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SYNTHESIS OF NANOSILVER IN PLASMA-LIQUID MICRODISCHARGE SYSTEM

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Abstract. This paper presents the results of investigation of the plasma-liquid system with the secondary discharge supported by atmospheric pressure microdischarge in the vortex Ar flow. The plasma treated fluids were aqueous solutions of $AgNO_3$. The microplasma discharge was powered by a DC supply. The plasma channel behaviour was characterized by photo/video recording, also plasma was studied using emission spectroscopy technique. The working liquid and firm products created after the treatment were studied also.

Keywords: microdischarge, secondary discharge, Ag nanoparticles, plasma-liquid system.

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1. Introduction

For a long time, an active study of the interaction between plasmas and liquids (solutions, in particular) were performed. Classic systems have two electrodes, one of which is immersed in a liquid [1]. There is another approach in which liquid plays a function of an electrode in a secondary discharge. Thus, the principal generator of discharge can serve different types of discharges. Today atmospheric pressure microdischarges are one of the promising discharge types [2]. Microplasma is characterized by high current density and relatively low gas temperature that makes it handy for the electrochemical applications of aqueous solutions.

Creation of plasma involving liquids becomes increasingly important in industrial applications [3]. The issues of water purification using plasma, the usage of plasma treated liquids in agriculture, the synthesis of nanosized particles, the reforming of hydrocarbons and others still remain open. Microplasma creates a unique environment for nanomaterial synthesis, which restricts their agglomeration and allows the formation of crystalline materials by selective heating. The key advantage of synthesis processes based on micro-plasma is the fact that all chemical processes happen at atmospheric or higher pressures and so the collision frequency will significantly increase, which may be favorable for the formation of particles [4]. It should be held in mind that the nanoparticles in the solution can become charged and make self-organized structures through interaction as a result of the Coulomb and Van-der-Waals forces.

The paper presents the results of studies of the plasma-liquid system with the secondary discharge supported by the microdischarge in the vortex Ar flow. The fluids were aqueous solutions of $AgNO_3$.

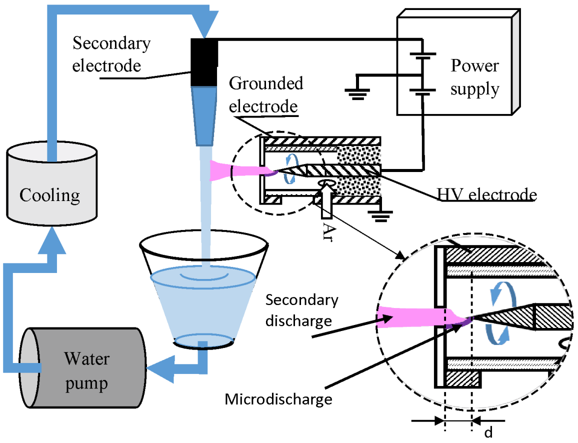

Figure 1. Schematic representation of studied plasma-liquid system with secondary discharge supported by microdischarge.

2. Experimental setup

A schematic representation of the studied plasma-liquid system with secondary discharge supported by atmospheric pressure DC microdischarge is shown in Fig. 1.

The source of microdischarge is axisymmetric plasma generator of microplasma jet. The peculiarities of the system and its detailed description one can find in [5]. Discharge power supply provides the output voltage of 7 kV (cathode). External grounded copper electrode had water cooling (anode). The electrodes of microdischarge were made from copper. The distance between the cathode and orifice of the anode ("d" in fig. 1) was 1 mm. Generated plasma was carried out by vortex flow of working gas (Ar) from discharge gap through a hole in the anode (d = 1 mm) in open air space. The gas flow was $G = 1\,\mathrm{L\,min^{-1}}$.

The secondary discharge was implemented by supplying the electric potential to a hollow graphite cylinder which has working fluid flowing through it. The cylinder is marked as a secondary electrode in Fig. 1. The discharge that burns between the working fluid and the microdischarge is the secondary discharge.

The study of the system parameters was carried out at 10 mA current of microdischarge and 5 mA secondary discharge current. The working liquid was $AgNO_3$ with NH_4OH (hydrate of ammonia) in excess. The concentration of Ag^+ ions in the solution was $50\,\mathrm{mM\,l^{-1}}$. 100 ml of this working liquid was treated for 15 min. The working liquid was diluted by distillate (1:2) for the absorption spectrum investigation.

Plasma system parameters were studied using optical emission spectroscopy method. Also, parameters of liquids and products, which were formed in the solution after plasma treatment were investigated by absorption spectroscopy and non-contact atomic force microscopy in air.

3. Results and discussion

It is known that the atmospheric pressure microdischarge is similar to glow discharge at low pressure. As was noted in [6], in the case where Ar was used as working gas for microdischarge at atmospheric pressure microplasma jet length was less than 3 mm. However, plasma region can be increased by secondary discharge generation supported by microdischarge. Photo and video recordings confirmed that the secondary discharge in argon looks like a set of individual channels fast moving in space [5]. With the decrease of camera exposure time, it was determined that the system has one channel, which quickly changes its position. Furthermore, the colour of the discharge jet varies along its length from white and blue at the source electrode area to purple at the surface of the liquid.

The emission spectra inside and outside the microdischarge system and absorption spectra of processed solutions were recorded using CCD-based spectrometer Solar TII (S-150-2-3648 USB) (operating in the wavelength range of 200–1080 nm). Emission spectra of microplasma inside microdischarge system contain atomic Ar lines and molecular OH bands, spectra outside the system also contain NO, N_2. Spectra are shown in Fig. 2.

Experiments show that microdischarge plasma is highly non-isothermal both inside ($T_v{}^*(OH)=1000\pm500\,K$ and $T_r{}^*(OH)=500\pm250\,K$) and outside ($T_v{}^*(N_2)=3000\pm500\,K$ and $T_r{}^*(N_2)=1500\pm250\,K$) MD system. The fact that plasma component composition dependends on gas atmosphere and does not contain electrode material, in addition to the non-isothermality of plasma shows that secondary discharge is of glow type.

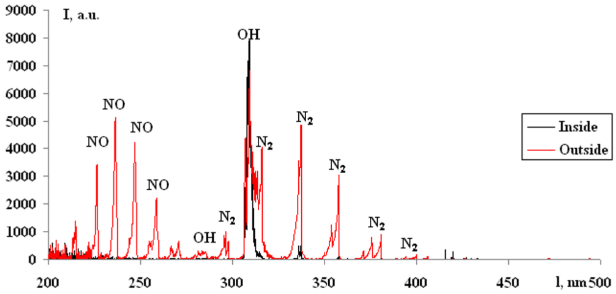

Figure 2. The emission spectra of plasma-liquid interface system with secondary discharge based on MD plasma.

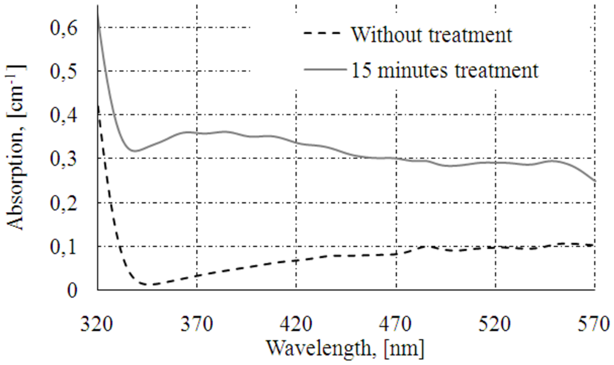

Figure 3. The absorption spectrum of the processed solution ($AgNO_3$+ NH_4OH) after 15 min processing.

The study of the absorption spectra is the simplest way to determine the presence of nanoparticles in the colloid solutions. This type of solutions features the absorption maximum, which corresponds to the plasmon resonance. The location and shape of the maximum depend on the material of the particles, their size and shape. According to [3, 7], the colloid solutions of Ag nanoparticles have maxima at 380 nm and 420 nm.

In this work, the solution of $AgNO_3$ and NH_4 was treated for 15 min. After the plasma treatment of the solution with the secondary discharge, the colour of the investigated liquid significantly changed and became darker. The absorption spectra of processed solutions (Fig. 3). The solid line corresponds to the absorption spectrum of the solution after the treatment. The dashed line shows the absorption spectrum of the untreated solution. The rise of the spectrum that begins at 340 nm corresponds to NO_3^- ion and H_2O_2. The spectum of treated solution shows the presence of weak maximum at 380 nm, which can be caused by the presence of Ag nanoparticles in the solution. In addition, the continuous absorption spectrum is present in the whole studied range of wavelength. This absorption can be caused by the strong scattering of the radiation in the solution due to the presence of the massive particles. These particles can appear as a result of coagulation.

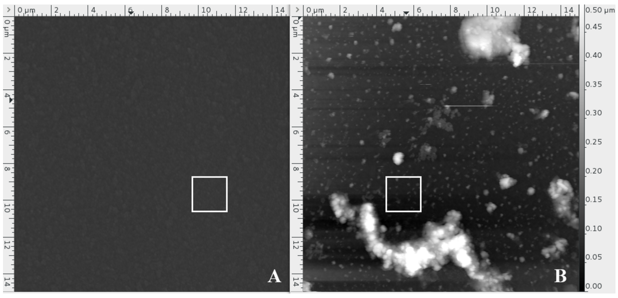

Figure 4. Microimages of clean substrate (A) and nanoparticles stranded substrate (B) field of view size 15× 15 µm.

The darkening of the solution can be observed after a single plasma treatment. This can be explained by the formation of sub-macroscopic sized metal even after a single treatment of working liquid. For more data, we analyzed substance which was formed in the liquid after the plasma treatment. The atomic force microscopy was conducted on the drop of treated liquid that was placed on a silicon wafer covered with a layer of cobalt silicide. Before the study, the liquid samples were dried out. To analyze the samples, we used a Smena NT-MDT microscope. Images of the surface obtained by this method are shown in Fig. 4.

Fig. 4 A shows the image of a clean wafer. Fig. 4 B shows the area covered with the solution. The figure shows that in the second case the size of the particles present on the wafer is 100 nm and more. This massive structures potentially appeared as a result of coagulation of a large number of particles. White squares in Fig. 4 are the areas that have been studied with more spatial resolution. The results are shown in Fig. 5. Along the lines in Fig. 5, cross-sections have been built. These sections are shown in Fig. 6.

The dashed chart in Fig. 6 corresponds to the surface profile of the clean wafer. The solid curve shows the profile of the surface with the presence of nanoparticles. The surface roughness is approximately 10 nm. The characteristic height of the nanoparticles is on the order of 100 nm and their lateral size is approximately 200 nm. However, the lateral size can be overestimated due to the specifics of atomic force microscopy.

Judging from the images the particles of a microscopic size and nano-sized particles with a characteristic size from tens to hundreds of nanometers are present on the substrate.

4. Conclusion

Experiments have shown that treatment of ammoniac silver nitrate solution with non-isothermal plasma of plasma-liquid system with secondary discharge supported by atmospheric pressure direct current microdischarge leads to silver nanoparticles formation. The size of the nanoparticles ranges from 10 to 100 nm. Besides the nanoparticles, the microparticles are observed on the substrate. Presumably, they are the result of the coagulation of individual nanoparticles.

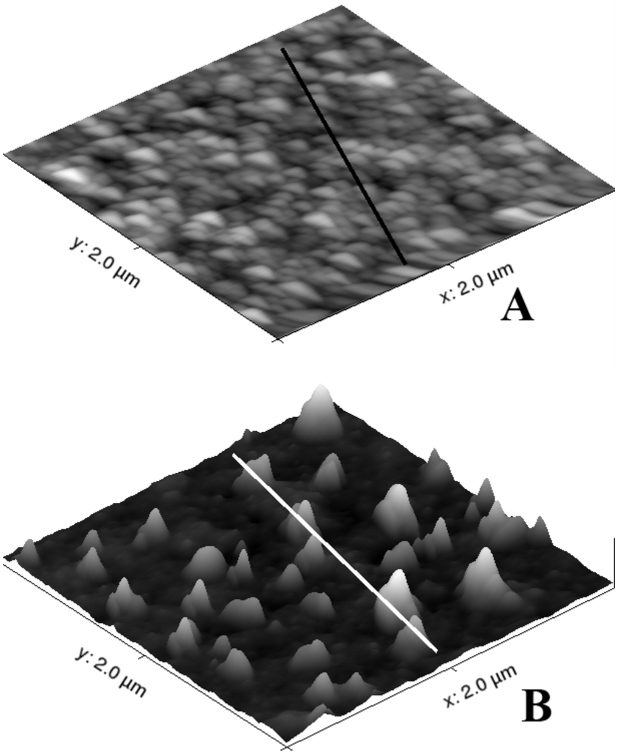

Figure 5. Microimages of clean substrate (A) and nanoparticles stranded substrate (B) field of view size 2× 2 µm.

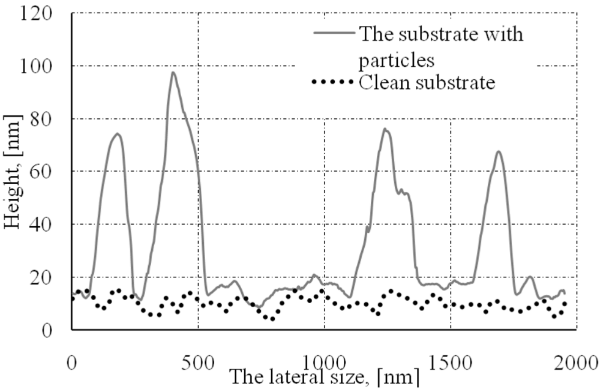

Figure 6. Cross-sections along the lines in Fig. 5. Black dots – clean substrate, Gray lines – nanoparticles stranded substrate.

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