Resonance light absorption of granular aluminium and silver films placed on a rough sublayer of multilayered ZnS

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Abstract. We report the spectrophotometric studies of two-layer granular films of aluminium and silver disjoint by ZnS layers. This multilayered system is prepared with two-stage deposition of Al and Ag separated by a thin ZnS film. Dipole–dipole interactions between the optical thin films in the multilayer sandwich are studied and optical absorption bands are identified at different stages of deposition procedure. The plasma frequency of aluminium is determined from the position of maximum of the high-frequency band, which is peculiar to the two-layer sample based on the granular aluminium film enclosed between the ZnS layers.

1. Introduction

Resonance in its simplest form, i.e. an external resonance of a linear oscillator, represents a well-known phenomenon. If the system is not so simple or has several degrees of freedom, another effect becomes possible. This is an internal resonance, i.e. a resonance between individual subsystems. Due to the internal resonance, individual subsystems exchange energy with each other. In other words, one can observe interaction of those subsystems. It is obvious that the external resonance can be considered as a special case of the internal one, where the energy of one of the subsystems is assumed to be infinite. In this case we deal simply with the impact of one subsystem on the other, rather than the interaction itself.

The aim of the present work is to study experimentally a possible effect of dipole–dipole interactions between the granules of two layers of different metals, which are separated by a thin dielectric layer with high dielectric permittivity, on resonant light absorption. To achieve this goal, we need to examine a simple mathematical model of interactions between two oscillators and predict the interaction resonance frequency of this system.

Let us use the simplest example of coupled oscillators [1]. To be specific, this can be two mathematical pendulums of lengths l_1 and l_2 with the same weight masses $m_1 = m_2 = m$ in the gravitational field. The pendulums are connected by a weightless spring with the elasticity coefficient k. In the linear approximation, the motion of such a conservative system with two

degrees of freedom is described by the equations of coupled oscillators:

$$\ddot{x}_1 + \omega_1^2 x_1 = (k/m)(x_2 - x_1),$$
$$\ddot{x}_2 + \omega_2^2 x_2 = (k/m)(x_1 - x_2).$$

(1)

Compound, i.e. interaction-imposed resonance frequencies $\omega'_{1,2}$ of the normal oscillations are then equal to

$$\omega'_{1,2} = \frac{\omega_1 + \omega_2}{2} + \frac{k}{2m\sqrt{\omega_1\omega_2}} \pm \sqrt{\left(\frac{\omega_1 - \omega_2}{2}\right)^{1/2} + \left(\frac{k}{2m\sqrt{\omega_1\omega_2}}\right)^2},$$

(2)

where ω_1 and ω_2 denote the frequencies of two independent resonance systems. From the equality $\omega_1^2 = \omega_2^2 = \omega_0^2$ in Eq. (1) one can obtain

$$\omega'_1 = \omega_0, \ \omega'_2 = \omega_0 + k/m\omega_0.$$

(3)

Assuming that $\omega_1\omega_2$ is large enough and $(\omega_1 - \omega_2)$ small, one can neglect the second and third summands in Eq. (2), resulting in

$$\omega'_{1,2} \approx (\omega_1 + \omega_2)/2.$$

(4)

When the two coupled oscillators are excited by an external periodic force in the way that the frequency of the external force coincides with one of the normal frequencies of the system, a resonance occurs, and the oscillation amplitudes for the both oscillators increase infinitely. In this case, the well-known reciprocity theorem [2] holds true: When an external force is applied to one oscillator, the other oscillates in the same way as if the first did whenever the external force has been applied to the second one.

A detailed theory of plasma resonance has been thoroughly studied [3]. In particular, it is known that the absorption band of colliding nanoparticles is given by a so-called Fröhlich frequency:

$$\omega_0 = \omega_p / \sqrt{\varepsilon_m + 2\varepsilon_0},$$

(5)

where ω_p is the plasma frequency of a metal of which exact value is insufficiently known so far, ε_m the dielectric constant determined by interband transitions in metals, and ε_0 the dielectric constant of environment of the granule.

In line with the above model, we are going to argue that silver and aluminium granules deposited on a rough ZnS layer would act as a system of coupled oscillators. The optical properties of such materials have been studied rather well. For instance, resonance-vibration frequencies have been determined with great accuracy, together with dispersion of the permittivity associated with the interband transitions [3].

2. Optical properties

A thin film of zinc sulphide has been deposited on a quartz substrate at the room temperature in high vacuum. Then we deposit granular silver films at 300°C, so that two plasma resonance bands appear [4]. The high-frequency band has the frequency $\omega_0^1 = 5.2 \times 10^{15}\,\text{s}^{-1}$. The electron microscopic images taken by us have revealed large granules with the filling factor $q = 0.03$, along with the granules of usual dimensions. The presence of these large granules also causes the appearance of the high-frequency band, with the resonant frequency equal to that of natural electron oscillations in the granule.

The relation (5) enables one to find the ε_m values, using the parameters known for the original film ($\omega_p = 13.5 \times 10^{15}\,\text{s}^{-1}$, $\omega_0 = 5.2 \times 10^{15}\,\text{s}^{-1}$ and $\varepsilon_0 = 1$ [3]) and those for the film put in immersion liquid ($\omega_0 = 4.6 \times 10^{15}\,\text{s}^{-1}$ and $\varepsilon_0 = 2.16$ [5]). The corresponding value is equal to $\varepsilon_{1m} = 4.74$ [3].

The optical properties of aluminium have been studied in Ref. [5], where a two-layer film of aluminium granules embedded in NaCl and KCL substrates are used as a modular system. It turns out that the plasma frequency for aluminium is $\omega_p = 22 \times 10^{15}\,\text{s}^{-1}$. It has been found using Eq. (5), the appropriate experimental data ($\omega_0 = 4.6 \times 10^{15}\,\text{s}^{-1}$) and the dielectric constant of the medium that surrounds the granules ($\varepsilon_0 = 2.65$ [5]). These data help in explaining the behaviour of the system in the case of dipole approximation, when the radiation propagates along the substrate, i.e. the dipole moment lies in the plane of the substrate.

The dipole–dipole interactions between the layers consisting of different nanoobjects have not been studied yet. However, it would be important to understand the interactions of the systems consisting of granules with the biological objects lying in a different plane. This would be useful, e.g., when creating biosensors. Hence, understanding of the effect of dipole interactions present in the plane perpendicular to the substrate represents an important issue. To establish such an interaction, we have set up the experiments described below.

3. Description of experimental procedure

To accomplish our tasks, we studied the resonance light absorption by granular aluminium and silver films, each of which was deposited on a rough surface of ZnS sublayer and covered by a layer of the same material on top. As a result, we obtained a multilayered 'sandwich' sample with the granular layers of silver and aluminium, which were 'immured' in ZnS. We chose fused quartz as a main substrate and ZnS as a sublayer and intermediate layers for the following reasons. First, the above substances are practically transparent in a wide spectral range (from 200 to 800 nm [6]). Second, the mentioned cover was repeatedly employed for testing the methods for obtaining a step-like relief by applying ZnS sublayers [7].

The samples were made in the following way. Fused silica substrates were thoroughly cleaned with a fine-grained "Crocus" powder, and then washed in water and wiped with pure alcohol immediately before being placed in a vacuum chamber. The quartz substrate was placed in a special furnace that allowed the substrate to be heated to 300°C in the 0.0066 Pa vacuum. The temperature was controlled with a thermocouple pressed against the substrate from the side opposite to deposited film. To obtain ZnS sublayer of a given thickness, we took an experimentally determined weight of ZnS. The resulting thickness of the sublayer was approximately equal to 50 nm.

Then 10–15 nm thick granular silver or aluminium films from the molybdenum boat were deposited on the rough surface of ZnS sublayer at the substrate temperature 300°C in the 0.0066 Pa vacuum. After that, a thin (50 nm) layer of ZnS was deposited on the granular film of the first metal. Finally, a granular film of the second metal was deposited. An additional 50 nm thick layer of ZnS was subsequently deposited on this film. In this manner, a multilayered sample was obtained (see Fig. 1).
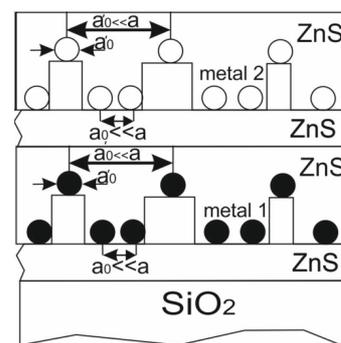

Fig. 1. System of two coupled oscillators: a implies the distance between islands and a_0 the island radius.

In the first series of our experiments, silver was used as the first metal and aluminium as the second, and vice versa for the second series of experiments. The granular films of aluminium and silver were 'immured' by ZnS, which could significantly change the dielectric permittivity ε_0 of the medium surrounding the metal granules.

The samples thus prepared were subjected to spectrophotometric measurements on a SF-26 spectrophotometer. While conducting the spectrophotometric experiments, both nonpolarized and p-polarized light beams were used. A beam of the p-polarized light was directed at the angle $\phi = 50$ deg with respect to the sample surface. The measurements were carried out each time after each of the metal or ZnS layers had been deposited.

4. Results

The experimental data obtained for SiO$_2$/ZnS/Al/ZnS and SiO$_2$/ZnS/Ag/ZnS samples are shown in Fig. 2. They are obtained with both non-polarized and p-polarized light beams. When the non-polarized light is used, one can clearly see that there are two absorption bands for the both samples. These are a low-frequency band with the resonance located at ω_{s1} and a high-frequency band with the ω_{s2} resonance. We have obtained $\omega_{s1}^{Ag} = 3 \times 10^{15}\,s^{-1}$ and $\omega_{s2}^{Ag} = 4.5 \times 10^{15}\,s^{-1}$ in the case of Ag, while the corresponding figures for the case of Al are equal to $\omega_{s1}^{Al} = 4.6 \times 10^{15}\,s^{-1}$ and $\omega_{s2}^{Al} = 6.2 \times 10^{15}\,s^{-1}$.

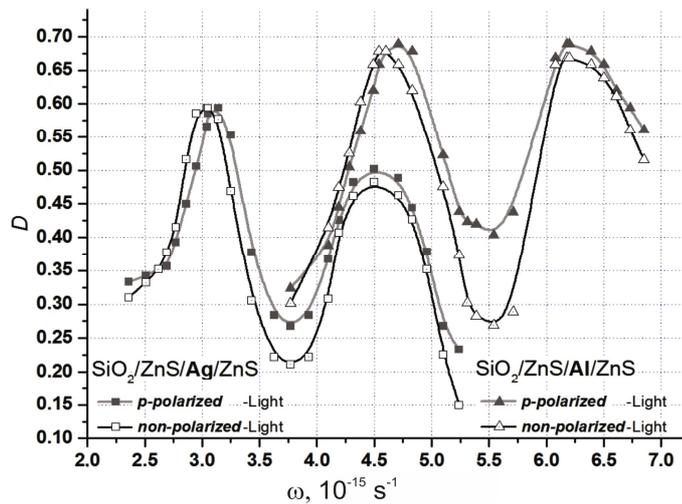**Fig. 2.** Absorption spectra for the sandwiches SiO$_2$/ZnS/Al/ZnS and SiO$_2$/ZnS/Ag/ZnS under analysis, as obtained using non-polarized light and p-polarized light incident at the angle $\phi = 50$ deg to the sample surface.

In case of the p-polarized light and SiO$_2$/ZnS/Al/ZnS and SiO$_2$/ZnS/Ag/ZnS sandwich-like samples (see Fig. 2), one can observe a regular pattern for the both silver and aluminium films. Namely, the high-frequency band is not shifted, whereas the low-frequency band shifts towards higher frequencies: $\Delta\omega_{s1}^{Ag} = 0.1 \times 10^{15}\,s^{-1}$ and $\Delta\omega_{s1}^{Al} = 0.15 \times 10^{15}\,s^{-1}$. This implies that the position of the high-frequency band in the both cases is determined by the natural frequencies ω_0 of free electron oscillations. Obviously, the appearance of two absorption bands follows immediately from the model of two-layer sample. Using Eq. (5) and the known values $\varepsilon_0^{ZnS} = 5.76$ [9] and $\varepsilon_m^{Al} = 1$ [10], it is easy to calculate the ω_p^{Al} parameter, assuming that $\omega_{s2}^{Al} = \omega_0^{Al}$. We arrive at the result $\omega_p^{Al} = \omega_0^{Al}\sqrt{1 + 2\varepsilon_0^{ZnS}} = 21.9 \times 10^{15}\,s^{-1}$.

The curves shown in Fig. 3 correspond to the spectral dependences of the optical density $D(\omega) = -\lg(I/I_0)$, with I and I_0 being respectively the emergent and incident light intensities. They have been obtained with the non-polarized light for the samples of the first experimental series (see Fig. 2), after subsequent deposition of the layers of the second metal and ZnS. In the case of SiO$_2$/ZnA/Ag/ZnS/Al/ZnS structure, the first metal is silver, and the second is aluminium. One can see that application of the granular film of the second metal does not result in additional absorption bands. The position of the corresponding maxima are $\omega_{s1}^{Ag\&Al} = 3.1\times10^{15}\,s^{-1}$ and $\omega_{s2}^{Ag\&Al} = 5.35\times10^{15}\,s^{-1}$. The curve obtained for the case of SiO$_2$/ZnA/Al/ZnS/Ag/ZnS presents similar $D(\omega)$ dependences obtained in the second experimental series, where the first metal is aluminium and the second is silver. The corresponding positions of the maxima are $\omega_{s1}^{Al\&Ag} = 3.5\times10^{15}\,s^{-1}$ and $\omega_{s2}^{Al\&Ag} = 5.4\times10^{15}\,s^{-1}$. Comparing the cases of SiO$_2$/ZnS/Al/ZnS/Ag/ZnS and SiO$_2$/ZnS/Ag/ZnS/Al/ZnS, one can see that the change in the order of metal layers does not produces significant changes in the absorption bands.

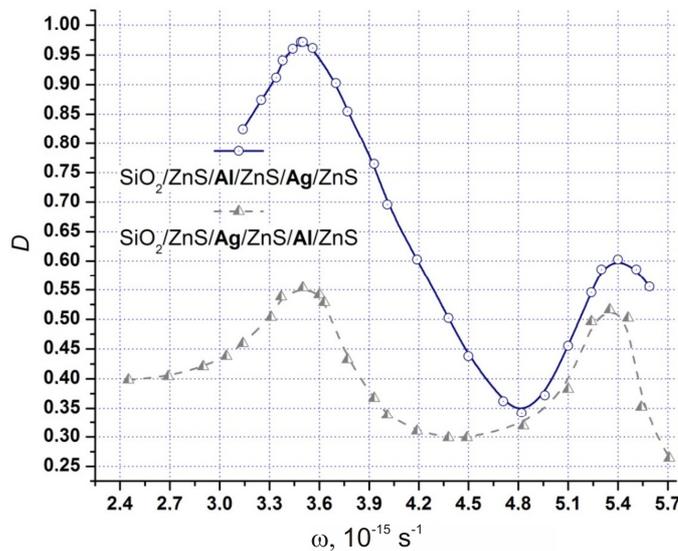**Fig. 3.** Absorption spectra for the sandwiches SiO$_2$/ZnS/Ag/ZnS/Al/ZnS and SiO$_2$/ZnA/Al/ZnS/Ag/ZnS under analysis, as obtained using *p*-polarized light.

It is also obvious that adding a layer of the second metal and the corresponding ZnS layers does not increases the number of bands, if compared with the case of single-metal sample. Assuming that there is the dipole–dipole interaction between the layers of different metals along the direction perpendicular to the layer plane, one can use the coupled-oscillator model (see *Zheng Yu. et al., 2017. Ukr. J. Phys. Opt.* **18**: *225–231*). When the two oscillators with the natural frequencies ω_1 and ω_2 interact with each other, the oscillations with the eigenfrequencies $\omega_{1,2} = (\omega_1 + \omega_2)/2$ should arise in the oscillator system. They are to be compared with the frequencies $\omega_{s2\,calculated}^{Ag\&Al} = \dfrac{\omega_{s2}^{Ag} + \omega_{s2}^{Al}}{2} = \dfrac{4.5 + 6.2}{2}\times10^{15}\,s^{-1} = 5.35\times10^{15}\,s^{-1} \approx \omega_{s2\,exp\,erimental}^{Ag\&Al} = 5.4\times10^{15}\,s^{-1}$ obtained by us. Balancing the calculated values with the experimental ones, one concludes that the locations of the high-frequency maxima for the samples of SiO$_2$/ZnS/Al/ZnS/Ag/ZnS and SiO$_2$/ZnS/Ag/ZnS/Al/ZnS correspond roughly to the mean value of the frequencies obtained for the high-frequency bands peculiar to the SiO$_2$/ZnS/Al/ZnS and SiO$_2$/ZnS/Ag/ZnS samples.

After changing the order of layers, one does not have any essential changes in the data. Thus, we have proven that there are the dipole–dipole interactions between the layers of the metal granules. Note that this fact is of a fundamental importance while creating biosensors, in which the dipole-dipole interactions between the layers result in Raman scattering.

5. Conclusion

In the present work we have confirmed the presence of the dipole–dipole interactions between the granular layers of different metals, which are separated by the intermediate layer of ZnS. The plasma frequency of aluminium $\omega_p = 21.9 \times 10^{15}\,s^{-1}$ has been determined from the maximum position of the high-frequency band found for the two-layer sample based on the granular Al film enclosed between the ZnS layers. A comparison of our results with those reported in Ref. [5] allows us to confirm that our calculations based upon the model of system of two coupled oscillators are correct.

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Анотація. *Описано спектрофотометричні дослідження двошарових гранульованих плівок алюмінію і срібла, розділених шарами ZnS. Таку багатошарову систему приготовлено шляхом двостадійного висадження Al і Ag, розділених тонкою плівкою ZnS. Досліджено диполь–дипольні взаємодії між оптичними тонкими плівками в багатошаровому сендвічі та визначено оптичні смуги поглинання на різних етапах процедури осадження. Виходячи з позиції максимуму високочастотної смуги для двошарового зразка на основі гранульованої алюмінієвої плівки, укладеної поміж шарами ZnS, встановлено плазменну частоту алюмінію.*