APPLICATION OF RIGOROUS COUPLED WAVE ANALYSIS TO INVESTIGATE NANOWIRE-BASED SURFACE PLASMON RESONANCE

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1. Introduction

Surface plasmons are excited when a thin conducting metal film is placed between the two optical media. At a specific incident angle, the surface plasmons resonantly couple with a light in an appropriate polarization. Since the energy of the incident light is absorbed in this resonance, the reflected intensity shows a minimum at the resonance angle. Such a phenomenon has been widely used in a variety of sensing applications, since it provides rapid, label-free and array-based sensing capability in real-time for biochemical reactions on a surface.[1,2,3,4] In a conventional schematic of surface plasmon resonance (SPR) based biosensors, a glass slide with a thin gold coating is mounted on a prism. Light passes through the prism and slide, then reflects off the gold film and passes back through the prism to a detector.[5] Changes in reflectivity versus angle or wavelength give a signal that is proportional to the concentration of biomaterial near to the surface. By measuring the resonance shift, it is possible to quantify the surface reactions of interest. These biochemical reactions include antibody-antigen interactions, DNA hybridization, biomaterial and cell receptor interactions, and other adsorption processes.

The highest sensitivity of a conventional SPR biosensor is approximately 1 pg/mm^2,[6,7] corresponding to 5×10^{-7} of refractive index unit. Although an SPR based biosensor is extremely simple in structure and commercially available as an economic alternative to such more expensive sensing techniques, it suffers from insufficient sensitivity in some applications, for example, those that require the sensing of aerosol release of toxins. In order to get over the limitation on the sensitivity, nanoparticle based SPR biosensors have drawn tremendous interests in recent years. It has been empirically shown that applying nanoparticles on the thin film of an SPR biosensor can significantly enhance its sensitivity by 1-2 orders of magnitude.[8,9]

The goal of this study is to numerically investigate the sensitivity enhancement of nanoparticle-based SPR biosensors using well-established rigorous coupled wave analysis (RCWA).[10,11] In our calculations, we approximated two-dimensional Au nanoparticles to one-dimensional Au nanowires. For a given polarization of light, the difference of the optical properties between the two structures is insignificant, and we corroborated these polarization effects by comparing our calculation results with the published experimental data of other groups.

As a result of our calculations, use of RCWA shows that the binding of biomaterial with Au nanowires leads to remarkably larger changes of resonance angles than those observed in the absence of the Au nanowires. And the strong dependence of the resonance angle shift on nanowire period is also presented. Our studies demonstrate the potential for significant improvement in the sensitivity of SPR biosensors by controlling the design parameters of nanowires.

2. Numerical Model

In Maxwell's equations, the linearly polarized light can always be divided into two mutually independent polarizations, transverse electric (TE) and transverse magnetic (TM) modes. Once, one of the two transverse field components is known, the other may be obtained from the curl relation of the Maxwell's equations. Among many existing rigorous methods, the coupled-wave analysis formulated by Moharam and Gaylord is unique because of its versatility and simplicity. Its numerical implementation uses only elementary Maxwell's equations, and do not require any sophisticated numerical techniques or approximations. RCWA may be applied to one-dimensional nanowires (gratings) that have continuous or discontinuous permittivity variations. The permittivity in a metallic grating region is written as a Fourier series expansion

$$\varepsilon(x, z) = \varepsilon(x + \Lambda, z) = \sum_m \varepsilon_m(z) \exp(j2\pi mx / \Lambda), \tag{1}$$

where Λ is the grating period, ε_m is the Fourier component of the grating dielectric function, $2\pi/\Lambda$ is the grating vector, and $j = (-1)^{1/2}$. The light source is assumed as a unit-amplitude monochromatic plane wave with a wavelength λ and incident at an angle θ relative to the z-axis. And the electromagnetic fields inside a grating are given by wave equations

$$\nabla^2 E + \nabla(E \cdot \frac{\nabla \varepsilon}{\varepsilon}) + k^2 \varepsilon(x, z)E = 0, \tag{2}$$

$$\nabla^2 H + \frac{\nabla \varepsilon}{\varepsilon} \times \nabla \times H + k^2 \varepsilon(x, z)H = 0, \tag{3}$$

where E is the electric field, H is the magnetic field, $\varepsilon(x, z)$ is the complex permittivity, k $(= 2\pi/\lambda)$ is the wave number in vacuum. One of the above two general wave equations may be selected and simplified for particular incident wave polarizations. The electric or magnetic field inside a grating region is expanded in terms of space harmonic components. And at the boundaries of each layer, the tangential components of the electric and magnetic fields must be continuous.

When the particle size is smaller than 100 nm, the calculation becomes difficult and the convergence problem is not easy to solve due to extremely rapid variations of the field that occur on very short distances. However, convergence can be achieved in a calculation work of every case by including a sufficient number of harmonics. We suggest to the reader interested in the details of RCWA and its improvements to read references (10, 11).

3. Application to a nanowire-based SPR biosensor

The nanoparticle induced sensitivity enhancement mechanisms in SPR biosensors are governed by various interactions among the substrate, biomaterials, and nanoparticles. In our calculation, we model nanoparticle-based SPR biosensors as multilayer systems and numerically analyze the sensitivity enhancement using RCWA. The randomly patterned gold nanoparticles binding with biomaterial are approximated to one-dimensional nanowires whose directions are parallel to x-axis because the incident light has TM polarization. In this modified SPR biosensor as shown in Figure 1, biomaterial is sandwiched between a gold film and a layer of nanowires, and biomaterial layer is considered to be purely dielectric because its thickness is thin enough to neglect the effects of loss and absorption.
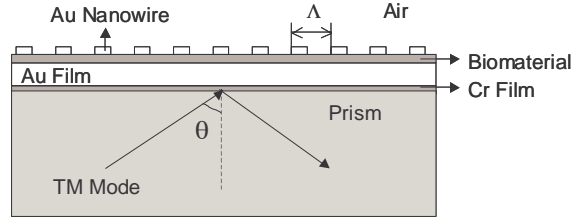

Figure 1. Multilayer configuration of a nanowire-based SPR biosensor. Each layer corresponds to a glass prism, a binding film of Cr (2nm), Au metal film (40nm), biomaterial (here, 1,6-hexanedithiol (HDT) 1nm), one-dimensional Au nanowires (20nm), and air, respectively. We use well-known dielectric functions (n, k) of glass prism (1.5151, 0), Cr (3.48, 4.36), Au (0.18, 3.0), and biomaterial (1.52643, 0) at the wavelength of 633 nm.[12] The incident light is monochromatic (633 nm) and the polarization is TM mode.

We calculate a conventional SPR configuration with or without biomaterial layer and the results of the resonance angles are 45.295° and 45.125°, respectively. As shown in Figure 2, only minor change of 0.17° is observed, and thus it is confirmed that the presence of a biomaterial only weakly affects the conventional SPR response. However, use of Au nanowires on a surface of biomaterial results in a resonance angle of 46.460° and a dramatic shift 1.335° of a resonance angle. In this calculation, the dimension of Au nanowire is 20 nm in width and height, and the nanowire period is set to 400 nm. The shiftness of a nanowire-based SPR biosensor is about 7.85 times larger than that of the conventional one.

While fixing the geometry of nanowires, varying nanowire period from 1 um to 200 nm affects the SPR response as shown in Table 1. In the result of RCWA, we find that, as grating period is decreased,

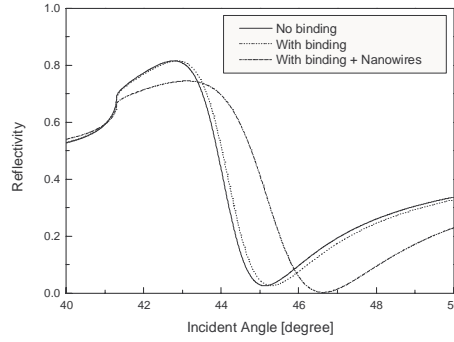the response of the biosensor becomes more sensitive.

Figure 2. SPR curves (reflectivity vs. incident angle) of a 40 nm thick Au metal film on a dielectric glass prism (solid line), binding with biomaterial on a bare Au film (dotted line), and the nanowire layer is additionally adsorbed onto biomaterial layer (dashed line). In the calculation, the period of nanowire gratings is 400 nm. The calculated resonance angles are 45.125° (solid line), 45.295° (dotted line), and 46.460° (dashed line), respectively.

Period [nm]	SPR Angle [degree]	Shift of SPR Angle [degree]
200	48.190	3.065
400	46.460	1.335
600	46.170	1.045
800	46.160	1.035
1000	46.055	0.930

Table 1. SPR angle and its shiftness are shown as varying the period of nanowire gratings of a SPR biosensor from 200 nm to 1 um.

We define a parameter of sensitivity enhancement factor (SEF) to represent the influence of Au nanowires. This parameter is given by

$$SEF = \frac{\Delta\theta_{N\_SPR}}{\Delta\theta_{C\_SPR}} = \frac{\theta_{N\_SPR\_SAM} - \theta_{C\_SPR}}{\theta_{C\_SPR\_SAM} - \theta_{C\_SPR}},$$
(4)

where θ_{C_SPR} is the plasmon resonance angle of a conventional SPR configuration with a bare Au film, $\theta_{C\_SPR\_SAM}$ is that of a conventional SPR scheme with a bare Au film binding with biomaterial, and $\theta_{N\_SPR\_SAM}$ is that of one-dimensional nanowire-based SPR configuration shown in Figure 1. Using RCWA, it was already computed that θ_{C_SPR} is 45.125° and $\theta_{C\_SPR\_SAM}$ is 45.295°. Therefore the numerical results of Table 1 may be presented by use of SEF as shown in Figure 3.
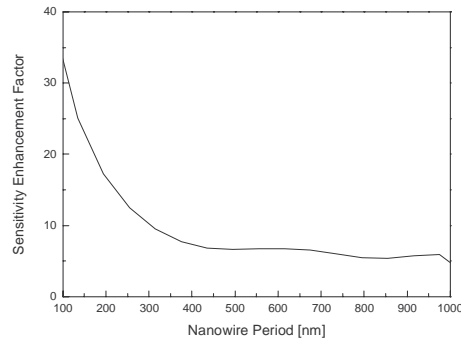

Figure 3. SEF curve of a nanowire-based SPR biosensor. The dimension of one-dimensional Au nanowires is 20 nm in width and height, and the grating period varies from 1000 nm to 100 nm.

As described previously, decreasing the grating period from 1000 nm to 100 nm brings about an improvement of SEF. Comparison of the reflectivity minimums' positions shows that a change of nanowire period from 100 nm to 1000 nm shows the decrease of SEF from 31.85 to 5.47 as shown in Figure 3. When the period is less than 300 nm, the calculated sensitivity enhancement of the nanowire-based SPR biosensor is more than ten-fold compared with the sensitivity of a conventional one. These results may be explained as a superposition of the following two effects.

As the period is decreased, the coverage or surface concentration of the nanowires gets higher. The large number density of nanowires per unit area may induce more localized plasmon resonances. Thus, this effect results in a damping of surface plasmon polariton (SPP) modes and a dominant excitation of localized surface plasmon (LSP) modes that leads to the emergence of strong extinction bands and to a giant amplification of the local electromagnetic field.

Moreover, for a single isolated nanowire, it is known that the plasmon resonance mainly depends on the nanowire size and shape as well as on the dielectric functions of the nanowire and surrounding medium. However, for an ensemble of nanowires, the electromagnetic coupling between nanowires arises and the interaction of nanowires is enhanced with a decrease of inter-nanowire spacing. Thus a strong interaction effect can present different resonance properties, resulting in an additional shift of resonance angle. In our calculation results of Figure 3, when the period is over 300 nm, the sensitivity enhancement effect by interacting nanowires is limited and insignificant. Thus it is confirmed that there is no distinguishable difference of SEF in this range. However, as the period is decreased less than 300 nm, the strong interactions between nanowires may induce an enormous enhancement of sensitivity.

4. Conclusion

We have investigated the sensitivity enhancement of a nanowire-based SPR biosensor using RCWA method. As the metallic nanoparticles allow a strong optical coupling of incident light that is known as localized surface plasmons, the RCWA may be applied to demonstrate these coupling effects between periodic nanostructures and the polarized electromagnetic waves. In our study, the periodic metallic nanostructures are approximated to one-dimensional nanowires. An application of RCWA to a SPR biosensor configuration involving Au nanowires onto a dielectric biomaterial layer shows a dramatic shift of a resonance angle. Especially, when the period of nanowire gratings is less than 300 nm, the calculated sensitivity enhancement is more than ten-fold compared with the sensitivity of a conventional SPR biosensor's configuration. These results are the superposition of the two effects, the increased density of nanowires exciting LSPs and the strong interactions between nanowires resulting in an additional shift of a resonance angle.

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