SURFACE PLASMONS AND TRANSIENT OPTICAL RESPONSE OF COPPER NANOPARTICLES

I.V. BLONSKII[1], **I.M. DMITRUK**[1,2], **O.A. YESHCHENKO**[2], **I.A. PAVLOV**[1], **V.M. KADAN**[1], **P.I. KORENYUK**[1], **A.A. ALEKSEENKO**[3], **A.M. DMYTRUK**[1]

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[1]**Instutite of Physics, Nat. Acad. Sci. of Ukraine**
(46, Nauky Prosp., Kyiv 03028, Ukraine),

[2]**Taras Shevchenko Kyiv National University**
(2, Academician Glushkov Prosp., Kyiv 03127, Ukraine),

[3]**Gomel Technical University**
(Gomel, Belarus)

For the femto-picosecond time range, we present the results of investigations of induced variations of the optical density $\Delta D(t)$, half-width $\Delta H/2(t)$, and spectral position of the maximum of the band of surface plasmons (SP) in copper nanoparticles incorporated into SiO_2 matrix under the excitation with femtosecond laser pulses. On this basis, a dependence of energy exchange efficiency between hot electrons and lattice on the dimensionality factor is analyzed, as well as the influence of high frequency field effects on the basic parameters of surface plasmon band.

1. Introduction

Figure 1,(*a,b*) presents two spectra of edge absorption of spherical nanoparticles of different materials incorporated into a dielectric matrix. One can see that the spectra are almost identical. The uncommonness of this result lies in the fact that, in one case (*a*), the spectrum corresponds to the well-known direct gap CdSe semiconductor (nanoparticles with the average size $d \approx 4.5$ nm), while in the other one (*b*) – to classic metal – Cu nanoparticles with the ensemble mean size $d \approx 45$ nm (see, e.g. [1] and references therein).

In the case of a semiconductor, the appearance of the absorption peak with a maximum at $\lambda_{\max} \approx 568.5$ nm is related to the excitation of excitons – bound electrons and holes, whose energy state on the nanometer scale is essentially influenced by the quantum confinement effect. Due to its action, changing the size of nanoparticles d, one can perform a controlled wide-range influence on the energy state of an exciton, whose dimensional shift $\Delta E_{\rm exc}^{0-D}(d)$ is determined from the well-known condition [2]

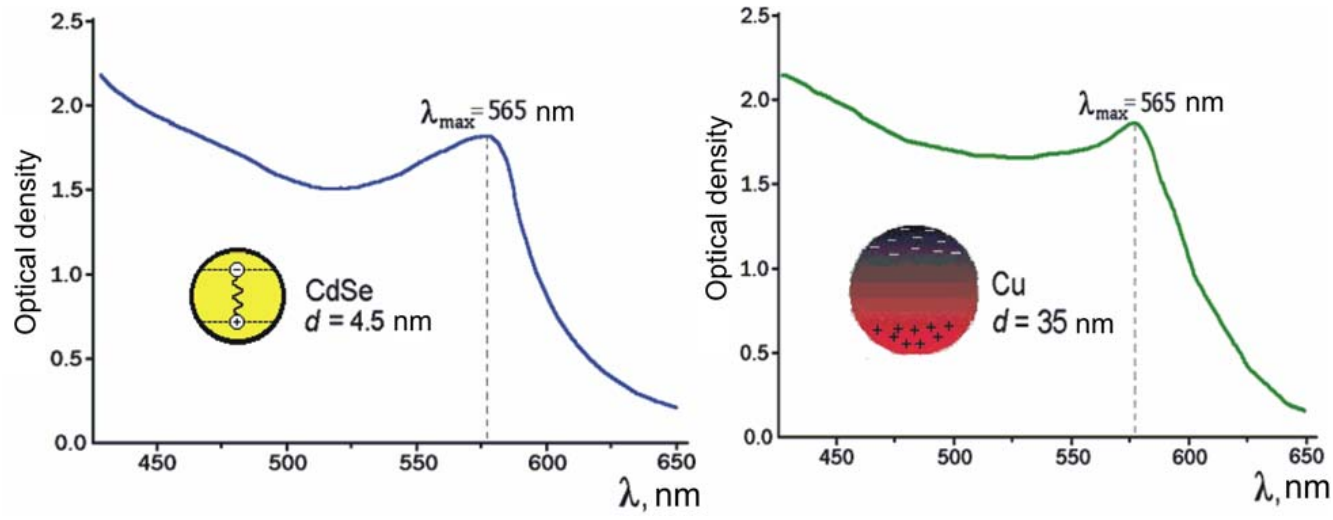
$$\Delta E_{\rm exc}^{0-D} = \frac{\pi^2\hbar^2}{2\mu_{\rm exc}d^2} - 1.786\frac{e^2}{4\pi\varepsilon d} - 0.248R. \qquad (1)$$

The first term on the right-hand side of expression (1) describes a shift of the exciton level with the reduced mass $\mu_{\rm exc}$ in a spatially confined quantum well with the size d, whereas the second and the third ones represent energy corrections to the energy of electron-hole interaction of higher orders. Another factor, which causes an increase of the energy of electron-hole interaction in excitons in quantum dots of semiconductors and therefore underlies the controlled change of the quantity $\Delta E_{\rm exc}^{0-D}$, is related to the realization of the so-called effect of dielectric amplification [3]. Its essence consists in the fact that, due to small sizes of semiconductor nanoparticles incorporated into a dielectric matrix, force lines of the electric field between an electron and a hole in an exciton pass through the dielectric matrix with an essentially lower permittivity ε than that in the material of a nanoparticle, thereby intensifying the interaction between the charges.

For the case of Cu nanoparticles, the appearance of the absorption band in the same spectral region as for CdSe nanoparticles is caused by the excitation of SP – dipole-active excitations localized at the interface of nanoparticles and the matrix (see, e.g., [4]). The resonance frequency of such excitations

$$\omega_{\rm SP} = \frac{\omega_{3D}}{\sqrt{\varepsilon_H(\omega_{\rm SP}) + 2\varepsilon_M(\omega_{SP})}} \qquad (2)$$

is specified by the resonance frequency of bulk plasmons ω_{3D} and also can be changed in a controllable way due to the other factors – the choice of matrices with different



a **b**

Fig. 1. Spectral distribution of the optical density $D(\lambda)$ of spherical nanoparticles: *a*) CdSe direct gap semiconductor; *b*) copper

permittivities $\varepsilon_M(\omega)$ with respect to the background permittivity of the material of nanoparticles $\varepsilon_H(\omega)$. Such a dependence results in a shift of the spectrum of plasmon absorption of light in metals from the far ultraviolet region specific of bulk materials to the visible region characteristic of nanoparticles of the same materials.

It follows from the considerations stated above that, by changing the size and the dielectric surrounding of nanoparticles, one can reach a situation where the spectra of edge absorption of light of metal and semiconductor nanoparticles are practically identical (Fig. 1).

At present, the influence of the dimensionality of a medium $\mathcal{D}$, sizes of nanoparticles d, and their dielectric surrounding on the energy spectrum, electron state density, and the basic properties determined by them are well-studied. As for the investigation of the influence of the same factors on the dynamic electron processes that determine the kinetic properties of electron excitations in nanomaterials, the situation is less satisfactory. Among such dynamic processes, one considers the electron scattering by electrons (e-e), phonons (e-ph), and developed surfaces of nanoparticles (e-s), as well as the Landau damping – the decay of collective electron excitations (plasmons) into single Fermi quasiparticles. All these dynamic processes occur on the time scale 10^{-15}–10^{-12} s, which complicates their experimental investigation (see [4,5]). After putting the Center for Collective Use of Equipment (CCUE) "Laser Femtosecond Complex" at the Institute of Physics of the NAS of Ukraine into operation, the investigations in this direction became available under our conditions. The methodical properties of the CCUE are described in detail in reviews [6, 7].

In this work, we present the results of experimental investigations that demonstrate the peculiarities of heating and cooling of the electron gas and their reflection in the transient optical response in Cu nanoparticles incorporated into a fused quartz matrix on their excitation with femtosecond laser pulses. The choice of such model objects for investigation is explained by the fact that, unlike all other metal nanoparticles where the excitation quantum energy of SP $\hbar\omega_{\rm SP}$ is essentially lower than the energy of interband transitions $E_{\rm I-B}$, Cu nanoparticles represent a unique case where the quantities $\hbar\omega_{\rm SP} = 2.18$ eV and $E_{\rm I-B} = 2.15$ eV are practically equal. This means that, under the photoexcitation of the samples with light of the same spectral composition that corresponds to such resonance transitions, there occurs the excitation of single electrons and coherent vibrations of conduction electrons due to phototransitions from plane d states of the valence band to the conduction band above the Fermi level. The last fact is important with regard for the used method of investigation. It is the so-called two-beam "pump-probe" technique. The function of the first ("pump") beam lies in the destabilization of the electron subsystem due to the realization of intraband transitions. The task of the second ("probe") beam delayed by various time intervals with respect to the "pump" one consists in the diagnostics of a state of the heated electron gas by means

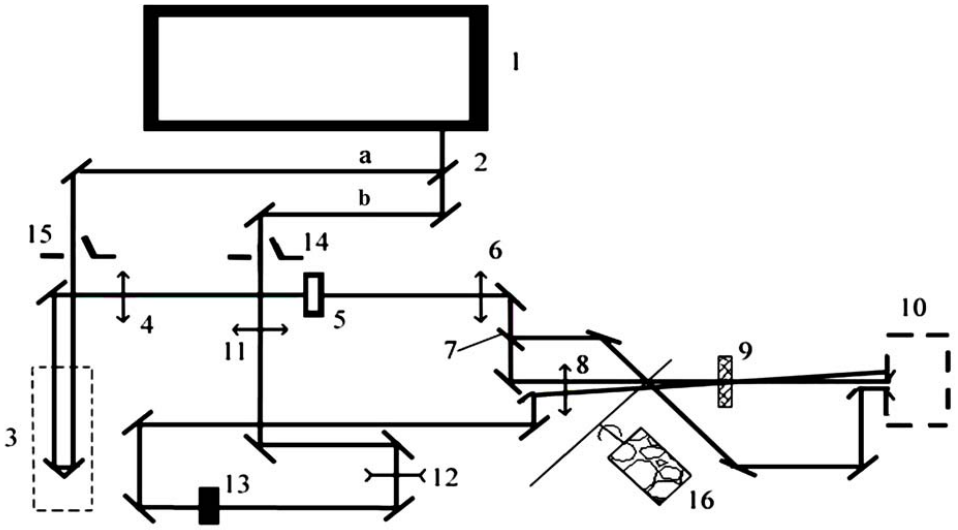


Fig. 2. Block diagram of the "pump-probe" technique for precise investigations of induced variations of optical characteristics of materials

of the excitation of SP in it and the study of the temporal evolution of the basic parameters of the plasmon band.

2. Method and Samples

The scheme of the created set-up is illustrated by Fig. 2 [7]. The initial beam of regenerative amplifier *1* is divided by semitransparent mirror *2* forming a probe beam "a" and a pump beam "b".

The "probe" beam "a" (20% of the initial beam) passes through optical delay line *3*, and then it is focused by lens *4* in a cell with heavy water or in sapphire plate *5* for the purpose of the generation of a "white continuum". White light is collimated by lens *6* and then is directed to investigated sample *9* with the help of a system of mirrors and lens *8*. A part of the "probe" beam detached with plane-parallel quartz plate *7* passes by the sample and is introduced into spectrograph *10* simultaneously with the beam that passed through the sample projecting on various regions of a CCD matrix. On the one hand, this allows one to obtain the absorption spectrum of a sample from one measurement and, on the other hand, decreases the noise level associated with fluctuations of the intensity of white light. The minimal step of the delay line amounts to 0.1 μm, which corresponds to the delay time of 0.67 fs.

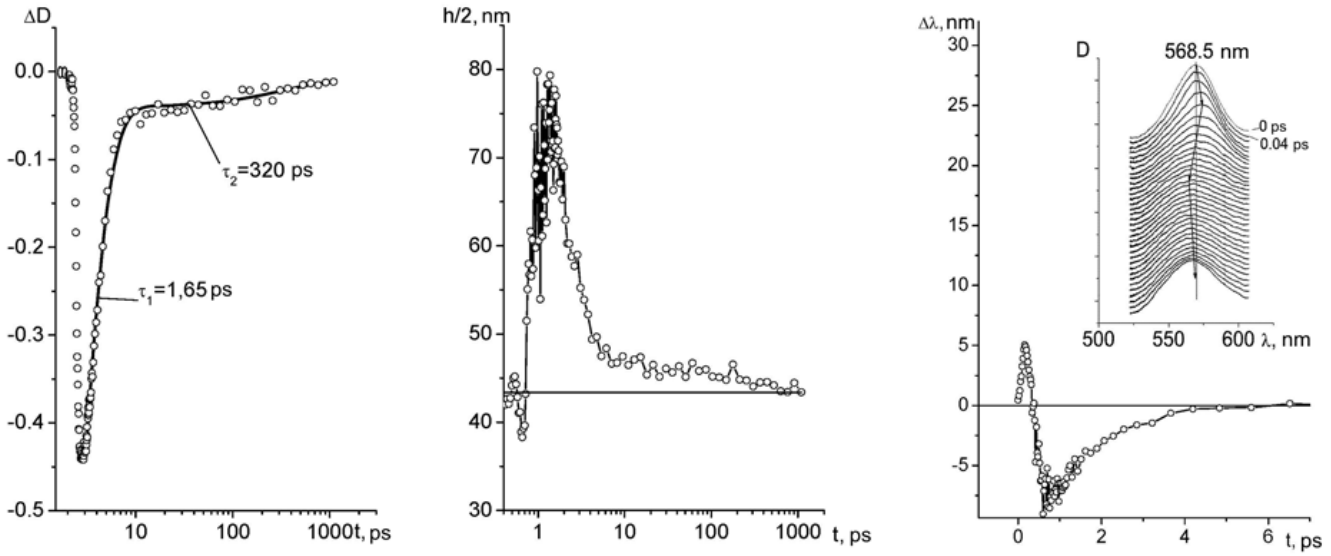
Pump beam "b" passes through a telescope formed by lenses *11* and *12* and nonlinear BBO crystal *13*, where the second harmonic is generated. The second harmonic is directed to sample *9* to the spatial region that coincides with the region of irradiation with the probe beam. Mechanical shutters *14* and *15* allow one to block beams "a" and "b", if necessary. The whole system is controlled automatically.

The created technique provides the following parameters of laser beams: "pump" – minimum pulse duration $\sim$ 100 fs; ranges of generation – 375–475 and 750–950 nm; repetition frequency – 1 kHz, maximum pulse energy – 1.7 mJ; "probe" – quasiwhite continuum 500 nm – 1 μm; pulse duration at a wavelength of 667 nm equals 180 fs. The range of delays between the "pump" and "probe" pulses is 1 fs–1.5 ns.

We have investigated the arrays of spherical Cu nanoparticles with the ensemble mean size $d \approx 47$ nm incorporated into a SiO_2 matrix obtained using the technology described in [8]. A fragment of the TEM image of such nanoparticles is presented in the same work. The ensemble variance of their size distribution function did not exceed 20%. At such values of the mean size of nanoparticles and the variance of their size distribution function, one can neglect the influence of the latter factor on the nonuniform expansion of the SP band.

3. Results and Discussion

Let us consider the results of experimental investigations of the kinetics of induced variations of the basic



a **b** **c**

Fig. 3. Results of induced variations of the parameters of the SP band in Cu nanoparticles at $T = 300$ K after the action of an "pump" femtosecond pulse: *a*) optical density $\Delta D(t)$ (pump pulse at $t = 2.5$ ps); *b*) half-width $\Delta H/2(t)$ (pump pulse at $t = 0.6$ ps); *c*) spectral position of the maximum $\Delta\lambda_{\rm SP}(t)$ (pump pulse at $t = 0.6$ ps) . The inset in Fig. 3,*c* shows the spectra of the SP band registered at various time moments after the "pump" pulse with a time step of 40 fs

parameters of the plasmon absorption band in Cu nanoparticles: optical density $\Delta D(t)$, half-width $\Delta H/2(t)$, and spectral position of the maximum $\Delta\lambda_{\rm SP}(t)$ (Fig. 3,*a*–*c*).

Figure 3,*a* illustrates the dependence $\Delta D(t)$. Here, one can see two typical time intervals of variation of ΔD that correspond to unities and hundreds of picoseconds. At first, let us consider the shortest time interval. One can see that, after the action of the "pump" pulse, there occurs the abrupt bleaching in the region of the absorption band that manifests itself in the time interval < 200 fs. As was shown in a number of works (see, e.g., [4, 5]), such a behavior of $\Delta D(t)$ in this time interval is caused by the processes of heating of the electron gas due to electron-electron collisions. The mean time of an elementary act of this scattering $\tau_{e-e} \approx 10^{-14}$ s [5]. According to the Landau theory of Fermi-liquid, it quadratically depends on the quantum energy $h\nu_{\rm ex}$ and the laser radiation intensity $I_{\rm ex}$, and in accordance with [15], has a form

$$\tau_{\rm e-e}^{-1} = K\frac{(\pi k_{\rm B}T_e)^2 + (h\nu_{\rm exc} - E_{\rm F})^2}{1 + \exp\left(-\frac{(h\nu_{\rm exc}-E_{\rm F})}{k_{\rm B}\cdot T_e}\right)}, \qquad (3)$$

where $K = 0.01$ eV^{-2}fs^{-1} is the electron-electron scattering constant, $T_{\rm e} \sim I_{\rm exc}$ is the effective temperature of the heated electron gas. The value of $T_{\rm e}$ can be calculated based on the so-called 2T Kaganov model [9] that combines two heat conduction equations for electrons and phonons via the parameter of energy interchange between nonequilibrium electrons and the lattice $G(T_{\rm e},\ T_{\rm lat})$. Using the well-known tabulated values of thermal parameters of (bulk) copper, it is easy to demonstrate that, at the excitation intensity used in the experiment $I_{\rm exc} = 4.510^{11}$ W/cm^2, $T_{\rm e} \approx 800$ K, in this case $\tau_{\rm e-e} \approx 10^{-14}$ s. It is worth noting that, in the framework of the accepted approximations, the change of the dielectric response of the medium induced by a femtosecond excitation pulse $\Delta\varepsilon \sim \Delta D$ adiabatically follows the variation of $T_{\rm e}$ [4, 5]. The subsequent relaxation of $\Delta D(t)$ to the state close to the initial one in the time region ~ 1.65 ps is due to the thermalization of electrons provided by the processes of their scattering by phonons and on the surface of nanoparticles. A more long-term component $\tau_2 = 320$ ps of the dependence $\Delta D(t)$ is related to the cooling of heated nanoparticles. Comparing the thermalization times obtained under close experimental conditions for spherical Cu nanoparticles $\tau_{e-T}^{\rm 0D} \approx 1.65$ ps and Cu films of 30 nm in thickness $\tau_{e-T}^{\rm 2D} \approx 2$ ps [10], it is possible to conclude that, with decreasing dimension of a medium, the effectiveness of the electron thermalization somewhat increases. But today it is still difficult to analyze this fact in more details. The answer

to this question is in future, because it is necessary to analyze a number of reasons influenced by the dimension factor as a whole: the densities of electron and phonon states and the probability of quantum-mechanical transitions related to them, "cutoff" of the long-wave part of the acoustic phonon spectrum in nanoparticles along with the possibility of the excitation of "breathing" oscillations in overheated nanoparticles, relaxation effects like the "bottleneck" one, and a number of others (see [1] and references therein). At present, this problem is considered as a "hot spot" in the physics of electron processes in nanostructures.

In spite of the uncertainty of answers to the question about the dependence of the effectiveness of relaxation processes on the dimensionality of a medium $\mathcal{D}$, there is a greater definiteness in their dependence on the size of nanoparticles d. In this connection, let us consider Fig. 4 from [11] that demonstrates the dependence of $\tau_{\rm rel}$ on the size d of Au nanoparticles. Similar dependences are also typical of nanoparticles of other noble metals. The observed increase of the relaxation rate of electrons heated by radiation of a femtosecond laser is explained by the rise of the contribution of surface scattering and can be satisfactorily described by the expression

$$\tau_{e-s}^{-1} = \tau_0^{-1} + \frac{V_{\rm F}}{\alpha d}, \tag{4}$$

where $V_{\rm F}$ is the Fermi electron velocity, α is the number of collisions of electrons with the surface before the achievement of the thermalized state, and τ_0^{-1}denotes the dimension-independent component of the electron scattering.

It is evident that, at typical values of $V_{\rm F} = 10^7$ cm/s and sizes of nanoparticles ~ 10 nm, the time of an elementary act of the electron scattering on the surface $\tau_{e-s} \approx 10^{-13}$ s. Moreover, with decrease in the size of nanoparticles, the quantity τ_{e-s}^{-1} will grow, and its efficiency can exceed that of electron-phonon relaxation ($\tau_{e-{\rm ph}}^{-1} \approx 10^{12}$ s^{-1}) and compete with the electron-electron scattering efficiency ($\tau_{\rm e-e}^{-1} \approx 10^{14}$ s^{-1}).

Another dynamic process that can determine the lifetime of plasmons in Cu nanoparticles is the Landau damping – the loss of coherence in a system of conduction electrons due to the transmission of their energy to one-particle excitations. Such a process occurs in the case where the phase velocity of a plasmon wave is close to the velocity of single electron excitations. As was already mentioned in Introduction, the peculiarity of Cu nanoparticles that differs them from all other metals is the almost complete coincidence of the frequencies of SP and interband transitions. Due to this fact, the radiation

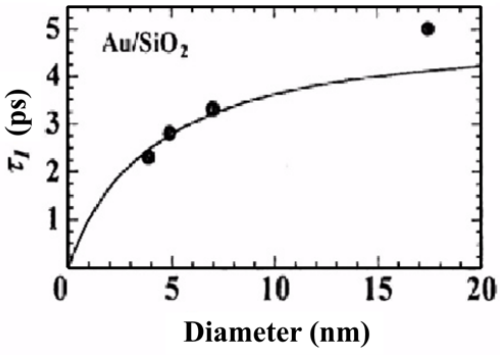


Fig. 4. Typical form of the dimension dependence of the relaxation time of hot electrons in nanoparticles of noble metals (see [11])

of the same spectral composition simultaneously excites SP and free charge carriers that can promote the collisionless dissipation of the energy of SP. In this connection, let us pay attention to the temporal evolution of the halfwidth of the plasmon band $H/2(t)$ that directly reflects the damping time of SP (Fig. 3,*b*). In the Cu nanoparticles under study (without the action of an "pump" femtosecond radiation) the damping time of SP (obtained by the band width) amounted to $\tau_{\rm SP} \approx 40$ fs. Under the action of an "pump" femtosecond pulse that heated conduction electrons, the band width in the time interval < 1 ps increased by 40 %, which corresponded to the reduction of the damping time of plasmons by $\sim$ 15 fs. With a further cooling of the electron gas, the band gets narrower with the tendency to approach the initial width, Fig. 3,*b*. But the stationary value of the plasmon band width in Cu nanoparticles still exceeds the corresponding parameter in nanoparticles of other metals (see [1]). To our mind, the latter fact can indicate the peculiarities of damping processes in the plasma of Cu nanoparticles. This result seems to be important in view of the following considerations. There are the results explaining the peculiarities of such collisionless damping in 3D, 2D, and 1D structures [12]. As for 0D structures, the question on features of the Landau damping is still open. In this connection, Cu nanoparticles can appear to be fortunate model objects for the experimental investigation of such relaxation process.

In conclusion, let us consider the alternating-sign behavior of the spectral position of the plasmon band maximum and its nature. This result was partially elucidated in works [13, 14]. As one can see from Fig. 3, the action of an "pump" pulse in the initial time interval (< 0.2 ps) results in a shift of the band maximum

to the long-wave spectral region. Then, in the time interval 0.2–0.6 ps, the direction of this shift changes its sign. At the final stage (0.6–5 ps), the sign of the shift direction again changes, and the position of the SP band maximum returns to its initial value of 568.5 nm. The maximal shifts of the band toward the red and blue spectral regions appeared to be approximately equal and dependent on $I_{\rm exc}$. At $I_{\rm exc} = 4.5 \times 10^{11}$ W/cm^2, the maximal shift of the band toward the red spectral region amounted to $\Delta\lambda_{\rm SP} \approx 5$ nm. Evidently, the observed alternating-sign behavior of the dependence $\Delta\lambda_{\rm SP}(t)$ reflects the nonelementary character of the processes running during various time intervals in the case of the interaction of femtosecond laser pulses with Cu nanoparticles incorporated into fused quartz. Its explanation requires allowance, first of all, for the basic effects that accompany the interaction of femtosecond pulses with such materials: the high-frequency Kerr effect, formation of plasma in a SiO_2 matrix, heating and cooling of electrons in nanoparticles, *etc.* Let us analyze the thresholds of their appearance and their influence on the value of $\omega_{\rm SP}$ with regard for dependence (2). It is appropriate to associate the shift to the long-wave spectral region observed in the initial time interval ($<$ 0.2 ps) with an increase of the denominator in expression (2) that occurs due to the action of the Kerr effect with the instantaneity specific of the latter (10^{-15} s) resulting in a change of the refractive index of the medium n according to the relation

$$n = n_0 + n_2 I_{\rm exc}, \tag{5}$$

where n_0 stands for the initial value of the refractive index; $n_2 = \frac{2\pi}{n_0}\chi^{(3)}$ is its increase in the laser wave field; $\chi^{(3)}$ is the nonlinear cubic-in-field component of the susceptibility.

It is easy to demonstrate that, in order to provide an experimentally observed reduction of the energy of SP by $\Delta\hbar\omega_{\rm SP} \approx 0.02\hbar\omega_{\rm SP}$ (shift of the band to the red spectral region by $\Delta\ \lambda_{\rm SP} \approx 5$ nm), it is sufficient to achieve an increase of the refractive index by several percent, which is quite realistic at $I_{\rm exc} = 4.5 \times 10^{11}$ W/cm^2 and, with regard for the huge growth of the susceptibility $\chi^{(3)}$ (that exceeds the value of the corresponding parameter in bulk materials by three orders of magnitude [15]), is specific of such nanocomposites. It is natural that, when the action of the Kerr effect comes to the end, the refractive index of the medium (mainly that of the SiO_2 matrix) relaxes to the initial value, n_0, which is accompanied by the inversion of the sign of the dependence $\Delta\lambda_{\rm SP}(t)$ and the shift of the band to the initial position at 568.5 nm in 0.34 ps after the action of the pump pulse.

The following shift of the SP band to the blue spectral region in the time interval 0.34–0.6 ps and its final return to the initial position (568.5 nm) in 5 ps after the action of the pump pulse are qualitatively similar to the behavior observed earlier in [16] and can be explained by the combined contribution of the temporal evolution of the distribution function of photoexcited electrons and the induced surface polarization in metal nanoparticles.

4. Conclusions

Thus, the results presented in this work testify to the fact that the study of the interaction of femtosecond laser pulses with metal nanoinclusions in a dielectric surrounding requires a further deeper investigation of the physical reasons with regard for the dimension factor and the dispersion of nanoparticles. It is also worth noting the importance of the influence of a dielectric surrounding on electron processes in metal nanoparticles similarly to the action of the same factor in nanoparticles of the semiconductor nature in dielectric matrices.

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ПОВЕРХНЕВІ ПЛАЗМОНИ І НЕСТАЦІОНАРНИЙ ОПТИЧНИЙ ВІДГУК НАНОЧАСТИНОК МІДІ

І.В. Блонський, І.М. Дмитрук, О.А. Єщенко, І.А. Павлов, В.М. Кадан, П.І. Коренюк, А.А. Алексєєнко, А.М. Дмитрук

Р е з ю м е

У фемто-пікосекундному часовому діапазоні представлено результати досліджень наведених змін оптичної густини, півширини та спектрального положення максимуму смуги поверхневих плазмонів у наночастинках міді, інкорпорованих в матрицю SiO_2, при їх збудженні фемтосекундними лазерними імпульсами. На їх основі аналізується залежність ефективності енергообміну між гарячими електронами і ґраткою від розмірного фактора та вплив високочастотних польових ефектів на базові параметри смуги поверхневих плазмонів.