Bonding of single-layered Cu$_2$O nanospheres on Cu substrates in irradiating near-infrared femtosecond laser pulses

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We investigated the bonding mechanism of single-layered Cu$_2$O nanospheres (NSs) on Cu thin films. When near-infrared femtosecond laser pulses were focused and irradiated on the Cu$_2$O NS films containing the NSs and reducing agents on Cu thin film-coated Si substrates, single-layered NSs were bonded just above the substrates after rinsing the non-bonded NSs. The minimum pulse energy for the single bonding on the Cu thin film-coated Si substrates was smaller than that on Si substrates. The electromagnetic enhancement was calculated between the Cu$_2$O NSs and Cu thin films by simulating the finite element method. The enhancement was estimated using a transverse mode of the linear polarization of the incident femtosecond laser pulses. The experimental and simulation results indicated that the single-layered NSs were bonded on the Cu thin films by femtosecond laser pulse-induced local heating and melting due to the localized plasmon enhancement between the Cu$_2$O NSs and substrates. © 2022 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

1. Introduction

A direct writing technique using femtosecond laser pulse-induced multi-photon absorption has been recognized as a robust tool for three-dimensional (3D) microfabrication. Multi-photon absorption occurs in the high-intensity region, which is beyond the threshold intensity. Therefore, photoinduced reactions occur only around the focal spot of the femtosecond laser pulses. To date, 3D microstructures of photopolymers and noble metals are fabricated using photosensitive polymers, organic–inorganic hybrid materials, and noble metal ions. For example, 3D microstructures of SCR-500 photopolymers, such as a spiral structure and a small bulb, have been successfully fabricated using two-photon polymerization. The sub-diffraction limit spatial resolution has been attained with the intensity threshold for photopolymerization. Organic–inorganic photosensitive materials have also been used in femtosecond laser pulse-induced multi-photon absorption. Finer microstructures fabricated using this technique have been employed for biological applications such as drug delivery and scaffold for cell culture. Noble metal microstructures with Au and Ag have also been fabricated using multi-photon-induced reduction. Ag and Au ions in AgNO$_3$ and HAuCl$_4$ were used as raw materials. Surfactants such as nitrogen-containing alkyl carboxylate n-decanolsarcosine sodium and polyvinylpyrrolidone (PVP), were also mixed with the ions to reduce the growth of precipitated spatial regions. However, the application of this technique to common metals, such as Cu and Ni, have not been reported because common metals are difficult to be photochemically precipitated. To overcome this problem, multi-photon absorption-induced thermochemical reduction have been applied to fabricating Cu-based 3D microstructures. Cu$_2$O nanoparticle ink containing Cu$_2$O nanospheres (NSs) and a reducing agent, was reduced and sintered to form Cu microstructures using femtosecond laser pulse-induced multi-photon absorption. The Cu$_2$O NS ink exhibited high transparency at both near-infrared (NIR) and green femtosecond laser pulses and intense absorption at half of their wavelength. In addition, the multiphoton absorption properties were examined using the z-scan method. Both femtosecond laser pulses have achieved 3D Cu microfabrication using multiphoton absorbed thermochemical reduction which is induced only around the high-intense focal point inside the Cu$_2$O NS ink. By comparing to the conventional inkjet printing, the technique allows us to write 3D Cu microstructures directly inside the ink without coating and sintering the ink layer by layer. In addition, the technique achieves vacuum free metal direct writing. In this technique, using NIR femtosecond laser pulses, single-layered Cu$_2$O NSs only adjacent to Cu thin films were bonded on Cu thin film-coated glass substrates when the femtosecond laser pulses were irradiated at low pulse energy and scanning speed conditions. It was considered that the localized plasmon resonance enhanced the electromagnetic field between the Cu$_2$O NSs and the Cu thin film, inducing the local heating and melting. However, the mechanism has not been elucidated because localized plasmon resonance is generally studied for metallic NSs on dielectric substrates or media.

Dielectric NSs on metal substrates have been recently reported for optical and optoelectric applications. For example, Cu$_2$O NSs placed on various substrates such as indium tin oxide, Si substrates, and Au films were investigated to enhance the Raman scattering. The enhanced Raman scattering by Cu$_2$O NSs on Au thin films occurred by large electromagnetic field enhancements. Dielectric Si NSs on metal substrates were also investigated experimentally and theoretically. When a p-polarized incident light (TM mode) was irradiated to the NSs on the metallic substrates, the electromagnetic field was simulated to be enhanced. Dielectric NSs on metallic substrates such as Al, Ag, Au, and Cu substrates, have been calculated using numerical simulations. It was revealed that the field enhancement in the gap between a dielectric NS and the metallic substrates was induced from surface plasmon polaritons of the metal substrates.
In this study, we investigated the mechanism of single-layered bonding of Cu$_2$O NSs on Cu thin film-coated Si substrates. We hypothesized that Cu$_2$O NSs were bonded on Cu thin film-coated Si substrates by electromagnetic field enhancement between the NSs and substrate surface. Figure 1 shows a schematic illustration of the bonding mechanism hypothesis. By considering a previous study on dielectric NSs on metallic substrates, when femtosecond laser pulses were irradiated to a Cu$_2$O NS ink film on a Cu thin film, the pulses passed through the NSs, and the electromagnetic field between the Cu$_2$O NSs on substrate surface was enhanced via a localized plasmon resonance. The enhanced electromagnetic field locally heated the boundary of the Cu$_2$O NSs and Cu thin film, indicating that the single-layered Cu$_2$O NSs were bonded on the substrate surface. To validate the bonding mechanism hypothesis, the dependence of the bonding states on the laser irradiation conditions such as pulse energy and scanning speed were experimentally evaluated. Then, the electromagnetic field analysis was also performed to consider the bonding mechanism.

2. Experimental and simulation methods

2.1. Femtosecond laser pulse irradiation method

A Cu$_2$O NS ink containing monodispersed Cu$_2$O NSs, PVP, and 2-propanol was prepared via a previously reported method. Cu$_2$O NSs were synthesized using a polyol method. Cu(NO$_3$)$_2$·2.5H$_2$O (0.20 g) and PVP (M$_w$ ~ 55 000, 0.09 g) were separately dissolved in ethylene glycol (12 ml), simultaneously adding the prepared cupric nitrate and PVP solutions to ethylene glycol (20 ml), which was heated at 160 °C for 30 min using an oil bath. After heating the mixed solution at 160 °C for 30 min using an oil bath. The injection rate of both cupric nitrate and PVP solutions was 100 ml min$^{-1}$. After heating the mixed solution at 160 °C for 15 min, Cu$_2$O NSs in the suspension solution were generated. The Cu$_2$O NSs were separated centrifugally under the condition that the rotation rate and duration were 14 500 rpm and 30 min, respectively. The separated Cu$_2$O NSs were washed two times using ethanol under the same centrifugal separation condition. Finally, the separated Cu$_2$O NSs were dispersed into 2-propanol (3.6 ml) mixed with PVP (M$_w$ ~ 55 000, 0.09 g) to prepare a Cu$_2$O NS ink.

The Cu$_2$O NS ink was spin-coated on Cu thin film-coated Si substrates (t ~ 545 μm) or bare Si substrates (t ~ 545 μm). The spinning rate and duration were 500 rpm and 10 s, respectively. The ink film was baked at 80 °C for 8 min to dry the film. The thickness of the Cu$_2$O NS ink film was ~1 μm. The Cu thin films on Si substrates were deposited via radiofrequency (RF) magnetron sputtering. The RF power, operating pressure of Ar gas, and deposition duration were, 30 W, 1 Pa, and 5 min, respectively, to deposit the Cu thin films with a thickness of ~100 nm.

NIR femtosecond laser pulses (FemtoFiber pro-NIR, TOPTICA Photonics AG) were focused on the substrate surface, Cu thin film-coated or bare Si substrates, by passing through the Cu$_2$O NS ink films. The wavelength, pulse duration, and repetition rate of the laser pulses were 780 nm, 120 fs, and 80 MHz, respectively. The laser pulses were focused on the substrate surface using an objective lens with a numerical aperture of 0.80. The Cu$_2$O NS films on the substrates were scanned in the XY directions using an XYZ-mechanical stage. Finally, non-sintered Cu$_2$O NSs on the substrates were removed by rinsing the substrates in ethanol after the femtosecond laser pulses were irradiated at various laser irradiation conditions, such as scanning speed and pulse energy. The scanning speed was fixed to 100 μm s$^{-1}$ and the pulse energy was varied in the range of 0.066–0.131 nJ.

2.2. Experimental analysis

A NS size distribution of Cu$_2$O was evaluated using images observed using a field emission-scanning electron microscope (FE-SEM, SU8230, Hitachi High-Tech). The images were processed using ImageJ to produce binary images and determine the Cu$_2$O NS diameter. The advantage of the FE-SEM observation is not to be affected by the agglomeration of the NSs. In contrast, the number of the NSs observed using FE-SEM images is not so much than the evaluation using a laser diffraction scattering technique. Therefore, we observed some area of a substrate coated with Cu$_2$O NSs. An absorption property of the Cu$_2$O NS ink film on SiO$_2$ glass substrate was evaluated using an ultraviolet–visible spectrometer (UV2600, Shimadzu). The cross-sectional observation of the Cu$_2$O NSs bonded on the substrates was also observed using FE-SEM. The cross-sections were polished using an Ar milling (IB-09020CP, JEOL).

2.3. Electromagnetic field analysis

The electromagnetic field analysis was performed using the finite element method (FEM, Comsol Multiphysics v5.6). The calculation model was simplified such that Cu$_2$O NSs were periodically placed as close packing in the XY plane to analyze the electric field around the boundary of Cu$_2$O NS and Cu thin film. To evaluate the polarization dependence on the enhancement of electromagnetic field, both sphere [Figs. 2(a) and 2(b)] and cylinder models [Figs. 2(c) and 2(d)] of Cu$_2$O on Cu thin film-coated and bare Si substrates were designed, respectively. The material properties used in the FEM simulation are shown in Table I.

3. Results and discussion

3.1. Cu$_2$O NS ink film

Figure 3(a) shows FE-SEM images of Cu$_2$O NSs synthesized using the polyol method. Spherical nanoparticles were formed. Some nanoparticles were slightly angular, which was caused by the anisotropic growth of the NSs.

Fig. 1. (Color online) A hypothesis on the bonding mechanism of single-layered Cu$_2$O NSs on Cu thin film-coated substrates.
Figure 3(b) shows the size distribution of the Cu$_2$O NSs. The mode diameter of the Cu$_2$O NSs was 0.130 μm. The diameter of 10% and 90% were 0.110 and 0.145 μm, respectively. Almost monodispersed Cu$_2$O NSs were synthesized. An absorption coefficient of Cu$_2$O NS ink film is shown in Fig. 3(c). Although the high transmittance at the laser wavelength, 780 nm, was seen, intense absorption at half wavelength, 390 nm, was seen. These results agreed with those of the Cu$_2$O NSs of ∼100 nm in diameter reported previously.13

3.2. Investigation of minimum pulse energy and bonding state

Figure 4 shows the bonding states of Cu$_2$O NSs on Cu thin film-coated or bare Si substrates. The bonding states were classified into four, single-layered, multilayered, melted NSs, and laser-induced periodic surface structures (LIPSS), in order of the increase in the irradiated pulse energy.28–31 The Si substrates were not ablated in all types after irradiating femtosecond laser pulses. The original shape of the Cu$_2$O NSs was maintained for the single-layered NSs and surface of multilayered NSs. The minimum pulse energies required for the single-layered Cu$_2$O NS bonding on the Cu thin film-coated and bare Si substrates were 0.066 and 0.109 nJ, respectively. Although the thermal diffusion on the Cu thin film-coated Si substrates was larger than that on the bare Si substrates, the minimum energy for bonding on the Cu thin film-coated Si substrates was smaller than that on the bare Si substrates. It is thought that the localized plasmon resonance enhanced the electromagnetic field between the Cu$_2$O NSs and Cu thin film. Figure 4(c) shows the FE-SEM images and EDS mappings of the cross-sectional of single- and multi-layered Cu$_2$O NSs on a Cu thin film-coated Si substrate. The NSs were bonded on the Cu thin film without significant deformation of the NSs. The interface between the Cu thin film and the Si substrate was not remarkably changed because Cu thin film exhibits high thermal conductivity. Both single- and multi-layered Cu$_2$O NSs were not reduced completely as shown in Cu and O elemental mappings. These results suggest that the contact points of Cu$_2$O NSs and Cu thin film were heated locally when the low pulse energy was irradiated.

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**Table I.** Material properties used in the FEM simulation.

| Material          | Refractive index $n$ | Extinction coefficient $k$ | Absorption coefficient |
|-------------------|----------------------|----------------------------|------------------------|
| Cu$_2$O NSs       | 2.262                | 0.025                      | 4027                   |
| Cu thin film       | 0.247                | 4.855                      | 782100                 |
| Si substrates      | 3.71                 | 0.0077                     | 1240                   |

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Figure 3(b) shows the size distribution of the Cu$_2$O NSs. The mode diameter of the Cu$_2$O NSs was 0.130 μm. The diameter of 10% and 90% were 0.110 and 0.145 μm, respectively. Almost monodispersed Cu$_2$O NSs were synthesized.

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![Figure 2](image_url) (Color online) (a) Cu$_2$O NSs and (b) Cu$_2$O cylinder models to calculate electromagnetic fields.

![Figure 3](image_url) (Color online) (a) FE-SEM image of synthesized Cu$_2$O NSs, (b) the size distribution of Cu$_2$O NSs, and (c) linear optical absorption of Cu$_2$O NS ink thin film.
3.3. Electromagnetic field analysis in the simulation
To evaluate the effect of localized plasmon resonance enhancement on the single-layered bonding of Cu$_2$O NSs on Cu thin film, the cross-sectional image of the simulation model, the electric field intensities, and absorbed electric field intensities in the Z-axis are shown in Figs. 5(a)–5(c), respectively. The electromagnetic field was enhanced on the Cu thin film-coated Si substrates using the sphere model shown in Fig. 2(a). The absorbed electromagnetic field was also enhanced between Cu$_2$O NSs and Cu thin film. By contrast, there was no enhancement on the bare Si substrates calculated using the model shown in Fig. 2(b). The p- and s-polarized incident lights (TM and TE modes) were irradiated to the Cu$_2$O cylinder model shown in Figs. 2(c) and 2(d) to evaluate the polarization dependency on the enhancement. Figure 5(d) shows the electric field intensity distribution. The electromagnetic enhancement was induced by irradiating only the p-polarized incident light. The calculated results suggested that the electromagnetic enhancement was induced by localized plasmon resonance. By considering both experimental and simulation results, the localized plasmon resonance enhanced the electromagnetic field between the Cu$_2$O NSs and Cu thin film coated on Si substrates, indicating that the Cu$_2$O NSs were bonded on the Cu thin films by local

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**Figure 4.** (Color online) (a) Relationship between pulse energy and bonding state on Cu thin film-coated and bare Si substrates. (b) SEM images of the typical four bonding states on Cu thin film-coated Si substrates, single-layered, multi-layered, melted NSs, and LIPSS. (c) FE-SEM images and EDS images of the cross-sectional single-layered NSs and multi-layered NSs on Cu thin film-coated Si substrate.

**Figure 5.** (Color online) Simulation models of (a) Cu$_2$O NSs on Cu thin film-coated Si substrate, (b) electric field intensities, and (c) absorbed electric field intensities on Cu thin film and bare Si substrates. (d) Electric field intensity distributions for a Cu$_2$O cylinder on Cu thin film-coated Si substrates.
heating and melting. Therefore, the contact points between Cu$_2$O and Cu become local heating points in this technique because Cu becomes the seed to reduce Cu$_2$O NSs to Cu in the reductive sintering process as previously reported. This technique is vacuum free, and is useful for application to the direct writing of 3D microstructures such as 3D electrical wiring of metal electrodes, and fabrication of plasmonic devices.

4. Conclusions
In this study, we investigated the bonding mechanism of single-layered Cu$_2$O NSs on Cu thin films.

(1) The minimum pulse energy required for single-layered bonding of Cu$_2$O NSs on Cu thin film-coated Si substrates was smaller than that on the bare Si substrates, although the thermal diffusion of the Cu thin film-coated Si substrates was larger than that of the Si substrates.

(2) In FEM simulation, the electromagnetic field enhancement was calculated between the Cu$_2$O NSs and Cu thin films when the p-polarized incident light (TM mode) was irradiated to the Cu$_2$O NSs. From these experiments and simulations results, it was found that the bonding of the single-layered Cu$_2$O NS was induced by the local heating and melting between the Cu$_2$O NSs and Cu thin film due to the electromagnetic field enhanced by the local plasmon resonance. This technique is useful for application to the direct writing of 3D microstructures and fabrication of plasmonic devices.

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