Particle Element and Size Simultaneous Measurement Using LIBS

Muneaki Wakamatsu  Non-member  (Waseda University The Graduate School of Information, Production and Systems)
Satoshi Ikezawa  Member  (Waseda University The Graduate School of Information, Production and Systems)
Toshitsugu Ueda  Member  (Waseda University The Graduate School of Information, Production and Systems)

Keywords: LIBS, time measurement, laser breakdown, particle measurement technology

We have developed high-sensitivity in-situ measurement technology based on photons with visible to ultraviolet wavelength bands. This measurement technology builds on plasmatizing particle technology and a high-sensitivity measurement technology for measuring photons from the plasma. Thus, we have established a technology for measuring particle sizes and the constituent element content of particles with 10% accuracy.

The method of using light (photons) as a means for measuring a variety of quantities in situ is advantageous, as it is non-intrusive to the object being measured and can precisely measure the quantity in real time. The size of particles, which is for example often a pivotal issue in the semiconductor manufacturing process, and that can be measured at present, is limited to 0.1 µm. Another serious problem we face is that it is impossible to identify the constituents that compose the particles \(^{1(2)}\). In this paper, we will report on the technologies necessary for particle measurement \(^{3}\) based on laser-induced breakdown spectroscopy (LIBS) which we propose as a solution to the problems mentioned above \(^{4(5)}\).

In this paper, we will report how we built the experimental system necessary for LIB-based particle measurement. We will also report the results of particle measurement using sodium chloride, lithium chloride, and a mixture of sodium chloride and lithium chloride, and give our consideration of the results.

The experimental system is shown in Figure 1. We used a commercially available flash lamp–excited Nd:YAG laser for the experimental system. This laser features a pulse duration of 8 ns, an output power of 300 mJ/pulse (maximum), and a repetition frequency of 10 Hz. In this system, a lens with a 150-mm focal length was used to condense laser beams. Using a particle generator, we produced salt particles 30 to 50 nm in diameter by dispersing salt water into the atmosphere to evaporate the water and dry out the salt particles. The salt particles thus produced were introduced through a pipe to a particle counter, in order to monitor the amount and sizes of the produced particles. On the other hand, the particles introduced into the cell are broken down by condensed pulse laser beams and turned into a plasma. Plasma produced at this point, and the light emitted as the result of energy transition due to recombination are separated into their spectral components by means of spectrometers. The resulting spectral data is recorded on a streak camera as a function of time. Then, the data is fed to a computer for signal processing. The time resolution available with a streak camera is 10 ps or higher.

Using the standard samples containing sodium chloride and lithium chloride in different ratios, we conducted a test of constituent measurement. In the test, we measured the content of NaCl and LiCl in the standard samples from the spectrum intensity of sodium and lithium.

Figure 2 shows the results of this test. The measurement deviation from the theoretical figure is as small as 8%.

---

---

---

---

---

---
Particle Element and Size Simultaneous Measurement Using LIBS

Muneaki Wakamatsu*  Non-member
Satoshi Ikezawa*  Member
Toshitsugu Ueda*  Member

We have developed high-sensitivity in-situ measurement technology based on photons with visible to ultraviolet wavelength bands. This measurement technology builds on plasmatizing particles technology and a high-sensitivity measurement technology for measuring photons from the plasma. Thus, we have established a technology for measuring particle sizes and the constituent element content of particles with 10% accuracy.

Keywords: LIBS, time measurement, laser break down, particle measurement technology

1. Introduction

The method of using light (photons) as a means for measuring a variety of quantities in situ is advantageous. The size of particles, which is for example often a pivotal issue in the semiconductor manufacturing process and that can be measured at present, about 40 nm(1). Serious problem we face is that it is impossible simultaneously to identify the constituents that compose the particles and to measure the size of particles(2,3). In this paper, we will report on the technologies necessary for particle measurement(4) based on laser-induced breakdown spectroscopy (LIBS) which we propose as a solution to the problems mentioned above(5).

In this paper, we will report how we built the experimental system necessary for LIB-based particle measurement. We will also report the results of particle measurement using sodium chloride, lithium chloride, and a mixture of sodium chloride and lithium chloride, and give our consideration of the results.

2. Experimental System

In order to measure the size and constituents of particles, we have assumed the following process of laser plasma formation.

1. The volume of a particle increases as evaporation begins in particle surfaces by laser radiation.
2. Evaporated substance quickly ionizes once the intensity of a laser beam exceeds the breakdown threshold.
3. The ionized substance absorbs the energy of the laser beam and becomes hotter as it continues receiving laser pulses. The substance cools down slowly when it stops receiving laser pulses.
4. In the beginning, the absorption coefficient of the laser beam is dependent on solid absorption. A gas plasma produced in this case is transparent. The scale of a gas plasma is nearly the size of a particle, where we believe a plasma involves resonance. Assuming the plasma temperature is sufficiently high, then the laser absorption coefficient is large enough for plasma resonance to take place.

The experimental system is shown in Figure 1. We used a commercially available flash lamp excited Nd:YAG laser for the experimental system. This laser features a pulse duration of 8 ns.
output power of 300 mJ/pulse (maximum), and repetition frequency of 10 Hz. In this system, a lens with a 150-mm focal length was used to condense laser beams. Using a particle generator, we produced salt particles 30 to 50 nm in diameter by dispersing salt water into the atmosphere to evaporate the water and dry out the salt particles. The salt particles thus produced are introduced through a pipe to a particle counter, in order to monitor the amount and sizes of the produced particles. On the other hand, the particles introduced into the cell are broken down by condensed pulse laser beams and turned into a plasma. Plasma produced at this point and the light emitted as the result of energy transition due to recombination are separated into their spectral components by means of spectrometers and the resulting spectral data is recorded on a streak camera as a function of time. Then, the data is fed to a computer for signal processing. The time resolution available with a streak camera is 10 ps or higher.

2.1 Production of Particles Using JSR's NANOMASTER particle generation system, we generated the particles from salt water. For comparing with the measurement result of the LIBS, we measured the particle size and number of produced particles which varied depending on the concentration of salt water with the TSI's SMPS (Scanning Mobility Particle Sizer). The SMPS is constituted of the DMA (Differential Mobility Analyzer) and the CPC (Condensation Particle Counter). The DMA passes particles which have particular mobility. And after that the particular mobility particles are counted with CPC. In the tests, we used five types of salt water with different concentrations ranging from 1 mol/l to 0.001 mol/l. Like the standard particle-dispersed liquid, these types of saline were turned into liquid particles using the NANOMASTER, along with dry air, so that the liquid was removed and the particles were produced. The flow rate of the gas used to dry the particle-dispersed salt water was approximately 60 l/min, the same rate used when the liquid of standard particles was prepared. The results of this test are shown in Figure 2. The diameter of salt particle is calculated of geometric mean of four hundreds times measured particles. From the figure, we can understand that salt particles approximately 30 to 50 nm in diameter are produced as the salt water concentration is varied and the size is monotonous to the concentration. In order to produce particles other than those of salt, we tested a lithium solution in the same way as the salt water. The test results were almost the same as those of the salt water in terms of the particle size and the number of particles produced.

One of our research objectives, however, was the simultaneous measurement of multiple constituents. In order to meet this objective, it is necessary to generate particles that contain plural constituents in a variety of ratios. To produce these particles, we mixed the solutions of salt and lithium chloride in arbitrary ratios to form material solutions. The distribution of particle sizes was measured using the SMPS. The constituents of the particles thus produced are thought to contain NaCl and LiCl in the same ratio as the mixing ratio of the original solution. By using this same method, we could produce particles that contained NaCl and LiCl in arbitrary ratios. According to our tests, the average particle size and size distribution of the multi-constituent particles produced are almost the same as those obtained using the solution of salt, regardless of the ratio at which the above-mentioned two types of solution are mixed.

2.2 Breakdown Testing Methods The region in which laser beams can be condensed onto particles to cause breakdown is shaped like an extremely thin cylinder, measuring only 0.1 mm in diameter in the case of the laser currently being used in our tests. Accordingly, the system is configured so that particles are jetted in a straight line from a nozzle mounted within the breakdown cell to reach the focal point of the laser. Assuming the average particle-to-particle distance is close to the diameter of focusing, laser pulses, even when emitted at any desired timing, will always hit particles and cause them to break down.

Now, we will discuss the concentration of particles produced by the particle generator and the distance between particles at the tip of the nozzle from which the particles are jetted into the breakdown cell. Figure 3 shows the breakdown cell. In the case of the breakdown cell, particles are introduced from the top of the nozzle and forcibly expelled by a vacuum pump from a pipe mounted on the bottom of the nozzle.

Figure 4 shows the results of calculating an average particle-to-particle distance when particles are introduced into the breakdown cell, assuming the concentration of particles in the air is $10^9$ to $10^{12}$ pieces/cc under atmospheric pressure.

![Fig. 2. Sizes of Salt Particles Produced from Solutions at Different Concentrations. Square:experimental result. Line:approximatation](image)

![Fig. 3. The breakdown cell](image)
The particles disperse into the break down cell, the instant the particles are shoot out from the nozzle. Then the cubic root of the concentration is particle-to-particle distance. It is known that the concentration of actual salt water ranges from $0.3 \times 10^7$ to $1.6 \times 10^7$ pieces/cc. Consequently, we can obtain a particle-to-particle distance of 0.05 to 0.12 mm, almost the diameter of a pulsed laser beam, by depressurizing the breakdown cell with the vacuum pump to an atmospheric pressure of 0.2 to 0.6. This means particles can be broken down every time a laser beam is emitted. Reducing the internal pressure of the breakdown cell is also effective for strengthening spectral signals, as proven by our test results, which we will discuss later.

A statistical variation occurs in the particle-to-particle distance in actual applications, however. We will discuss statistical approaches under these conditions in our consideration of the test results.

3. Test Results

In our tests, particles produced by the system were introduced to the breakdown cell, where an Nd:YAG laser beam was condensed onto the particles to break them down. Emissions produced at this point were separated into spectral components using spectrometers to measure the components as a function of time. In these measurements, we were able to distinctly observe the spectral line of sodium (D line), a component of salt, as shown in Figure 5.

The salt particles used in these tests exhibited problems in that the particle sizes varied from the average by an order of magnitude and the particle concentrations varied several-fold. For the sake of accuracy, it is necessary to process the test results so that individual particles are statistically evaluated one by one.

3.1 Statistical Considerations

In our tests, we anticipated that particles would break down 100% when the particle-to-particle distance was made almost equal to the width of the region where the plasma was produced. In practice however, particles are not distributed in a uniform manner. For this reason, statistical consideration must be given to the probability at which laser light hits particles\(^6\). For example, consider the conditions mentioned above, i.e. that the volume of mean space occupied by a single particle is almost the same as the volume of the region where breakdown takes place. The probability at which \(n\) particles are contained in the plasma under the above mentioned conditions is considered to be approximately consistent with the Poisson distribution.

Under these conditions, the probability at which \(n\) particles are contained in the plasma is

$$P_n = \frac{a^n}{n!} \exp(-a)$$

\(P_n\) is the probability at which \(n\) particles are contained in the plasma, and \(a\) is the particle density in an average volume of plasma. In an example where \(a = 1\), calculations made according to the equation shown above proved that the probabilities for the laser light to hit 1) no particles, 2) one particle, 3) two particles, and 4) three or more particles are 37%, 37%, 19%, and 6%, respectively. In this example, the average number of particles contained in the plasma where the particles have been broken down was approximately 1.5. Therefore, the particle size obtained as the result of measurement must be corrected by assuming that 1.5 particles are contained in the plasma.

With conventional systems, particle size measurement has only been possible by calculations made from the average particle size.
We have modified our earlier system in order to observe stochastic phenomena, so that we can measure not only the average of 100 measurements but also individual phenomena. In addition, we dealt with stochastic phenomena with the understanding that particles are contained in the plasma only when a signal from the sodium particle is being sensed during breakdown.

Figure 6 shows the results of measuring the probability of being able to detect the sodium signal when the particle concentration is changed by varying the internal pressure of the breakdown cell. According to these results, it is assumed that several particles are contained in the plasma produced by breakdown. From these test results, it is now possible to measure individual particles separately by reducing the particle density and thereby keeping the probability of the sodium signal being contained in the emission to less than 0.5.

3.2 Testing and Evaluation Based on Statistical Methods

In the tests discussed above, we conducted various experiments under the conditions that the number of particles in the volume of plasma is 1.1 and the probability of breakdown is 0.29. Note that the average particle number in this case is 1.5.

The experiments were conducted so that the sodium spectrum and D line emitted in the LIBS process of NaCl particles were measured. More specifically, the spectrum of sodium (588.6 [nm]) was measured individually 400 times, and the frequency distribution of the intensity of individual spectra was measured. Figure 7 shows the normalized histogram obtained from test results.

An intensity twice the average background intensity was defined as the threshold, and spectra having intensity levels higher than that intensity were accumulated in the histogram.

The background intensity was measured in the following manner. Pure water was sprayed with argon and introduced into the cell, where light from the Nd:YAG laser was condensed so that particles containing no salt were broken down. The emissions produced at this point were separated into their spectral components by means of a spectrometer, and the components were measured as a function of time.

We measured the spectrum from widths of 588.6 [nm] to 589.2 [nm] 400 times, and calculated the average from the 400 measurements.

In this research, we used a scanning mobility particle sizer (SMPS) as our standard particle-measuring instrument. Figure 8 shows the result of measuring NaCl particles using the SMPS.

The vertical axis is a scale obtained by dividing the particle concentration by the particle size. This is because we took into account the fact that the resolution of the SMPS is proportional to the particle size, as shown in the following equation.

\[ \Delta D = \frac{q_a}{q_{sh}} D \]  

where

- \( \Delta D \): Particle size resolution
- \( q_a \): Aerosol flow
- \( q_{sh} \): Sheath flow
- \( D \): Particle size

When comparing the results of LIBS measurement with SMPS measurement, it is observed that their variances differ greatly and it seems infeasible that the figure shows the results of measuring the same particles. Accordingly, we made the following assumptions:

- In LIBS particle size measurement, it is possible to measure particle sizes larger than 30 [nm].
- On the other hand, the result of SMPS measurement shows that a concentration distribution of particles with sizes from 10 [nm] to about 300 [nm] was obtained.
- Therefore, in the LIBS measurement, part of the distribution of particles was measured.
Under the above-mentioned assumptions, we evaluated the range of particle sizes measurable by LIBS, using the following method.

The results of SMPS-based particle concentration measurement were normalized by the average volume. The particle concentration was multiplied by an S-type weighting function to sweep \( V_0 \). The results of LIBS-based particle concentration measurement were normalized by the average intensity. Then, a value of \( V_0 \) at which the concentration distribution agrees with that of the SMPS measurement was determined. An exponent of 6.78 representing the gradient of the weighting function was determined so that the gradient agrees with that of the LIBS-based particle size distribution. Figure 9 shows the results of predicting agreement between the two concentration distributions.

Distribution matching was verified by \( \chi^2 \) verification. Since \( \chi^2 = 3.22 \) at \( V_0 = 3.05E + 5 \) [nm\(^3\)] and therefore the level of significance is 5%, the matching will not be rejected.

\[
f = \frac{1}{1 + \left( \frac{V}{V_0} \right)^{6.78}}
\]

where

\( V \): Volume of particles
\( V_0 \): Volume at which \( f \) equals 0.5 at \( V = V_0 \)

Since the distribution of SMPS-based particle volumes and the distribution of LIBS-based emission intensity are in agreement with each other, it is now possible to evaluate the emission intensity for each particle volume.

The test conditions were such that 1) a 0.1mol/l solution of NaCl was sprayed with a 60l/min flow of argon, 2) NaCl particles thus produced were introduced to the cell, 3) where light from the Nd:YAG laser was condensed onto the particles to break them down, 4) the emissions produced at this point were separated into their spectral components with a spectrometer, and 5) the components were measured as a function of time.

### 3.3 Multi-constituent Measurements

Using the standard samples containing sodium chloride and lithium chloride in different ratios that are discussed in paragraph 2(1) “Production of Particles,” we conducted a test of constituent measurement. In the test, we measured the content of NaCl and LiCl in the standard samples from the spectrum intensity of sodium and lithium.

Figure 10 shows the results of this test. The spectrum intensity is the integrated value of 100 times measurement. The measurement deviation from the theoretical figure is as small as 8%.

### 4. Summary

As discussed heretofore, we have developed technologies for measuring airborne particles using laser induced breakdown spectroscopy (LIBS).

These technologies will hopefully allow for higher-sensitivity measurement, i.e., measurement of extremely small particles, compared with methods based on conventional catoptric particle counters or microwave induced plasma (MIP) mass spectrometry. The simultaneous measurement of particle sizes and constituents is an essential technology in the fields of not only future semiconductor manufacturing, but also precision machining, pharmaceutics, bioengineering materials manufacturing and many others.

(Manuscript received Jul. 28, 2006, revised Mar. 22, 2007)

### References


Muneaki Wakamatsu (Non-member) Muneaki Wakamatsu was born in Tokyo, Japan, on August 25, 1965. He received the B.E. and M.E. degree in electrical engineering from Tokyo University of Agriculture and Technology, Tokyo, Japan, in 1988 and 1990 respectively. Since joining Yokogawa Electric Corporation in 1991, he has been engaged in developing IC tester and bare-board tester. Now, he is engaged in measurement standard. Mr. Wakamatsu is a member of Instrument and Control Engineers of Japan.
Satoshi Ikezawa  (Member) Satoshi Ikezawa was born in Saitama, Japan, on August 24, 1974. He received the B.A. degree in physics from Kitasato University, Kanagawa, Japan, in 1999. He received the master degree from Waseda University in 2006.

Toshitsugu Ueda  (Member) Toshitsugu Ueda was born in Nara, Japan, on October 4, 1945. He received the B.E. and M.E. degree in electrical engineering from Shinshu University, Nagano, Japan, in 1969 and 1971 respectively. He received Ph.D. degree from Tokyo Institute of Technology in 1988. Since joining Yokogawa Electric Corporation in 1971, he has been engaged in developing low noise amplifiers, mechanical resonators, micro machining technologies and sensors using above mentioned technologies for temperature, pressure and displacement. Now he is a professor of Waseda University. He received Awards from Society of Instrument and Control Engineers of Japan in 1987 and 1994, and Awards from Japan Institute Invention and Innovation in 1985 and 1987. Dr. Ueda is a member of the Institute of Electrical Engineers of Japan, and Society of Instrument and Control Engineers of Japan.