



Long-range surface plasmon resonance sensors fabricated with plasma polymerized fluorocarbon thin films



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ABSTRACT

A rapid and simple approach to prepare the dielectric buffer layers is of crucial importance for the development of long-range surface plasmon resonance (LRSPR) sensors. In this regard, we describe for the first time the use of plasma polymerized fluorocarbon thin films as the dielectric buffer layers for the construction of LRSPR sensors. The fluorocarbon films were achieved by radio frequency plasma polymerization of perfluorooctyl ethylene (PFOE) at continuous wave mode with an input power of 60 Watts. The resulting ppPFOE exhibited good adhesion with both the glass substrate and the gold superstrate, and also remained relatively stable in aqueous solutions as seen by optical waveguide spectroscopy (OWS). The obtained LRSPR sensor consisting of a SF11–ppPFOE–Au structure was employed for the detection of both the bulk refractive index variation and the protein adsorption.

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1. Introduction

Recently long-range surface plasmon resonance (LRSPR) has attracted considerable attention because of their potential applications for cellular studies [1–3] and the detection of pathogens [4–6]. Compared with conventional surface plasmon resonance (cSPR) in the Kretschmann's configuration, LRSPR exhibits a stronger surface electric field strength, a narrower resonance dip, as well as, a longer penetration depth up to several micrometers [7–11]. Consequently, a LRSPR sensor has an extended detection range from metallic surface compared to a cSPR sensor. The multilayered structure required for the excitation of LRSPR usually contains an optimum thickness of dielectric (so-called buffer layer) embedded between glass substrate and thin metallic layer (e.g., Au) [12–14]. The refractive index of the dielectric buffer layer should be identical/similar to that of sensing medium (e.g., water) in order to obtain a symmetric coupling of the surface plasmon modes on both surfaces of thin metallic layer [15–17].

When taking the refractive index and film thickness control into account, the selection of dielectric buffer materials is limited to several fluoride-containing materials, including evaporated magnesium fluoride (MgF_2) [14,18], sputtered polytetrafluoroethylene

(PTFE) [19,20], as well as, spin-coated fluoropolymers [15,21,22]. Since MgF_2 is harmful to human health and has trace solubility in aqueous media, most LRSPR sensors are fabricated by spin-coating two commercially available fluoropolymers: (1) Teflon AF-1600 (DuPont, USA), a polytetrafluoroethylene copolymer with a refractive index $n_d = 1.3065$ at $\lambda = 632.8 \text{ nm}$ [14,15]; (2) Cytop (Asahi Glass Co. Japan), a polydecafluorooctaheptadiene with a refractive index $n_d = 1.3368$ at $\lambda = 632.8 \text{ nm}$ [21,22]. Both fluoropolymers are soluble in the specific solvents provided by the corresponding suppliers. The film thickness (d) can be tuned by adjusting the spin-coating speed and the solution concentration. In order to promote the adhesion of the fluoropolymers onto glass substrates, the glasses should be coated firstly with a fluorosilane solution [7]. After spin-coating the fluoropolymer, the thin film needs to be baked in a series of steps at elevated temperatures in order to remove the specific solvent [14,21]. Therefore the whole fabrication process contains multi-steps, and is time-consuming and tedious, which limits the wide application of LRSPR sensor.

An alternative approach to prepare fluorocarbon thin film is plasma polymerization (pp) of various fluorinated precursors [23–25]. Some merits associated with plasma polymerization technique include simple operation, one-step and solvent-free process, easy control of film thickness, good adhesion onto various substrates, etc. Therefore, plasma polymerization of perfluorooctyl ethylene (PFOE) was carried out in this work in order to obtain a fluorocarbon thin film with good adhesion onto the glasses. PFOE

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is chosen here as the precursor because it has a sufficient vapor pressure, thus avoiding the need of carrier gases and making the deposition process easy.

The multilayered structure supporting LRSPR was prepared by plasma polymerization of PFOE directly onto the glass slides, and followed by the deposition of a thin Au layer using a thermal evaporator. The thickness of the ppPFOE film was controlled by adjusting the deposition time. Optical waveguide spectroscopy (OWS) was employed to determine both the thickness and the refractive index of the ppPFOE. The stability of the ppPFOE in water was also investigated since LRSPR sensors are supposed to be used in aqueous media. The obtained LRSPR sensor was used for the investigation of bulk refractive index variation and protein adsorption as compared with cSPR.

2. Experimental

2.1. Materials and substrates

Perfluorooctyl ethylene (97%) was purchased from Sigma-Aldrich (Shanghai, China), and was degassed by three freeze-thaw cycles before use, without any further purification. Deionized water was used throughout the experiments. Ethylene glycol (99%) was obtained from Aladdin (Shanghai, China). Lysozyme was purchased from Energy Chemical Co., China. The glass substrates used for all SPR, OWS and LRSPR measurements were 25×25 mm SF11 slides ($n_g = 1.7786$ at $\lambda = 632.8$ nm), which were cleaned using 2% Hellmanex solution, rinsed with copious deionized water, and dried with pure nitrogen gas. For SPR and OWS measurements, the SF11 slides were coated with approximately 2 nm of Cr and 52 nm of Au (or Ag), which were thermally evaporated. For the construction of LRSPR sensors, a plasma polymerized fluorocarbon films was deposited directly on a SF11 slides without any pretreatments, thereafter an Au film of 21.9 nm thick was thermally evaporated onto the fluorocarbon layers.

2.2. Plasma deposition of ppPFOE

Deposition of ppPFOE films was carried out in a custom-built, capacitively coupled radio frequency (13.56 MHz) plasma reactor as described before [26,27]. The tubular Pyrex glass chamber, enclosed in a Faraday cage, was 40 cm in length and 11 cm in diameter. The plasma power was generated by a plasma power generator, which passed through a matching unit, and was delivered to the reactor via a coil around the exterior of glass tube. The reaction chamber was evacuated down to 6×10^{-3} mbar using a rotary pump. A baratron was connected to the chamber in order to monitor its pressure. A side arm at reactor inlet allowed for the introduction of PFOE vapors. The monomer pressure during plasma deposition was ca. 0.1 mbar. The plasma depositions were carried out at a continuous wave (CW) mode with an input power of 60 W. The deposition time was adjusted to obtain the desired thickness.

2.3. LRSPR, SPR and OWS measurements

LRSPR, SPR and OWS measurements were carried out in a custom-built SPR setup based on the Kretschmann configuration, which had been described before [28–30]. A He-Ne laser ($\lambda = 632.8$ nm, laser power < 5 mW) was used as light source. The light beam passed through two polarizers and a chopper, and then was reflected from the prism base, which was detected by a photodiode and a lock-in amplifier. While LRSPR and SPR could be excited only by p-polarized light (TM polarisation), both p- and s-polarized (TE polarization) were employed for OWS measurements. In contrast to SPR, OWS allowed for the simultaneous determination of both the refractive index and the thickness of plasma polymerized

films, provided that two waveguide modes were excited. All samples were attached to a flow cell for liquid exchange. A peristaltic pump was employed to introduce different liquids into the flow cell at a flow rate of 1 ml/min. The LRSPR, SPR and OWS spectra (i.e., the reflectivity vs. incident angle curve) could be fitted using the WASPLAS software, which was based on the Fresnel's multireflection theory and developed by Max-Planck-Institute for Polymer Research, Mainz, Germany. The figure of merit (FOM) was calculated using the following equation according to the literature [8,15]:

$$FOM = \frac{\Delta\theta_{res}}{\Delta\theta_{FWHM} \times \Delta n_s}$$

Here $\Delta\theta_{res}$ is the angular shift of the resonance dip. $\Delta\theta_{FWHM}$ is the full width at half maximum (FWHM) of the resonance dip, and Δn_s for the bulk refractive index change on sensor surface. The protein density on the surface is calculated using de Feijter's equation [31,32]:

$$M = d_A \times \frac{n_A - n_s}{dn/dc}$$

Here, d_A and n_A are the thickness and the refractive index of the adsorbed protein layer, respectively. n_s is the refractive index of a surrounding medium on a metal surface. dn/dc is the refractive index increment, which is equal to approximately $0.182 \text{ cm}^3/\text{g}$ for proteins [32]. The refractive index of lysozyme is $n_A = 1.480$ as reported previously [32].

3. Results and discussion

When used as the dielectric buffer layer in a LRSPR sensor, the thin film should fulfill several requirements, including a suitable refractive index, an optimum thickness, a low surface roughness, as well as, a good adhesion with substrates. In biosensor applications, the sensor architectures should also show sufficient stability in aqueous medium. Therefore, based on our experiences about plasma polymerization of PFOE, the ppPFOE films used in the study were prepared at a CW mode with an input power of 60 Watts.

3.1. Refractive index and thickness of ppPFOE films

OWS is a powerful optical technique for the analysis of thin films [28]. When at least two waveguide modes are observed in both p- and s-polarized OWS spectra, one can obtain the thickness and the refractive index simultaneously from the fitting of the OWS spectra. Fig. 1A gives the p-polarized OWS spectra of a series of ppPFOE films at different deposition time. Five sample positions were measured at ambient atmosphere at room temperature. The standard deviation originated from different positions is lower than 1.5%. From Fig. 1A, it is apparent that, when increasing deposition time from 5 to 8 min, the waveguide mode shifts to a higher angle. When further increasing the deposition time to 10 min, a new waveguide mode appears, and eventually the OWS spectrum of 23 min deposition shows five waveguide modes. The OWS spectra measured with s-polarized light also confirm the similar trend (data not show here).

After the fitting of OWS spectra with WASPLAS program (based on Fresnel's equation), one can find that the ppPFOE thicknesses are proportional to the deposition time, as shown in Fig. 1B. The calculated deposition rate is 68.4 nm/min with a linearity $r = 0.995$. These results indicate that plasma polymerization method allows for a good control over the film thickness. The refractive indices of various ppPFOE films are also shown in Fig. 1A. The average refractive index of ppPFOE films in air is $n_d = 1.3756 \pm 0.0022$. The refractive index value is consistent with the spectroscopic ellipsometer result of $n_d = 1.3710$ (data not shown here). The ppPFOE's refractive index

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