

#### ION ASSISTSANCE INFLUENCE ON THE STRUCTURE OF a-C:Ag FILMS DEPOSITED BY PULSE-PLASMA DEPOSITION TECHNIQUE

I. A. Zavidovskiy, O.A. Streletskiy, O.Yu. Nishchak, A.V. Pavlikov, N.F. Savchenko Lomonosov Moscow State University, Faculty of Physics

Ion-Surface Interactions 2021, Yaroslavl', Russia

## Pulse-plasma deposition set-up

# **TEM and EELS studies**





#### **Deposition parameters**

Pressure: 10<sup>-3</sup> Torr; Atmosphere: Argon; Discharge power 500 W; Deposition time: 10 min; Pulse frequency 1 Hz; Two sets of the samples were deposited: for the first set, ion assistance current and energy were varied. Their simultaneous increase led to the emergence of small (~3-5 nm) silver nanoclusters. This effect is related to the formation of irradiation-induced defects playing a role of favorable centers of Ag nucleation. Size of large clusters increases with energy/current rise due to the nanoparticles surface mobility enhancement by ion assistance leading to nanoparticles aggregation. EELS shows minimum of  $sp^2$ -hybridized atoms fraction for 100 ev/10 mA-assisted sample and its further increase with ion current/energy. This data is in accordance with the subplantation theory, which predicts the existence of optimum ion energy ensuring structure densification and defects reduction. Apparently ion energy increase to 200+ eV leads to the disordering and sparcification of amorphous carbon structure.



Pulse length: 1 ms; Ion assistance: 100-600 eV, 10-30 mA (20-80 µA/cm<sup>2</sup>) Relative surface of sputtered silver ~10%.

#### **UV-Vis absorbtion spectra**



Contribution of several components can be distinguished: at 320-330 nm,  $\pi$ - $\pi^*$ transition related to sp<sup>2</sup>-hybridized carbon atoms is observed. Its narrow component represented by peak at 300-360 nm is probably related to polymeric substructure. Peaks related to amorphous graphite are usually wider, therefore we suggest that  $\pi$ - $\pi^*$  transition related to amorphous phase peaking at the same wavelength also contributes to  $0^{-650}$  overall slope of the spectra. Sp<sup>2</sup> content increase at 100-400 eV energy shift correlates with the UV-Vis spectra slope shift.

Absporbtion in 400-600 nm range is typical for surface plasmon resonance (SPR) of silver nanoclusters. Emergence and rise of the wide peak at 370-560 nm is assigned to the faceting of the silver nanoclusters. Faceting is known to increase plasmonic peak intensity due to local field enhancement on small curvature radii. Significant width of the peak centered at 440 nm can be ascribed to broad nanoclusters size distribution.

Second set of the samples was deposited at fixed assistance current of 10 mA  $(20 \ \mu\text{A/cm}^2)$  and various assistance energy. Similarly to the previous case, nanoparticles of 2 sizes were observed. Energy enlargement, however, led to the nanoclusters faceting rather than to the clusters size variation. Probably in this case ion assistance effect is comparable to the one of the annealing: recrystallization of damaged clusters takes place, leading to their orientation. As observed via EELS, sp<sup>2</sup>-hybridized atoms fraction increase takes place at 100-400 eV range, while slight change in atoms hybridization ratio is observed at 400-600 eV range.

## Raman spectroscopy



Raman spectra were measured at 488 nm excitation wavelength. They show prominent D- and G-lines related to amorphous carbon phase. The increase of D/G relative intensity, as well as G-line position shift to lower wavenumbers for 400 eV-assisted sample confirms EELS data indicating the sp<sup>2</sup>-hybridized atoms content rise. D-line broadening observed for 600 eV-assisted sample indicates the disordering of carbon matrix with assistance energy increase. Emergence of the lines in the vicinity of 1200 and 1400 cm<sup>-1</sup> typically indicates the formation of

trans-polyacetylene induced by ion-assisted decomposition of the residual hydrogen.

However, lines positions are shifted from 1150 cm<sup>-1</sup> (C-C) and 1550 cm<sup>-1</sup> (C=C) positions typical for pure trans-polyacetylene. We suggest that cis-polyacetylene fragments, C-N and C-H<sub>x</sub> bonds may also contribute to the spectra and induce the line positions shift.

# Conclusions

Amorphous carbon coatings with silver inclusions were deposited by ion-assisted pulse-plasma deposition. Simultaneous increase of ion current and energy led to the formation of the defects. They acted as favorable nucleation centers, which formation increased the number of 3-5 nm-sized Ag particles. Presence of larger (20-40 nm) particles was attributed to particles coalescence induced by ion irradiation-enhanced surface diffusion of silver.

When ion assistance energy was increased at constant discharge current, silver nanoclusters faceting was observed. Ion energy increase from 100 eV to 400 eV led to sp<sup>2</sup>-hybridized atoms content rise, while further energy increase to 600 eV didn't lead to graphite content change, alghough disordering of carbon matrix took place. UV-Vis absorbtion spectra variation with ion assistance energy was observed. Emergence of the SPR-related peak at 400-600 eV assisting energies was assigned to silver nanoclusters faceting. Spectra slope shift at 100-400 eV was caused by sp<sup>2</sup>-hybridized atoms content rise.

The reported study was supported by RFBR, project № 20-32-90077. I.A. Zavidovskiy acknowledges the support of Theoretical Physics and Mathematics Advancement Foundation "BASIS".