Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/0S65-05
Chinese Physics
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and IOP Publishing Ltd

LARGE AND EXTREMELY FAST THIRD-ORDER NON-LINEARITY OF Ag NANOPARTICLES EMBEDDED INTO A Cs_xO SEMICONDUCTOR MATRIX*

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(Received 14 March 2001)

The third-order optical nonlinearity of Ag-O-Cs thin films, where Ag nanoparticles are embedded into a Cs_xO semiconductor matrix, was measured by the femtosecond optical Kerr technique. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, of the thin films was estimated to be 1.1×10^{-9} esu at the incident wavelength of 820 nm. The response time, i.e. the full width at half-maximum of the Kerr signal, is as fast as 114 fs only. The intrinsic third-order optical nonlinearity can be attributed to the intraband transition of electrons from the occupied state near the Fermi level to the unoccupied state. It is suggested that such a nonlinearity is further enhanced by the local field effect that is present in the metallic nanoparticles composite thin films.

Keywords: optical Kerr effect, metallic nanoparticles, third-order nonlinearity
PACC: 4265, 6146, 7866W

I. INTRODUCTION

With the development of photon devices, nonlinear optical (NLO) materials that have not only a large third-order nonlinear coefficient, but also a rapid optical response speed, are required. Nanocomposite thin films formed by nanoparticles embedded into a dielectric or semiconductor matrix have been widely studied, in recent years, in terms of their linear and nonlinear properties. Their special electric and optical properties allow to apply such materials in photoelectric and optical devices.[1−3] Since the nanoparticles composites, in general, are macroscopically isotropic, their nonlinear response is mainly of third order. Third-order optical nonlinearity can be studied by many methods, such as generated four-wave mixing (DFWM),[4] z-scan,[5] and the optical Kerr effect (OKE).[6] On this basis, a time-resolved technique was developed to describe the temporal behavior of the nonlinear response.

This allows not only to measure the third-order nonlinear optical susceptibility, $\chi^{(3)}$, but observe the relaxation process of a nonlinear response. However, the latter is restricted by the time resolution of the experimental system, namely, the duration of the output laser pulse.

A typical nanoparticles composite thin film system is composed of nonlinear metal particles (preferably noble metal particles) such as Au, Ag, and Cu, randomly embedded in a linear matrix, for example, SiO_2, Al_2O_3, TiO_2 and BaO.[7−9] Considerable theoretical and experimental efforts have been made to investigate the optical nonlinearity of such thin films. It is believed that, due to the surface plasma resonance,[10] local field enhancement,[11] and quantum size effect of the embedded metal nanoparticles,[12] these types of nanoparticles composites are just one type of materials with both a larger third-order non-linearity and a faster response speed. Using the DFWM configuration, Ricard *et al.*[13] reported the first experimental study on NLO properties of metal colloids (silver and gold colloids). They observed a dominant nonlinear response on the 28-ps

*Project supported partly by the National Natural Science Foundation of China (Grant No. 60071017) and the Natural Science Foundation of Beijing, China (Grant No. 2992019).
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time scale and therefore assigned the nonlinearity to the conduction electrons of the small metal particles. Hache *et al.*[1] performed a similar experiment, but with a better time resolution. They recorded a faster nonlinear response on a 5-ps time scale. As for solid-state thin films, the most exciting result, an ultrafast response of an Au:SiO_2 nanoparticles system on the 240 fs time scale, was obtained by Inouye *et al.*[6] in 1998 in a femtosecond optical Kerr experiment, where the width of the incident laser pulses used was 500 fs. However, the wavelength in Ref.[6] was selected to be near the surface plasma resonance frequency of 0.53μm, which is in the visible region.

In this paper, we present a femtosecond time-resolved third-order NLO investigation of Ag-O-Cs composite thin films, which are traditional but still interesting photoemissive materials in the visible and near-infrared region.[14,15] Their structure consists of nano-scale Ag particles embedded in a Cs_xO ($2 \leq x < 3$) semiconductor matrix.[16] A larger and extremely fast NLO response has been observed in the thin films. The typical magnitude of $\chi^{(3)}$ is about 1.1×10^{-9} esu and the related response time is as fast as 114fs only. In our experiment, the used wavelength of the incident laser pulses was 820nm, which is in the near-infrared region and considered to be more significant for the applications available in optical devices.

II. EXPERIMENT

In the preparation of Ag-O-Cs thin films, silver films were deposited onto the transparent glass substrate by a vacuum thermal evaporation method. Their thickness was controlled by stopping the deposition while the light transmissivity dropped to 30%. The base vacuum of the deposition system was about 5×10^{-5}Pa. The silver films were then exposed to the pure oxygen gas at a pressure of 10 Pa for oxidation with the glow discharge method.[14] The oxidation process was interrupted when the transmissivity was raised to nearby 100%. Finally, at a temperature of 150°C the evaporated cesium was introduced to deoxidize the silver oxide to the Ag and Cs_xO composite until the maximum photoemission current was attained. Moreover, the thin films were activated by the excess silver to obtain more sensitive photoelectronic response in the near-infrared region. The sample of Ag-O-Cs thin films fabricated with this method was studied with transmission electron microscopy (TEM). It can be described by Ag nanoparticles with an average radius of 5 nm being randomly dispersed in the Cs_xO semiconductor matrix, as shown in Fig.1. Usually, in order to obtain a more uniform size distribution of the Ag nanoparticles and improve the stability of the thin films, the sample was annealed at a temperature of 100°C for more than 2 h in air. The total thickness of the sample employed in this study was approximately 50nm.

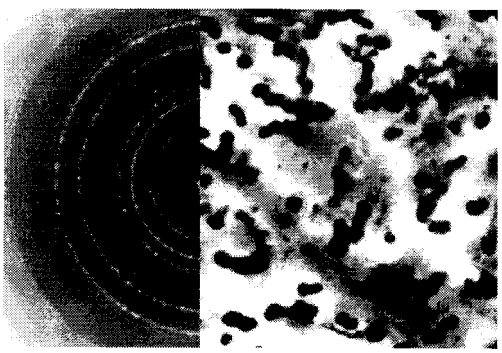


Fig.1. Transmission electron micrograph and transmission electron diffraction image of Ag-O-Cs thin films.

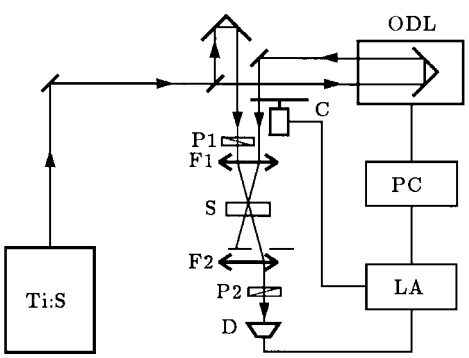


Fig.2. System for measuring the femtosecond optical Kerr effect of Ag-O-Cs thin films.

The NLO measurements were performed using a Ti:sapphire laser (Mira 900F, Coherent, USA). The laser wavelength was centered at 820nm and the width of the output pulse was 120fs. The average energy of a single pulse on the sample was 24nJ and the repetition ratio amounted to 76MHz. Figure 2 shows the system for measuring the femtosecond time-resolved optical Kerr effect of Ag-O-Cs thin films. The beam from the laser was divided into pump and probe beams with an intensity ratio of 10:1. The polarization of the probe beam was rotated by 45° with respect to the linear polarization of the pump beam. The pump beam was led through an optical delay line (ODL) driven by a step-by-step motor in order to adjust the optical path between the pump and probe beams during the measurement. Two beams, i.e. the pump and

probe beams, finally intersected by being focused on the surface of the Ag-O-Cs sample. The third-order nonlinearity induced by the pump and probe pulses generated a Kerr signal that passed through the analyzer and was detected by the photodiode. To improve the signal-to-noise ratio, the pump and probe beams were chopped in each frequency, f_1 or f_2, and the optical Kerr signal was detected at the sum frequency (f_1+f_2). All measurements were controlled by a computer (PC) program. The time-resolved NLO response can be obtained from the data acquisition and conversion system, which is also controlled by the computer.

Ⅲ. RESULTS AND DISCUSSION

A typical temporal behavior of the optical Kerr signal observed for Ag-O-Cs thin films is shown in Fig.3. The insert displays the response of the reference sample, CS_2, obtained under identical experimental conditions. The FWHM of the Kerr signal is as fast as 114 fs only, i.e. shorter than any others that have been reported up to now for nanocomposite thin films. Such a fast response of Kerr signal seems to be amazing, because the response time is slightly shorter than the width of the incident pulse, 120fs. From Fig.3, we can also see that the temporal behavior is decomposed into two delay components: A fast component (part A-B) with a time of 100fs and a subsequent slow component (part B-C) with a time of more than 1ps. In Fig.3 the dashed line is drawn for a better illustration of the slow delay component.

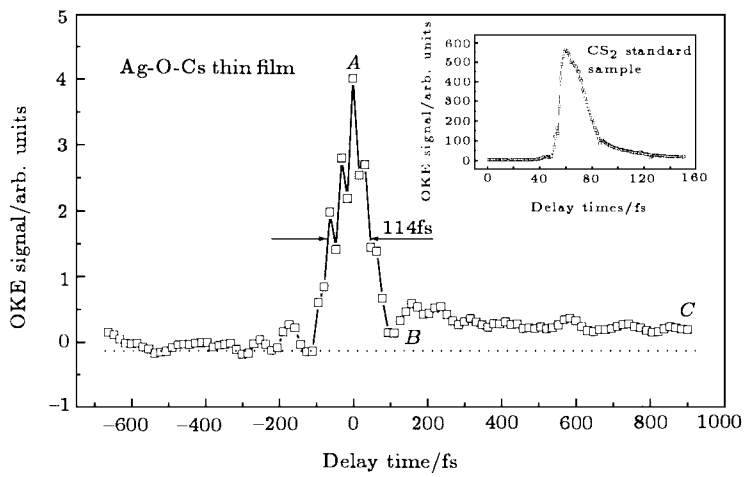


Fig.3. Time-resolved optical Kerr effect of Ag-O-Cs thin film at 820nm.

For metallic nanocomposites, an intrinsic NLO third-order susceptibility was dominantly caused by the electrons in the nanoparticles. There are three possible carrier transition contributions which are related to the action of the pump beam:[17] Intraband transitions, interband transitions, and hot electron transitions. In our experiment, the fact of the response time of the Kerr signal being even shorter than the width of the incident pulse indicates that such a nonlinear response could be assigned exclusively to the contribution of the electrons in the metallic nanoparticles. Furthermore, due to the wavelength of the incident pump laser pulses used being in the near-infrared region, third-order optical nonlinearity certainly is to be attributed to the intraband transition of electrons from the occupied state near the Fermi level to the unoccupied state. The aberrance of the electron cloud, related to the electron transition, finally results in a variation of the refractive index of the sample and the polarization direction of the probe beam is therefore changed. Consequently, the probe beam that is blocked by the two vertical polarizers in the beginning can partly pass through the analyzing polarizer now and is observed as a Kerr signal.

Usually, the intrinsic susceptibility caused directly by the aberrance of the electron cloud is so weak that it can hardly be observed. The reason why nonlinear response can still be observed here, as mentioned by Shalaev *et al.*,[11] is believed to lie in the fact that the intrinsic susceptibility is further enhanced by a local field that especially exists in the metallic nanoparticles composite thin film of random

or fractal structure. The Kerr nonlinearity enhancement factor according to Ref.[11] is strongly increased towards to the long-wave part of the spectrum and on the average reaches values of $\sim 10^4$ at 1μm by numerical simulation. This means that our experimental result obtained at 820 nm can be well explained by the intraband transition of electrons near the Fermi level and the local field enhancement effect.

As mentioned above, the intrinsic optical nonlinearity originates from the electron transition induced by the pump beam. We therefore believe that the two decay components of the temporal behavior observed in the optical Kerr effect are correlated with the different relaxation processes of the non-equilibrium electrons in the Ag nanoparticles.[18] One is the thermal equilibrium process between the electron and the lattice system in the Ag nanoparticles. It is exhibited by the fast decay (part A-B) in the temporal behavior, which generally is on the femtosecond scale. The other is the thermal diffusion process from the Ag metallic nanoparticles to the Cs_xO matrix, which is exhibited by the slow decay (part B-C) of the order of picoseconds. Here, the extremely fast response is probably due to the Cs_xO semiconductor matrix that is considered to be superior to the other dielectric media, such as SiO_2 or Al_2O_3, when Ag nanoparticles are embedded.

For the Ag-O-Cs thin film sample employed, we can estimate the third-order nonlinear susceptibility, $\chi^{(3)}$, by comparison with that of CS_2, as[4]

$$\chi^{(3)} = \chi^{(3)}_{CS_2} \sqrt{\frac{I}{I_{CS_2}}} \frac{n^2}{n^2_{CS_2}} \frac{d_{CS_2}}{d} \frac{\ln(1/T)}{(1-T)\sqrt{T}} \qquad (1)$$

where $\chi^{(3)}_{CS_2}$ is the third-order nonlinear susceptibility of CS_2, I and I_{CS_2} are the Kerr signal intensities, n and n_{CS_2} are the refractive indices, d and d_{CS_2} are the thicknesses of the sample and the reference material CS_2, respectively; and T is the transmission coefficient of the sample at the incident wavelength. In our experiment the parameters were taken to be: $\chi^{(3)}_{CS_2} = 1\times10^{-13}$esu,[19] n=2.23, n_{CS_2}=1.62, d=50nm, d_{CS_2}=1mm. The transmission coefficient, T, of the sample at 820nm was measured to be 0.275. Hence, we obtained the value of $\chi^{(3)}$ from Eq.(1) as 1.1×10^{-9}esu for a typical sample of Ag-O-Cs composite thin films. The value seems to be much smaller than that obtained by the others in the Ag nanoparticle systems, where the incident nanosecond or picosecond laser pulses induce an unavoidable thermal effect.[20] However, such a thermal effect is considered to be negligible on a femtosecond time scale. Therefore, the value of nonlinear susceptibility obtained should still be large enough for the thin films, with only 50 nm in thickness, when excited by near-infrared laser pulses.

IV. CONCLUSION

An ultrafast response faster than the pulse width of the incident laser pulse has been observed in the Ag-O-Cs thin films in a femtosecond optical Kerr experiment. The third-order nonlinear susceptibility $\chi^{(3)}$ of the thin films is estimated to be as large as 1.1×10^{-9}esu on the femtosecond time scale. The intrinsic third-order optical nonlinearity is attributed to the intraband transition of electrons from the occupied state near the Fermi level to the unoccupied state. Such a nonlinearity is further enhanced by the local field effect that is present in the metallic nanoparticles composite thin films.

ACKNOWLEDGEMENT

The authors gratefully thank Prof. Q. D. Wu, member of Chinese Academy of Sciences, for the valuable discussions.

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