Sensitivity Enhancement of Graphene-Based Surface Plasmon Resonance Biosensor Using Germanium Nanowires Grating

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Abstract—In this study we proposed a new surface plasmon resonance (SPR) configuration for enhancement of biosensor sensitivity with high absorbing molecules on the sensor surface. The proposed SPR structure consists of a germanium nanowires grating coated with three graphene layers while the addition of titanium layer between gold and fused silica (substrate) prevents the gold oxidation. For transverse magnetic (TM) mode, the changes in the electric and magnetic fields are presented. As a result of numerical study, the reflection and transmission characteristics of the SPR sensor are shown. The new structure increases 60% more resolution of SPR angle in compared to the known graphene-based SPR structure. Therefore, the proposed SPR configuration could potentially open a new possibility of graphene-based SPR for sensitivity and high throughput assessment of multiple biomolecular interactions.

Index Terms—graphene-based SPR, germanium nanowires grating, numerical analysis, COMSOL multiphysics

I. INTRODUCTION

In many biomedical studies and diagnostics, detecting of relevant antigens, antibodies or proteins of virus is one of the main common methods [1]-[4]. The assays based on the SPR technique are increasing rapidly and the number of reported researches has been quickly growing [5]-[8]. In recent years, some additional thin films with excellent optical properties have been proposed to enhance the performance of SPR biosensors, such as magnetic nanoparticles [9], gold nanoparticles [10], [11], electropolymerized molecularly imprinted polythiophenes [12], nanoelectronics [13], carbon nanotubes [14] and silicon layers [15].

The technique of the SPR is very sensitive to a refractive index variation in sensing medium. This variation occurs due to binding of analyte (in a liquid sample) to their affinity ligands (that immobilized on the chip surface) when the liquid sample comes in contact to the sensor surface. Therefore, material which is in contact with the liquid sample (top layer of sensor), in terms of

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refractive index and absorption of molecules, is influential and important [16], [17].

The graphene layer is basically provided the scope for new surface functionalization, which can be used for anchoring ligands to the SPR chip. Compared with gold, the most advantages of using graphene layers can be pointed to its efficiency in adsorption of biomolecules passivation of the sensor surface against oxidation, highly hydrophilic layered material, and be able to control the SPR response by controlling the number of coated graphene layers. Owing extraordinary optical properties of graphene as mentioned, the researchers would interest to utilize it and its derivations in their biosensor applications [18]-[22]. Because of the specific nature of graphene, the refractive index of this material in the visible range was estimated to be $n=3+iC\lambda/3$, where λ is the wavelength in μm and the constant C equals 5.446 μm^{-1} [23].

When the sample containing analyte molecules comes into the graphene surface, the molecules get adsorbed on graphene surface. Then it produce a layer which its refractive index is higher than a buffer solution (water) and it affects the SPR angle. As mentioned, the performance of SPR sensor depends on the biomolecular adsorption. Hence, the material type of upper surface which immobilizes the biomolecules (ligands) on chip, plays an important role. Although researchers have gained the great achievement, the number of publications devoted to graphene-based SPR biosensors, is still surprisingly low in sensitivity (smaller increase of the resonance angle with additional graphene layers) and facile detection [24]-[26].

In the present study, to enhance the sensitivity of the SPR sensor for biomolecules, we have placed a nanowires grating of high refractive index dielectric (germanium) onto three graphene layers. To see the points of proposed structure, simulations have been carried out for both conventional and introduced graphene-based SPR configurations.

II. THEORY AND DESIGN CONSIDERATION

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In order to get the plasmon resonance with photons, the energy and momentum should be preserved which is obtained by the following equation [27]:

$$K_{sp} = K_{ev} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_D + \varepsilon_M}} = \frac{\omega}{c} \sqrt{\varepsilon_p} \sin \theta_{res}$$
(1)

where *Ksp* and *Kev* are the wave vectors of the propagation constant of the surface plasmon and the evanescent wave, ε_M and ε_D are the dielectric constant of metal and dielectric layer respectively, and *c* is the speed of light.

The scattering parameters (S-parameters) are complexvalued wavelength dependent matrices expressing device characteristics (e.g., transmission and reflection of electromagnetic energies) using the amount of absorption or transmission. For a two-port device, the S-parameters are defined as [28]:

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}$$
(2)

where S_{11} is the S-parameter for the reflected wave and S_{21} is the S-parameter for the transmitted wave. Furthermore,

$$S_{11} = \sqrt{\frac{Power \ reflected \ from 1}{Power \ incident \ on 1}} \tag{3}$$

, and

$$S_{21} = \sqrt{\frac{Power \ delivered \ to \ 2}{Power \ incident \ on 1}} \tag{4}$$

The magnitudes of S_{II} ($|S_{II}|$) gives the normalized reflectance. And, the normalized reflectance for this multilayer SPR is calculated as follows,

$$S_{11} = \left| \frac{M_{11}}{M_{12}} \right|^2 \exp(i\varphi_{11})$$
 (5)

where φ_{11} contains the phase information of S_{11} and

$$M = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = I_{01}L_1I_{12}L_2I_{23}L_3 \dots I_{jk}L_k$$
(6)

$$I_{jk} = \begin{bmatrix} 1 & r_{jk} \\ r_{jk} & 1 \end{bmatrix} \quad and \quad L_j = \begin{bmatrix} e^{id_z k_{zj}} & 0 \\ 0 & e^{-id_z k_{zj}} \end{bmatrix}$$
(7)

The reflectance (*R*) is represented by a 2×2 M-matrix, which is a serial product of the interface matrix (I_{jk}) and the matrix of layer (L_j). The sensitivity of SPR sensor (*S*) is obtained by differentiating the reflectance directly with respect to $n_{binding}$. Here, r_{jk} , k_{zj} , and d_j represent the Fresnel reflection coefficient, the wave-vector in the z-direction, and the thickness of *j*-th layer, respectively. r_{jk} and k_{zj} are given by:

$$r_{jk} = \frac{\left(\frac{k_{zj}}{\varepsilon_j} - \frac{k_{zk}}{\varepsilon_k}\right)}{\left(\frac{k_{zj}}{\varepsilon_j} + \frac{k_{zk}}{\varepsilon_k}\right)} \quad , \ k_{zj} = \sqrt{\left(\frac{\omega}{c}\right)^2 \left[\varepsilon_j - \varepsilon_0 \sin^2\theta\right]}$$

$$\tag{8}$$

where ω is the angular frequency, *c* is the speed of light in free-space, d_j and ε_j are thickness and the optical constant of the *j*-th layer.

In the most commonly of graphene-based SPR biosensors, the configuration consists of five layers namely, prism, adhesion, noble metal, graphene, and sensing medium that contains the ligand-analyte binding. The different strategy is proposed within the framework of the proposed design. For our analysis, we consider a prism (fused silica) placed with germanium nanowires onto three graphene layers. The binding medium, as known sensing medium, is in contact to graphene layers and periodic germanium nanowires, with thickness 200 nm. This medium is limited from top by a SF10 material.

In this study, both introduced SPR structures are numerically simulated at a free space wavelength of 633 nm. For this wavelength of light source, the applied refractive index of fused silica, titanium, gold, graphene, germanium nanowires, and SF10 are 1.457, 2.705+i3.767, 0.2+i3.32, 3.0+i1.149, 5.39+i0.69, and 1.723 respectively. As a single graphene layer has a thickness of 0.34 nm, thus, the three used graphene layers have total thickness of 1.02 nm. The cross section of a germanium nanowires (with grating period 140 nm) is circle with diameter 50 nm. Although these nanowires can be produced to smaller diameters [29], [30], however, the diameter of nanowires is minimized due to the available lab equipment to make possible in future fabrication.

The performance of the grating depends on the polarization of the incident wave. Since the transverse magnetic (TM) polarization excites the surface plasmons, the TM mode is considered. For this mode, the electric field vector is pointing in the *xy*-plane and perpendicular to the direction of propagation (parallel to *x*-axis), whereas the magnetic field has only a component in the *z*-direction. The angle of incidence is for both cases swept from 0 to $\frac{9\pi}{20}$, with a pitch of $\frac{\pi}{400}$.

Fig. 1 shows a three dimensional schematic of the proposed graphene-based SPR biosensor. A uniform gold film is coated on a fused silica prism via an adhesive of 5 nm thick titanium layer [31], [32]. The biomolecular reactions of ligand-analyte binding are modeled as a 200 nm thick dielectric layer where is located on the graphene surface and germanium nanowires.

Here the optical response of a Kretschmann surface plasmon resonance biosensor is used featuring a germanium nanowire grating and patterned ligand immobilization of surface receptors by combining graphene layer and germanium nanowires. At an initial stage, the refractive index of an immobilized ligand is set to be 1.332 and this value gradually increases with the quantity of ligand-analyte binding to 1.432.



Figure 1. The modeled germanium nanowires grating is designed in conventional Fresnel model and their corresponding parameters



Figure 2. The simulated electromagnetic field distributions of the conventional and proposed graphene-based SPR biosensor for TM mode

This study numerically confirms that new design can improve the tuning range (long range surface plasmon polaritons) and sensitivity of localized SPR sensors due to the graphene layers with germanium nanowires coated on the gold. The numerical analysis shows the sensitivity improvement of graphene-based SPR sensors originating from the germanium nanowires onto graphene thin film. The plasmon field distribution is studied in TM mode for the absorption or scattering enhancement effect of the germanium nanowires grating using rigorous propagation analysis by Comsol Multiphysics. The finite element method (FEM) is applied to analyze the two-dimensional (2D) germanium nanowires grating deposited on the fused silica (as substrate) by a smooth titanium adhesion layer.

III. RESULTS AND DISCUSSION

It is based on the assumption that the enhancement of localized plasmons can be demonstrated by the coupling phenomenon between the periodic germanium nanowires and the incident light with an appropriate polarization.

The diameter of 50nm germanium nanowires and thickness of 5nm titanium layer along with the three graphene layers have been optimized to achieve the best performance of the sensor in terms of sensitivity and full width at half maximum (FWHM). In Maxwell's equations, the general linearly polarized case can always be divided into two mutually independent fundamental polarization modes, TE and TM polarizations. For TE polarization, no resonance is found in the range of incident angles. For TM polarization, the resonance position is in the vicinity of 633 nm and the FWHM is about 25% improved as less as broadening of the SPR curve is good candidate for affinity-based sensing. As the output from the model, Fig. 2 shows the electric and magnetic fields for the TM case.



Figure 3. Simulated reflectance diagram using TM polarization for conventional and proposed biosensor configuration, observed resonance angle is 59.2



Figure 4. Transmission coefficients for conventional and proposed biosensor configuration

According to the proposed biosensor configuration, the sum of all coefficients is consistently less than 100. This is because of the dielectric losses in the germanium nanowires grating. This is more apparent in TM mode, as Fig. 3 and Fig. 4 show. Another important feature of the TM mode in the proposed graphene based-SPR structure is that there is a sharp specular reflection around 60 degree. It shows a germanium nanowires grating over gold thin film (as high refractive index dielectric) can be used to enhance the sensitivity of SPR sensor.

This mainly occurs because the germanium nanowires grating increases the field intensity of the excitation light at the sensing medium. Therefore, use of the germanium nanowires grating can possibly improve the sensing of biomolecules efficiently because it increases the mobility of electrons in graphene at the surface.

IV. CONCLUSION

We have numerically simulated and analyzed a state of the art graphene-based SPR sensor using germanium nanowire onto graphene layers compared to the conventional configuration. It is anticipated the germanium nanowire grating can be more effective in the usual graphene based-SPR biosensors. The proposed SPR configuration has not been implemented experimentally and wants to show the sensitivity could be dramatically improved by optimizing the thickness of layers and exploring more on material of layers and their patterns. This article provides a promising potential for biological sensing applications to fabricate a highly sensitive and more accurate biosensor.

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