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Interband electronic transitions and scattering of excess free carriers from a surface in nonlinear spectroscopy of ultrathin metal films

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***Abstract*. Based on degenerate four-photon spectroscopy of ultrathin (10 – 20-nm thick) Ni, Au, and Pt films, a conclusion is made about a dominating role of interband electronic transitions in the formation of a nonlinear response of the metals in the visible spectral range. It is shown that an excited electron subsystem in films of thickness less than the mean free path is thermalized and cooled due to rapid inelastic scattering of excess free carriers on the film surface. The estimates performed for the Ni film showed that up to 10 % of 20-ps pump-pulse energy could be scattered in this way producing the surface deformation. Upon spatially nonuniform excitation, the efficient 'direct' generation of surface acoustic waves is possible.**

Keywords: *interband electronic transitions, excess free carriers, nonlinear spectroscopy of thin metal films.*

1. Introduction

The physical properties of ultrathin metal films are extensively studied because they are promising for a variety of practical applications in many fields of science and technology, for example, in nano- and microelectronics, microwave technology, optics, etc. Vast experimental data are accumulated to date, which have been obtained by various non-optical [1 – 3] and optical [4 – 6] methods. The study of the ultrafast relaxation of 'collision' excitation of an electron subsystem by ultrashort laser pulses especially attracts recent attention [3, 7, 8 – 11].

However, despite extensive studies in this field, processes proceeding in ultrathin metal films are not adequately studied. This is explained, in particular, by the fact that most of the parameters used for the description of nonequilibrium processes [temperatures of the electron (T_e) and phonon (T_{ph}) subsystems, the Fermi-level energy, the characteristic relaxation time, etc]. cannot be measured directly. Their values can be estimated only from indirect measurements. For this reason, the authors of papers devoted to the study of kinetic phenomena in metals proceeding after the collision 'heating' of metals by ultrashort laser pulses quite often make contradictory conclusions [10, 11].

In this paper, we study the role of the interband electronic transitions in the formation of a nonlinear-optical response in the visible spectral region in ultrathin metal films.

2. Role of interband electronic transitions in nonlinear spectroscopy of metal films

The application of the methods of coherent nonlinear spectroscopy [12] for studying physical properties of ultrathin metal films allows the solution of many of the problems mentioned above. Thus, one of the methods of nonlinear spectroscopy, the so-called degenerate four-photon spectroscopy (DFPS) [13], is based on the writing of the permittivity grating in a sample under study. The written grating has a dynamic nature and is fabricated due to an interference pattern (spatially nonuniform distribution of the intensity I) produced by two pump pulses with the same carrier frequency propagating at an angle to each other. Simultaneously with writing, the reading of the grating is also performed during which the spectral dependence of the self-diffraction efficiency $\eta(\lambda)$ of one of the pump pulses is measured. The DFPS can give information on the resonance mechanisms of nonlinearity, i.e., identify both the position and width of the corresponding resonances in a nonlinear response and the ratio of their amplitudes.

We obtained nonmonotonic spectral dependences $\eta(\lambda)$ for ultrathin (10 – 20-nm thick) Ni, Au, and Pt films by the method of DFPS (Fig. 1). These data were interpreted using the model [13] of the electronic part of the nonlinear response of metal films, which takes into account the real band structure of a sample, all types of possible one- and two-photon interband electronic transitions in the Brillouin zone, and saturation effects. The agreement between the experimental data (Fig. 1, dashed curves) and the numerical simulations (Fig. 1, solid curves) for Ni (Fig. 1a) and Au (Fig. 1b) films shows that precisely such nonmonotonic spectral dependences should be formed due to interference of several coherent contributions to the electronic nonlinear response of the metal films under study. Such interfering components appear due to the presence of several types of simultaneously proceeding interband electronic transitions.

A very important role of the interband transitions in the formation of the nonstationary response of metal films (Ni, Au, and Cu) to an ultrashort optical pulse was recently pointed out by the authors of papers [14, 15] in the interpretation of the experimental data obtained by the probe – beam method. Because the interband transitions, in contrast

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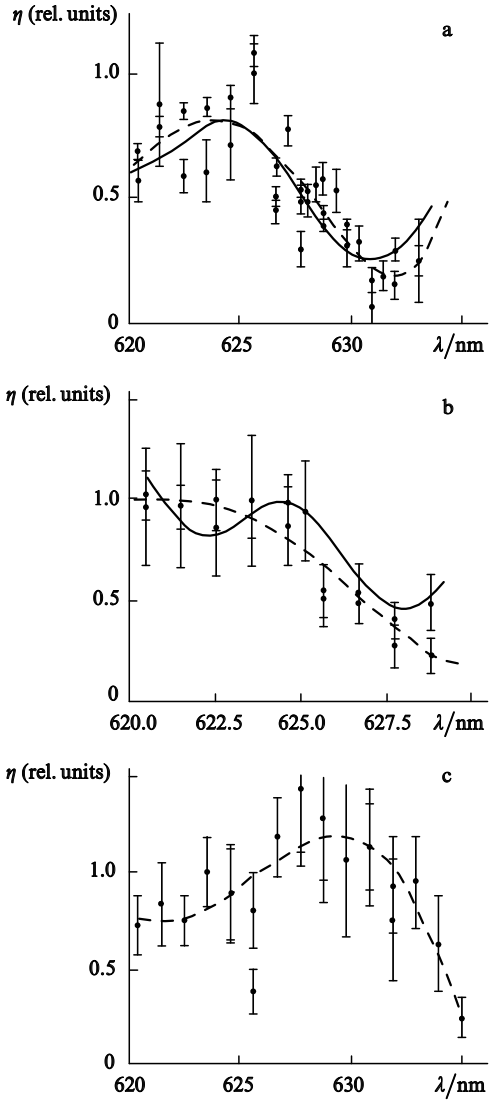

Figure 1. Dependences of the self-diffraction efficiency η on the pump wavelength λ for ultrathin Ni (a), Au (b), and Pt (c) films obtained by the DFPS method (dots), using the polynomial approximation (dashed curves), and calculated using the model [13] (solid curves).

to absorption of light by free carriers, inevitably result in the appearance of 'excess' free carriers, the consideration of the latter can drastically alter the usual concept of physical mechanisms of energy exchange between optically excited electronic and phonon subsystems.

3. Features of relaxation processes in ultrathin metal films

Nonequilibrium processes in metals are usually described with the help of the so-called two-temperature model [16]. It is assumed that after absorption of an ultrashort light pulse, the electronic subsystem ceases to be in the thermal equilibrium with the lattice. In this case, the electron temperature T_e differs from the phonon temperature T_{ph} due to the finite rate of energy exchange. The possibility of migration of excitation in the space (for example, over the coordinate x) is taken into account by the diffusion terms in the corresponding kinetic equations (thermal balance equations), which can be written, in the simplest one-dimensional case, in the form

$$c_e(T_e)\frac{\partial T_e}{\partial t} = -G_{eph}(T_e - T_{ph}) + \varkappa_e\frac{\partial^2 T_e}{\partial x^2} + F(x,t),$$
$$c_{ph}(T_{ph})\frac{\partial T_{ph}}{\partial t} = -G_{eph}(T_{ph} - T_e). \quad (1)$$

Here, $c_{e,ph}$ are specific thermal capacities of the electron and phonon subsystems; $\varkappa_e$ is the thermal diffusivity; $F(x,t)$ is the 'thermal' source (the absorbed pump intensity); $G_{eph} = c_e/\tau_e = c_{ph}/\tau_{ph}$ is the constant of electron–phonon interaction; and $\tau_{e,ph}$ are the characteristic times of variation in temperatures of the electron and phonon subsystems. Because $c_{ph}/c_e = \tau_{ph}/\tau_e \sim 10^3$ for metals [16], the total specific thermal capacity is $c = c_e + c_{ph} \simeq c_{ph}$; for example, we have $c \simeq 4 \times 10^2$ J kg^{-1} K^{-1} for Ni [17].

The system of equations (1) is often modified to take into account the specific features of a particular problem (the dimensionality, the presence of other degrees of freedom, specific features of energy transfer, etc.) When the spatially nonuniform pump is used, the spatially nonuniform variation in T_e and, hence, in T_{ph} takes place. The latter results in the lattice deformation and generation of acoustic waves. However, this indirect (thermal) mechanism of generation of sound [18] proves to be too slow (the characteristic time of about several picosecond) and inefficient.

Upon optical excitation of excess free carriers in ultrathin metal films, the 'direct' deformation mechanism of energy transfer to a surface proves to be efficient [19, 20]. When the kinetic energy of free carriers is certainly lower than the work function (~ 8 eV for Ni [17]) and $l < l_e$ (where l_e is the mean free path of free carriers), these excess carriers are scattered from the sample surface, producing the excess pressure on it. Although scattering of carriers from the surface is 'coherent' under stationary conditions (i.e., is elastic) [21], a part of the electronic energy is inevitably spent due to the appearance of the excess pressure, because the recoil momentum exists. Spectroscopic studies of ultrathin metal films and films exhibiting high-temperature superconductivity performed by various methods confirm indirectly an important role of the direct mechanism of the energy exchange between the electron and phonon subsystems [3, 4, 6–11, 13]. The estimates of the characteristic time of thermalization and cooling of the electron subsystem (200–800 ps) made by the authors of the above papers well correlate with the time of ballistic flying (at the velocity equal to the Fermi velocity v_F) of a free carrier over the distance l.

A part of the energy that can be transferred to excess carriers on the film surface for time τ_p can be estimated using the gas-kinetic theory. Below, we consider excitation of an ultrathin Ni film of thickness $l = 20$ nm by a 20-ns pump pulse with the energy density $W_p = 5 \times 10^{-4}$ J cm^{-2} and the photon energy $W_\omega = 2$ eV, in accordance with the experimental conditions [13].

For the absorption coefficient $\alpha_p = 2 \times 10^5$ cm^{-1}, the concentration δn_e of excess carriers can be estimated as

$$\delta n_e = \frac{\alpha_p W_p}{W_\omega} = 3.1 \times 10^{20}\ \text{cm}^{-3}, \quad (2)$$

which amounts to $\sim 3\,\%$ of the initial concentration of free carriers in Ni [17].

Let us assume now that during collisions of excess carriers, having the mass m_e and moving at the mean (Fermi) velocity v_F, with a massive 'wall' (surface), the normal pro-

jection $p_z = m_e v_z$ of their momentum changes its sign, while the surface itself receives the recoil momentum and uniformly (i.e., under the conditions of balance of forces) is displaced by the distance Δl for the time τ_p (Fig. 2a). Then, after the averaging over spatial degrees of freedom, the momentum transferred to the surface during each collision event is

$$2\langle p_z \rangle = \frac{2}{\sqrt{3}} m_e v_F, \tag{3}$$

while the total momentum ΔP_z imparted to the surface with the area S for the time τ_p and the pressure P_e produced by excess carriers on the film can be estimated as

$$\Delta P_z = \frac{4}{3}\delta n_e E_F \tau_p S, \quad P_e = \frac{\Delta P_z}{\tau_p S} = \frac{4}{3}\delta n_e E_F, \tag{4}$$

where $E_F = m_e v_F^2/2$ is the Fermi energy. The total displacement Δl of the film boundary for the time τ_p and its velocity v_s are determined by the expressions

$$\Delta l = \chi P_e l, \quad v_s = \frac{\Delta l}{\tau_p} = \frac{4}{3}\chi \frac{\delta n_e E_F l}{\tau_p}, \tag{5}$$

where $\chi = 6 \times 10^{-7}$ atm^{-1} [17] is the compressibility of Ni. From here, we obtain the energy ΔW_e imparted to the surface in each electron collision and the energy density W_s stored in the unit surface for the time τ_p:

$$\Delta W_e = 2 m_e v_z v_s = \frac{8}{3\sqrt{3}}\chi \frac{m_e v_F \delta n_e E_F l}{\tau_p},$$
$$W_s = \frac{8}{9}\chi \delta n_e^2 E_F^2 l \simeq 1.7 \times 10^{-6} \text{ J cm}^{-2}. \tag{6}$$

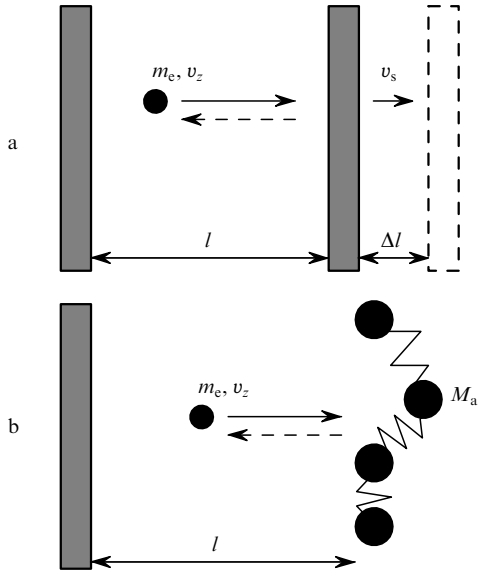

Figure 2. Scheme of the direct electronic energy transfer from excess free carriers to the film surface upon their inelastic scattering from a massive 'wall' (a) and upon the interaction of an electron with an atom (b).

The value of W_s in (6) is less than one percent of the pump-pulse energy.

The loss W_s increases quadratically with increasing $\delta n_e \propto W_p$, in qualitative accordance with the features of the optical 'breakdown' of the films that we observed with increasing W_p. This breakdown always began when the frequencies of two pump pulses were exactly matched and resulted in the formation of a distinct one-dimensional interference grating.

The above assumption about the balance of the excess electron pressure and the pressure appearing in the film during its surface deformation is not sufficiently reliable. By discarding this assumption, we consider the scattering of an excess electron by one of the atoms on the surface (Fig. 2b). When the modulus $|p_z|$ of the electron momentum changes weakly, the average energy W_a imparted to a Ni atom with the mass $M_a \gg m_e$ in each collision can be estimated as

$$W_a = 2\frac{\langle p_z^2 \rangle}{M_a} = \frac{4}{\sqrt{3}}\frac{m_e}{M_a} E_F, \tag{7}$$

and the energy density is

$$W_s = \frac{4\sqrt{2}}{3}\frac{m_e^{1/2}}{M_a}\delta n_e E_F^{3/2}\tau_p \simeq 1.7 \times 10^{-5} \text{ J cm}^{-2}. \tag{8}$$

Expression (8) does not contain l explicitly. Because the total number of free carriers involved in the process is proportional to l, a part of the energy lost by each of them should be also proportional to l. Note that the authors of paper [22] have already pointed out the dependence of the rate of interband electronic relaxation on l for ultrathin silver films in two-photon photoemission experiments. The value of W_s estimated from (8) is an order of magnitude higher than that estimated from (6). Therefore, up to 10 % of the electronic energy can be converted to the deformation energy of the surface for the time $\tau_p = 20$ ps.

4. Conclusions

The analysis of our DFPS experiments with ultrathin Ni, Au, and Pt films have shown that the interband transitions play a dominating role in the formation of their nonlinear response, at least in the visible spectral region. The interference of several such contributions explains, in our opinion, the extremely high sensitivity of the DFPS to the intraband relaxation time, which was pointed out in paper [13]. The appearance of excess free carriers in the conduction band removes the prohibition on their inelastic scattering from the surface [21] and opens up a fast and efficient channel of the electronic energy relaxation in ultrathin metal films, which was considered earlier, for example, in papers [19, 21]. In films of thickness l less than the mean free path l_e of free carriers, the thermalization and cooling of the collisionally excited electron subsystem occur predominantly due to rapid inelastic scattering of excess free carriers from the surface.

Our estimates have shown that from 1 % to 10 % of the electronic energy can transfer to the deformation energy of the surface of the film of thickness $l = 20$ nm for the time $\tau_p = 20$ ps. Transverse surface acoustic waves can be directly excited using spatially modulated light beams. The properties of this relaxation channel are similar to those of the optical 'breakdown' of ultrathin metal films that we observed in the interference field of two frequency-matched pump beams and indicate the possible reason for the dependence of the rate of electronic relaxation on l observed in paper [22].

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