Copper Nanoparticle Composites in Insulators by Negative Ion Implantation for Optical Application *

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Steady-state and laser-induced transient surface plasmon bands of copper nanoparticle composites, fabricated by ion implantation, were studied by optical measurements. Negative ion implantation has been applied to generate the Cu nanoparticles with a narrow distribution in amorphous SiO₂, MgO_{2.4}(Al₂O₃) and LiNbO₃ with various refractive indices. The Cu nanoparticles were embedded within a depth of 100 nm by implantation of 60 keV Cu⁻. The surface plasmon band in steady-state absorption spectra resulted from formation of nanoparticles in the various substrates and shifted to red with increasing refractive index of the matrix. Transient absorption was measured with the technique of pump-probe femtosecond spectroscopy. The transient bleaching band also shifted in parallel with the steady-state plasmon resonance. The bleaching recovered in several picoseconds due to energy transfer from the excited electron system to the phonon system via the electron-phonon interaction. The electron-phonon coupling constant, g , of Cu nanoparticles in amorphous SiO₂ was obtained to be a value of 2.4×10^{16} W/m³K.

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1. Introduction

Metal nanoparticle composites, *i.e.*, metal nanoparticles dispersed in an insulator, have a high potential for optical applications with enhanced nonlinear optical properties.¹⁻⁴⁾ The unique properties with picosecond response is attributed to surface plasmon oscillation modes,⁵⁻⁷⁾ but the large optical nonlinearity is limited around surface plasmon resonance in the visible light region. For optical device applications, it is imperative to tune the resonance band for a photonic signal. To meet the concrete demands, the expected optical bands are 1.3 and 1.5 μ m for optical communications of trunk network, 850 and 650 nm for a local area network using plastic fibers⁸⁾ and 405 nm for high-density optical recording in future.⁹⁾ The optical property of nanoparticle composites depends on both morphology changes of a matrix and nanoparticles. Selection of matrix substrates is also vital to tune the optical band of nanoparticle composites.

The negative ion implantation at high currents has enabled us to form self-assembled metal nanoparticles in insulating substrates without applying post-implantation annealing.¹⁰⁾ Especially the negative ion implantation has the advantage of application to various insulating substrates, because of alleviation of surface charging of insulators in balance with secondary electron emission.¹¹⁾ The nanoparticles are located around a projectile range near the surface with a narrow depth distribution. The thin composites with two-dimensional structure are promising as integrated photonic device applications.

In this paper, we present nonlinear transient spectra of Cu nanoparticle composites, fabricated by negative ion implantation, in amorphous SiO₂, MgO_{2.4}(Al₂O₃) and LiNbO₃ with various refractive indices. We discuss tuning of the surface plasmon resonance of Cu nanoparticle composites, depending on the matrix, and the electron-phonon coupling constant of Cu nanoparticles, with consideration for future device applications.

2. Experimental Procedures

Negative Cu ions of 60 keV were produced by a Cs-assisted plasma-sputter-type ion source with a cusp magnetic field. The implantation technique has already been described elsewhere.¹²⁾ The dose rate ranged from 1 to 10 μ A/cm², with a total dose of 3×10^{16} ions/cm². Insulating substrates used were amorphous (a-)SiO₂, magnesium aluminate spinel MgO_{2.4}(Al₂O₃) single crystal of (100) plane and x-cut LiNbO₃ single crystal. The refractive index of the substrates, determined by spectroscopic ellipsometry, is $n = 1.47$ at 600 nm for a-SiO₂, 1.7 for MgO_{2.4}(Al₂O₃), and 2.2 for LiNbO₃. The diameter of the substrates was 15 mm and the thickness was 0.5 mm. A Cu mask with $\phi 6$ mm quadri-holes was screwed onto the substrate to avoid the local beam heating and charging if any.

Steady-state absorption spectra of the Cu nanoparticle composites were measured in a photon energy range from 0.5 to 6.5 eV using a dual beam spectrometer. Transient absorption experiments were conducted using the femtosecond pump-probe method. We used an output pulse from an optical parametric amplifier (OPA) with sum-frequency generation as a pump pulse. The OPA was pumped by a regenerative amplified Ti:sapphire laser system. The wavelength of the pump pulse was tuned, near the surface-plasmon resonance, to 574 nm (2.16 eV). The typical output energy of the OPA was 16 μ J at 1-kHz repetition rate and the pulse duration was a few hundreds of femtoseconds. To probe the change on the nonlinear absorption caused by the pump pulse, we used the white-light probe pulse generated through the self-phase modulation process in the water flow cell by the amplified pulse. The white light ranged from 400 nm to 800 nm. The pump beam was overlapped with the probe beam in the sample after traveling through a variable delay line. The diameters of the probe and the pump beams were both about 0.1 mm. The typical energy density of the excitation pulse was 36 mJ/cm², on a sample. We measured the absorption spectra by a 35 cm single monochromator with dual-diode ar-

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rays. The transient absorption spectrum was obtained by dividing the absorption spectrum with pumping by that without pumping. All the optical experiments were carried out at ambient temperature.

3. Results and Discussion

Figure 1 shows cross-sectional TEM images of a-SiO₂ implanted at 1 $\mu\text{A}/\text{cm}^2$ to 3×10^{16} ions/cm². The projectile ranges of 60 keV Cu for SiO₂, estimated with the TRIM code,¹³⁾ is 45 nm (± 15 nm). The spheres of Cu particles of about 2 nm in diameter are located within a narrow depth 100 nm near the surface. The nanoparticles spontaneously grow near the surface by a radiation-enhanced diffusion and precipitation of Cu solutes during implantation. Nanoparticle morphology in the composites is greatly dependent on the implantation conditions. At the higher dose rates up to 100 $\mu\text{A}/\text{cm}^2$, the enhanced diffusion is promoted and spherical Cu nanocrystals of 10–15 nm in diameter grow near the surface in amorphous and crystalline SiO₂.^{14,15)} On the other hand, nanoparticles in MgO_{2.4}(Al₂O₃) remain below 2–3 nm in diameter because of the radiation resistance.¹⁶⁾ Detailed studies on formation and morphology of the Cu nanoparticle by high-current negative ion implantation have been reported elsewhere.^{10,14–16)}

Steady-state absorption spectra of Cu nanoparticle composites in various transparent substrates are shown in Fig. 2. An absorption peak around 2 eV is due to the surface plasmon resonance and corresponds to formation of Cu nanoparticles in the substrates. The origin of the resonance is attributed to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field and the surface plasmon exists at the surface of the nanoparticle faced on the matrix. The resonant condition is given by the following equation:^{5,17)}

$$\varepsilon'_p(\lambda) + 2\varepsilon'_m(\lambda) = 0, \quad (1)$$

where ε'_p is the real component of dielectric constant of the metal, ε'_m is that of the medium and λ is the wavelength. The resonance position depends on both metallic particles and the substrate. According to eq. (1), the surface plasmon peak shifts to red with the increase of ε'_m because ε'_p diverges to negative infinity toward red according to the Drude model. The measured plasmon peak of Cu nanoparticle composites located at 2.14, 2.11 and 2.01 eV for a-SiO₂, MgO_{2.4}(Al₂O₃)

Fig. 1 Cross-sectional TEM images of a-SiO₂ implanted with 60 keV at a dose rate of 1 $\mu\text{A}/\text{cm}^2$.

and LiNbO₃, respectively as shown in Fig. 2 and well agrees with the estimated ones for Cu in a-SiO₂ ($\varepsilon'_m = 2.16$), MgO_{2.4}(Al₂O₃) ($\varepsilon'_m = 2.9$) and LiNbO₃ ($\varepsilon'_m = 4.8$), using the Maxwell-Garnett theory.^{18,19)} Figure 3 shows the transient absorption spectra, immediately after the excitation by the pumping laser, of Cu nanoparticle composites in the various substrates. The bleaching of the surface plasmon band is seen around the steady-state plasmon resonance. The transient positive absorption is also observed at the wings of bleaching and competes with the bleaching in intensity. The spectra show an overall similar shape among the various substrates. The optical results show the nanoparticle effectively forms in the different substrates by the implantation, because the surface plasmon peak and the transient absorption are charac-

Fig. 2 Steady-state absorption spectrum of Cu nanoparticle composites in of a-SiO₂, MgO_{2.4}(Al₂O₃) and LiNbO₃ implanted with a total dose of 3×10^{16} ions/cm². Dose rates are 1 $\mu\text{A}/\text{cm}^2$ for a-SiO₂ and 10 $\mu\text{A}/\text{cm}^2$ for MgO_{2.4}(Al₂O₃) and LiNbO₃.

Fig. 3 Transient absorption spectra, right after the excitation, of Cu nanoparticle composites in a-SiO₂, MgO_{2.4}(Al₂O₃) and LiNbO₃.

teristic of metal nanoparticles.^{5,18)} The formation in LiNbO₃, which is known as a photorefractive material, is promising as a composite material for photonic application. The transient bleaching and the positive wing are expected to be used specifically as the optical switching. It is capable to tune the band of an optical signal by selection of substrates. The nanoparticle composites can be applied to an optical switching at 1.9–2.3 eV (650–540 nm), including a wavelength for the local network, as demonstrated in Fig. 3. The transient bleaching is attributed to the change in the electronic temperature in the nanoparticle. The free electrons in nanoparticles are excited by a pumping pulse and the electronic temperature easily reaches several hundreds of degrees. The bleaching spectrum with the positive wing recovers in several picoseconds. The recovery reflects the cooling process of the excited electrons with energy transfer to the lattice in the nanoparticles.^{20,21)}

Figure 4 shows transient bleach recovery of the Cu nanoparticle composites in a-SiO₂ where the probe is located at the peak of the bleaching band. The abrupt recovery in several picoseconds corresponds to the decrease of the electronic temperature, that is, energy transfer from the excited electron system to the phonon system in the nanoparticle via the electron-phonon couplings. The residual slow decay is due to energy transfer from the nanoparticles to the host matrix. The relaxation behavior in the nanoparticle can be expressed by the two-temperature model, which describes the energy exchange between the electrons and phonons in nanoparticles by the coupled equations.^{22–24)} In the limit of low pump power, where the change in lattice temperature can be neglected, time evolution of the electron temperature is given by^{25,26)}

$$\gamma T_e \frac{dT_e}{dt} = -g(T_e - T_l), \quad (2)$$

where T_e is the electronic temperature, T_l is the lattice temperature, and g is the effective electron-phonon coupling constant.

The γ denotes the electron heat capacity constant, where $\gamma = 71 \text{ J/m}^3\text{K}^2$ for Cu. In the limit, the electronic energy relaxation time is also given by $\gamma(T_0 + \Delta T)/g$, where T_0 is the ambient temperature and ΔT is the electronic temperature increment induced by the pump pulse. Extrapolation of the measured time constants to zero power by plotting the relaxation time vs. relative pump power yields an estimate of g (from $\tau = \gamma T_0/g$). The inset in Fig. 4 shows a linear extrapolation of the relaxation time as a function of the relative pump power. The intercept shows 0.89 ps and yields $g = 2.4 \times 10^{16} \text{ W/m}^3\text{K}$ for the as-implanted Cu nanoparticles. The bulk electron-phonon coupling constant is approximately given by^{24,27)}

$$g_{\text{bulk}} = \frac{\pi^2 m_e n_e c_l^2}{6\tau_m(T_e)T_e}, \quad (3)$$

where n_e is the number density of free electron, m_e is the mass of electron, c_l is the longitudinal speed of sound in the metal, τ_m is the electron mean free time between collisions and the equation yields $g_{\text{bulk}} = 14.0 \times 10^{16} \text{ W/m}^3\text{K}$ for Cu.²⁴⁾ On the other hand, the energy transfer in the nanoparticle also occurs thorough electron-surface interactions, which couple an acoustic surface mode and a capillary surface mode with electrons.^{25,28,29)} The acoustic and capillary mode coupling constants, g_A and g_C respectively, are given by²⁵⁾

$$g_A = \frac{1}{16\pi} k_B \frac{v_F}{R^2} n_e \frac{m_e}{P} \left(\frac{\omega_D}{C_l} \right)^2 \left(\frac{V_0}{\varphi_0} \right)^2, \quad (4)$$

$$g_C = \frac{3}{16\pi} k_B \frac{v_F}{R} n_e \frac{m_e \omega_l^2}{\sigma} \left(\frac{V_0}{\varphi_0} \right)^2 \quad (5)$$

where k_B is Boltzmann's constant, v_F is the Fermi velocity, R is the particle radius, ρ is the density of metal, ω_D is the Debye frequency, V_0 is the Fermi energy, φ_0 is the work function, ω_l is the maximum frequency of the capillary modes, and σ is the surface tension. The acoustic and capillary mode coupling constants show inverse dependence on the particle radius and are estimated to be $g_A = 7.15 \times 10^{14} \text{ W/m}^3\text{K}$ and $g_C = 8.99 \times 10^{15} \text{ W/m}^3\text{K}$ for Cu nanoparticles with the radius of 1 nm. The estimated surface couplings are small relative to the bulk phonon coupling. Therefore the bulk electron-phonon coupling mainly contributes to the relaxation of excited electrons in the Cu nanoparticle and the size dependence can be neglected. It is considered that the difference between calculated bulk coupling and our measured value is ascribed mainly to the different mean free time, which reflect defects and imperfect structure in the nanoparticle. However, the transient response is possible to improve within 3 ps from over 10 ps by a suitable post-implantation annealing as we reported before.^{30,31)} Our result is also comparable to that found by Bigot *et al.*⁴⁾ ($= 3.0 \times 10^{16} \text{ W/m}^3\text{K}$ for Cu nanoparticles with $R = 10 \text{ nm}$ in doped glass), Tokizaki *et al.*³⁾ ($= 8.0 \times 10^{16} \text{ W/m}^3\text{K}$ for Cu nanoparticles with $R = 4 \text{ nm}$ in doped glass), Elsayed-Ali *et al.*²⁰⁾ ($= 10.0 \times 10^{16} \text{ W/m}^3\text{K}$ for a Cu thin film), Broson *et al.*³²⁾ ($= 4.8 \times 10^{16} \text{ W/m}^3\text{K}$ for a Cu thin film). There is no inferiority of the g -constant in comparison with the nanostructure with 2D distribution in various insulating substrates by other techniques on the as-implanted Cu nanoparticle composites by negative ion implantation.

Fig. 4 Time resolved data for Cu nanoparticles in a-SiO₂. The insert shows a linear extrapolation of lifetime as a function of the relative pump power.

4. Summary

We have been investigated Steady-state and transient absorption around the surface plasmon resonance and the electron-phonon coupling of Cu nanoparticle composites in a-SiO₂, MgO₂·4(Al₂O₃) and LiNbO₃, fabricated by negative ion implantation. The surface plasmon band in steady-state absorption shifts with the change of dielectric constant of the medium. The transient bleaching band also shifts in parallel with the steady-state plasmon resonance in the range of 2.0–2.15 eV and the transient absorption bands cover the range of 1.9–2.3 eV. The optical band can be tuned with selection of the medium. The electron-phonon coupling constant of as-implanted Cu nanoparticles in a-SiO₂ exhibits a value of $g = 2.4 \times 10^{16} \text{ W/m}^3\text{K}$. The nanoparticle fabrication by negative ion implantation is successfully attained in various insulating substrates and the nanoparticle composites have the advantage of 2D distribution and tuned optical band for the optical device application.

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