Characterization of optically inhomogeneous polymer layers with silver nanoparticles by spectroscopic ellipsometry

A I Lihachev, P N Brunkov, A V Nashchekin, V A Tolmachev and M V Vasileva
Ioffe Institute, Polytekhnicheskaya Str. 26, St. Petersburg, 194021, Russia
E-mail: Lihachev@mail.ioffe.ru

Abstract. In this work it was shown the applicability of the spectroscopic ellipsometry technique for characterization of an optically inhomogeneous polymer film with silver NPs. The histogram of silver NPs distribution based on SEM images shows the largest number of NPs have a size in the range 15-35 nm and the filling factor as large as 6%. By using the possibilities of ellipsometry it was suggested a 3-layer inhomogeneous structure with different sizes of silver NPs covered by thin polyamide-6 film. Also existence of localized plasmon resonance in such NPs was observed by optical absorption measurements.

1. Introduction
Nowadays there is an increased interest in nanoscale layered structures that are widely used in optoelectronic devices [1], biosensor applications [2] and various purposes functional systems [3]. One of the most attractive of these structures are materials with metal nanoparticles (NPs) due to their unique optical properties. Localized surface plasmon resonance (LSPR) is the collective oscillation of the conduction electrons of metallic NPs excited by the incident light field. Due to the interaction of NPs electromagnetic field with nearby bioobjects the concentration of the bioobject can be determined by measuring of the LSPR spectral position shift. In this regard, using of glasses with silver NPs with LSPR in the blue part of the spectrum is perspective for biosensor applications.

In our work we use K-8 glass substrates with synthesized NPs on top. Our preliminary experiments show that silver NPs have not enough adhesion on glasses and can be partially flushed in liquid environment. The perspective way to fix NPs on glass surface is cover it by thin polymer film. We used polyamide-6 (PA-6) for NPs coating. PA 6 is biocompatible polymer, that is promising for further biological applications [4].

Nanosized structure characterization requires development of layers thickness and composition measuring methods, and of the morphology analysis. Along with Auger spectroscopy, diffraction of slow and fast electrons, and atomic force microscopy (AFM), the ellipsometry method [5] occupies a special place, making it possible to determine the optical characteristics of homogeneous layers, as well as their thickness down to one nanometer.

In this paper the ellipsometry method is used to characterize an optically inhomogeneous polyamide-6 film with silver NPs on the glass surface. Film thickness was measured by AFM
and ellipsometry techniques. Particles on the glass surface were observed by scanning electron microscopy (SEM). In this paper we suggest the approach of optical methods for the optically inhomogeneous layers thickness evaluation.

2. Experimental

2.1. Silver nanoparticles synthesis and characterization

Ag NPs were synthesized on K-8 glass surface by ion exchange technique [6] and subsequent reduction in water vapor [7]. The thickness of glass was 1 mm. Ion exchange temperature was 350°C, reduction temperature was 325°C. This conditions are optimal to get the narrowest spectral LSPR peak. On the glasses for ellipsometry one of the surfaces was made opaque to reduce reflection from back surface. Figure 1 shows SEM image of NPs on the K-8 surface using JSM-7001F (Jeol, Japan). The image processing made by ImageJ free software allowed us to draw a histogram of NPs size distribution. From the histogram it was estimated that the largest number of NPs has a size in 15-35 nm. The filling factor was 6%. The optical absorption measurements of this structure is correspond to LSPR in silver NPs (figure 2).

2.2. Polyamide-6 coating

The thin PA-6 films were deposited on top of the glasses with Ag NPs by spin coating. The thickness of the polymer film was varied by changing the PA-6 concentration dissolved in formic acid. Concentrations were 1, 1.2, 1.5 and 3 weight percentages. Centrifuge rotational speed was 4000 rpm. Coating time was 60 seconds. Also conventional Si substrates were coated with PA-6 of each concentration for comparative measurements by AFM and reflective ellipsometry.

Thickness control measurements were made on Si substrates by atomic force microscope Dimension 3100 (Veeco, USA). Substrates were scratched, then scratch profile was written by AFM probe and thickness was measured on this profile (figure 3). After that PA-6 films thickness on Si substrates was measured by Ellipse-1891 ellipsometer (Russia). Example of Ψ ellipsometric parameter for 124 nm film fitting showed on figure 4. Measurement results are
Table 1. Results of comparative measuring the thickness of PA-6 films by AFM and ellipsometry with different concentrations of the polymer.

| Concentration, weight % | Thickness, nm | AFM  | Ellipsometry |
|-------------------------|---------------|------|--------------|
| 1                       | 20 ± 5        | 29 ± 5 |
| 1.2                     | 40 ± 5        | 48 ± 5 |
| 1.5                     | 120 ± 5       | 124 ± 5 |
| 3                       | 625 ± 5       | 634 ± 5 |

presented in table 1. As can be seen from the table, results of films thickness measuring by AFM and ellipsometry correlate well.

Figure 3. AFM thickness profile of PA-6 film on Si substrate.

Figure 4. Fitting of Ψ ellipsometry parameter for 124 nm PA-6 films on Si substrates.

2.3. Ellipsometry measurements of glasses with NPs
K-8 glasses with Ag NPs covered by different thicknesses of PA-6 films (refractive index n = 1.524) and opaque back surface were measured by spectroscopic ellipsometry technique at 70 degree angle. Further, in “Spectroscan” software Ψ and Δ ellipsometry parameters were simulated with Maxwell-Garnett approximation. In standard way the structure model was very simple: one PA-6 layer containing Ag with filling factor close to one obtained from the histogram (6%). But experimental and theoretical fitting was not sufficient enough. So we suggested multi layer model with different thicknesses and silver filling factors in every layer. The best fitting results were achieved in four layer model (table 2). Layers 1–3 corresponds to NPs with different size. These results are in a good agreement with histogram of NPs size distribution (see inset on the figure 1). Layer 4 means PA-6 thin film that cover NPs. Figure 5 shows Ψ ellipsometric fitting parameter for 124 nm polyamide-6 film.

Relatively good agreement of fitting peaks position with experimental peaks can be seen on figure 5. Experimental curve has less magnitude because of broad NPs size distribution.
Table 2. Four layer model for 124 nm thick PA-6 film.

| Layer   | Thickness, nm | Ag containing, % |
|---------|---------------|------------------|
| Layer 4 | 69.2          | 0.0              |
| Layer 3 | 30.5          | 0.5              |
| Layer 2 | 25.0          | 1.0              |
| Layer 1 | 16.6          | 2.0              |
| K-8 glass Substrate | -        |

Figure 5. Fitting of Ψ ellipsometric parameter for 124 nm thick polyamide-6 film.

leaved out of account in structure model. Other reason for no coincidence of experimental and calculated “wings” of curves is near refractive indexes of glass and polyamide-6, that greatly complicates the ellipsometric evaluation in inhomogeneous multi-layered structures with resonant peculiarities.

Thus, a promising method for estimating the thickness of inhomogeneous layers is proposed. It should be emphasised that the coating polymer layer thickness estimating accuracy increases significantly with increasing of refractive indices difference.

3. Conclusion

Thus the perspective of use of the spectroscopic ellipsometry for characterization of an optically inhomogeneous polymer films with silver NPs was shown. The histogram of silver NPs distribution based on SEM image analysis shows the largest number of NPs have a size in the range 15-35 nm and the filling factor as large as 6%. By using the possibilities of spectroscopic ellipsometry it was suggested a 4-layer inhomogeneous structure model with different sizes of silver NPs covered by thin polyamide-6 film. Also existence of localized surface plasmon resonance in such NPs was observed by optical absorption measurements.
Acknowledgements
SEM characterization were performed using equipment owned by the Federal Joint Research Center “Material science and characterization in advanced technology” with financial support by Ministry of Education and Science of the Russian Federation.

References
[1] Sakamaki Y et al. 2017 Optics Express 25(17) 19946
[2] Wijaya E et al. 2011 Current Opinion in Solid State and Materials Science 15(5) 208
[3] Zhou J et al. 2018 Quantum Electron 24(4) 6101306
[4] Zucca P et al. 2014 Molecules 19 14139
[5] Azzam R M A and Bashara N M 1977 Ellipsometry and Polarized Light (Netherlands, Amsterdam: North-Holland Publishing Company)
[6] Tervonen A et al. 2011 Optical Engineering 50 071107
[7] Kaganovskii Y et al. 2007 Journal of Physics: Conference Series 61 508