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Pump-probe third harmonic generation kinetics of gold nanoparticle-attached aluminum-doped zinc oxide substrate

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ABSTRACT

Size-aligned gold nanoparticles (AuNPs) of 5, 10, and 20 nm were attached on aluminum-doped zinc oxide (Al–ZnO) substrates chemically using for the first time 3-aminopropyl-trimethoxysilane as a linker molecule. By using these substrates, we present the pump-probe studies of the AuNPs deposited on the Al–ZnO with the different particle sizes and inter-particle distances. The obtained results may be a consequence of interaction of surface Plasmon resonances with the intra-band contributions to the nonlinear optical susceptibilities and to the interactions with the phonons.

1. Introduction

The gold nanoparticles (AuNPs) present an enhanced interest due to possible applications in nonlinear-optical nanocomposite materials with a photonic crystal structure [1]. They may be incorporated into different dielectric matrices like polymers, glasses etc. Their optical nonlinearities were enhanced by the local Lorentz field effect. Furthermore, the highest optical nonlinearity was achieved by appropriate matching the NP sizes and inter-particle distances. Generally this sensitivity is determined to arise from structural properties including particle size, shape, spacing, and orientation polarization effects. The latter are crucial for linear and nonlinear optical responses of AuNP arrays. The major requirements to these NPs besides the high nonlinear optical susceptibilities are low losses due to absorption/scattering, good optical quality, and mechanical stability [2]. Usually the third-order nonlinear optical properties of AuNPs is achieved due to combination with extending the π-conjugated length of the ligands [3], or by ion implantation nanotechnology allowing to fabricate materials with almost any desirable metallic structures, with high size dispersion [4]. Principal roles in these cases play surrounding dielectric hosts [5]. Crucial contribution to the enhancement of the third-order susceptibilities give interaction of the surface plasmon resonances which for the AuNPs are strongly dependent on the volume fraction of the NP sizes, their inter-particle distances, morphological parameters, laser pulse duration and substrate resistance [6–8].

In the present work we study the AuNP-attached aluminum-doped ZnO (Al–ZnO) coated glass substrates. The interface between the ZnO and the metallic NPs should favor enhanced nonlinear optical susceptibilities [9]. Because the pump-probe experiments are more sensitive than the usual nonlinear optical experiments [10] in the present work we present the pump-probe studies of the AuNPs deposited on the Al–ZnO substrate with the different particle sizes and inter-particle distances.

2. Experimental

As the source of size-aligned AuNPs, gold colloid solutions of 5, 10 or 20 nm purchased from Sigma-Aldrich were used. Trichloroethylene and 3-aminopropyltrimethoxysilane (APTMS) were also obtained from Sigma-Aldrich. Aluminum-doped zinc oxide (Al-ZnO) coated glasses were purchased from Geomatec Co. Ltd., Japan.

Initially, a piece of Al–ZnO, was cleaned with trichloroethylene, ethanol and water successively. After drying at 40 °C, the substrate was immersed in ethanol containing 2% APTMS (v/v) at room temperature. Next the APTMS-modified Al–ZnO, was washed with ethanol, and subsequently dried with nitrogen blowing. Then, the APTMS-modified substrate was dipped in the solution of AuNPs (i.e., Au colloid from Sigma-Aldrich, as received) for 2 h at room temperature. After washing with water, the AuNP-attached substrate was dried at 40 °C. Fig. 1 shows the FE-SEM images of AuNP-attached Al–ZnO, recorded using a JSM-7400F field-emission scanning electron microscope (FE-SEM, JEOL, Japan).

The third harmonic generation (THG) was measured using a Q-switched Nd:YAG laser. The pulse duration and the pulse repetition rate were 12 ns and 10 Hz, respectively. The peak power density was continuously changed up to 700 MW/cm^2. A thin-film sample of AuNP-attached Al–ZnO substrate was mounted on a goniometer and rotated around an axis perpendicular to the laser beam. The laser beam was linearly polarized in a direction parallel to the rotational axis. The THG intensities of the AuNPs attached on the Al–

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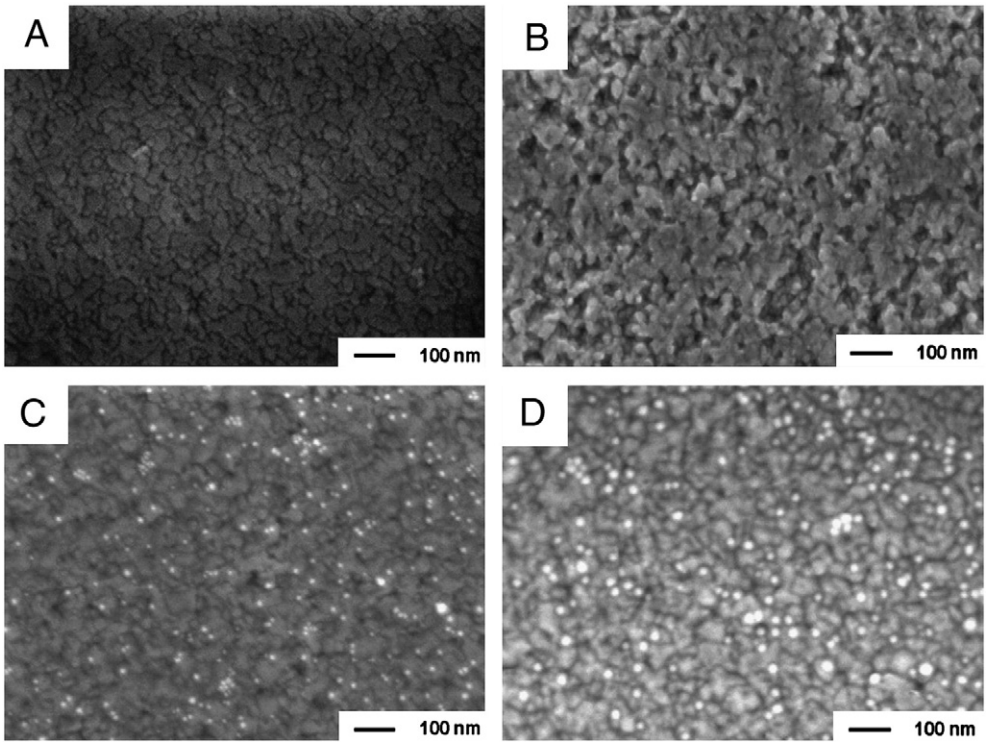

Fig. 1. FE-SEM images of AuNP-attached Al–ZnO substrates. (A) Base Al-ZnO, (B) 5-nm, (C) 10-nm, and (D) 20-nm AuNPs were chemically attached using APTMS on the Al–ZnO substrates.

ZnO were measured as function of laser incident angles. THG from the bare Al–ZnO substrate was also measured as a control. The THG intensity from the studied AuNPs showed a monotonic function of laser incident angles, while the film showed Maker fringe pattern, corresponding to consecutive optical path length variations. The third order NLO susceptibility of the AuNPs/ITO thin film was calculated by comparing the measured THG peak intensity of the film and that of the substrate using the equation reported elsewhere [11], assuming the film thickness to be much thinner than the coherence length of the film. We also assumed that the effect of the refractive index difference between the deposited film and the substrate for calculation is negligible. For the calculations we have extracted the third order susceptibility of substrate equal to 10^{-14} esu. The fundamental beam was split by beam splitter for two channels. The first one fundamental and the second one pumping. The delaying time between these two channels was varied with increment up to 15 ps.

3. Results and discussion

Fig. 1 shows the FE-SEM images of AuNP-attached Al–ZnO substrates. In Fig. 1B and C, it is recognized that the size aligned AuNPs pf 10 nm and 20 nm were attached on the surfaces. However, in the case of 5 nm AuNPs, the clear observation of AuNPs was possible as shown in Fig, 1B, which is due to the resolution the FE-SEM used. However, because the attached AuNPs of 5 nm increases the surface conductivity, a clearer image of Al–ZnO could be observed in Fig. 1B in comparison with the bare Al–ZnO of Fig. 1A.

Following Fig. 2 one can see that the maximal achieved THG signal is observed for the 5 nm samples. And for 20 nm samples the signal is compared with the noise. From the Al–ZnO substrates, it is interesting that the optimal pump-probe delaying time is varied within the 100 + 150 ps. Such times are typical for phonon relaxation processes which may be particularly crucial during the interactions with SPR and the phonon excitations. At higher pump-prove delaying times one can observe decrease of the THG which is disappeared at delaying times about 600 ps. The measurements were performed in different places of the samples and they show that the deviations of the experimental results from the average values did not exceed 3.5%. The enhancement of the temperature due to the laser photothermal effects did not exceed 0.4 K which excludes thermal factor in the effect. Moreover the incident beam diameter was changed within the 0.1–4 mm and after the output signal was averaged.

During the performed measurements beam waist at the focal plane which controlled by charge-coupled camera device and which was carried from 20 up to 75 mm was very crucial. To be ensured that the measurements are performed for the THG signal we have performed the reference measurements for the CS_2 material.

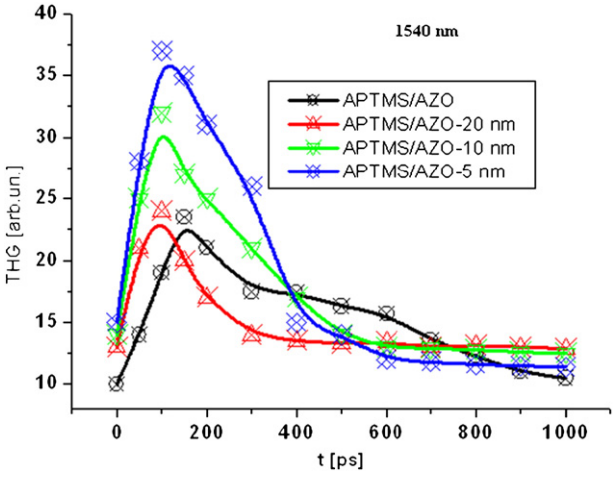

Fig. 2. Pump-probe dependence of the third harmonic generation for the 10 ns Er:glass laser for the fundamental frequency 1540 nm. The ratio between the fundamental and THG intensities was equal to 5:1. The samples indicated as APT MS/AZO correspond to the base Al–ZnO; samples APT MS/AZO-(20 nm, 10 nm, 5 nm) correspond to the samples with the attached NP of the corresponding sizes.

In order to take into account reflection losses additional determination of the reflection signal originated from the pumping and probing beams were done. To avoid an influence of the scattering background all the measurements were done using the lock-in amplifier which allows to discriminate the parasitic signals.

To explain the clear observed size dependences of the THG one can consider three principal mechanisms [12,13]: the hot-electron transitions, inter-band and intra-band contributions. However, due to the hot electron and the inter-band transitions should not be sensitive to the AuNPs and only the intra-band transitions within the s–p conduction band may be sensitive to the AuNPs. Another factor may be formation of the photoinduced phonons [8].

Generally the decrease of the third-order susceptibility, for example module of the third order susceptibility with decreasing sizes was also observed using the degenerate fourth wave mixing [14,15]. It is crucial that the maximum of the third order susceptibility is closely connected with the SPR features which in turn are dependent on the nanoparticle sizes and inter-particular distances [6].

The results presented in this work are in principal agreement with the obtained size-dependent results for other metallic NP [16]. However, in this work we show that the NLO susceptibilities are substantially dependent also on the pump-probe delaying times which are close to phonon interactions with the plasmons. This may be crucial for other studies of the metallic nanoparticles. Additionally gold nanoparticles may be promising in formation of the novel structural architecture [17] and for the photoinduced piezooptical effects which also are described by the fourth rank tensors [18].

4. Conclusions

Using the pump-probe third harmonic generation measurements for the AuNP-attached Al–ZnO substrates we have established that that the maximal achieved THG signal is observed for the 5 nm samples. And for 20 nm samples the signal is compared with the noise. From the Al–ZnO substrates, it is interesting that the optima pump-probe delaying time is varied within the $100+150$ ps. Such times are typical for phonon relaxation processes which may be particularly crucial during the interactions with SPR and the phonon excitations. At higher pump-probe delaying times one can observe decrease of the THG which disappears at delaying times about 600 ps. The studied effects are caused by a specific interaction of the size-dependent surface plasmon resonance's with the phonon subsystem. Some additional contribution may be also caused by multi-photon excitations [19].

References

[1] Tsuchiya Kosuke, Nagayasu Satoshi, Okamoto Shigeru, Hayakawa Tomokatsu, Hihara Takehiko, Yamamoto Katsuhiro, et al. Opt Express 2008;16:5362–71.
[2] Canfield Brian K, Jefimovs Konstantins, Vallius Tuomas, Turunen Jari, Kauranen Martti. J Opt A Pure Appl Opt 2005;7:S110.
[3] Lv Jing, Jiang Li, Li Cuihong, Liu Xiaofeng, Yuan Mingjian, Xu Jialiang, et al. Langmuir 2008;24(15):8297–302.
[4] Stepanov AL. In: Barret P-H, Palmer M, editors. High-power and femtosecond lasers. New York: NOVA Sci. Publ. Inc.; 2009. p. 27.
[5] Pincon N, Palpant B, Prot D, Charron E, Debrus S. Eur Phys J D 2002;19:395.
[6] Coso R, Equejo-Isidro JR, Solis J, Gonzalo J, Afonso CN. J Appl Phys 2004;95:2755.
[7] Han JB, Chen DJ, ding S, Zhou HJ, Han YB, Xiong GG, et al. J Appl Phys 2006;99:1.
[8] Kityk IV, Ebothe J, Fuks-Janczarek I, Ali Umar A, Kobayashi K, Oyama M, et al. Nanotechnology 2005;16:1687.
[9] Ozga K, Kawaharamura T, Ali Umar A, Oyama M, Nouneh K, Slezak A, et al. Nanotechnology 2008;19:185709.
[10] Kityk IV. J Non-Cryst Solids 2001;292(1–3):184–201.
[11] Kulyk B, Sahraoui B, Krupka O, Kityk IV. J Appl Phys 2009;106:093102 (1–6).
[12] Yang L, Becker K, Smith F, Magruder RH, Haghund IIIRF, Yang R, et al. J Opt Soc Am B Opt Phys 1994;11:457.
[13] Flytzanis C. J Phys B At Mol Opt Phys 2005;38:5661.
[14] Liao HB, Wen W, Wong GKL. J Appl Phys 2003;93:4485.
[15] Ma G, Sun W, tong S, Shen Z, Qian S. Opt Lett 2002;27:27.
[16] Couris S, Koudoumas E. Nonlinear optiocal response of molecules, solids and liquids: methods and applications. In: Papadopoulos MG, editor. Trivandrum, India: Research Signpost; 2003. p. 231–2540. Ch. 10.
[17] Zeng Shuwen, Liang Yennan, Lu Haifei, Wang Libo, Dinh Xuan-Quyen, Yu Xia, et al. Mater Lett 2012;67:74.
[18] Ozga K. Chem Phys Lett 2004;385:255.
[19] Plucinski KJ, Makowska-Janusik M, Mefleh A, Kityk IV, Yushanin VG. Mater Sci Eng 1999;B64:88.