Dispersion curve-based sensitivity engineering for enhanced surface plasmon resonance detection

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Manipulation of dispersion curve for enhancing surface plasmon resonance (SPR) detection is proposed. Based on strong correlation between slope of dispersion curve and SPR angle shift, it is confirmed that dispersion curve characteristics can be employed as an analysis tool to evaluate SPR sensor performance and to predict anomalous plasmonic behaviors. Complicated resonance shift in SPR angle, especially in the presence of metallic nanograting, such as negative shift, can be controlled reliably by engineering the dispersion curve. As it has a dependence on geometrical parameters of metallic films and gratings, dispersion relation engineering is also useful in optimizing the sensor sensitivity. For a wavelength of \( \lambda = 630 \text{ nm} \), introduction of a gold nanograting shows a significant improvement in sensitivity by more than 5 times, compared to a traditional thin-film-based SPR structure. In addition, we find that use of a longer wavelength in near-infrared region can be advantageous for avoiding a negative SPR shift and obtaining a narrow and deep SPR curve. Our approach is expected to extend the applicability of dispersion-based sensitivity engineering technique to a variety of SPR platforms for highly enhanced SPR detection.

1. Introduction

Resonant coupling between conduction electrons and polarized incident light, called surface plasmon resonance (SPR) contributes to a collective charge oscillation at a dielectric-metal interface. Since SPR condition is sensitive to a variation in refractive index of a sensing medium in proximity to a metallic substrate, one can measure an adsorption of target analytes by tracking a change in resonance angle. However, despite several unique advantages of an SPR biosensor, such as rapid, quantitative, and label-free detection, it often suffers from an insufficient sensitivity, especially for biomolecules at very low molecular weights [1].

Recently, dispersion relation has been investigated to interpret the manner of light coupling to surface plasmons in a variety of SPR configurations such as a curved metal-dielectric interface [2], metal-dielectric slot waveguide [3], sinusoidal metallic gratings [4], and subwavelength Gaussian grooves [5,6]. Enhanced coupling in surface plasmons by means of metallic nanoparticle arrays was explored by measuring a dispersion relation experimentally based on angle and wavelength scanning methods [7,8]. More interestingly, manipulation of dispersion curve by an added SiO\(_2\) overlayer on top of a silver film was utilized to expand the color dispersion of SPR-based holography to incident angle because the angular separation for color reconstruction is relatively small for the case without SiO\(_2\) layer [9]. Inspired by those previous works, we found a possible link between dispersion relation and SPR sensor sensitivity, since dispersion relation in dielectric-metal interface relates the angular frequency of the surface plasmon field to its wave vector magnitude depending on the optical constants of dielectric and metallic materials and its curve is slightly displaced due to a refractive index change in the dielectric medium. This gives us a hint that sensitivity characteristics of SPR biosensor can be controlled by engineering the dispersion curve.

A number of studies for amplifying the SPR signal have been demonstrated [10,11]. For example, alternative SPR configuration with a periodic gold nanograting on a gold film was suggested to improve the angular sensitivity while maintaining its intrinsic label-free strategy [12,13]. In principle, this approach could serve as an effective way to increase a surface reaction area and to generate a highly confined localized surface plasmon mode, thereby boosting a field-matter interaction [4,14]. While a resonant excitation of localized plasmons on a nanostructured metallic film enables to improve the sensitivity by more than an order of magnitude, highly distorted SPR curve associated with multiple localized plasmon mode excitations results in an abrupt change in magnitude or sign of the sensitivity [15,16]. Similar to an anomalous blue-shift occasionally found in a localized SPR biosensor, a negative shift in an SPR system indicates that the resonance angle...
shifts to a smaller angle during the binding event on the substrate surface, which is opposite to a typical positive shift to a larger SPR angle. Since descriptions and remedies on such exceptional plasmonic responses in the presence of metallic nanostructures are unclear yet, it has been often unsuccessful to control the sensitivity characteristics reliably [17].

Hence, in this study, we intend to demonstrate graphically that dispersion curve of SPR structure can be used to find a correlation with SPR angle shift and to characterize an overall sensor sensitivity in visible and near-infrared wavelengths. If sensitivity characteristics are not predictable and reliable, that may adversely affect the performance in the SPR detection because of increased uncertainty in sensor output and high standard errors in measurement. On the other hand, once the nature of sensor sensitivity is a priori known by virtue of dispersion relation, we can guarantee SPR signal amplification reproducibly and suggest an experimental design to meet a practical demand for recognizing a specific target molecule.

2. Simulation methods

To obtain a dispersion curve profile and to determine a sensor sensitivity, we employ two different simulation methods depending on the configuration of SPR substrate. First, for thin-film-based traditional SPR structure based on the Kretschmann configuration as illustrated in Fig. 1(a), transfer matrix method (TMM) is used to calculate the reflectance curves and to display the dispersion characteristics graphically. In TMM computation, the reflectance is represented by \(2 \times 2\) matrix, which is a serial product of the interface matrix and the layer matrix [18,19]. The details of our TMM algorithm can be found elsewhere [20,21]. A smooth gold film with a thickness of \(d_m\) is deposited on a glass prism substrate. As the prism angle increases from 1.40 to 1.45, the thickness of the dielectric and metallic nanostructures [30,31]. Suitable space-harmonic orders are required to accomplish convergence and to improve calculation accuracy as the field rapidly changes in short distance when grating size is less than a wavelength \(\lambda\) [32].

In TMM and RCWA computation, both wavelength scanning from 380 nm to 1500 nm with an increment of 10 nm and angle scanning from 50° to 90° with an increment of 0.01° are performed to obtain the reflectance and dispersion characteristics for a given SPR configuration. Wavelength dependent optical constants of glass substrates, gold, and chromium are referred to the previous reports and publications [33,34].

3. Results and discussion

In order to explore a relation between dispersion curve and SPR angle shift, we consider a traditional SPR configuration consisting of prism substrate, chromium adhesion film, gold film, and PBS ambience. TMM calculation is performed when a 45-nm thick gold film is coated on different types of glass substrates, such as BK7, SF10, and LaSF9 via an attachment of 2-nm thick chromium adhesion layer. The resonance shift is determined by finding a change in SPR angles when a refractive index of 5 nm thick binding layer increases from 1.40 to 1.45. Note that, SPR curves with minimum reflectance larger than 0.2 are discarded in computing SPR angle shift since a shallow resonance curve is not appropriate practically for precise and accurate detection.

Fig. 1. Schematic of (a) conventional and (b) gold nanograting-mediated SPR systems. A gold film with a thickness \(d_m\) is deposited on a prism substrate after 2-nm chromium adhesion layer. Rectangular gold nanogratings with a thickness \(d_g\) a period \(\Lambda\) and a width \(w\) are regularly deposited on a thin gold film. Reflective index of a 5-nm-thick binding layer covering the whole substrate surface uniformly is assumed to change from 1.40 to 1.45 before and after a binding reaction of target molecules. The superstrate is assumed as PBS solution.
Fig. 2. 2D dispersion curve and correlation analysis between SPR angle shift (square in black) and slope of dispersion curve (solid line in red) for conventional SPR system when prism substrate is assumed to be (a) BK7, (b) SF10, and (c) LaSF9. White dot in dispersion curve indicates the position of resonance with a minimum reflectance. The color bar indicates the reflectance values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
obtainable sensitivity with no need of calculating all the resonance angles and their shifts before and after a binding event. As a result, the derivative of dispersion curve can be used for optimizing the sensitivity of the sensor system at both angle and wavelength interrogation modes. It is also found that, when a refractive index of prism substrate gets larger, resonance condition moves to a smaller angle and thus a light source at shorter wavelength becomes more advantageous for a greater sensitivity. We confirm that our findings in Fig. 2 are consistent with previous experimental data [35].

Another sensitivity engineering study based on a dispersion relation is demonstrated to examine an effect of gold thickness $d_m$ on the sensor sensitivity when a gold film is deposited on SF10 prism substrate via 2-nm thick chromium adhesion film. Calculation results of the dispersion and sensitivity characteristics as a function of gold thickness is shown in Video 1 linked to Fig. 3. Together with an evidence of a strong correlation between slope of dispersion curve and SPR angle shift, it is observed that for all cases, SPR detection at a shorter wavelength allows to get a higher sensitivity while it has a low dynamic range. To overcome this limitation, we can change an incidence wavelength by tuning it to a band-edge wavelength. Moreover, angular sensitivity in SPR detection is exponentially decreased with an increasing wavelength and the peak value obtained is gradually reduced when $d_m$ is increased.

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In the Video 1, the reflectance curves at $d_m < 40$ nm may suffer from a broad and shallow dip in the visible band. On the other hand, a gold film thicker than 60 nm provides a degraded sensitivity in a visible region and a broad and shallow resonance dip in near-infrared wavelength larger than $\lambda = 1000 \text{ nm}$. Since a thin gold film ranging from 40 nm < $d_m$ < 50 nm efficiently produces a resonant plasmon excitation in both visible and near-infrared wavelengths, a gold film at this thickness range has been generally used in practical SPR biosensors. If a wavelength of $\lambda = 630 \text{ nm}$, one of the most commonly used spectral line, is chosen as a light source to excite surface plasmons, the optimized gold film thickness is determined to be $d_m = 45 \text{ nm}$ with a maximum resonance angle shift of 0.26°, which corresponds to a sensor sensitivity of 5.2°/refractive index unit (RIU) and its full-width at half maximum (FWHM) is 12.6°. It is also important to note that, while an SPR biosensor operating at a longer wavelength tends to provide a smaller angular sensitivity, SPR angle at a lower momentum is accompanied by a narrower width in reflectance curve, which is favorable for realizing a higher imaging sensitivity as shown in Fig. 3. To guarantee a robustness to inaccuracies in the sensor system, such as power fluctuation of the light source, detector noise, and angular positioning error, the systematic resolution should be improved toward a higher angular sensitivity and a narrower curve width [36,37].

In addition, based on a well-known correlation between plasmon field amplitude and refractive index sensitivity of SPR biosensor, we calculate the plasmonic field distribution at the sensor surface using finite-difference time-domain (FDTD) method. For conventional SPR system with $d_m = 45$ nm in Fig. 1(a), illumination light with a wavelength varying from 400 to 1000 nm is incident on the structure under its resonance condition. On the assumption that the field of an incident beam is of unit amplitude, Fig. 4 shows the correlation between maximum field amplitude and slope of dispersion curve when a wavelength varies from 400 nm to 1000 nm. All values of field amplitude are calculated from FDTD simulations. The SPR structure consists of SF10, 2-nm chromium adhesion, 45-nm gold film, and a binding layer in water ambient.
presents that a maximum field amplitude of $E_X$ component is found at the gold surface and its value is highly correlated with a slope of dispersion curve. For a given gold thickness of $d_m = 45$ nm, visible light with a shorter wavelength at around $\lambda = 450$ nm allows for a significant increase in the field amplitude at the binding site, which can be used to improve the sensitivity in detecting layered biomolecular interactions. This verifies a possibility of utilizing the characteristic in dispersion curve to estimate the sensitivity performance of SPR biosensor and to select an optimal wavelength with better sensitivity and higher field amplitude.

Subsequently, an improved SPR scheme with a periodic gold nanograting onto a thin gold film is investigated. Fig. 5(a) shows the dispersion curve and its correlation study between slope of dispersion relation and SPR angle shift when a gold nanograting with a period of $\Lambda = 100$ nm and a width of $w = 50$ nm is deposited on a substrate consisting of 45-nm thick gold film, 2-nm thick chromium layer, and SF10 prism. Dashed lines indicate the spectral range with a negative shift. The color bar indicates the reflectance values. (b) SPR curves for conventional and gold nanograting-mediated configurations at $\lambda = 630$ nm with a change in a refractive index from 1.40 (solid lines) to 1.45 (dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (a) 2D dispersion curve and correlation analysis between SPR angle shift (square in black) and slope of dispersion curve (solid line in red) for gold nanograting-based SPR system when a grating thickness $d_g$ changes from 5 nm to 40 nm with a step of 5 nm (Video 2). A nanograting with a period of $\Lambda = 100$ nm and a width of $w = 50$ nm is formed on a substrate consisting of 45-nm thick gold film, 2-nm thick chromium layer, and SF10 prism. Dashed lines indicate the spectral range with a negative shift. The color bar indicates the reflectance values. (b) SPR curves for conventional and gold nanograting-mediated configurations at $\lambda = 630$ nm with a change in a refractive index from 1.40 (solid lines) to 1.45 (dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Grating thickness and period effects will be discussed as proof for validity of utilizing the correlation between dispersion relation and sensitivity of nanograting structure.

In Video 2 linked to Fig. 5(a), when a grating thickness varies from 5 nm to 40 nm with a step of 5 nm, the distribution of resonance position in the dispersion curve tends to bend downward notably. For a small grating thickness, back-bending happens at short wavelengths because dispersion curve bends backward the
light line in the vicinity of the surface plasmon energy instead of increasing asymptotically to the surface plasmon energy at infinite momentum [38]. Contrary to a typical positive SPR shift, the wavelength associated with a negative shift, change in resonance signal to a smaller angle according to adsorption of a binding layer, has been considered less feasible for practical applications due to broad and shallow SPR curve characteristics despite its high-sensitivity feature. Interestingly, however, it is found that the back-bending exactly overlaps the spectral range with a negative shift, implying that an anomalous behavior of the negative shift becomes obviously predictable and avoidable as long as back-bending in the dispersion relation is a priori known.

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For a gold nanograting thicker than 10 nm, dispersion curve rapidly bends toward a longer wavelength and a higher incidence angle. Such movement becomes prominent for a thicker gold nanograting and the 40-nm thick nanograting makes the upper boundary of dispersion curve restricted at the wavelength of 1000 nm. Of importance is that the bended dispersion curve can lead to a decrease of gradient value due to a reduced contrast in wavelength as no SPR excitation is found in the visible band. As a result, a decreasing peak sensitivity value, which is consistent with a lower slope of dispersion curve, is obtained at a near-infrared wavelength with an increasing $d_g$. If the wavelength of $\lambda=630$ nm at which a peak sensor sensitivity of $5.2^\circ$/RIU is obtained for a conventional SPR system, is chosen and compared, the optimized thickness of a gold nanograting is $d_g=10$ nm because of a large resonance shift of 1.40°, indicating an enhanced sensitivity of 28.0°/RIU by more than 5.3 times, and a fairly good FWHM of 17.6° as shown in Fig. 5(b). When $d_g$ is less than 5 nm, sensitivity enhancement of about 2 times is not as significant as expected. On the other hand, further increment of $d_g$ larger than 15 nm leads to a highly broad SPR curve of FWHM over 271°.

Furthermore, an effect of grating period $\Lambda$ on dispersion relation and SPR angle shift is investigated when a period varies from 30 nm to 170 nm with an increment of 10 nm for fixed fill factor $f=w/\Lambda=0.5$ and $d_g=10$ nm. While the dispersion curves for individual periods are not presented, distribution of resonance position tends to bend downward slowly with a decreasing period, which resembles the data in Fig. 5(a). As shown in Fig. 6, displacement of dispersion relation according to the grating period is attributable to a slight increase in SPR angle shift when the wavelength of incidence beam is fixed at $\lambda=630$ nm. The highest sensitivity is found to be 29.6°/RIU at $\Lambda=80$ nm, i.e., 5.7 times improvement. A greater, but negative value in the slope of dispersion curve is observed at $\Lambda<50$ nm. However, its SPR curve characteristics are not practically feasible due to broad curve width and shallow reflectance dip.

For a relatively large period of $\Lambda>100$ nm, higher order diffraction by grating begins to take place. A complex dispersion behavior such as back-bending at short wavelengths less than 600 nm may lead to an abrupt change in sensitivity and thus a negative shift is found at around $\Lambda=500$ nm. In short, if the wavelength of $\lambda=630$ nm is chosen, a notable improvement in sensitivity is achievable until the period is reduced to $\Lambda=80$ nm. On the other hand, bended dispersion curve can produce a negative shift for a period less than 50 nm and therefore, use of a longer wavelength in near-infrared region is more appropriate for avoiding an unwanted negative shift and realizing a narrow and deep SPR signal.

4. Conclusion

In this study, we explored traditional and gold nanograting-mediated SPR schemes based on analysis of dispersion curve that allows to estimate the sensor sensitivity at a wide range of incidence wavelength and angle. Based on a strong correlation between slope of dispersion curve and SPR angle shift, it was found that we can evaluate SPR sensor performance more reliably and control anomalous plasmonic behaviors more predictably. Enhancement of SPR angular sensitivity in the presence of a gold nanograting was analyzed through a manipulation of dispersion curve by adjusting geometric parameters of a gold nanograting. Compared to a conventional bare gold film, the proposed SPR substrates with a gold nanograting provided a larger SPR angle shift at $\lambda=630$ nm by more than 5 times, due to the bended dispersion curve toward a longer wavelength and a higher incidence angle. We also presented an additionally improved sensor sensitivity by selecting optimal values in thickness and period of the gold nanograting. Our results are expected to extend the applicability of dispersion curve-based sensitivity engineering to a variety of SPR platforms for realizing a highly enhanced SPR detection.

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References
