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 SiO$_2$, MgO$_{2.4}$(Al$_2$O$_3$) and LiNbO$_3$ 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 SiO$_2$ was obtained to be a value of 2.4 x 10$^{16}$ W/m$^3$K.

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. The unique properties with picosecond response is attributed to surface plasmon oscillation modes, 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 from 1.3 to 1.5 $\mu$m for optical communications of trunk network, and 850 nm and 650 nm for a local area network using plastic fibers. Insulating substrates used were amorphous (a-)SiO$_2$, magnesium aluminate spinel MgO$_{2.4}$(Al$_2$O$_3$) single crystal of (100) plane and x-cut LiNbO$_3$ single crystal. The refractive index of the substrates, determined by spectroscopic ellipsometry, is $n = 1.47$ at 600 nm for a-SiO$_2$, 1.7 for MgO$_{2.4}$(Al$_2$O$_3$), and 2.2 for LiNbO$_3$. The diameter of the substrates was 15 mm and the thickness was 0.5 mm. A Cu mask with 6 mm quadri-holes was screwed onto the substrate to avoid the local beam heating and charging if any.

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. The dose rate ranged from 1 to 10 $\mu$A/cm$^2$, with a total dose of $3 \times 10^{16}$ ions/cm$^2$. Insulating substrates used were amorphous (a-)SiO$_2$, magnesium aluminate spinel MgO$_{2.4}$(Al$_2$O$_3$) single crystal of (100) plane and x-cut LiNbO$_3$ single crystal. The refractive index of the substrates used were amorphous SiO$_2$, magnesium alumina spinel MgO$_{2.4}$(Al$_2$O$_3$) and LiNbO$_3$ with various refractive indices. The Cu nanoparticles were 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 SiO$_2$, MgO$_{2.4}$(Al$_2$O$_3$) and LiNbO$_3$ 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.

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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-SiO$_2$ implanted at 1 µA/cm$^2$ to $3 \times 10^{16}$ ions/cm$^2$. The projectile ranges of 60 keV Cu for SiO$_2$, estimated with the TRIM code, is 45 nm ($\pm$15 nm). The spheres of Cu particles of about 2 nm in diameter are located within a narrow depth 100 nm near the surface. The nanoparticles spontaneously grow near the surface by a radiation-enhanced diffusion and precipitation of Cu solutes during implantation. Nanoparticle morphology in the composites is greatly dependent on the implantation conditions. At the higher dose rates up to 100 µA/cm$^2$, the enhanced diffusion is promoted and spherical Cu nanocrystals of 10–15 nm in diameter grow near the surface in amorphous and crystalline SiO$_2$. On the other hand, nanoparticles in MgO$_2.4$(Al$_2$O$_3$) remain below 2–3 nm in diameter because of the radiation resistance. Detailed studies on formation and morphology of the Cu nanoparticle by high-current negative ion implantation have been reported elsewhere.

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:

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

where $\varepsilon'_p$ is the real component of dielectric constant of the metal, $\varepsilon'_m$ is that of the medium and $\lambda$ 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 $\varepsilon'_m$ because $\varepsilon'_p$ 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-SiO$_2$, MgO$_2.4$(Al$_2$O$_3$) and LiNbO$_3$, respectively as shown in Fig. 2 and well agrees with the estimated ones for Cu in a-SiO$_2$ ($\varepsilon'_m = 2.16$), MgO$_2.4$(Al$_2$O$_3$) ($\varepsilon'_m = 2.9$) and LiNbO$_3$ ($\varepsilon'_m = 4.8$), using the Maxwell-Garnett theory. 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. 1 Cross-sectional TEM images of a-SiO$_2$ implanted with 60 keV at a dose rate of 1 µA/cm$^2$.

Fig. 2 Steady-state absorption spectrum of Cu nanoparticle composites in of a-SiO$_2$, MgO$_2.4$(Al$_2$O$_3$) and LiNbO$_3$ implanted with a total dose of $3 \times 10^{16}$ ions/cm$^2$. Dose rates are 1 µA/cm$^2$ for a-SiO$_2$ and 10 µA/cm$^2$ for MgO$_2.4$(Al$_2$O$_3$) and LiNbO$_3$.

Fig. 3 Transient absorption spectra, right after the excitation, of Cu nanoparticle composites in a-SiO$_2$, MgO$_2.4$(Al$_2$O$_3$) and LiNbO$_3$. 
teristic of metal nanoparticles. The formation in LiNbO$_3$, 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. 

The formation in LiNbO$_3$, where the evolution of the electron temperature is given by

$$\frac{dT_e}{dt} = -\frac{g(T_e - T_0)}{\varepsilon},$$

where the change in lattice temperature can be neglected, time evolution of the electron temperature is given by

$$\gamma T_e \frac{dT_e}{dt} = -g(T_e - T_0),$$

where $T_e$ is the electronic temperature, $T_0$ is the lattice temperature, and $g$ is the effective electron-phonon coupling constant. The $\gamma$ 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 $\Delta T$ 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 gives $0.89$ 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

$$g_{\text{bulk}} = \frac{\pi^2 n_e \epsilon_1^2}{6m_0(T_e/T_e)}.$$  

Figure 4 shows transient bleach recovery of the Cu nanoparticle composites in a-SiO$_2$ 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. 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

$$\gamma T_e \frac{dT_e}{dt} = -g(T_e - T_0),$$

where $g$ is the particle radius, $\gamma$ is the density of metal, $\epsilon_1$ is the longitudinal speed of sound in the metal, $\tau_m$ 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. On the other hand, the energy transfer in the nanoparticle also occurs through electron-surface interactions, which couple an acoustic surface mode and a capillary surface mode with electrons. The acoustic and capillary mode coupling constants, $g_A$ and $g_C$, respectively, are given by

$$g_A = \frac{1}{16\pi} \frac{v_F}{R} \frac{m_e}{\rho} \frac{\omega_0}{\epsilon_1} \frac{V_0}{\phi_0}$$

and

$$g_C = \frac{3}{16\pi} \frac{v_F}{R} \frac{m_e \sigma}{\sigma} \frac{V_0}{\phi_0},$$

where $K_B$ is Boltzmann’s constant, $v_F$ is the Fermi velocity, $R$ is the particle radius, $\rho$ is the density of metal, $\omega_0$ is the Debye frequency, $V_0$ is the Fermi energy, $\phi_0$ is the work function, $\epsilon_1$ is the maximum frequency of the capillary modes, and $\sigma$ 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 reflects 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. Our result is also comparable to that reported before. Our result is also comparable to that reported before. Our result is also comparable to that reported before.

Fig. 4 Time resolved data for Cu nanoparticles in a-SiO$_2$. 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 absorption 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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REFERENCES


