Fabrication of gold and silver nanoparticles with pulsed laser ablation under pressurized CO₂

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Abstract
Pulsed laser ablation (PLA) has become a promising method for the synthesis of nanoclusters for photonics, electronics and medicine. In this work PLA in pressurized CO₂ has been applied for fabrication of gold and silver nanoparticles. Laser ablation was performed with an excitation wavelength of 532 nm under various pressures (0.1–20 MPa), temperatures (40–80 °C) of CO₂ medium and ablation times (1500–9000 s). On the basis of the experimental result, it follows that structures of gold (Au) and silver (Ag) nanoparticles were significantly affected by the changes in CO₂ density. The structures of gold and silver nanoparticles also changed with an increase of ablation time. From a field-emission scanning electron microscopy (FE-SEM) image of the fabricated gold nano-structured particles on silicon wafer, it was seen that a network structure of smaller gold particles was fabricated. A similar morphology of particles fabricated from silver plate was observed. Silver particles contain nanoparticles with large-varied diameter ranging from 5 nm to 1.2 µm. The mechanism of nanoparticles fabrication could be observed as follows. Bigger gold/silver particles melted during the ablation process and then ejected smaller spherical nanoparticles, which formed nanoclusters attached on the molten particles.

Keywords: pulsed laser ablation, gold, silver, nanoparticles, supercritical CO₂

Classification number: 4.02

1. Introduction
Due to the unique characteristics of laser energy in broad applications for the nanotechnologies, there have been many important developments of laser processing methods in modern industry, especially for the urgent needs of nano-scale metallic particles and related laser processes [1]. In recent years, control of particle size, shape and distribution has become an important issue of particle fabrication with laser ablation [2–8]. Many attempts have been made for laser ablation on solid, in liquid or gas surroundings, for nanoparticle formations [9–12].

Fabrication of nanoparticles under laser ablation of solids either in gas or in vacuum has been extensively explored during the last decade. This pulsed laser ablation (PLA) technique has become a promising method for the synthesis
Figure 1. Schematic diagram of PLA with a high-pressure cell.

of nanoclusters for photonics, electronics and medicine. It provides a possibility for chemically clean synthesis nanoparticles production. In addition, the distribution of cluster size could also be controlled by carefully choosing the laser irradiation parameters and properties of the medium. Furthermore, PLA allows for easy production of colloidal metal nanoparticles. Formation of Au and Ag nanoparticles under ablation of corresponding solids by pulsed Nd:YAG laser has been reported recently [13–19]. Kamat et al [14] reported that the 40-60 nm silver particles produced by the citrate reduction method in aqueous medium undergo fragmentation when subjected to 355 or 532 nm laser-pulse excitation. Selectivity for fragmenting silver clusters into smaller ones can be achieved with the choice of the excitation wavelength. Takami et al [15] studied the irradiation of a pulsed Nd:YAG laser at 532 nm to gold particles of less than 50 nm in aqueous solution. They found that the non-spherical gold particles between 20 and 50 nm in diameter disappeared, whereas the number of gold particles of spherical shape less than 10 nm increased. The shape change and size reduction are considered to occur through melting and vaporization of the gold particles. Simakin et al [19] reported that the laser ablation of Au and Ag targets in water by a Cu vapor laser generates Au and Ag sols. They reported that the metal nanoparticles obtained after evaporation are disc-shaped (diameter in the 20-60 nm range, thickness of few nanometers). In this work PLA under pressurized CO$_2$ was used to produce the gold and silver nanoparticles. Supercritical CO$_2$ is an interesting fluid with critical temperature (31 $\degree$C) close to the ambient and an easily achieved critical pressure of 7.4 MPa. CO$_2$ is an inert, inexpensive, easily available, odorless, tasteless, environment-friendly and generally regarded as safe (GRAS) solvent. Compared with liquids, the higher diffusivity in supercritical fluid allows increased reaction rates when the diffusion limitations are great. Having zero surface tension, the supercritical fluid allows complete penetration into a metal cavity. Furthermore, the lower viscosity of supercritical fluid in comparison with liquids can reduce the solvent-cage effects and therefore increase the initiator efficiency. Since the solvent power of supercritical fluid is directly related to its density, a large variation of solubility can be achieved by simply changing the pressure and temperature of the system. Moreover, by simple pressure reduction, phase change is observed, and the supercritical fluid is transformed to a gas and the system exits without leaving any residues. Kuwahara et al [20] conducted the laser ablation of a copper target under pressurized CO$_2$ at 40 $\degree$C. They explained that the laser ablation efficiency at high pressure is several tens or hundreds of times greater than at low pressure, therefore, the PLA in supercritical CO$_2$ can be assumed to be influenced by the CO$_2$ density. An ablation crater of copper plate with a depth of 6.9 $\mu$m was found by ablating at 25 MPa with an irradiation time of 500 s. When the gold plate was subjected as a target, its surface morphology after ablation was also affected by CO$_2$ density and pressure [21]. In the present work the effects of temperature, pressure and ablation time on the fabrication of Au and Ag nanoparticles is presented.

2. Experimental section

2.1. Materials

Au and Ag plate (purity: 99.99%, thickness: 0.5 mm) commercial products purchased from Nilaco, Japan, were used for PLA target. They were used without further treatment. Silicon (Si) wafer (P, Low, 100 type, Nilaco, Japan) was used to collect the generated Au and Ag nanoparticles during experiments. CO$_2$ (purity: 99.95%) as a medium was obtained from Uchimura Co., Japan.

2.2. Experimental setup and procedure

The experimental apparatus used in this work was shown in figure 1. PLA was carried out in a high-pressure chamber (SUS 316, 110 ml volume, AKICO, Japan) with three sapphire windows. The second harmonic of a Q-switched pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray INDI-40-10, wavelength: 532 nm, pulse energy: maximum 200 mJ cm$^{-2}$ pulse, pulse duration: 8 ns, repetition frequency: 10 Hz) was used. The target was fixed in the center of a high-pressure chamber. Incident angle of the laser beam was 30$\degree$ and the laser was located 1 m from the target. Au or Ag plate (size: 1 $\times$ 1 cm) was used as the target. Liquid CO$_2$ was pressurized and pumped into the chamber using a high-performance
liquid chromatography (HPLC) pump (Jasco PU-1586, Jasco, Japan). A Si wafer was placed perpendicular to the target to collect nanoparticles. A thermocouple was inserted to the inside of the chamber, directly contacting the chamber area which controls the temperature of the PLA process. K-type thermocouples were also inserted into the chamber wall to measure the radial temperature distribution. Therefore, the chamber temperature could be controlled by a temperature controller at various temperatures (40–80 °C). The pressure of the system was varied from 0.1 to 20 MPa. A back-pressure regulator (BPR; AKICO HPB-450 SUS-316) was used to maintain a constant pressure. After the setting temperature and pressure were reached, PLA was performed for 1500–9000 s. The laser beam was collimated by a 1 mm diameter of aperture without any focusing lens. Au and Ag nanoparticles generated on the Si wafer were observed by FE-SEM (Hitachi, SU8000) and characterized by fast Fourier transformation (FFT). Particle size distribution of Au and Ag nanoparticles was also performed using image analyzer software (Image J 1.42). It was well known that SEM had capability for detecting particle diameters and morphologies, but the resolution is lost at extreme magnifications. However, SEM remains a quick method for observing the produced particles and it requires a very small sample size to operate.

3. Results and discussion

It was well known that Au and Ag nanoparticles with different sizes and shapes have been attracting much attention due to their unusual size, optical properties electrical properties, and magnetic properties. The production of Au or Ag nanoparticles by PLA is one of the alternative methods to chemical reduction technique. They were directly irradiated by pulse laser without chemical reagent as a surfactant to control the size of particles. It is a simple and versatile technique that has gained much attention because of its capability and feasibility in the production of large quantities of nanoparticles from metals. Here, under pressurized CO\(_2\), the effects of temperature, pressure and ablation time on the fabricated Au and Ag nanoparticles were observed. Typical FE-SEM images of the Au nanoparticles at various temperatures, pressures and ablation times are shown in figures 2–4, respectively. The ablations were carried out at 10 MPa and 40 °C. The conditions were maximum points of Au ablation [22].

The morphology of Au particles was basically sphere-like structure. Figures 2(a) and (b) show the FE-SEM images of Au nanoparticles at 40 and 60 °C, respectively. To be exact, the ablation was carried out at various temperatures of 30, 40, 60 and 80 °C. However, Au particles could not be collected at 30 and 80 °C due to the low ablation flux [22]. At 40 and 60 °C, the Au nanoparticles have similar structure. A bigger Au nanoparticle is surrounded by a network structure of smaller-sized Au nanoclusters in ensembles of 300–800 nm length. The network structure of Au nanoclusters may modify the properties of Au nanoparticles. Unfortunately, the absorption spectrum of the particles was not measured in this work. The attached Au nanoclusters on the Au nanoparticles may occur due to the fast coagulation and quenching of the Au atoms in the dense CO\(_2\) environment. The medium adjacent to the laser-exposed area of the target contains a significant amount of Au nanoclusters, which favors their growth and the formation of network structure [19]. As observed on the FE-SEM image, the Au nanoclusters were also spread on the Si wafer.

In figure 3 the Au particles structure varied as the pressure changed. At 5 MPa big rod-like-shaped particles were observed. At this condition, the ablation flux was low, resulting in slow melting gold. At 7 MPa, a network structure of small-sized Au nanoclusters was formed. At this condition a small amount of Au nanoclusters could be observed. Upon increasing pressure up to 10 MPa, the abundant network structure of Au nanoclusters was clearly fabricated. Clustering of Au nanoparticles in the expanding plume critically depends on the relative relevance of different interaction mechanisms between ablated metals and ablation environment including scattering, slowing down, diffusion, recombination, shock wave formation and propagation. All these mechanisms are affected by ablation medium and pressure [23]. At 20 MPa the Au nanoparticles could not be observed clearly by FE-SEM. In figure 3(d) Au-like particles are examined; however at this magnification the particles look like Au-film on the Si-wafer. It might be due to a high CO\(_2\) density pressing the Au particles to adhere on the Si-wafer.

From figure 4, the morphology of Au particles was almost unchanged with increasing ablation time. A big spherical Au particle was fabricated with the network structure of Au nanoclusters on its surface. However, the number of Au nanoclusters on the surface of the big Au particle increases with an increase in ablation time (figures 4(c) and (d)).
Moreover, with increasing ablation time, a melting big Au particle was observed. Cloud-like Au nanoclusters were formed on the surface of big Au particles. It can be explained that the increasing ablation time causes the increasing heat transfer and absorbed energy on the surface of particles that resulted in the melting of particles.

Typical FE-SEM images of the Ag particles at various temperatures, pressures and ablation times are shown in figures 5, 6 and 7, respectively. The ablations were carried out at 7 MPa and 40 °C, respectively. The conditions were maximum points of Ag ablation [24, 25]. Similar to Au particles, the morphology of Ag particles was basically
Figure 5. FE-SEM image of Ag nanoparticles fabricated by PLA at 7 MPa for various temperatures: (a) 30 °C, (b) 40 °C, (c) 60 °C, and (d) 80 °C.

Figure 6. FE-SEM image of Ag nanoparticles fabricated by PLA at 40 °C for various pressures: (a) 5 MPa, (b) 7 MPa, (c) 9 MPa, (d) 10 MPa, (e) 15 MPa and (f) 20 MPa.

sphere-like in structure. However, in the ablation of Ag plate, neither the size nor shape changed. The fabrication of Ag nanoparticles was different from the Au nanoparticles. Ag particles contain larger-sized Ag nanoparticles with larger-varied diameter ranging from 3 nm to 1.2 µm. At 40 and 60 °C bigger Ag particles melted during the ablation process and then ejected smaller spherical Ag nanoparticles, which surrounded the molten Ag particles (figures 5(b) and (c)). Moreover, the abundant smaller Ag nanoparticles were spread on the Si wafer. In these conditions, the ablation flux was strong, resulting in abundant Ag nanoparticles. On the other hand, at 30 and 80 °C the ablation was low, resulting in a small amount of Ag particles. Moreover, the Ag nanoclusters were fabricated in these conditions.

As shown in figure 6, the Ag particles structure varied as the pressure changed. At 5, 10 and 15 MPa, the Ag nanoclusters were fabricated. In these conditions, the ablation flux was not strong enough. On the other hand, at near critical pressure of CO₂ (7 and 9 MPa), a 500 nm Ag particle was formed and tended to melt into smaller Ag
nanoparticles. In these conditions the ablation flux was very strong, resulting in the melted nanoparticles. At 20 MPa, the lowest ablation flux [25], a piece of irregular Ag particle was observed. Ablation times affected the Ag nanoparticles formation (figure 7). At short ablation time, a big Ag particle was fabricated (figure 7(a)). The big Ag particle tended to be melted for further ablation time due to the increasing absorbed laser energy. Furthermore, the melting Ag particle ejected smaller Ag nanoparticles that tend to be connected to each other to form a network structure of Ag nanoclusters (figure 7(d)). As observation on the FE-SEM image, abundant Ag nanoclusters were spread on the Si wafer.

Based on the FE-SEM image of Au and Ag nanoparticles fabricated at various ablation times, the mechanism of nanoparticles fabrication might be proposed as follows. Initially big Au or Ag particles were formed. With increasing ablation time, bigger Au or Ag particles melted during the ablation process and then ejected smaller spherical nanoparticles, which formed nanoclusters attached on the molten particles. However, the smaller silver nanoparticles were also formed around the bigger silver particles. In other words, the nanoclusters were produced via direct cluster ejection upon the pulse laser material interaction. This process occurred due to the fast energy absorption by the target, which leads to the explosive decomposition of a substantial volume of the rapidly heated target material. The target material decomposition might occur through either phase-explosion or photomechanical spallation or fragmentation mechanisms. These processes took place in volume rather than on the surface and led to the ejection of a mixture of clusters. Simultaneously, the collision-affected condensation and evaporation of CO$_2$ medium in the ablated plume was also influenced on the nanoclusters formation. In this case, the process is similar to the phenomena taking place in aggregation sources. The presence of pulse laser may eject small molecules and clusters in the ablated plume producing diatomic or more molecules which represent cluster formation.

4. Conclusions

Au and Ag nanoparticles were successfully fabricated by PLA under pressurized CO$_2$. The PLA was carried out at pressures of 0.2–20 MPa, temperatures of 20–80°C for 1500–9000 s. On the basis of the experimental result, structure of both Au and Ag nanoparticles were significantly affected by the changes in CO$_2$ pressure and temperature, and the ablation time. The morphology of Au and Ag particles were basically sphere-like in structure. A network structure of small Au nanoparticles was fabricated. Ag particles contain nanoparticles with large-varied diameter ranging from 5 nm to 1.2 µm. The mechanism of nanoparticles formation was also proposed. Based on the results, we conclude that this method may also be used to obtain advanced nano-structured materials.

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