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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.

Keywords: 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.

2. 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 $x10^{-8}$ 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.

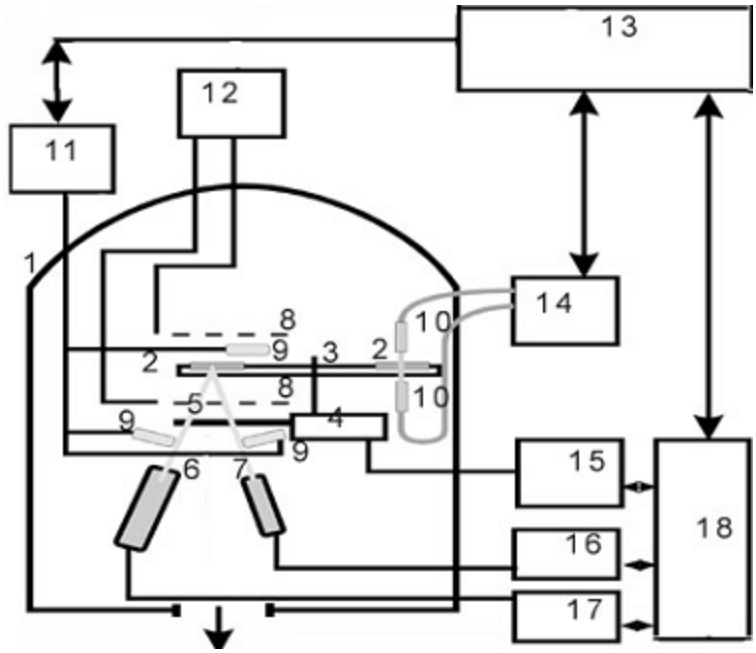


Fig.1. Scheme of the deposition installation:

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. Table 1 is summarising experimental data for Au-filled PTFE films. Ellipsometry data presented in the table 1, obtained using isotropic model.

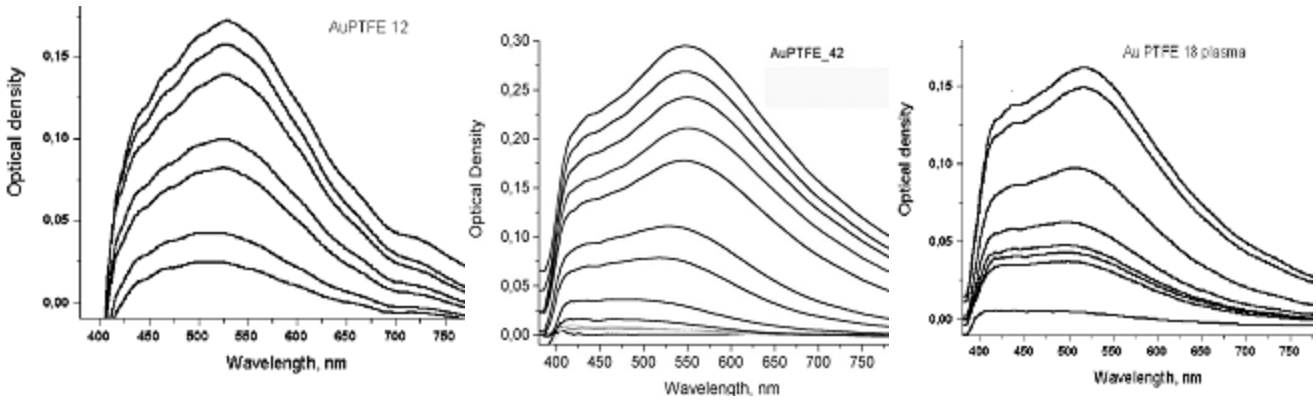


Fig.2. Evolution of absorption spectra of Au–filled PTFE films, recorded during their growth: Au_{12} and Au_{42} deposited without plasma treatment, Au_{18}- deposited with plasma treatment.

For the film, contained 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 exhibit more sharp shift to certain film thickness – about 25 nm and farther 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.

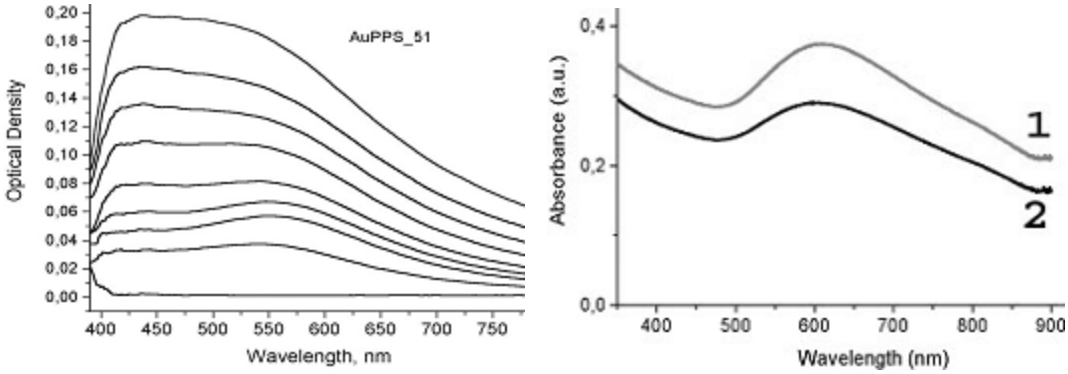
Table 1. Preparation and characterization of Au-filled PTFE films

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 dependent on thickness of the film and deposition conditions.

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 farther growth the relative intensity of the band 425 nm



a b

Fig.4. Evolution of absorption spectra of Au-PPS films:

a – deposited without plasma treatment filled with 20% Au, b- deposited with plasma treatment filled with: 1 - 20, and 2 - 15 Au (vol. %).

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 it position during film thickness increase. This is true for all films studied with 5-30 Au vol.% concentration.

TEM images showed big 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 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 by: 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 making 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 nano-clusters attracted attention for various applications [4,5]. But all these systems were deposited from solutions. For the best of our knowledge, 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.

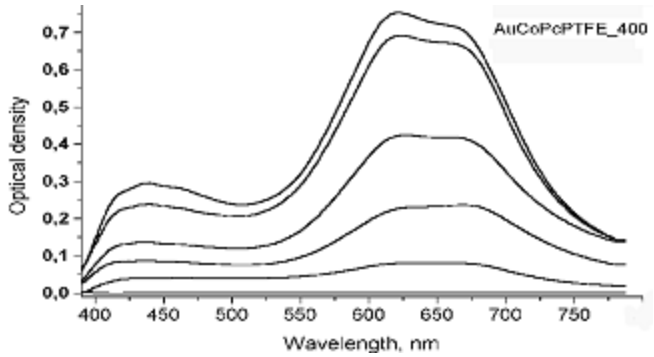


Fig. 5. Evolution of CoPc-Au-PTFE film spectrum.

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 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

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