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Evanescent Field Monitoring for Signal Enhancement of Gold Nanoparticles Filled Surface Plasmon Resonance Sensing

[Chardchai Korjittavanit, Rardchawadee Silapunt, and Boonsong Sutapun]

***Abstract*—The signal enhancement using the evanescent electric field monitoring in the gold nanoparticles (AuNPs) filled surface plasmon resonance (SPR) biosensing is of interest here. The profiles of average evanescent electric fields in a direction normal to the gold/saline layer interface of the 2-dimensional (2D) system are generated at various surface AuNP densities. The shift of the corresponding power density profile increases consistently with the density. The SPR curves associated with dielectric effects from AuNPs are next determined. It shows that the SPR curve shift also possesses the similar characteristic to that of the evanescent field. The evanescent field approach may thus be a potential tool for analyzing SPR signal enhancement.**

***Keywords*— Electric field distribution, Gold nanoparticles, Maxwell-Garnett, SPR enhancement, Surface plasmon resonance (SPR)**

I. Introduction

Surface plasmons or surface plasmon polariton (SPP) is an electromagnetic wave propagating along the metal-dielectric interface where the absolute value of the real part of a metal's complex dielectric constant layer is larger than the dielectric constant of a dielectric layer. To employ SPP in sensing, the resonance by matching excited light and SPP momentum at the surface or surface plasmon resonance (SPR) is necessary. SPR is widely and conveniently applied to biosensing applications since the dielectric constant of the dielectric medium becomes more sensitive to change induced by SPP. The conventional approach of monitoring a resonant angle shift of the SPR reflectance curve, can be used to detect bio substance concentrations at certain densities but the sensitivity of the sensor becomes worse for small and low-mass biomolecules. Localized surface plasmons (LSPs) phenomena of gold nanoparticles (AuNPs) filled in the dielectric layer to amplify signal shifting are then introduced. It is found that the signal intensity can be enhanced substantially in DNA or protein diagnostics using the AuNPs SPR technique [1-2]. Nevertheless, further resolution improvement to account for lower biomolecular density or smaller biomolecule detection is still in great need.

Chardchai Korjittavanit and Rardchawadee Silapunt
King Mongkut's University of Technology Thonburi
Thailand

Boonsong Sutapun
Suranaree University of Technology
Thailand

In this paper, we present an approach to increase the SPR sensing sensitivity the AuNPs filled SPR biosensing system, by monitoring the profile of the evanescent field decay in a dielectric, in a direction normal to the gold/dielectric interface at various surface AuNP surface coverage. The shifts associated with densities of the equivalent power density profiles calculated by average evanescent electric fields are easily noticeable. These profiles also contain information associated with field interactions [3-4]. The evanescent field approach may then be a potential tool to understand and improve the SPR signal enhancement.

Maxwell's equations are employed to compute SPP evanescent electric field distributions in the 2D system of interest. The computational tool is MATLAB. We also create the SPR profile of the AuNPs filled SPR sensing structure using WINSPALL [5], the Fresnel model based calculation software, by utilizing the widely known modified Maxwell-Garnett (MG) model under the Kretschmann geometry to determine the AuNPs effective dielectric constant. The results are analyzed and compared. Section II includes brief theories on the SPPs, LSPs, and modified MG model, and setup parameters. Section III presents the results and discussion. The conclusions are finally presented in section IV.

II. Brief Theory

A. *SPPs at a Single Interface*

Fig. 1 show the 2D single interface structure filled with AuNPs. The lower (z < 0) and upper (z > 0) half spaces are metallic and dielectric layers, respectively. We can obtain general TM solutions for the electric fields using Maxwell's equations in the upper half space, assuming a flat interface as [6]

$$E_x(z) = -iA\frac{1}{\omega\varepsilon_0\varepsilon_d}k_d e^{i\beta x}e^{-k_d z} \qquad (1a)$$

$$E_z(z) = -A\frac{\beta}{\omega\varepsilon_0\varepsilon_d}e^{i\beta x}e^{-k_d z} \qquad (1b)$$

where A is the amplitude constant, β is the propagation constant of the SPP, ε_d is the dielectric constant of the dielectric, ε_o is the free space permittivity = 8.854×10^{-12} F/m, ω is the angular frequency (rad/s), $k_d = \alpha_d + ip_d$ is the component of the wave vector with the attenuation constant α_d (S/m) and the phase constant p_d (rad/m), respectively.

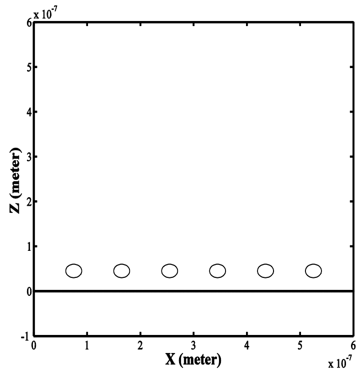

Figure 1. Metallic NPs integrated SPR structure

The propagation constant β is calculated from a dispersion relation of the SPP traveling at the interface between two layers as

$$\beta = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}\ , \tag{3}$$

where ε_m is the complex dielectric constant of the metal layer which is a function of ω, and c is the light velocity.

The magnitude of the evanescent electric field $\vec{E}_0$ or $|\vec{E}_0| = \sqrt{E_x(z)^2 + E_z(z)^2}$ is then calculated at every point in our model spaces to account for the electric field distribution, and averaged out to obtain the average decay field. Note that, the coupling effects of LSP and AuNPs are not yet included.

B. *Localized Surface Plasmon*

Adding AuNPs is an important step to improve the SPR sensitivity. We employ a quasi-static approximation to investigate coupling of AuNPs of size d, where $d << \lambda$ located in the dielectric medium. By assuming a spherical geometry for the AuNP, the distribution of the electric field can be expressed as [4, 6]

$$\vec{E}_{in} = \frac{3\varepsilon_d}{\varepsilon_{NP} + 2\varepsilon_d}\vec{E}_0 \tag{4a}$$

$$\vec{E}_{out} = \vec{E}_0 + \frac{3\vec{n}(\vec{n}\cdot\vec{p}) - \vec{p}}{4\pi\varepsilon_0\varepsilon_d}\frac{1}{r^3} \tag{4b}$$

$$\vec{p} = \varepsilon_0\varepsilon_d\alpha\vec{E}_0 \tag{5}$$

$$\alpha = 4\pi a^3\frac{\varepsilon_{NP} - \varepsilon_d}{\varepsilon_{NP} + 2\varepsilon_d}\ , \tag{6}$$

where $\vec{E}_{in}$ and $\vec{E}_{out}$ are electric field vectors inside and outside a gold sphere respectively, ε_{NP} is the dielectric function of a metallic nanoparticle, $\vec{n}$ is the unit vector in the direction of point p, r is the magnitude of the position vector $\vec{r}$ pointing toward point p, a is the NP sphere radius, and α is the polarizability of a small sphere of sub-wavelength diameter in the electrostatic approximation. $\vec{E}_0$ is obtained via TM solutions described above.

C. *Modified Maxwell-Garnett (MG) equations*

The modified MG theory is employed to estimate the effective dielectric function (ε_{eff}) of composite materials (or the dielectric in our study) with metallic NPs inside which can be found using

$$\varepsilon_{eff} = \varepsilon_d\left(\frac{\varepsilon_{NP}(1+2f) + 2\varepsilon_d(1-f)}{\varepsilon_{NP}(1-f) + \varepsilon_d(1+f)}\right), \tag{7}$$

where f is volume fraction of metallic NPs that can be calculated by the ratio of the area occupied by NPs to the total area. The real ($\varepsilon_{eff,r}$) and imaginary ($\varepsilon_{eff,i}$) components of ε_{eff} can be described as

$$\varepsilon_{eff,r} = \varepsilon_d + \left(\frac{AC + BD}{C^2 + D^2}\right) \tag{8}$$

$$\varepsilon_{eff,i} = \left(\frac{BC - AD}{C^2 + D^2}\right), \tag{9}$$

where $A = f(\varepsilon_{NP,r} - \varepsilon_d)$, $B = f\varepsilon_{NP,i}$, $C = \varepsilon_d + g(\varepsilon_{NP,r} - \varepsilon_d) - f\gamma(\varepsilon_{NP,r} - \varepsilon_d)$, and $D = g\varepsilon_{NP,i} - f\gamma\varepsilon_{NP,i}$. $\varepsilon_{NP,r}$ and $\varepsilon_{NP,i}$ are the real and imaginary components of ε_{NP} respectively, g is a geometry factor and equal to 1/3 for a spherical NP, and γ represents the field interaction factor by metallic NPs which is

$$\gamma = \frac{1}{3\varepsilon_d} + \frac{K}{4\pi\varepsilon_d}\ , \tag{10}$$

where K is the dielectric field at a location of particle created by adjacent particles or by surrounding materials. The K term can be omitted when the dipolar interactions are negligible.

D. *Setup Parameters*

The SPR model structure is a 2D rectangular with width×height = 1,600×500 nm^2. The p-polarization light wavelength of 820 nm is employed throughout the study. The interface is at z = 0 as shown in Fig. 1. The gold film with the thickness of 50 nm is located in the lower half with the complex dielectric constant obtained from the Drude model of $\varepsilon_m = -25.5782 + 1.6106i$. The saline solution with the dielectric constant of $\varepsilon_d = 1.904$ occupies the upper half. In our model, the 2D uniform array of 15 nm-diameter AuNPs is placed in the saline layer at 50 nm above the interface. The AuNPs surface density is varied from 0 to 0.2. The dielectric function of AuNPs is defined as ε_{NP} and also determined by the Drude model. The average decay electric field of the conventional SPR sensing is first determined as a reference. Then the modified MG equations are employed to calculate for the effective dielectric constants of the AuNPs filled dielectric layer at each density. The calculation window covers from the interface to the AuNPs top. The SPR data based on the Fresnel model are then computed using WINSPALL and plotted in MATLAB. The average evanescent fields produced by the AuNPs filled SPR system at different surface densities are then computed. Note that, $K = 0$ is assumed to account for negligible interaction between NPs.

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III. RESULTS AND DISCUSSION

A. *SPP Evanescent Field Decay*

Fig. 2 shows the distribution of the SPP electric field propagating along the gold/saline interface. The average evanescent electric field decays exponentially with the distance in the direction normal to the interface is shown in Fig. 3. The reflection of the SPP at the interface is realized by the SPR profile as illustrated in Fig.4. The SPR angle is around 63.5°.

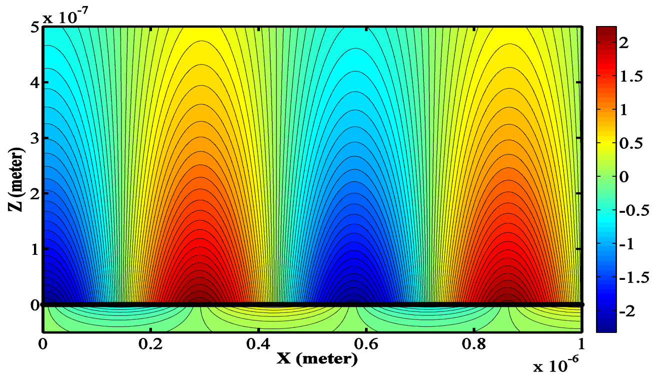

Figure 2. Electric field distribution of the SPP at 820 *nm* wavelength.

B. *SPR Curve Shift Dependence on AuNPs Surface Densities*

We apply the modified MG equations to determine effective dielectric constants of the AuNPs filled saline layer and collect SPR data at different AuNPs surface densities. Fig. 5 shows that both real and imaginary effective dielectric constants increase with surface densities. There appears a shift in the SPR curve when AuNPs are included as shown in Fig. 6. The greater SPR shifts are achieved with higher effective dielectric constants. The angle shifts from 0 to 0.02 and 0.05 surface densities are 0.5° and 1.3°, respectively.

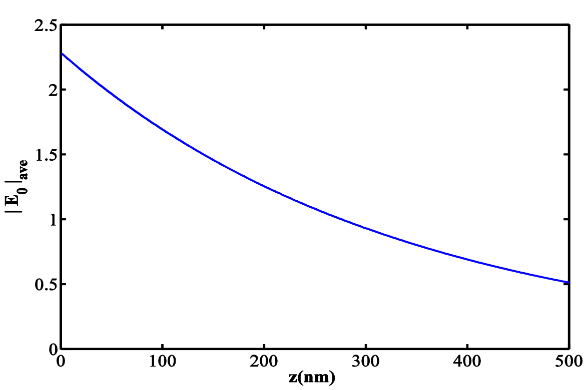

Figure 3. The SPP average decay field in saline solution.

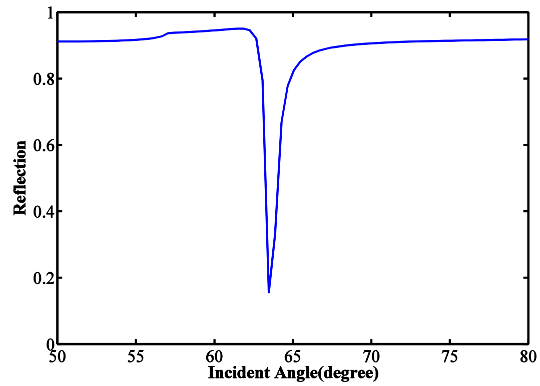

Figure 4. The conventional SPR profile of the gold/saline structure at 820 nm incident wavelength.

C. *Evanescent Field Decay Dependence on AuNPs Surface Densities*

Fig.7 depicts the example of the electric field distribution at 0.05 surface density where the interaction of AuNPs on the field propagation is quite obvious. The z-axis average evanescent field profiles at different surface densities are computed and shown in power density related term, $|E_0|^2$ in Fig. 8. The interactions of AuNPs to the surrounding medium in each profile are clearly observed. It can also be seen that the profile shift from the 0 density line is greater as the density increases, agree well with SPR data. The inset shows fairly distinct shifts at two smallest surface densities (0.02 and 0.05) (around 2 and 6 V^2/m^2). These similar shifting behaviors suggest the evanescent field approach as a promising tool to understand and improve the SPR signal enhancement.

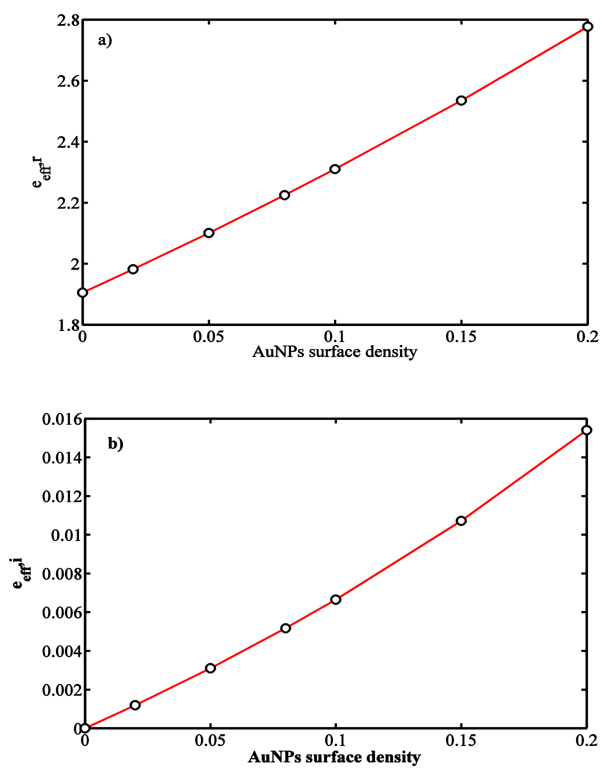

Figure 5. a) real and b) imaginary effective dielectric constants at different AuNPs surface density.

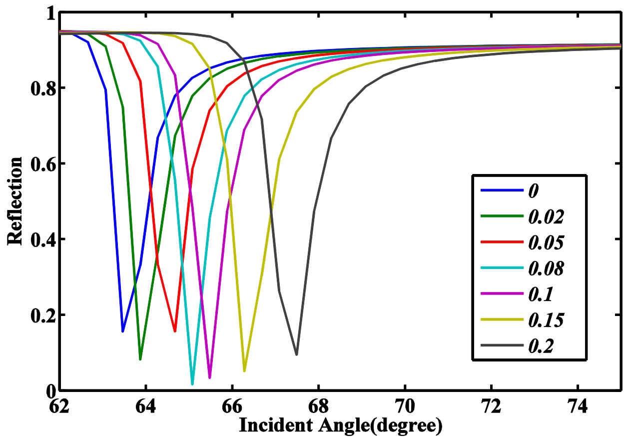

Figure 6. SPR profiles at various AuNPs surface densities.

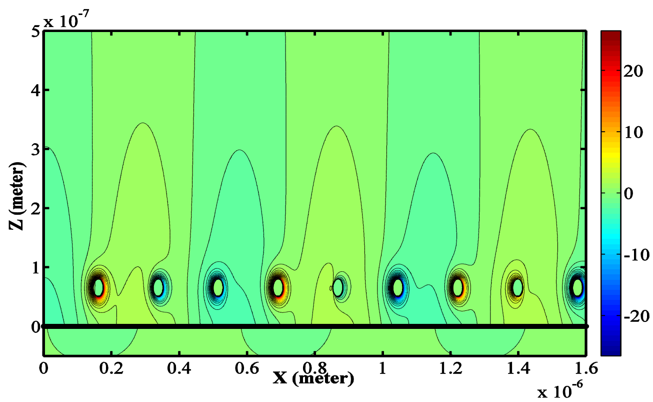

Figure 7. The electric field distribution at the 0.05 surface density.

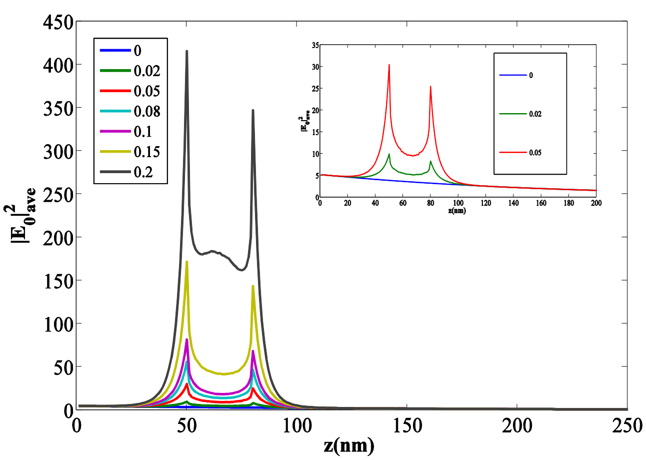

Figure 8. Related power density profiles of the evanescent field at various AuNPs surface densities as a function of the distance in z direction. The inset shows profiles at 0 – 0.05 surface density.

IV. Conclusions

Our study shows that AuNPs strongly respond to the SPPs excitation, which is significant to sensitivity enhancement of the SPR biosensors. The evanescent field profile clearly indicates the couplings between AuNPs and surrounding media. The shift of the evanescent power density profile increases as the AuNP density increases, agree well with SPR data. The evanescent field monitoring approach can then provide better understandings on SPR signal enhancement mechanisms that will help improve SPR detection sensitivity. Future work includes the application of the evanescent field monitoring to other AuNPs structures such as 2x1 array and non-uniform structures.

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About Authors:

Chardchai Korjittavanit was born and raised in Thailand. He is currently studying in senior year at Department of Electronic and Telecommunications Engineering at KMUTT. His senior project is about Electric field monitoring of SPR of gold nanoparticles enhancement. His topic of interests include Telecommunication and Networking related areas.

Rardchawadee Silapunt received her B.Eng. degree in Electrical Engineering from Chulalongkorn University, Thailand, in 1996, M.S. and Ph.D. degrees in Electrical Engineering from University of Wisconsin-Madison, USA in 1998 and 2004, respectively. She is currently a lecturer at King Mongkut’s University of Technology Thonburi, Thailand. Her research interests are plasmonics, nanophotonics, and recording head technology in hard disk drives.

Boonsong Sutapun received his B.S. degree in Physics from Khon Kaen University, Thailand, in 1990, M.S. degree in Electrical Engineering from Washington University, USA in 1995 and Ph.D. degree in Electrical Engineering and Applied Physics from Case Western Reserve University, USA in 2000. He is currently a lecturer at Suranaree University of Technology, Thailand. His research interests are biophotonics, plasmonics, and optical devices.