Proc. Int. Conf. Optical Properties of Nanostructures, Sendai, 1994
Jpn. J. Appl. Phys. Vol. 34 (1995) Suppl. 34-1, pp. 137-139

Study of Diffusion and Carrier Recombination for Cu_2O Ultrafine Particles in Organosols

X. Q. Zhang, Y. M. Chen, J. L. Zhao, W. P. Qin, X. W. Fan and S. H. Huang
Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, *China*

The diffusion coefficient and carrier recombination time have been obtained by time-delayed four-wave mixing with incoherent light for Cu_2O ultrafine particles in the organosols at room temperature. The results, $D=0.011$ cm^2/s, $T_R=1.2$ ns. The diffusion processes was discussed.

KEYWORDS: carrier recombination time, diffusion coefficient, time-delayed four-wave mixing with incoherent light

1. Introduction

Recently time-delayed four-wave mixing with incoherent light (TDFWM-IL) was developed and attracted much attention. Morita and Yajima[1] gave the background of TDFWM-IL theoretically on the basis of the two-level model and derived the conclusion that when this technique was used to measure the dephasing time and population relaxation time, the time resolution was limited by the coherent time of the excitation light field used rather than by its overall duration. It opened up a new technique with which ultrafast relaxation time could be measured with nanosecond pulse lasers or even cw lasers. The technique has been applied to measure the dephasing time[1-4], population relaxation time[4,5] and optical Kerr relaxation time[6].

Population relaxation time can be usually obtained by fitting the tail of the trace of the TDFWM-IL signal with theory. However, because only small portion in the tail of the signal is related to the population relaxation time, the error in fitting must be large. Besides, diffusion, energy transfer and thermal motion affect to the TDFWM-IL signal, and shorten the decay time of the dynamic grating, the population relaxation time such obtained is usually different from the intrinsic one.

In this paper, we present a new method, which allows us to extract the carrier recombination time and diffusion coefficient from relative intensities of two diffracted peaks and the constant background. We demonstrate this technique with nanosecond pulse laser for Cu_2O ultrafine particles at 300 K and 338 K, respectively.

2. Theory

In four wave mixing with phase conjugation configuration, I_1, the forward pump beam (or I_3, the backward pump beam) and I_2, the probe beam interfere within the sample, generate a dynamic grating with period of $\lambda/2\sin(\theta/2)$ [or $\lambda/2\cos(\theta/2)$], where λ is the wavelength of the light and θ is the angle between I_1 and I_2. Backward pump beam (or forward pump beam) is diffracted by this grating, conjugation wave I_s along the direction opposite to the probe beam is thus produced. The intensity $I_s(\tau)$ is measured as a function of delay time $-\tau$ of I_2 to I_1. There are two peaks in the trace of $I_s(\tau)$ around $\tau=0$ and $\tau=-T$, if T, the delay time of I_3 to I_1, is nonzero. Since the diffractive efficiency is dependent not only on the carrier recombination but also on the diffusion, the intensities of the two peaks are generally inequal. Under the condition $T \gg \tau_c$, $T \gg T_2$ and T_{11}, $T_{12} \gg \tau_c$, the shapes of the peaks can be approximated by[2,6 8-10]

$$I_s(\tau) \propto 1+\frac{2\sqrt{2}T_{11}^2}{\sqrt{\pi}\tau_c(T_{11}+T_{12})}\exp[-(2\tau^2/\tau_c^2)] \quad (1)$$

$$I_s(\tau+T) \propto 1+\frac{2\sqrt{2}T_{12}^2}{\sqrt{\pi}\tau_c(T_{11}+T_{12})} \times \exp[-2(\tau+T)^2/\tau_c^2], \quad (2)$$

where the first order coherent function of the laser is assumed to be $\exp(-\tau^2/\tau_c^2)$, τ_c is the coherent time of the light, T_2 is the dephasing time of the sample, T_{11} and T_{12} are the decay time constants of the two dynamic gratings, respectively.

The decay time constants of the two gratings can be expressed as[7]

$$\frac{1}{T_{11}}=\frac{1}{T_R}+\frac{16\pi^2 D\sin^2(\theta/2)}{\lambda^2} \quad (3)$$

$$\frac{1}{T_{12}}=\frac{1}{T_R}+\frac{16\pi^2 D\cos^2(\theta/2)}{\lambda^2} \quad (4)$$

where D is diffusion coefficient and T_R is carrier recombination time.

Letting $I_o=I_s(\tau=\infty)$, $I_{M1}=I_s(\tau=0)-I_o$ and $I_{M2}=I_s(\tau=-T)-I_o$, from Eqs. (1-4), the diffusion coefficient and the carrier recombination time can be determined by

$$T_R=\frac{\sqrt{\pi}\tau_c(\sqrt{I_{M1}}+\sqrt{I_{M2}})\sqrt{I_{M1}I_{M2}}\cos\theta}{2\sqrt{2}I_o[\sqrt{I_{M2}}\cos^2(\theta/2)-\sqrt{I_{M1}}\sin^2(\theta/2)]} \quad (5)$$

$$D=\frac{\sqrt{2}}{8\pi^{5/2}}\frac{\lambda^2}{\tau_c\cos\theta}\frac{\sqrt{I_{M1}}-\sqrt{I_{M2}}}{\sqrt{I_{M1}}+\sqrt{I_{M2}}}\frac{I_o}{\sqrt{I_{M1}I_{M2}}} \quad (6)$$

In short, the decay time of the grating is dependent not only on the material but also on the period of the transient grating. Since diffusion, energy transfer and thermal motion contributes differently to the two gratings, T_{11} is longer than T_{12}, so the trace of the TDFWM-IL signal intensity $I_s(\tau)$ exhibits two peaks with different intensities around $\tau=0$ and $\tau=-T$, and the relative intensity of the two peaks is generally different for materials. Under the condition $\tau_c \ll T_{11}$, T_{12}, the two peaks are all symmetrical about $\tau=0$ and $\tau=-T$ with a constant background, and the separation between the two peaks is T. Diffusion coefficient and carrier recombination time can be obtained from the ratios of the intensities of the constant background and to each of the two peaks in TDFWM-IL signal.

3. Experimental Results and Discussion

The experimental setup for TDFWM-IL is shown in Fig. 1. The light source was from the second harmonic of a Q-switched Nd:YAG Laser with a pulse

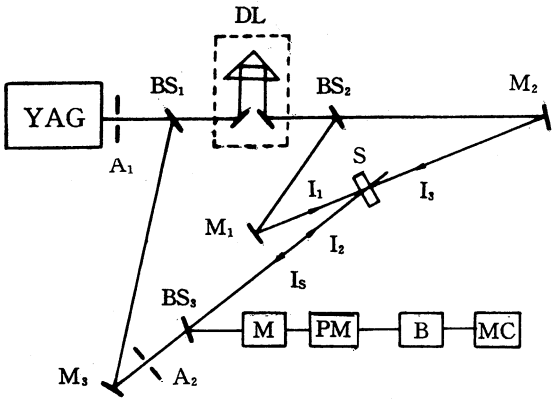

Fig. 1 Experimental setup for TDFWM-IL. BS_1 and BS_2 are the beam splitters; BS_3, the glass plate; DL, the delay line; PM, photomultiplier; A_1, A_2, the apertures; S, the sample; B, the boxcar; MC, the microcomputer; M_1, M_2, M_3, the reflective mirrors; M, the monochrometer.

duration of 10 ns, a repetition rate of 10 Hz and a coherent time of 28 ps. The output of the laser pulse is split by the beam splitters BS_1 and BS_2 into three beams, a weak probe beam and two equally intense counterpropagation pump beams, which incident upon the sample. In all measurements, the probe beam is incident at an angle θ of 15° with respect to the forward pump beam, the delay time T between the beams I_1 and I_2 is 510 ps. The delay time τ of beam I_2 with respect to beam I_1 was changed by the delay line. The phase-conjugation signal was split by a glass plate BS_3 and detected with a photomutiplier after passing through a boxcar averager, the signal was stored and processed in a microcomputer. The signal intensity $I_s(\tau)$ was measured as a function of the delay time τ. To avoid the saturation effect we have to use a pump beam energy lower than the saturation energy. Therefore the signal intensity versus the pump beam energy should be measured first to determine the saturation limitation.

We have measured $I_s(\tau)$ for Cu_2O ultrafine particles in the organosols at room temperature, as shown in Fig. 2, where the dots represent the experimental curve while the solid line is a fitting with Eqs. (1) and (2). The trace of the TDFWM-IL signal was well fitted as shown in Fig. 2 by Eqs.

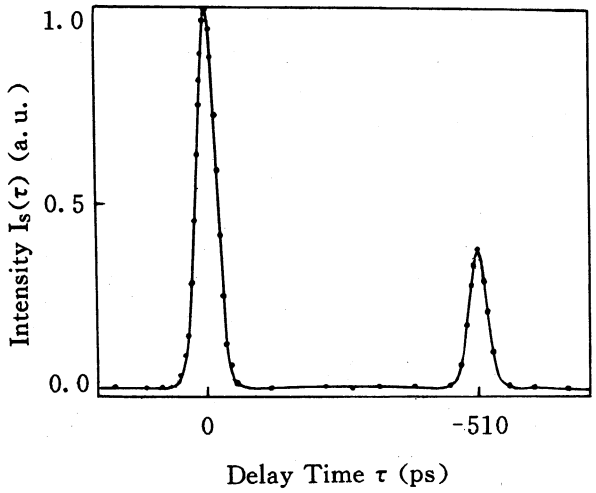

Fig. 2 Normalized TDFWM-IL signal intensity as a function of delay time for Cu_2O ultrafine particles at room temperature.

(1) and (2). This indicates that the experimental curve is in agreement with the theory. By Eqs. (5) and (6) we have got $T_R=1.2$ ns and $D=0.011$ cm^2/s. As can be seen from Fig. 2, two symmetrical peaks from large and small period gratings are observed corresponding to the delay time $\tau=0$ and $\tau=-510$ ps, respectively, and the intensity of the $\tau=-510$ ps peak is weaker than that of the $\tau=0$ peak. This phenomenon can not be attributed to carrier diffusion because the size of the ultrafine particles is much smaller than the periods of the two gratings, carriers are effectively confined within the particles. We attribute $I_s(-510\text{ ps})/I_s(0)<1$ to the Brownian movement, since the delocalization

of the excited particle makes the small period grating suffer more serious deterioration than the large period one.

Similarly $I_s(\tau)$ for Cu_2O ultrafine particles has also been measured at 338 K, as shown in Fig. 3. In the same way, the carrier recombination time and diffusion coefficient were obtained to be 0. 91 ns and 0. 016 cm^2/s, respectively. The speed of Brownian movement increases with temperature rise, so

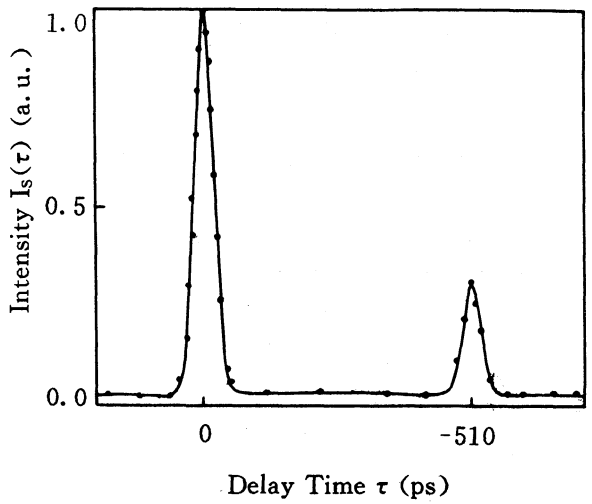

Fig. 3 Normalized TDFWM-IL signal intensity as a function of delay time for Cu_2O ultrafine particles at 338 K.

the diffusion coefficient at high temperature is larger than one at low temperature. Rate of nonradiation transition increases with a rise in temperature. Hence the carrier recombination time at high temperature is smaller than one at low temperature. These are in agreement with the experimental results.

In Figs. 2 and 3, the two peaks are symmetric about $\tau=0$ and $\tau=-T$, respectively, with a constant background and separated by $T=510$ ps, just as the theory predicted. In addition, the TDFWM-IL technique has been applied to measure the carrier diffusion coefficient in CdS:Cu. The obtained coefficient is in good agreement with that determined by another method[8]. The experimental results indicated that the technique is correct.

4. Conclusion

The diffusion coefficient and carrier recombination time can be derived from the relative intensities of the constant background and the two peaks around $\tau=0$ and $\tau=-T$ in TDFWM-IL. The two parameters have been got by this method for Cu_2O ultrafine particles in the organosols at 300 K and 338 K, respectively. These results are in agreement with the dynamical behavior of the light-matter interaction. Brownian movement accelerates decay of the dynamic grating, and weaken the peak intensity corresponding to the small period grating. The experiments showed the validity of the theory.

Acknowledgements

This work was supported by the National Natural Science Foundation of China and the Science Fund of the Laboratory of Excited State Processes. Changchun Institute of Physics, Chinese Academy of Sciences.

1) N. Morita and T. Yajima: Phys. Rev. **A30**(1984)2525.
2) X. Cheng and T. Kobayashi: Mol. Cryst. Liq. Cryst. **A182** (1990)139.
3) X. Mi, H. T. Zhou, R. H. Zhang and P. X. Ye: J. Opt. Soc. Am **B6**(1989)184.
4) T. Kobayashi, A. Terasaki, T. Hattori and K. Kurokawa: Appl. Phys. **B47**(1988)107.
5) N. Morita, T. Tokizaki and T. Yajima: J. Opt. Soc. Am. **B4** (1987)1269.
6) K. Kurokwa, T. Hattori and T. Kobayashi: Phys Rev. **A36** (1987)1298.
7) H. J. Eichler: Spectroscopy of Solid State Laser Type Materialed. B. Dibartole, Plenum, New York, 1987. P451
8) X. Q. Zhang, J. L. Zhao, W. P. Qin, K. Dou and S. H. Huang: Acta Phys. Sinica **42**(1993)417.
9) J. Y. Liu, S. H. Huang, W. P. Qin and J. Q. Yu: J. Lumin. **54**(1993)319.
10) P. M. Fu, 2. H. Yu, X. Mi and P. X. Ye: J. physique. **48** (1987)2089.