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Laser Breakdown Spectrochemical Analysis of Microparticles in Liquids

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A focused pulsed laser beam was irradiated on a $CaCO_3$ microparticle in water, and a laser breakdown of single microparticle was induced. In the laser breakdown plasma emission spectrum, the emission lines of Ca I and Ca II were observed, while these lines did not appear for the Ca^{2+} aqueous solution. Hence this method is effective for analysis of microparticulate impurities in liquids.

Recently, technologies such as semiconductor and biochemical engineering require extremely pure liquid reagents including ultrapure water. Particularly fine and ultrafine particulate impurities in solution, which become the cause of breaking the insulation between the wiring patterns on ultralarge scale integrated circuits, need to be removed. Therefore, a novel method for detecting and analyzing such particulate impurities has been desired. We have presented a laser breakdown acoustic method, in which an optical breakdown of the ultrafine particles is induced by irradiation of a focused pulsed laser beam and the ultrafine particle is counted individually by detecting the strong acoustic emission accompanying its plasma formation.[1,2] In addition to the acoustic emission, laser breakdown of the particulate substances accompanies a plasma emission, which may allow to perform spectrochemical analysis. This method has been applied for gas, liquid and solid samples.[3-5] Therefore, there is a possibility of spectrochemical analysis of the particulate substances in liquids as well as counting by the acoustic method. In the present paper, a laser breakdown plasma emission spectrum of a $CaCO_3$ particle is reported and the spectrochemical analysis of the particle components are discussed. In comparison with the laser breakdown plasma emission spectrum of the $CaCO_3$ particle in water, that of Ca^{2+} aqueous solution is examined.

An experimental setup of the laser breakdown spectrometer is shown in Fig. 1. The beam source is a pulsed Nd-YAG laser, and the excitation beam is the 1064 nm fundamental emission line. The near infrared fundamental emission line was selected so as not to obstruct obtaining a visible and ultraviolet spectrum. The laser breakdown threshold of the particulate substances was on the order of 10^{10} W/cm^2 and those of the liquid medium and air were 10^{11} and 10^{12} W/cm^2, respectively.[1] Hence the output energy of the excitation beam was set at 150 mJ and

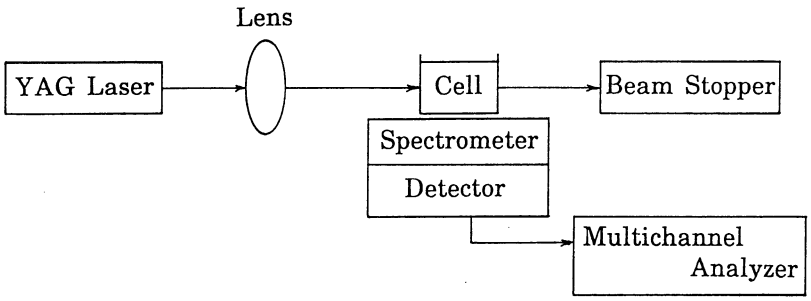

Fig. 1. A block diagram of the experimental apparatus.

focused with a convex lens of 50 mm focal length. Under these conditions, the power density of the focal region, where the laser breakdown was induced, was calculated to be 2.0×10^{13} W/cm^2, and this was sufficient for laser breakdown of both the $CaCO_3$ turbid particle and the Ca^{2+} aqueous solution.

A rectangular quartz cell used had the dimensions of 100 mm, 50 mm,and 100 mm for the width, length,and height, respectively. The excitation beam passed along the 50 mm length direction, and laser breakdown was induced at the center of the cell. Every side of the cell was made of quartz, and the laser breakdown plasma emission was collected through a lens from one side of the cell. The collected laser breakdown plasma emission was focused on the entrance slit of the concave grating polychrometer of 250 mm focal length. The spectrally resolved plasma emission was detected by a microchannel plate image intensifier and a 1024 channel photodiode array; hence the total wavelength resolving power of the present spectroscopic system was about 0.1 nm for a spectral range of about 100 nm.

The samples used were a $CaCO_3$ particle turbid solution and a Ca^{2+} aqueous solution. The sizes of the $CaCO_3$ particles, as determined by scanning electron microscope observation, ranged from 5 to 15 μm. Powdered $CaCO_3$ particles were dispersed in ultrapure water in which particulate impurities larger than 0.2 μm were completely removed. The weight concentration of the $CaCO_3$ turbid solution was adjusted to 33 ppm(μg/ml) by stepwise dilution. At this sample concentration, the particle number expectation in the focal region, in which the calculated volume was 1.3×10^{-4} ml, was estimated to be about 1.0. Under this condition, only one $CaCO_3$ particle was expected to be broken down for every pulse shot. The Ca^{2+} aqueous solution was prepared in the same manner as the $CaCO_3$ turbid solution. The concentration of Ca^{2+} was 14 ppm, at which the Ca concentrations were kept the same for both solutions.

The laser breakdown plasma emission spectrum of the $CaCO_3$ turbid particle was measured in the spectral range between 350 - 450 nm. The repetition rate of the excitation beam was 10 pps. The laser breakdown plasma emission spectrum was obtained by accumulating the plasma emission spectrum data for ten times. The obtained spectrum is shown in Fig. 2. The spectrum for Ca^{2+} solution was then measured under the same experimental conditions and is also shown in the same figure.

In the spectrum of the $CaCO_3$ particle, the Ca II lines at 393.4 nm and 396.9 nm, and the Ca I line at 422.7 nm are clearly seen on top of the white background

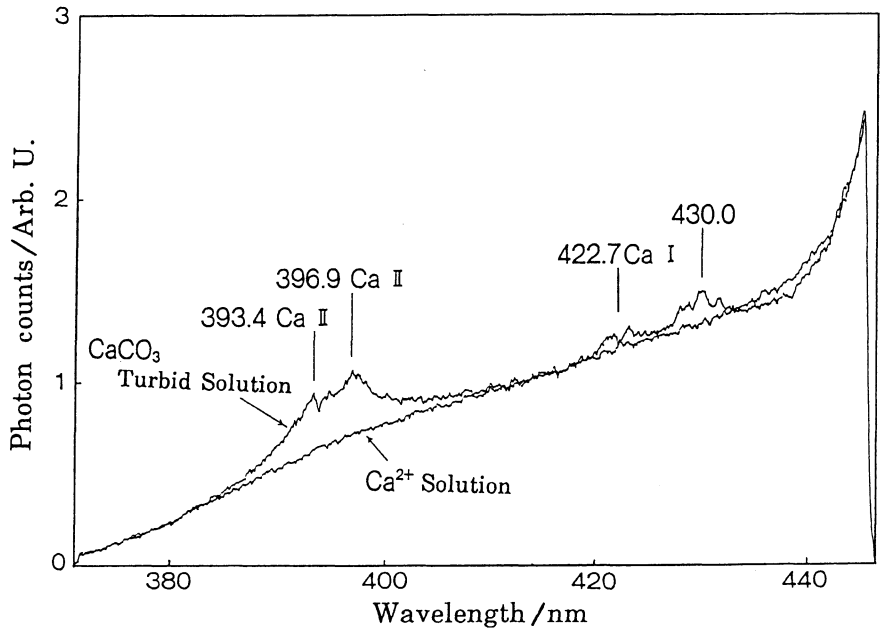

Fig. 2. Laser breakdown plasma emission spectra of a $CaCO_3$ microparticle and Ca^{2+} aqueous solution.

which is considered to be due to radiative recombination and black body radiation in the plasma. Therefore, spectrochemical analysis of the particle component by laser breakdown spectroscopy is verified. The spectral lines of carbon and oxygen do not appear in the observed spectral region, because these lines lie in the ultraviolet region. At 430.0 nm, triplet emission lines, which are assigned to neither the Ca I nor Ca II lines, are also observed. Assignment of these emission lines is not clear presently, however these lines may be assigned to the emission lines of Ca ions in higher valence states in the breakdown plasma. The two spectral lines of Ca II appear to be rather broad. The broadening of the spectral lines is considered to be due to Stark effect under high electron density which was estimated at 10^{18} cm^{-3} in underwater laser breakdown plasma.[6] Self absorption effect can be seen at the Ca I 422.7 nm line, which also seems to be resulted from the high electron density in the induced plasma.

These Ca I and Ca II emission lines shown in the laser breakdown plasma spectrum of the $CaCO_3$ particle do not appear in the spectrum of Ca^{2+} aqueous solution. In the case of particle breakdown, laser breakdown plasma is formed at the particle because the breakdown threshold of the particle is lower than that of liquid medium,[1,7] while in the case of the Ca^{2+} solution, the laser breakdown is induced in the whole part of the focal region in the solution. The Ca atoms in the $CaCO_3$ turbid solution are spatially localized as a particle in comparison with Ca^{2+} ions in aqueous solution, although the macroscopic Ca concentrations are the same in both samples. Hence, the concentration of Ca in the particle breakdown plasma is considered to be higher than that of the breakdown plasma in the Ca^{2+} aqueous solution. Therefore, the Ca II and Ca I lines appear only in the spectrum of the $CaCO_3$ particle breakdown plasma emission because of the high concentration

of Ca in the plasma. Therefore, laser breakdown spectrochemical analysis is more sensitive for turbid solutions than for true solutions.

The excitation potential of Ca II from the ground state of neutral Ca including its ionization potential is 15.2 eV, while the one photon energy of the excitation beam is 1.2 eV. Hence it is difficult to attribute the laser breakdown mechanism of the particle to multiphoton processes, because absorption of over 13 photons is required for the multiphoton processes. Thermal excitation processes may be responsible for these emission lines.[8)]

The spectrochemical analysis of particulate substances by laser breakdown spectroscopy has been verified. The counting and analysis of the ultrafine particle with the laser breakdown acoustic spectroscopy, in which the acoustic and plasma emission are measured at same time, is expected to be an effective method for characterization of particulate substances in liquids. The detailed characterization of the laser breakdown plasma and the mechanism of the laser breakdown of particles in liquids are now under investigation.

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