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Nonlinear Optical Response of Metal Nanoparticle Composites for Optical Applications

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Optical response is studied for Cu nanoparticle composites with numerical calculation of the local electric field inside a metal nanoparticle. Negative Cu ion implantation was applied to fabricate Cu nanoparticle composites in amorphous SiO_2 and single crystals of $SrTiO_3$ and TiO_2. The surface plasmon resonance reflected an enhancement of the local field with red shift. Complex nonlinear optical constants were evaluated by the z-scan method with a tunable femtosecond laser system over a range from 2.0 to 2.3 eV. Third-order optical susceptibility of Cu nanoparticle composite exhibited an absolute value of 5.1×10^{-9} esu at 2.1 eV. The real part indicated negative values over the range and the imaginary part changed from positive to negative toward the higher photon energy. The both parts steeply vary with the photon energy near the surface plasmon resonance. The dispersion roughly reflects the fourth power of the local field factor.

Key words: Ion implantation, Cu nanoparticle, Nonlinear Optical Constant, Local field factor

1. INTRODUCTION

Metal nanoparticle composites, consisting of dispersed metal nanocrystals and insulating matrix, have large optical nonlinearities at the surface plasmon resonance [1-4]. The nonlinearities recently attract much attention for application to the near-field optics, photonic device and photonic sensors because of interaction with an enhanced electric-magnetic field around a metal nanoparticle [5]. To design photonic devices, it is necessary to evaluate nonlinear constants of nanoparticles at the particular wavelength and the dispersion. However there have been very few experiment studies [6] of metal nanoparticle composites. For Cu nanoparticle composites, nonlinear optical constants at several wavelengths for the pulse duration of picoseconds have been only reported [7,8]. The optical properties reflect the local electric field inside a metal nanoparticle. Ion implantation is one of the most powerful techniques to fabricate metal nanoparticles in insulating substrates. The negative ion implantation has enabled us to form metal nanoparticles in various insulators [4].

In this paper, we present optical absorption and nonlinear optical constants of Cu nanoparticle composites, fabricated in insulators by negative ion implantation. We discuss enhancement of the surface plasmon resonance by the local field factor, the photon energy dispersion of complex third-order optical susceptibility, $\chi^{(3)}$ for pulse duration of 200 fs with numerical calculations of the local field factor.

2. EXPERIMENTAL

Negative Cu ions of 60 keV were produced by a Cs-assisted plasma-sputter-type ion source with a cusp magnetic field. The details of the techniques have already been described elsewhere [9]. The dose rate was fixed at 10 $\mu A/cm^2$, achieving a total dose of 1×10^{17} $ions/cm^2$. Insulating substrates used were amorphous (a-)SiO_2 and single crystals of $SrTiO_3$ and TiO_2. Implanted samples were annealed at 800°C for a-SiO_2, and at 300°C for $SrTiO_3$ and TiO_2, for 1 hour in an Ar gas flow after the ion implantation. Ellipsometry measurements were made using a multi-angle spectroellipsometer with a rotating polarizer (SOPRA, GESP). The ellipsometry spectra were obtained in the range from 200 to 850 nm at incident angles of 55°, 60° or 65°. Complex dielectric constants of the substrate were obtained from measurements with unimplanted samples. Steady-state absorption spectra were measured using a dual beam spectrometer. Measurements of nonlinear optical constants were carried out by means of the z-scan method [10] with a tunable femtosecond-laser system providing pulses of about 200 fs at 1 kHz. These pulse duration and repetition rate are possible to avoid a thermal refraction [6]. We used an output pulse from an optical parametric amplifier (OPA) with sum-frequency mixing, generated by an idler light and a residual input pump laser. The wavelength was tuned over a wide visible range of 540 - 610 nm. The focal length of the lens was 60 mm. The beam waist at the focal point of the apparatus was about 20 μm. The maximal peak

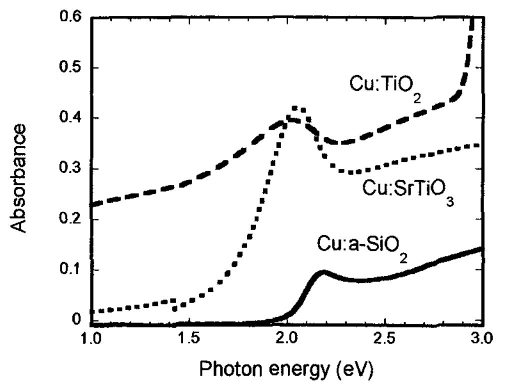

Fig. 1 Absorption spectrum of Cu nanoparticle composites fabricated in various substrates.

intensity on the spot was 8 × 10^{11} W/cm^2. All the optical experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows optical absorption spectrum of Cu nanoparticle composites fabricated in various substrates by negative ion implantation with annealing after implantation. Absorption peaks around 2 eV indicate the surface plasmon resonance corresponding to formation of Cu nanoparticles in the substrates. The peak shifts to red and increases with increasing dielectric constant of the substrate. Optical absorption of metal nanoparticle composites is written by

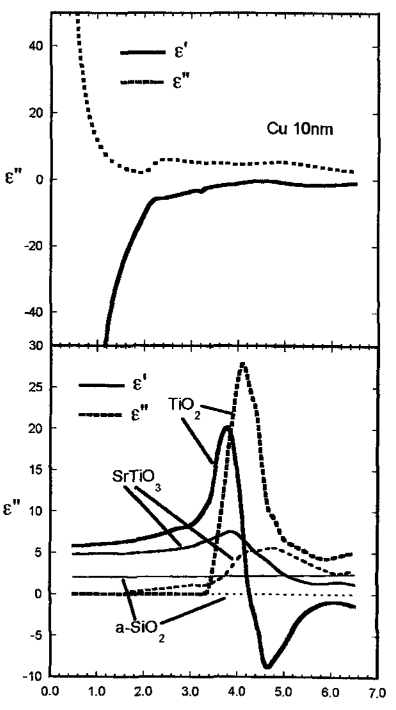

Fig. 2 Complex dielectric constant of Cu nanoparticle with a radius of 10 nm and substrates.

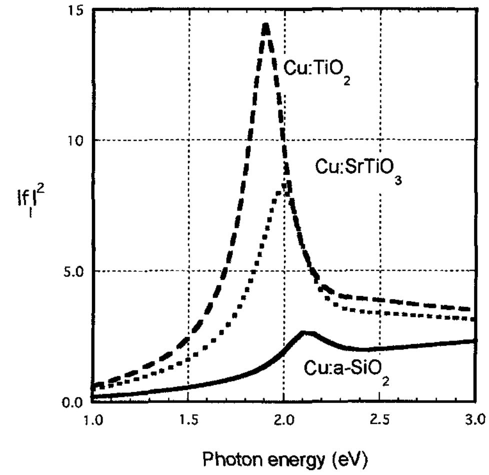

Fig. 3 Numerical Calculation of $|f_l|^2$ values of Cu:a-SiO_2, Cu:$SrTiO_3$ and Cu:TiO_2.

$$\alpha = p\frac{\omega}{n_0 c}|f_l|^2 \varepsilon_m{}'', \quad (1)$$

where p is the volume fraction of the metal nanoparticles, n_0 denotes the linear refractive index, c and ω represent the velocity and frequency of light, respectively [1]. The local field factor, f_l, is the ratio between the internal field in a spherical nanoparticle and the applied external field and is given in Maxwell-Garnett approximation by

$$f_l = \frac{3\varepsilon_d(\omega)}{\varepsilon_m(\omega) + 2\varepsilon_d(\omega)}, \quad (2)$$

where $\varepsilon_d(\omega)$ and $\varepsilon_m(\omega)$ denote the complex dielectric constants of matrix substrate and metal nanoparticle, respectively. The local field factor depends on both the metal particle and substrate. Figure 2 shows complex dielectric constant of Cu and the substrates. The dielectric constants of the substrates are evaluated by spectroscopic ellipsometry and that of Cu nanoparticles used includes a size effect through the mean free path of collisions between free electrons in the Drude model, where the radius of Cu nanoparticle is 10 nm [11]. The real parts around 2 eV represent negative and positive for Cu and substrates, respectively. The surface plasmon resonance corresponds to a minimum of the denominator in eq. (2). Numerical calculations of $|f_l|^2$ spectra for a Cu nanoparticle in a-SiO_2, $SrTiO_3$ and TiO_2 are shown in Fig. 3. With increasing dielectric constant of the matrix substrate, the resonance is enhanced with red shift. Absorption spectra as shown in Fig. 1 strongly reflect the enhanced factor.

Optical nonlinearities of the nanoparticle composite at the surface plasmon resonance are defined by a third-order optical susceptibility. The effective susceptibility $\chi_{eff}^{(3)}$ of metal nanoparticle composites is

$$\chi_{eff}^{(3)}(\omega;\omega,-\omega,\omega) = p f_l^2 |f_l|^2 \chi_m^{(3)}(\omega;\omega,-\omega,\omega), \quad (3)$$

where $\chi_m^{(3)}$ denotes the third-order optical susceptibility of metal particles [1]. The effective nonlinear optical

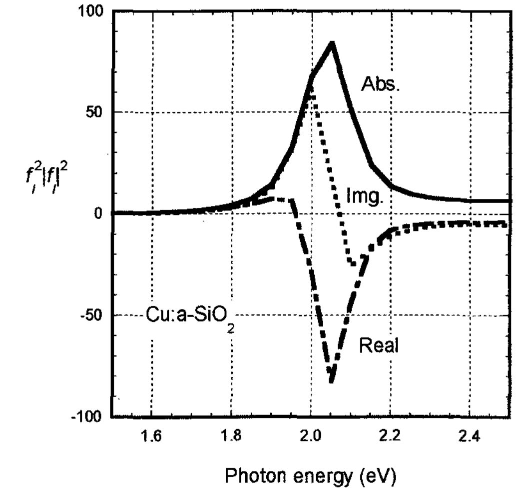

Fig. 4 Calculated dispersion curves of the fourth power of the local field factor. Solid curve: absolute value, dotted curve: the real part, dashed curve: the imaginary part.

susceptibility is enhanced by the fourth power of the local field factor, $f_l^2|f_l|^2$. Figure 4 shows numerical calculation of dispersion curves of $f_l^2|f_l|^2$ value for a Cu:a-SiO_2 nanoparticle composite. The real part of the fourth power term exhibits a negative peak near the surface plasmon resonance. The imaginary part shows a first derivative curve and the sign changes from positive to negative toward the higher photon energy. Complex third-order optical susceptibilities of a Cu nanoparticle composite are evaluated by the z-scan method [12,13]. Typical z-scan profiles of the Cu nanoparticle composite and an unimplanted a-SiO_2 are shown in Fig. 5. Optical nonlinearity of the substrate is negligible in the measurement. The measured absolute values of Cu:a-SiO_2 exhibit 5.1 × 10^{-9} esu around the surface plasmon resonance as shown in Fig. 6 and are about 10 times less than reported ones for the pulse duration of 6 ps [7,8]. The magnitude depends on the pulse duration and repetition rate. However, the measured values bear comparison with values of Ag:glass composites [6] and Au:SiO_2 composites [14] for the pulse duration of a few femtoseconds and the result shows the Cu:SiO_2 composites fabricated by ion implantation have an enough potential for applications [15]. The real part represents negative sign over the range and is maximized with a value of -3.1 × 10^{-9} esu at 2.1 eV. The imaginary part increases with photon energy and exhibits a value of +1.6 × 10^{-9} esu at 2.1 eV. Beyond 2.1 eV the sign turns to negative and the value largely decreases toward the higher photon energy. The measured dispersion is relatively similar to the calculated one as shown in the Fig. 3. However, the measured values steeply vary with the photon energy near the surface plasmon resonance. It is considered that the behavior may be reflected $\chi_m^{(3)}$ of the Cu nanoparticle and morphology of the composite. The measured dispersion of the complex effective nonlinear susceptibility is sensitive to the photon energy. The result suggests that it is important to evaluate dispersions

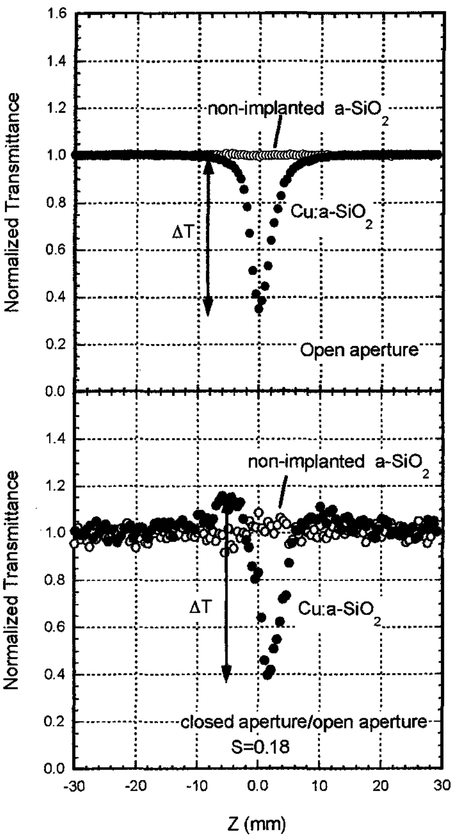

Fig. 5 Typical z-scan profiles of the Cu nanoparticle composite and an unimplanted a-SiO_2 measured by use of an open aperture and a closed aperture at 2.1 eV.

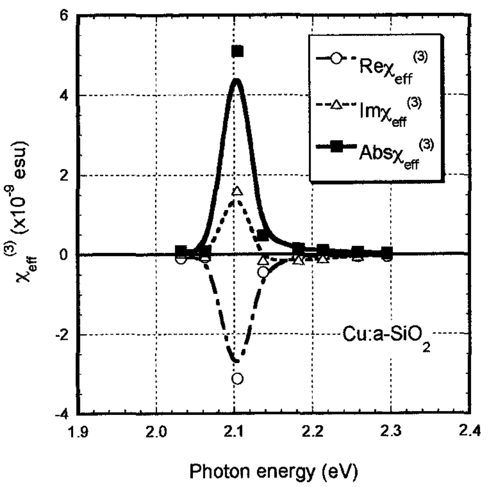

Fig. 6 Measured complex third-order optical susceptibilities $\chi_{eff}^{(3)}$ of a Cu:a-SiO_2 nanoparticle composite. Open circles denote the real part of $\chi_{eff}^{(3)}$, open triangles the imaginary part and closed squares the absolute values.

for photonic application. Additionally, we have expected metal nanoparticles in $SrTiO_3$ and TiO_2 with the higher dielectric constant to show the larger $\chi_{eff}^{(3)}$

enhanced by the local field factor.

4 CONCLUSIONS

Optical response of Cu nanoparticle composite fabricated by negative ion implantation is evaluated with numerical calculation of the local field factor. The surface plasmon peak strongly reflects an enhancement by the local field factor. Third-order optical susceptibility for the pulse duration of 200 fs exhibits values of 5.1×10^{-9} esu around the surface plasmon resonance. Both the real and imaginary parts steeply vary with the photon energy near the surface plasmon resonance. The dispersion roughly reflects the fourth power of the local field factor.

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