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Self-Referenced Dual Mode SPR Sensing using Sandwiched ITO Layer: Long Range vs. Short Range SPR Referencing

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Abstract: A dual mode prism based SPR sensor was theoretically modeled with an ITO layer sandwiched between the metal and the substrate to obtain self-referenced operation. The configuration was compared with existing dual mode SPR configurations.

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1. Introduction

Surface plasmon resonance (SPR) is the phenomenon of excitation of electromagnetic (EM) oscillations at a metal-dielectric interface when the wave vector of the incident light becomes equal to that of the surface plasmon (SP) modes supported by the structure. As a result of SP excitation, a drop in optical power of the light reflected from the interface is observed. The SPR condition is highly sensitive to any changes in the refractive indices of both the metal and the dielectric medium which reflects as a change in the resonance parameter. The concept of long range surface plasmons (LRSPs) was first proposed by Sarid [1] and later experimentally observed by his colleagues [2]. In such a configuration, a thin metallic layer is sandwiched between two transparent insulators (IMI) of almost similar refractive indices (RIs) and the SPs get excited at both the interfaces of the metal film. While the two plasmon modes superimpose, they lead to two new super-modes called symmetric and anti-symmetric plasmons. The anti-symmetric super-mode is termed as long range (LR), while the symmetric one is called short range surface plasmon (SRSP) mode. LRSPs possess large penetration depth and propagation length, while the SRSPs possess short propagation length and small penetration depth as compared to conventional SPR [3]. A good number of reports are available in literature on the excitation of both kinds of surface plasmons, and their applications in sensing, etc. [3]. Most of these sensors utilize either Teflon or Cytop as sandwich layer. The high penetration depth of LRSPR provides the advantages of probing the plasmonic field deep into the analyte medium and hence larger interaction volume. Additionally, the larger propagation length provides larger time for interaction of the plasmonic field with the analyte, which eventually leads to improvement in sensitivity. Further, the LRSPs possesses higher resolution than the conventional SPR.

Recently, self-referenced sensors have gained lots of interest due to their reliability over conventional sensors [4, 5]. The self-referencing provides accurate prediction of the analyte concentration due to simultaneous detection of the same measurand. In self-referencing, desirably, one of the SPR modes must preferably be fixed with respect to change in the refractive index of the analyte. Few studies on self-referenced sensing utilizing simultaneous excitation of long and short range SPR have already been reported in the literature [5]. However, in all such reports, both the SPR resonances vary with a change in the analyte concentration/RI. A schematic of the SPR geometry for excitation of dual SPR modes is presented in Fig.1. A *p-polarized* beam incident on the IMI structure (where the other dielectric is the medium surrounding metal) excites both LR- and SR- SPR.

Fig. 1. Schematic of dual mode SPR geometry in a Kretschmann configuration

2. Results and discussion

The n-layer model and dispersion relations of Ag, ITO, and SiO₂ were considered from ref. [6], while that of Teflon and Cytop were taken from [7] & [8] respectively. When a thin film of indium tin oxide (ITO) is sandwiched between the optimal metal-prism configuration of conventional SPR, two SPR modes are observed, which can be

seen in Fig. 2(a), for varying thickness of ITO. The SPR resonance at the smaller wavelength (λ_1) corresponds to LRSR while that on longer wavelengths (λ_2) to SRSR. From Fig. 2 (a), it can be concluded that the optimum ITO thickness is the one around 200-250 nm, as it corresponds to the maximum contrast of the SPR curve. Fig. 2(b) presents the variation of λ_1 and λ_2 with change in RI for the near optimum configuration. From the curves, it is clear that when the RI of the surrounding medium is increased from 1.33 to 1.37, almost linear red shift in λ_1 is observed, while the variation of λ_2 is shorter. Therefore, this dip can be chosen as the reference dip. The thickness of Ag layer was also varied to reach the optimum configuration. It can be seen that for Ag thickness of 60 nm, with 150 nm ITO, the overall shift in λ_2 is less than 0.5 nm. Hence, this scheme can be used for self-referenced sensing. Control simulations were performed on widely used materials for dual SPR: SiO₂, Teflon® AF-1600 and Cytop as sandwich layers. Figure 3(a) presents the SPR spectra for optimal SF11/SiO₂/Ag structure (parameters given in inset) for varying RI. It can be seen that even though, the contrast of the SRSR dip is quite low, this configuration can be used for self-referenced operation. What makes ITO special over SiO₂ can be found in Fig. 3(b), where we can see the effect of the imaginary part of the ITO refractive index. Unlike SiO₂, ITO works as a plasmonic material in the IR region of EM spectrum. Since, the SRSR dip falls on the edge of NIR, small absorptions in the ITO lead to the desirable contrast of the SRSR dip. This dip is not purely SR-SPR, as it has partial plasmonic character of ITO as well.

Fig. 2. (a) SPR spectra for varying thicknesses of ITO at 53.5° angle of incidence and 46.7 nm thickness of Ag film. The spectra are used for the optimization of ITO thickness. (b) Response curves for nearly optimum structures: Optimization of Ag thickness for self-referencing.

Fig. 3. (a) SPR curves for varying refractive indices of the analyte at the optimum self-referencing Ag/SiO₂ structure at 57° angle of incidence, (b) Effect of the imaginary part of dielectric function of ITO on the SPR response.

Fig. 4. (a) SPR curves for varying analyte refractive indices at optimum Ag/Teflon structure, (b) Response curves for nearly optimum SF11/Cytop/Ag structure at 53.5° angle of incidence.

The SPR spectra for optimum configuration of Teflon as a sandwich layer are presented in Fig. 4(a). No self-referencing configuration with stationary dip could be achieved. However, the LRSPR dip, being less responsive to RI variations, can be used for referencing purposes. Similar studies were performed on configurations with Cytop as the sandwich layer. It was found that similar to ITO case, the prediction of the optimum thickness for Cytop is ambiguous. Hence, the SPR spectra were modeled for various combinations. Fig. 4(b) present the response curves for λ_1 and λ_2 variation with change in RI for Cytop thickness of 200 and 250 nm. Similar to Teflon case, both λ_1 and λ_2 show red shift with an increase in RI. Further, only the LRSPR dip can possibly be used as reference dip. So, it can be seen that ITO and SiO₂ can be used for SRSP referenced sensing, while Teflon and Cytop for the LRSP referenced. The choice of the mode of referencing depends on the size of the analyte and volume of sensing. For, analytes very small in size and close to the interface, SRSPs can be utilized for detection. Hence, LRSP mode can be used for self-referencing. However, since the LRSPR possesses the large penetration depth and propagation length, the analytes of bigger size and larger sensing volumes can be detected using them. Hence, SRSPs can be used for self-referencing. One crucial factor here is the large sensitivity and detection accuracy of LRSPR which makes them better and preferable candidate with large figure of merit (FOM) for sensing applications. A detailed study of the present configuration can be found in [9].

3. Conclusions

A self-referenced SPR sensor utilizing ITO as a sandwich layer in between metal and the SF11 glass substrate was theoretically studied. The advantages of the present sensor over the conventional dual mode sensors was discussed in context of self-referencing.

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