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Sensitivity enhancement of a nanocomposite-based fiber optics sensor with platinum nanoparticles

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In this paper, sensitivity enhancement of a nanocomposite-based optical fiber sensor with platinum nanoparticles is investigated. This optical fiber sensor is based on the surface plasmon resonance in the nanocomposite layer coating the core of optical fiber. A comparison is carried out for sensitivity between an optical fiber sensor based surface plasmon resonance with platinum layer and the one with nanocomposite layer. The nanocomposite layer consists of platinum nanoparticles with varying volume fraction which is arrayed in a host dielectric material of InN or TiO_2. We show that the sensitivity of the sensor with a nanocomposite layer containing platinum nanoparticles is bigger than the sensitivity of the sensor with a platinum layer for all the values of refractive index of sample media. Also, the effect of the thickness of the nanocomposite layer and the volume fraction of platinum nanoparticles on the spectrum of the transmitted power has been investigated.

Keywords: surface plasmon resonance, sensor, nanocomposite, platinum, sensitivity.

1. Introduction

In recent years, many researchers try to find various sensing techniques which may be used for fast and accurate measurement of numerous physical, chemical and biochemical parameters. The optical excitation of a surface plasmon wave at the interface between a metal and a dielectric is called surface plasmon resonance (SPR). The SPR -based optical fiber sensors have attracted great attention due to enormous potential for measuring with high sensitivity, including the measurements of the concentration of an analyte in a complex sample, the specificity, affinity, biomolecular interaction kinetics [1–5]. The surface plasmon wave can be excited by the evanescent field of the incident p-polarized light. This p-polarized light can excite the surface plasmon wave resonantly if the wave vector and the frequency of the incident p-polarized light coincide with that of the surface plasmon wave. The incident angle, the wavelength of the light and the dielectric constants of both metal and dielectric are important items for resonance condition. The reflectance spectrum shows a sharp dip at the resonance angle (angular interrogation) or at the resonance wavelength (wavelength interrogation). This resonance angle or wavelength is most sensitive to variations in the refractive indices of the metal layer and the dielectric adjacent to the metal and their geometrical sizes. Therefore, the variations in the refractive index of sensing medium can be detected by measuring the variations in the reflected spectrum and its dip. Commonly, SPR has been studied by Kretschmann's configuration that is based on attenuated total internal reflection [6, 7]. Kretschmann's configuration based on the prism-coupled configuration that a high refractive index prism is coated with a thin metal film. The surface plasmon waves are excited by an evanescent wave from a high refractive index prism at the total reflection condition. The optical fiber based SPR sensing has many attractive advantages, such as miniaturization and integration, remote sensing, continuous analysis, real time and *in situ* monitoring [8–10]. In optical fiber based SPR sensor, the glass prism is replaced by a fiber core. Optical fiber based SPR sensing has been investigated by numerous experimental and theoretical research studies [11–13]. In this way, a SPR-based fiber optic sensor has been fabricated for the detection of low content of water in ethanol [11] and a SPR-based optical fiber sensor has been reported for the detection of urea in liquid [12]. A theoretical analysis of a SPR-based optical fiber sensor with four-layer is studied in [14] and the effect of the thickness of metal layer and sensing layer on the spectrum of the transmitted power and wavelength has been studied. It has been shown that sensitivity of the SPR-based sensor is enhanced by using of conducting metal oxides along with plasmonic metals [15].

So far as gold and silver metals have been widely used as SPR active materials for SPR-based sensor because they have considerable amount of charge carriers. However, the SPR sensors based on these metals have small sensitivity and therefore these are not suitable for sensing of gas samples. Also, the SPR sensors based on these metals have the SPR resonance dips in UV region. Therefore, a nanocomposite-based fiber optic SPR sensor has been reported to sensing of gas samples in a visible region [16]. Generally, the nanocomposites consist of nanoparticles of gold (Au), silver (Ag), copper (Cu) and aluminum (Al) with their varying volume fractions embedded in host dielectric material like titanium oxide (TiO_2) and indium nitride (InN) [17, 18]. A fiber optic sensor with a nanoparticle layer coated on the core of the optical fiber has been analyzed in which nanoparticles layer of four metals (ITO, Au, Ag and Cu) was considered [19]. Recently, a novel approach is proposed to embed sensing under extreme temperature conditions by integration of Au-nanoparticle based plasmonic nanocomposite thin films with optical fibers [20]. In other research, a fiber optics SPR sensor with a metal–semiconductor core–shell nanocomposite layer is studied [21]. A SPR-based fiber optic sensor is designed for the detection of manganese ions in aqueous medium using nanocomposite of ZnO-polypyrrole [22]. The performance of a fiber optic SPR sensor based on silver-gold alloy nanoparticle film is theoretically analyzed in terms of its signal-to-noise ratio (SNR) [18].

Recently, platinum (Pt) metal has attracted researcher's interest as a metal layer in SPR-based optical fiber sensor and a highly sensitive SPR sensor with Pt layer coated on the core of the optical fiber has been theoretically studied [23]. Platinum metal has prolonged stability, high melting point, high reflectivity. Platinum is an important metal in optoelectronic devices, solar cells, sensors, automotive industry and anti-cancer drugs [24]. SHAH *et al*. studied an SPR fiber sensor with bilayers of Pt-ZnO and they showed sensitivity of sensor enhance by increasing the Pt layer thickness [15]. Their proposed sensor was composed of the platinum layer and ZnO layer and the highest sensitivity was calculated to be 3160 nm/RIU for the sensing layer with refractive index 1.37. In this paper, for this refractive index of the sensing layer, we present the highest sensitivity of 3200 nm/RIU with only one nanocomposite layer. We studied an SPR-based optical fiber sensor with Pt-TiO_2 or Pt-InN nanocomposite layer and it has been shown that the sensitivity of the sensor with nanocomposite layer containing platinum nanoparticles is bigger than the sensitivity of sensor with platinum layer, for all the values of refractive index of sample media. The paper is organized as follows. In Section 2, we introduce a theory of the fiber sensor. In Section 3, the numerical results are demonstrated for our proposed SPR fiber sensor. In Section 4, the paper is concluded.

2. Theory

The SPR sensing is based on the principle of ATR with Kretschmann's configuration. In the proposed SPR-based fiber optic sensor, the sensing system is a three layer system consisting of a fiber core–nanocomposite layer–sensing medium as shown in Fig. 1.

The plastic cladding around of the core is removed from the middle portion of a step index multimode fiber. Then, it has been coated with a thin nanocomposite layer of thickness *d*. Finally, it is surrounded by the sensing medium. The fiber has the numerical aperture and core diameter, 0.24 and 600 nm, respectively. The light from a polychromatic source is launched into one of the ends of the optical fiber with suitable optics. Then, we detect the transmitted light at the other end of the optical fiber. The transmitted power will show a sharp dip at a resonance wavelength that is dependent on the refractive index of sensing medium. The core of optical fiber is the layer I and it is assumed to

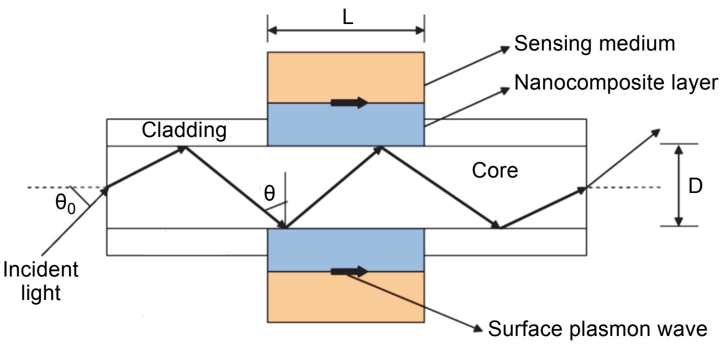

Fig. 1. Schematic diagram of SPR-based fiber optic sensor.

be made of fused silica. The refractive index of fused silica is dependent on the wavelength according to Sellmeier's dispersion relation as,

$$n_1(\lambda) = \sqrt{1 + \frac{a_1\lambda^2}{\lambda^2 - b_1^2} + \frac{a_2\lambda^2}{\lambda^2 - b_2^2} + \frac{a_3\lambda^2}{\lambda^2 - b_3^2}} \tag{1}$$

where λ is the wavelength in μm, and a_1, a_2, a_3, b_1, b_2 and b_3 are Sellmeier's coefficients. The values of these coefficients are given as, $a_1 = 0.6961663$, $a_2 = 0.4079426$, $a_3 = 0.8974794$, $b_1 = 0.0684043$ μm, $b_2 = 0.1162414$ μm and $b_3 = 9.896161$ μm [25].

The composite layer is the layer II. In the nanocomposite media, the nanoparticles of one component material are embedded in a continuous host dielectric matrix of the other component [17]. Here, the particle sizes of nanoparticles are much smaller than the wavelength of the incident radiation. Therefore, we can use the Maxwell–Garnett model for calculating the effective dielectric constant of nanocomposite [26]. According to this model, the effective dielectric constant of nanocomposite is given as,

$$\varepsilon_{\text{eff}} = \varepsilon_2\left(\frac{\varepsilon_1 + 2\varepsilon_2 + 2f(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - 2f(\varepsilon_1 - \varepsilon_2)}\right) \tag{2}$$

where ε_1 is the dielectric constant of metal nanoparticles of component 1, and ε_2 is the dielectric constant of host dielectric matrix of component 2; f is the volume fraction of nanoparticles of component 1. The nanoparticles of permittivity ε_1 are distributed in the host dielectric of permittivity ε_2 either on a lattice or randomly but uniformly on average. The volume fraction f = (volume of nanoparticle)/(volume of unit cell). In Eq. (2), the effective dielectric constant of nanocomposite is assumed to be independent of the particle size and shape of the nanoparticles. In this paper, the Pt metal is assumed as component 1. InN or TiO_2 are considered as component 2. The dielectric constant of Pt metal is written according to the Drude model as,

$$\varepsilon_1 = 1 - \frac{\lambda^2\lambda_c}{\lambda_p^2(\lambda_c + i\lambda)} \tag{3}$$

where λ_p and λ_c are the plasma wavelength and the collision wavelength of Pt, respectively. Here, $\lambda_p = 2.415 \times 10^{-7}$ m and $\lambda_c = 1.795 \times 10^{-5}$ m [27]. The dielectric constant of host dielectric matrix InN according to the Drude model is given as [28],

$$\varepsilon_2 = \varepsilon_\infty\left(1 + \frac{w_{LO}^2 - w_{TO}^2}{w_{LO}^2 - w^2 - iw\gamma} - \frac{w_p^2}{w^2 + iw\Gamma}\right) \tag{4}$$

Here, ε_∞ is the high frequency dielectric constant, ω_{LO} and ω_{TO} are longitudinal optical and transverse optical frequencies of phonon mode, ω_p is the plasma frequency, γ and Γ are the two corresponding damping constants. The values of parameters are: $\varepsilon_\infty = 7.5$, $\omega_p = 4100$ cm^{-1}, $\Gamma = 1382$ cm^{-1}, $\omega_{LO} = 590$ cm^{-1}, $\omega_{TO} = 450$ cm^{-1} and $\gamma = 120$ cm^{-1}.

The refractive index of host dielectric matrix TiO_2 is given by the empirical formula as [29],

$$n_{TiO_2} = \sqrt{5.913 + \frac{0.2441}{\lambda^2 - 0.0843}} \tag{5}$$

The last layer is the sensing medium. The refractive index and the dielectric constant of sensing medium are n_s and $\varepsilon_s = n_s^2$, respectively. Therefore, the resonance condition for excitation of surface plasmon wave would be

$$\frac{2\pi}{\lambda} n_1 = \mathrm{Re}\{K_{sp}\} \tag{6}$$

where

$$K_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_s}{\varepsilon_m + \varepsilon_s}} = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m n_s^2}{\varepsilon_m + n_s^2}}$$

is the propagation constant of the surface plasmon wave, and c is the speed of light in vacuum. The propagation constant of the surface plasmon wave (K_{sp}) is dependent on the refractive index of sensing medium. If the refractive index of sensing medium is changed, the resonance condition will be satisfied at some other value of wavelength. Therefore, the variation in the refractive index of sensing medium can be measured by the variation in resonance wavelength.

2.1. Transmitted power

The reflected intensity of p-polarized incident light can be calculated by using the matrix method for N-layer model [30]. This light is launched into one end of the fiber from a collimated source. The power at another end of the fiber between the incident angles θ and $\theta + \mathrm{d}\theta$ would be [30] $\mathrm{d}P \propto P(\theta)\mathrm{d}\theta$, where the angular power distribution of rays guided in the fiber is given as [31],

$$P(\theta) = \frac{n_1^2 \sin\theta \cos\theta}{(1 - n_1^2 \cos^2\theta)^2} \tag{7}$$

Here, n_1 is the refractive index of the fiber core and θ is the angle of the ray with the normal to the core-cladding interface. Finally, for p-polarized light, the normalized transmitted power in an optical fiber based SPR sensor can be calculated as

$$P_{trans} = \frac{\int_{\theta_{cr}}^{\pi/2} R_p^{N_{ref}(\theta)} P(\theta)\mathrm{d}\theta}{\int_{\theta_{cr}}^{\pi/2} P(\theta)\mathrm{d}\theta} \tag{8}$$

where $N_{ref}(\theta) = L/(D\tan\theta)$ and $\theta_{cr} = \sin^{-1}(n_{cl}/n_1)$. Here, θ_{cr} is the critical angle of the fiber and n_{cl} is the refractive index of the fiber cladding; N_{ref} is the total number of light reflections performed by a ray; L and D are the length of the exposed sensing region and the fiber core diameter, respectively. Also, the sensitivity of a SPR sensor with wavelength interrogation is defined as the change in resonance wavelength per unit change in refractive index of the sensing medium [32]. Therefore, sensitivity $S = \delta\lambda/\delta n$, where $\delta\lambda$ is the shift of the resonant wavelength, and δn is the refractive index variation of the sensing layer.

3. Results and discussion

For numerical calculations, the following values of the parameters have been used: numerical aperture of the fiber is 0.24, fiber core diameter $D = 600$ μm and length of the exposed sensing region $L = 15$ mm. In this paper, nanocomposites consisting of Pt nanoparticles with different volume fraction embedded in host dielectric matrices of TiO_2 and InN have been studied. Firstly, we try to optimize the thickness of nanocomposite layer and volume fractions of nanoparticles. Therefore, the transmitted output power of SPR-based fiber optic sensor has been investigated for different value of the thickness of nanocomposite layer and volume fractions of nanoparticles.

3.1. Nanocomposite TiO_2

Figure 2**a** shows the transmitted output power spectrum of SPR sensor for 40, 50, 60 and 70 nm thick Pt-TiO_2 nanocomposite layers with fixed volume fractions of 0.85 with refractive index of sensing medium $n_s = 1.37$. The results show that the resonance wavelength rises with the increasing thickness of nanocomposite layer and the resonance dip broadens. In Fig. 2**b**, the transmitted output power spectrum of SPR sensor

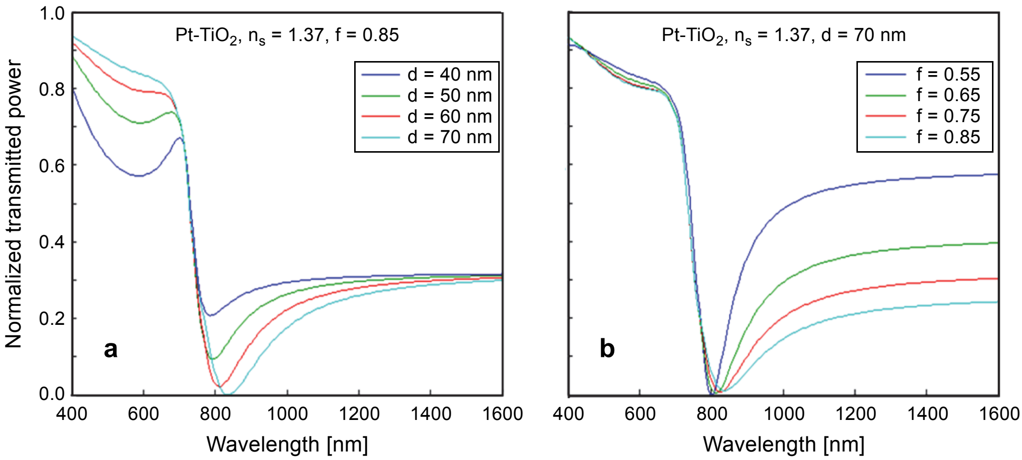

Fig. 2. Normalized transmitted power *vs*. wavelength for 40, 50, 60 and 70 nm thick Pt-TiO_2 nanocomposite layers with fixed volume fractions of 0.85 (**a**), and for 70 nm thick Pt-TiO_2 nanocomposite layer with various volume fractions of 0.55, 0.65, 0.75 and 0.85 (**b**).

has been plotted for 70 nm thick Pt-TiO_2 nanocomposite layer with volume fractions f = 0.55, 0.65, 0.75 and 0.85 for refractive index of sensing medium n_s = 1.37. It can be seen that the resonance wavelength rises with the increasing volume fraction of nanoparticles. The increase in the nanocomposite layer thickness, from 40 to 70 nm, shifts the resonance wavelength from 790 to 830 nm. The increase in the volume fraction of the nanoparticles (0.55 to 0.85) shifts the resonance wavelength about 25 nm. Also, the resonance dip of SPR sensor has been broadened with the increasing volume fraction of nanoparticles. There is a decrease in the real part of the dielectric constant of the nanocomposite layer with an increase in the volume fraction f. This means that as we increase the volume fraction of nanoparticles in the nanocomposite layer, the real part of the nanocomposite dielectric function becomes more negative. Therefore, according to Eq. (6), for a given change in sensing layer index δn, greater volume fraction of nanoparticles gives a larger shift in resonance wavelength. Therefore, the sensitivity of the SPR fiber sensor increases with an increase in the volume fraction f.

3.2. Nanocomposite InN

Figure 3**a** illustrates the transmitted output power spectrum of SPR sensor for Pt-InN nanocomposite layers holding the volume fraction 0.85 with thicknesses 40, 50, 60 and 70 nm for the refractive index of sensing medium n_s = 1.37. Also, in Fig. 3**b**, the transmitted output power spectrum of SPR sensor has been plotted for 70 nm thick Pt-InN nanocomposite layer with volume fractions of 0.55, 0.65, 0.75 and 0.85 for refractive index of sensing medium n_s = 1.37. Figures 3**a** and 3**b** show that resonance wavelength rises with the increasing volume fraction of nanoparticles and with the increasing thickness of nanocomposite layer. Also, the broadening of the resonance dip of SPR sensor has been seen with the increasing either thickness of nanocomposite layer or volume fraction of nanoparticles.

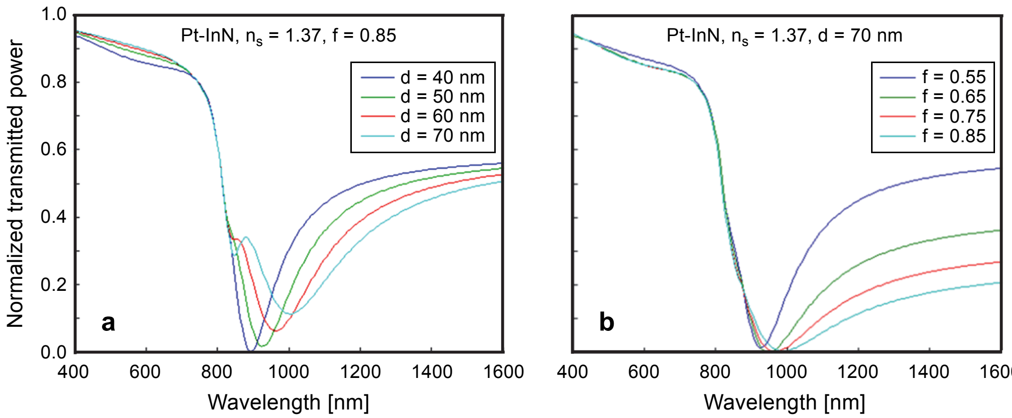

Fig. 3. Normalized transmitted power *vs*. wavelength for 40, 50, 60 and 70 nm thick Pt-InN nanocomposite layers with fixed volume fractions of 0.85 (**a**), and for 70 nm thick Pt-InN nanocomposite layer with various volume fractions of 0.55, 0.65, 0.75 and 0.85 (**b**).

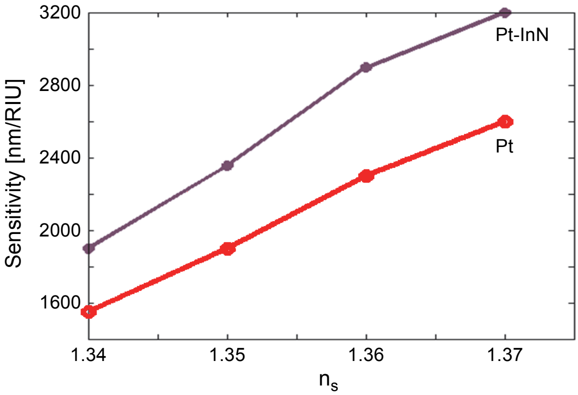

Fig. 4. Variation in sensitivity of SPR-based fiber optic sensor with refractive index of sensing medium for Pt metal and Pt-InN nanocomposite layers.

Also, the optimum value of nanocomposite layer thickness and the volume fraction of nanoparticles are important to be investigated in order to achieve the maximum sensitivity from the SPR fiber optic sensor. Therefore, the sensitivities of SPR-based fiber optic sensor for a number of thickness values of Pt-TiO_2 and Pt-InN nanocomposite layers with different volume fractions of nanoparticles have been investigated. Finally, our results show that the SPR-based fiber optic sensor has highest sensitivity for Pt-InN nanocomposite layer with 70 nm thickness and volume fraction 0.85. In Fig. 4, the sensitivity of SPR-based fiber optic sensor *vs*. the refractive index of the sensing medium is plotted for Pt metal and Pt-InN nanocomposite layers. In this figure, we select the Pt layer thickness 70 nm, the Pt-InN nanocomposite layer thickness 70 nm and the volume fraction 0.85. These curves have been calculated from the second order polynomial fit of the resonance wavelength *vs*. the sensing layer refractive index curve. Figure 4 shows that the sensitivity of the SPR sensor increases linearly with the increase in the refractive index of the sensing medium for Pt metal layer as well as Pt-InN nanocomposite layer. The slope of sensitivity of SPR sensor over the refractive index of the sensing medium is almost same for both of Pt metal and Pt-InN nanocomposite layers. But, the sensitivity of SPR-based fiber optic sensor with Pt-InN nanocomposite layer is more than the sensitivity of the sensor with Pt metal layer. Because the nanocomposite layer has a large value of the real part of its dielectric constant the nanocomposite layer increases the shift between the resonance wavelengths for a given change in the refractive index of the sensing layer. Figure 4 shows that the SPR fiber sensor with Pt-InN nanocomposite layer has the highest sensitivity 3200 nm/RIU.

4. Conclusions

The SPR-based fiber optic sensor with Pt-TiO_2 and Pt-InN nanocomposite layers coated on the core of the optical fiber has been studied. The sensitivity of the SPR-based fiber optic sensor is investigated for various thicknesses (40–70 nm) of nanocomposite layer and various volume fractions of Pt metal nanoparticles. In this study, the host dielectric matrices of TiO_2 and InN are considered. The simulations show that the sensitivity of the proposed SPR sensor increases linearly with the increase in the refractive index of the sensing medium for Pt metal layer as well as Pt-InN nanocomposite layer. Finally, the SPR-based fiber optic sensor has highest sensitivity for Pt-InN nanocomposite layer with 70 nm thickness and volume fraction 0.85.

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