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Grain size effect on the optical properties of thin silver films

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The characterization of the optical constants of metals is an extensive task and dates back to many decades ago. In present work, particular emphasis has been placed on calculations of the dielectric function of thin silver films performed using both photometric (reflection and transmission) measurements. Silver thin films were deposited on glass substrates via radio-frequency sputtering. The thickness of the thin films is in the range of 10 to 100 nm. The optical constants (refractive index and extinction coefficient) and the parameters for the Drude optical model (damping constant, Γ and plasma frequency, ω_p) of the films were calculated. It was established that the value of Γ strongly depends on the thickness due to a size effect in the metal films. When the thickness of the silver films decreases, the magnitude of the imaginary part of the dielectric function becomes smaller than its bulk value. This feature should be taken into account in the design and simulation of the most optical metamaterials with metal-dielectric meta-atoms.

Keywords: silver films, modified Drude model, complex permittivity, grain-size effect

INTRODUCTION

Thin silver films have attracted much attention owing to their peculiar optical properties [1-2]. They have found many applications in different optical devices such as solar cells, light emitting diodes, to improve the properties of organic semiconductor materials and to launch new metamaterials [3].

Widely used techniques for fabrication of metal films on a dielectric substrate are vacuum evaporation, cathode sputtering and electron beam physical vapor deposition. It is well-known the fact that the deposition conditions (deposition rate, vacuum pressure and kind and temperature of substrate) control the aggregation of grains during the deposition of thin metal films [4, 5]. On its part, the size of the crystalline grains building the metal coatings affect the electrical and optical properties of the metals layers [6].

The object of investigation of the present work is the influence of the deposition rate and film's thickness on the optical properties of thin silver coatings obtained by RF (radio-frequency) sputtering method.

EXPERIMENTAL DETAILS

The silver coatings were deposited by RF cathode sputtering (13 MHz) in argon atmosphere. The partial pressure of Ar was p ~ $5.10^{-2}$and 10^{-1} Pa. The deposition rate was controlled by variation of the applied cathode voltage. The thickness of thin films was controlled after film deposition by profilemeter "Talystep".The data for the thickness showed that the increase of the argon leads to an increase of the deposition rate from 1 to 3 nm/s.

The transmittance (T) and reflectance (R) were measured by a UV–VIS–NIR spectrophotometer Cary 5E (Australia) in the range 350–2000 nm to an accuracy of ΔT = ±0,1% and ΔR = ±0,5%.

RESULTS AND DISCUSSION

Theory

The Drude model is suited for description of the optical function of metals. In the present work we used the modified Drude model, which takes into account the constant offset for interband transitions [7]. According to this model, the complex permittivity, ε(ω), as a function of the angular frequency is given by the following equation:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2+\Gamma^2} + i\frac{\omega_p^2\Gamma}{\omega(\omega^2+\Gamma^2)} \quad (1)$$

where $\varepsilon_\infty$is the relative dielectric constant (for the silver $\varepsilon_\infty = 9$ [7]). $\omega_p = \sqrt{n_e e^2/\varepsilon_0 m}$ is the metal plasma frequency, where n_e is the number of free

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electrons, e and m are the electron's charge and mass, respectively. Γ is a damping parameter and it is related with the electron mean free path, l and the Fermi velocity v_F by:

$$\Gamma = \frac{v_F}{l} \qquad (2)$$

For the bulk silver, the parameters in (2) have the following values: l = 4.375×10^{-8} m and v_F = 1.4×10^6 m/s [7]. The refractive index, n, extinction coefficient, k and film thickness, d were calculated from the transmittance or reflectance spectra [8]. The real and imaginary parts of the complex permittivity, ε = ε'+iε" can be calculated from the refractive index and extinction coefficient by the following equations:

$$\varepsilon' = n^2 - k^2 \quad \text{and} \quad \varepsilon'' = 2nk \qquad (3)$$

The Drude parameters were determined by fitting the obtained data for the refractive index. Furthermore, the results for the optical parameters were used for calculation of the theoretical reflectance spectra. In Fig. 1 it is given the fit of the reflection spectra of thin silver films with thickness 16 nm obtained by *rf* sputtering with deposition rate 1 and 3 nm/s. The results for the fitting parameters, ω_p and Γ are given in Table 1. It is seen that the plasma frequency is close to that for bulk metal [7], while Γ depends on the deposition rate and thickness of the film.

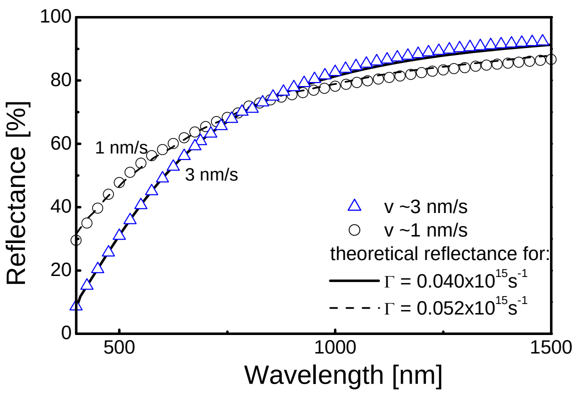

Fig. 1. Measured and theoretically calculated reflectance spectrum of silver coatings with thickness 16 nm and deposition rate 1 and 3 nm/s.

In Fig. 2 data are presented for the real and imaginary part of the permittivity, refractive index, n and extinction coefficient, k for thin films with thicknesses 16 and 41 nm and deposition rate 3 nm/s.

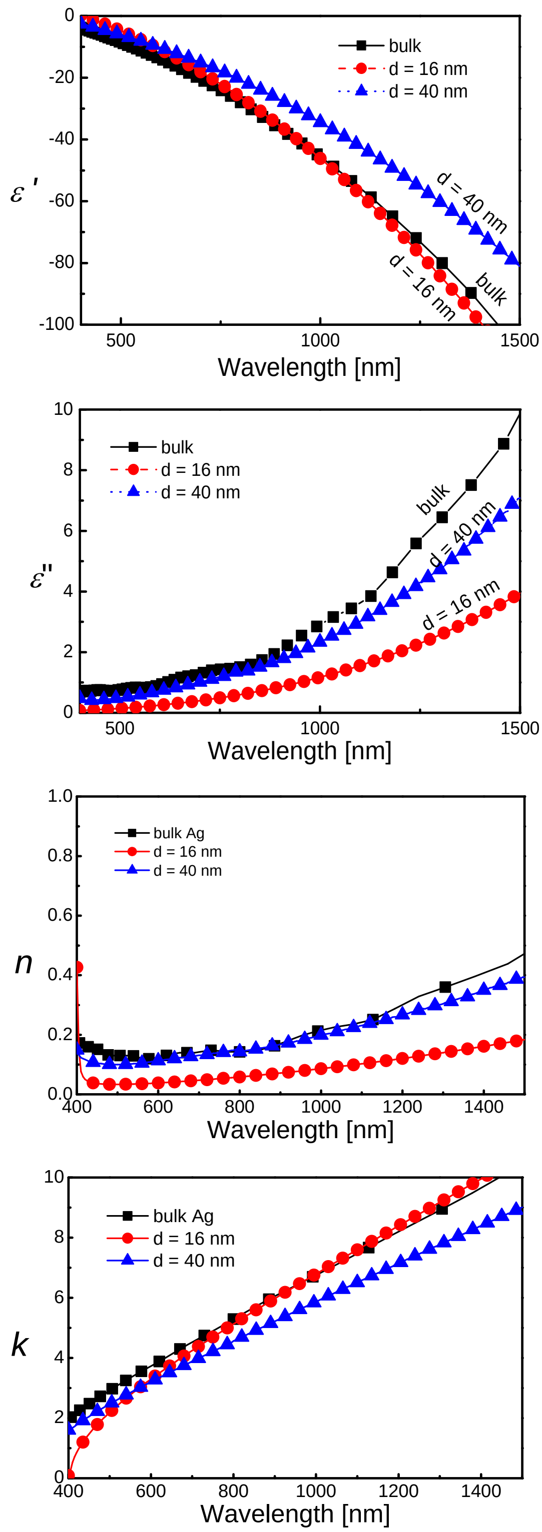

Fig. 2. Comparison of the dispersions of the real and imaginary part of the complex permittivity, refractive index and extinction coefficient of the thin silver films in the present study and bulk metal published in [9].

Table 1. Drude parameters - metal plasma frequency, ω_p, damping parameter, Γ, size-limited mean free path, l_1 and size of the film's grains, R_m

Film thickness, *d* [nm]	Deposition rate [nm/s]	ω_p [s^{-1}]	Γ [s^{-1}]	l_1 [m]	R_m [nm]
16	1	13.6×10^{15}	5.2×10^{13}	3.5×10^{-8}	17.1
16	3	14.6×10^{15}	4.01×10^{13}	2.8×10^{-8}	19.4
41	3	13.4×10^{15}	1.07×10^{14}	1.3×10^{-8}	10.1

Influence of thin oxide overlayer

The existence of a thin oxide layer on the metal surface is a well-known fact. Usually it leads to reduction of the reflectance. According to [10] the thickness of the silver oxide varies in the range of 1-10 nm and the refractive index - between 2.3 - 2.75 in the spectral range 400-1200 nm [11]. The authors of the latter work report a value of $n = 2.51$. Further, we use the optical parameters plotted in Fig. 2 and the calculated thickness to theoretically compute the reflectance spectrum of a double layered Ag_2O/silver structure. The calculation procedure is described in [8]. The comparison between the reflectance spectrum of a silver layer and the theoretical one for a double layered structure from Ag_2O and Ag is shown in Fig. 4. This result shows that the consideration of a very thin Ag_2O layer with thickness 1-2 nm significantly reduces the discrepancy between the theoretical and experimental reflectance spectrum.

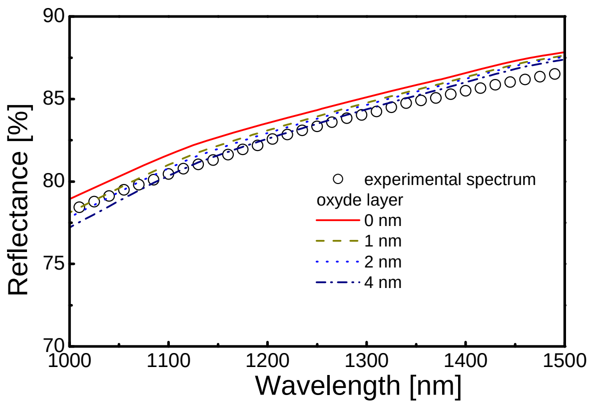

Fig. 3. Comparison of the measured reflectance spectrum of silver film ($d = 16$ nm) to the theoretical reflectance spectra calculated considering a silver oxide overlayer with different thicknesses.

Grain size effect

Usually Γ in the Drude model (formula (1)) is considered to be a constant at a given temperature. Due to shortening of the mean free path of electrons, the fixed value for Γ, however is no longer valid, when thickness of the film become tens of nanometers. The effective mean free path, l is reduced in the following manner [7]:

$$\frac{1}{l_1} = \frac{1}{l} + \frac{1}{R_m} \qquad (4)$$

where R_m represents the size of the metal particle and l_1 is the size-limited mean free path of electrons. Using equation (2) and the data for Γ from Table 1 we can find the values for l_1. Inputting the obtained data for the size-limited mean free path in formula (4) the size of the silver grains is determined. The results show that increasing of the deposition rate from 1 to 3 nm/s would change the average size of the layer's grains from 17.1 to 19.4 nm. These values are in agreement with the published data for the average crystallite size of thermally evaporated silver films [5].

CONCLUSION

In the present work it is analyzed the influence of the deposition rate and thickness on the optical properties of thin silver layers. It was established that the introducing of a thin oxide overlayer with thickness 2-4 nm and refractive index 2.51 reduces the discrepancy between the theoretical and measured reflectance spectra. The metal plasma frequency ω_p and damping constant, Γ are determined applying the Drude model. On the base of the dependence of Γ on the thin film's thickness it was calculated that the average size of the metal crystallites is 17.1 and 19.1 nm.

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ВЛИЯНИЕ НА РАЗМЕРА НА КРИСТАЛИТИТЕ ИЗГРАЖДАЩИ ТЪНКИ СЛОЕВЕ ОТ СРЕБРО ВЪРХУ ОПТИЧНИТЕ ИМ СВОЙСТВА

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(Резюме)

Определянето на оптичните константи на тънки метални покрития е сложна задача и по нея се работи от много десетилетия. В настоящата работа, особен акцент е поставен върху изчисленията на диелектричната функция на тънки слоеве от сребро чрез използване спектрофотометрични измервания на коефициентите на пропускане и отражение. Тънките слоеве бяха отложени върху стъклени подложки чрез радиочестотно катодно разпрашване. Дебелината на тънки слоеве беше в интервала от 10 до 40 нанометра. Оптичните константи (показател на пречупване и показател на поглъщане) и параметрите на дисперсионния модел на Drude (коефициент на затихване, Г и плазмена честота, ω_p) бяха определени от спектрите на отражение и пречупване. Резултатите показаха, че Г силно зависи от дебелината на слоевете.