Jpn. J. Appl. Phys. Vol. 39 (2000) pp. 5132–5133
Part 1, No. 9A, September 2000

Short Note

Ultrafast Optical Switching in a Silver Nanoparticle System

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(Received February 2, 2000; accepted for publication June 28, 2000)

An ultrafast response of a silver nanoparticle system, as fast as 360 fs, was observed in a femtosecond optical-Kerr-shutter experiment. The ultrafast response is attributed to a self-diffraction of a pump pulse due to transient grating. We estimated $\chi^{(3)}$ of the silver nanoparticle system to be 1.5×10^{-7} esu in the femtosecond region.

KEYWORDS: femtosecond optical Kerr shutter, silver nanoparticle

In a noble-metal nanoparticle system dispersed in a transparent matrix, an absorption peak due to a surface plasmon is generally observed in the visible region. In particular, in a SiO_2 glass matrix, the absorption peak appears near the edge of the band-to-band transition from the valence d-band to the Fermi surface. These systems have been actively investigated both in basic and applied research fields, because of its strong enhancement of the third-order nonlinear optical susceptibility $\chi^{(3)}$ around the peak of the surface-plasmon resonance.[1,2)]

In a silver nanoparticle system, Uchida *et al.* obtained a nonlinear susceptibility $\chi^{(3)}$ of $\sim 7.6 \times 10^{-8}$ esu from a degenerate four-wave mixing (DFWM) experiment with a two-beam configuration in the nanosecond region.[2)] They also reported the size dependence of the nonlinear susceptibility. Recently, Hamanaka *et al.* reported the nonlinear response of silver nanocrystals embedded in a glass matrix.[3)] The temporal behavior of the nonlinear response was described by two characteristic response times: the faster one is less than a few picoseconds and the slower one is over one hundred picoseconds.[2–6)] Such a nonlinear response has been explained by the thermalization process between electrons and lattice subsystems in a metal nanoparticle and the thermal diffusion process from the metal nanoparticle to the host matrix.[2,4,5)] Recently, in a gold nanoparticle system, we have succeeded to observe an ultrafast response of 240 fs and investigated the origin of this response.[5–7)]

In the present report, we study the ultrafast response by the pump-probe method and the optical-Kerr-shutter (OKS) method in a silver nanoparticle system.

Silver nanoparticles embedded in a SiO_2 glass matrix were prepared by a multitarget rf magnetron sputtering system. Details were reported elsewhere.[1,8)] The mean diameter of the particles was about 21 nm. The sample was 300 nm thick and the concentration of Ag in the film was 8.8 at.% ($Ag/Ag + SiO_2$).

In the pump-probe experiment and femtosecond optical-Kerr-shutter (OKS) experiment, we used frequency-doubled pulses of a Ti:Al_2O_3 regenerative amplifier. The typical energy density of the excitation pulse was $20\,\mu J\,cm^{-2}$, which corresponds to the power density of $35\,MW\,cm^{-2}$ at the position of the sample. The repetition rate of the output pulse was 200 kHz. The full-width at half maximum (FWHM) of the incident pulse width was about 600 fs at the position of the sample. As a probe pulse, we used part of the frequency-doubled pulse. In the OKS experiment, the polarization plane of the pump beam was rotated by $\pi/4$ from that of the probe beam. The nonlinear medium was placed between a polarizer and an analyzer in the cross-Nicol configuration, where the probe beam could not pass through the analyzer without the pump beam. A third-order nonlinearity induced by the pump and probe pulses generates a Kerr signal that passed through the analyzer. The Kerr signal was detected by a photomultiplier tube. To improve the signal-to-noise ratio of the observed Kerr signal, the pump and probe beams were chopped at frequencies f_1 and f_2, respectively, and the sum frequency ($f_1 + f_2$) component of the signal was picked up by a lock-in amplifier.

Figure 1 shows an absorption spectrum of an Ag/SiO_2 composite thin film at 301.5 K (solid curve). One can recognize a clear absorption peak at 406 nm. The absorption peak is assigned to the surface-plasmon resonance of silver nanoparticles dispersed in the glass matrix. The absorption in the high-energy (short wavelength) side corresponds to the absorption due to the band-to-band transition from the valence d-band to the Fermi surface. The dashed curve indicates the spectrum of the incident laser pulse.

Figure 2 shows the temporal change of the optical density (ΔOD) at the peak of the surface-plasmon band. Delay time (ΔT) is the time separation between the pump and probe pulses. The temporal behavior is decomposed into a fast-rise component and two decay components, as reported previously.[5,6)] Decay time constants were obtained by a fitting with exponential functions. The best-fitted curve is shown as a solid curve in the figure. The fast decay constant is 1.3 ps and the slow decay constant is more than 100 ps. In the fitting, we apply a constant, 100 ps, as a slow decay constant. In our previous paper,[5)] we noted that the fast decay component is

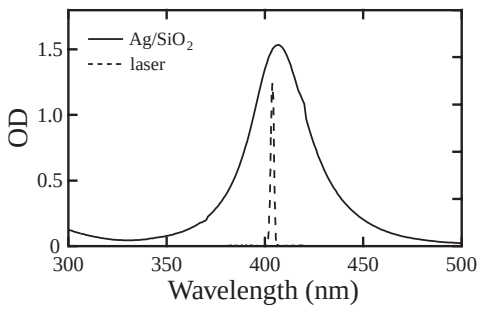

Fig. 1. Absorption spectrum of a silver nanoparticle system dispersed in SiO_2 matrix (solid curve). The dotted curve shows the spectrum of the incident laser pulse.

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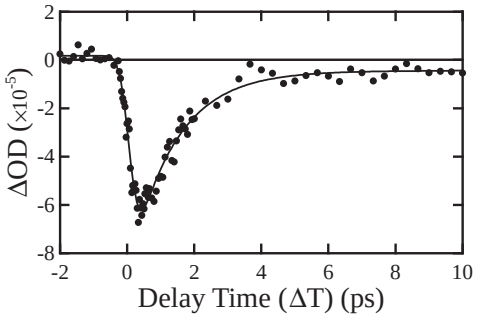

Fig. 2. Time evolution of bleaching signal measured at the absorption peak of the surface-plasmon band (dots). The fitting result is also shown (solid curve).

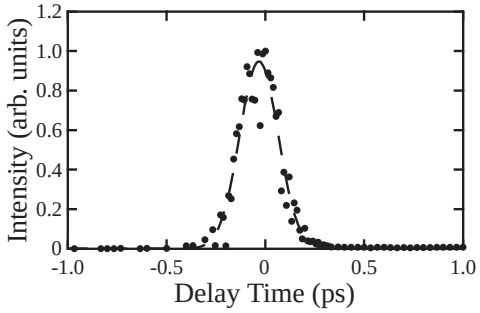

Fig. 3. Temporal behavior of the Kerr signal (dots). The fitting result by a Gaussian curve is also shown (dashed curve).

mainly governed by the thermal equilibrium process between the electrons and the lattice subsystems in the metal nanoparticle, while the slow decay component originates from a thermal diffusion process from the metal nanoparticle to the host matrix.[2] The fast rise component should originate from an integral of the incident pulse.[5]

The temporal behavior of the observed Kerr signal is shown in Fig. 3. The intensity of the signal increases and decreases sharply at approximately $\Delta T = 0$. The FWHM of the Kerr signal is 360 fs. We consider a simple model to explain this ultrafast response which is similar to the one proposed in the case of the gold nanoparticle system,[6,7] where two laser pulses strike the nonlinear material. When the time separation of the two pulses is within the field correlation time, the two pulses coherently interfere with each other. Bleaching of the absorption due to silver nanoparticles is induced at the bright part of the interference pattern, which causes transient grating. The transient grating lasts as long as the bleaching remains, which is shown in Fig. 2. The transient grating generated by the interference between two incident beams, i.e., a pump and probe pulse with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, respectively, has a wave number $\boldsymbol{k}$ ($\boldsymbol{k} = \boldsymbol{k}_1 - \boldsymbol{k}_2$). The transient grating diffracts the incident pulse itself to yield a Kerr signal. The incident beam with the wave vector of $\boldsymbol{k}_1$ is diffracted by the transient grating in the directions of $\boldsymbol{k}_1 \pm \boldsymbol{k}$ (i.e., $\boldsymbol{k}_2$ and $2\boldsymbol{k}_1 - \boldsymbol{k}_2$). Since the pump beam has a wave vector $\boldsymbol{k}_1$, part of the pump beam is diffracted in the direction of the wave vector $\boldsymbol{k}_2$. Because the polarization plane of the pump beam is rotated by $\pi/4$ from that of the probe beam, half of the diffracted pump beam can pass through the analyzer and is observed as a Kerr signal.

From the diffraction efficiencies of the Kerr signal, one can estimate the nonlinear susceptibility $\chi^{(3)}$ compared with that of a reference sample, $\chi^{(3)}_{\mathrm{ref}}$, as[9]

$$\chi^{(3)} = \chi^{(3)}_{\mathrm{ref}} \sqrt{\frac{I_{\mathrm{sig}}}{I_{\mathrm{ref}}}} \frac{n^2}{n_{\mathrm{ref}}^2} d_{\mathrm{ref}} \frac{\alpha \exp(\alpha d/2)}{1 - \exp(-\alpha d)}, \qquad (1)$$

where I_{sig} and I_{ref} are the diffraction efficiencies, n and n_{ref} are the linear refractive indices, d and d_{ref} are the thicknesses of the sample and reference material, respectively. α is the absorption coefficient at the surface-plasmon peak of the silver nanoparticle system. The value was taken to be $1.16 \times 10^5\,\mathrm{cm}^{-1}$. We used a fused silica plate as a reference sample to avoid a contribution of the two-photon absorption process. We assumed a value of $\chi^{(3)}_{\mathrm{ref}}$ as 2.9×10^{-14} esu.[10] The index, n, is taken to be the same as that of glass, 1.5, because the volume fraction of silver nanoparticles is still small even in our sample. From eq. (1), we obtained a value of 1.5×10^{-7} esu for $\chi^{(3)}$. This value is almost equal to that reported elsewhere in the case of the nanosecond region.[2] This might be attributed to the special feature of our sample, which is the high density of silver nanoparticles.

In this case, the figure of merit, $\chi^{(3)}/\alpha$, is appropriate to characterize nonlinear materials containing metal or semiconductor particles with different volume fractions. We estimate the figure of merit to be 1.3×10^{-12} esu cm. The value of $\chi^{(3)}/\alpha$ of the silver nanoparticle whose diameter is 20.8 nm is shown to be 1.4×10^{-11} esu cm in the nanosecond region.[2] The figure of merit in the femtosecond region is smaller than that in the nanosecond region. As previously noted,[5,11] a nonlinear response depends on the incident pulse width, when the response concerns an accumulation effect of the incident pulse. It is considered that the difference in $\chi^{(3)}/\alpha$ values in each time region is caused by this phenomenon because the accumulation effects would be small in the femtosecond region.

In summary, we observed an ultrafast response of a silver nanoparticle system. The response time was as fast as 360 fs in the femtosecond OKS experiment, as in the case of that observed in the gold nanoparticle system.[7] The origin of the ultrafast response is attributed to the self-diffraction of a pump pulse due to transient grating. We also estimated $\chi^{(3)}$ of the silver nanoparticle system to be 1.5×10^{-7} esu in the femtosecond region as is the case with that of the gold nanoparticle system.[6]

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