Optical properties of thin graphene oxide films and their biosensing applications

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Abstract. Graphene oxide (GO) is a promising platform to realize immobilization matrices for plasmonic biosensors. Here, we discuss various aspect of the deposition of GO thin films, their optical properties, and the influence of GO linking layers on biosensing sensitivity. Using spectroscopic ellipsometry, we obtain dielectric functions of thin GO films deposited by spray-coating in the visible and near-infrared ranges. In addition, we demonstrate that the optimization of GO linking layers may sufficiently increase the sensitivity of SPR biosensing.

1. Introduction

Surface plasmon resonance (SPR) biosensing is a widely used technique in biochemical studies and pharmacology that provides quantitative analysis of biomolecular reactions. In recent years, many research papers have been published on the use of graphene oxide (GO) linking layers to improve biosensing sensitivity [1-5]. One of the advantages of GO linking layers is their universality because the same GO sensor chips can be used both for small-molecule interaction and for biomolecular reactions such as antibody-antigen interactions [6, 7]. However, to optimize GO sensor chips we need to determine optimal conditions for the deposition of GO films and obtain their optical properties. In present work, we investigate GO thin films using spectroscopic ellipsometry and use obtained complex refractive index represented with Cauchy model in the simulation of SPR excitation in thin gold films coated with GO linking layers. Obtained results give us the optimal configuration of GO sensor chips for using in highly-sensitive SPR biosensing.

2. Deposition and characterization of thin graphene oxide films

Different methods can be used for the deposition of graphene oxide thin films from an aqueous solution including spin-coating, spray-coating, dip-coating and drop-casting [8]. In this work, we use
spray-coating, which allows to deposited uniform and homogeneous GO films with controlled thickness. The analysis of the structure and optical properties of the deposited GO films was performed using atomic force microscopy (AFM), optical spectrometry, and spectroscopic ellipsometry.

1. **Spray-coating**
Graphene oxide films were deposited on p-type silicon wafers with 90-nm-thick thermally-grown SiO2 layer using a spray-coating technique, see Figure 1 (a-b). An airbrush JAS 1127 with a nozzle with a diameter of 0.2 mm was connected to compressed air with a pressure of 1.8 bar. For the deposition, we used GO water solution (Graphene Laboratories Inc., USA) with a concentration of 0.5 g/l, which contains GO flakes with a diameter of 0.3-0.7 µm. The substrate temperature was kept constant during the deposition process. The films were deposited under atmospheric pressure in a continuous spraying regime and at the deposition rate of about 1 ml/min. Graphene oxide flakes solution concentration was 0.5 mg/ml. Before the film deposition substrate was ultrasonicated in acetone for 2 min., then cleaned with IPA and then treated in oxygen plasma during 10 minutes in the DienerFemto plasma system. Thicknesses and roughnesses (height root mean square or RMS) of the thin GO films were collected from 6x6 um atomic force microscopy (AFM) maps on the NeaspecNeaSNOM microscope.

2. **Optical absorption**
Optical absorption spectra of the GO films are shown in Figure 2. Measurements within 200-3300 nm spectral range were performed with a two-beam spectrophotometer Agilent Technologies Cary 5000. The spectra were measured for the GO flakes water solution in the quartz cell with 1-cm-long optical path. In addition, spectra were obtained for GO thin films on quartz and glass substrates.

**Figure 1.** GO films deposited on SiO2/Si substrates (a) and their characterization by optical microscopy (b).

**Figure 2.** Optical absorption of GO films on glass/quartz substrates and GO water solution with a concentration of 0.5 g/l. The inset shows absorption in UV and VIS spectral ranges.
3. Optical parameters

![Figure 3](image)

Figure 3. Real (a) and imaginary (b) parts of refractive index of GO films with thicknesses of 25 and 38 nm.

Dielectric functions of GO films are depicted in Figure 3. Spectroscopic ellipsometer VASE produced by J.A. Woollam Co performed measurements in the wavelength range 300 – 3100 nm. For ellipsometry modelling, we used the standard dielectric Cauchy Model with absorption part (the wavelength \( \lambda \) is in the units of nanometers):

\[
n = A_n + \frac{B_n}{\lambda^2}; k = A_k + \frac{B_k}{\lambda^2}
\]  

(1)

Fitting parameters \( A_n, B_n, A_k, B_k \) calculated for the 38-nm-thick GO film are equal 2, 9232, 2 and 15575 respectively.

![Figure 4](image)

Figure 4. (a) Schematic representation of the SPR biosensor with an SPR sensor chip comprising the graphene-oxide-linking layer; (b) The sensitivity to refractive index changes of such sensor chips depending on the thickness of the GO linking layer.

3. Plasmonic biosensing

Coating of SPR sensor chips with thin dielectric films allows increasing biosensing sensitivity [4,9]. We studied the dependence of the sensitivity to refractive index changes (SRI) on the GO linker layer thickness according to the Kretschmann SPR excitation configuration displayed in Figure 4(a). Using the transfer matrix model [10], we analyzed the reflection from a multilayer structure composing the
following layers: 1) the glass layer; 2) a 50-nm-thick gold film; 3) a GO linking layer; 4) the top aqueous layer with RI of 1.33.

The dependence of biosensing sensitivity on the thickness of GO linking layers is presented in Fig. 4(b). For sufficiently thin GO layers, the sensitivity to refractive index (RI) changes is almost proportional to their thicknesses reaching its maximum at 13, 39, 75 and 105 nm at the wavelengths of 633, 880, 1315, and 1550 nm, respectively. Therefore, the deposition of GO linking layers of the optimal thickness provides an opportunity to double the biosensing sensitivity and perform more accurate SPR analysis.

4. Conclusions
We have considered in detail the optical properties of thin GO films deposited by spray-coating and their applications in plasmonic biosensing. Thin films spray-coating deposition of GO films from an aqueous solution is an inexpensive and suitable for mass production method. In addition, the sensitivity of SPR biosensors can be improved by adding linking GO layer and further sensor structure optimization. We found optimal thicknesses which maximize the sensor’s sensitivity to RI changes for four common laser lines. For numerical simulation of SPR excitation, we use the optical properties of GO films obtained from spectrophotometric and spectroscopic ellipsometry measurements. As a result, we obtained that optimization of the thickness of GO linking layers may double the sensitivity to RI changes providing more accurate biosensing analysis.

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