Preparation of Nanoparticles by Excimer Laser Ablation of Calcium Iron Complex Oxide

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Nanoparticles of various materials such as metal, semiconductor and oxide have been studied because of their unique physical and/or chemical properties, which are different from those of the bulk materials. For example, nanoparticles of Si have photoluminescent properties (Yamada et al., 1996). Those of Au and Co oxide in SiO_2 have nonlinear optical properties for optical devices (Kineri et al., 1995) and cause optical transmittance change by ambient gases for gas-sensor (Koshizaki et al., 1994), respectively. Their unique properties result from quantum size effects, and interface and/or surface effects.

Nanoparticles have been prepared by physical vapor deposition techniques. Granqvist and Buhrman (1976) reported the preparation of ultrafine metal particles using resistive evaporation. Some research groups have reported that sputtering can be also used to prepare nanoparticles (Hahn and Averback, 1990; Chow and Edelstein, 1992; Haas and Birringer, 1992; Terauchi et al., 1995). Since the development of laser induced chemical vapor deposition, some lasers such as CO_2 and Nd:YAG lasers have been used for the preparation of particles. Si and Si_3N_4 particles have been prepared from SiH_4 in the gas phase using laser induced chemical vapor deposition, using CO_2 lasers (Cannon et al., 1982) and using Nd:YAG lasers (Caceres et al., 1995). Kato (1976) reported the production of ultrafine particles from refractory oxide using CO_2 laser evaporation, where the CO_2 laser was used for heating the evaporation source.

Recently, the fabrication of nanoparticles using laser ablation has also been reported. Johnston et al. (1992a,b) investigated the generation of AlN and Al_2O_3 nanoparticles by XeCl excimer laser ablation of Al in N_2 and O_2 atmosphere. Si nanoparticles have been prepared by ArF excimer laser ablation of a Si wafer in inert gas of He (Yoshida et al., 1995). Juang et al. (1994) also reported the preparation of glass nanoparticles in air at atmospheric pressure with KrF excimer and Nd:YAG laser ablation. These preparation methods using laser ablation have the following advantages. The contamination of the particles is suppressed and this technique can be applied to many kinds of materials such as metals, intermetallic compounds, simple oxides, complex oxides, and polymers. The ablation process can be easily controlled by the energy and the wavelength of the irradiating laser. In the case of the evaporation technique using a resistance or induction heating, the thermal evaporation processes of the stoichiometric compound are not so easily controlled because of vapor pressure differences for the different elements. In addition, with the ablation technique nanoparticles with a narrow size dispersion are more easily obtained than by the spray pyrolysis technique.

It is well known that complex oxides such as perovskite type and spinel type oxides have various functionality originating from their stoichiometry and crystallinity. Some of these complex oxides such as calcium iron complex oxide are very useful materials for photoelectrodes, photocatalysts and gas sensors (Matsumoto et al., 1989). The complex oxide nanoparticles have more unique properties than simple component nanoparticles such as metal and simple oxide nanoparticles. However, it is very difficult to prepare complex oxide nanoparticles by evaporation because of their multicomponents and high melting point. As mentioned above, Kato (1976) studied the production of particles of refractory complex oxides such as Mg_2SiO_4, $MgAl_2O_4$ using a CO_2 laser. However, there are few studies of the preparation of complex oxide nanoparticles using laser ablation.

Pulsed excimer laser ablation has been usually used for the preparation of thin films of complex oxide such as high T_c superconductors of YBCO. In this technique the film composition easily matches with that of the target, because the excimer laser ablation mechanism is based on both a photoinduced process and a thermal process (Venkatesan, 1994). In addition complex oxide films are deposited through atoms, molecules, and molecular ions formed by excimer laser irradiation. If the reaction of these species is controlled, complex oxide nanoparticles can be also prepared by this technique.

In this article, the preparation and characterization of calcium iron complex oxide nanoparticles using ArF excimer laser ablation is demonstrated.

Experimental Studies

The target material for the excimer laser ablation was $CaFe_2O_4$ pellets prepared by the usual ceramic technique. α-Fe_2O_3 and $CaCO_3$ powders were stoichiometrically mixed,

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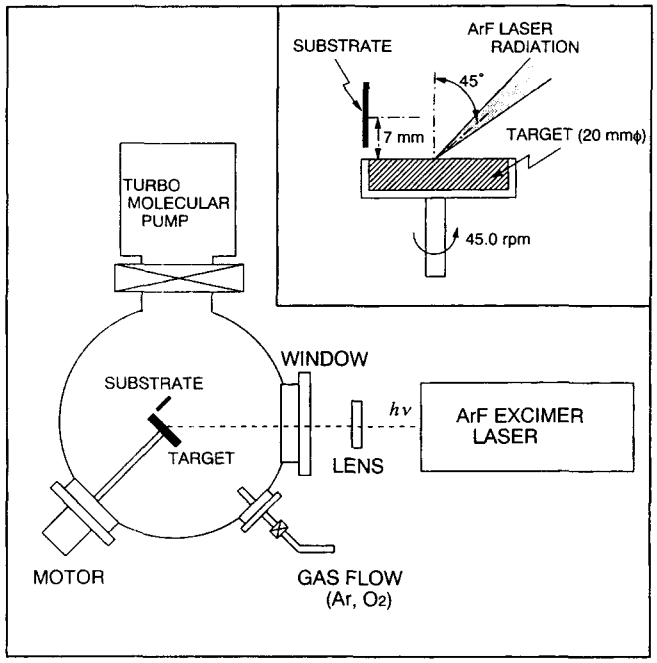

Figure 1. Laser ablation apparatus.

followed by calcining at 1,100°C for 5 h in air and firing again under the same conditions. Finally, the $CaFe_2O_4$ pellets were prepared by pressing into a pellet and sintering at 1,100°C for 5 h. The size of the $CaFe_2O_4$ pellets was 20 mm in diameter and 4 mm thick. These pellets were determined to be single-phase $CaFe_2O_4$ by powder X-ray diffraction analysis (Rigaku RAD-C). The relative densities of these sintered pellets were ca. 75%. Silicon wafers (100) (Sumitomo Sitix Co.) were used as substrates and the typical root mean square and maximum height of the surface roughness were 0.14 nm and 0.5 nm, respectively.

The preparation system is shown in Figure 1. A Lambda Physik ArF excimer laser (wavelength = 193 nm: LPX110i) was used for the ablation. The repetition rate and pulse width of laser were 10 Hz and 17 ns, respectively. The laser light was irradiated onto the target through a lens for 50 s and its power was varied from 50 to 200 mJ/pulse. A $CaFe_2O_4$ target was put on the rotating target holder in the ablation chamber and was rotated at 45.0 rpm during the irradiation by the ArF laser. Nanoparticles were deposited on the substrates at room temperature. A substrate was placed at an off axial position against the target in the chamber, as shown in Figure 1. The ablation atmospheres were varied from 0.133 Pa to 133 Pa of oxygen and argon.

Morphological observations of nanoparticles were performed using an atomic force microscope (AFM: Digital Instruments Nanoscope III). The AFM images were used to determine the size distributions of the nanoparticles. The composition and the chemical states of Fe and Ca in the nanoparticles were investigated by X-ray photoelectron spectroscopy (XPS: PHI 5600ci). The X-ray source was monochromated Al Kα (14kV, 100W). The atomic ratios of Fe/Ca in the nanoparticles were calculated from the Ca2p and Fe2p peak areas. The structures of the nanoparticles were examined by powder X-ray diffraction analysis (Rigaku RAD-C).

Results and Discussion

Usually, a substrate for film deposition by laser ablation is placed parallel to the target. As is well known, in the case of film depositions of complex oxides such as high-Tc superconductor by excimer laser ablation, a serious problem in film quality is droplet-like large particles, where particle size ranges from several hundreds of nanometers to several micrometers. The target temperature can be over the boiling point immediately upon the laser irradiation, resulting in explosive spouting of the molten target which flies directly to the substrate. Thus, droplet-like large particles are mainly emitted in a vertical direction to the target (Kinoshita et al., 1994). Actually the calcium iron complex oxide particles deposited on the substrate mounted parallel to the target at a distance of 1 cm had a very wide size distribution, where droplet-like large particles were observed. Therefore, the substrate was oriented vertically to the target as shown in Figure 1, in order to avoid the large particle deposition of complex oxides.

Typical AFM images of the top and surface of the calcium iron oxide nanoparticles which were deposited at 200 mJ/pulse in 66.6 Pa of Ar are shown in Figures 2 and 3. Nanoparticles were clearly observed and almost the same images were obtained from different parts on the substrate. As can be seen in Figure 3, the image of each nanoparticle is almost hemispherical, indicating that the real shape of these nanoparticles is spherical. Juang et al. (1994) reported that soda-lime glass microspheres could be prepared by excimer laser ablation. The shape of Si particles prepared by ArF excimer laser ablation of an Si wafer was also spherical (Yoshida et al., 1995). These results suggest that "spherical" particles can easily be prepared by laser ablation. No primary particles were observed on the surfaces of the deposited nanoparticles by AFM under high magnification. It is ambiguous, however, whether primary particles exist in the nanoparticles only from AFM observation.

The size distributions of the nanoparticles prepared at 200 mJ/pulse in 66.6 Pa of Ar (a) and O_2 (b) are shown in Figure 4. (d_{gm} is the geometric mean size of the particle.) The size of these nanoparticles was determined from AFM images. The curves in the figure show calculated distributions using the log-normal distribution function (LNDF). As can be seen, the nanoparticle size range was from 2 to 26 nm and the size distributions matched very well with the log-normal distribution. The geometric mean size and dispersion of the nanoparticles prepared in Ar were 14.0 nm and 0.19, respectively. The nanoparticles prepared by this technique were nearly monodispersed according to Fuchs' criteria (Fuchs and Sutugin, 1966) for monodispersed particles: dispersion = α = σ/mean dia. < 0.2. The dispersion of the nanoparticles prepared in O_2 was larger than that of the nanoparticles prepared in Ar. This tendency was observed for nanoparticles at all pressure ranges used in the experiment, suggesting that ablated species may react with O_2 gas in the atmosphere.

Nanoparticle size as a function of ambient pressure of Ar and irradiated laser power is shown in Figure 5. The nanoparticle size increased with ambient pressure and laser power. The maximum and minimum mean sizes of the nanoparticles prepared by laser ablation were 16.5 nm and 8.5 nm, obtained with 200 mJ/pulse in 133 Pa of Ar and 50 mJ/pulse in 0.133 Pa of Ar, respectively. Thus, the nanoparti-

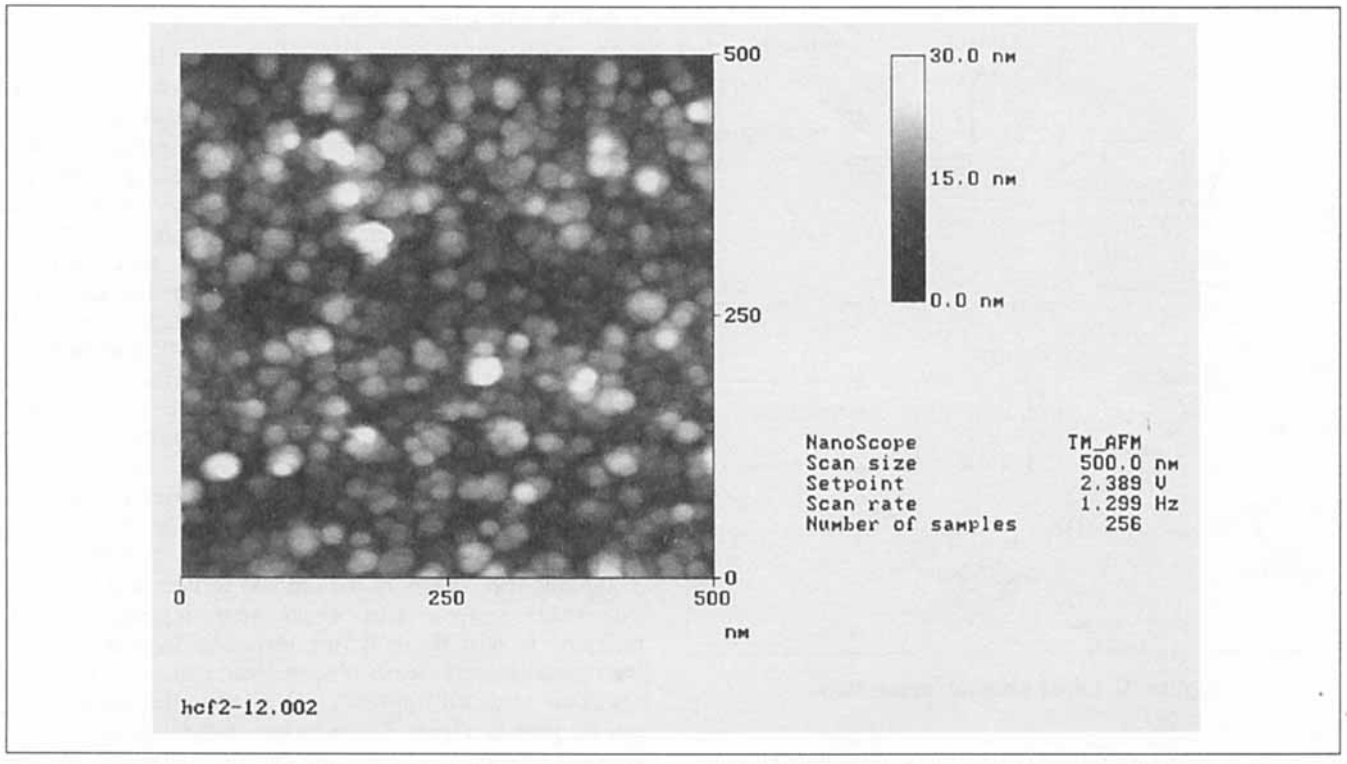

Figure 2. Typical AFM image from above of the calcium iron oxide nanoparticles deposited at 200 mJ/pulse in 66.6 Pa of Ar.

cle size can be more easily controlled in the smaller size range than in the 20 nm range by ambient pressure and laser power.

The sizes of the metal particles prepared by evaporation can be described by

$$d_m = CP^{1/3} \tag{1}$$

where d_m is mean size (nm) of the particle, P is ambient pressure (Pa) during the evaporation, and C is a proportional constant which is determined by the ambient gas species, the materials, and the evaporation temperature (Granqvist and

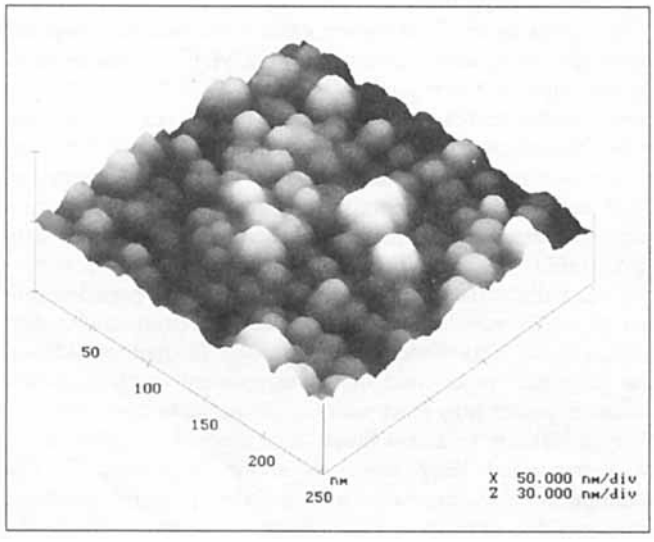

Figure 3. Typical AFM surface image of the calcium iron oxide nanoparticles deposited at 200 mJ/pulse in 66.6 Pa of Ar.

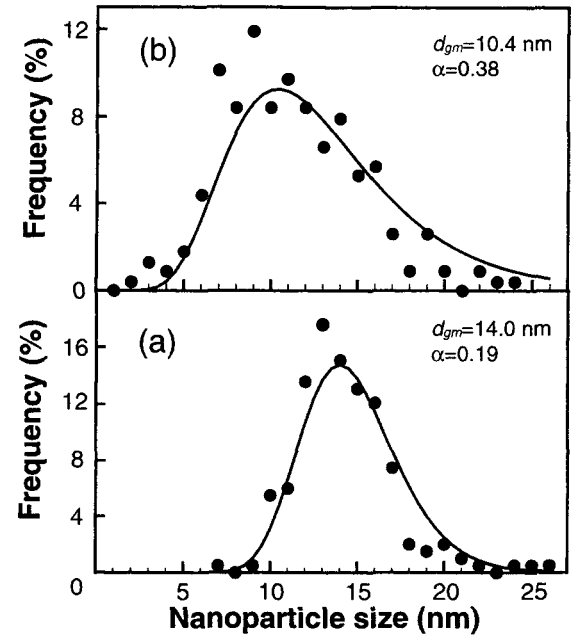

Figure 4. Size distributions of nanoparticles prepared at 200 mJ/pulse in 66.6 Pa of Ar (a) and O_2 (b) atmospheres.

The curves in the figures represent the calculated distributions obtained using the log-normal distribution function.

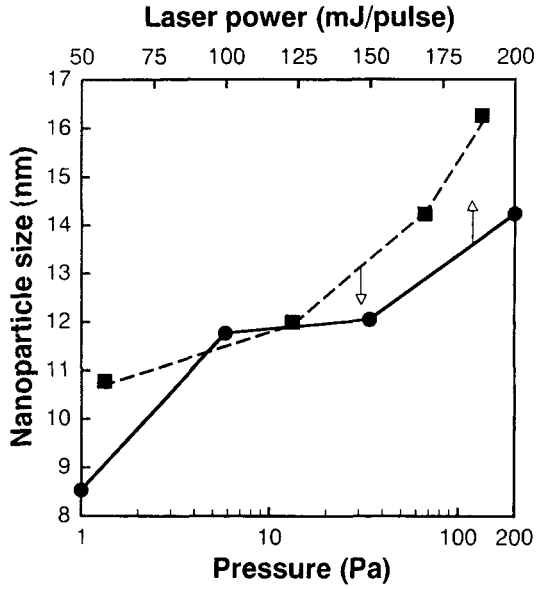

Figure 5. Nanoparticle size as a function of ambient pressure of Ar and irradiating laser power.

The nanoparticles were prepared under a constant pressure of 66.6 Pa (solid line) or at constant laser power of 200 mJ/pulse (broken line).

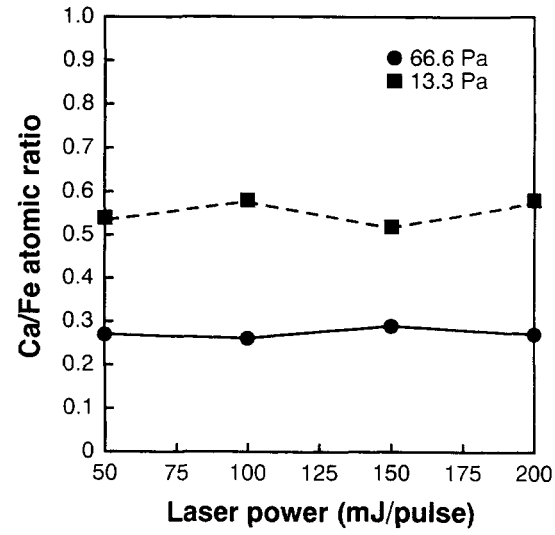

Figure 7. Ca/Fe atomic ratio in the nanoparticles as a function of irradiating laser power.

The nanoparticles were prepared under a pressure of 66.6 Pa and 13.3 Pa of Ar.

Buhrman, 1976). Yoshida et al. (1995) also reported that the sizes of the silicon particles prepared using ArF excimer laser ablation followed the above equation. In our case, the sizes of the prepared iron complex oxide nanoparticles did not follow Eq. 1, indicating that the formation process of the complex oxide nanoparticles is different from the above case. The pressure dependence of the particle size of tin oxide prepared using reactive evaporation with r.f. oxygen gas plasma did not follow the above equation either (Ogawa et al., 1981). These deviations from Eq. 1 may result from the particle formation process where the evaporated or ablated species react with oxygen species (molecular, atomic, ionic, or radical).

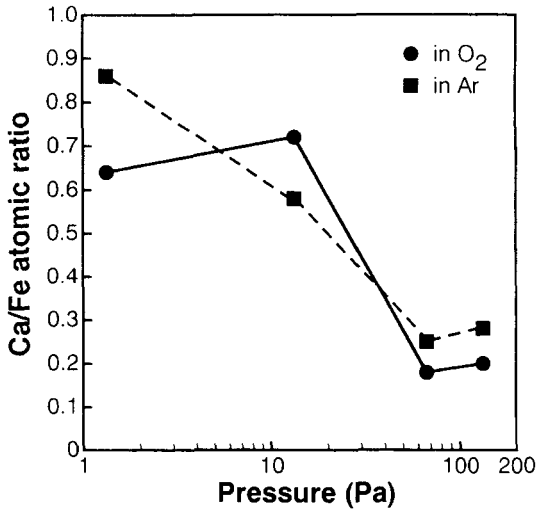

Figure 6. Ca/Fe atomic ratio in the nanoparticles as a function of ambient pressure of Ar and O_2.

The nanoparticles were prepared at 200 mJ/pulse.

The Ca/Fe atomic ratios calculated from XPS data were almost constant in different analyzed parts of a substrate where the nanoparticles were deposited. The Ca/Fe atomic ratios in the nanoparticles as a function of ambient pressure and irradiated laser power are shown in Figures 6 and 7, respectively. The Ca/Fe atomic ratios are also dependent on the ambient pressure as well as particle size. The Ca/Fe atomic ratios in the nanoparticles decrease with increasing ambient pressure, indicating that the composition of the nanoparticles can also be controlled by pressure. The Ca/Fe atomic ratios in the nanoparticles were independent of the laser power, as shown in Figure 7.

The $Fe2p_{3/2}$ peak positions in binding energy for the samples prepared in Ar and O_2 atmospheres were from 710.5 eV to 710.7 eV and 711.0 eV, respectively. The $Ca2p_{3/2}$ peak position in binding energy for all samples was from 356.5 to 346.9 eV. These peaks positions were different in binding energy from that of the $CaFe_2O_4$ target and very close to that of Fe_2O_3 (711.0 eV, McIntyre, 1977) and CaO (346.7 eV, Franzen, 1977). These results suggest that the chemical states of Fe and Ca in the nanoparticles are similar to those of Fe_2O_3 and CaO. According to the X-ray diffraction analysis of the nanoparticles, all nanoparticles were amorphous. Consequently, the nanoparticles prepared by laser ablation can consist of amorphous Fe_2O_3 and CaO.

The fact that the composition did not depend upon laser power may be indicative that the material is ablated as clusters from the molten target and preferential loss of Ca from the cluster surface during the flight to the substrate. The dependency of nanoparticle size upon ambient pressure during ablation suggests that the nanoparticles may be formed through a vapor condensation process where the nucleation and growth of the particles will proceed. However, it is not yet possible to determine the mechanism of the nanoparticle formation process. This technique is very useful for the

preparation of monodispersed spherical nanoparticles of complex oxide, in which the size and composition of the nanoparticles can be easily controlled by pressure and laser power.

Conclusions

In summary, we have demonstrated a new method for preparing nanoparticles of calcium iron complex oxide with a diameter range from 2 to 26 nm using ArF excimer laser ablation. From AFM observation, it was determined the shape of the nanoparticles was spherical. The size distribution of the nanoparticles deposited on the substrates placed at off axial positions against a target was very narrow and followed a log-normal distribution. The size of the nanoparticles was dependent on both the ambient pressure and laser power. The Ca/Fe atomic ratios in the nanoparticles were dependent on the ambient pressure but were independent of laser power. By this technique, the size and composition of nanoparticles can be easily controlled by the laser power and pressure during the laser ablation. In addition the nanoparticles obtained were nearly monodispersed. It was inferred from XPS and XRD measurements that the nanoparticles prepared by laser ablation consisted of amorphous Fe_2O_3 and CaO.

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