Ultrafast dynamics of nonequilibrium electrons in a gold nanoparticle system

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Transient absorption spectra were measured to investigate the nonlinear response of a gold nanoparticle system by the femtosecond pump-probe method. We obtained temporal changes of electron temperatures and effective damping constants by fitting transient absorption spectra with Mie scattering theory. In the ultrafast region, the nonlinear response originates mainly from the hot electron system which is heated by the incident pump pulse. It is noteworthy that the lattice temperature plays an important role even in the first step of the nonlinear response through the change of the effective damping constant. In the long-time-scale region, over 10 ps, both the electron and the lattice temperatures contribute to the nonlinear response comparably. The origin of the effective damping constant is also discussed with the surface scattering and the e-p scattering processes. [S0163-1829(98)05617-3]

I. INTRODUCTION

In a noble-metal nanoparticle system, such as gold or copper, an absorption peak due to a surface plasmon is frequently observed in the visible region. Particularly, in a SiO_2 matrix, the absorption peak appears near the edge of the band-to-band transition from the valence d band to the Fermi surface. This system has been actively investigated both in basic and applicable research fields, because the strong enhancement of the third-order nonlinear optical susceptibility $\chi^{(3)}$ has been observed around the peak of the surface-plasmon resonance.[1–3] The mechanism of the large $\chi^{(3)}$, however, has not yet been clarified.

The particle-size dependence and host-matrix dependence of the absorption spectrum have been discussed in copper systems with Mie scattering theory.[4] The study took into account two contributions to the dielectric function $\varepsilon(\omega)$, a Drude term $\varepsilon_{\mathrm{intra}}(\omega)$ originating from free electrons and an interband term $\varepsilon_{\mathrm{inter}}(\omega)$ reflecting the band-to-band transition. As for the time response of nonlinear optical properties, the transient reflectivity measurement and the transient absorption measurement clarified that transient changes of reflectivity and absorption recovered in a few picoseconds.[5,6] The time constant of the recovery strongly depended on the pump-pulse energy density.[5] The origin of the time response was ascribed to the cooling process of nonequilibrium electrons through the electron-phonon coupling.[7]

The following is the widely accepted model for the whole relaxation process in a metal nanoparticle system with ultrafast light excitation. First, surface plasmons are excited when a pump pulse strikes nanoparticles. Plasmons lose their coherence instantaneously through an electron-electron (e-e) scattering process and change into a quasiequilibriated hot electron system within 100 fs.[8] As the hot electron system loses its energy through an electron-phonon (e-p) coupling process, the phonon system becomes hot. After 5–10 ps, a quasiequilibrium state is formed between the electron system and the phonon system in a nanoparticle. In a long time scale over 100 ps, the heat transfer from the nanoparticle to the host matrix should be a dominant process. Recently, several studies have tried to justify the nonlinear response through this model.[5–7] In these studies, electron temperatures are calculated as a function of time from the macroscopic energy-balance equation for the one-dimensional heat flow with the incident pulse energy. However, the relation between the nonlinear response and the electron temperature has not been clarified directly.

In the gold nanoparticle system, Hache and co-workers made an optical Kerr experiment in the picosecond region and discussed the origin of large $\chi^{(3)}$.[3] They suggested that the large $\chi^{(3)}$ originates from the hot electron which smears the Fermi-Dirac distribution and modifies the absorption coefficient. Assuming that the pulse duration was much longer than the time constant of the cooling of hot electrons, they theoretically estimated the value of $\mathrm{Im}\{\chi^{(3)}\}$ caused by the hot electron as 1.1×10^{-7} esu, which was almost as large as the result obtained by the optical Kerr experiment (7.5×10^{-8} esu).[3]

Recently, Perner and co-workers reported temporal change of the effective damping constant in a gold nanoparticle system.[9] They estimated the damping constant by fitting the surface-plasmon resonance peak to a simple Lorentzian line shape. They suggested that the nonlinear response originates from the broadening of the surface plasmon band, which reflects the increase of the effective damping constant through the rise of the electron temperature. This suggestion is quite different from the discussion by Hache and co-workers where the smearing effect of the Fermi-Dirac distribution plays an important role in the nonlinear response.[3]

In this study, transient absorption spectra are measured by

a white-light pump-probe method and the temporal behavior of the electron temperature and the damping constants in the dielectric function are discussed with Mie scattering theory. Considering the smearing effect of the Fermi-Dirac distribution and changes of damping constants simultaneously, we demonstrate that the electron temperature is the most characteristic parameter for describing the nonlinear optical response. We also discuss the temporal behaviors of the electron and the lattice temperatures, taking into account thermal diffusion processes from a gold nanoparticle to the host matrix. We found that the thermal diffusion process is considerable even in the ultrafast region. It is suggested that the transient change of the effective damping constant in $\varepsilon_{\text{intra}}(\omega)$ mainly comes not from the e-e scattering but the e-p scattering process.

II. EXPERIMENT

Gold nanoparticles embedded in a SiO_2 glass matrix were prepared by a sputtering method. The SiO_2 and gold layers were constructed alternately on the SiO_2 base glass plate. After an annealing treatment, gold nanoparticles were precipitated and dispersed in the SiO_2 glass matrix. Details were reported elsewhere.[2] The mean diameter of the particles was 7.6 nm with a deviation of 2.4 nm. The sample was 480 nm thick and the volume fraction was 0.027. This high volume fraction was a special feature of this method.

In the femtosecond pump-probe experiment, we used the output pulse from the optical parametric amplifier (OPA) as a pump pulse. The OPA was pumped by the Ti:Al_2O_3 regenerative amplifier. The typical pulse energy of OPA was 1 μJ. The pulse duration was less than 200 fs. Since OPA had a wide tunability for a wavelength of the pump pulse, we set the wavelength to the surface-plasmon resonance. The typical energy density of the excitation pulse was 1.4 mJ cm^{-2}, corresponding to the total energy input of 3×10^{-4} pJ per particle. To probe the change of the optical density (ΔOD) caused by the pump pulse, we used the white-light pulse generated through the self-phase modulation process in the water flow cell by the amplified pulse. The white light covered from 450 nm to over 1.2 μm. We measured absorption spectra of the sample by a 27.5 cm single monochromator with dual-diode arrays. To improve the signal-to-noise ratio, we monitored simultaneously the spectrum of the white-light pulse itself as a reference. The ΔOD spectrum was obtained by subtracting the absorption spectrum with no pump pulse from that with the pump pulse at each delay time τ, where τ is the time separating the probe pulse from the pump pulse. The chirping effect of the probe pulse, which is caused by the group velocity dispersion, was estimated with a cross-correlation method and ΔOD spectra were corrected by a simple calculation. All experiments were executed at room temperature (301.5 K).

III. RESULTS

Figure 1 shows an optical density (OD) spectrum of a Au/SiO_2 composite thin film at 301.5 K (solid curve). One can clearly recognize an absorption peak at 2.33 eV along with a slightly increasing background. The origin of the peak is assigned to a surface-plasmon resonance. The background

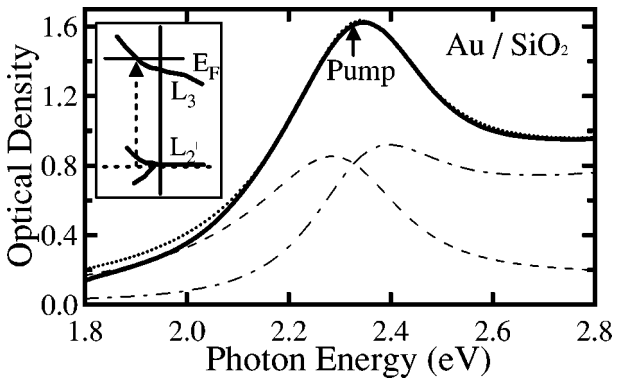

FIG. 1. Absorption spectrum (solid curve) of the Au nanoparticles in the SiO_2 matrix. The fitting curve (dotted curve) by Mie scattering theory is also depicted. The related band structure of gold is depicted as an inset. The arrow corresponds to the pump photon energy. The broken and chain curves show contributions of the surface plasmon and the band-to-band transition in the absorption spectrum, respectively.

is originated from an optical transition of valence electrons in the d band to the Fermi surface as shown in the inset. The arrow indicates the photon energy of the pump pulse used in the pump-probe experiments.

Typical time-resolved differential optical density spectra (ΔOD) obtained by the white-light pump-probe method are shown in Fig. 2 at several delay times, τ's. At $\tau=-1.0$ ps, the spectrum clings closely to the zero line. At $\tau=0.4$ ps, the OD decreases significantly around the peak of the surface plasmon and increases on both sides of the peak. As the delay time increases, the whole magnitude of the ΔOD becomes small. In any case, the ΔOD spectrum crosses the zero line at two points. We show dash-dotted lines to emphasize the movements of the crossing points. At $\tau=0.4$ ps, the

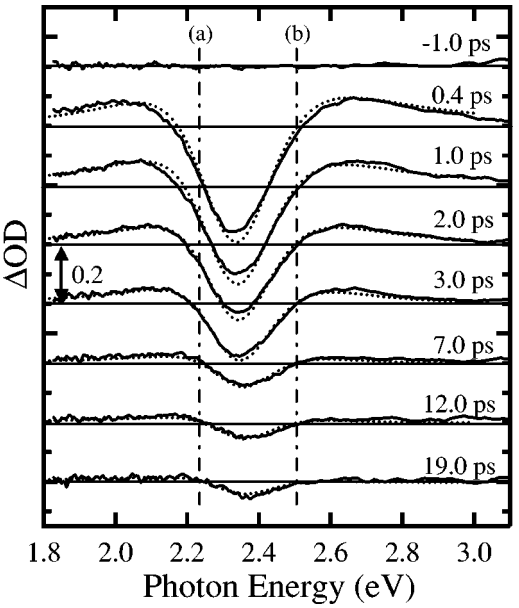

FIG. 2. Transient differential absorption spectra for various delay times (solid curves). Fitting curves by Mie scattering theory are also shown by broken curves. Chain lines (a) and (b) are depicted to emphasize the movement of the crossing points as mentioned in the text.

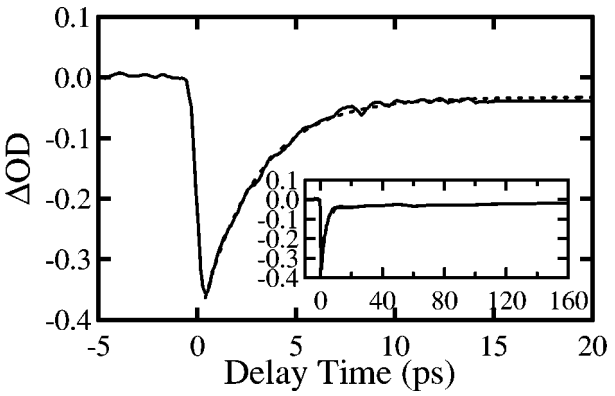

FIG. 3. Time evolution of ΔOD measured at the absorption peak of the surface-plasmon band. In the inset, we show a long-time-scale behavior.

crossing point in the low-energy side is at 2.16 eV. This point moves to the high-energy side as τ increases. After $\tau > 7$ ps, the position is unchanged to be 2.25 eV. In contrast, the crossing point in the high-energy side hardly moves from the initial point. A close look at the movement of the points reveals that the transient change of the absorption spectrum is not a simple symmetrical broadening of the absorption peak.

Figure 3 shows a temporal change of the ΔOD at the peak of the surface-plasmon band. The inset represents a long-time-scale behavior. The temporal behavior is decomposed into two decay components, the fast decay component (less than 3 ps) and the slow decay component (more than 100 ps). It is suggested that the fast decay constant reflects the thermal equilibrium process between the electron system and lattice system in the metal nanoparticle and the slow decay constant comes from the cooling process by a thermal diffusion from the metal nanoparticle to the host matrix.[5,13] The decay constants of the fast and slow components are estimated as 2.8 and 120 ps by a fitting. The result of the fitting is shown as a broken curve in Fig. 3.

IV. DISCUSSION

A. The origin of the nonlinear response

It is reported that the absorption spectrum of a nanoparticle can be reproduced in terms of Mie scattering theory.[1,4] For the analysis of optical nonlinear response of a nanoparticle, the theory is applicable and successfully describes temporal behaviors of transient absorption spectra.[10]

The dielectric function of gold can be written in the form

$$\varepsilon(\omega)=\varepsilon_{\text{intra}}(\omega)+\varepsilon_{\text{inter}}(\omega), \tag{1}$$

where $\varepsilon_{\text{intra}}(\omega)$ is the Drude part originating from the free electron

$$\varepsilon_{\text{intra}}(\omega)=1-\frac{\omega_p^2}{\omega(\omega-i\gamma_{\text{eff}})}, \tag{2}$$

and $\varepsilon_{\text{inter}}(\omega)$ is the interband part originating from the band-to-band transition

TABLE I. Fixed parameters of the gold nanoparticle sample.

Parameter	Value	Source
Particle diameter R_0 (nm)	7.6	Ref. 2
Sample thickness d (nm)	480	Ref. 2
Number density N	1.17×10^{23}	Ref. 2
Dielectric constant $\varepsilon_{\text{glass}}$	2.25	Ref. 10
Plasma frequency $\hbar\omega_p$ (eV)	8.2	Ref. 18
Gap energy $\hbar\omega_g$ (eV)	1.7	Ref. 3

$$\varepsilon_{\text{inter}}(\omega)=K\int_{\omega_g}^{\infty}dx\,\frac{\sqrt{x-\omega_g}}{x}[1-F(x,\Theta_e)]\times\frac{(x^2-\omega^2+\gamma_{ee}^2-2i\omega\gamma_{ee})}{(x^2-\omega^2+\gamma_{ee}^2)^2+4\omega^2\gamma_{ee}^2}, \tag{3}$$

where ω_p is an effective plasma frequency, γ_{eff} is an effective plasma damping constant, $F(x,\Theta_e)$ is an energy distribution function of conduction electrons whose energy is $\hbar x$ at temperature Θ_e, and γ_{ee} represents the damping constant in the band-to-band transition. We assume a dispersionless d band and a parabolic conduction band with a gap energy $\hbar\omega_g$.

By using Mie scattering theory, we can calculate the absorption spectrum $\alpha(\omega)$ of nanoparticles embedded in the glass matrix as[1]

$$\alpha(\omega)=\frac{2\pi R_0^2 N}{\chi_0^2}\sum_{l=1}^{\infty}(2l+1)\ \text{Re}\,[a_l(\chi_0,\chi_i)+b_l(\chi_0,\chi_i)], \tag{4}$$

$$\chi_0=\frac{R_0\omega}{c}\sqrt{\varepsilon_{\text{glass}}},\quad \chi_i=\frac{R_0\omega}{c}\sqrt{\varepsilon(\omega)}. \tag{5}$$

where a_l and b_l are Mie scattering coefficients.[1] Here, R_0 is the diameter of the nanoparticle, N is the number density of nanoparticles in the sample, c is the velocity of the light, and $\varepsilon_{\text{glass}}$ is the dielectric constant of the glass matrix. In Fig. 1, we show the best fitted absorption spectrum calculated by Eq. (4) as a dotted curve. Fixed parameters used in the calculation are listed in Table I. The electron temperature Θ_e is also fixed as 301.5 K. Remaining parameters, two damping constants, are determined by the least-squares method as $\hbar\gamma_{\text{eff}}=0.450$ eV and $\hbar\gamma_{ee}=0.158$ eV. The dotted curve reproduces the absorption spectrum excellently. In the following analysis, we apply Eq. (4) to analyze the transient absorption spectra. Contributions of the Drude part and the interband part are also depicted as a broken curve and a chain curve, respectively. From these curves, one can see the following points. The Drude part mainly contributes to the absorption in the low-energy region. On the other hand, the interband part is dominant in the high-energy region. It is noteworthy that contributions of the Drude part and the interband part are comparable at the peak of the surface-plasmon band.

Time-resolved differential absorption spectra are analyzed by Eq. (4) with three running parameters, Θ_e, γ_{eff}, and γ_{ee}. Best fitted curves at each delay time are depicted in Fig. 2 as dotted curves. These curves excellently reproduce the

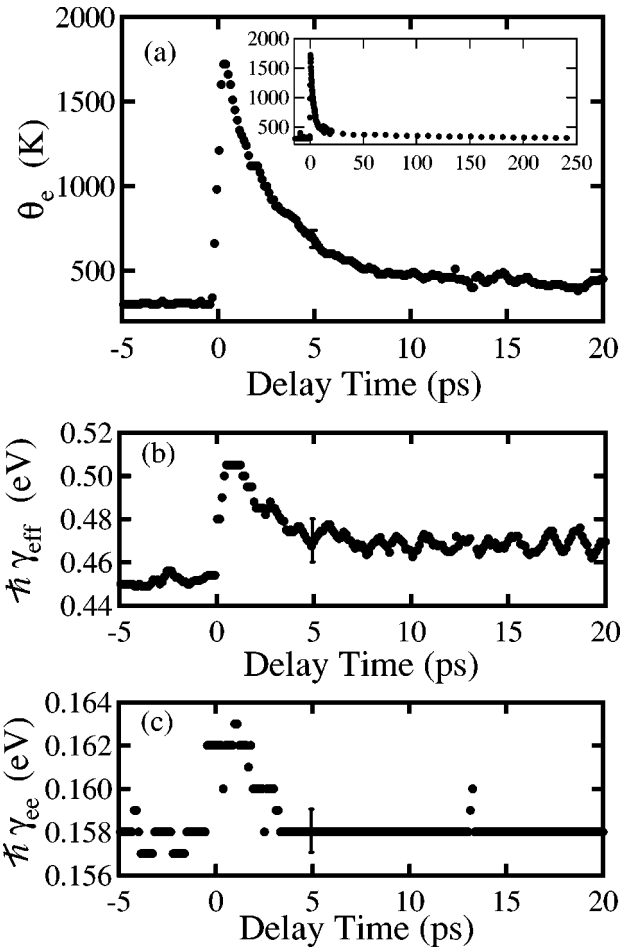

FIG. 4. (a) Fitting results of the electron temperature at each delay time (closed circles). The inset shows a temporal change of the electron temperature in the long-time-scale region. (b) Temporal change of the damping constant $\hbar\gamma_{\rm eff}$. (c) Temporal change of the $\hbar\gamma_{ee}$. The degree of errors corresponds to allow a 5% change in the mean-square error for each running parameter.

bleaching around the absorption peak of the surface plasmon and the absorption increase in both sides of the absorption peak.

Figures 4(a)–4(c) show temporal changes of fitting parameters. The inset in Fig. 4(a) shows a temporal change of Θ_e in a long time scale. One can recognize that the electron system cools down with two characteristic time constants of a few picoseconds and over hundred picoseconds. After the rapid increase of Θ_e to 1700 K, the electron temperature decreases to 400 K with a decay constant of 2.8 ps. The electron temperature gradually cools down with a time constant of 120 ps. It is suggested that the fast decay constant reflects the thermal equilibrium process between the electron system and the lattice system in a metal nanoparticle and the slow decay constant comes from the cooling process by a thermal diffusion from the gold nanoparticle to the host matrix.[5,13]

In Fig. 4(b), one can see a rapid increase of the $\hbar\gamma_{\rm eff}$ from 0.450 to 0.505 eV around $\tau=0$ and a decrease with the decay constant of 1.7 ps. The temporal change of the γ_{ee} is shown in Fig. 4(c). The magnitude of the change is almost as large as its standard deviation. Therefore, the change of the

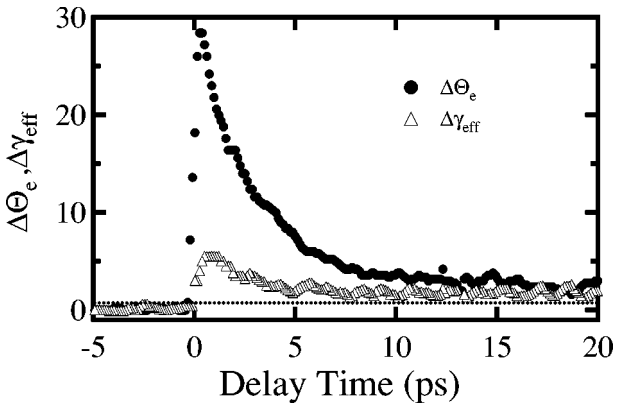

FIG. 5. Temporal changes of $\Delta\Theta_e$ and $\Delta\gamma_{\rm eff}$, which are defined in the text. Dotted line corresponds to the value of 1.

γ_{ee} barely affects the transient change of the absorption spectrum. In the following discussion, we ignore the change of the γ_{ee}.

To clarify the most effective parameter in transient absorption spectra, we introduce normalized magnitudes of changes of parameters, defined as $\Delta\Theta_e(t)=[\Theta_e(t)-\Theta_0]/\delta\Theta_e(t)$ and $\Delta\gamma_{\rm eff}(t)=[\gamma_{\rm eff}(t)-\gamma_0]/\delta\gamma_{\rm eff}(t)$, where Θ_0 is the initial temperature of the electron and γ_0 is the initial effective damping constant ($\Theta_0=301.5$ K, $\hbar\gamma_0=0.450$ eV). $\delta\Theta_e(t)$ and $\delta\gamma_{\rm eff}(t)$ are degrees of error to allow a 5% change in the mean-square error for each running parameter. A typical value is plotted for each spectrum at $\tau=5.0$ ps. The temporal change of $\Delta\Theta_e$ and $\Delta\gamma_{\rm eff}$ are shown in Fig. 5. A dotted line indicates a value of 1 which means that the change in the parameter and the error are comparable. We can reasonably conclude that the electron temperature Θ_e is the most effective parameter for the nonlinear optical response so far as $\tau<5.0$ ps. The parameter Θ_e is five times more efficient than $\gamma_{\rm eff}$ around $\tau=0$. Other parameters only affect details of the transient absorption spectrum.

In the region of $\tau>10$ ps, the electron temperature Θ_e contributes to the transient absorption spectrum as well as the damping $\gamma_{\rm eff}$. This result means that the $\gamma_{\rm eff}$ becomes more important in the quasiequilibrium state between the electron and phonon systems. In the time region $\tau>10$ ps, therefore, we should consider both contributions for the nonlinear optical response. As will be discussed latter, an increase of the phonon temperature plays an important role in the $\gamma_{\rm eff}$ in the long time scale.

In contrast with our result, Perner *et al.* reported that the $\gamma_{\rm eff}$ in the Drude term is most effective for the nonlinear optical response in the gold nanoparticle system.[9] Damping constants were estimated by fitting the surface-plasmon absorption band as a single Lorentzian line shape. In the analysis, the electron temperature only affects the transient absorption spectrum through the change of the damping constants. Our results demonstrate that the change of the electron temperature mainly affects the transient absorption through the smearing effects of the electron distribution function, especially in the region of $\tau<5$ ps. This means that the ΔOD spectrum should not be considered as a simple broadening of the spectral band shape in the gold nanoparticle system.

In the analysis by Hache *et al.*,[3] it is suggested that the

large $\chi^{(3)}$ is caused by the rise of the electron temperature which induces a change in the electron distribution function. Our results evidently indicate that the temporal change of Θ_e is the main origin of the nonlinear response and the large $\chi^{(3)}$ in a gold nanoparticle system.

B. Nonequilibrium thermodynamics in the metal nanoparticle system

In the previous section, we obtained the temporal change of the electron temperature Θ_e. To discuss the cooling process of the hot electron system, we should consider nonequilibrium thermodynamics in a metal nanoparticle system with the host matrix. In this section, we try to estimate the temporal change of the lattice temperature with the electron-phonon (e-p) coupling model, taking into account the thermal diffusion to the glass matrix.

It is reported that the relaxation dynamics of the electron temperature in a metal nanoparticle can be described by usual e-p coupling model.[5–7,11] In the model, the metal system is described as a couple of subsystems, an electron system and a phonon system. The electron system is characterized by an electron temperature Θ_e and the phonon system is characterized by a lattice temperature Θ_l, where each subsystem is assumed to be in local equilibrium. The energy transfer between the subsystems occurs through the e-p coupling. The time evolution of the temperatures are obtained with heat equations

$$C_e(\Theta_e)\frac{\partial \Theta_e}{\partial t} = -G(\Theta_e - \Theta_l) + p(t), \tag{6}$$

$$C_l \frac{\partial \Theta_l}{\partial t} = G(\Theta_e - \Theta_l), \tag{7}$$

where G reflects the e-p coupling constant, $C_e(\Theta_e)$ and C_l are electronic and lattice heat capacities, and $p(t)$ represents a direct heat input to the electron system by the pump pulse. For gold, $C_e(\Theta_e)=\gamma\Theta_e$ with $\gamma=67.3$ J m^{-3} K^{-2}, $C_l=2.49\times10^6$ J m^{-3} K^{-1} in the room-temperature region. The electron temperature is heated by the absorption of the pump pulse. The initial heat input can be calculated from the initial rise of the electron temperature. A simple calculation indicates that the input energy is about 2.3×10^{-5} pJ/particle which corresponds to 1/13 of the total energy input as mentioned in Sec. II. In addition, from Eqs. (6) and (7), we can estimate that a rise of the lattice temperature should be about 40 K in the quasiequilibrium state, which is quite different from our experimental results. The equilibrium temperature is about 400 K and corresponds to 100 K rise of the lattice temperature from the room temperature. These facts strongly suggest that the initial energy of hot electrons flows to other pathways than the e-p coupling. We should consider the nonequilibrium thermodynamics including an energy transfer to the lattice system through the scattering processes or a thermal diffusion to the glass matrix.

To investigate the nonequilibrium thermodynamics of the whole system, at first, we consider a thermal diffusion from a metal nanoparticle to the glass matrix by a simple diffusion equation,

$$\frac{\partial \Theta_{\rm glass}}{\partial t} = D_{\rm glass}\nabla^2\Theta_{\rm glass} \tag{8}$$

where $D_{\rm glass}$ is the diffusivity of heat in the glass matrix. For the silicate glass, $D_{\rm glass}=8.4\times10^{-3}$ cm^2 s^{-1} at room temperature.[12] From Eq. (8), we obtain the thermal distribution function outside of the metal nanoparticle as a function of the distance r and time t. Thermal diffusion inside of the metal nanoparticle should be neglected, because diffusivity of gold, $D_{\rm gold}$, is nearly 10^3 times larger than $D_{\rm glass}$. This means that the inside of the metal nanoparticle has an uniform thermal distribution. When we assume the thermal continuity at the surface of the nanoparticle ($r=R_0/2$) with the glass and the uniformity of the lattice temperature in the nanoparticle, we obtain the following energy-balance equation:[13]

$$C_l V_0 \Theta_{l0} = C_l V_0 \Theta_l(t) + C_{\rm glass}\int_{r=R_0/2}^{\infty} 4\pi r^2 \Delta\Theta_{\rm glass}(t,r)\,dr, \tag{9}$$

where Θ_{l0} is an initial lattice temperature of the gold nanoparticle in the aftermath of the pump pulse, $C_{\rm glass}$ is a heat capacity of the glass taken as $C_{\rm glass}=1.63\times10^6$ J m^{-3} K^{-1}, $\Delta\Theta_{\rm glass}(t,r)=\Theta_{\rm glass}(t,r)-\Theta_0$ ($\Theta_0=301.5$), and $V_0=4/3\pi(R_0/2)^3$.[12] By using the analytic solution of Eq. (8), we can derive the temporal change of the lattice temperature inside the metal nanoparticle from Eq. (9) as

$$\Theta_l(t) = \frac{\Theta_{l0}-\Theta_0}{1+3\dfrac{C_{\rm glass}}{C_l}\{[(2D_{\rm glass}t)^{3/2}/\sqrt{2\pi}(R_0/2)^3]e^{(R_0/2)^2/4D_{\rm glass}t}\ \mathrm{erfc}\ (R_0/2)/\sqrt{4D_{\rm glass}t}) + 2D_{\rm glass}t/(R_0/2)^2\}} + \Theta_0. \tag{10}$$

From Eqs. (6) and (7) with $G=(3.0\pm0.5)\times10^{16}$ W m^{-3} K^{-1} reported by Fann and co-workers in a gold film,[11] we can reasonably assume that the electron system and the lattice system are enough equilibrated after $\tau\geqslant10$ ps. In the region, we can consider that the lattice temperature is the same as the electron temperature. By using the electron temperature at $\tau=10$ ps represented in Fig. 4(a), we estimate the temporal change of the lattice temperature from Eq. (10). The calculated temporal change of the lattice temperature is shown in Fig. 6 by a broken curve. The broken curve traces the temporal change of the electron temperature well in the region of $\tau>7$ ps, justifying the assumption of the equilibrium between the electron and the lattice system in the time region.

The result shows that the initial temperature of the lattice system should be nearly 950 K in the aftermath of the inci-

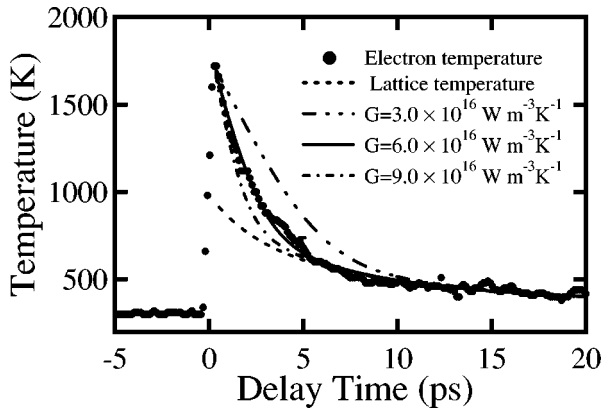

FIG. 6. The temporal change of the lattice temperature (broken curve). Fitting curves of the electron temperature by Eqs. (6) and (7) with three G's are also shown by using the lattice temperature. We show calculated results with $G=3.0\times10^{16}$ W m^{-3} K^{-1} as dash-dot-dotted curve, $G=6.0\times10^{16}$ W m^{-3} K^{-1} as solid curve, and $G=9.0\times10^{16}$ W m^{-3} K^{-1} as chain curve.

dence of the pump pulse. We can estimate the total input energy as 3.9×10^{-4} pJ/particle from the initial rises of the electron and the lattice temperatures. This value is nearly the same as the value estimated experimentally from the energy density of the incident laser pulse. The results mean that a large proportion of the incident energy is spent to heat up the lattice system in the first step of the relaxation process of hot carriers.

To understand the direct energy input to the lattice system, the first point to notice is an absorption process of the pump pulse in a gold nanoparticle system. In case of the excitation at the peak wavelength of the surface plasmon band, the incident pump pulse is absorbed by both the surface plasmon band and the band-to-band transition as described in Sec. IV A. It is natural to consider a heating of the electron system through the excitation of surface plasmons. On the other hand, a generation of electron and hole pairs through the band-to-band transition should lead to a nonradiative surface recombination of electron and hole pairs. The surface recombination will cause a heat input to the lattice system. As discussed in the next section, a typical surface-scattering rate estimated from an effective plasma-damping constant is 1×10^{14} s^{-1}. This value corresponds to the time constant of 10 fs. Thus, it is likely that the nonradiative surface recombination of electron-hole pairs generates phonons in the aftermath of the pump pulse. In a similar way, we should take into account the possibility of heat input to the lattice system through a scattering process between plasmons and phonons at the surface. As a result, it is concluded that all the absorbed energies through the band-to-band transition and 86% of the absorbed energies by the surface plasmon are spent to heat up the lattice system.

The initial temperature of the lattice system seems to be a very high temperature. If the surface scattering processes heat up the lattice system, it is natural to consider a thermal distribution in the metal nanoparticle at the initial stage of the excitation. Such a thermal distribution has the possibility of the generation of a coherent strain wave. Strain wave generation is reported in the case of gallium and tin nanoparticle systems.[14] In our experimental ΔOD data, however, no oscillation due to the strain waves is observed, indicating that the coherent strain wave is not evident in our case. Therefore, we do not take into account the generation of the coherent strain wave in our discussion.

We try to discuss the cooling process of the electron system. In the previous section, we pointed out that the fast decay constant reflects the thermal equilibrium process between the electron system and the lattice system in the metal nanoparticle.[5,13] The thermal equilibrium process between the electron system and lattice system is usually described by Eqs. (6) and (7). From the equations, we can see that the e-p coupling constant G governs the thermal equilibrium process. In Fig. 6, we show temporal changes of the electron temperature calculated from Eqs. (6) and (7) with several G's by using the lattice temperature obtained above. The result with $G=6.0\times10^{16}$ W m^{-3} K^{-1} reproduces quite excellently the temporal change of the electron temperature. This value is about two times larger than the result of the gold film.[11] The reason is not clear at present, though a mesoscopic effect would play an important role in increasing the e-p coupling constant of the nanoparticle system.

In summary, we obtained the temporal change of the lattice temperature taking into account the thermal diffusion to the glass matrix with Eqs. (6)–(9). The total energy flow in the metal nanoparticle system can be understood quantitatively, indicating that the lattice temperature should play an important role still in the first stage of the nonequilibrium state.

C. The origin of the damping constant in the Drude term

There are still open questions on the damping mechanism of free electrons in the metal nanoparticle system. In this section, to investigate the electron dynamics in the nonequilibrium state, we discuss the temporal change of the damping constant since it reflects the electron dynamics such as the e-e scattering process and the e-p scattering process.

As shown in Fig. 4(b), $\hbar\gamma_{\rm eff}$ increases rapidly around the delay time $\tau=0$ from 0.450 to 0.505 eV. First, let us consider the e-p scattering process which has a linear dependence on the lattice temperature. We get

$$\hbar\gamma_{\rm eff}(\Theta_l)=\Gamma_{\rm sur}+\Gamma_{e-p}\Theta_l, \tag{11}$$

where $\Gamma_{\rm sur}$ is a constant which mainly reflects the impurity scattering process, and the second term represents the e-p scattering process. We show the calculated result of Eq. (11) as a solid curve in Fig. 7. The best fitting parameters are $\Gamma_{\rm sur}=0.427$ eV and $\Gamma_{e-p}=8.28\times10^{-5}$ eV K^{-1}. The curve almost reproduces the temporal change of $\gamma_{\rm eff}$.

The result leads to the following important conclusion. Transient response of the $\gamma_{\rm eff}$ is mainly governed by the e-p scattering term. We also recognize from Fig. 5 that the lattice temperature is a considerable parameter for describing the nonlinear response through the temporal change of $\gamma_{\rm eff}$ as well as the temporal change of Θ_e in the long time scale over 10 ps. If we consider an e-e scattering process, it is expected that the damping constant shows a quadratic dependence of Θ_e.[9,15] From the temporal behavior of Θ_e, one can easily imagine a more drastic change of $\gamma_{\rm eff}$ in the first step of the excitation. Such behavior, however, cannot be extracted in

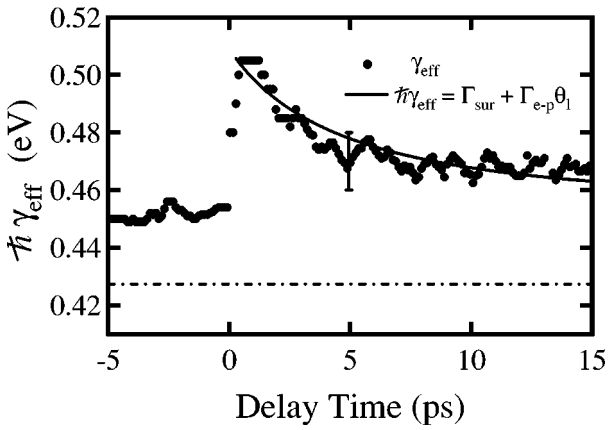

FIG. 7. Damping constant $\hbar\gamma_{\mathrm{eff}}$ at each delay time (closed circles) with fitting curves; solid curve is a fitting result by Eq. (11). Dash-dotted line indicates the value of Γ_{sur} in Eq. (11) .

the temporal change of γ_{eff}. Thus, we can conclude that only the e-p scattering process should contribute considerably in the temporal change of γ_{eff}.

Comparing the magnitudes of each term in Eq. (11), we found that even around $\tau=0$, the ratio of Γ_{sur} and $\Gamma_{e-p}\Theta_l$ is about 6. The value of Γ_{sur} (0.427 eV) is much larger than the value reported in bulk ($\Gamma_{\mathrm{bulk}}=0.170$ eV).[16] In our case, it is suggested that scattering by a structural fluctuation on the metal-glass interface induces the dephasing process of plasmons. If we assume that the electron dephases within a round trip from one point to another point on the surface, the damping energy due to the process is described as $hV_F/(2R_0)$. For our gold nanoparticle, the value is estimated as 0.272 eV. If we calculate the $\Gamma'_{\mathrm{sur}}=\Gamma_{\mathrm{bulk}}+hV_F/(2R_0)$, we obtain $\Gamma'_{\mathrm{sur}}=0.442$ eV. This value is nearly the same as the Γ_{sur} obtained experimentally. This means that the surface of the nanoparticle plays an important role in the damping process of electrons through the collision at the metal-glass interface. Zhou *et al.* and Yang *et al.* also used a similar expression to explain the effective damping constant.[16,17] To confirm this point, the size dependence of Γ_{sur} should be studied quantitatively.

V. CONCLUSION

Nonlinear optical response of gold nanoparticles was investigated by the white-light pump-probe method. We analyzed transient absorption spectra by Mie scattering theory. The temporal changes of the electron temperature and the effective damping constant in the Drude term were obtained from the analysis. The nonlinear response was found to originate mainly from the hot electron which was heated by the incidence of the pump pulse in the subpicosecond region. By taking into account the thermal diffusion process from metal nanoparticle to the host matrix, the total energy flow in the metal nanoparticle system was explained quantitatively. We found that the lattice temperature is also raised even in the first stage of the nonequilibrium state. We also estimated the e-p coupling constant G as 6.0×10^{16} W m^{-3} K^{-1}. This value is about two times larger than the result of the gold film.[11] The reason is not clear at present, though a mesoscopic effect would play an important role in increasing the e-p coupling constant of the nanoparticle system.

The effective damping constant γ_{eff} in the Drude term could be described by the surface scattering process and the e-p scattering process. It should be noted that the lattice temperature is a considerable parameter to describe the transient absorption spectrum through the change of the γ_{eff} in the quasiequilibrium state between the electron and the lattice systems.

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