# Degenerate four-wave mixing study of Au fine particle doped glass

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Abstract

Nonlinear optical property of Au fine particle doped glass was studied by degenerate four-wave mixing method. It was found the third order nonlinear susceptibility $\chi^{(3)}$ was as large as $10^{-8}$ esu, and the response time was faster than 40 pico second and the hot electron excitation electronic was responsible for the fast response, but it was found that there was slow component which arose from the thermal grating. This slow component can be attributed to the excitation of lattice vibration of Au fine particle.

## I INTRODUCTION

There are growing interests in nonlinear optical properties of metal fine particle embedded in glass or polymer matrixes, or suspension in solution because of their large nonlinearity.[1-10] Particularly, Au fine particle system is attracting a lot of studies since the pioneering study by Ricard et al.[2] We can see the developments of Au system in the reviewing article by Halperin.[11] As to the nonlinearity of Au fine particle system, Hashe et al[3] proposed three contributions, i.e. intraband transition, interband transition, and hot electron excitation. In the present study, we report the determination of $\chi^{(3)}$ and time response of Au fine particle doped glasses which were made by traditional melting technique and advanced sputtering and ion-implantation methods employing degenerate four-wave mixing method and the results were analyzed in terms of the mechanism of Hashe et al. As will be shown later, Au fine particle doped glasses are promising material because of their large nonlinearity.

## II. EXPERIMENTAL

Degenerate four-wave mixing(DFWM) study was performed employing a frequency doubled Nd:YAG laser in the phase conjugate geometry. The laser generates 7 nano second and 40 pico second light pulses at 532 nm. The polarization of light pulses was controlled by half-wave plates and glan polarizers. The phase conjugate signal and probe pulse were recorded simultaneously using a streak camera. The experimental set up of the DFWM system is illustrated in Fig.(1).

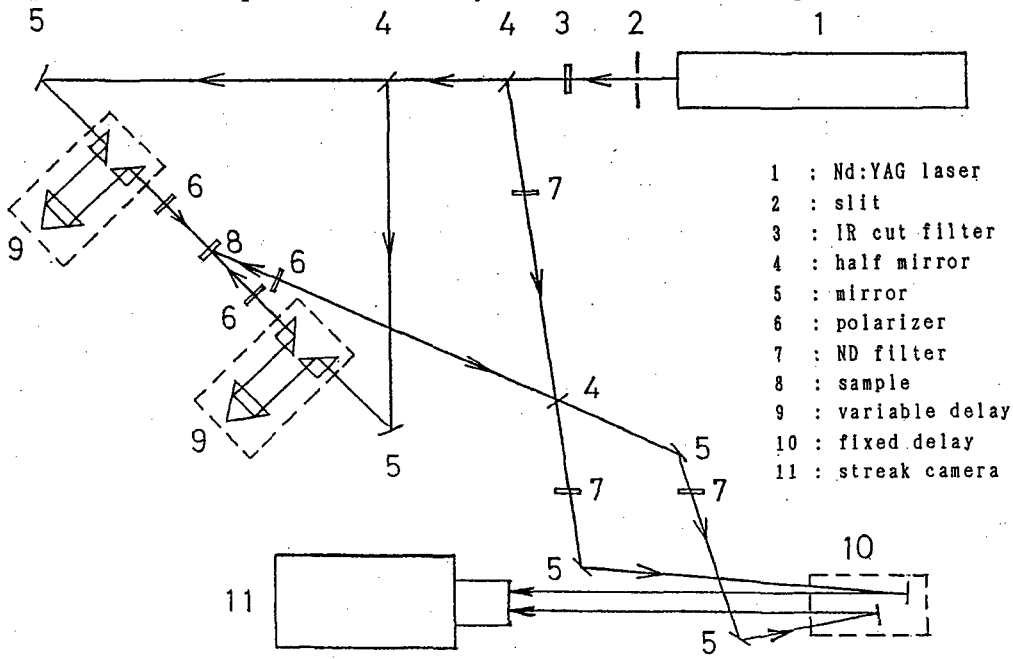



Fig.(1) Experimental set up of DFWM system.

Au fine particle doped glass prepared by melting method was commercially available. In the sputtering method, silica and gold target were simultaneously sputtered in Ar gas, and Au fine particle silica glass films were deposited on silica glass plates. Ion implanted glasses were prepared by implanting $Au^+$ ion into silica glass.[12] In both cases, Au fine particles were formed by heat treatment. The diameter of Au fine particles was

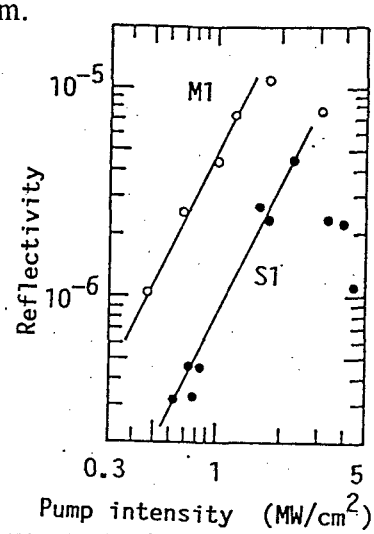



Fig.(2) Reflectivity vs pump.

determined by full width at half maximum of absorption band.[13] The diameter thus obtained was in the range from 5 nm to 10 nm. The typical example of absorption spectra are reproduced in Fig.(3).

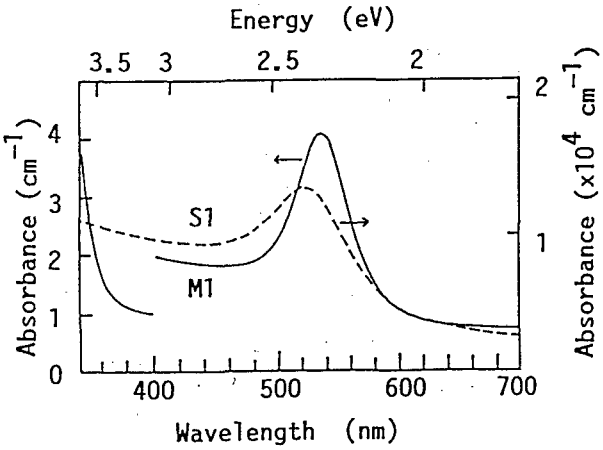



Fig.(3) Absoption spectra of SampleM1(melting) and S1(sputtering).

## III. RESULTS AND DISCUSSIONS

### (1) Nano Second Study

The logarithmic plots of the dependence of the reflectivity of phase conjugate signal vs the pump intensity are illustrated in Fig.(2). The slopes are close to a value 2 in the region of the pump intensity less than 2 MW/cm$^2$ for glasses prepared by melting(M1) and sputtering(S1) methods.

This indicates that the following equation is valid.

$$R^{1/2} = 24\pi^3 L/\lambda cn^2 \chi^{(3)} (I_1 I_2)^{1/2}\ T(1\text{-}T)/\ln(1/T), \qquad (1)$$

where R denotes reflectivity of phase conjugate signal, I's denote pump intensities , and T denotes transmittance. Then using Eq.(1), we could determine $\chi^{(3)}$ values of three types of glasses, which were obtained by melting method(M), sputtering method(S), and ion implantation method(I), and the results are summarized in Table(I). As shown in Table(1), the $\chi_m^{(3)}$ values estimated from the volume fraction are in the same order, therefore the large $\chi^{(3)}$ can be attributed to high concentration of Au particle.

Table(1) Third order nonlinear susceptibilities of Au fine particle doped glasses.

| Glass | $\chi^{(3)}$ (esu) | Thickness (mm) | Au concentration | Diameter (nm) | $\chi_m^{(3)}$ (esu) |
|---|---|---|---|---|---|
| M1 | $2.5\times10^{-11}$ | 0.92 | 0.0033 wt% | 8.8 | $7\times10^{-8}$ |
| S1 | $3.5\times10^{-8}$ | $4.3\times10^{-4}$ | 0.89 at% (8.1 wt%) | 5.8 | $3\times10^{-8}$ |
| I1* | $1.2\times10^{-7}$ | $1.9\times10^{-4}$ | <6.3 at% (<40 wt%) | 5.8 | $8\times10^{-8}$ |

*This glass is prepared by ion-implantation and see ref.[12] in more detail.

(2) Pico Second Study

In the study which employed a laser to generate 40 psec. light pulse, we observed $\chi^{(3)}$ vales and the temporal behavior of phase conjugate signal. The $\chi^{(3)}$ values obtained for Au doped glass and carbon disulfide($CS_2$), and are summarized in Table(2). As shown in Table(2),

Table(2) Third order nonlinear suceptibilies obtained by 7 nano sec. and 40 pico sec. pulses.

| | $\chi^{(3)}$ (esu) 7 ns | $\chi^{(3)}$ (esu) 40 ps |
|---|---|---|
| $CS_2$ | $1.7\times10^{-12}$ | $2.9\times10^{-12}$ |
| Au-doped glass | $2.5\times10^{-11}$ | $3.6\times10^{-12}$ |

the $\chi^{(3)}$ values of carbon disulfide are almost identical for nano second experiment and pico second experiment. The values of $\chi^{(3)}$ of M1 sample, however, are found to be different by the factor of ten. Based on this observation, we performed the measurement of temporal behavior of glass sample, and the result is illustrated in Fig.(3). Fig.(3) indicates that there are two components of the relaxation, i.e. fast component which is faster than the light pulse width, and slow component which has the relaxation time around few nano

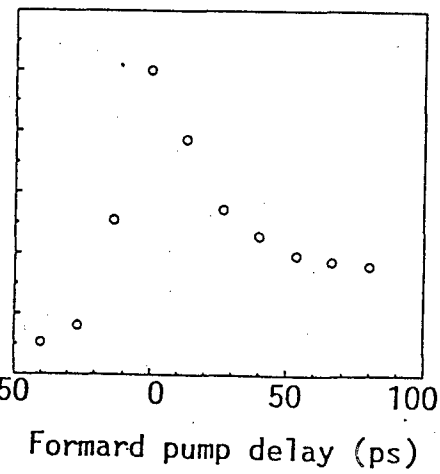


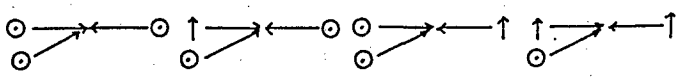

Fig.(3) Temporal response.

second. This observation can be explained as follows. The relaxation of hot electron is fast enough to response with in the pulse width, but the slow component arose from the excitation of lattice vibrations of Au particle.[7]

(3) Tensor Components

The results reported above were performed using the light pulses which have all vertically parallel polarization. In order to discuss the tensor components of $\chi^{(3)}$, we performed experiments which have different polarization of pump beams employing nano second pulse, and the results are summarized in Table(III). It is well known[3] that the hot

Table(3) Tensor components of $\chi^{(3)}$.

| Glass | $\chi^{(3)}_{xxxx}$ | $\chi^{(3)}_{xyxy}$ | $\chi^{(3)}_{xxyy}$ | $\chi^{(3)}_{xyyx}$ |
|---|---|---|---|---|
| |  | | | |
| M1 | 1 | 0.42 | 0.55 | 0.02 |
| M2 | 1 | 0.46 | 0.55 | 0 |
| S2 | 1 | 0.32 | 1.07 | 0 |
| S3 | 1 | 0.57 | 0.65 | 0 |

electron excitation is responsible to the phase conjugate reflection in the spacial configuration ( $\chi_{xyxy}$ and $\chi_{xxyy}$), and the interband transition contributes to the reflection in the temporal grating configuration ( $\chi_{xyyx}$ ).

The values of $\chi_{xyxy}$ and $\chi_{xxyy}$ are comparable in the case of the glasses prepared by melting method. In our geometry of DFWM experiment the small-spaced and large-spaced gratings are estimated to be 180 nm and 1 mm, respectively. Therefore the size of the particle is smaller than the grating periods in both cases. Thus, our findings described above is reasonable as we can expect almost same contribution from small-space grating and large-space grating.

For the results of glasses prepared by sputtering method, similar argument is possible except sample S2. In the case of sample S2, the sample thickness is comparable to the small-space grating, and this results in the fact that only few rows of excited Au particle by the interference of the probe and backward beams. This effect must be

responsible to the observation for sample S2. It must be noted that the sum of $\chi_{xyxy}$ and $\chi_{xxyy}$ is larger than $\chi_{xxxx}$. We have two possible reasons for this observation. One is that the phases of the susceptibility are shifted from each other and the other is the effect that both large-spaced and small-spaced gratings cancel out in the copolarized configuration.The latter effect arises when Au particle, which are excited to form a grating between the rows of other grating. As the sum of $\chi_{xyxy}$ and $\chi_{xxyy}$ of M1 and M2 is almost equal to $\chi_{xxxx}$, the first mechanism deemed to be implausible by the reason that the phase shift is owing to the difference of the mechanisms which contribute to the reflection in the configuration of $\chi_{xyxy}$ and $\chi_{xxyy}$. The second reason is more possible as it can explain the difference between the glass prepared by melting method and the one prepared by sputtering method. The main difference of those glasses is the concentration of Au particle, it can be possible to explain the observation as follows. The mean distance between the neighboring Au particles, which can be estimated from the volume fraction, is about 10 nm and 150 nm for sample S1 and sample M1. The former is smaller than the period of the small-spaced grating while the latter is comparable. By this reason, it is possible to explain the above observation by the reason that the larger amount of Au particles are excited to form a grating between the rows of the other grating in the glass prepared by sputtering method compared to the glasses prepared by melting method.

## IV. CONCLUDING REMARKS

The large nonlinear susceptibility was obtained for Au doped glasses prepared by sputtering method and ion implanting method because of the high concentration of Au fine particle, whereas $\chi_m^{(3)}$ was found to be a same order of magnitude for all the samples. The time dependent study indicated that there are two relaxation mechanisms. The one is the fast electronic process and the other is the slow relaxation of electron to excite the lattice vibration modes.

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