage pulse itself consisted of time-damped oscillations with a duration of about 20-30 ns.

The maximum value of the voltage drop on the discharge gap was 30 kV, taking into account the positive and negative components of the voltage pulse amplitude.
The maximum amplitude of the current pulse reached 100 A. The highest pulsed power of the discharge was reached in the first 100 ns from the moment of its ignition and was about 3 MW. The second maximum pulsed power was 1.5 MW and was observed at the time from the start of discharge ignition $t = 150$ ns. The energy of a separate electric pulse was 0.77 J. Oscillograms of voltage, current, and power pulses of an overvoltage nanosecond discharge between electrodes from the Ag$_2$S connection are presented in Fig. 3. The voltage pulses consisted of oscillations that decayed in time, and their total duration reached 400-450 nanoseconds. The magnitude of the voltage drop in the discharge gap reached 30 kV, and the maximum amplitude of the current pulse was 100 A. The magnitude of the impulse power of the discharge was about 3 MW. The energy of the electric pulse was 0.77 J.

In the spectral range of 200-350 nm, gas-discharge plasma radiated, and the main sources of radiation in this range of 200-350 nm were singly charged silver ions and silver atoms (Fig. 4) [9].

![Fig. 3 - Oscillograms of current pulses, voltage and pulsed power of an overvoltage nanosecond discharge in air ($p$(Air)) = 101 kPa, $d$ = 2 mm and $f$ = 1000 Hz)](image.png)

![Fig. 4 - Emission spectrum of an overvoltage nanosecond discharge in air at atmospheric pressure)](image.png)

### 4. PLASMA PARAMETERS

The transport parameters of the discharge plasma (the ratio of components 200 Pa : 101 kPa and 1000 Pa : 101 kPa) were determined numerically and calculated as the total integral of the electron energy distribution function for a mixture of silver sulfide vapor and air at atmospheric pressure. EEDF were calculated by solving the Boltzmann kinetic equation in the two-dimensional approximation using the program [12].

The range of changes of the parameter $E/N = 1-1000$ Td ($1 \times 10^{-17} - 1 \times 10^{-14}$ cm$^2$/e) included the values of the reduced electric field that were implemented in the experiment. These values of the reduced electric field were 306 Td and 102 Td, as well as 304 Td and 101 Td for the duration of 50 ns and 100 ns voltage pulses (Fig. 3) from the beginning of the discharge burning.

The absolute values of the effective cross-sections of the processes that were taken into account during modeling, as well as their dependence on the electron energies, are taken from the database [12]. The effective cross sections for the excitation and ionization of a silver atom by electrons were taken from [13-15].

Figure 5 shows the dependences of the average energy of electrons in the plasma of the vapor-gas mixture Ag$_2$S: Air = 200 : 101000 Pa and Ag$_2$S : Air = 1000 : 101000 at the total pressure $p = 101200$ Pa and 102000 on the reduced electric field strength. The mean energy of discharge electrons for vapor-gas mixtures of silver sulfide-air increases almost linearly from 0.1365 eV to 16.44 eV (Fig. 5 (1)) and from 0.1372 to 15.87 (2) with an increase in the reduced electric field strength from 1 to 1000 Td. At the same time, a pattern of increased rate of change was observed in the range of 1-200 Td for both the first and second mixtures.

![Fig. 5 - Dependences of mean energy of electrons in the plasma of the vapor-gas mixture on the reduced electric field strength: 1 – Ag$_2$S – air = 200 : 101000; 2 – Ag$_2$S – air = 1000 : 101000 at a total pressure $p = 101200$ Pa and 102000 Pa)](image.png)
The temperature and electron drift speed (Table 1) decrease from 132.124 to 81.490 K and from 4.7×10⁷ to 2.8×10⁶ m/s for the first mixture, and from 126.440 to 76.595 K and 4.6×10⁷ to 2.8×10⁶ m/s for the second mixture, when the reduced electric field strength changes from 615 to 305 Td, respectively. The electron concentration values increase from 2.9×10¹⁶ to 8.5×10¹⁹ m⁻³ for the first mixture and from 2.0×10¹⁸ to 8.6×10¹⁹ m⁻³ for the second mixture.

Fig. 6 presents the results of the numerical calculation of the dependence of the excitation rate constants of the spectral lines of silver atoms on the reduced electric field strength in mixtures of silver sulfide vapors and air for the ratio of partial pressures of 200-101000 Pa (a) and 1000-101000 Pa (b).

The excitation rate constants are characterized by a high value, which is associated with the values of the absolute effective cross sections of the corresponding processes. In the range of the reduced electric field strength of 305 Td-615 Td, in which experimental studies of electrical and optical characteristics of the discharge were carried out, they were within the range of $k = 10^{-17}$-10⁻¹⁸ m⁶/c.

**Table 1 – Transport properties of electrons for the mixture: Ag₂S – air = 200 Pa – 101 kPa and Ag₂S – air = 1000 Pa – 101 kPa**

<table>
<thead>
<tr>
<th>$\tau$, ns</th>
<th>$E/N$, Td</th>
<th>$\varepsilon$, eV</th>
<th>$T$, K</th>
<th>$V_{dr}$, m/s</th>
<th>$N_e$, m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>615</td>
<td>11.39</td>
<td>132 124</td>
<td>4.7×10⁵</td>
<td>2.0×10¹⁹</td>
</tr>
<tr>
<td>75</td>
<td>307</td>
<td>7.025</td>
<td>81 490</td>
<td>2.8×10⁴</td>
<td>8.5×10¹⁹</td>
</tr>
</tbody>
</table>

**Fig. 6 – Dependences of the rate constants of collisions of electrons with silver atoms on the reduced electric field strength in plasma on a mixture of silver sulfide vapors and air 200-101000 Pa (a) and 1000-101000: 1 – elastic scattering of electrons on atoms 2 – excitation of the state of the silver atom ($E_{th} = 3.78$ eV), 3 – excitation of the state of the silver atom ($E_{th} = 3.66$ eV), 4 – ionization of silver atoms (threshold energy 8.00 eV).**

5. CHARACTERISTICS OF THE SYNTHESIZED FILMS

The method of synthesis of thin films from materials of sputtered electrodes was the same as in [16]. In Fig. 7, the characteristic spectrum of Raman scattering radiation of a semiconductor laser with a generation wavelength of 785 nm is given. The laser beam probed the area of the film surface with a diameter of 1-2 microns. The average radiation power of the laser that generated radiation at a wavelength of 785 nm was 32 mW, and the radiation power of lasers at wavelengths of 532 and 632.8 nm was 9.2 and 60.6 mW, respectively. Identification of Raman scattering spectra was carried out on the basis of [17]. A Renishaw InVia™ confocal Raman microscope (UK) spectrometer was used to study thin films. The exposure time was 10 seconds.

Films were analyzed using all three available laser wavelengths – 532, 633 and 785 nm. The spectrum of Raman light scattering of the film (Fig. 7), which was studied using radiation at a wavelength of 532 nm, was characterized by bands in the range of 100-300 cm⁻¹, in particular at 248 cm⁻¹. A broad band in the range of 210-250 cm⁻¹, in particular the maximum at 248 cm⁻¹,

**Fig. 7 – Spectra of Raman scattering of radiation from a semiconductor laser at a wavelength of 785 nm by a thin film, which was synthesized from the products of electrode erosion in an air plasma of atmospheric pressure.**
which is caused by Ag₃S nanoparticles, is associated with asymmetric longitudinal vibrational modes of Ag–S–Ag bonds [17]. These bands were also observed in Ag₃S samples and in the spectrum of α-Ag₃S [17].

Two bands at 432, 457 cm⁻¹ were also observed, which are associated with symmetric bending in the plane of O-S-O bonds (scissor oscillations), and a weak band at 618 cm⁻¹ is associated with asymmetric bending in the plane of O-S-O bonds (oscillatory vibrations) [17]. The sharp and intense band at 969 cm⁻¹ is associated with the symmetric stretching of S-O bonds, and was 3.3 times larger than the bands in the range of 100-300 cm⁻¹. This band also prevailed in [17], where the authors studied the spectra of silver sulfite Ag₂SO₃ and silver sulfate Ag₂SO₄.

Also, a band at 1037 cm⁻¹ was observed in the Raman spectrum, which is associated with asymmetric stretching of S-O bonds [17].

A broad band in the range of 1460-1600 cm⁻¹ is associated with the oscillations of silver and sulfur oxide compounds, which are released during the photoinduced decomposition of Ag₂S. In [17], the maximum at ~1435 cm⁻¹ is explained by the photodecomposition of Ag₂S, which may be caused, as the authors of this article explain, by the high power of the laser or by the relatively long duration of the measurement.

In the Raman spectrum of the thin film, which was synthesized from the products of an overvoltage nanosecond discharge between the electrodes of the superionic conductor Ag₃S at atmospheric air pressure, when lasers at wavelengths of 632.8 nm and 785 nm were used for the experiment, the same maxima were observed as in the study using radiation at 532 nm. They only differed in intensity.

When examining the sample using laser radiation at λ = 632.8 nm, the band at 969 cm⁻¹ was pronounced, and the bands in the range of 100-300 cm⁻¹ were less pronounced, which are 2.5 times smaller than the band at 969 cm⁻¹.

6. CONCLUSIONS

The study of the destruction products of the electrodes of an overvoltage nanosecond discharge between the electrodes of a superionic conductor (Ag₃S) in atmospheric air revealed the following characteristics of this discharge in atmospheric air:

– the cause of the ignition of a spatially homogeneous discharge is the formation of X-ray radiation and run-away electrons in the discharge. They also play the role of an auristic preionization system in the discharge;

– the study of the spectra of Raman scattering of light by thin films showed that they are identified with the corresponding spectra of macroscopic polycrystalline samples.

The study of plasma transport parameters in a mixture of silver sulfide vapor and air established that in the range of reduced electric field strength 305 Td-615 Td, the mean energies of electrons varied in the range of 6.603-11.39 eV, the values of their largest energies corresponded to the values of 53.38 eV-182.8 eV for the first mixture, and for the second mixture 53.16 eV-156.2 eV. The value of electron concentration was 2.0·10⁻⁹ m⁻³-8.6·10¹⁰ m⁻³.

The excitation rate constants of the spectral lines of silver atoms in the mixture Ag₂S – Air = 200 Pa – 101000 Pa = 328.068 nm, 338.289 nm, 405.54 nm are within the range of values (0.5427-0.2132)·10⁻¹³ m⁶c⁻¹, (0.5730-0.1789)·10⁻¹⁶ m⁶c⁻¹, respectively, and they had higher values than for the mixture with a high partial pressure of silver sulfide (1000 Pa). The excitation rate constant of the silver ion spectral line λ = 424.06 nm is within the range of (0.2535·10⁻¹⁶-0.2568·10⁻¹⁷) m⁶/s. The maximum value of the excitation rate constant of the spectral line of silver atoms λ = 328.068 nm was (0.5427·10⁻¹⁰) m⁶c⁻¹ for a reduced electric field strength of 615 Td in a mixture of silver sulfide vapors with air with a partial pressure ratio of 200-101000 Pa.

The study of the Raman light scattering spectra of thin films, which were obtained by depositing the products of the erosion of the electrode material and the products of the destruction of air molecules in a powerful nanosecond discharge on a solid substrate installed near the electrode system, showed that they mainly consist of silver sulfide, silver sulfite (Ag₂SO₃) and silver sulfate (Ag₂SO₄).

REFERENCES

12. BOLSIG+ software.
Синтез тонких плівок на основі сульфіду срібла в повітрі при атмосферному тиску в газовому розряді

О.К. Шуаїбов, О.Й. Мінія, О.М. Малінін, Р.В. Грицак, А.О. Малініна, А.І. Погодін, З.Т. Гомокі
ДВНЗ «Ужгородський національний університет», Народна пл.3, 88000 Ужгород, Україна

Приведено характеристики перенапруженого високовольтного наносекундного розряду в повітрі атмосферного тиску між полікристалічними електродами виготовленими з суперіонного провідника – сульфіду срібла (Ag₂S). В процесі мікронікших неоднорідностей на робочих поверхнях електродів в сильному електричному полі в міжелектродний простір, за рахунок утворення ектонів, вноситься пари сполуки Ag₂S і продуктів її дисоціації в плазмі. Це створює передумови для синтезу тонких плівок з даного матеріалу, які мають властивості суперіонних провідників та фотовольтаїчних сполук і можуть осаджуватися на діелектричній підкладці, встановлений розрядного проміжку. Були досліджені просторові та електричні властивості наносекундних розрядів перенапруги та спектри комбінаційного розсіювання синтезованих тонких плівок та їх поверхні. Параметри плазми розряду моделювалися у су- міші парів суперіонного провідника Ag₂S та повітря. Чисельні розрахунки проводилися за допомогою програми, що роз’язує рівняння Больцмана для функції розподілу енергії електронів. Транспортні характеристики електронів розряду і константи швидкості електронних процесів були розраховані залежно від значень параметра $E/N$ в експериментальному діапазоні 1-1000 Тд досліджень властивостей розряду. Приведені спектри Раманівського розсіювання світла тонких плівок, що були синтезовані з продуктів ерозії електродів в плазмі повітря.

Ключові слова: Перенапруження наносекундний розряд, Суперіонний провідник, Тонкі плівки, Спектр випромінювання, Плазма.