Nonlinear Optical Properties of the Au-SiO₂ Nanocomposite Superresolution Near-field Thin Film

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A Au-SiO₂ superresolution nanocomposite active nonlinear optical thin film is fabricated reproducibly by cosputtering method with the size of Au nano particles around 2 to 10 nm. Results of the Z-scan indicate that these nanocomposite Au-SiO₂ films have nonlinear optical properties and enhanced transmittance at the focusing position. For a 15-nm-thick Au-SiO₂ nanocomposite thin film, the transmittance can be 135% for a sample with an average grain size of around 5 nm.

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1. Introduction

The superresolution near-field structure (super-RENS) is one of the most important research topics in the field of ultrahigh-density optical recording.¹⁾ The super-RENS has the advantages of simpler recording head design, less mechanical damage, and higher recording speed than the old near-field optical recording method using a near-field optical pickup head. The key of the super-RENS is to use a novel disk structure which consists of an active nonlinear optical layer sandwiched between two dielectric protection layers on a recording layer; and the near-field optical effects can occur between the active nonlinear optical layer and recording layer. The precision of the near-field optical distance between the active thin film and recording layer can be well controlled by the sputtering process of super-RENS. Different materials have been used recently in order for the nonlinear optical layer to achieve smaller recording mark size and stable carrier-to-noise ratio (CNR). After the as-deposited Sb nano sized thin film was first used as the active nonlinear optical layer^{1–4)} with a CNR of more than 10 dB for 90 nm recording marks, the AgO_x thin film subsequently demonstrated a 10 dB higher CNR.^{5–9)} According to the direct near-field optical measurements on Sb-type super-RENS and AgO_x-type super-RENS, the effects of localized surface plasmon (LSP) are proposed to be the key mechanism behind the super-RENS.^{3,7)} The enhancement of local optical intensity in near-field and the nonlinearity of the enhancement are closely related to the LSP, which was calculated using finite difference time domain (FDTD) method as well.⁸⁾ Because of the instability of AgO_x at high temperature, a PtO₂-type super-RENS¹⁰⁾ and a nanostructured ZnO-type super-RENS¹¹⁾ were reported very recently. For a relatively high readout laser power, the PtO₂-type super-RENS can provide a 30 dB CNR for 100 nm recording marks. The nanostructured ZnO-type super-RENS on the other hand was able to provide a more than 47 dB CNR with a relatively low readout laser power for 100 nm mark trains.¹²⁾ In this paper, we intend to introduce a new type of active nonlinear optical layer which is a SiO₂ and Au nanocomposite thin film, and demonstrate its nonlinear

optical properties. The enhancement factors for different Au and SiO₂ ratios are determined at various incident laser powers (10 to 100 μW) as well.

2. Experimental

2.1 Sample preparation

A cosputtering method is used to fabricate the active nonlinear optical thin film of super-RENS.¹³⁾ Two targets of SiO₂ and Au are simultaneously rf-sputtered with argon. A nanocomposite thin film consisting of SiO₂ and Au can be made easily, and the ratio of Au to SiO₂ is controlled by the powers of two sputtering guns. The sample structure used in this study is glass/ZnS-SiO₂(170 nm)/Au-SiO₂(15 nm)/ZnS-SiO₂(20 nm). The cosputtered 15 nm Au-SiO₂ nanocomposite thin film is sandwiched by two spacer layers of ZnS-SiO₂ on a glass substrate. Figure 1 shows the top view of the transmission electron microscope (TEM) micrographs, and the inset is the electron diffraction patterns of this 15 nm Au/SiO₂ nanocomposite thin film. The sputtering powers of SiO₂ in Figs. 1(a), 1(b) and 1(c) are 200, 300 and 400 W, respectively, and is maintained at 10 W for Au. The bright-field TEM images shown in Fig. 1 clearly display the gold nanoparticles embedded in SiO₂ with random distribution and irregular shape. The size of these nanoparticles is around 2 to 10 nm. The electron diffraction patterns shown in the insets of Fig. 1 demonstrate that these nanoparticles are Au crystal with FCC structure. The average grain diameters of the gold nanoparticles shown in Figs. 1(a), 1(b) and 1(c) are 4.95, 4.21 and 2.96 nm, respectively.

2.2 Optical measurement

The nonlinear optical properties of the SiO₂ and Au nanocomposite thin films are investigated by the confocal Z-scan method. The Z-scan method¹⁴⁾ is a single-beam optical system for measuring nonlinear absorption and refraction. The intensity-dependent saturable absorption and reverse saturable absorption could be spatially separated by the Z-scan measurements. The schematic of the experimental setup for our confocal Z-scan system is shown in Fig. 2. The light source is a Q-switched Nd:YAG semiconductor pulse laser with a wavelength of 532 nm, pulse width of 0.7 ns, and 15.79 kHz repetition rate. To study the nonlinear optical properties in a microscopic region, a Mitsutoyo long-

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Fig. 1. Transmission electron microscope (TEM) micrographs and electron diffraction patterns (inset) of the Au/SiO₂ nanocomposite thin films for various ratios of Au in SiO₂. The sputtering power of Au is fixed at 10 W. The sputtering powers of SiO₂ are 200, 300 and 400 W, for (a) M2-200-10, (b) M2-300-10 and (c) M2-400-10, respectively.

Fig. 2. Schematic of the experimental setup of confocal Z-scan measurements.

working-distance ($WD = 13$ mm), high-numerical-aperture ($NA = 0.55$) objective lens is used to focus the laser beam. A beam splitter behind the sample is used to split the transmission light for the transmission-mode (T-mode) measurements, i.e., a lens is followed to collect all the transmitted light, and the close-aperture-mode measurements, i.e., an aperture is used to control the passing-through light at the near optical axis. The Z-scan movement of the sample at the focal region is precisely positioned using motorized stage. An adjustable attenuator is used to control incident laser power from 0.5 to 120 μ W. The reflectance and transmittance of the sample can be measured simultaneously by the photo detectors D4 and D3/D2, and the incident laser power at the sample surface is monitored by an optical power meter (D1). The super-RENS sample is placed with the Au-SiO₂ nanocomposite thin film layer facing the collecting lens and on a motorized stage along the optical axial direction (Z-axis). The positive scanning direction is to move the sample from the focusing objective side toward the collection lens. The Z-scan position marked 0 is set at the focusing of the Au-SiO₂ nanocomposite thin film. Results of the transmittance and reflectance at different positions along the optical axis can be acquired and plotted simultaneously,

Fig. 3. Experimental results of the dependence of the transmittance or reflectance on the position of the Z-scan for various input laser powers. (a) shows the results on a referenced cover glass with incident laser power of 100 μ W. (b), (c), (d), (e) and (f) show the results of M2-200-10 super-RENS sample with incident laser powers of 10, 20, 30, 40, and 50 μ W, respectively.

and the optical properties such as the absorption and refraction can be analyzed.

3. Results and Discussions

Figure 3 shows the Z-scan results of the transmittance and reflectance of a glass/ZnS-SiO₂(170 nm)/Au-SiO₂(15 nm)/ZnS-SiO₂(20 nm) sample, M2-200-10, as shown in Fig. 1(a). The position 0 is set at the focusing position on the active nonlinear optical thin film, i.e., 15 nm nanocomposite thin film of Au and SiO₂. Figure 3(a) shows the results of the glass substrate at the incident laser power of 100 μ W as a reference. Two peaks at the positions of 25 μ m and 125 μ m in the right column of Fig. 3(a) indicate the reflection occurring at the air-glass interface. The distance between the two peaks is around 0.12 mm, which is the thickness of the glass substrate. The linear transmittance of the glass substrate is displayed on the left column of Fig. 3(a), and no dependence of the incident laser power is found.

Figures 3(b), 3(c), 3(d), 3(e) and 3(f) are the results of

different incident laser powers, i.e., 10, 20, 30, 40 and 50 μW , respectively. It is similar to that of Fig. 3(a). The reflectance shown in Figs. 3(b), 3(c), 3(d), 3(e) and 3(f) displays two peaks at the positions of 28 μm and 125 μm . The most important thing is that there is a spike happened before the first peak was previously observed. This spike resulted from the existence of the 15 nm Au-SiO₂ nanocomposite thin film. The value of reflectance can be two times more than that of the glass substrate. The results of transmittance in Figs. 3(b), 3(c), 3(d), 3(e) and 3(f) clearly show the nonlinear optical absorption of the 15 nm Au-SiO₂ nanocomposite thin film. The threshold laser power for the observation of nonlinear response is around 10 μW . The dip in transmittance indicates a positive absorption of the Au-SiO₂ nanocomposite thin film. Results show a spike is aroused at the absorption dip when the incident laser power is more than 20 μW . As shown in Fig. 3(d), a sharp and strong spike occurred at the focusing position when the incident laser power exceeded 30 μW . This spike is considered to be caused by the excitation of the localized surface plasmon of the gold nanoparticles that are randomly embedded in the SiO₂.^{15,16} The size, shape, and distribution of the gold nanoparticles, and their environments, i.e., SiO₂ in this case, are important issues for the generation of strong localized surface plasmon.

In order to investigate the connection between the strong nonlinear effect and the properties of the Au-SiO₂ nanocomposite thin film, three cosputtered samples, M2-200-10, M2-300-10 and M2-400-10, are fabricated with clear distinction as shown in Figs. 1(a), 1(b) and 1(c). Figure 4 shows the ratio of the transmittance value at the focusing position to the out-of-focus position for various incident laser powers. The circles shown in Fig. 4 are the reference results of the glass substrate, and a linear response is found. Square, rhombus and triangular symbols indicate the results for the Au-SiO₂ nanocomposite thin film samples, M2-200-10, M2-300-10 and M2-400-10, respectively. Clearly, a nonlinear response can be found with these three samples. For the incident laser power of 60 μW , the transmittance at the focusing point of Au-SiO₂ nanocomposite thin film is 135%, 118% and 112%, for M2-200-10, M2-300-10 and M2-400-10, respectively. The relationship between the

enhancement and the grain size, shape and density of distribution of the Au nanoparticles embedded in the SiO₂ thin film is a complicated issue; however, the tendency shows that the larger Au nanoparticles (only in the range from 2 nm to 10 nm) gain stronger enhancement. A detailed and quantitative analysis of their relationships requires computing for the ensemble effects of the localized surface plasmons using the actual volume ratio and grain size of all three samples. It is not an easy task to achieve using only the two-dimensional TEM images shown in Fig. 1. Instead of the estimated computation, we have measured the absorption spectra of three samples, and their results show a broad peak centered around 530 nm with redshift of the absorption peak for large-grain samples such as M2-200-10. Absorption spectra indicate the ensemble effects of the plasmon band of these gold grains embedded in SiO₂. We found that the absorption peak is around 30%, 23% and 17% for M2-200-10, M2-300-10 and M2-400-10, respectively, which correspond well with the Z-scan measurements (35%, 18% and 12%, respectively, for 532 nm wavelength) at the power of 60 μW . The strong absorption of M2-200-10 is in good agreement with the larger interaction coefficient of the larger grain size. Because the absorption of the M2-200-10 sample is almost two and three times that of M2-300-10 and M2-400-10 samples, respectively, the saturation powers of the M2-200-10 and M2-300-10 samples at the incident laser powers of 50 μW and 80 μW agree well with each other, and the expected saturation power of the M2-400-10 will be around 140 μW . These experimental results indicate that, for a 532 nm wavelength, the plasmonic excitations and saturations of the three samples can be clearly obtained in Fig. 4.

4. Conclusions

We found a novel active nonlinear optical layer for the super-RENS, which is a nanocomposite thin film with Au nano particles embedded in SiO₂. A cosputtering method is used to fabricate this nanocomposite thin film, and TEM micrographs of the film demonstrate a random and uniform distribution of the Au nanoparticles of 2 to 10 nm. Results of the Z-scan on these nanocomposite thin films indicate nonlinear optical properties and strong enhancement in transmittance. The excitation of the localized surface plasmons of the Au nanoparticles and the optical interactions between them should be the key factors. Based on the studied samples, an average 5 nm grain size of the Au nanoparticle sample (Fig. 1(a), M2-200-10) gains more enhancement in transmittance (135%) than a 4 nm or 3 nm average-grain-size sample, as shown in Fig. 1(b) or Fig. 1(c). The reason of why the ensemble effects of the LSP are stronger than that of other samples requires more quantitative study; however, a novel active layer with more than 30% optical enhancement is found and can be fabricated reproducibly under a well-controlled cosputtering process.

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Fig. 4. Ratio of the transmittance value at the focusing position to that of out-of-focus position for various incident laser powers.

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