

Giant Surface Plasmon Resonance Switching of Gold Nanoparticles Based on Ultrafast Phase Change of GeSbTe

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ABSTRACT

We discussed switching behavior of localized surface plasmon resonance (LSPR) of Au nanoparticles (AuNPs) associated with phase change of a GeSbTe (GST) substrate. We observed difference in the magnitude of LSPR shift and damping depending on the degree of interaction (contact area) between AuNPs and the GST film. In a static measurement, LSPR spectra of AuNPs on a crystalline GST were visibly different from those on amorphous GST, which result is almost consistent with numerical simulation. In strong contrast to this, in a dynamic measurement, we obtained giant switching of LSPR, spectral shift and reduction of scattering intensity, upon repeated amorphization and crystallization by alternate irradiations of femtosecond laser and cw annealing laser.

Key words: femtosecond laser, localized surface plasmon, nonthermal phase change

1. INTRODUCTION

Phase change materials such as chalcogenide GeSbTe (GST) compounds are widely used for rewritable optical and electronic memory applications. This is because GST meets all the requirements for data storage materials: high contrast between the amorphous and the crystalline phase in refractive index and resistance, fast write and erase speeds as well as non-volatility, and low energy consumption. Regarding the write speed, recently we demonstrated sub-picosecond nonthermal amorphization of a GeSbTe thin film with femtosecond laser pulse excitation [1]. Also in the process of erasing, we have found that for nonthermally amorphized phase, crystallization proceeds more efficiently than for the melt-quenched amorphous phase [2].

Localized surface plasmon resonance (LSPR) of metal nanoparticle provides us with a strong and highly confined electromagnetic field. The resonance can be modulated and damped by the variation of dielectric function of the surrounding medium. By combining this unique property of LSPR with the femtosecond phase change with high contrast refractive index, we can achieve ultrahigh density storage and ultrafast switching devices and, more interestingly, neuron-inspired devices by using plasticity and threshold responses of phase change materials.

In this presentation, we demonstrated switching behavior in the LSPR of gold nanoparticles on a GST thin film upon phase change between crystalline and amorphous phase.

2. EXPERIMENTS

The sample investigated was gold nanoparticles (AuNPs) with a diameter of 85 nm embedded in a polymer (polyvinyl alcohol) thin film and partially covered with a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) film, as shown in Fig. 1(a). The thickness of GST film was 30 nm. By changing the thickness d of the polymer film, we can control the degree of interaction (contact area) between an AuNP and the GST film. For $d > 85$ nm, AuNPs were not in contact with the GST film. We also investigated LSPR behavior of AuNPs directly dispersed on a GST(20 nm)/ SiO_2 (10 nm) thin film (Fig. 1(b)).

LSPR scattering from individual AuNPs was observed with a dark-field optical microscope setup under white light illumination using a color CCD camera. Single-particle scattering spectra were measured by using a liquid-nitrogen-cooled multi-channel CCD spectrometer. For amorphization of the GST film a single femtosecond pulse ($\lambda = 800$ nm) was delivered through a microscope objective and was focused on an AuNP and the underlying GST film. A

continuous wave (cw) laser diode ($\lambda=830$ nm) was used to erase the amorphous region by thermal annealing crystallization.



FIG. 1: Schematic of sample structure

3. RESULTS & DISCUSSION

Figures 2(a) and (b) are dark-field optical micrographs for $d=100$ nm and 30 nm, respectively. In both images left half part is as-deposited amorphous phase and right half part is crystalline phase created by laser annealing. In the case of polymer thickness $d=100$ nm, where there was a 15 nm average gap between AuNPs and the GST film, AuNPs exhibit various colors depending on their LSPR frequency. We do not see visible difference in color distribution between the amorphous and crystalline area. In the case of $d=30$ nm, on the other hand, AuNPs do not exhibit specific colors and look almost white (broad spectrum) as shown in Fig. 2(b). Large contact area with the GST film probably causes strong damping of LSPR due to a significant large imaginary part $\text{Im}\epsilon$ of dielectric constant of GST. Brighter scattering in the amorphous area implies less LSPR damping, which corresponds to smaller $\text{Im}\epsilon$ (for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ $\text{Im}\epsilon(\text{cry}) > \text{Im}\epsilon(\text{amo})$ in visible wavelength).

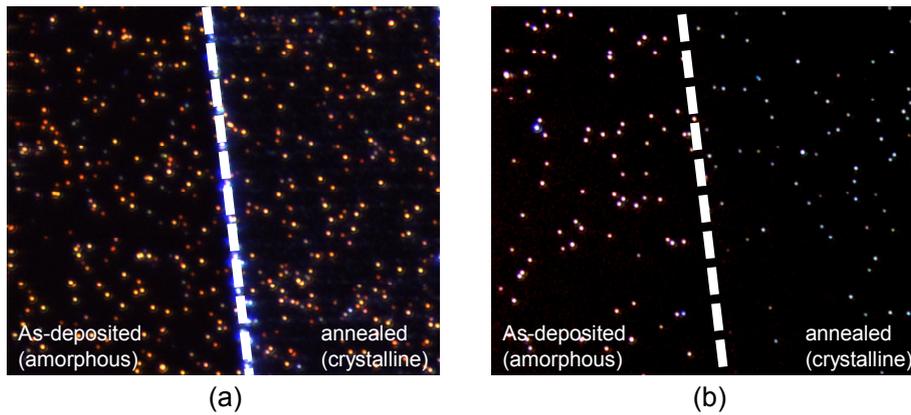


FIG. 2: Dark-field optical micrographs of AuNPs partially covered with a GST film for PVA thickness of 100 nm (a) and 30 nm (b).

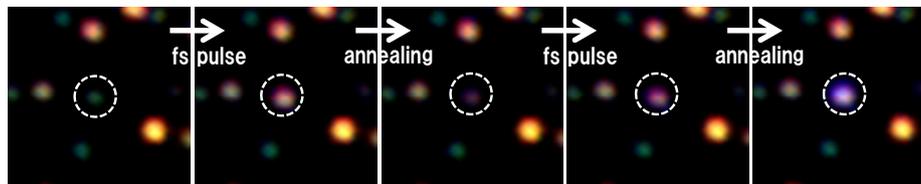


FIG. 3: LSPR switching of a single AuNP partially covered with a GST film upon phase change. The AuNP was irradiated with a femtosecond laser pulse and annealing laser alternately.

For appropriate d , at which AuNPs undergoes less LSPR damping compared to the case in Fig. 2(b), we expect a peak shift of LSPR (change in color of scattered light) upon phase change of the GST film. Figure 3 shows sequential dark-field optical micrographs of a single AuNP (encircled) taken during repeated amorphization and crystallization of the underlying GST film by alternate irradiations of femtosecond laser and cw annealing laser. A drastic and dynamic change in color of AuNP was observed. In particular a large blue shift cannot be accounted for even qualitatively in the context of optical interaction between AuNP and GST. Transformation of the polymer film, such as melting and resolidification, might be responsible for the LSPR switching.

We also investigated LSPR switching of AuNPs directly dispersed on a GST/SiO₂ film (Fig. 1(b)). Figures 4(a) and 4(b) are micrographs and scattering spectra of two different single AuNPs. In some cases, as shown in Fig. 4(a), we obtained LSPR switching just with a change of its scattering cross section and not accompanied by a change in spectral shape. In other cases AuNPs exhibit a LSPR peak shift as shown in Fig. 4(b). Among these kinds of results, one of the most drastic change is shown in Fig. 5. Upon the irradiation with a femtosecond pulse for amorphization, the LSPR scattering was completely suppressed and laser annealing led to recovery of the scattering. In all measurements we confirmed repeatability of the switching process.

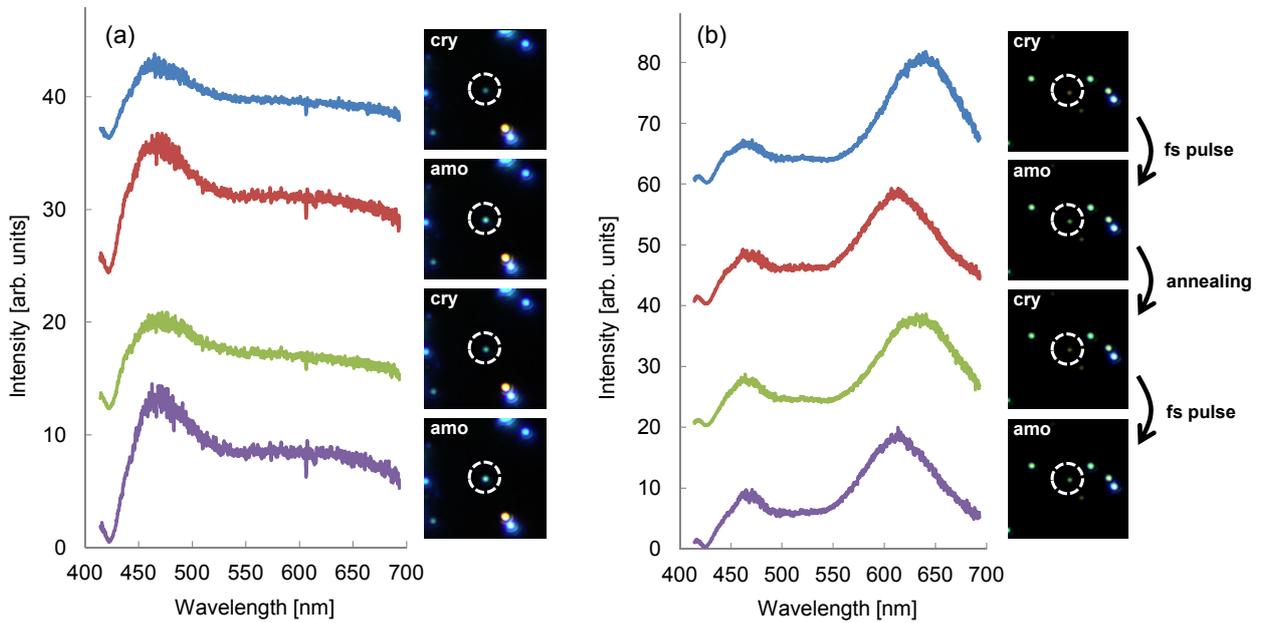


FIG. 4: LSPR switching of single AuNP dispersed on a GST thin film upon phase change. The AuNP was irradiated with a femtosecond laser pulse and annealing laser alternately.

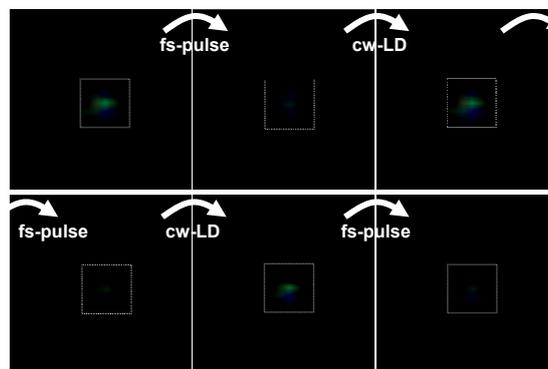


FIG. 5: A complete LSPR switching of AuNP on a GST thin film upon phase change.

We conducted numerical simulation to understand LSPR switching mechanism. Although we obtained small shift and damping of LSPR, significantly high contrast switching as shown above was not reproduced. One possible explanation is that a strong electric field originating from localized spatial charges generated by the photoexcitation may attribute to the modification of plasmon oscillation.

4. CONCLUSION

We demonstrated LSPR switching of Au nanoparticles through the interaction with a phase-change GeSbTe thin film. In dynamic measurements, where alternate irradiations of femtosecond laser and cw annealing laser was given, giant LSPR shift and damping was observed with good repeatability. The ultrafast and high contrast switching mechanism will be implemented in future active nanophotonic devices.

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REFERENCES

1. M. Konishi, H. Santo, Y. Hongo, K. Tajima, M. Hosoi, and T. Saiki: "Ultrafast amorphization in Ge₁₀Sb₂Te₁₃ thin film induced by single femtosecond laser pulse", *Appl. Opt.* **49** (2010) 3470
2. K. Tajima, N. Kitamura, Y. Hongo, and T. Saiki: "Crystallization behavior of amorphous GeSbTe nonthermally amorphized by femtosecond laser pulse irradiation", EPCOS 2011, poster presentation

Biographies

Toshiharu Saiki was born in Tokyo, Japan in 1965. He received the B.S. and M.S. degrees in physics, and the Ph.D degree in applied physics from the University of Tokyo. In 1993, he joined the Kanagawa Academy of Science and Technology (KAST), where he later became a project leader. He had been an Associate Professor in the Department of Electronics and Electrical Engineering at Keio University since 2002 and Professor since 2009.

His current research interests include near-field optical microscopy and spectroscopy in semiconductor quantum-confined systems and nanoparticles and biomolecules in solution, and ultrafast spectroscopy of phase change materials. He has developed a highly sensitive near-field scanning optical microscope (NSOM) with a spatial resolution of 10 nm and has demonstrated real-space mapping of exciton wavefunctions confined in a quantum dot.