Research Article

Rigorous Coupled-Wave Analysis of Surface Plasmon Enhancement from Patterned Immobilization on Nanogratings

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We numerically evaluate the optical response of a Kretschmann surface plasmon resonance (SPR) biosensor featuring metallic nanogratings and patterned immobilization of surface receptors. Parameters are chosen such that the biosensor is operated near the generated bandgap of the surface plasmon dispersion. In this paper, we demonstrate that the sensitivity can be increased by concentrating the surface receptors and adsorbed analytes on regions where the field intensity is the greatest. Specifically, a surface presenting receptors on the grating mesas is shown to be twice as sensitive as that of a uniformly functionalized corrugated surface. The grating geometries are also studied; it is found that higher aspect ratio features show increased SPR response. The analysis differs from existing studies of enhanced SPR as the sensitivity improvement originating from the concentration and mapping of surface receptors to the plasmon field distribution is studied rather than the absorption or scattering enhancement effect of the nanostructures.

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1. Introduction

Current and future demands for biosensors for use in point-of-care clinical diagnosis require increasingly compact and sensitive devices. Metallic nanogratings are studied owing to their capacity to perturb a propagating surface plasmon wave; it has been shown that these perturbations create strong field gradients and modify the surface plasmon dispersion relation. The development of novel surface functionalization techniques including polymer matrices, self-assembled monolayers, and nanocolloidal particles adds further potential for sensitivity improvements [1–5].

In a traditional surface plasmon resonance (SPR) biosensor configuration, known as the Kretschmann or Attenuated Total Reflection (ATR) configuration, surface plasmon waves are excited on a metallic-dielectric interface via a high refractive index prism [6]. Incident photons, propagating with increased momentum through the prism, are coupled to a surface electron density wave (surface plasmon) at a specific energy and momentum, collectively referred to as the resonance condition. The coupling of energy is observed as a dip in the reflectance spectrum when measured as a function of incident angle or wavelength of the excitation light.

It has been shown that sensitivity of the SPR biosensor can be increased by the modification of the metallic surface with a periodic grating for both propagating and localized surface plasmon. Numerous studies have been presented in which nanoposts, nanowires, and gratings are used for enhancement [7–14]. Unlike grating-coupled SPR [6] and localized SPR spectroscopy [15, 16], in the presented configuration, the coupling to the plasmon mode is achieved via a dielectric prism in a traditional setup. As a result of the surface corrugations, the electric field intensity of the propagating surface plasmon is redistributed between the grating mesa and trough. In this article, the focus is not on the surface plasmon enhancement due to the presence of the nanostructures, as previously explored elsewhere. Rather, we seek to determine whether there is a significant increase in sensitivity if the surface receptors are immobilized specifically where the field intensities are at their strongest, thus allowing the detection of lower concentrations of biomolecules than for a uniform distribution. In this context, we assume that the biosensor interface is not saturated with the adsorbed biomolecules, and thus we hypothesize that concentrating the adsorption to regions of field enhancement is advantageous. Furthermore, we will examine the effect of

FIGURE 1: (a) SPR surface grating configuration, (b) single surface biomolecule active medium (dark gray), (c) active medium uniformly distributed along the grating, (d) active medium in the grating trough, (e) active medium on the grating mesa.

the grating duty factor, the grating height, and the underlying gold thickness on the SPR response for the concentration of adsorbed surface receptors and analytes.

2. Model and Simulation Methods

The SPR interface consists of thin layer of gold of thickness t on top of which a binary grating of depth h and period Λ is introduced (Figure 1(a)). A high index glass (SF10) serves as the substrate and also as the coupling prism in the standard Kretschmann SPR setup. Surface receptors are immobilized on the gold surface. The biomolecules or analytes of interest are captured by the receptors as the sample solution flows over them. In this model, the change in optical properties due to the adsorption of the surface receptors/analyte is simulated as a small refractive index change of an active medium from 1.30 to 1.33 and then from 1.33 to 1.36. A background refractive index of 1.30 is assumed to be typical for background buffer (aqueous or solvents). Four different receptor immobilization patterns are considered. First, the adsorption of a single receptor-analyte complex is modeled. In this case, it is represented by a $5\text{ nm} \times 10\text{ nm}$ active element per period (Figure 1(b)). Then, configurations

FIGURE 2: Angular reflectance spectrum at 820 nm and 970 nm wavelength.

in which the surface receptors are placed uniformly over the entire grating (Figure 1(c)), exclusively in the trough (Figure 1(d)), and exclusively on the mesa (Figure 1(e)) are modeled. The SPR angular resonance shifts are calculated for various index changes of the active medium (from 1.33 to 1.60) for all configurations to model the capturing of analytes by the surface receptors. A planar surface is also included in the comparison. While this study focuses on the enhancements from the mapped immobilization and not on the effect of the nanostructure, the conventional planar or flat surface serves as a control for the comparison. Furthermore, a large refractive index change is modeled instead of a typical refractive index change associated with the adsorption of analytes (10^{-5}RIU), as to model a wide range of analyte types and buffer conditions.

The simulations were carried out using a proprietary rigorous coupled wave analysis (RCWA) code. In the literature, RCWA has been extensively employed to study metallic corrugated surfaces, with significant pioneering work by Moharam and colleagues [7, 10, 17–20]. A period of 250 nm and laser wavelength of 820 nm and 970 nm were chosen so that the biosensor operates near and above the bandgap in the dispersion map. It has been demonstrated that, for periodic structures, operating near the bandgap is more sensitive [8]. The optical properties of the metal and substrate were taken from Johnson and Christy [21] and the manufacturer, respectively. Calculations were carried out using 100 harmonics in order to obtain an accuracy of 1×10^{-3} , with 1 nm resolution in the grating depth axis and 512 steps per grating period. Only TM polarization is considered. An initial grating thickness t of 25 nm and grating height h of 25 nm were chosen.

3. Results and Discussion

3.1. Field Concentration and Patterned Reception Immobilization. Figure 2 shows reflectance as a function of the

FIGURE 3: (a) Field intensity (E_z) distribution, with higher strength at the edge and on the mesa, (b) sensitivity of the SPR to displacement of a single analyte along grating surface, for an illumination wavelength of 970 nm.

incident angle for the two different wavelengths (820 nm and 970 nm). An evanescent field scattering off a grating receives a momentum change equal to an integral multiple of the grating vector. Consequently, multiple resonances are observed for 820 nm illumination. The reflectance curve is shallow and broad. Generally, a narrower resonance is preferred for determining the resonance angle precisely, such as the response for 970 nm illumination.

The grating redistributes the field intensity of the propagating surface plasmon wave such that the highest field intensity is found near the grating edge, and with higher field strength on the grating mesa rather than in the trough as shown in Figure 3(a). The SPR response from the adsorption of a single biomolecule complex on the grating surface is simulated. Both the adsorption of the surface receptor (active medium index change from 1.30 to 1.33) and the adsorption of the analyte (from 1.33 to 1.36) are compared (Figure 3(b)). The sensitivities for both refractive index changes are similar, suggesting a linear response for the index range. The SPR response or sensitivity, defined as the

FIGURE 4: Resonance shift for 970 nm operating wavelength for immobilization on the mesa, trough, or uniform across the grating and also for the flat (conventional SPR) surface.

FIGURE 5: Field distribution (E_z) for 820 nm at (top) 56.2° incident angle (first resonance dip) and (bottom) 69.8° (second resonance dip)—See Figure 2.

angular shift of the resonance minimum per refractive index unit (RIU) change, is calculated at different points along the grating surface. A sensitivity of 0.1 deg/RIU is observed when the adsorption of the receptor and analyte is on the mesa, compared to 0.03 deg/RIU in the trough. It peaks at 0.24 deg/RIU at the grating edge where the field intensity is the greatest.

The intensity distribution over the grating surface and consequently the selective sensitivity of the plasmon wave suggest that one can significantly enhance the SPR biosensor by guiding, selectively, the immobilization of surface receptors, such as antibodies for the detection of proteins, or

FIGURE 6: (a) Sensitivity for grating duty factor from 20%–80%. (b) SPR curves for increasing gold thickness ($t = 5$ to 40 nm) and for each thickness, an increasing grating height ($h = 5$ to 40 nm), as indicated by the arrow. (c) Sensitivity for gold layer thickness (t) and grating height (h).

oligonucleotide probes for the detection of DNA, onto the more sensitive area of the grating surface.

The grating structure is simulated with the active medium uniformly distributed along the entire grating (as in Figure 1(c)), concentrated on the mesa (Figure 1(d)) and in the trough (Figure 1(e)). For a fair comparison, an equal total concentration of biomolecules is assumed over a grating period. In the case of the uniformly distributed surface, this results in a lower surface density. For a 50% duty factor grating, the latter surface analyte density is half that of the selectively functionalized mesa or trough surfaces. In these simulations, the active medium refractive index is changed from 1.33 to 1.60 to model an increasing surface analyte concentration. Numerically, the active medium represented as a grid of $5 \text{ nm} \times 10 \text{ nm}$ areas covering the entire mesa, trough, or both. The refractive indices of each area are increased

accordingly. On the uniformly or evenly distributed active medium (that is equally distributed on the mesas and in trough), only the refractive index of every second $5 \text{ nm} \times 10 \text{ nm}$ area is changed, such that in the three immobilization cases, the effective refractive index changes are the same over the entire grating.

The resonance shift for the functionalized mesa is almost twice that of the uniformly covered grating and almost 3 times that of a conventional (planar) interface, while a small response is measured when the analyte is adsorbed in the trough (Figure 4). This gives rise to another possibility for enhancement. By selecting a second excitation laser wavelength or angle for which the field intensities are localized in the trough, as exemplified by Figure 5 for measurement at 820 nm, one could implement a two-analyte detection system or a differential measurement SPR approach. In the

FIGURE 7: Figure of merit for different grating geometries. The grating with 5 and 10 nm underlying gold layer is not included.

former approach, two types of receptors can be immobilized to the different parts of the gratings. The latter case requires that either the mesa or trough is passivated to repel any analyte adsorption.

3.2. Grating Geometry and Duty Factor Effect with Mapped Immobilization. The effects of the metallic grating height and the grating duty factor are also examined with the mapped immobilization of surface receptors. The plasmon field distributions are dependent on the features of the metallic gratings. For an initial binary grating with a depth of 25 nm and underlying gold thickness of 25 nm as described in the previous section, RCWA calculations of the angular resonance shift are obtained for grating duty factors from 20% to 80%. For these simulations, the immobilization of surface receptors is assumed to be exclusively on the grating mesas, where field concentrations are the greatest, at 970 nm wavelength. Furthermore, an equivalent effective refractive index change is assumed in all cases, as to model an equal adsorption of analytes. It assumes that in an actual system the surface and solution concentrations have reached equilibrium, with unsaturated surface receptors. Shown in Figure 6(a), the results point to an increased SPR response for gratings with smaller duty factors. As discussed, increased field concentrations are observed near the grating mesa edges (Figure 1(a)) and thus point toward a greater response when analytes are increasingly concentrated on the mesas. However, in practice the smaller grating mesas are harder to implement given the small feature sizes; furthermore, the smaller effective coverage area reduces the accessibility of the solution analyte to the surface receptors, thus reducing the probability of binding. The optimum duty cycle is thus best determined experimentally.

While the previous analysis has been carried out on a binary grating structure with 50% duty factor, 25 nm depth,

and 25 nm underlying gold, the latter two parameters can also be optimized for a mapped immobilization. Similar to a planar SPR interface configuration, increasing the underlying metallic film narrows the angular resonance curve. A thin gold underlayer increases the loss of the propagating evanescent wave, reducing its propagation length, resulting in broad resonance responses (Figure 6(b)). The presence of the surface corrugations, while perturbing the electromagnetic field distribution and allowing for enhanced responses from the mapped immobilization, can be viewed as a change in the surface refractive index. By increasing the grating height, one can observe a shift toward a larger angular resonance response. The sensitivity with respect to an index change localized at the grating mesa increases with the higher aspect ratio features, suggesting a higher field gradient in these cases, as shown in Figure 6(c).

A higher sensitivity is generally observed for gratings with deep troughs and a thinner underlying gold layer ($t = 15$ – 20 nm). For a very thin gold layer ($t = 5$ – 10 nm), the SPR resonance dips are generally broad, and the sensitivity is only weakly dependent on grating height. For shallow gratings and a thick gold layer, the resonance dips are narrow, much like planar interfaces. However, they show increased sensitivity with an increased grating height. The latter effect points to the advantage of corrugated surfaces in plasmonic biosensing. The effect of the nanograting on the SPR curves can also be measured by the figure of merit. It is defined as the ratio of the sensitivity and the full-width half maximum (width of the SPR curves) [22]. The figure of merit for the different grating geometries is shown in Figure 7. As one would expect, an increase in the underlying gold layer thickness results in an increased figure of merit due to the narrower SPR responses. As the grating height increases, both the angular sensitivity and width of the SPR curves increase, resulting in a generally constant figure of merit with a peak value at 15–30 nm in grating height depending on the gold thickness t . Again, in practice, a compromise must be made between the degree of resonance shift and the width of the SPR curves for the measurement setup and fabrication process.

A number of methods have been reported for the fabrication of nanometric metallic gratings or periodic structures, generally based on a metallic lift-off process of an electron-beam patterned polymeric resist or fast-replication techniques [23]. Features smaller than 100 nm have been demonstrated [24]. Various techniques can also be employed for the exclusive functionalization of the periodic corrugated features (mesa/trough) including microcontact printing, dip-pen patterning, or masking techniques [25–30]. Typically, molecules that are known to self-assemble on metallic surfaces (alkanethiol) are employed [31]. They are either applied uniformly to a surface and then selectively removed to form different patterns by laser ablation [32] or directly applied to a masked surface with exposed features. Self-assembled monolayers can be readily functionalized using a variety of chemistries for the attachment of surface receptors (antibodies, oligonucleotides) or can be modified using for example poly(ethylene) glycol, well-known to repel biomolecule adsorption [33]. In another work, we have

demonstrated that functionalized metallic nanogratings with dimensions in the range modeled can be fabricated [30]. In practical uses, the effect of the mapped immobilization can be applied to both conventional propagating and localized SPR biosensors where nanostructures are employed with surface plasmon field redistribution. Optimization of the duty factor also requires additional experimental analysis. The increased signal from the concentration of the surface receptors/analytes on the grating mesas, mapped to the field distribution, was shown to increase with smaller duty factors; however one would also expect a counter effect due to the reduced binding probability of the smaller functionalized area. The latter is best measured experimentally.

4. Conclusion

In conclusion, we have demonstrated numerically that the targeted immobilization of surface receptors onto the nanostructured biointerface of a surface plasmon-based biosensor, in a Kretschmann configuration, can increase the detection sensitivity. The guided immobilization allows the concentration of the index change (surface adsorption) to be targeted to zones of high field intensity generated by the grating. Coupled with the enhancement from operating the SPR-biosensor near the generated bandgap [8], one can anticipate a significant improvement in the performance of these biosensors. While the enhancements shown here are limited, an optimization of the grating geometry and duty cycle, within the limits of current fabrication techniques, can further improve the sensitivity of the patterned SPR biosensing method.

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