Enhanced Photoemission of Nanostructured Metal Films Supporting Localized Plasmon Resonances*

V. V. Khromov, N. B. Leonov, S. G. Przhibel'skii, E. V. Vaschenko,† and T. A. Vartanyan
St. Petersburg State University of Information Technologies, Mechanics and Optics,
Birzhevaya linija 16, St. Petersburg 199034, Russia
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In the present work the photoelectric emission from island sodium films was investigated. Appreciable deviations from Fowler’s law as well as an increase of the photoelectrons yield for the island films were discovered. The dependences of the photoeffect efficiency on the films structural parameters, on the polarization and the angle of incidence of the laser radiation were studied. [DOI: 10.1380/ejssnt.2009.563]

Keywords: Photoemission (total yield); Photoelectron emission; Plasmons; Alkali metals; nano-particles; nano-films

I. INTRODUCTION

Ensembles of metal nanoparticles deposited on transparent dielectric surfaces are investigated for a long time, owing to their optical properties defined by the excitation of localized plasmons. Basic mechanisms of the field enhancement on the nanoparticles surface were elucidated, and the use of metal nanoparticles in such applications as confocal microscopy, biosensing, near field optics, informatics has already begun. The resonance increase of the absorption cross section, which can largely exceed the geometrical cross section of the metal nanoparticle, the field enhancement near the metal particle surface in comparison with the field of the incident wave, and also the spatial localization of the field in the regions that are considerably smaller than the wavelength of the optical radiation as well as the possibility of plasmon excitation transfer between nanoparticles are used in these applications.

In the present work an attempt of studying the influence of the localized plasmon excitation on the photoelectron emission process from an ensemble of interacting metal nanoparticles was undertaken. A research of an external photoeffect from an isolated metal particle located on a dielectric substrate is impossible owing to the effect of particle charging. This effect becomes especially dramatic for the particles in the nanometer size regime. In the previous work we have shown, that it is possible to prepare island metal films in which the charging effect can be minimized by the nonzero conductivity of the tunnel contacts between particles [1]. This allowed us to investigate the photoelectric effect in small metal particles on dielectric surfaces.

It is necessary to notice, that the dependence of the metal clusters electronic properties on their size was investigated in great detail and very carefully during last years [2, 3]. In particular, in [3] the ionization thresholds (work function) of alkaline metals clusters Li, Na, K have been measured. It was noticed that the experimentally obtained values of work function for nanoparticles containing several thousand atoms tally with values of work function for massive metals and the dependence of the photoionization efficiency for these particles on the radiation frequency submits to Fowler’s law. It is necessary to underline that in this work the clusters were produced by condensation of alkali metal vapors in a buffer gas. In our work we investigated the photoelectric emission from the island sodium films that were evaporated on a surface of transparent dielectric materials, in particular, glass and sapphire. That allowed us to control and to change over a wide range the size, the concentration and the shape of nanoparticles.

In this research of photoelectric effects in metal nanoparticles the main attention was given to the mutual influence of collective electronic excitations and single-particle excitations of electrons. The manifestations of collective electronic excitations are well-known and have been investigated in detail from the point of view of purely optical effects. At the same time field enhancement on the surface and in the volume of nanoparticles, connected with excitation of localized plasmons in it, can lead to the effective formation of single-particle excitations and, consequently, to the formation of electrons with the energy lying above Fermi level. This process is well-known and widely used in optoelectronics. On the other hand, the excitation transfer from a collective mode to a single electron can be considered as one of the plasma damping mechanisms. Below it is shown that in the system, which we investigated this mechanism is rather efficient and essentially influences on the spectral, polarization and angular characteristics of the photoelectric emission.

II. EXPERIMENTAL

The experiments were performed with island sodium films that were evaporated in an evacuated vacuum cell in the gap situated between two electrodes on sapphire windows of the cell. To enable the photoelectric emission measurements the third electrode was soldered in near the second window. Such design of the cell allowed us to measure both film’s optical characteristics on spectrophotometer SF-56 and film’s photoelectric properties (photoelectric emission and photoconductivity of the film). Be-
FIG. 1: Extinction spectrums, obtained for island sodium films (film $\ll 1\gg$ and film $\ll 2\gg$), which were investigated in the experiment (the position of short-wave plasmon resonance for films: $\ll 1\gg$ - 464 nm (2.68 eV), $\ll 2\gg$ - 385 nm (3.22 eV)).

Before the beginning of each experiment the old film was removed by warming up the window of the cell and, then, a new film was deposited.

In our experiments the size of the particles was in the range of 20-100 nm. Two plasmon resonances were observed in the optical extinction spectra of the films. These resonances correspond to the collective oscillations of all electrons along each of two axes of an ellipsoid that approximates the shape of the metal nanoparticles on dielectric substrate (Fig. 1) [4]. Electron oscillations along the third axis of an ellipsoid could be excited only at oblique incidence of p-polarized radiation (this resonance falls out of the range of wavelengths displayed in Fig. 1). The film $\ll 1\gg$ has been prepared by evaporation of sodium in the cell. The film $\ll 2\gg$ has been obtained by heating of the film $\ll 1\gg$ at temperature 40 $^\circ$C for several minutes.

The films extinction as well as the particles size and shape were defined by the conditions of the films evaporation and its thermal processing after evaporation. These procedures allowed us to change the position of the short-wave plasmon resonance within 350-500 nm.

The results obtained in such cells were compared with the results for photoelectric emission obtained in a specially made cell where the sodium continuous film of 0.5 mm thickness was evaporated.

For measurement of the spectrum of photoelectric emission the continuous arc lamp radiation passed through monochromator was used, the value of photocurrent was registered by digital multimeter Atakom IWATSU ABM-4403.

III. RESULTS AND DISCUSSION

1. The quantum efficiency of photoelectric emission from an island sodium film is compared to photoemission from the continuous metal film in Fig. 2. Besides that, we evaporated an island film in which short-wave plasmon resonance coincided with the maximum in the selective spectrum of photoelectronic emission from continuous metal. In spite of the fact that another film’s parameters weren’t optimized, one could see that the quantum efficiency of the photoemission from an island film is larger than that from a massive metal by more than an order of magnitude.

2. The distinct correlation between the form of the spectrum of the selective photoeffect from island sodium films and the spectral position of the short-wave plasmon resonance has been established. It was revealed, that the maximum of the photoelectric emission spectrum moves concerning the maximum in the photoemission spectrum of the continuous film towards the short-wave plasmon resonance (Figs. 1 and 3).

3. The Fowler’s law

$$I \sim (h\nu - \phi)^2,$$

(1)
where $h\nu$ is the energy of photons, $\varphi$ is work function for the metal for island sodium films was checked up. Using photoelectric emission spectra, that have been measured for the films (Fig. 3), we drew dependences of $I^{1/2}$ on the photon energy $h\nu$. The work function values of each metal film were found as well. It was shown, that the value of work function $\varphi = 2.25 \pm 0.05$ eV coincides with that for bulk sodium, $2.27$ eV [5]. In all investigated cases Fowler’s law was strictly carried out, except for the film in which the plasma resonance is located in immediate proximity of the photoeffect threshold. In the last case the dependence of the photoemission current on the photon energy deviated from the square-law (Fig. 4). This effect is explained by an enhancement of the optical field on the surface and in the volume of metal nanoparticles owing to the plasmon resonance.

4. The dependences of the photoelectric emission from the island films on the polarization and the angle of incidence of exciting radiation were investigated. For vectorial effect studying we illuminated island sodium film with the continuous diode laser of 8 mW power on the wavelength of 377 nm. Especially for the experiment we evaporated the film in which the short-wave plasmon resonance maximum was observed at 380 nm. Hence, it is close to the frequency of the exciting radiation.

Let us remind, that for a plane surface of massive metal the vectorial effect consists in the following: for the radiation with $s$-polarization (the electrical vector of light wave is parallel to the substrate plane) the photocurrent is small and doesn’t depend on the angle of incidence. For the radiation with $p$-polarization (the electrical vector has a component, which is perpendicular to substrate plane) the photocurrent sharply increases when the angle of incidence grows [6]. Figure 5 plots the photocurrent dependence on the angle of incidence for $s$- and $p$-polarized light. Since in our experiments the film’s excitation was made from an outer side of the cell, these dependences were corrected with account of the substrate reflection [7]. As one can see from Fig. 5 the vectorial effect for island films differs significantly from the similar effect for the plane metal surface.

The obtained experimental results show that the basic characteristics of the photoelectric emission from metal island films in the spectral range of localized plasmons excitations differ considerably from the similar characteristics of massive metal. These differences are explained by opening of an additional channel for creation of one-particle electronic excitations related to the decay of plasmon oscillations. Such supposition explains all received experimental results. First of all it concerns the observed enhancement of the photoelectric emission that is related with the resonance character of the plasmon oscillations in nanoparticles.

The influence of plasma oscillations on the photoelectric emission out of a nanoparticle is due to the field enhancement inside it. In the case of the nanoparticles of ellipsoidal shape the internal field is homogenous, thus, the field enhancement factor in the nanoparticle characterized by the resonance frequency $\nu'$ is uniquely defined by the relation

$$ g(\nu, \nu') = \frac{\left| E_1 \right|^2}{\left| E_0 \right|}, $$

where $E_0$ is the electric field amplitude of the incident radiation with frequency $\nu$, while $E_1$ is that inside the nanoparticle. The field enhancement factor may be obtained using the known relations [8] for the ellipsoids made of a material with a dielectric permeability

$$ \varepsilon(\nu) = \varepsilon_1 + i\varepsilon_2, $$

$$ E_1 = \frac{E_0}{1 + (\varepsilon(\nu) - 1)L}, $$

where $L$ is the depolarization factor related to the corresponding axis of the ellipsoid. Although $L$ may be easily related to the ratio of the ellipsoidal axes we are not going
to use this relation in the following. Instead, the absorption cross section \(\gamma(\nu, L)\) of an ellipsoidal nanoparticle of volume \(V\) is found via [8]

\[
\gamma(\nu, L) = \frac{2\pi V\nu}{c} \frac{1}{3} \left\{ \varepsilon(\nu) - 1 \right\} \left[ \frac{1}{1 + \varepsilon(\nu) - 1/L} \right],
\]

where \(c\) is the speed of light. Substituting the explicit form of the dielectric permeability one finds

\[
\gamma(\nu, L) = \frac{2\pi V\nu}{cL^2} \frac{\varepsilon_2(\nu)}{[\varepsilon_1(\nu) - 1 + 1/L]^2 + \varepsilon_2^2(\nu)}.
\]

If the imaginary part of the dielectric permeability is small the absorption cross section reaches a sharp maximum when the term in the square brackets in the denominator turns to zero. This happens at the resonance frequency \(\nu'\) that is the root of the equation

\[
\varepsilon_1(\nu') - 1 + \frac{1}{L} = 0.
\]

That means that the resonance frequency \(\nu'\) may be used to characterize the nanoparticle shape instead of the depolarization factor \(L\). As the islands in the film had different shapes their absorption spectra were different. Hence, the absorption spectrum of the whole film was inhomogeneously broadened. It is defined by the formula

\[
S(\nu) \propto \int d\nu' \gamma(\nu', \nu') f(\nu'),
\]

there \(f(\nu')\) characterizes the resonance frequencies distribution.

On the other hand, on account of the field enhancement factor, the Fowler’s law reads as

\[
I \propto (h\nu - \varphi)^2 g(\nu, \nu') E_0^2.
\]

Accordingly, the photoemission current from the film with the inhomogeneous broadening of plasmon resonances equals to

\[
I(\nu) \propto (h\nu - \varphi)^2 E_0^2 \int d\nu' g(\nu, \nu') f(\nu').
\]

Comparing the expressions for the absorption cross section and the field enhancement factor one finds the following relation

\[
g(\nu, \nu') = \frac{\varepsilon_1(\nu, \nu')}{2\pi V \varepsilon_2(\nu)},
\]

with the use of which we finally arrive to the relation the absorption spectrum \(S(\nu)\) and the modified Fowler’s relation \(I(\nu)\)

\[
I(\nu) \propto \frac{(\nu - \nu_0)^2}{\nu^2} S(\nu),
\]

where \(\nu_0 = \varphi/h\) is the frequency of the photoemission threshold.

The obtained connection between the photoemission and absorption spectra was employed to rationalize the observed deviations from the Fowler’s law. The photoemission spectrum was computed according to the above formula using the measured extinction spectrum that in this size regime coincides with the absorption spectrum, \(S(\nu)\), and the known optical properties of sodium. Figure 6 plots the experimental data points for the film, which demonstrated the largest deviation from Fowler’s law, along with the computed results.

Considerable inhomogeneous broadening of the extinction spectrum implies that only a small part of all islands in the film are in resonance with the incident radiation. For this reason deviations from the Fowler’s law are not very spectacular. Despite that the photocurrent enhancement in resonance islands is great enough to provide for appreciable enhancement of the photocurrent from the whole film as compared to the continuous metal surface.

The experimental results obtained for the angular and polarization dependencies of the photoemission current can be described by the following model. It was assumed, that the islands shapes may be approximated by ellipsoids and the frequencies of plasma oscillations parallel to the substrate surface are in resonance while the frequencies of plasma oscillations normal to the substrate surface are out of resonance with the incident radiation. For this reason the enhancement factor for the field component parallel to the substrate surface \(g_1\) differs from the enhancement factor for the field component perpendicular to the substrate surface \(g_2\). In the case of \(s\)-polarization the electric field of the incident wave is parallel to the substrate plane independent of the incidence angle. Hence, the field enhancement factor does not depend on the incidence angle in this case and the effective radiation intensity in given by the formula \(g_1 E_0^2\).

On the other hand, in the case of \(p\)-polarization the electric field vector lies in an incidence plane and has a component parallel to the substrate surface, \(E_0 \cos \alpha\), as well as a component normal to it, \(E_0 \sin \alpha\), where \(\alpha\) is the angle of incidence. The enhancement factor for the first component is \(g_1\), while for the second component it is \(g_2\). That is why the effective radiation intensity in the island...
is given by the formula
\[
g_1 E_0^2 \cos^2 \alpha + g_2 E_0^2 \sin^2 \alpha = g_2 E_0^2 \left( \frac{g_1}{g_2} - 1 \right) \cos^2 \alpha + 1 \right].
\] (13)

By changing the angle of incidence, we change also the dimension of the illuminated spot on the substrate, hence, the quantity of excited islands changes as well. This quantity is proportional to $1 / \cos \alpha$. So, the expected dependence of the photocurrent on the angle of incidence is given by
\[
I_s \propto g_1 E_0^2 \frac{1}{\cos \alpha}
\] (14)
for s-polarization and
\[
I_p \propto g_2 E_0^2 \left( \frac{g_1}{g_2} - 1 \right) \cos \alpha + \frac{1}{\cos \alpha} \right] \] (15)
for p-polarization. Angular dependence of the photoemission current for s-polarization shown in Fig. 5 agreed well with the first formula, while the angular dependence for p-polarization was used to estimate the ratio $g_1 / g_2$. The best fit, shown in Fig. 5 was obtained with $g_1 / g_2 = 8$.

Although it is tempting to compare this value with the overall enhancement of the photoemission current from the island metal film relative to that from a bulk metal surface it is not possible to make such a comparison in a straightforward manner. First of all, due to the inhomogeneous broadening, both values, $g_1$ and $g_2$, are to be understood as the mean values over the resonance frequency distributions that are not known. In the above discussion of Fowler’s law this difficulty was alleviated for $g_1$ using the measured extinction spectrum at normal incidence. This procedure does not work for $g_2$. Hence, its mean value is not available yet. Second, due to the Fresnel reflection, the field amplitude on the bulk metal surface is reduced as compared to the incident field. Thus, the photoelectron emission from the bulk metal surface is reduced as well. The exact value of this reduction is difficult to estimate because of the macroscopic roughness of the bulk metal surface used in our experiment. These arguments preclude from comparing of the enhancement factors directly. Nevertheless, closeness of the overall enhancement of the photoemission from the island metal film relative to that from a bulk metal surface and the enhancement factor obtained from the angular dependence of photoemission current suggests the conclusion that the mean value of $g_2$ is not very different form unity. Thus, the above assumption that the laser light is out of resonance with the plasmon oscillations perpendicular to the substrate surface is justified.

IV. CONCLUSIONS

In the present work the dependence of the photoemission current on the position of plasma resonances in the island sodium films has been revealed. It has been found out, that for the films with plasma resonances located in the immediate proximity of the photoeffect threshold, Fowler’s law is inapplicable. It was noticed, that the photoemission current density from sodium island metal films supporting localized plasmon resonances is an order of magnitude larger than from the surface of bulk sodium. The dependence of the photoemission current from the island metal films on the state of polarization as well as on the angle of incidence of the optical radiation was studied. During the research it was found, that for p-polarized light the decrease of the photoemission current with the growth of the angle of incidence is observed, and for spolarization, on the contrary, the increase is observed.

All results obtained in this research were explained by an influence of localized plasmon excitation on characteristics of the photodetector process.

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