Semi-Empirical Plasmon Coefficients of Metals for Nanoplasmonics

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The paper considers a program for determining the plasmonic parameters of some metals using the least squares method based on experimental data. Analytical expressions are obtained for the real part of the dielectric function as a function of the wavelength of the incident light. It is found that in all metals at a wavelength of the incident light $\lambda > 0.7$ μm, nanoplasmons can be formed. The dependence of the dielectric constants of Au, Ag, Cu, Al, Ni, Pt, Zn, and Ti nanoparticles, which are used for solar energy today, on the wavelength is studied. Also, the wavelengths that create the nanoplasmonics effect are determined. It is found that the plasmonic wavelength for gold, silver and platinum nanoparticles is equal to 142.9 nm, 79.1 nm, and 163.9 nm, respectively. Among metal nanoparticles, Al has the shortest plasmon wavelength and Pt has the longest wavelength. Metal nanoparticles are introduced into silicon-based solar cells mainly to modify photons in the infrared spectrum to photons in the visible range, because silicon mainly absorbs photons in the visible range but cannot absorb photons in the infrared range. In order for a metal nanoparticle to convert infrared photons into visible photons, the plasmon wavelength must be larger. Therefore, Pt nanoparticle is considered to have the best plasmon coefficient for input into silicon solar cells. The real part of the dielectric constant is spread over the Taylor series and the unknown coefficients are determined by the least squares method. One of the main parameters is the wavelength-independent part of the dielectric coefficient. It is equal to 8.76, 14.154, 26.95, 4.830, 0.189, 6.72, and 3.688 for Au, Ag, Cu, Al, Ni, Pt, Zn, and Ti, respectively. Therefore, it is found that Pt has the smallest dielectric coefficient and Al has the largest. The smallest error in the calculation according to the least squares method occurs in Pt and the largest error occurs in Al.

Keywords: Least squares method, Dielectric function, Nanoplasmonics, Plasmonic frequency, Nanoparticle.

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1. INTRODUCTION

It is known that the nanoplasmonic effect is observed in metal nanoparticles embedded in the semiconductor surface of solar cells [1]. Fluctuations in the electron density of metal nanoparticles have a resonant frequency – localized plasma resonance (LPR) in the visible and infrared parts of the spectrum [2]. Therefore, the main task of nanoplasmonics is the study of optical and electrophysical processes caused by LPR. LPR is caused by the formation of potential charges in the surface charge and oscillations of electrons in the medium under the action of an external electromagnetic field. The resonant properties of metal nanoparticles (plasmons) and the accumulation of an electromagnetic field around them make it possible to observe many new effects. Based on these effects, optoelectronic devices with plasmonic nanoparticles, nanoscale lasers, and highly efficient solar cells have been proposed and implemented [3].

There are two different methods for theoretically calculating the resonant frequency of a plasmon and the distribution of the corresponding electromagnetic fields inside and outside the nanoparticle. With the sources given in the first method, the system of Maxwell equations is solved using analytical solutions available for different frequencies or numerical methods, and depending on the frequency, different characteristics are obtained [4]. For example, this may be the scattering or absorption cross section. The maximum value of the cross section corresponds to the plasmon resonance, and the corresponding distribution of the electromagnetic field characterizes the structure of plasmons.

In another, more convenient way of describing the plasmonic properties of nanoparticles, the main role is played not by resonant frequencies, but by the dielectric functions corresponding to them [5]. This method is based on the fundamental properties of plasmons and allows you to simultaneously characterize particles of the same shape [6], but made of different materials, as well as to better understand the nature of plasmons. In this method, the main attention is paid to studying the influence of the shape of nanoparticles on their electromagnetic and optical properties. In both methods, the frequency dependence of the permittivity of metals plays an important role [7].

2. MATERIALS AND METHOD

2.1 Theory

Let us consider important particular cases of wave propagation in metals. The expression for the dielectric constant of metals [3]

$$\varepsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i\gamma)} \qquad (1)$$

has a different character at lower and higher frequencies. At high frequencies, the second term in the denominator of the expression can be neglected, then the permittivity is determined by the expression:

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$$\varepsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2}. \tag{2}$$

This nature of dispersion phenomena at high frequencies is due to the inertia of free electrons: in the time interval between two scatterings, the electron performs multiple oscillations, since $T << \tau$.

When $\omega < \omega_{pl}$, the permittivity is negative, and the refractive index is imaginary. This means that a wave of this frequency cannot propagate in metals due to the presence of strong absorption, which is not associated with energy absorption. In this case, the permittivity is real. In practice, when $\omega < \omega_{pl}$, total internal reflection of the incident wave occurs. When $\omega > \omega_{pl}$, the refractive index is real, and the metal becomes transparent to radiation. When $\omega << \gamma$, expression (1) can be reduced to the form:

$$\varepsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i\gamma)} \approx i\frac{\omega_{pl}^2}{\omega\gamma}. \tag{3}$$

Therefore, the permittivity in this case is imaginary. Such waves penetrate the metal at short distances from the wavelength in vacuum. For them, the reflection coefficient is close to unity, i.e., they are practically reflected from the surface.

At intermediate frequencies, expression (1) is used for the permittivity. In this case, the dielectric constant has a complex value, and the refractive index has real and imaginary parts that are different from zero, depending on the frequency.

At the same frequencies, the wave vector of a surface plasmon is greater than the wave vector of a free photon, and therefore it is impossible to excite surface plasmons by ordinary photons [3]. Surface plasmons are also excited at frequencies where the permittivity of one of the media at the metal-external interface is negative, i.e., under conditions

$$\begin{gathered} \varepsilon_{\text{м}}(\omega) \cdot \varepsilon_{\text{в}}(\omega) < 0, \\ \varepsilon_{\text{м}}(\omega) + \varepsilon_{\text{в}}(\omega) < 0. \end{gathered} \tag{4}$$

Thus, nanometals embedded in the surface of semiconductors behave differently depending on the frequencies of the electromagnetic radiation incident on them. Therefore, the study of the dependence of the complex permittivity of metal nanoparticles embedded in the silicon surface on the frequency (wavelength) of incident electromagnetic waves is one of the topical problems of nanoplasmonics. In particular, the dielectric function of a metal nanoparticle and the semiconductor surrounding it is strongly related to the wavelength of the incident light, taking into account changes in the electric field at the boundary, depolarization, and radiation losses.

As is known [1], the real part of the permittivity of metals depends on the wavelength of the incident light as

$$\operatorname{Re}\varepsilon = \varepsilon_\infty - \frac{(\lambda/\lambda_p)^2}{1+(\lambda/\lambda_f)^2} = \varepsilon_\infty - \frac{\lambda_f^{\,2}}{\lambda_p^{\,2}}\frac{\lambda^2}{\lambda^2+\lambda_f^{\,2}}. \tag{5}$$

We expand this expression in a Taylor series in powers of $\lambda(\lambda^2)$:

$$\begin{aligned} \operatorname{Re}\varepsilon &= \varepsilon_\infty - \frac{\lambda_f^{\,2}}{\lambda_p^{\,2}}\left(\left(\frac{\lambda}{\lambda_f}\right)^2 - \left(\frac{\lambda}{\lambda_f}\right)^4 + \left(\frac{\lambda}{\lambda_f}\right)^6\right) = \\ &= \varepsilon_\infty - \frac{\lambda^2}{\lambda_p^{\,2}} + \frac{\lambda^4}{\lambda_p^{\,2}\lambda_f^{\,2}} - \frac{\lambda^6}{\lambda_p^{\,2}\lambda_f^{\,4}}. \end{aligned} \tag{6}$$

On the other hand, according to the results of the experiment, it is possible to determine the relationship between any two physical quantities using the least squares method. Presenting the results of the experiment between $Re\varepsilon$ and λ [8] as

$$\operatorname{Re}\varepsilon = A_0 + A_1\lambda^2 + A_2\lambda^4 + A_3\lambda^6, \tag{7}$$

it is possible to determine the coefficients A_i by the least squares method. Further, comparing expressions (6) and (7), we can obtain

$$\varepsilon_\infty = A_0, \;\; \lambda_p = 1/\sqrt{-A_1}, \;\; \lambda_f = 1/\lambda_p\sqrt{A_2}. \tag{8}$$

3. RESULTS AND DISCUSSION

On Visual Basic-6.0, a program was developed to study the dependence of the permittivity of metals on the wavelength of incident electromagnetic waves. The results obtained using this program were sent to MS Excel, described using graphs, compared with experimental results and used to calculate the main parameters of silicon-based solar cells with the introduction of metal nanoparticles.

Table 1 – Plasmon parameters of metals

	ε_∞	λ_p	λ_f	χ^2
Au	8.764	0.1429	7.489	0.204
Cu	6.13	0.1502	3.255	0.320
Ag	14.154	0.0791	0.691	0.135
Al	26.95	0.0501	0.775	1.072
Ni	4.830	0.1308	0.909	0.047
Pt	0.189	0.1639	1.296	0.028
Zn	6.720	0.0845	0.632	0.573
Ti	3.688	0.1485	0.713	0.089

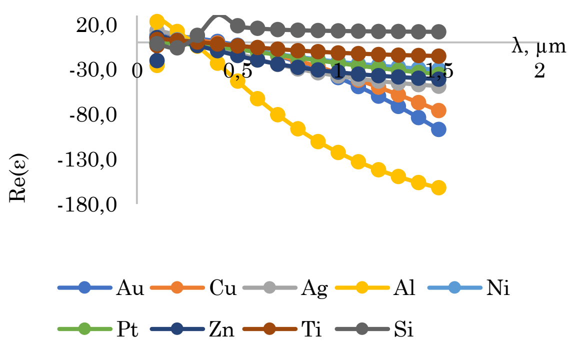

Fig. 1 – Dependence of the real part of the dielectric function of metals on the wavelength of the incident light, $Re\varepsilon = f(\lambda)$

As an example, the plasma coefficients of metals such as gold (Au), silver (Ag), copper (Cu) and platinum (Pt) were determined from the results of the experiment presented in [9] using the program. The calculation results are given in Table 1. The results obtained practically agree with the results of [1, 3, 10].

Fig. 1 shows the dependence of the real part of the dielectric function of metals like (Au), silver (Ag), copper (Cu) and platinum (Pt) on the wavelength of the incident light, built on the basis of parameters determined using the least squares method. The figure also shows the dielectric function of silicon (Si) [10].

4. CONCLUSIONS

It can be seen from the graphs that in all metals at a wavelength of incident light $\lambda > 0.7$ μm, conditions (4) are satisfied, i.e., nanoplasmons can be formed.

Thus, in this work, a program has been developed for determining the plasmon coefficients of metals, and analytical expressions for the dielectric functions of metals have been obtained. One of the main problems in photovoltaics today is to increase the efficiency of solar cells. In this article, metal nanoparticles that can be incorporated into solar cells have been studied. In our theoretical studies, the dielectric coefficient of each metal nanoparticle, plasmon wavelength and squared error in calculation have been determined. In conclusion, according to the obtained results, it has been proved that the nanoplasmonic effect can occur in each of the studied metal nanoparticles. When inserting them into a solar cell, it is necessary to pay attention to the material of the solar cell, because each nanoparticle has a different plasmon wavelength. For example, it turned out that platinum is the most suitable nanoparticle for a silicon-based solar cell.

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Напівемпіричні плазмонні коефіцієнти металів для наноплазмоніки

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У роботі розглянуто програму для визначення плазмонних параметрів деяких металів методом найменших квадратів на основі експериментальних даних. Отримано аналітичні вирази для дійсної частини діелектричної проникності як функції довжини хвилі падаючого світла. Встановлено, що в усіх металах при довжині хвилі падаючого світла $\lambda > 0{,}7$ мкм можуть утворюватися наноплазмони. Досліджено залежність діелектричної проникності наночастинок Au, Ag, Cu, Al, Ni, Pt, Zn та Ti, які сьогодні використовуються для сонячної енергетики, від довжини хвилі. Також визначено довжини хвиль, які створюють ефект наноплазмоніки. Установлено, що плазмонна довжина хвилі для наночастинок золота, срібла та платини дорівнює 142,9, 79,1 та 163,9 нм відповідно. Серед металевих наночастинок Al має найкоротшу плазмонну довжину хвилі, а Pt має найдовшу довжину хвилі. Металеві наночастинки вводяться в кремнієві сонячні елементи головним чином для зміни фотонів в інфрачервоному спектрі на фотони у видимому діапазоні, оскільки кремній переважно поглинає фотони у видимому діапазоні, але не може поглинати фотони в інфрачервоному діапазоні. Для того, щоб металева наночастинка перетворювала інфрачервоні фотони у видимі фотони, довжина хвилі плазмона повинна бути більшою. Тому вважається, що наночастинка Pt має найкращий плазмонний коефіцієнт для введення в кремнієві сонячні елементи. Дійсна частина діелектричної проникності розподіляється по ряду Тейлора, а невідомі коефіцієнти визначаються методом найменших квадратів. Одним з основних параметрів є незалежна від довжини хвилі частина коефіцієнта діелектричної проникності. Для Au, Ag, Cu, Al, Ni, Pt, Zn і Ti вона дорівнює 8,76, 14,154, 26,95, 4,830, 0,189, 6,72 і 3,688. Тому встановлено, що Pt має найменший коефіцієнт діелектричної проникності, а Al – найбільший. Найменша похибка розрахунку за методом найменших квадратів має місце в Pt, а найбільша – в Al.

Ключові слова: Метод найменших квадратів, Діелектрична проникність, Наноплазмоніка, Плазмонна частота, Наночастинка.