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RESEARCH PAPER

Studying the Optical Properties of Nanostructure Au/TiO_2 Bi-layer Films using the SPR Technique for Biosensing Applications

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ABSTRACT

Surface plasmon resonance (SPR) is an optical technique that can be used for sensitive optical sensor and biosensor applications. Surface plasmon resonance (SPR) biosensors consisting of alternate layers of gold (Au) and Titanium dioxide (TiO_2) thin film have been proposed as a high sensitivity property. Simulation analysis (in Matlab program) has been made for SPR of gold layer with thickness (10, 30 and 50 nm) and (TiO_2) layer with different eight thicknesses (from 10 to 100 nm), which deposited on high refractive index glasses (N_LASF9 glass prism), while the final sensing medium is the air. The analysis achieved for different wavelengths in the visible band (500-700 nm) and different refractive index (0, 0.04, 0.08 and 0.12). The properties of SPR angle θ_{SPR} have been calculated from the incident angle θ_{SPR} plot. The SPR sensitivity (S) calculated within this study. The results show that the best sensitivity and maximum sensitivity is (116.66) for thickness TiO_2=40 nm, and thickness Au =50 nm at wavelength 700 nm. for the studied refractive index.

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INTRODUCTION

Surface Plasmon Resonance (SPR) property appears on the surfaces of some metals and is the result of the collective movement of free electrons present in the nanoparticle when light falls on them [1]. The SPR occurs when polarized light hits an electrically conductive surface at the interface between two media, and thus this generates charge density waves of electrons called plasmons, which leads to a reduction in the intensity of the reflected light at a certain angle called the angle of resonance [2]. When considering optical properties of thin metal films surface plasmon technique is widely used. [3-5]. The material (TiO_2) Titanium oxide is one of the minerals that have great importance in optical applications because it has many optical properties [6]. In addition to the transmittance to the visible and far-infrared range of the electromagnetic spectrum [7]. Films manufactured from these oxides are highly durable and have a high refractive index, so they are suitable for applications of anti-reflective coatings and multi-layer optical coatings [8]. In (2015) Borges, J., used TiO_2/Au thin films to study the physical and chemical properties of proteins, whereby a TiO_2/Au membrane was prepared and then heat treated. Au by a DC magnetic splatter method was detected and the membrane efficiency was 8.3%, at a temperature of 300°C, and 500°C [9]. In (2016) researchers DINGYI FENG

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used gold-coated fiber of infrared wavelengths to make a Tilted fiber Bragg gratings (TFBG) sensor and used a single- and double-sided tilt angle. 50 layers of gold were deposited with a thickness of nanometers; the experimental results show the similarity of the TFBG-SPR sensors with perfectly uniform precipitation-based processes. One of the precipitation conditions is that the precipitates are oriented appropriately in the direction of the tilt level, and this is considered difficult to apply, as it must be within 5 nanometers. [10]. In (2017) Md. R. Hasan et al proposed numerically demonstrate a two-layer circular lattice photonic crystal fiber (PCF) biosensor based on the principle of surface plasmon resonance (SPR). The finite element method (FEM) with circular perfectly matched layer (PML) boundary condition is applied to evaluate the performance of the proposed sensor. A thin gold layer is deposited outside the PCF structure, which acts as the plasmonic material for this design [11]. In (2020) Keyi Li et al proposed a different surface plasmon resonance biosensor by incorporating emerging two-dimensional material blue phosphorus and graphene layers with plasmonic gold film theoretically. They can provide sensitivity up to 1.4731 × 105 °/RIU, [12]. In (2021) Farah J. et al proposed an optical sensing applications and biosensors. Simulation analysis (using Matlab) has been done for SPR for gold (Au) layer with thickness (40 nm) and Polyvinyl Alcohol (PVA) polymer with various thickness (10, 20, 30, 40, 50, 60, 70 and 80 nm) deposited on glass prism type D-ZLAF50_Dense lanthanum flint. The analysis was taken for different wavelengths from ultra- violet of wavelength 100 nm to near infra-red wavelength of 1000 nm. The SPR sensitivity (S) was calculated. The maximum obtained sensitivity was 207.5 for (PVA) thickness of 30 nm and 40 nm, Δn= 0.08 at wavelength 800 nm and 1000 nm, respectively. The best sensitivity in visible region (700 nm) was 158.33 for thickness 20 nm, Δn= 0.12. [13].

In this study a simulation program was constructed in Matlab Program by adopting the Fresnel equations of reflectivity of electromagnetic waves in range Visible and using the transfer matrix for a system consisting of a semicircular prism on which two layers were deposited: The second is TiO_2 with a thickness of (10-100 nm) and the first is gold with a variable thickness started (10 nm, 30 nm, 50 nm, 80 nm). The simulations were presented to prompt a determination to understand the shape of the resonances when the sensor head (gold thin film) biosensor was applied as a pollutant gas.

MATERIALS AND METHODS

Electromagnetic waves at metal dielectric interfaces

To find the state that allows the presence of a surface electromagnetic wave propagating at the interface between two different media. We consider two semi-infinite media with complex dielectric functions M_1 and M_2 divided by a planar interface parallel to the x direction as is represented in Fig. 1. Each of the electromagnetic

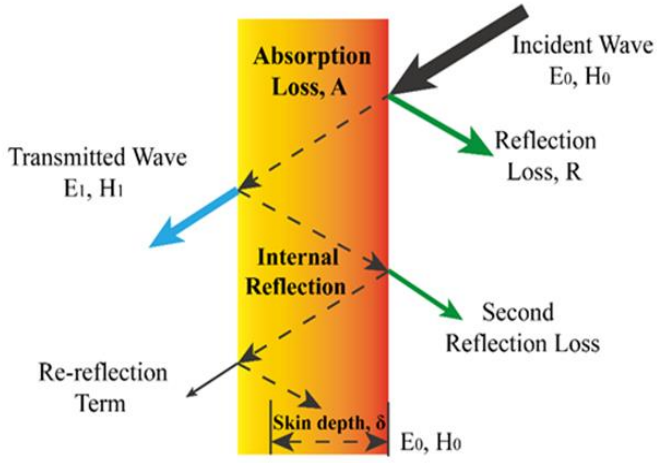

Fig. 1. The interface between two semi-infinite mediums is demonstrated. It's worth noting that the electromagnetic field is TM polarized [15].

fields must satisfy Maxwell's equations and the boundary conditions for electromagnetic fields. It is necessary to consider two different possible states of polarization of the electromagnetic wave: transverse magnetic wave (TM) and transverse electric wave (TE), where the magnetic field or the electric field is respectively perpendicular to the plane of incidence [14].

(a) Transverse Magnetic (TM) polarization

While we look for traveling, electromagnetic waves for easy way Expression the fields in the two semi-infinite media is the following. [16]:

$$Ej = \left(E_X j, 0, E_Z\right) exp\left(i\left(M_X j_X + M_Z, j_z\right) - i\omega t\right) \quad (1)$$

$$Hj = \left(0, H_y j, 0\right) exp(i(M_X, j_X + M_Z, j_z) - j\omega t) \quad (2)$$

Where j= 1, 2.

The dispersion relation of the surface Plasmon is [16]:

$$\beta = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (3)$$

The expression for the normal component of the wave vector obtained [16].

$$M_j, Z = \frac{\omega}{C}\sqrt{\frac{{\varepsilon_1}^2}{\varepsilon_{1+}\varepsilon_2}} \quad (4)$$

That β is called propagation constant and M is the wave vector, ε_1 and ε_2 of dielectric material and metal, respectively. Is the light angular frequency, C is the speed of light.

(b) Transverse Electric TE polarization

Since we are looking for magnetic field is parallel to the incidence plane, the boundary co1nditions and Maxwell's equation lead to the relations [17]:

$$M_{Z_{0_1}} + M_{Z_{0_2}} = 0, \quad (5)$$

$$M_{X,1} = M_{X,2} \quad (6)$$

That, together lead for equation [17]:

$${M_1}^2 = \left(\frac{\omega}{C}\right)^2 M_1 \quad (7)$$

$${M_2}^2 = \left(\frac{\omega}{C}\right)^2 M_2 \quad (8)$$

Methodology: Measurement of the optical constants of Au and TiO_2 layers

The Simulation analysis (in Matlab) consists of four media, such as glass prism (half-sphere type N-LASF9_ glass), deposited on it layer of gold with the thickness (10, 30, 50) nm, and TiO_2 with different thickness from (10 to100) nm step10 nm with the final medium (sensing polluting gases), using the excitation light beam different wavelengths from 500 to 700 nm (Fig. 2).

The wave vector of the surface plasma wave suffers a perturbation ΔM respect to the wave vector β. The dispersion relation of the surface plasmon, is [18]:

$$\beta = \frac{\omega}{C}\sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} = \beta' + \beta'' \quad (9)$$

, since ω is the light angular frequency, c is the speed of light,ε_1 and ε_2 are the complex dielectric functions for medium1 and medium2 respectively . So β characteristic of two semi-infinite media, and can be written. [18]:

$$\beta' = \beta + \Delta M \quad (10)$$

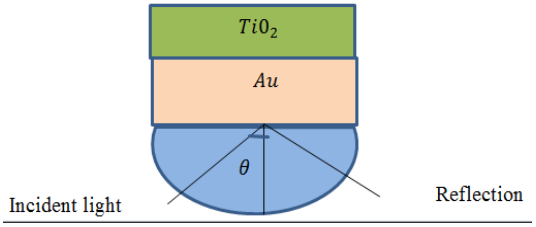

Fig. 2. Schematic diagram of the proposed SPR sensor (Au and TiO_2)

That real part of ΔM causes a displacement of the resonance position compared to Re(β), while its imaginary part is related with the presence of the prism and the finite thickness of the metal layer. This new term ΔM can be approximated as the contribution of the intrinsic damping, which represents the joule loss in the metal, and the intrinsic damping, which represents the joule loss in the metal, and the radiation damping which represents the energy lost by back-coupled radiation. For metals generally used in SPR experiments such as aluminum, gold or silver, it exists an analytic approximation of the SPR curve near the angle of resonance θ_{SPR} which is given by [19]:

$$R = 1 - \frac{4I_m(\beta)I_m(M)}{n^2M^2(\sin\theta - \sin\theta_{spr}) + I_{m(\beta r)^2}} \quad (11)$$

And I_m is imaginary part and M_0 the vacuum of wave vactor, surface Plasmon resonance is the requires wave vector of the incident light in the plane of the surface (M_x) match the wave vector of the SP wave in metallic films M_{SP} [20]:

$$M_x = n_p\left(2\pi/\lambda\right)\sin\theta \quad (12)$$

$$M_{sp} = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}} \quad (13)$$

M_1 and M_2 represent complex dielectric constant of dielectric material and metal, respectively.

n_p: is the refractive index of the prism. λ and θ: are wavelength and angle of incident light, respectively. The matching relationships for SPR are M_x=M_{SP} [20] where

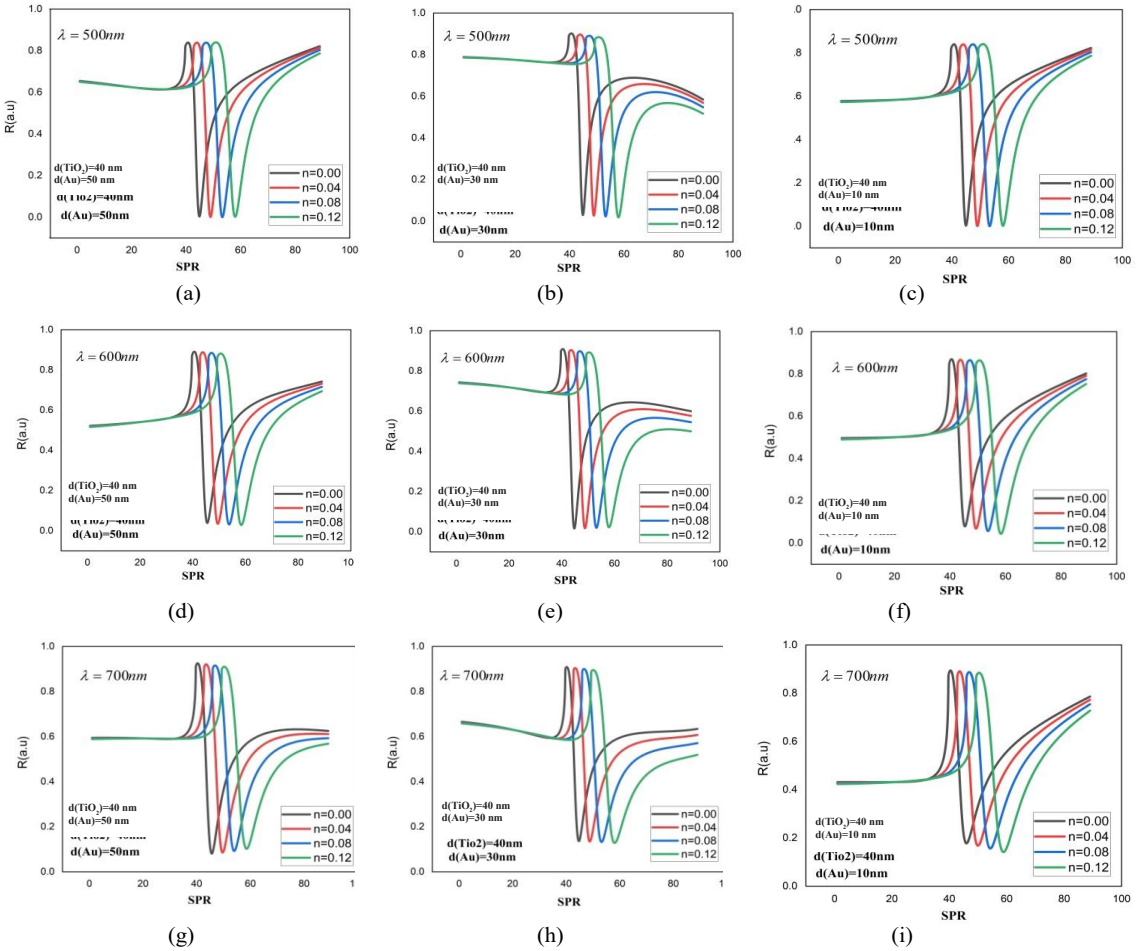

Fig. 3. The relation between reflectance with incident angle for different thickness TiO_2 and wavelength (λ) = 500, 600 and 700 nm.

$$\theta_{SPR} = \sin^{-1}\sqrt{\frac{M_1 M_2}{M_2(M_1 + M_2)}} \quad (14)$$

Where the resonant angle is can be adjusted by controlling the angle of incidence in order to match the propagation constant of the plasmon waves and the sensitivity of the sensor to changes in the refractive index of an analyte placed in direct contact with the sensor surface is defined by [13]:

$$S_{n=}\frac{\partial\theta_{spr}}{\partial n} \quad (15)$$

where θ_{SPR} is the resonant angle , =how that for wavelengths of electromagnetic waves in the visible range, and using noble metals such as gold the ratio of the losses terms reaches 1 when the thickness is approximately 50 nm. Further, it is possible to demonstrate that the full width half maximum (FWHM) of the curve of reflectivity is proportional to the imaginary part of the wave vector of the plasma wave, that is to the losses of the systems [13].

RESULTS AND DISCUSSION

The film thickness of a single metal-based SPR sensor has to be such that the resonance curve produced by a sensor structure under consideration not only shows the maximum possible loss in reflectivity and absorption but also produces the slimmest possible FWHM of the reflectivity curve. The thickness range for a gold film-based SPR sensor would be (10, 30, and 50) nm. Fig. 3a, b, c, d, e, f, g, h and i show the relationship between reflectivity as a function of the angle of incidence of the light ray. Where shown that the SPR curves resulting from the simulation of the proposed system consisted of a gold layer and a titanium layer for different states

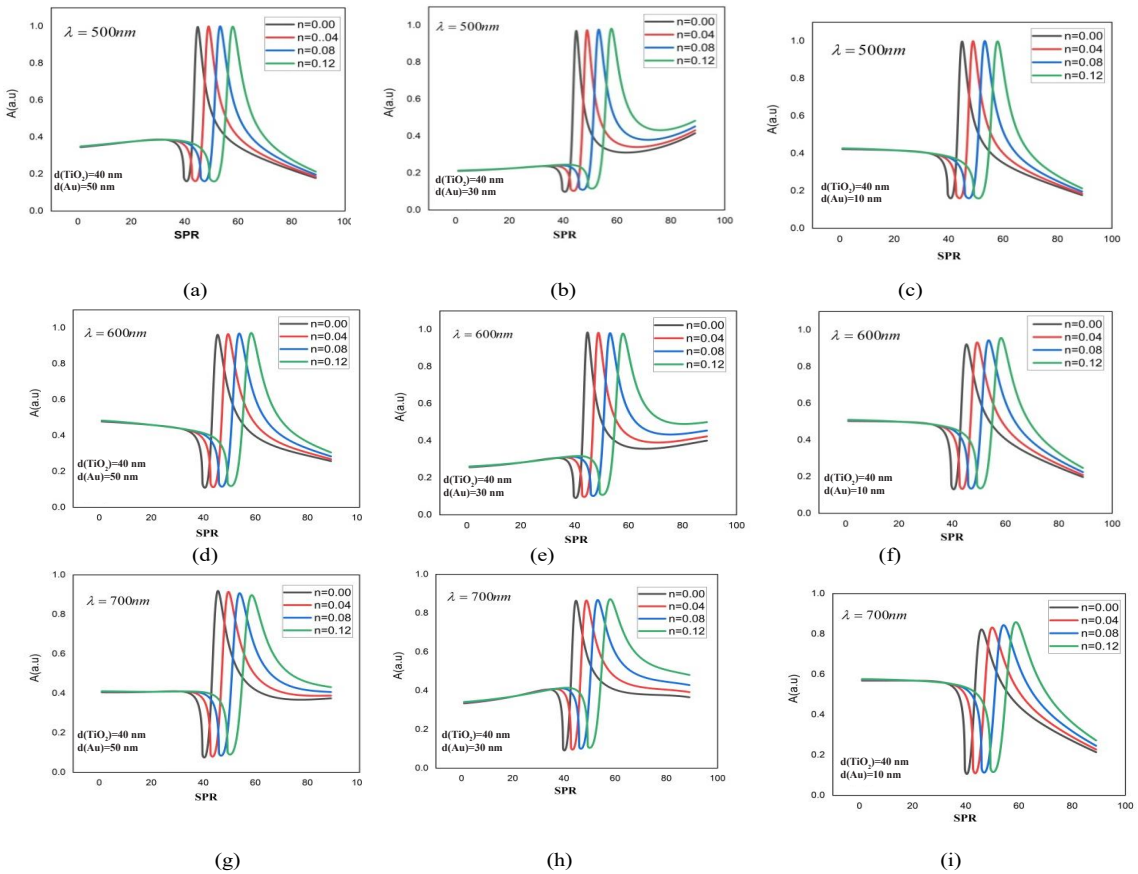

Fig. 4. The relation between absorption with incident angle for different thickness TiO_2 and wavelength (λ) = 500, 600 and 700 nm.

of titanium thicknesses and different wavelengths. Any minimum reflectivity value corresponds to the maximum energy loss due to the high absorption of the light beam within the sensor system. The excitation of the surface plasmon is determined by the angle of resonance of the surface plasmon. The surface plasmon resonance revealed by the curves in this figure can be determined as follows There is SPR at λ= 500 nm for TiO_2 thickness is 40 nm and Au thicknesses are (10,30,50 nm) ,The best SPR at Au thickness d=50 nm in λ= 500 nm see Fig. 3a, b and c. There is SPR at λ=600nm for TiO_2 thickness is 40 nm and Au thicknesses are (10, 30, 50 nm). The best SPR at Au thickness d=30 nm in λ=600 nm see Fig. 3d, e and f. There is SPR at λ=700 nm for TiO_2 thickness is 40 nm and Au thicknesses are (10, 30, 50 nm), the best SPR at Au thickness d=50 nm in λ=700 nm see Fig. 3g, h and i. The surface Plasmon resonance angle (θspr) shifts to a higher angle when λ=500 nm especially at TiO_2 thicknesses 40 nm and Au 50 nm.

Fig. 4a, b, c, d, e, f, g, h and i shows the relationship between absorption as a function of the angle of incidence of the light ray. Where shown that the SPR curves resulting from the simulation of the proposed system consisting of a gold layer and a TiO_2 layer for different states of titanium thicknesses and different wavelengths. Any maximum value of absorption corresponds to the minimum energy loss due to the Low absorption of the light beam within the sensor system. The excitation of the surface plasmon and is determined by the angle of resonance of the surface plasmon. The surface Plasmon resonance revealed by the curves in this figure can be determined as follows. There is SPR at λ= 500 nm for TiO_2 thickness is 40 nm and Au thicknesses are (10, 30, 50 nm). The best SPR at Au thickness d= 50 nm in λ= 500 nm see Fig. 4a, b and c. There is SPR at λ= 600 nm for TiO_2 thickness is 40 nm and Au thicknesses are (10, 30,50 nm) .The best SPR at Au thickness d= 30 nm in λ=600 nm see Fig. 4d, e and f. There is SPR at λ=700 nm for TiO_2 thickness is 40 nm and Au thicknesses are (10, 30,50 nm)

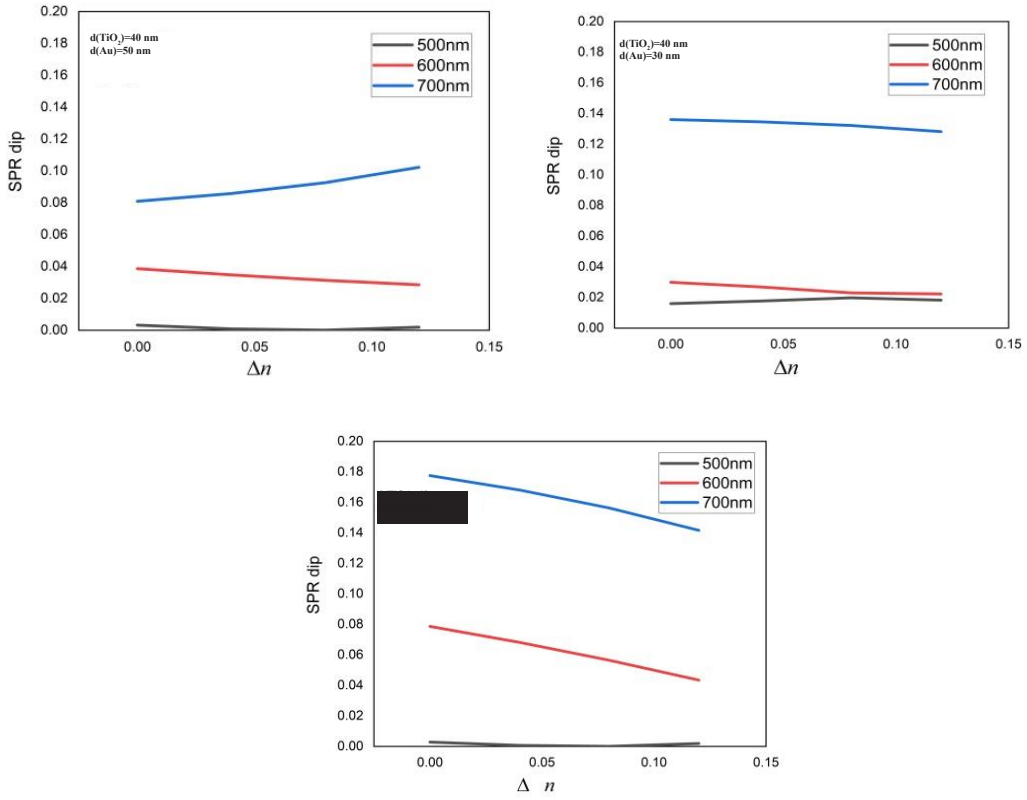

Fig. 5. The variation of SPR dip length (Ld) with the change of refractive index of layers for different thickness (Au) and wavelength (500,600,700 nm.)

.The best SPR at Au thickness d=50 nm in λ=700 nm seeing Fig. 4g, h and i.

The surface Plasmon resonance angle (θ_{SPR}) shifts to a higher angle when λ=500 nm especially at TiO_2 thicknesses 40 nm and Au 50 nm.

The properties of SPR dip length (Ld) against the changing of the refractive index of sensing medium increased length are shown in Fig. 5. It has been noted that the decreased plasmonic bottom length(SPR dip length) with increased TiO_2 thickness at the wavelengths 500, 600, and 700 nm. It is noticed that there is an observable increase in the length when increasing the wavelength from 500, 600 to 700 nm at the same thickness of TiO_2, meaning a further improvement in the plasmonic resonance.

On the other hand, Fig. 3 Illustrated the relation between reflectance with incident angle, that once the thickness increases from (10-100) nm, the dip of SPR all thickness of TiO_2 layers appear and become sharper at 500 nm. Also, Fig. 4 Illustrates the relation between absorption with incident angle, that once the thickness increases from (10-100) nm, the dip of SPR for all thicknesses of TiO_2 layers becomes severer at 500 nm.

Table1, it shows the sensitivity values and thicknesses for two layers of TiO_2 and Au within the visible range. The best result of sensitivity at thickness of (d=40 nm) for TiO_2 when using wavelength 500-700 nm and thickness of Au (d=50 nm) at wavelength 700 nm.

CONCLUSION

In summary, differences in the performance of SPR sensing to prism-based for Au layer (10, 30,50 nm) following the addition of the layers of TiO_2 (10-100 nm) were investigated in this paper. The performance of the Au/TiO_2 layers was analyzed and numerically simulated. Finally, the sensitivity and the properties of θ_{SPR} calculated from curve reflectance with incident angle θ_{incid} for each structure were obtained via simulations involving changes in the refractive index of the sensitive layer. Numerical simulation results showed the following points; the biosensor Au-TiO_2 layer deposited on prism gave SPR dip at wavelength 500,600 and 700 nm and shows no appearance for wavelength 500 in the viable range. The best SPR is in the wavelength 500 nm at TiO_2 thickness d=40 nm, Au thickness d=50 nm at Δn=0.12 and for the wavelength 600nm, TiO_2 thickness at d=40 nm. Au thickness d=50 nm at Δn=0. The findings of this work can be used as a theoretical foundation for making major adjustments to SPR sensors to improve their sensitivity.

The best result of sensitivity at thickness of (d=40 nm) for TiO_2 when using wavelength 500-700 nm and thickness of Au (d=50 nm) at wavelength 700 nm.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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