JOURNAL OF APPLIED PHYSICS **98**, 114314 (2005)

Surface-plasmon resonance sensing of alcohol with electrodeposited polythiophene and gold nanoparticle-oligothiophene films

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(Received 19 May 2005; accepted 21 October 2005; published online 13 December 2005)

Electrodeposited films of polythiophene or gold nanoparticles (NPs) capped with conjugated oligothiophenes prepared on thin gold films are employed in a Kretschmann-type surface-plasmon resonance detector. The polythiophene films selectively respond to alcohol (ethanol or methanol) and toluene vapors but not to hexanes or water vapors, while the nanoparticle/oligothiophene films respond only to alcohol vapors of the solvents tested. For both films, the response to vapors consisted of the minimum in the reflectance curve (θ_0) shifting to a higher angle as the thickness of the film increased. Slight increases in dielectric constant were also observed. The NPs do not result in an enhancement in sensitivity, contrary to theoretical predictions that suggest greater sensitivity may be achieved due to localized surface-plasmon effects associated with the presence of the Au NPs in the dielectric. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2138373]

I. INTRODUCTION

In recent years, there has been growing interest in developing techniques to selectively detect alcohol vapors for applications in the chemical, biomedical, and food industries. Currently, the most widely used methods for detecting alcohol vapors are infrared spectroscopy[1,2] and fuel-cell-based sensors, which measure changes in current flow to determine the alcohol concentration.[3,4] Both of these methods have limitations: infrared spectroscopy is not very selective and it is susceptible to interference from other organic compounds such as toluene and xylenes.[5,6] Fuel-cell-based detection is quite selective but suffers from a lack of sensitivity (detection limit ~200 ppm).[4]

Surface-plasmon resonance (SPR) is a method of vapor detection that promises both high sensitivity[7] (<100 ppm) and tunable selectivity.[8–10] Deposition of an organic polymer on top of a thin gold film increases the selectivity of a SPR-based sensor relative to bare gold, taking advantage of the solubilities of different vapors in the organic layer. The resulting variations of the refractive index and thickness after exposure to a vapor give rise to a selective response, dependent on the specific chemical properties of the organic layer. For example, layers of isoprene rubber,[10] poly(methyl methacrylate),[8] or polyethylene glycol[11] result in selectivity towards hydrocarbons, benzene, and alcohols, respectively.

Improvements in the sensitivity of a SPR sensor with respect to the response from a bare gold layer may also be attained by attaching metal nanoparticles (NPs) to the surface of the thin metal film.[12–14] NPs may be attached to the metal film by means of a bifunctional cross-linker such as a dithiol (on a Au film), and multilayers can be achieved by successively dipping in solutions of NP and cross-linker.[15] Such layer-by-layer assembly is tedious and the buildup of multiple layers may take several hours or even days depending on the thickness desired and the efficiency of the NP and cross-linker adsorption. The presence of the NPs results in a larger plasmon angle shift and changes in reflectivity (R),[13] which enhances the detection sensitivity of the SPR device.[16,17] The enhanced sensitivity has been attributed to interactions between the localized surface plasmons (LSP) of the Au NPs and the propagating surface plasmons (PSP) of the Au substrate.[13,14]

Thin films of NPs and organic layers deposited on the metal layer of SPR detectors thus improve the sensitivity and selectivity of SPR sensors, respectively, so combining these approaches by embedding NPs in an organic polymer may be advantageous. An approach to the preparation of such NP thin films is electrodeposition, which is much faster than layer-by-layer assembly.[18–20] We have previously shown that networks of gold NPs ($d_{\text{core}} \sim 1.7$ nm) can be readily electrodeposited onto a conducting substrate using conjugated oligothiophene linkers [Fig. 1(a)].[20] The thickness of the deposited NP film can be controlled via the deposition time and the solution concentration, and deposition of a 1–2-μm-thick film takes a few seconds or less. After deposition, a cross-linked conjugated network surrounds the NPs. Here we probe the SPR response of these films to solvent vapors.

II. EXPERIMENT

The Kretschmann optical setup shown in Fig. 1(b) was used for the SPR measurements.[21] Surface plasmons were excited with a p-polarized He–Ne laser ($\lambda = 632.8$ nm). The prism and sample were mounted on a θ-2θ rotation platform (resolution of 0.1°). A small glass chamber with an access port was sealed to the back of the prism using silicone cement. The port was fitted with a rubber septum to permit

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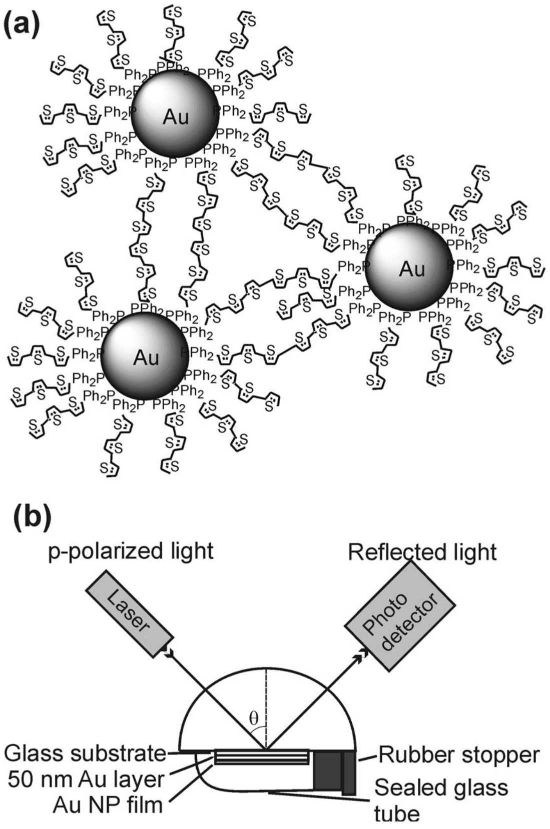

FIG. 1. (a) Schematic diagram of the electrodeposited Au NP network. (b) Kretschmann-type configuration to measure SPR.

exposure of the modified gold film to different vapors. The thin gold films were prepared by first cleaning the glass slides with piranha (1 H_2O_2:2 H_2SO_4) solution (caution: piranha solution should be handled with extreme care), rinsing with de-ionized water, and drying with a stream of N_2. Deposition of 1–2 nm of Cr followed by 50 nm of Au using an evaporation system was carried out on the clean glass substrate. The Au NP/oligothiophene (NPOT) film was electrodeposited on the 50 nm gold film following the previously described procedure.[20] A deposition time of 100 ms at 2 V was used for a solution containing 1 mg of Au NP per 5 ml of CH_2Cl_2 and 0.1M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6). Polythiophene (PT) was electropolymerized onto a 50 nm gold film with a deposition time of 3 s at 1.5 V using a solution containing 2 mg of 2,2′-bithiophene per 5 ml of CH_2Cl_2 and 0.1M n-Bu_4NPF_6. The freshly electrodeposited films were held in the same solution at 0 V for 1 min to electrochemically reduce them. These conditions gave a ~60-nm-thick NPOT film [thickness determined by atomic force microscope (AFM)] and a ~7-nm-thick PT film, respectively.

III. RESULTS AND DISCUSSION

The reflectivity as a function of the angle of incidence for a 50-nm-thick unmodified gold film (A) and the same film with a ~7 nm PT film electrodeposited on the surface (B) is shown in Fig. 2(a). The minimum in the reflectance curve (θ_0) shifts towards larger angle and the peak absorption width (Γ_w) is broader for B compared to the unmodified film A. The experimental SPR curves were fitted to Fresnel's equations with variable film thickness and dielectric constant, using a least-squares algorithm (Fig. 2).[22] The fit to B yields a dielectric constant of the PT layer (ϵ^*_{PT}) of 2.40 +0.12i, similar to the literature value (2.33+0.04i).[23]

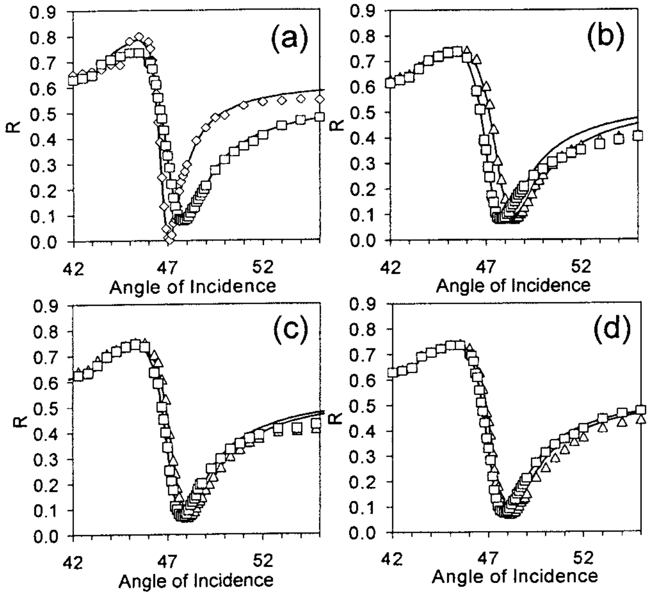

FIG. 2. SPR plots of reflected intensity as a function of the angle of incidence for (a) a 50-nm-thick gold film (◇) and a 7-nm-thick PT film on a 50 nm gold film in air (□). PT on a 50 nm gold film before (□) and after (△) exposure to (b) methanol, (c) ethanol, and (d) toluene. Solid line is the theoretical fit obtained from Fresnel's equations with variable film thickness and dielectric constant, using a least-squares algorithm.

The SPR response of the PT-modified layer B was tested upon exposure to vapors of five solvents (hexanes, toluene, ethanol, methanol, and water). Several drops of liquid solvent were introduced to the glass chamber via a syringe. After 10 min of equilibration to allow a saturated atmosphere to form, the SPR response of B was measured. Exposure to hexanes or water resulted in no change in the SPR response. On the other hand, methanol, ethanol, and toluene [Figs. 2(b)–2(d)] resulted in shifts of θ_0 to a slightly higher angle but the minimum reflectivity ($R_{\min}$) did not change. Fitting the data shows that the thickness of the PT layer increases with exposure to either of the alcohols or toluene but only a small change in the dielectric constant was observed (Table I).

The reflectivity as a function of the angle of incidence for a 50-nm-thick gold film with a ~60 nm NPOT electrodeposited on the surface (C) is shown in Fig. 3(a). The minimum reflectivity increases significantly when the NPOT is present. The measured dielectric constant of the NPOT film (Table I) agrees well with the value predicted by the Maxwell-Garnett theory (1.21+0.13i), which assumes that the dielectric constant (ϵ_{calc}) is simply a weighted average dielectric constant of the two components,

$$\epsilon_{\mathrm{calc}} = (1-\varphi)\epsilon_{\mathrm{PT}} + \varphi\epsilon_{\mathrm{Au}}, \tag{1}$$

where φ is the volume concentration of Au (Ref. 20) and ϵ_{PT} and ϵ_{Au} are the dielectric constants of electropolymerized polythiophene[23] and gold,[24] respectively. This approximation

TABLE I. SPR minimum (θ_0), thickness (d), differential reflectivity ($\Delta R_{\max}$), and real and imaginary (img) parts of the dielectric constant for the fourth layer (ϵ_4) from fitting using Fresnel's equations before and after exposure to organic vapors.

Sensor type	Organic vapor	θ_0 (deg)	θ_0' (deg)	d (nm)	d' (nm)	$\Delta R_{\max}$	ϵ_4	ϵ_4 (img)	ϵ_4'	ϵ_4' (img)
PT/50 nmAu	toluene	47.8	48.1	7.2	8.4	0.12	2.39	0.15	2.40	0.12
	methanol	47.8	48.4	7.2	10.2	0.32	2.39	0.12	2.40	0.12
	ethanol	47.8	48.0	7.1	8.3	0.14	2.41	0.08	2.42	0.09
NPOT/50 nm Au	methanol	50.6	51.2	68.6	77.3	0.08	1.23	0.13	1.25	0.15
	ethanol	50.6	51.4	60.8	72.5	0.07	1.23	0.16	1.26	0.15

is expected to hold for homogenously distributed NPs.[25,26] Electron microscopy of the electrodeposited film confirms that this is the case.[20] PT and the cross-linked oligothiophenes used here are expected to have similar dielectric constants.

The SPR response of the NPOT-modified layer C was tested upon exposure to the same five solvent vapors tested with B. In this case, exposure to hexane, toluene, and water resulted in no change in the SPR response. On the other hand, both methanol [Fig. 3(a)] and ethanol [Fig. 3(b)] resulted in shifts of θ_0 to a higher angle (0.6° and 0.8° shifts, respectively). $R_{\min}$ also increased with exposure to methanol and slightly with exposure to ethanol. Fitting the data shows that the thickness of the NPOT layer increases, and the dielectric constant increases slightly, with exposure to methanol or ethanol (Table I).

Increases in the SPR minimum angle and reflectivity after exposure of a dielectric layer to organic vapors has been previously attributed primarily to changes in the thickness of the dielectric medium (film swelling). Very small changes in the refractive index caused by vapor adsorption may also contribute.[27] Recently, a poly[3-(6-methoxyhexyl)thiophene] (P6OME) film spin cast onto a SPR gold substrate was used to detect organic vapors.[9] A 0.2° shift in θ_0 was reported after exposure to toluene due to an increase in film thickness and a slight change in dielectric constant. This shift is similar to the 0.3° shift in θ_0 and slight change in dielectric constant observed for B after exposure to toluene. However, P6OME also showed a response to hexane whereas B did not. The response depends on the solubility of a vapor in the film, which is related to the polarity of the vapor and polymer. The alkyl groups present in the P6OME film increase the solubility of hexanes in this medium relative to electropolymerized PT.

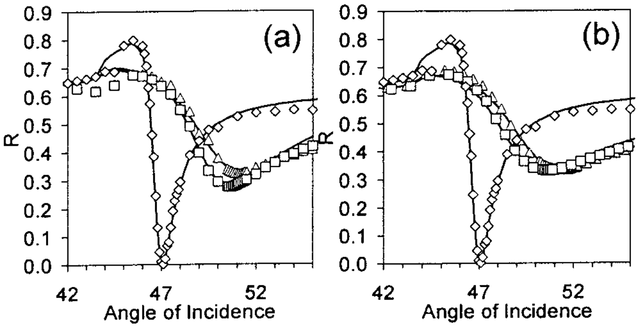

FIG. 3. SPR plots of reflected intensity as a function of the angle of incidence for a 50-nm-thick gold film (◇), a ~60-nm-thick NPOT film on a 50 nm gold film in air (□), and NPOT film on a 50 nm gold film after exposure to selected vapors (△), (a) methanol and (b) ethanol. Solid line is the theoretical fit obtained from Fresnel's equations with variable film thickness and dielectric constant, using a least-squares algorithm.

The selectivity of B and C towards alcohols can be attributed to the partially oxidized nature of the electrodeposited film. Oxidative cross-linking results in positive charge remaining on the conjugated polymer or linkers (compensated by the presence of negative $[PF_6]^-$ ions in the film). Prior to use, the films are reduced electrochemically; however, this is an incomplete process and some charges remain. The partially oxidized nature of the NPOT film is evidenced by the presence of phosphorus and fluorine from the $[PF_6]^-$ ions in energy-dispersive x-ray (EDX) analysis of the films and the higher binding energy of the Au $4f_{7/2}$ peak in the x-ray photoelectron spectrum (XPS) of NPOT relative to unlinked NPs.[20] The static contact angle measured for a water drop on the surface of C was $(64\pm3)°$. This indicates that C is slightly more hydrophilic than oxidized polythiophene,[28] suggesting a possible explanation why B also responds to the less polar solvent toluene. The lack of response to water for both B and C could be due to either low vapor pressure (23.74 mm Hg at 25 °C) for water compared to either alcohol or to poor solubility of the highly polar water molecules in the polymer.

Previous work by Lyon and co-workers[16,17] demonstrated that a Au NP layer adsorbed on a gold film results in changes to θ_0, Γ_w, and $R_{\min}$, and these changes are linked to enhanced detection sensitivities. Roy and Fendler[14] calculated SPR plots for analyte detection and predicted larger θ_0 shifts and improved detection sensitivities with Au NPs present compared to without. According to Roy and Fendler,[14] addition of Au NPs to a dielectric material such as in C should introduce LSP and PSP interactions leading to increased sensitivity. Although a larger increase in θ_0 for C ($\Delta\theta_0 = +0.8°$) in response to ethanol compared to B ($\Delta\theta_0 = +0.2°$) and a larger increase in $R_{\min}$ for C compared to B in response to methanol were observed, lower alcohol detection sensitivities for C compared to B can be seen from the respective SPR plots (Figs. 2 and 3). This is because from a practical detector standpoint, it is not the total transformation of the curve that is important in SPR sensing but rather the maximum change in reflectivity that can be observed at a fixed angle,

$$\Delta R_{\max} = \frac{R' - R}{R}, \quad (2)$$

where R and R' are the reflectivities before and after exposure to an analyte, respectively. Table I tabulates the values of $\Delta R_{\max}$ for B and C, and B is shown to have a larger detectable response to the organic vapors. We therefore do not find evidence to support improved detection sensitivities from the incorporation of Au NPs into PT for use in a SPR device.

Although no evidence was found for an increase in sensitivity from incorporating Au NPs into PT, there does appear to be an improvement in selectivity. The selectivity of C towards alcohols and lack of response towards toluene give it an advantage over traditional infrared detection of alcohols which is susceptible to interference. For example, Intoxilyzer 5000©, a widely used instrument for measuring ethanol in motorist's breath, is susceptible to reporting false positive readings for ethanol in the presence of methyl-substituted aromatics such as toluene and xylenes.[5] This is because methyl-substituted aromatics have a similar IR absorption as ethanol at 3.48 and 3.39 μm where the instrument is calibrated to detect ethanol. Since C is selective towards alcohols due to its partially oxidized nature, it appears to be immune to interference from nonpolar aromatic solvents. The information delivered by C in an SPR sensor could eliminate false positives introduced by methyl-substituted aromatics.

IV. CONCLUSIONS

The response of electrodeposited PT and NPOT films employed in a Kretschmann-type SPR configuration was found to be selective when exposed to selected organic vapors. There is a detectable response to ethanol, methanol, or toluene for PT and ethanol or methanol for NPOT. The films show changes in θ_0, $R_{\min}$, and dielectric constant after exposure to alcohol vapors. Although we do not find a significant improvement in sensor sensitivity in incorporating Au NPs in this application, it is possible that the general approach for a one-step embedding of metal NPs into dielectric materials may prove useful in other SPR sensors.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and one of the authors (J.Y.) would like to acknowledge the support of the Canadian Institute for Advanced Research.

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