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High-sensitivity sensor based on surface plasmon resonance and heterodyne interferometry

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Abstract

A common-path, heterodyne interferometric system for investigation of the phase variations under surface plasmon resonance (SPR) is presented. With the combination of SPR and total internal reflection (TIR), the system has the merits of avoiding direction change in the output light and increasing sensitivity. The system utilizes a pair of orthogonally linearly polarized beams with heterodyne frequency of 60 kHz as the light source. Because the two beams are perfectly collinear, the noises resulting from the ambient conditions are greatly reduced. Compared to reflectivity variation measurement, which is widely used in traditional SPR, the phase variation measurement using common-path, heterodyne techniques is approximately an order of magnitude higher in sensitivity and thus can be used as a high-sensitivity-demanded biosensor.

Keywords: Surface plasmon resonance; Sensors; Interferometers; Waveguides; Phase measurement

1. Introduction

The evanescent wave of a surface plasmon is a powerful tool to detect binding of analytes to thin receptor films on the sensor surface. Most research has focused on investigating the energy transfer from the incident wave to the surface plasmon wave (SPW). The surface plasmon resonance (SPR) manifests itself on a dip in the angular dependence of the intensity of the reflected light. The energy of the light beam is used to excite surface plasmons, which then quickly decay and dissipate as heat during their propagation.

Several methods have been employed to monitor the excitation of SPR by measuring the reflection coefficient from the sensor interface. These include analysis of angle modulation [1], wavelength modulation [2], and intensity modulation [3]. The angle modulation technique involves measuring the reflected intensity dip versus the change of reflective index over a range of incident angles. Because of its simplicity and ease of use, this technique has been studied extensively and pushed to the commercial end. However, it has been demonstrated that the absorption in the sample medium strongly influences the minimum high at the dip [4]. Furthermore, the low signal-to-noise ratio at the dip and the difficulty of determining the minimum of a smooth-curved dip give rise to the detection limit of this method not above the range of physiological concentrations for most biomolecules, making in vivo measurement impossible. A technique combining the dip-position and the dip-height measurement has been demonstrated a moderate improvement [5]. The wavelength modulation technique is similar to the angle modulation one. It involves measuring the reflected intensity dip versus the change of refractive index (RI) over a range of incident wavelengths. The intensity modulation techniques involve measuring the intensity at a fixed value of incident angle or incident wavelength directly. Unfortunately, these techniques not only suffer the drawback of angle modulation but are also disadvantaged by its limited dynamic range. The advantage of such intensity detection is its simplicity. However, the measurement accuracy is degraded due to dc shift in the light source, receiver, and amplification circuit.

Higher detection sensitivity is always desirable for improving sensing performance. Fortunately, it has been found that the phase can change much more abruptly than the intensity as the refractive index or thickness of a binding layer on the surface has been changed [6]. Several methods

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have been employed to monitor the excitation of SPR by measuring the phase change from the sensor interface. These include analysis of polarization state [7], shear interferometry [8], Mach–Zehnder interferometry [9,10], and heterodyne interferometry [11,12]. The polarization state method is based on measurement of the ratio of the p- and s-polarized components in reflected light. A RI sensitivity of 3×10^{-5} was reported [7]. Spatial interference patterns which image the angular dependencies of the SPR reflected light phase have demonstrated by the shear interferometry. The poor spatial resolution of interference patterns limits the method to be an impractical one. The Mach–Zehnder interferometry, always containing a pair of spatial-separated reference and measurement paths, has been successfully applied to the measurement of phase changes in SPR [9,10]. The sensitive dependence of phase changes on the environment due to the different paths for reference beam and measurement beam, respectively, makes this type of interferometry noisier than that of heterodyne interferometry. In contrast to the TE wave, in which the phase keeps unchanged after being reflected from the SPR interface, the TM wave exhibits a strong phase shift character. The relative phase shift between the collinear TE and TM waves gives raise to the common-path heterodyne interferometer being realized. Because its reference (i.e. the TE wave) and measurement (i.e. the TM wave) beams are collinear, this type of interferometry is the most immune one to the environment.

In this paper, we present an interferometric sensor based on surface plasmon resonance and heterodyne interferometry. With the SPR device, the sensor further contains a total internal reflection (TIR) device. The TIR not only enhances the relative phase shift between the TE and TM waves but also keeps the output beam to be parallel or anti-parallel to the input beam, which is important for the detector to avoid tracing the output beam to achieving maximum sensitivity. The interferometric system utilizes a pair of orthogonally linearly polarized beams generated by two acousto-opto-modulators. They are perfectly collinear so that the noises resulting from the environment are greatly reduced. Compared to the technique of reflectivity variation measurement, which is widely used in traditional SPR, the phase variation measurement using common-path, heterodyne techniques is estimated to be an order of magnitude higher than that of the previous one in sensitivity and thus can be used as a high-sensitivity-demanded biosensor. The developed sensor was used to distinguish the methanol, water, and ethanol. Experimental results confirmed that the RI sensitivity down to 2×10^{-7} was detectable.

2. Principles of experimental design

In this experiment, the numerical simulations of SPR were performed on a three-layer (Bk7 glass–gold–air) system to model our experimental conditions. The permittivities of Bk7 glass prism (ε_3), gold film (ε_2), and air (ε_1) used in the experiment were $\varepsilon_3 = 2.293$, $\varepsilon_2 = -12 + 1.26i$, and $\varepsilon_1 = 1.0$, respectively. The incident light was from a stabilized He–Ne laser with wavelength of 633 nm.

A schematic diagram of the developed high-sensitivity sensor combing a common-path heterodyne interferometer, a SPR device, and a TIR device is shown in Fig. 1. Two acousto-opto-modulators, one excited at 40 MHz and the other excited at 40.06 MHz, were used to split the incoming laser light from a linearly polarized, stabilized He–Ne laser into two linearly orthogonally polarized beams having a frequency difference of 60 kHz. These two lights were emerged into one beam through a polarization beam splitter (PBS_2). The single beam having TE and TM components with frequency ω_1 and ω_2, respectively, was further imparted into two beams by a beam splitter (BS). One of the beams was interfered after a polarizer (Pol_1) and then was converted into electrical signal by a photo-detector (PhD_1), and it served as the reference signal for the experiment. The other one impinged onto a metal/air interface where the SPW occurred when the incident angle matched to the SPR conditions. The reflected beam was further reflected at a second glass/air interface where the TIR occurred. Information caused by the SPR and further amplified by the TIR were carried in the TE and TM waves, respectively, and interfered at a polarizer (Pol_2). The optical signal was then converted into an electrical signal at a photo-detector (PhD_2), which served as the measurement signal. The reference signal I_r and measurement signal I_m have the forms:

$$I_r \propto E_{so}E_{po}\cos(\Delta\omega t), \tag{1}$$

$$I_m \propto |r_p|E_{so}E_{po}\cos(\Delta\omega t + \phi), \tag{2}$$

where E_{so} and E_{po} are the real amplitudes for TE wave and TM wave, respectively, $\Delta\omega$ represents the beat frequency of TE and TM waves, and ϕ stands for the phase shift between TE and TM waves after undergoing both the SPR and TIR.

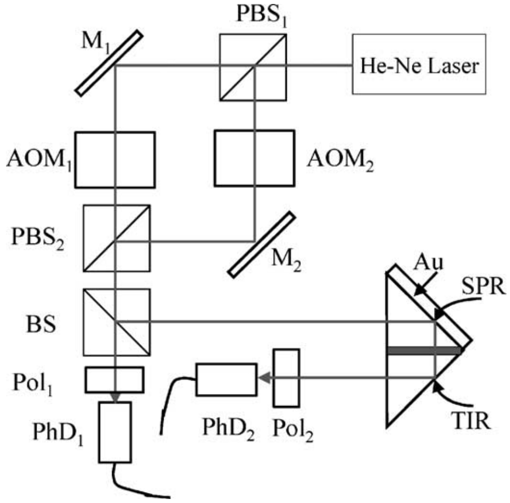

Fig. 1. Schematic configuration of an experimental set-up. PBS, polarizing beam splitter; M, mirror; BS, beam splitter; AOM, acousto-opto-modulator; Pol, polarizer; PhD, photo-detector.

Here we assume that the reflected intensity of the TE wave is unchanged after exciting both SPR and TIR, and that the reflected intensity of the TM wave is only altered by the excitation of the SPR. The real-time phase shift ϕ can be obtained simply by an electronic phase meter. In the experiment, a commercial dual-phase lock-in amplifier was used (not shown in figure). By taking the ratio of I_m to I_r, which can be directly read out by the lock-in, the reflection coefficient r_p of the TM wave was also obtained simultaneously.

3. Experimental results and discussion

A right-angle prism (Bk7 glass) having one side-face being coated with 47 nm gold film was used as a SPR device. The other side-face of the prism was without any coating but exposed to the air, and served as the TIR device. It can be also realized by putting another right-angle prism, as a TIR device, with its side-face adjacent to the side-face of the SPR device. There is an inconvenience to measure the phase or intensity using a single SPR device. Angle between the reflected and incident beams always varies as the incident beam, or the SPR device itself, is scanned. This implies that the photo-detector should scan accordingly. In our experiments, this problem is overcome by the combination of a SPR and a TIR device. The reflected beam from the combination sensor (undergoes a SPR reflection and a TIR reflection) is always anti-parallel to the incident beam no matter how the incident beam is scanned.

The use of combined SPR and TIR structure is not only improving the advantage of spatial orientation but also enhancing the phase shift variation by adding an extra phase shift caused by the effect of total internal reflection. A second simulated curve showing the phase difference between the TE and TM waves, according to the Fresnel's equations [13], as a function of the incident angle of the TIR device is given in Fig. 2. Due to the phase difference between the TE and TM waves, the phase shift after the SPR device is further amplified. The same permittivity for glass prism was used and the refraction index for air was $n_z = 1.0$.

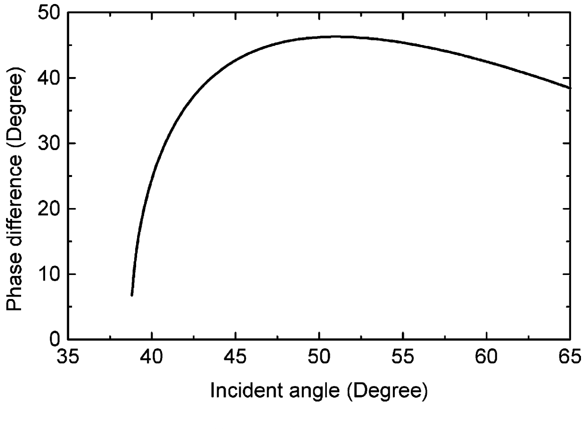

Fig. 2. Simulated phase difference between the TE and TM waves. The refractive indices for the two mediums are $n_2 = 1.515$ and $n_1 = 1.0$, respectively.

To verify experimental system, we first put the SPR device on a precision rotary table (resolution: 0.001°), then the phase shift and intensity reflection variations were recorded simultaneously by a lock-in amplifier, respectively. The measured phase shift (solid line with square symbol) and the simulated phase shift are shown in Fig. 3. They are matched to each other so that the usefulness of our system is verified. To demonstrate the improvement in the sensitivity of using the TIR device, both phase shift variations for the SPR device only and the combined SPR and TIR device were recorded (see Fig. 4). The slop of phase shift for the combined sensor is steeper than that for the SPR device only around the resonance angle, implying that the sensitivity (defined by the ratio of incremental phase shift to incremental incident angle) of combined SPR and TIR is superior. The sensitivity for the SPR only is about $K = 1400$ while that for the combined SPR and TIR is about $K = 2250$. For applications requiring the highest sensitivity, the combined SPR and TIR would be one of the best candidates.

With the high-sensitivity sensor, many chemical substances can be detected and verified. The methanol (permittivity: 1.329), water (permittivity: 1.33), and ethanol (permittivity: 1.3612) were put into a fluid cell, respectively, and attached

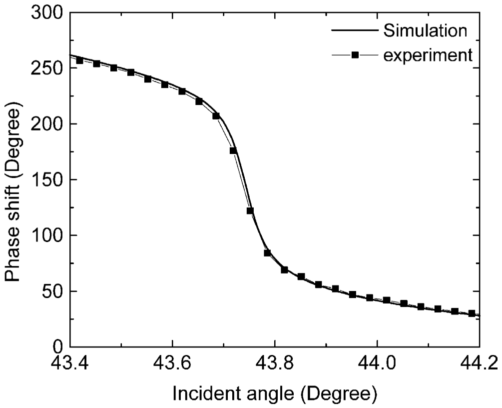

Fig. 3. Comparison of simulated and measured results for a SPR with gold film: 47 nm.

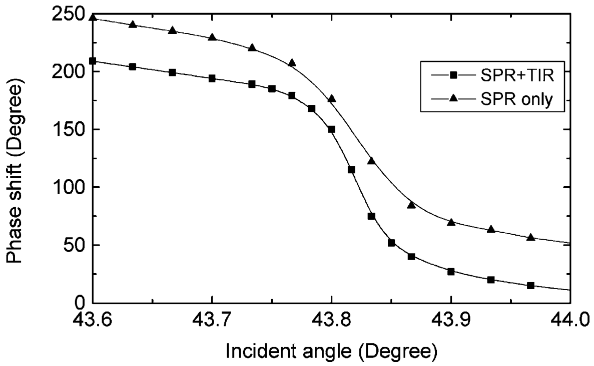

Fig. 4. Comparison of measured phase shift between the SPR device and the combined SPR and TIR devices. The metal film is Au: 47 nm.

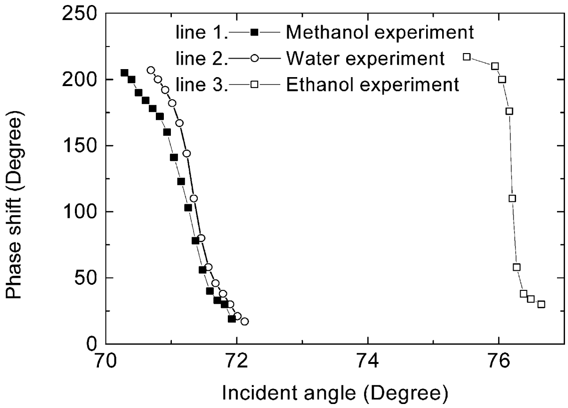

Fig. 5. The phase shift variations vs. incident angle for methanol, water, and ethanol.

onto the gold surface, the SPR detection surface, to see the phase shift variation versus incident angle. The results are shown in Fig. 5. The ethanol will get maximum phase shift (i.e. the resonance angle) near 76° while the methanol and water will all be near 71°. There are 5° apart for permittivity-difference of about 0.03. Our system is a high sensitive sensor in distinguishing different fluid or gas substances by means of detecting its permittivity. Even the methanol and water, their permittivity-difference is as small as 8×10^{-4}, they can be easily distinguished (see Fig. 5). Because the lock-in amplifier used in the experiments is with phase resolution, $\Delta\varphi$, of better than 0.01°, the permittivity-difference, δn, between the methanol and water is 8×10^{-4}, and the phase-shift difference, $\delta\varphi$, between the methanol and water is about 40° (see Fig. 5), RI sensitivity

$$\mathrm{RI} = \frac{\Delta\varphi}{\delta\varphi/\delta n} \tag{3}$$

is estimated to be 2×10^{-7}, the best RI sensitivity compared to other reports [7,11].

4. Conclusions

A collinear, heterodyne interferometric system based on combined SPR and TIR devices was proposed and realized. This new scheme can provide an enhanced sensitivity of real-time phase detection. The spatial variations of orientation of the reflected beam are overcome. Both the phase variation and intensity variation measurements can be simultaneously obtained on the same system. They are perfectly collinear so that the noises resulting from the environment are greatly reduced. Compared to the technique of reflectivity variation measurement, which is widely used in traditional SPR, the phase variation measurement using common-path, heterodyne techniques is estimated to be higher in sensitivity and thus can be used as a high-sensitivity-demanded biosensor.

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