Sensitivity Calculation of An Optical Plasmon Sensor Based on Semiconductor Nanoparticles of Different Shapes

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ABSTRACT

The paper deals with the influence of the geometric shape of a semiconductor nanoparticle on the sensitivity of an optical plasmon sensor built on its basis. An ellipsoidal Indium-Tin Oxide (ITO) nanoparticle is considered as an example. It is shown that the sensitivity of such a sensor is proportional to the semiaxis dimension of the ellipsoid along which the polarization of the incident radiation is directed.

Keywords: Semiconductor nanoparticles; Localized surface plasmon resonance (SPR); absorbtion cross section; optical plasmonic sensor

Introduction

At present, almost all areas of human activities involve the use of nanoparticles for solving various technical issues [1-6]. One of the most perspective nanoparticles applications is biosensors [7-10]. Noble metals are mostly used materials for nanoparticle production due to their low reactivity, biological compatibility [11], high stability and catalytic activity [12]. Nevertheless, noble metal nanostructures have some important disadvantages: high cost and much limited ability to change a density of the free charge carriers [13]. The latter makes almost impossible to tune surface plasmon resonance parameters. From this point, semiconductor nanoparticles are rather cheap and flexible solution of this problem due to the doping opportunity (concentration of free charge carriers can be altered in the wide ranges that corresponds to the plasmon resonance frequencies in the diapason from the terahertz to the visible part of light spectrum) [14]. As a matter of fact, semiconductor materials are widely used in the biosensors design. For example, CdS and PbS nanoparticles are used for biomolecules labeling [15],

polyaniline semiconductor films is a rather perspective solution for potentiometric biosensor development [16]. One more intriguing application is proposed in the work [17] devoted to *Escherichia coli* detection with use of photoluminescence-based quantum semiconductor biosensor. Despite the variability of approaches and applications, consideration of semiconductor nanoparticles plasmonic properties in the context of biosensor development is far from the exhaustive. This is the point to which the present work is devoted.

The processes of absorption and scattering of electromagnetic radiation on semiconductor spherical nanoparticles were considered earlier [18,19]. Based on the results obtained, a model of an optical plasmon sensor based on semiconductor nanoparticles was proposed [20]. This work is a continuation of the aforementioned works and sets the task of generalizing the model of an optical plasmon sensor to semiconductor nanoparticles of ellipsoidal shape, since the previously proposed model [20] is only

a special case for specific nanoparticles. An analysis of the literature showed that this issue had not been investigated earlier, and the model [20] showed the promising prospects of using semiconductor nanoparticles in sensors based on surface plasmon resonance.

Materials and Methods

We find the photoabsorption cross section using the optical theorem:

$$\sigma_{abs}(\omega) = \frac{4\pi\omega\sqrt{\varepsilon_m}}{c} \operatorname{Im}\alpha(\omega) \qquad (1)$$

where ω is the frequency of laser radiation, ε_m is the dielectric permittivity of the medium in which the nanoparticle is placed, c is the speed of light in vacuum, $\alpha(\omega)$ is the dynamic polarizability of the nanoparticle.

The calculation $\alpha(\omega)$ is performed within the dipole approximation, i.e. for a nanoparticle, the maximum linear size d of which is significantly less than the wavelength λ of the incident radiation:

$$\lambda \gg 2\pi d\sqrt{\varepsilon_m} \qquad (2)$$

The geometry of a nanoparticle [21] is the ellipsoid. A rectangular coordinate system XYZ is introduced, the origin of which coincides with the geometric center of the ellipsoidal nanoparticle, and the axes OX, OY, OZ are directed along the semiaxes of the ellipsoid a, b, f respectively.

It is assumed that the electromagnetic wave is polarized along one of the i-th axis (i = X, Y, Z).

The expression for the polarizability along each of the axes is written as follows [21]:

$$\alpha_i(\omega) = abf\frac{\varepsilon(\omega)-\varepsilon_m}{3\varepsilon_m + 3L_i\left(\varepsilon(\omega)-\varepsilon_m\right)}, i = X, Y, Z, \qquad (3)$$

where $\varepsilon(\omega)$ – dielectric permittivity of a semiconductor nanoparticle.

Geometric coefficients L_i expressed as:

$$L_x = \frac{abf}{2}\int_0^\infty \frac{dq}{(a^2+q)\,p(q)}, \quad L_y = \frac{abf}{2}\int_0^\infty \frac{dq}{(b^2+q)\,p(q)}, \quad L_z = \frac{abf}{2}\int_0^\infty \frac{dq}{(f^2+q)\,p(q)}$$

(4)

where, $p(q) = \sqrt{\left(q+a^2\right)\left(q+b^2\right)\left(q+f^2\right)}$,

$$L_x + L_y + L_z = 1$$

Dielectric permittivity of a semiconductor target $\varepsilon(\omega)$ for sufficiently low frequencies (in comparison with the band gap of the considered semiconductor) can be described by the classical Drude model [22,23]:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \qquad (5)$$

where ε_∞ – high frequency dielectric permittivity, γ – relaxation constant, ω_p – plasma frequency.

The Drude parameters $(\varepsilon_\infty, \omega_p, \gamma)$ included in (5) can be found from the reference literature or determined from the absorption curves for the nanoparticles under consideration.

Below are the results of calculations of the photoabsorption cross section of ellipsoidal ITO nanoparticles [24]. ITO nanoparticles with Sn doping levels of 8 and 10 percent are considered, for which ω_p=1.72 eV, γ = 0.22 eV and ω_p=1.89 eV, γ = 0.15 eV correspondingly. In both cases ε_∞=4.08, dielectric permittivity ε_m = 1.

Let us choose the following values of the semiaxes of an ellipsoidal nanoparticle: a = 6 nm, b = 12 nm, f = 16 nm.

The curves in Figure 1 have the maxima that correspond to plasmon resonances. For both nanoparticles, the plasmon resonance amplitude increases with an increase in the length of the axis along which the radiation is polarized, and the plasmon resonance maximum shifts to a lower frequency region.
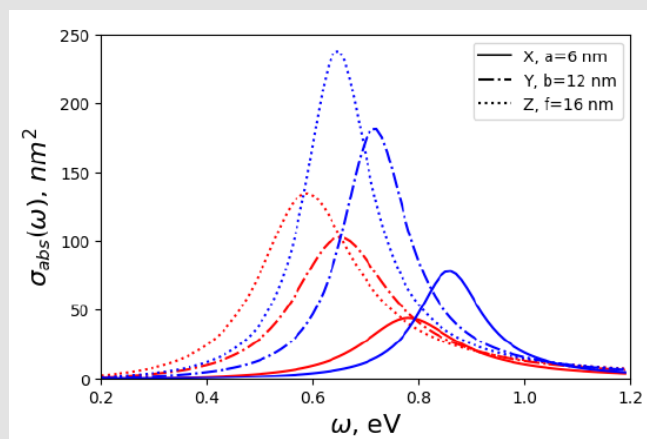
Figure 1: Dependence of the photoabsorption cross section for ITO nanoparticles with a doping level of 8% (red curves) and 10% (blue curves).

Discussion

The position of the plasmon resonance maximum ω_{res} can be found from the condition:

$$\frac{\partial \sigma_{abs}(\omega_{res})}{\partial \omega} = 0 \qquad (6)$$

After performing mathematical transformations, we obtain the expression:

$$\omega_{res} = \frac{\omega_p}{\sqrt{\varepsilon_\infty + \dfrac{1-L_i}{L_i}\varepsilon_m}} \qquad (7)$$

Expressing ω_{res} in terms of the wavelength λ_{res} and taking into account that $n = \sqrt{\varepsilon_m}$ we obtain the expression:

$$\lambda_{res} = \frac{2\pi c \sqrt{\varepsilon_\infty + \dfrac{1-L_i}{L_i}n^2}}{\omega_p} \qquad (8)$$

Let us construct dependences (8) of the wavelength of the maximum of the photoabsorption cross section λ_{res} on the geometric coefficient L_i for ITO nanoparticles.

From Figure 2 it follows that the dependencies $\lambda_{res}(L_i)$ are monotonically decreasing with increasing L_i, which corresponds to a decrease in the linear size of the nanoparticle along the i-th axis. At equal n, a larger shift of the maximum is observed for ITO nanoparticles with an 8% doping level. An increase in the refractive index n of the medium leads to an increase in the shift in the position of the maximum of the photoabsorption cross section for each type of nanoparticles at fixed L_i. This effect underlies the principle of operation of optical plasmon sensors and allows one to determine the characteristics of the medium in which the nanoparticle is placed [20].

An important characteristic of such a sensor is the magnitude of the position shift λ_{res} when the refractive index of the medium surrounding the nanoparticles changes - the sensitivity parameter S_λ [19], which can be defined as follows:
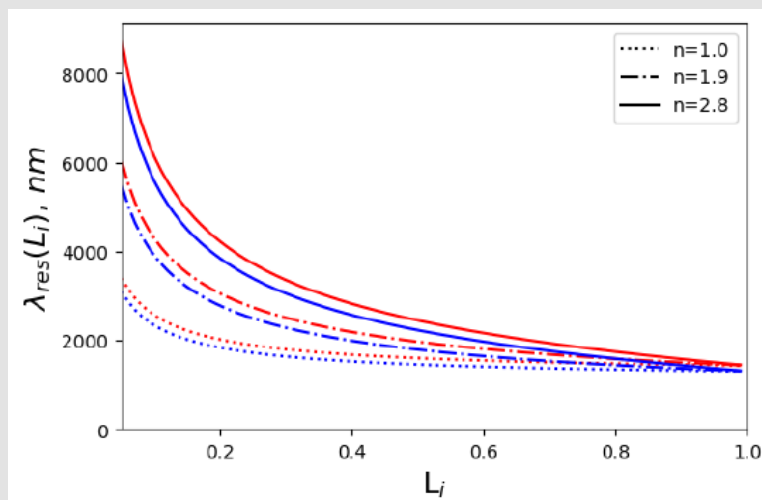
Figure 2: Dependence of the position of the maximum of the photoabsorption cross section on the geometric factor L_i for ITO nanoparticles with a doping level of 8% (red curves) and 10% (blue curves) at different refractive indices of the medium n.

$$S_\lambda = \frac{\partial \lambda_{res}}{\partial n} \qquad (9)$$

Substituting (8) into (9), we obtain the expression for the sensitivity of an optical plasmon sensor on an ellipsoidal nanoparticle:

$$S_\lambda = \frac{2\pi c}{\omega_p}\frac{1-L_i}{L_i}\frac{n}{\sqrt{\varepsilon_\infty + \dfrac{1-L_i}{L_i}n^2}} \qquad (10)$$

From expression (10) it is seen that the sensitivity S_λ, among others, is influenced by the value of the parameter L_i. Let us investigate the influence of this parameter on the value S_λ. From Figure 3 it follows that a decrease in the parameter value L_i leads to an increase in the sensitivity parameter S_λ, which corresponds to the stretching of a nanoparticle along the direction of radiation polarization, and the sensitivity of ITO nanoparticles with an 8% doping level, at the same L_i, is higher than for an ITO nanoparticle with 10% - doping level. The dash-dotted curves in this graph correspond to the spherical case when $L_i = 1/3$.
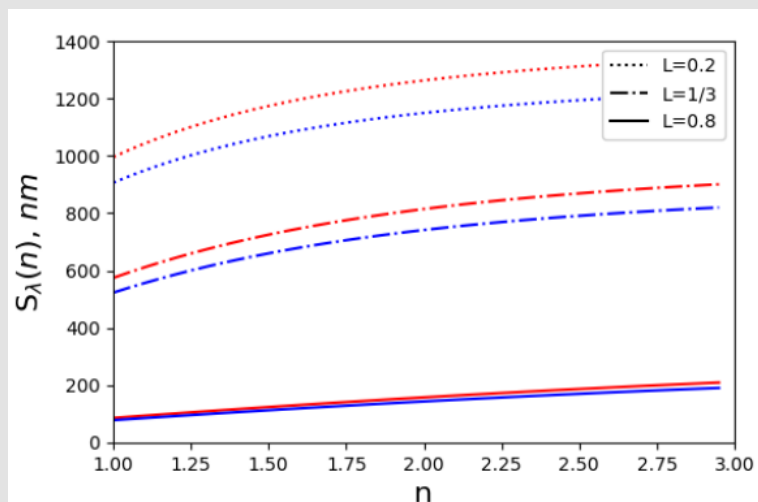
Figure 3: Dependence of the sensitivity parameter S_λ on the refractive index of the environment at various values of the parameter L_i for ITO nanoparticles with a doping level of 8% (red curves) and 10% (blue curves), as in Figure 1 and Figure 2.

Conclusion

Within the framework of the dipole approximation, the photoabsorption cross section for ellipsoidal ITO semiconductor nanoparticles with a doping level of 8 and 10 percent was calculated. It is shown that the amplitude of the plasmon resonance increases with an increase in the size of the nanoparticle (the length of the semi-axis of the ellipsoid), along which the radiation is polarized, and the maximum of the plasmon resonance shifts to a lower frequency region. At equal refractive indices n, a larger shift of the plasmon resonance maximum is observed for ITO nanoparticles with an 8% doping level.

The calculation of the sensitivity of an optical plasmon sensor, which can be built on the basis of ellipsoidal nanoparticles, has been performed. It was found that stretching a nanoparticle along the direction of radiation polarization leads to an increase in the sensor sensitivity, and the sensitivity for ITO nanoparticles with an 8% doping level, at equal, is higher than for an ITO nanoparticle with a 10% doping level.

Acknowledgement

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