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Surface Plasmon Resonance Device with Dielectric Mirror for Biochemical Sensing

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***Abstract* - We have reported a novel design of Surface Plasmon Resonance (SPR) device, which uses alternative dielectric layers to enhance the SPR signal quality and modulate its resonant position. Admittance loci method of thin film design has been used in the design of such a device. The fabricated device results in a calibration curve, y= 0.124x + 62.39 (R^2=0.99) of different glucose concentrations.**

I. Introduction

It has been an important subject for the studies of free electrons (plasma) behavior near the metallic-dielectric surface. Such a high density electron gas, which experience collective longitudinal excitation/oscillation, can have particle behavior and has been named "plasmons" for quanta representation in analogous to phonos, magnons and excitons [1,2]. Such phenomena were first discovered at early 20th century on metal grating and with prism coupling method later during 1970s [3]. It has been extensively used to study optical properties of metallic thin film, including index of refraction (n), extinction coefficient (k), thickness (d) and even roughness [4, 5]. The surface-localized electromagnetic wave with its electric field maximized at this surface will diminish exponentially on both sides with penetration distance from the interface. It can be used to probe the vicinity of metallic-dielectric interface in the range of several hundred nanometers [6]. However, its generation has to fulfill (1) surface active medium has a negative value for the real part of its complex dielectric constant (e.g. Au or Ag), (2) momentum matching between excitation and plasmons resonance. The changes in the reflective intensity (reflectance) are recorded as SPR spectra. This can apply for the design of SPR biochemical sensor to monitor the shift of SPR signal due to the presence of immobilized or captured molecules. Its unique characteristics of non-labeling and real-time monitoring have found special interests in biomedicine [7-13]. It has not been reported that a SPR device incorporated with dielectric mirror of alternating high/low refractive index materials [14, 15] as shown in the figure 1. In this paper, we will discuss the application of this method for the design of such a device and its performance [unpublished].

II. Materials and Methods

A. Design & simulation

Our design of novel SPR device is based on

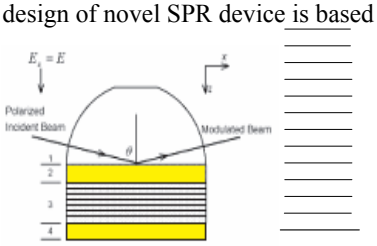

Fig. 2. Symmetric SPR device with DBR overlay structure and design.

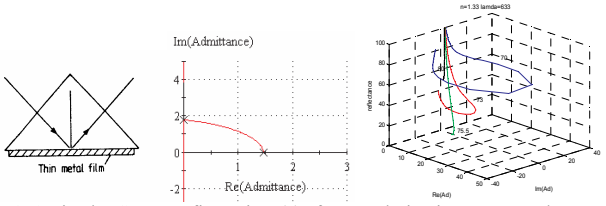

Fig. 2 As in the SPR configuration (a), for P-polarization wave under total internal reflection, a thin metallic film, (b) the admittance loci will leave the imaginary axis and could have the chance to approach the real axis to let the reflectance becomes zero, (c) 3D plot of the admittance loci (Re, Im) vs reflectance for different incident angles with prism (dense medium) n=1.5, gold film: d=50nm, water n=1.33, and the wavelength=633nm. The calculated critical angle is 62, and the reflectance SPR angle is around 74.5 degree, this is ATR angle.

corrugated grating structure and distributed Bragg reflector, which can be treated as dielectric mirror made from alternating high and low refractive index quarter-wave thick multilayers. Figure 2 shows a proposed model device, which has a symmetrical structure of Au/(SiO2, /TiO2)$_y$/Au (y=4). The simulation program is developed by using MATLAB 5.3 (Mathworks Inc) and the results were verified by using a commercial software package (Essential Macleod 8.5, Thin Film center Inc., USA).

The locus on the Re (Admittance) and Im (admittance) plane calls admittance diagram or admittance loci. It can be used to calculate the equivalent admittance (Ye), which moves its trajectory from the substrate admittance (Ys) as the thin film thickness changes. We can thus visualize the effect due to thin film dielectric properties. The effects of an ideal metallic thin film with either cases of Y = -ik or Y = n-ik can be viewed on the loci plot as moving from k to k on the Im axis or from (-n, k) to (n,-k) with bigger locus due to greater

k/n value. Total internal reflection (TIR) is another special case, which requires detail discussions. TIR occurs when the light leaves from denser medium into less denser medium and the angle of incidence is greater than the critical angle(θc).While incident angle is smaller than critical angle, the admittance is on the real axis. On the other hand, when the incident angle is larger than critical angle, the admittance will become an imaginary number. If we put a dielectric thin film, the admittance of the combination will move along the imaginary axis in a positive direction, and returning to starting point every half-wave of film thickness. One can make the admittance leave the imaginary axis by an absorbing layer (fig. 2b). Under appropriate incident angle and thickness of a metallic film, it can have near zero reflectance, which is surface plasmon resonance (SPR). As shown in the fig. 2c, a 3D plot of the admittance loci (Re, Im) vs reflectance for different incident angles with prism (dense medium) n=1.5, gold film: d=50nm, water n=1.33, and the wavelength=633nm. The calculated critical angle is 62, and the reflectance SPR angle is around 74.5 degree.

B. Materials

Standard glass slide for microscopy (SuperFrost–100, MENZEL-GLASER, German) is used as subtract for Au thin film deposition. a. glass slide. All deposited materials (SiO2, TiO2, Cr, Au) are purchased with purity > 99.99%. The glucose calibration solution was made by dilution of super-saturation of D-(+)-glucose (Sigma, USA) in ddH2O.

C. Fabrication

BK7 glass slides (refractive index = 1.51) were cleaned with piranha solution, and rinsed with Nanopure water, and finally rinsed with ethonal. The Au film was deposited by evaporation of ~ 1 nm of Cr followed by ~50 nm of Au at a pressure of ~ $1.6*10^{-6}$ torr using an E-beam evaporator (Model number, Maker, Nation) in Precision Instrument Development Center (PIDC, Hsin-Chu). The deposition rate was 0.1-0.2 nm/s. The thickness of the chromium and gold were monitored by a quartz crystal microbalance, which has been carefully calibrated according to the different characteristics of deposited materials. The substrate is heating to different temperature during the evaporation of gold layer (100℃) and dielectric layers (300℃) to improve the quality of thin films and adherence, which is critical for multilayer structure.

D. Verification

The fabricated devices were verified by using a spectrophotometer for spectral measurement in transmittance mode (SD2000, Ocean Optics Inc.) and an imaging ellipsometer (EP3, Nanofilm Inc.) for optical properties of thin film and SPR spectra. The measured external angle (θ_{ATRe}) and the calculated internal angle (θ_{ATR}) are related by $\theta_{AT\,\mathrm{Re}} = \sin^{-1}[\sqrt{\varepsilon_0}\,\sin(\theta_{ATR} - \Psi)] + \Psi$, where Ψ= 45 in our experiment.

III. Results & Discussion

Novel SPR device, which use alternative dielectric layers of high/low materials (Au/(SiO2, /TiO2)$_y$/Au (y=4)) to modulate its resonant properties has been proposed and

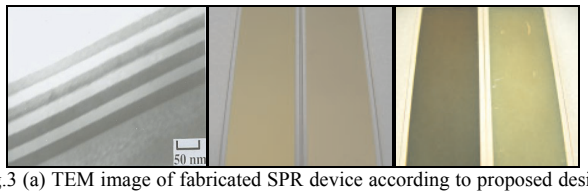

Fig.3 (a) TEM image of fabricated SPR device according to proposed design structure; (b) reflective image of new device (left) vs a traditional SPR one (right); (c) transmittance image.

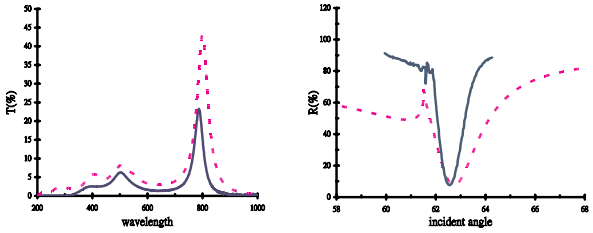

Fig. 4 (a) Transmitive spectra of theoretical calculation (dashed line) and measurement (solid line). (b) Reflective spectra near SPR angle of theoretical calculation (dashed line) and measurement (solid line).

implemented by using above mentioned design method for the goal of zero reflectance. TEM image (figure 3a) clearly identifies the alternative structure of high/low refractive index of Glass/(TiO2/SiO2)$_4$. The appearance of the new device has higher reflectivity (fig. 3b) and lower transmittance in the visible range (fig. 3c), compared to a traditional one.

Although, there are about 5% and 25% errors in the visible and NIR range of the transmittance spectrum, the overall shape and peak positions of fabricated SPR device are rather close to the theoretical calculation as shown in figure 4a. For the SPR spectra, as predicted, the fabricated SPR device has a resonant peak at 62.54 degree rather than 74 degree for a traditional one (fig. 4b) when interfaced to ddH2O with a BK7 coupling prism. However, the measured SPR curve has broader half maximum band width (HMBW) than the calculated one. These errors might be due to 1) the responsive efficiency of detector in the UV and NIR regions, 2) true thickness of each layer, and 3) the deviations of refractive index in nanometer thickness and the one used in the model calculation. Figure 5 shows the results from three different concentrations of glucose solutions (10%, 20%, 40%) to measure the linear response of this device. It was found that the angle shift is 63.55, 64.7 and 67.46, respectively. The linear regression of this calibration curve was found to be y= y = 0.124x + 62.392, R^2 = 0.9948.

Biomolecular interactions were tested by immobilizing antigen (SP, Starch Phosphorylase, MW = 220 kDa) on the multilayer device and then applied the monoclonal antibody (MW = 160 kDa). 4ng/ul of antigen is immobilized by linker with –COOH terminal on the film and the analyte sample is 5ng/ul in this test. With the binding of antigen and antibody, it results in 0.07 degree of resonant angle shift. Table 1 shows the comparisons between the multilayer device and single 50nm Au film. It has better resolution and its calculated sensitivity is about 14.3 pg/mm^2.

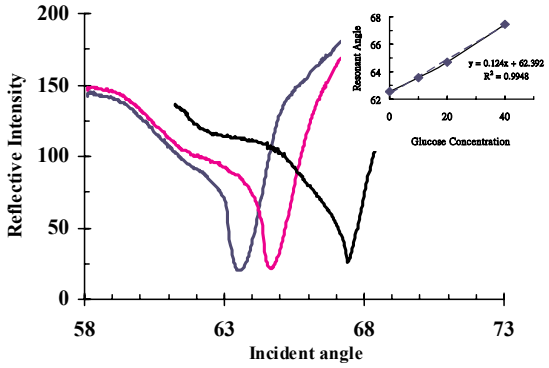

Fig. 5 SPR responses of fabricated device to three different concentration of glucose solutions (10%, 20%, 40%), peak positions are 63.55, 64.7 and 67.46, respectively. The calibration curve is calculated to be y = 0.124x + 62.392, R^2 = 0.9948.

Table. 1 Comparisons of the single Au layer and multilayer. θ_{SPR} is the original resonance angle. θ_{Δ} is the resonance angle shift causing by antibody binding. The ratio of θ_{Δ} /HMBW means the resolution.

	θ_{SPR}	HMBW	θ_{Δ}	θ_{Δ}/HMBW
Single Au	73.9	6.18	0.32	5.2%
multilayer	62.54	1.03	0.07	6.8%

IV. Conclusion

In this report, we proposed and implemented a novel SPR device design, which uses alternative dielectric layers to enhance the SPR signal quality and modulate its resonant position. Admittance loci can be used for the detail design of such a multilayer structure. The results from transmittance, ellipsometry and SPR spectra indicate the performance of this device can be specifically design for the of biochemical applications, especially in the solution phase.

Acknowledgment

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