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PDMS-based Optical Leaky Waveguide Coated with Self-assemble Au-NPs for Bio-analytical Detections

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Abstract: This paper presents a novel method for fabricating PDMS-based optical leaky waveguides coated with self-assembled gold nano-particles (Au-NP) for bio-analytical detection utilizing the localized surface plasmon resonance (LSPR) effect. In the presented method, a PDMS optical waveguide is first cast in Teflon tubing to form a cylindrical leaky waveguide structure. The de-molded PDMS optical waveguide is then modified with PDDA molecules and coated with a layer of 13 nm Au-NPs for inducing the LSPR effect. The fabricated LSPR sensor is finally connected to multi-mode optic fibers for guiding the detection light. The measured sensitivity of the PDMS waveguide based LSPR sensor for detecting diluted glycerol solutions was 7.25 AU/RIU and 325.97 nm/RIU. Experimental results of a label-free detection of DNA hybridization show that the presented PDMS waveguide based LSPR sensor has a good linear response and has a detection limit of about 10pM, confirming the detection performance of the developed PDMS waveguide-based LSPR sensor.

Keywords: PDMS waveguide; localized surface plasmon resonance; LSPR, PDDA molecule; SDS; multi-mode optic fiber

Introduction

Surface plasmon resonance (SPR) is widely applied in biological and chemical sensing for characterizing and quantifying the interactions of bio-molecules [1-3]. The typical advantages of SPR detection methods include high sensitive response, kinetic study in real-time, and label-free biological sensing [4, 5]. SPR detection is sensitive to the local change in the refractive index (RI) within a few 100nm of a metal surface. Optic-fiber based bio-sensors have the characteristics of being small, low-cost and having good compatibility with SPR detection schemes. In general, waveguide-based SPR sensors have been fabricated by spattering a thin layer of gold on etched optic fibers [6, 7]. However, coating a uniform metal layer on a cylindrical surface is of great difficulty. Therefore, a new method was developed to fabricate fiber-based SPR sensors which uses a self-assemble process to deposit gold-NPs on the etched optic fiber [8].

Recently, nano particles (NPs) have been widely used for bio-sensing applications, especially in use for integration with SPR-based biosensors [9]. The developed process has been termed *localized surface plasmon resonance* (LSPR) [10]. LSPR is a resonance phenomenon of free electron waves on the surface of nano-structure metal particles or nano-scale rough surfaces [11]. Surface plasmon resonance effect can be greatly enhanced from to the greater surface area and greater electron density of gold NPs (Au-NPs) [12]. Recently, the surface confined binding constant of Alzheimer's disease was measured and detected using a Au-NP-based localized SPR sensor [13]. As mentioned, LSPR has been usually achieved by coating metal nano-particles on the surface of an etched optic fiber [8, 14, 15]. Nevertheless, the etching process for exposing the core of an optic fiber is difficult to control [16, 17].

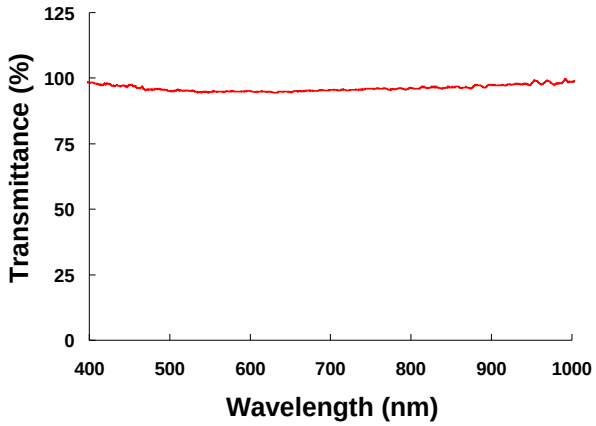

Figure 1. Measured optical transmittance of PDMS film with the thickness of 3.0 mm. The transmission rate is higher than 95% in the measured range.

In addition, the etched optic fiber is fragile and can be easily damaged during post processing processes. [18]

This paper presents a novel method to fabricate fiber-based LSPR sensors utilizing a cast Polydimethylsiloxane (PDMS) leaky waveguide. PDMS is a popular and widely used material in the micro-electro-mechanical-system (MEMS) community. PDMS has excellent optical properties including highly optical transparency, good flexibility and high bio-compatibility. It is an excellent material for optical applications due to its high refractive index of 1.5 and high transparency in the VIS-NIR wavelength. Figure 1 shows the measured optical transmittance of a 3.0 mm-thick PDMS film. The high transmission property of PDMS made it an ideal material for optical waveguide application.

In our novel approach, a glass-based fiber etching processes is not required, meaning that the fabrication process is more simple and reliable. A novel process of achieving surface flatness is utilized to improve the optical performance of the leaky waveguide. The evaluation of the surface morphology, insertion loss, and the Au-NP's coating behavior prior to performing real bio-analytical applications is presented below. This is followed by an evaluation of the developed PDMS waveguide-based LSPR sensor using a complementary ssDNA binding test.

Yi-Chieh Chen received his B.S. from the Department of Industrial Education, National Taiwan Normal University in 2006. He earned his M.S. from the Institute of Mechanical and Electromechanical Engineering, National Sun Yat-sen University in 2008. His research interest is in developing new MEMS-based optical sensors.

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Sensor Design

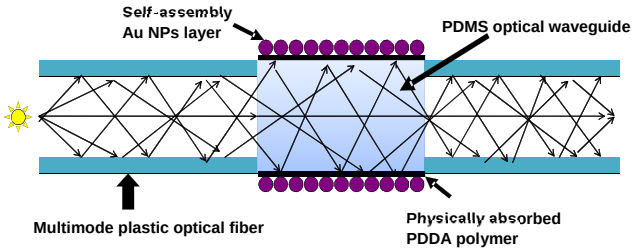

Figure 2. Schematic presentation of the proposed PDMS waveguide for LSPR detection.

Figure 2 presents the design concept of the proposed method for the PDMS waveguide-based LSPR sensor. The PDMS leaky waveguide was first cast in Teflon tubing and then connected with two multi-mode optic fibers for leading the detection lights in and out of the tubing. Au-NPs of 13 nm in size were then deposited onto the cast PDMS waveguide using a self-assembly process with the assistance of positively charged PDDA molecules (Poly-diallyl-dimethyl-ammonium chloride).

Materials and Method

(a) Fabrication

In the present approach, 13 nm Au-NPs were coated on the PDMS surface with the assistance of a positively charged polymer of PDDA to form an optical waveguide capable of LSPR detection. Since PDMS is a hydrophobic material, the coating of PDDA molecules and Au-NPs onto the PDMS surface is challenging. In this regard, an atmospheric plasma treating process was used to effectively enhance the coating ratio and speed of Au-NPs. Figure 3 presents a simplified schematic for the fabrication process of the proposed PDMS optical waveguide based LSPR sensor. First, a PDMS elastomer was filled into the Teflon tubing (diameter of 500 μm and length of 15 mm). The PDMS elastomer was then cured in an oven at a temperature of 100°C for 30 min (Figures 3(a) and 3(b)). Since there was no adhesion problem

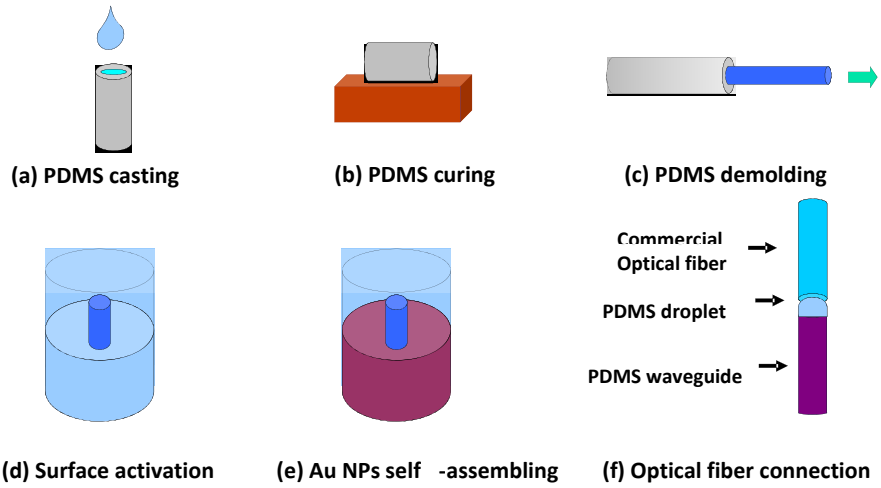

Figure 3. Simplified schematic for fabricating the gold nano-particle coated PDMS optical waveguide.

between the PDMS elastomer and the Teflon tubing, the cast PDMS core could be easily pulled out of the tubing for de-molding (Figure 3(c)). Once the PDMS waveguide was cast, its surface was then smoothed again by being treated with oxygen plasma and then immersed into a 1% PDDA solution (Sigma, USA) for 8hr (Figure 3(d)). Then, the positively charged PDDA molecules could absorb a layer of gold-NPs on the surface of the PDMS optical waveguide (Figure 3(e)). Commercial plastic optic fibers (500 μm POF, Unice Optic Ltd. TAIWAN) were polished at the cutting ends for leading the detection lights. The NP-coated PDMS waveguide was cut to 10 mm and finally connected to the optic fibers with PDMS polymer via a novel self-alignment process (Figure 3(f)).

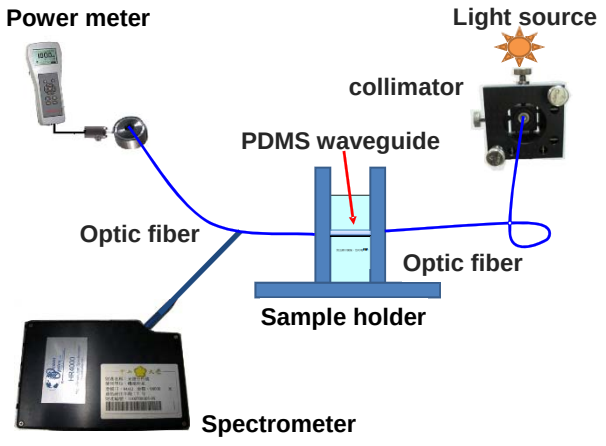

Figure 4. Illustration of the experimental setup.

(b) Experimental setup and apparatus

Figure 4 illustrates the experimental setup for LSPR detection demonstrated in this study. A PDMS optical leaky waveguide of 10.0 mm coated with Au-NPs was used in the present study for bio-analytical detection without fluorescence labeling. To build the sensing system, a continuous-wavelength light source (350-850 nm, 150 W, L150, D&R Co., TAIWAN) was fed into the lead-in optic fiber via a SMA coupler (ES01T, Onset, TAIWAN). The PDMS waveguide was fixed in a drilled polycarbonate standard cuvette (10 mm x 10 mm x 30 mm) for solution-based detections. The output of the other end of the sensor was connected to a power meter (SOLO PE, Gentec EO., CANADA) for insertion loss measurement, and to a UV-VIS-NIR spectrometer (HR4000, Ocean Optics, USA) for wavelength resolved SPR measurement. Note that the detections were performed inside a constructed light-shielding box to eliminate the noise from the background lights. Diluted glycerol solutions with various concentrations and conjugated ssDNA molecules were used for evaluating the sensing performance of the developed PDMS-based localized surface plasmon resonance sensor.

Results and Discussion

In order to enhance the optical performance of the PDMS leaky waveguide, the cast PDMS waveguide was coated with a thin layer of diluted PDMS to reduce the surface roughness of the cast PDMS structure. Figure 5(a) shows the SEM image of the fabricated PDMS optical waveguide after the surface smoothening process, confirming the excellent surface quality of the fabricated PDMS leaky waveguide. The coating uniformity of the Au-NPs layer is an important issue for LSPR detection performance. Since this study used physical absorption between the opposite charges for PDDA and Au-NPs, the coating Au-NPs tended to form a single layer. Figure 5(b) presents the close-up view of the Au-NPs coated PDMS leaky waveguide. The image indicates that the coating

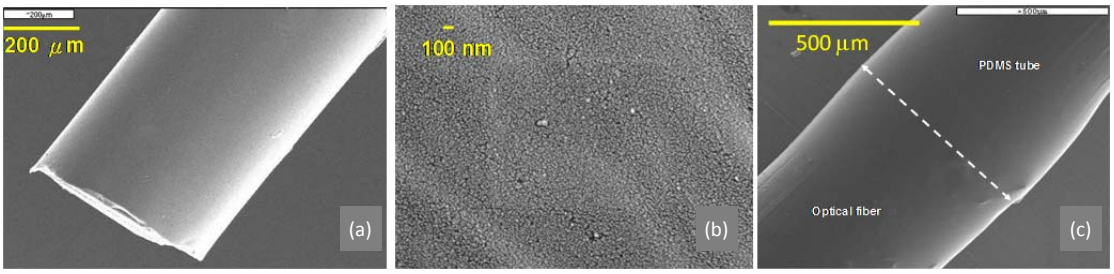

Figure 5. SEM images of (a) the fabricated PDMS optical waveguide, (b) the close-up view of the gold nano-particle coated PDMS surface and (c) close-up view of the connection region for the PDMS waveguide and the plastic optic fiber.

layer of the Au-NPs was quite uniform and dense. Figure 5(c) shows an SEM image of the close-up view for the connection region between the plastic optic fiber and the PDMS optical waveguide. Results show that the interface between the optic fiber and the PDMS optical waveguide disappeared after the connection. The images presented in Figure 5 confirm excellent surface smoothness and that a uniform coating of Au-NPs were achieved with this presented method.

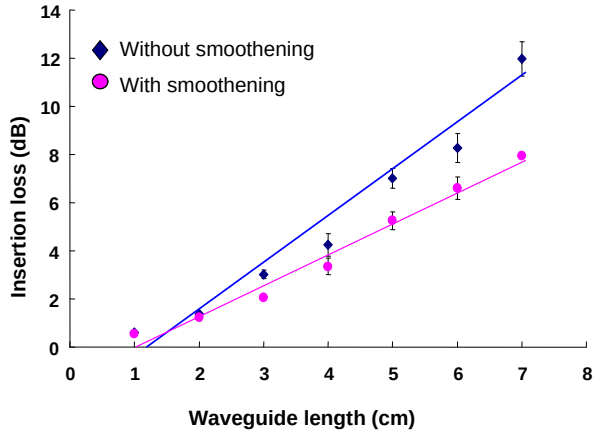

Figure 6. Measured insertion loss of the fabricated PDMS optical waveguides with and without the surface smoothing.

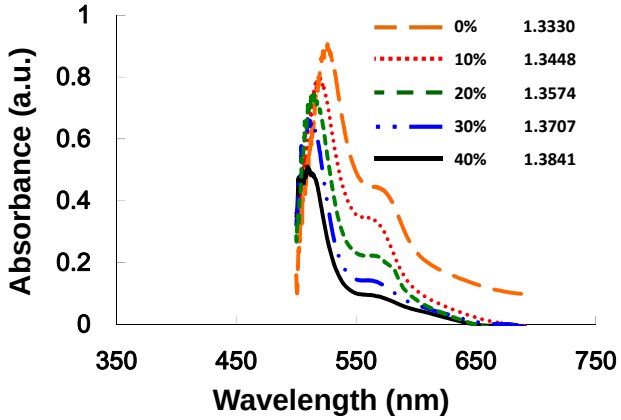

Figure 7. Optical spectra for measuring different concentrations of diluted glycerol solutions.

In order to further evaluate the optical performance of the PDMS waveguide enhanced by the post PDMS coating process, the insertion loss for the PDMS leaky waveguides was measured, as shown in Figure 6. Results indicate that the post PDMS coating process significantly reduced the optical losses of the PDMS leaky waveguides. The measured insertion losses were 1.71 dB/cm and 1.14 dB/cm for the waveguides with and without post smoothening process, respectively.

Figure 7 shows the optical spectra for measuring diluted glycerol solutions with concentrations from 0% to 40%. Since the reflective index of glycerol is around 1.474, the corresponding reflective indexes for the measured sample solutions were 1.333, 1.344, 1.357, 1.371 and 1.384, respectively. Since the reflective index of PDMS material is about 1.43 and the reflective index of 40% glycerol is around 1.3841. Glycerol of higher concentration resulted in smaller reflective index change between the PDMS leaky waveguide and the surrounding media. The leakage of the wavelength increased and less light was detected. Therefore, the calculated absorbance appeared higher compared with the values of detecting glycerol solutions of lower concentrations. In this regard, greater optical losses and noise would happen while measuring high reflective index solutions.

The sharp and narrow spectrum obtained by the Au-NP coated PDMS waveguide also confirms the nice coating results of Au-NPs on the PDMS waveguide. Further, the significant wavelength shift and absorption peak reduction confirm the successful performance of the proposed PDMS-based LSPR sensor. The calculated sensitivity for the developed LSPR sensor was 7.253 AU/RIU and 325.97 nm/RIU for absorbance and wavelength shift measurement, respectively.

Prior to the label-free DNA hybridization detection, the immobilization kinetic of the probe ssDNA on the LSPR sensor was investigated. Thiolated ssDNA with the sequence of 5'Thiol-AAGGCCTTCCGGAAT was used as the probe ssDNA. The thiol group on the thiolated ssDNA binds onto the surface of Au-NPs and forms covalent

bonds, resulting in the change of the optical properties on the binding surface. For this immobilization test, the LSPR sensor was immersed into a 100 μM thiolated ssDNA solution, and the peak absorbance was recorded every 30 min after immersion. Figure 8 presents the measured absorbance at different time stages. Results show that the immobilization of the probe ssDNA reached saturation after 2.5 hr. The LSPR sensor was then used for sensing the target complementary DNA molecules.

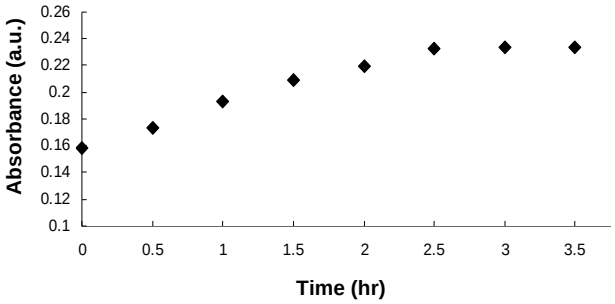

Figure 8. Measured absorbance change versus the time for single-strain DNA probe immobilization.

In order to obtain a stable baseline for DNA conjugation testing, the probe immobilized LSPR sensor was immersed in a 3.0 mL PBS solution at a temperature of 36°C for 5 min. Complementary ssDNA solutions with the concentration from 100 μM to 100 pM were prepared for this test. A 30 μM prepared ssDNA solution was injected into the PBS solution for DNA conjugation, resulting in a sample concentration from 1 pM to 1 μM. The conjugation reaction was performed for 1 hr to ensure total reaction for the DNA samples. Figure 9 presents the relationship between the measured absorbance changes versus the concentration of the target complementary ssDNA. The values were averaged from three independent tests using the same LSPR sensor. There was a good linear response between the peak absorbance and the concentration. It is observed that at extreme low concentration conditions (lower than 10^{-9} M), the measured absorbance values reached the detection limit of the measuring apparatus such that absorbance change was not significant and resulted in small standard errors. A detection limit of 10 pM was achieved without using the delicate measurement techniques. Experimental results confirm the high detection performance of the proposed LSPR sensor fabricated using the presented method. The developed method provides a simple and low-cost way to fabricate high-performance waveguide-based optical sensors.

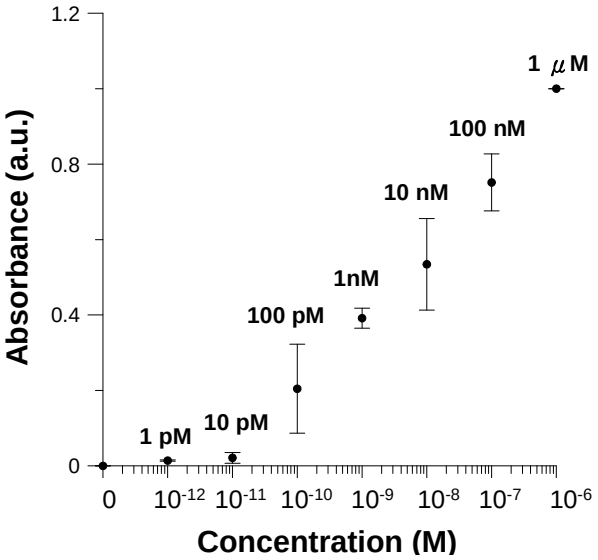

Figure 9: Measured absorbance change versus the concentration for detecting the complementary single-strain DNA target.

Conclusion

This research proposed a novel polymer-based optical waveguide made with PDMS for optical detection applications. Alternative to other fiber-based sensors, the proposed optical sensor used PDMS waveguide as the main sensing component. Uncured PDMS polymer was cast in Teflon tubing to form the PDMS rod. Since the reflective index of PDMS is as high as 1.43, the bare PDMS could be an optical waveguide so long as the reflective index of the surrounding media is smaller than 1.43. The cast PDMS waveguide was then connected with plastic optical fibers to form the proposed optical waveguide system. The measured insertion losses with and without performing the surface coating procedure were 1.14 dB/cm and 1.71 dB/cm, respectively. Liquid samples with different refractive indexes were used to demonstrate the LSPR sensing ability of the fabricated optical waveguide. Label free DNA detection was also demonstrated by the system. The thiolated single strand DNA was modified on the PDMS optical waveguide as a DNA probe and bound with target DNA by DNA hybridization. The detection limit was measured at as low as 10pM. This research provides a simple and fast method to fabricate waveguide-based LSPR sensors.

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