UDC 681.327

K. P. Grytsenko[1,2], D. O. Grynko[1], M. V. Sopinskyy[1], S. Schrader[2]
[1] V.E. Lashkaryov Institute of Semiconductor Physics
45 Nauky pr., 03650 Kyiv, Ukraine
[2] Institut fur Plasma/Laser/Optronic der TFH Wildau, Bahnhofstraβe,
15745, Wildau, Germany

In situ investigation of gold nanoclusters growth in polymer matrices

Polytetrafluoroethylene (PTFE) and polyparaphenylene sulphide (PPS) films were filled with gold (Au) nano-clusters by co-deposition in a vacuum. Multi-component film, filled simultaneously with Au and dye was deposited for the first time. Film formation was studied using optical absorption spectroscopy ***in situ****. Electron microscopy and ellipsometry were used for film characterisation. Au nano-cluster diameter is in 2–8 nm range in PTFE matrix. At the film growth beginning small clusters with plasmon band about 480 nm were grown, than aggregation of clusters began, which made plasmon band shift to 520–550 nm, which is dependent on Au concentration. Treatment with plasma led to formation of smaller, but aggregated Au clusters. Ellipsometry showed that the part of clusters are elongated and stands perpendicular to substrate. If PPS was used as a matrix, the growth kinetics revealed two stepped mechanism. At the film growth beginning Au clusters with plasmon band about 600 nm were formed, but with film thickness growth intensity of band at 420 nm grows faster. The resulting film has most strong band at 420 nm. But plasma treatment led to formation of Au aggregates confined with PPS matrix with plasmon band at 620 nm.*

Key words*: nanocluster, gold, PTFE, PPS, optical spectra, plasma, plasmon.*

Introduction

Metal nanoclusters are studied for applications in sensors [1, 2], photonics devices and plasmonic structures [3], waveguides [4], films for photovoltaics [5], optical recording of information [6–13], including high density near-field optical recording [14]. Several methods were used for deposition of metal-filled polymer film from a gas phase. Methods include: magnetron sputtering of gold target in C_2F_3Cl [15, 16] or mixture of CH_4 and Ar gaseous media [17], co-sputtering of Econol and Au targets [18], vacuum co-deposition of metal and polymers, in particular, Au and PTFE [8] or ion co-sputtering of these materials [19, 20]. Novel method to produce metal-containing polymer film is the plasma enhanced chemical vapor deposition (PECVD) using organometal precursors [9–14]. Te and Se compounds were used for composite film deposition by PECVD, including the mixture of their diethyls. Later Sn, Sb and Pd filled composite films were produced and the possibility of optical recording of information on these films was shown.

The aim of this work is to research the growth kinetics and structure of the film obtained by Au and polymer co-evaporation in a vacuum.

Experimental details

Films were deposited using VUP-5M installation equipped with computerised control system. Starting pressure in the chamber was 10^{-3} Pa. Control system assigns necessary heating regimes for Au, dye and polymer evaporators. Data from quartz thickness monitors with $6 \cdot 10^{-8}$ kg/m^2 sensitivity, chamber pressure, boat currents and temperatures are displaying at computer screen. Rotating glass disc with attached Si, NaCl and quartz slides were used as substrates. Spectrometer Polytec with optical fibres, introduced through quartz window, was recording absorption spectra of film, growing on rotating disc. Spectra were displayed at computer screen ***in situ***. Spectra were recorded using one beam scheme. Polymer films were deposited by two methods: 1 — thermal evaporation for PPS, 2 — PTFE evaporation with vapor activation by electron cloud. Polymer vapors can be additionally treated by 40,68 MHz 20–70 W plasma. Fig. 1 presents the scheme of the installation used for film deposition. Boat and electronic control channel for the third component are not shown.

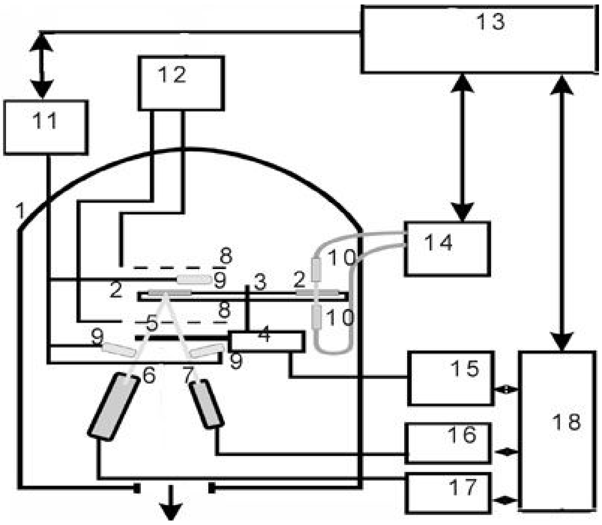


Fig. 1. Scheme of the deposition installation: 1 — vacuum chamber; 2 — substrates; 3 — system and 4 — motor for substrate rotation; 5 — shutter; 6 — evaporator-activator for polymer; 7 — evaporator for metal; 8 — RF electrodes; 9 — quartz crystals; 10 — fibres; 11, 15, 16, 17 — controllers of quartz monitors, motor, polymer and metal evaporators; 12 — RF generator; 13 — computer; 14 — optical absorption spectrometer Polytec; 18 — digital-to-analogue and analogue-to-digital converters

Absorption spectra of the deposited films were recorded by Perkin-Elmer Lambda 16 spectrometer. Optical properties of films were studied by multiple angle ellipsometry at 632 nm wavelength. Film thickness was controlled by ellipsometry and by atomic force microscopy (AFM) on step. Both isotropic and anisotropic models were used for ellipsometry calculations. Film structure was studied by transmission electron microscope (TEM) JEM-100EX.

Results and discussion

Fig. 2 shows evolution of absorption spectra of Au-PTFE films, grown both with and without plasma treatment. In Table 1 are summarised experimental data for Au-filled PTFE films. Ellipsometry data presented in the Table 1 are obtained using isotropic model.

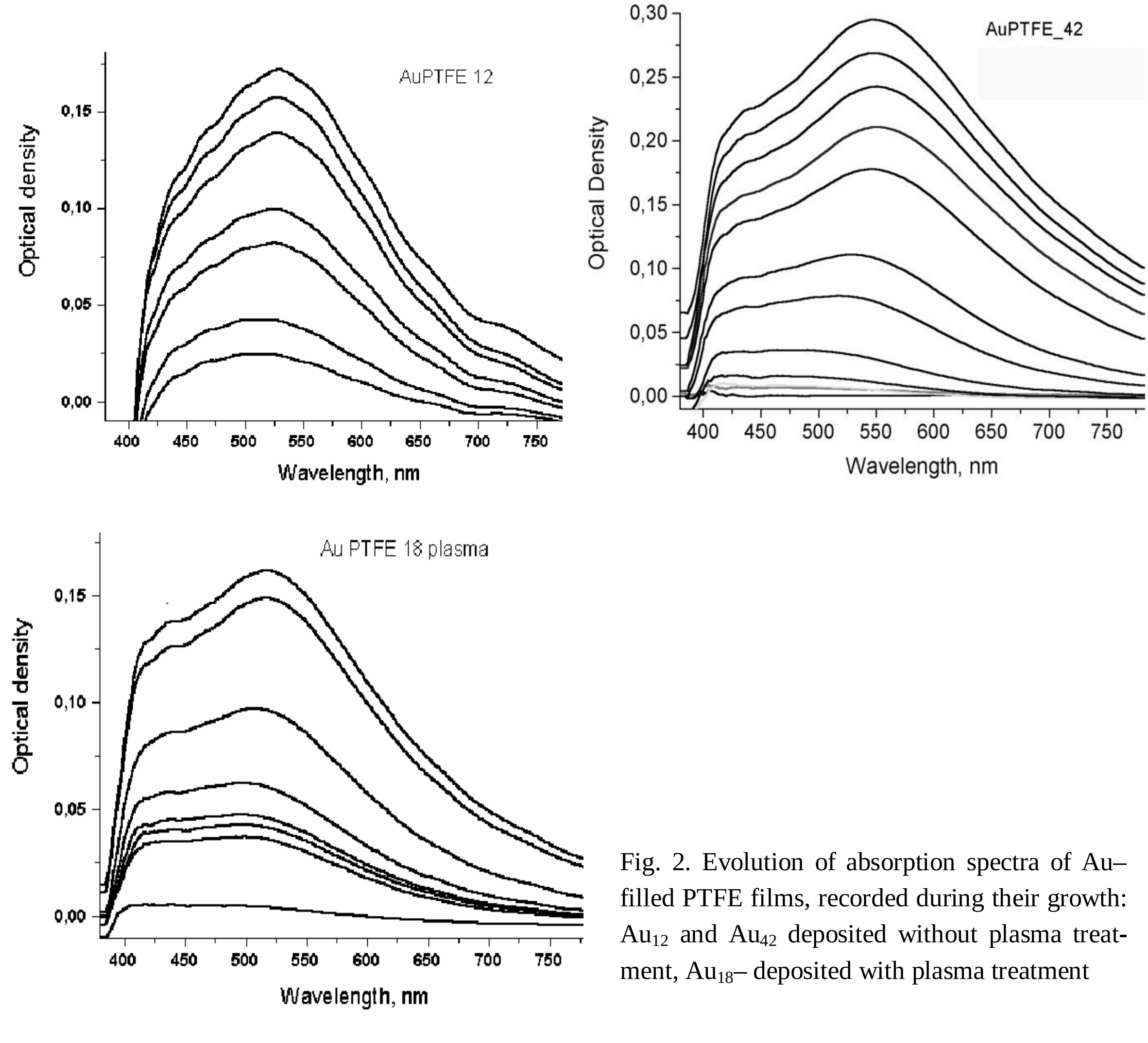


Fig. 2. Evolution of absorption spectra of Au–filled PTFE films, recorded during their growth: Au_{12} and Au_{42} deposited without plasma treatment, Au_{18}– deposited with plasma treatment

For the film, containing 12 vol. % of Au and deposited without plasma treatment, absorption band monotonously is shifting with film thickness growth from 480 nm to 520 nm. Plasmon band for the film deposited with 20 % of Au exhibits more sharp shift to certain film thickness — about 25 nm and further no changes. The behavior of plasmon band for the film containing 10 vol. % of Au and deposited with plasma treatment is like the latter one. The shift of plasmon band can be caused by Au clusters aggregation.

Table 1. Preparation and characterization of Au-filled PTFE films

No	Deposition parameters			Thickness, nm		*n*	*k*	Au, vol. %		Average cluster diameter, nm	
	I, mA	*V*, kV	*RF*, W	by AFM	by ellipsometry			quartz monitor	calculated		by TEM
PTFE$_{-2}$	7	1,2	0	–	212	1,36	0,003	0	–	–	–
PTFE$_{-4}$	8	1,2	40	–	261	1,37	0,000	0	–	–	–
Au$_{-12}$	3	1,2	0	56,7	57	1,78	0,078	12	10,8	5,4	4,5
Au$_{-14}$	3,5	1,2	40	–	51	1,79	0,070	10	–	–	4
Au$_{-15}$	4,5	2,0	40	–	61	1,46	0,037	7	–	–	5,5
Au$_{-17}$	7	1,8	0	40	37	1,68	0,071	5	–	–	3,5
Au$_{-18}$	8	2,2	40	74	60	1,61	0,12	10	8,6	1,9	6,5
Au$_{-42}$	7	2,0	0	60	60	1,80	0,228	20	21	5,5	4,4

Au-PTFE film parameters, calculated in the frame of isotropic and one-axis anisotropic model, are shown in the Table 2. Comparison of data obtained using both isotropic and uniaxial anisotropic models showed that the last one yields better approximation of experimental ellipsometric parameters and better correlation of film thickness values, obtained by ellipsometry and AFM. As can be seen from Table 2, degree and sign of birefringence and dichroism is dependent on thickness of the film and deposition conditions.

Table 2. Properties of Au-filled PTFE films calculated by isotropic and uniaxial anisotropic models using ellipsometry data

No	*h*, nm	*n*	*k*	n_o	$n_e - n_o$	k_o	$k_e - k_o$
Au–$_{12}$	57	1,78	0,078	1,803	–0,029	0,064	–0,01
Au–$_{14}$	51–53	1,80	0,070	1,73	+0,050	0,15	–0,0075
Au–$_{15}$	61–63	1,46	0,037	1,384	+0,0495	0,030	+0,028
Au–$_{17}$	40–41	1,56	0,105	1,52	+0,097	0,66	-0,25
Au–$_{18}$	74	1,61	0,12	1,605	+0,053	0,183	–0,072
Au–$_{42}$	60	1,89	0,144	1,80	+0,057	0,228	–0,128

Fig. 3 presents TEM images of all Au-filled polymer films. Normal law describes distribution of cluster size in the Au-PTFE film deposited without plasma. Cluster size is in 2–8 nm range. Distribution of Au clusters in PTFE in film deposited with plasma treatment are more wide. Smaller clusters were grown. But TEM image also revealed aggregates up to 13 nm diameter made from these small clusters.

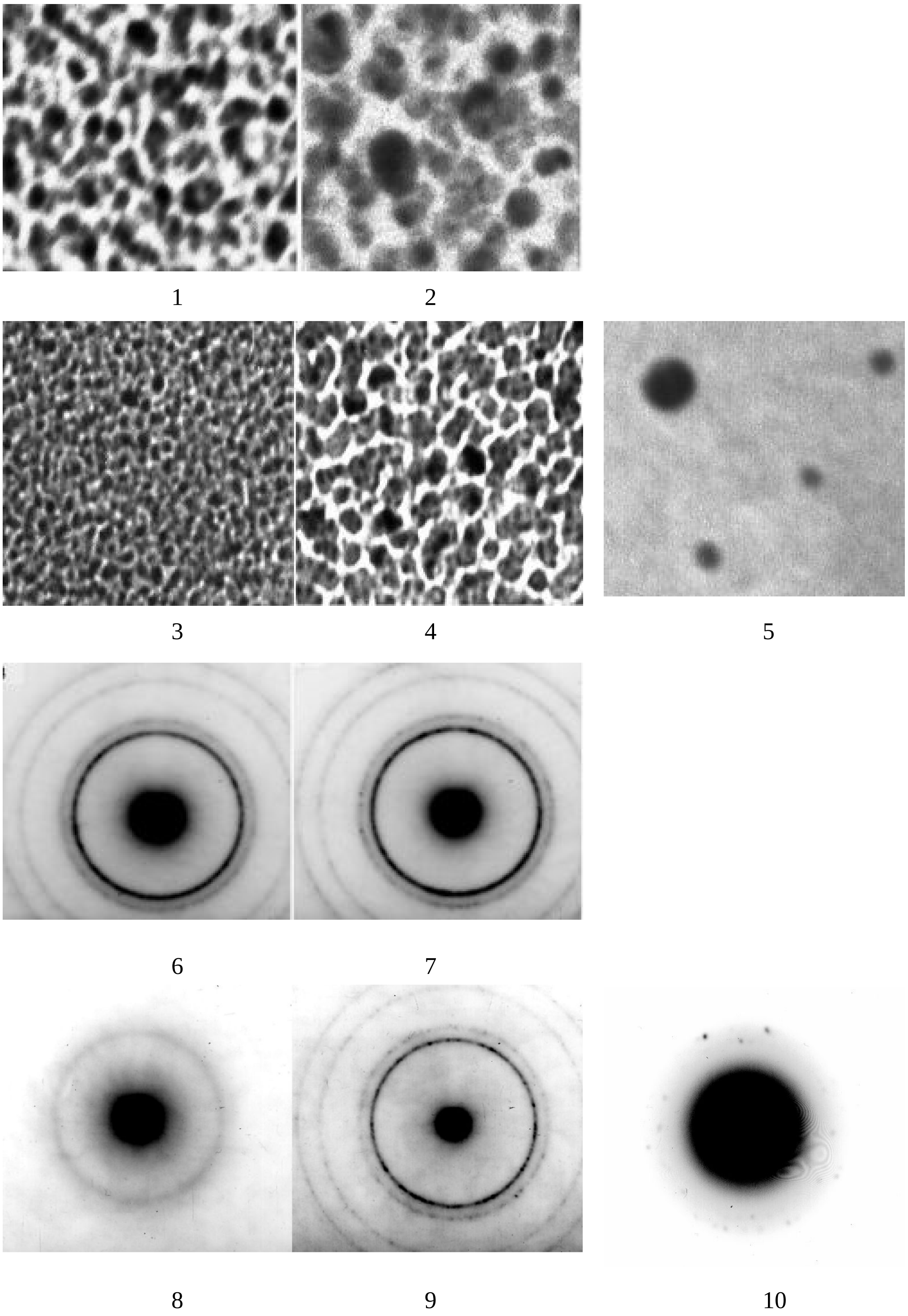
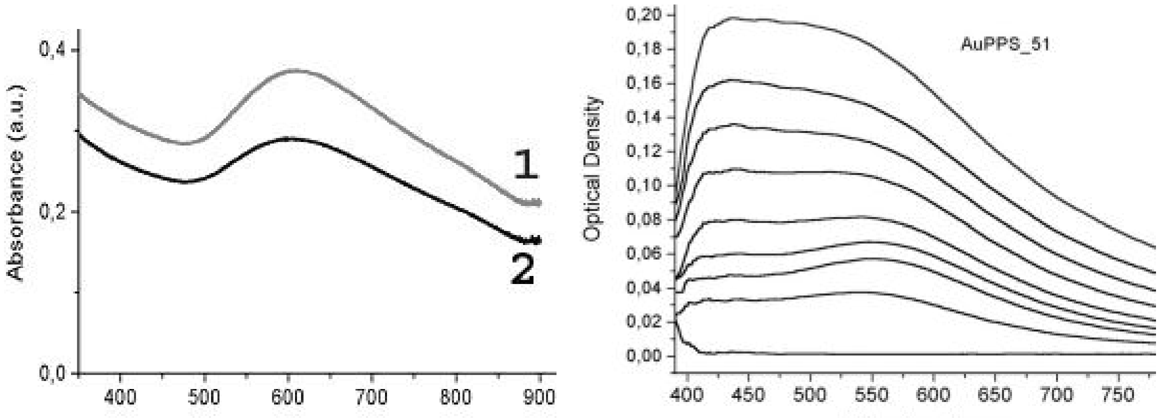


Fig. 3. TEM images of the Au-filled polymer films: 1 — Au_{12}; 2 — Au_{18}; 6 and 7 — their electron diffraction patterns; 3 — thermal evaporation of PPS; 4 — thermal evaporation of PPS with plasma treatment; 8 and 9 — their electron diffraction patterns; 5 and 10 — CoPc-Au-PTFE film. Magnification: 500 000

Au clusters have also been characterised using ellipsometry data. Maxwell-Garnett theory was used for calculations [24]. Au clusters were considered as nanocrystals embedded in PTFE matrix. The quasi-classical approximation [25] was used for the calculations of the dielectric constant as a function of the Au nanocrystals size. Volume fraction of the Au clusters calculated using this approach is close to the value obtained with quartz monitor. For the film deposited without plasma treatment calculated diameter of Au clusters is close to average size obtained by TEM. For the film deposited with plasma treatment calculated diameter of Au clusters is close to the minimal size obtained by TEM. This points out to the aggregation of Au clusters in the film deposited with plasma.

The difference in the film structure can be caused by: 1 — plasma can charge Au clusters, which can lead to their repelling; 2 — more chemically active CxFy species fix Au nuclei, increasing nuclei quantity but preventing their growth; 3 — cross-linked PTFE matrix resists Au diffusion and suppresses cluster growth; 4 — due to 2 and 3, the next layer of Au clusters is more favourable to grow onto already formed Au clusters.

Fig. 4 shows absorption spectra of Au-PPS films deposited with and without plasma treatment. Spectra show different mechanism of formation of film, grown without plasma treatment. At the film growth beginning plasmon band at 560 nm appeared. At initial stage of film thickness increase this band is shifted to 575 nm. This is evidence of formation of large Au clusters or aggregates. But with film thickness further growth the relative intensity of the band 425 nm increases more rapidly, than intensity of the band 575 nm. Final film spectrum has wide band at about 430 nm, but this can be the superposition of 580 nm and new 420 nm bands. Chemical reaction of Au with S can be suggested. In this case the formation of compound with new absorption band is possible. Film growth with plasma treatment revealed initial plasmon band at about 620 nm and no changes in its position during film thickness increase. This is true for all films studied with 5-30 Au vol. % concentration.



a

b

Fig. 4. Evolution of absorption spectra of Au-PPS films: a — deposited without plasma treatment filled with 18 % Au; b — deposited with plasma treatment filled with: 1 — 20, and 2 — 15 Au (vol. %)

TEM images showed large differences in the film structure (Fig. 3, 3,4). Film deposited without plasma is almost disordered mixture, while film deposited with plasma contained large Au cluster aggregates clearly divided one from other by polymer matrix. Electron diffraction patterns showed that in the former case film structure is far from the Au cluster structure in PTFE matrix (Fig. 3, 7,8). For the latter film Au cluster structure is almost the same as in PTFE matrix. The average diameter of Au clusters in PPS matrix is smaller (3 nm and 5,5 nm) than in PTFE matrix for both cases.

This can be explained in the following way: in the first case Au-S interaction is strong enough. So diffusion and cluster growth were suppressed. Au-S compound can be formed. In the second case plasma treatment makes organic species more active, therefore their interaction between them is stronger than with Au. But in the latter case plasma also can lead to decomposition of monomer to smaller species, so resulted deposit is less like original PPS than if film was deposited without plasma treatment. In both cases interaction of Au clusters with PPS decomposition products and matrix is stronger than interaction with PTFE ones, so cluster growth is suppressed more strongly.

Recently multi-component organic systems with Au nanoclusters attracted attention for various applications [4, 5]. But all these systems were deposited from solutions. We deposited three-component dye-Au-PTFE film in a vacuum for the first time. Fig. 5 presents evolution of absorption spectrum during CoPc-Au-PTFE film growth. Film composition Au:CoPc:PTFE (vol. %) is 6:44:50.

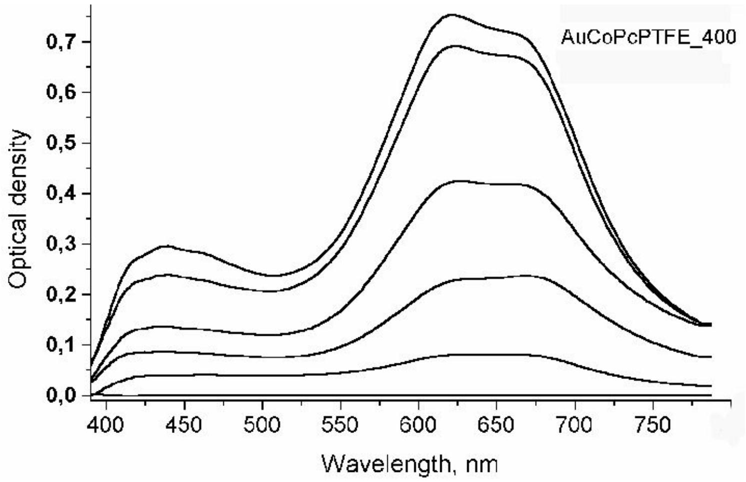


Fig. 5. Evolution of CoPc-Au-PTFE film spectrum

Spectrum represents superposition of Au plasmon band at 520 nm and CoPc absorption at 430, 610 and 670 nm. But 430 nm band of pure CoPc film is shifted to 420 nm in three-component film, intensity of 610 nm is weaker. The former effect may be caused by the contribution of small Au cluster absorption in the 420 nm region. The latter one can be due to that the Au clusters prevent CoPc aggregation and crystallisation, resulting in formation less organised CoPc clusters.

TEM investigations showed Au clusters about 2–7 nm diameter, rarely distributed in a matrix (Fig. 3,5) and only several aggregates. Most of clusters have perfect round shape. The distribution of CoPc and PTFE phases may be not resolved due to their almost equal density. At least no large aggregates or crystals were formed. This is caused by the fact that the each phase prevents the growth of another one. Electron diffraction pattern shows weak point reflexes (Fig. 3,10). This points to formation of crystallites with preferential orientation.

In summary we can make the conclusion that the use of optical spectroscopy ***in situ*** for film growth studies allows to discover transformations with film thickness increase. These investigations have to help to understand mechanism of the structure formation in multi-component composite system.

Conclusions

1. PTFE and PPS films filled with Au nanoclusters were deposited by co-evaporation in a vacuum.
2. Both PTFE and PPS based films showed nonlinear changes of optical spectrum during film growth.
3. Treatment of vapor by RF discharge led to aggregation but of more small Au clusters in the matrix.
4. Ellipsometry data showed that the films have anisotropy in optical properties, especially for films deposited with plasma.
5. Three-component dye-Au-PTFE film was deposited in a vacuum. Au clusters have round shape.

Acknowledgments

Deposition equipment was made in the frame of STCU Project 2348. Thanks to DAAD for granting of Polytec spectrometer system. Thanks to Mr. A. Kotko for TEM images.

1. *Yinon J.* Detection of Explosives by Electronic Nose // Anal. Chem. — 2003. — Vol. 1. — P. 99–105.

2. *Kim Y., Johnson R.C., Hupp J.T.* Gold Nanoparticles Sensing Heavy Metals // Nano Letters. — 2001. — Vol. 1, 4. — P. 165–167.

3. *Bozhevolnyi S.I., Volkov V.S., and Leosson K.* Localization and Waveguiding of Surface Plasmon Polaritons in Random Nanostructures // Phys. Rev. Lett. — 2002. — Vol. 89, N 18. — art. N 186801.

4. *Barca I.V., Brown A.P., Andrews M.P., Galstian T., et al.* Linear and Nonlinear Optical Response of Dye Anchored to Gold Nanoparticles // Canadian J. Chem. — 2002. — Vol. 80. — P. 1625–1633.

5. *Thomas K.G. and Kamat P.* Chromophore-Functionalized Gold Nanoparticles // Acc. Chem. Res. — 2003. — Vol. 36. — P. 888–898.

6. *Santussi S., Picozzi P.* Discontinuous Ag/Au Films as Nonerasable Media for Laser Writing // Thin Solid Films. — 1985. — Vol. 125. — P. 361–365.

7. *Yasuda N., Takeoka E. and Odzawa N.* Высоконадежные пленки для записи на оптических дисках // Kindzoku Khemen Gidzyutsu. — 1987. — Vol. 38, N 9. — P. 386–390.

8. *Petrov V.V., Gritsenko K.P., Kryuchin A.A.* Investigation of Film Structure Obtained by Coevaporation of Metals and Polytetrafluoroethylene in Vacuo // Dokl. Acad. Nauk. Ukr. SSR. — 1989. — Vol. 12. — P. 64–68.

9. *Gritsenko K.P.* Metal-Polymer Optical Storage Media Produced by PECVD // Thin Solid Films. — 1993. — Vol. 227. — P. 1–2.

10. *Gritsenko K.P., Kryuchin A.A., Krasovsky A.M.* Optical Recording of Information on Metal-Polymer Films, Produced by Plasma Dissociation of Te and Se Compounds // Ukr. Phys. J. — 1994. — Vol. 39, N 5/6. — P. 604–607 (Ukrainian).

11. *Gritsenko K.P.* Pd-Based Films Produced by PECVD // Proc. SPIE. — 1996. — Vol. 2776. — P. 291–299.

12. *Gritsenko K.P.* Polymeric metal-filled film for photothermal optical recording // Proc. SPIE. — 1997. — Vol. 3347. — P. 165–173.

13. *Gritsenko K.P.* Structure-Sensitive Pd-Based Optical Media Produced by PECVD // J. Sci. Appl. Photography. — 1998. — Vol. 39, N 5. — P. 419–437.

14. *Park Kang-Ho, Kim J., Song Ki-Bong, Lee Sung-Q., Kim J., Kim Eun-Kyoung.* Multi-Functional Probe Recording: Field-Induced Recording and Near-Field Optical Readout // ETRI J. — 2004. — Vol. 26. — P. 189–194.

15. *Kay E., Dilks A., Seybold D.* Metal-Containing Fluoropolymer Films, Produced by Simultaneous Plasma Etching and Polymerization // J. Appl. Phys. — 1980. — Vol. 51, N 11. — P. 5678–5687.

16. *Martinu L.* Deposition and Structure of Gold-Containing Plasma-Polymerized Halocarbon Film // Thin Solid Films. — 1986. — Vol. 40. — P. 307–319.

17. *Despax B., Leotard J.L.* Synthesis of Gold-Carbon Composites by Simultaneous Sputtering & Plasma-Polymerisation of Propane // Thin Solid Films. — 1989. — Vol. 168. — P. 81–88.

18. *Roy R.A., Messier R., Krishnaswamy S.V.* Preparation and Properties of R.F-Sputtering Polymer-Metal thin Films // Thin Solid Films. — 1984. — Vol. 109. — P. 27–35.

19. *Convertino A., Capobianchi A., Valentini A., Cirillo E.N.M.* A New Approach to Organic Solvent Detection: High-Reflectivity Bragg Reflectors Based on a Gold Nanoparticle / Teflon-Like Composite Material // Advanced Materials. — 2003. — Vol. 15, N 3. — P. 1103–1105.

20. *Cioffi N., Farella I., Torsi L., et al.* Correlation between Surface Chemical Composition and Vapor Sensing Properties of Gold-Fluorocarbon Nanocomposites // Sensors and actuators. — 2002. — Vol. B84. — P. 49–54.

21. *Gritsenko K.P., Krasovsky A.M.* Thin Film Deposition of Polymers by Vacuum Degradation // Chemical Reviews. — 2003. — Vol. 103, N 9. — P. 3607–3650.

22. *Fejfar A., Martinu L., Ostadal I.* Microstructure and Optical Properties of Gold-Doped Plasma-Polymerized Halocarbons // Vacuum. — 1989. — Vol. 39. — P. 19–22.

23. *Grytsenko K.P., Grynko D.O., Lozovsky V.Z., et al.* Preparation of Au Nanoclusters in Polymer Film by Co-Evaporation in a Vacuum // Proc. Conf. «Nowe Kierunki Modif. Zast. Tworzyw Sztucz». — Poland. — May 24–26. — 2004. — P. 79–84.

24. *Cohen R.W., Cody G.D., Coutts M.D., Abeles B.* Optical Properties of Granular Silver and Gold Films // Phys. Rev. B. — 1973. — Vol. 8, N 8. — P. 3689–3701.

25. *Lissberger P.H. and Nelson R.G.* Optical Properties of Thin Film Au-MgF_2 Cermets // Thin Solid Films. — 1974. — Vol. 21, N 1. — P. 159–172.

Received 15.11.2004.