

STABILITY OF PLASMA POLYMER - METAL NANOCOMPOSITES

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Abstract

The stability of plasma polymer matrix with functional metal fraction was investigated by UV/VIS and SEM techniques in this study. Compared are properties of Ag/plasma polymer nanocomposites where magnetron sputtered PTFE and nylon 6,6 serve as plasma polymer matrix. Silver was immersed into the matrix by two different ways: (i) in the form of nanoislands, formed by diffusive coagulation of deposited Ag atoms onto the plasma polymer, and (ii) by directly deposited Ag particles of size about of 11 nm grown in a gas aggregation cluster source. The Ag nanoislands or Ag nanoparticles were sandwiched in between plasma polymer layers with the top layer thickness that varied in the range 5-20 nm. Stability of prepared nanocomposites on air, in water and at elevated temperatures is investigated and compared in dependence on the matrix material as well as in dependence on the form of Ag nanoinclusions.

Keywords: Nanoparticles, plasma polymers, silver, nanocomposites, stability

1. INTRODUCTION

Silver nanoparticles (NPs) are due to their optical, electrical or bioactive characteristics used in impressive range of applications that span from highly sensitive biodetection (e.g. [1-4]), energy harvesting [5,6], antimicrobial protection [7-9], or are used as components of high-voltage, direct current electric power transmission systems [10] to mention some examples. Because of this, numerous methods were developed that enabled production of silver nanoparticles. From this point of view increasing attention receive approaches based on vacuum-based technologies such as magnetron sputtering or the use of so called gas aggregation sources (GAS). This is due to the fact that such techniques of nanoparticles production offer certain advantages as compared to the methods that utilize chemical synthesis, namely relative simplicity, possibility to coat virtually any substrate compatible with low-pressure conditions, low environmental burden, no need of laborious cleaning procedures and last, but not least, possibility to combine these deposition methods with other low-pressure deposition techniques [11]. The later enabled controlled production of silver containing nanocomposites with different architectures including not only classical nanocomposites in which NPs are homogeneously distributed in the matrix material [12,13], but also (multi)layered coatings [14,15] or films with vertical or horizontal gradients of density of embedded Ag NPs [16,17], that further widened the application potential of silver based nanocomposites.

As it was demonstrated in our recent work, magnetron sputtering and GAS deposition differ significantly in the mechanisms of formation of Ag nanoparticles [18]: whereas in the case of magnetron sputtering Ag NPs are created as the result of diffusive coagulation of deposited Ag atoms onto the substrate, silver nanoparticles are in the case of GAS created in the volume of aggregation chamber of GAS system and thus reach substrate in the form of beam of already formed NPs. The way in which nanoparticles are formed consequently influences their morphology and with it connected physico-chemical properties. In the case of magnetron sputtering the Ag NPs grow in the initial stages mostly laterally and thus form relatively smooth quasi 2D structures on substrates (such structures will be denoted in the subsequent text as nanoislands). In contrast, deposition of NPs created inside GAS results in much rougher nanoparticle films that are composed from individual and almost monodisperse NPs independently of the deposition time. However, the morphology is not the only parameter that influences applicability of produced silver nanoislands and nanoparticles. Similarly or in some

cases even more important is the stability of their properties: silver nanoparticles and their nanocomposites have often to be exposed to aqueous environment (e.g. in the case of biodetection or when used as antibacterial coatings) or higher temperature (e.g. during sterilization or under exposure to intense light) that can strongly modify their properties and thus also their functionality. Nevertheless, the systematic studies focused on stability of Ag based nanocomposites are still relatively sparse. In order to fill this experimental gap the properties and stability of bare Ag nanoislands and nanoparticles films or Ag nanoislands and nanoparticles films sandwiched between two types of plasma polymers that differ significantly in the chemical structure (magnetron sputtered poly(tetrafluoroethylene) and Nylon 6,6) is investigated in detail in this study.

2. EXPERIMENTAL

Two kinds of plasma polymers were used in this study: magnetron sputtered Nylon 6,6 (msNylon) and magnetron sputtered poly(tetrafluoroethylene) (msPTFE). These two plasma polymers were deposited in plasma reactors equipped by RF planar, water cooled magnetrons with either PTFE or Nylon 6,6 targets (81 mm in diameter, 3 mm thick, both sourced from Goodfellow). RF magnetron was powered by Cesar RF power supply (Advanced Energy) through a manually operated match box MFJ-962D (MFJ Enterprises). Applied RF power was 40 W in the case of msPTFE deposition or 50 W in the case of nylon sputtering. The sputtering was performed in argon atmospheres at pressure of 1.5 Pa and the thickness of deposited films of plasma polymers was determined by means of spectral ellipsometry (Woollam M-2000DI).

Silver nanoparticles and nanoislands were produced following the same techniques as described in detail in [18]. Here we only briefly summarize that DC nanoislands were produced by DC magnetron sputtering of Ag target in argon atmosphere. The pressure in the deposition chamber was 3.8 Pa, DC magnetron current was 40 mA and the distance between sputtering target and substrates was 20 cm. In the case of Ag NPs deposition by gas aggregation source the pressure in the aggregation chamber was 30 Pa, magnetron current was 100 mA and the distance between output orifice of aggregation chamber and substrate was 40 cm. In order to evaluate the role of the overcoat material on stability of produced Ag nanoislands and nanoparticles sequential deposition of base layer of plasma polymer (20 nm thick) - deposition of Ag nanoislands and nanoparticles - deposition of overcoat layer (thickness 5-20 nm) was performed. Morphology of coatings deposited on one-side polished Si wafers (ON semiconductors) before and after their immersion into water was evaluated by scanning electron microscopy (SEM) using Tescan Mira II microscope with acceleration voltage 15 kV and using secondary electron detector. Optical transmittance of coatings, that were deposited on soda lime glass slides (Marienfeld), was determined by means of UV-Vis spectrophotometer (U-2900, Hitachi) in the spectral range 325-1100 nm (scan speed 400 nm/min).

3. RESULTS

The first step of this study was the evaluation of stability of Ag nanoislands and Ag nanoparticles on air (examples of SEM images are presented in **Figures 1a** and **1b**). Due to the fact that both kinds of studied silver nanostructured films exhibit localized surface plasmon resonance (LSPR) peak whose intensity and position is very sensitive to properties of Ag nanoparticles, the ageing process was monitored by UV/Vis spectrophotometry. As can be seen in **Figures 1c** and **1d** the UV/Vis spectra recorded immediately after the deposition and then after 1, 3 and 7 days did not indicate any significant variation of properties of produced coatings even without any top overlay. Similar results were obtained also for samples in which Ag nanoislands and nanoparticles were coated with either msNylon or msPTFE films. This suggests good temporal stability of both nanoislands and nanoparticle films. This is an important finding as it enables to neglect intrinsic ageing of Ag films and nanocomposites in the subsequent experiments focused on the evaluation of their stability in water and at elevated temperature.

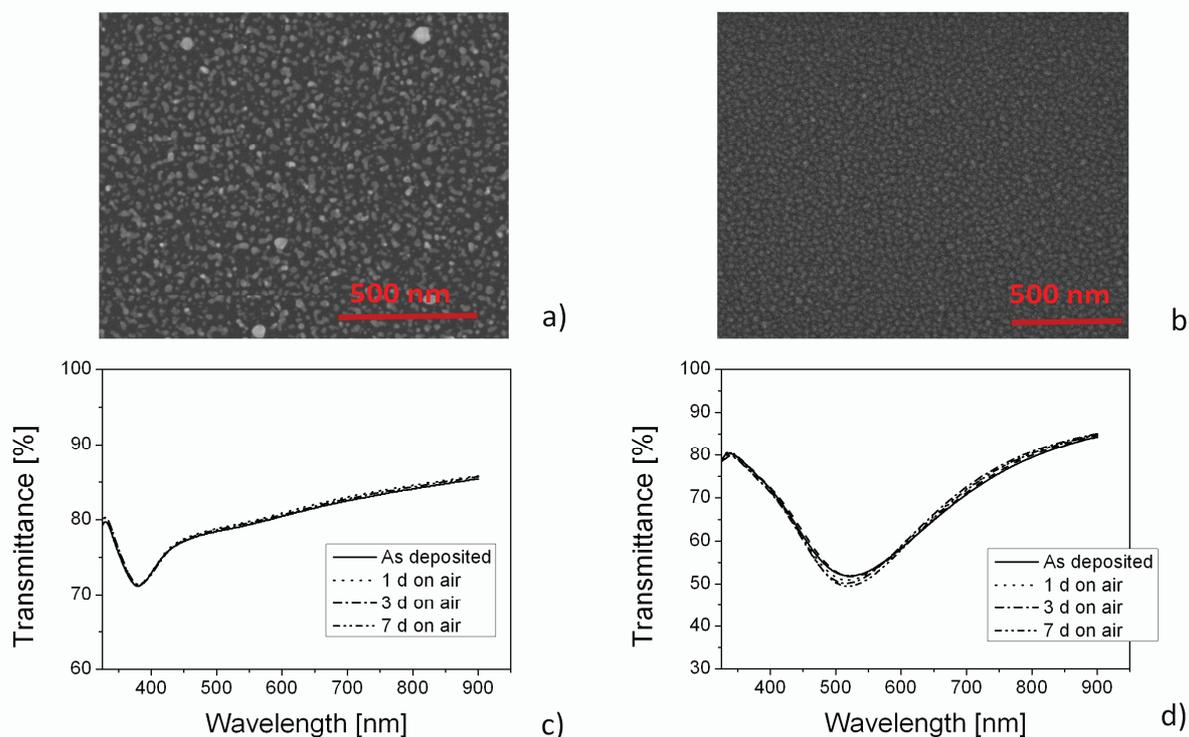


Figure 1 SEM images of a) Ag nanoparticle film and b) Ag nanoisland film deposited onto msPTFE. UV/Vis spectra of c) Ag nanoparticle and d) Ag nanoisland film deposited onto msPTFE, as function of storage time

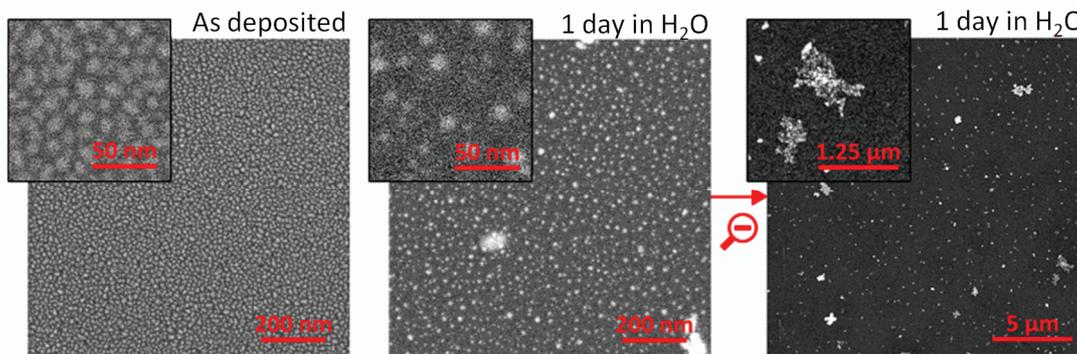


Figure 2 SEM images of Ag nanoislands deposited onto msNylon before and after 1 day immersion in water

The next step was study of stability of produced coatings in water in dependence on the overcoat material and its thickness. It was found that both Ag nanoislands and nanoparticle films deposited either on msPTFE and msNylon without any overcoat layer readily dissolve in water or are simply washed out. This is demonstrated in **Figure 2**, where examples of SEM images of Ag nanoislands deposited onto msPTFE acquired before immersion of the samples into water and after 1 day in water are compared: it can be seen that the surface density of Ag nanoislands is reduced (in this particular case from $(4.9 \pm 0.4) \cdot 10^3$ NPs/ μm^2 down to $(1.2 \pm 0.2) \cdot 10^3$ NPs/ μm^2). In addition, relatively big silver agglomerates were observed after soaking of the samples into water as it is evident from SEM image with bigger view filed. These agglomerates originate most likely from the sedimentation of dissolved silver during the drying of the samples. The changes in appearance of Ag films naturally resulted in pronounced alteration of their optical properties, namely in the decrease of the intensity of LSPR peak and its shift towards lower wavelengths (**Figure 3a**). This is consistent with increasing distance between individual Ag nanoislands or nanoparticles. This situation, e.g. dramatic change in appearance of Ag

nanoislands and nanoparticles after immersion into water, was also observed when they were overcoated with msNylon film independently of the thickness of the overcoat layer up to 20 nm, i.e. the highest thickness tested in this study (for example of evolution of UV/Vis spectra of Ag nanoislands films overcoated with 20 nm of msNylon see **Figure 3b**). This result is consistent with hydrophilic character of msNylon films (water contact angle 40° [18]) that contain polar functional groups and thus facilitates water permeation through them.

In contrast, when Ag nanoislands or nanoparticles were covered with hydrophobic msPTFE layer (water contact angle 110° [18]), the influence of water on them was largely reduced (see **Figures 3c** and **3d**). However, significant difference was observed between nanoisland and nanoparticle films. Whereas in the case of nanoislands 5 nm of msPTFE was sufficient to suppress the effect of water, at least at the time scale of 7 days, much thicker coating was necessary to stabilize Ag nanoparticles deposited by means of GAS. This difference is connected with different morphologies of nanoislands and nanoparticle films: whereas nanoislands deposited by magnetron sputtering form quasi 2D structures that are relatively smooth (root-mean-square roughness below 1 nm), Ag NPs deposition by GAS resulted in films with considerably higher root-mean-square roughness (around 32 nm). Due to the much higher vertical irregularities of such Ag NPs films as compared to Ag nanoislands more material is needed to fully cover all crevices and gaps in between them through which water can penetrate directly to Ag NPs and cause their dissolution or degradation.

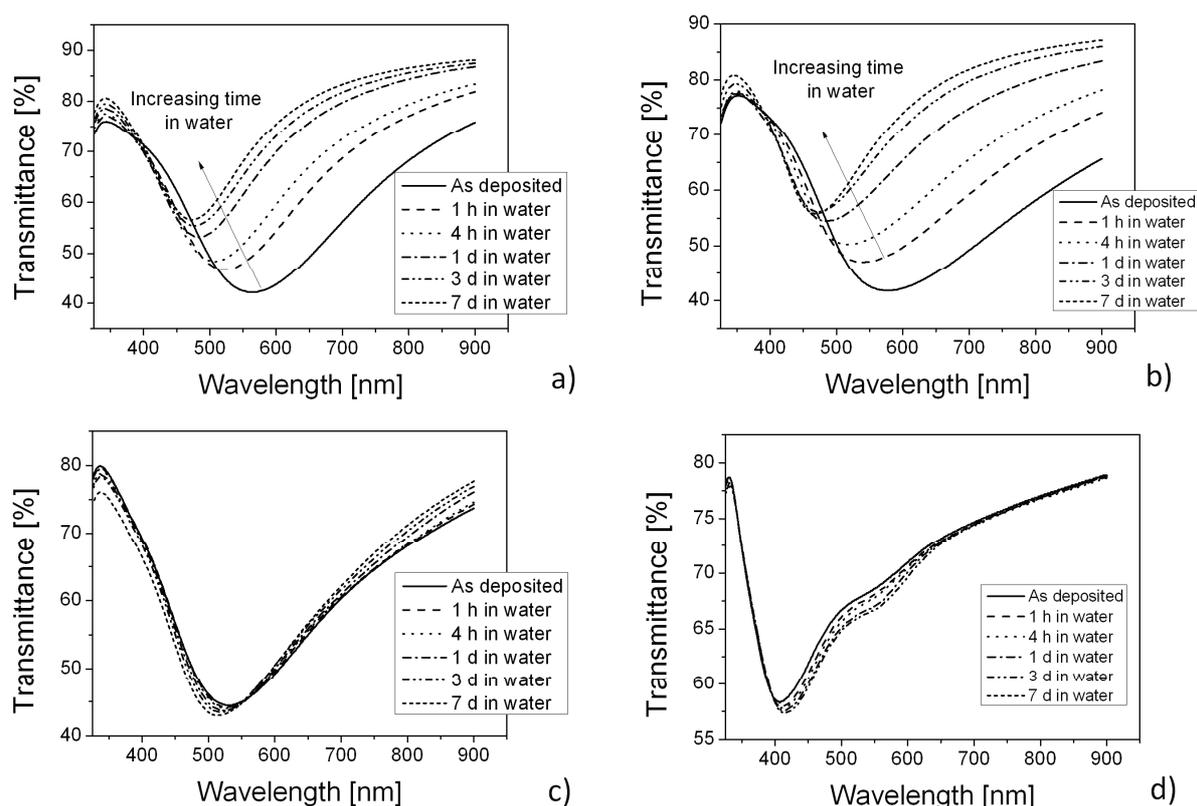


Figure 3 UV/Vis spectra of samples before and after immersion into water. a) Ag nanoislands deposited onto msPTFE, b) Ag nanoislands overcoated with 20 nm of msNylon, c) Ag nanoislands overcoated with 5 nm thick layer of msPTFE and d) Ag nanoparticles covered by 20 nm thick film of msPTFE

Finally, the effect of elevated temperature on produced samples was tested. It was found that bare Ag nanoisland and NPs films exposed for 30 min to temperatures higher than 75°C have tendency to coalesce (**Figure 4a**). This is accompanied by narrowing of the LSPR peak (**Figure 4b**) and its shift to lower wavelengths, which indicates increasing mean inter-particle distances. This effect was found to be significantly

reduced when Ag films were coated with either msNylon or msPTFE. However, whereas msPTFE stabilized Ag films up to 100°C (**Figure 4c**), msNylon was found to protect silver layers up to 150°C (**Figure 4d**).

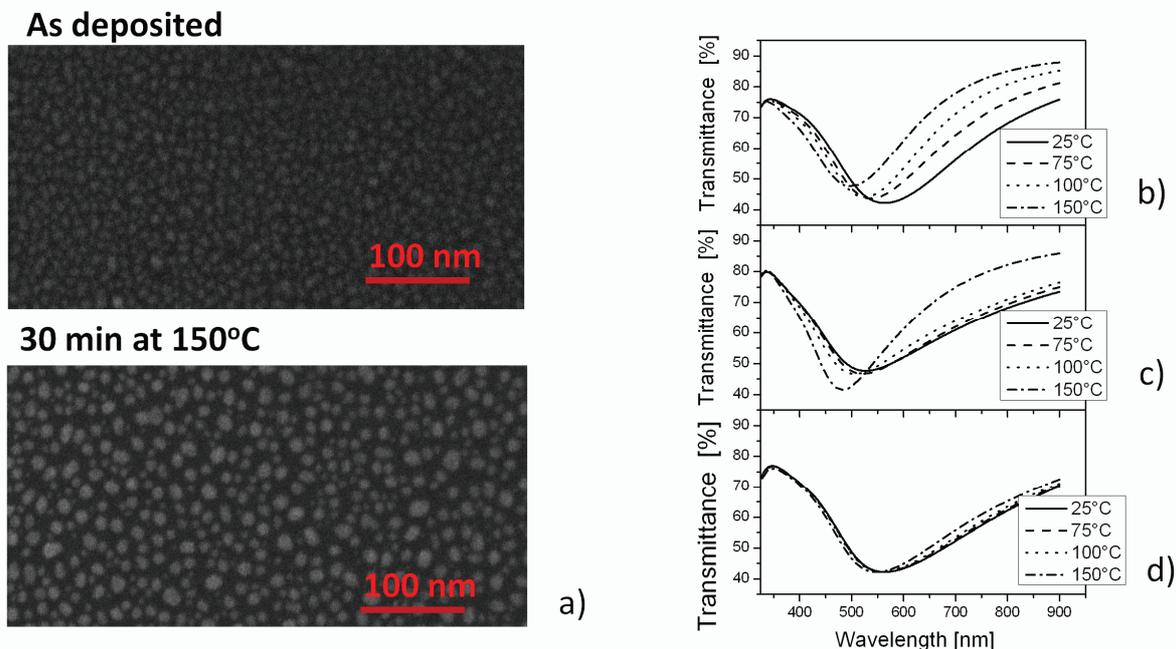


Figure 4 a) SEM images of Ag nanoisland films before and after heating. UV/Vis spectra of heated nanoisland films b) without any cover layer, c) coated with 5 nm thick film of msPTFE and d) coated with 5 nm thick film of msNylon

4. CONCLUSION

Stability of Ag nanoisland and nanoparticle films on air, in water and at elevated temperatures was studied in dependence on the presence and thickness of overcoat layer. It was found that whereas studied Ag films are stable on air, their morphology and optical properties are substantially altered when exposed to water or higher temperatures. These effects may be reduced by use of plasma polymer overcoat. However, chemical structure of plasma polymer plays an important role. It was demonstrated that hydrophobic msPTFE films significantly suppress effect of water. In contrast msNylon was found not be capable to prevent water from reaching Ag layer, but it offers better stabilization of Ag films exposed to heat. Finally, it was found that in general thicker films are needed to limit influence of water on films of Ag NPs as compared to Ag nanoisland layer. These results are of high importance especially from the point of view of assurance of functionality of Ag films and their nanocomposites, e.g. as antibacterial coatings or substrates for biodetection.

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REFERENCES

- [1] KNEIPP, K., KNEIPP, H., ITZKAN, I., DASARI, R.R., FELD, M.S. Ultrasensitive Chemical Analysis by Raman Spectroscopy, *Chemical Reviews*, 1999, vol. 99, no. 10, pp. 2957-2976.
- [2] WILLETS, K.A., VAN DUYNE, R.P. Localized Surface Plasmon Resonance Spectroscopy and Sensing, *Annual Review of Physical Chemistry*, 2007, vol. 58, pp. 267-297.

- [3] SHARMA, B., FRONTIERA, R.R., HENRY, A.I., RINGE, E. VAN DUYN R.P. SERS: Materials, applications, and the future, *Materials Today*, 2012, vol. 15, no. 1-2, pp. 16-25.
- [4] GILL, R., LE RUB, E.C. Fluorescence enhancement at hot-spots: the case of Ag nanoparticle aggregates, *Physical Chemistry Chemical Physics*, 2011, vol. 13, pp. 16366-16372.
- [5] KIM, S.S., NA, S.I., JO, J., KIM, D.Y., NAH, Y.C. Plasmon enhanced performance of organic solar cells using electrodeposited Ag nanoparticles, *Applied Physics Letters*, 2008, vol. 93, article no. 073307.
- [6] NAKAYAMAA, K., TANABE, K., ATWATER, H.A. Plasmonic nanoparticle enhanced light absorption in GaAs solar cells, *Applied Physics Letters*, 2008, vol. 93, no. 12, article no. 121904.
- [7] MORONES, J.R., ELECHIGUERRA, J.L., CAMACHO, A., HOLT, K., KOURI, J.B., RAMÍREZ, J.T., YACAMAN, M.J. The bactericidal effect of silver nanoparticles, *Nanotechnology*, 2005, vol. 16, no. 10, pp. 2346-2353.
- [8] PANÁČEK, A., Kvítek, L., PRUCEK, R., KOLÁŘ, M., VEČEŘOVÁ, R., PIZÚROVÁ, N., SHARMA, V.K., NEVĚČNÁ, T., ZBOŘIL, R. Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity, *Journal of Physical Chemistry B*, 2006, vol. 110, no. 33, pp. 16248-16253.
- [9] MARAMBIO-JONES, C., HOEK E.M.V. A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment, *Journal of Nanoparticle Research*, 2010, vol. 12, no. 5, pp. 1531-1551.
- [10] MAKASHEVA, M., VILLENEUVE-FAURE, C., BONAFOS, C., LAURENT, C., PUGLIARE, A., DESPAX, B., BOUDOU, L., TEYSSEDE, G., Dielectric engineering of nanostructured layers to control the transport of injected charges in thin dielectrics. *IEEE Transactions on Nanotechnology*, 2016, vol. 15, no. 6, pp. 839-848.
- [11] BIEDERMAN, H. Nanocomposites and nanostructures based on plasma polymers, *Surface and Coatings Technology*, 2011, vol. 205, supplement 2, pp. S10-S14.
- [12] DESPAX, B., PATRICE, R. Deposition of "Polysiloxane" Thin Films Containing Silver Particles by an RFAsymmetrical Discharge, *Plasma Processes and Polymers*, 2007, vol. 4, no. 2, pp. 127-134.
- [13] VAIDULYCH M, HANUŠ J, STEINHARTOVÁ T, KYLIÁN, O., CHOUKOUROV, A., BERANOVÁ, J., KHALAKHAN, I., BIEDERMAN, H. Deposition of Ag/a-C:H nanocomposite films with Ag surface enrichment, *Plasma Processes and Polymers*, 2017, article no. e1600256.
- [14] SCHÜRMAN, U., TAKELE, H., ZAPOROJTCHENKO, V., FAUPEL, F. Optical and electrical properties of polymer metal nanocomposites prepared by magnetron co-sputtering, *Thin Solid Films*, 2006, vol. 515, no. 2, pp. 801-804.
- [15] KUZMINOVA, A. BERANOVÁ, J., POLONSKYI, O., SHELEMIN, A., KYLIÁNA, O., CHOUKOUROV, A., SLAVÍNSKÁ, D., BIEDERMAN, H., Antibacterial nanocomposite coatings produced by means of gas aggregation source of silver nanoparticles, *Surface and Coatings Technology*, 2016, Vol. 294, pp. 225-230.
- [16] KÖRNER, E., AGUIRRE, M.H., FORTUNATO, G., RITTER, A., RÜHE, J., HEGEMANN, D. Formation and Distribution of Silver Nanoparticles in a Functional Plasma Polymer Matrix and Related Ag⁺ Release Properties, *Plasma Processes and Polymers*, 2010, vol. 7, no. 7, pp. 619-625.
- [17] PETR, M., KYLIÁN, O., HANUŠ, J., KUZMINOVA, A., VAIDULYCH, M., KHALAKHAN, I., CHOUKOUROV, A., SLAVÍNSKÁ, D., BIEDERMAN, H. Surfaces With Roughness Gradient and Invariant Surface Chemistry Produced by Means of Gas Aggregation Source and Magnetron Sputtering, *Plasma Processes and Polymers*, 2016, vol. 13, no. 6, pp. 663-671.
- [18] KRATOCHVÍL, J., KUZMINOVA, A., KYLIÁN, O., BIEDERMAN, H. Comparison of magnetron sputtering and gas aggregation nanoparticle source used for fabrication of silver nanoparticle films, *Surface and Coatings Technology*, 2015, vol. 275, pp. 296-302.