



DEVELOPMENT OF SEMI-QUANTITATIVE ANALYTICAL SYSTEM FOR METAL NANOPARTICLE INK USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Abstract- This paper describes the semi-quantitative analysis of metal nanoparticle ink using laser-induced breakdown spectroscopy (LIBS). LIBS can be used to obtain information about the density and chemical composition of silver particles or copper particles, even ultrafine particles. Metal particles have been attracting much attention because of their increased use in new micro-nano technologies. In this work, LIBS was used as a fine metal particle measurement system for nanometallic materials used in printing. Good spectral peak resolutions were obtained when the Ag spectra were recorded at wavelengths of 328.068 nm and 338.289 nm and Cu spectra at 324.754 nm and 327.396 nm.

Index terms: LIBS, laser, nanomaterials, in-situ measurement.

I. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is a unique technology that can be used to determine the distinct spectral signatures that are characteristic of almost all chemical species in various environments. Since the initial LIBS studies started with the discovery of the ruby laser in 1962 [1], LIBS has been extensively investigated for environmental monitoring [2-9], forensics [10], biological identification [11], industrial applications [12, 13], works of art [14, 15], and planetary applications [16-31]. Since the 1980s, many liquid miniaturization analytical techniques for LIBS have been reported to carry out proper chemical analysis of specimens [32-34]. The advantage of LIBS system is that it is compact and can be used as a in-situ measurement system for determining the elemental composition of various materials, regardless of their physical state (solid, liquid, or gas), and it does not require pre-processing. Despite the advantage, LIBS is often only used as an elemental analysis technique because of its insufficient stability of sensitivity for a quantitative analysis, as compared to other analysis techniques. Our research group has investigated and improved the LIBS system since the 1990s for use in quantitative analysis [35-37]. From our investigations, some important knowledge and information have emerged about the relationship between the time profile of the plasma emission intensity and the measurement conditions, particle size, type of ambient gas, and atmospheric pressure [38, 39]. This knowledge is used in the present work to improve our quantitative calibration techniques. Using the present LIBS system, it is possible to obtain information about the density of metal nanopaste ink. The nanoscale metal ink is attracting increased attention as a new material for use in interconnects for micro-devices and electrical circuit wiring with low temperature sintering. For example, the sintering time of silver nanoparticle ink is only 60 min at 200°C. The nanoscale silver particles are dissolved in an organic solvent (n-tetradecane) and formed by adding organic dispersant components. Rapid analysis is important for maintaining the dispersed state of the metal particles in the ink. The present work consumes only 1 mL of the sample for three measurements obtained from every 100 laser pulse shots and allows instantaneous LIBS measurement for the nanoscale metal ink.

II. EXPERIMENTAL SETUP ON LIBS SYSTEM

Figure 1 shows a schematic of the LIBS system. A Nd:YAG laser was operated at 1064 nm to generate a 50-mJ Q-switched pulse with a width of 8 ns (full width at half maximum, FWHM). The breakdown emissions were dispersed by a grating with a groove density of 1200 lines/mm, and the resulting electrical signal was recorded using a streak camera. The signal was processed, and the data were stored on a PC. Figure 2 shows a picture of the gas-flow assist ink-jet subsystem used for LIBS.

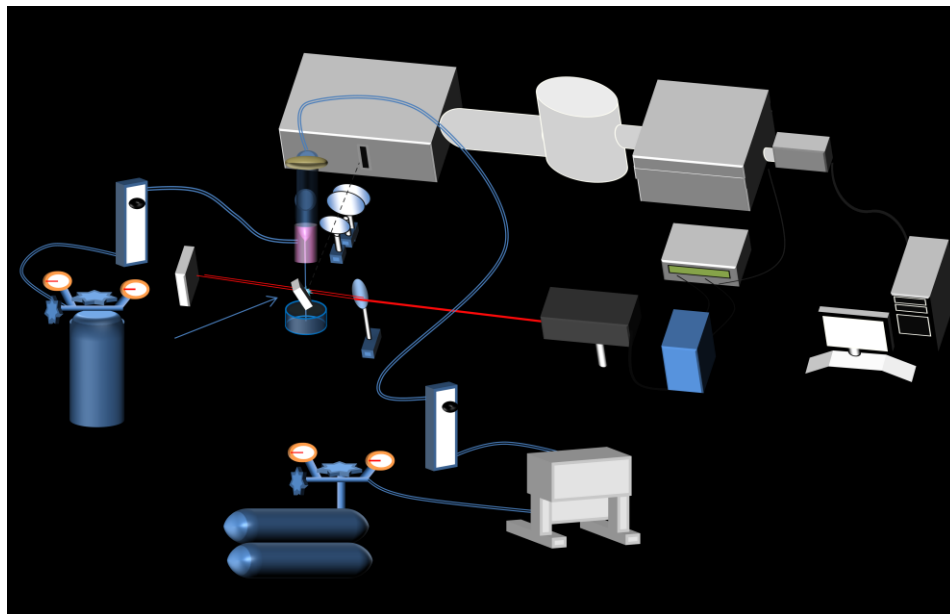


Figure 1. Schematic of LIBS system used for metal nanoparticle ink

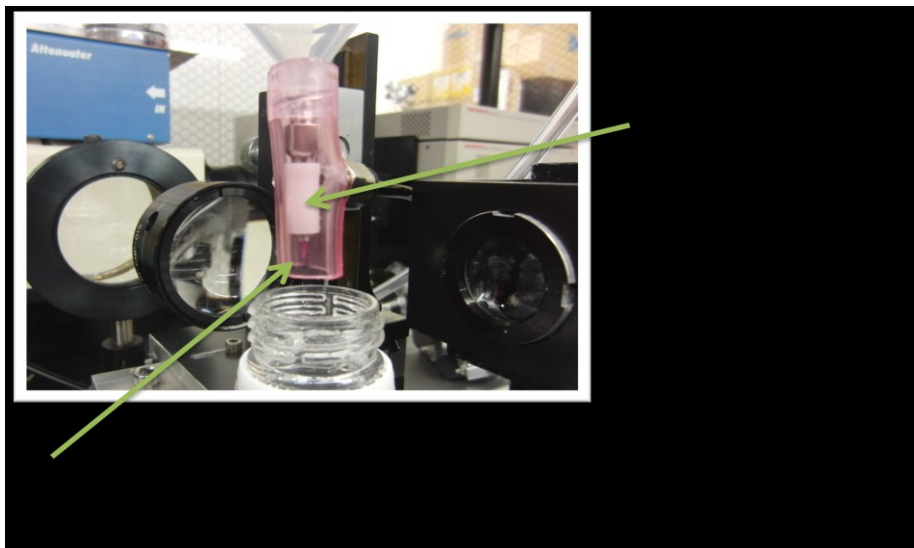


Figure 2. Picture of the gas-flow assist ink-jet subsystem for LIBS

The sampling system for LIBS measurement consists of an ink-jet nozzle and a gas flow assist system. The inner diameter of the nozzle is 30 μm . The ink is pushed out of the syringe under pressure from an air compressor, and the ink-jet hits a small area on the target plate that is crossed by a laser beam spot. As a defense against fire, argon gas is jetted out from a 10-mm orifice tube attached to the syringe. This ambient gas also facilitates the emission of the ink from the plasma. The gas flow rates are adjusted to be 0.2 L/min.

III. EXPERIMENTAL RESULTS

A. SILVER NANOPARTICLE INK

Silver nanoparticle ink was diluted by n-tetradecane by the same method as the LIBS experimental sample solution. The density of the solution was adjusted to 200, 400, 600, 800, and 1000 mg/L (see Figure 3). 1 mL was used for each LIBS measurement.



Figure 3. Silver nanoparticle ink adjusted for LIBS measurement

Figures 4 to 8 show the experimental data for the silver nanoparticle ink with density ranging from 200 mg/L to 1000 mg/L. These measurements were carried out using typical element-specific radiation emanating from silver at wavelengths of 328.068 nm and 338.289 nm. Each legends (1st, 2nd, and 3rd) indicate first, second, third experiments. The intensity of the signal was based on the data obtained for 100 laser pulse shots.

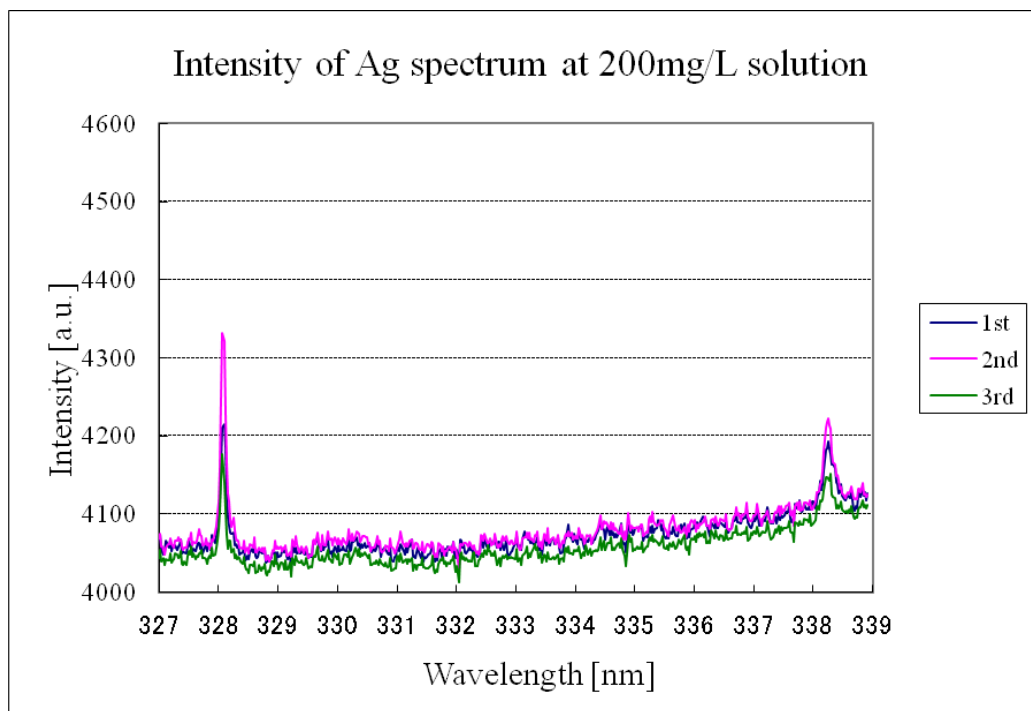


Figure 4. Variation in the Ag emission intensity from three measurements of 200-mg/L solution

Fig. 4 shows the intensity of silver spectrum using the spectra for 200-mg/L Ag nanoparticle solution sample. The graph shows that the limit of detection of the density on Ag nanoparticle solution is much lower. Figure 5 shows the intensity of silver spectrum using the spectra for 400-mg/L Ag nanoparticle solution sample. The peak intensity values are sensitive to the dispersion of each experiment.

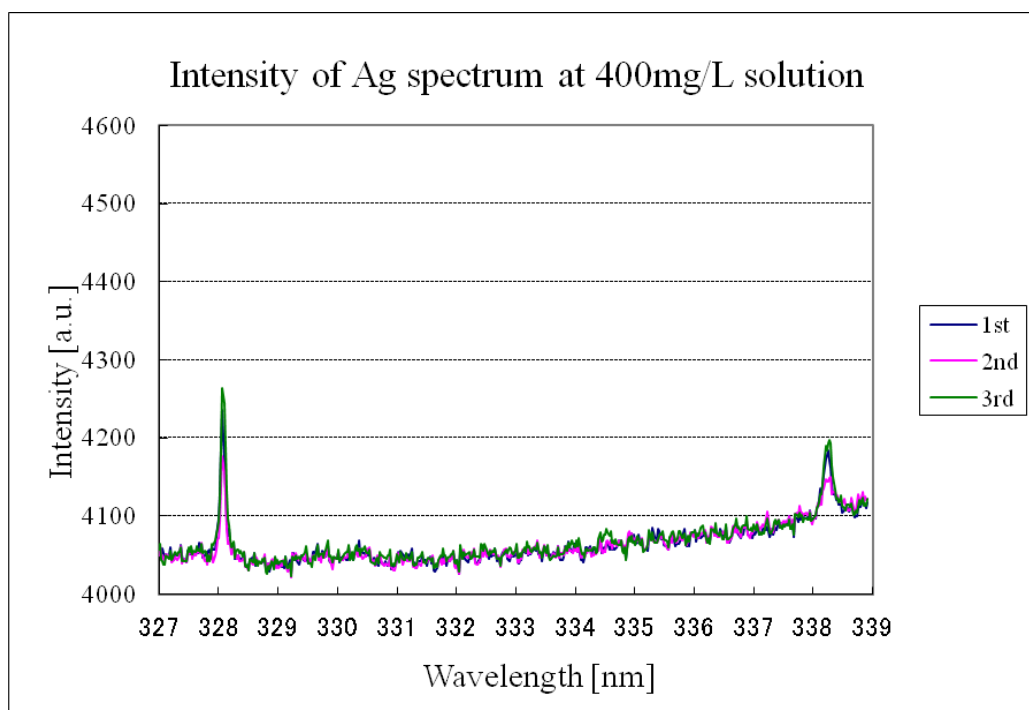


Figure 5. Variation in the Ag emission intensity from three measurements of 400-mg/L solution

Figure 6 shows the intensity of silver spectrum using the spectra for 600-mg/L Ag nanoparticle solution sample. Although the background levels are almost same, there are highly variable in peak intensities. Figure 7 shows the intensity of silver spectrum using the spectra for 800-mg/L Ag nanoparticle solution sample. The intensities have increasing tendencies to the density of the silver nanoparticle. Figure 8 shows the intensity of silver spectrum using the spectra for 1000-mg/L Ag nanoparticle solution sample. The peak intensity values are still highly variable on each experiment. To clarify the relation between the spectra peak intensities and solution density, the evaluation using calibration curve method was carried out.

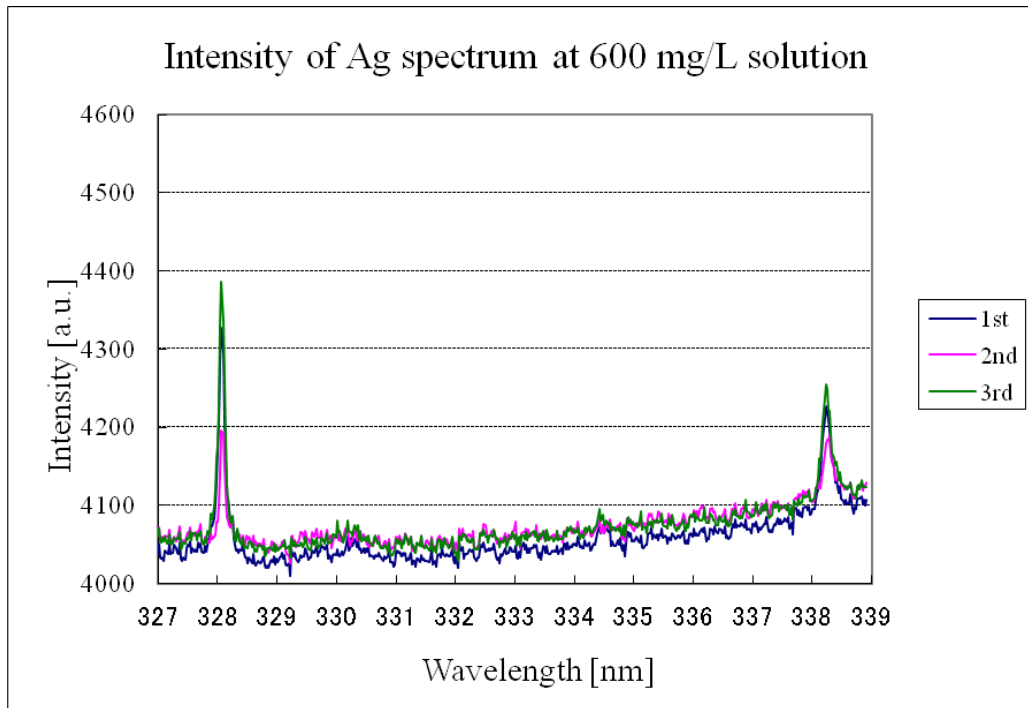


Figure 6. Variation in the Ag emission intensity from three measurements of 600-mg/L solution

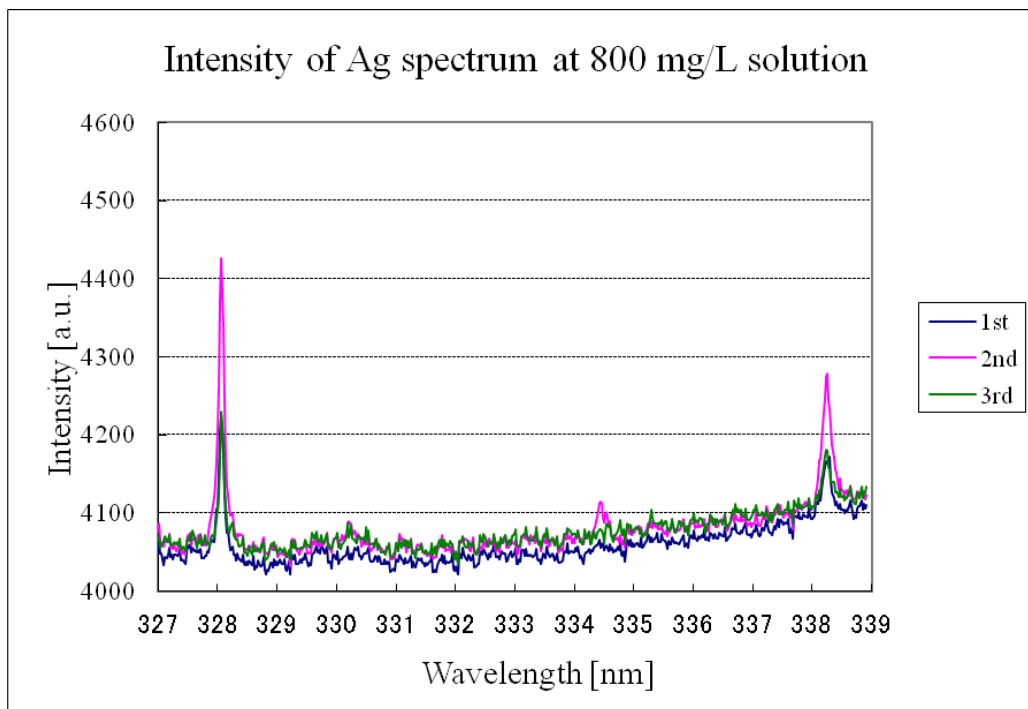


Figure 7. Variation in the Ag emission intensity from three measurements of 800-mg/L solution

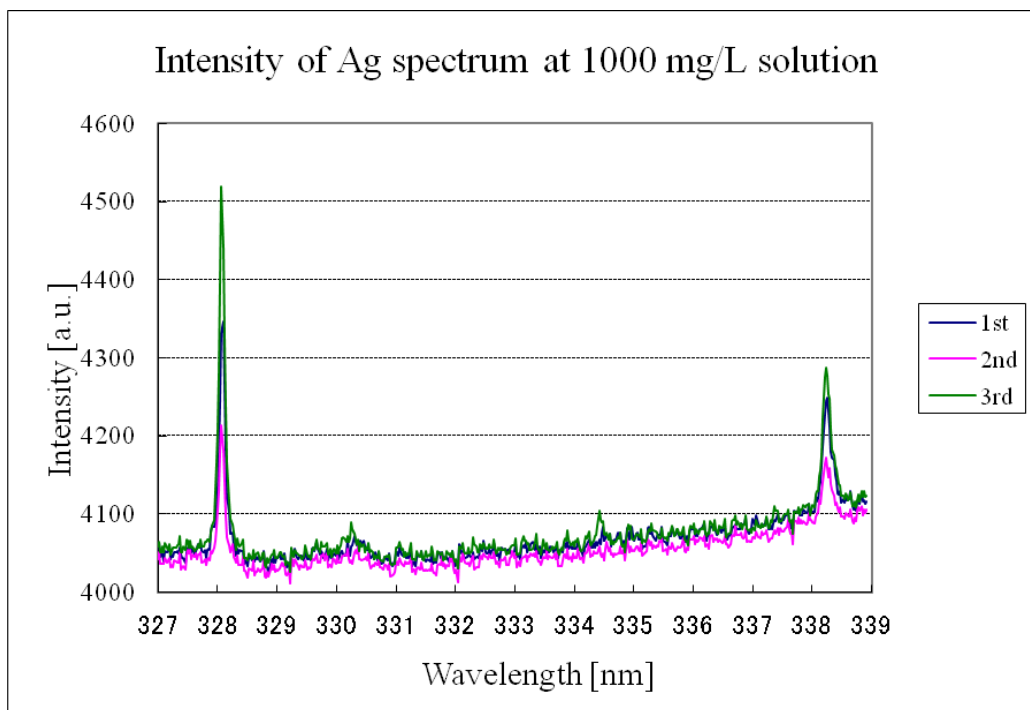


Figure 8. Variation in the Ag emission intensity from three measurements of 1000-mg/L solution

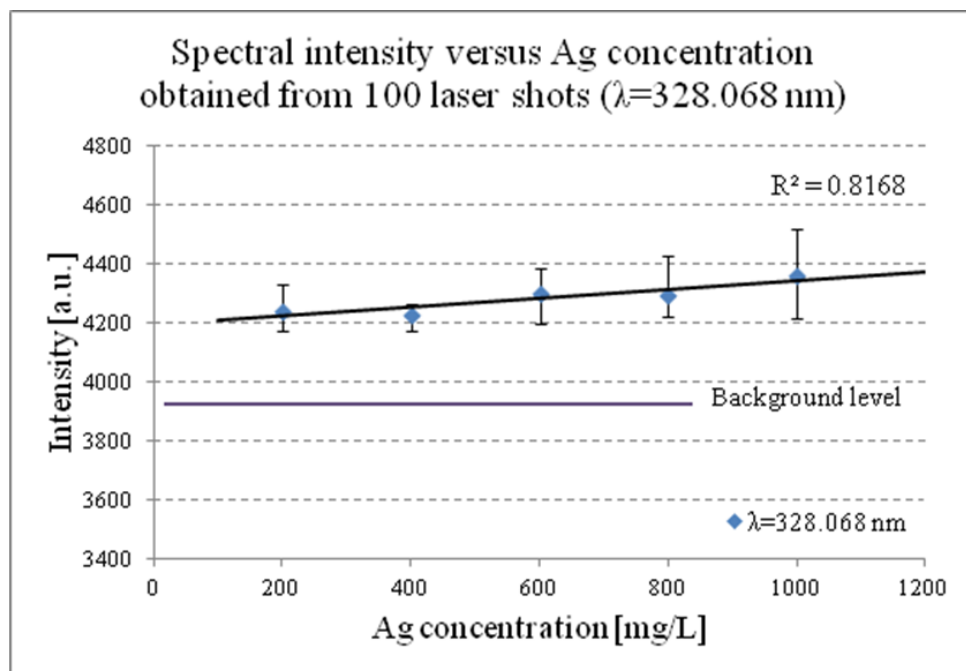


Figure 9. Calibration curve of spectral intensity versus silver concentration performed using silver atomic spectrum measurements at 328.068 nm obtained from 100 laser pulse shots

Figures 9 and 10 show that calibration curves obtained using the spectra for 200-mg/L to 1000-mg/L Ag nanoparticle solution samples used as ink-jet with argon ambient gas assist system.

In figure 9, the intensity values are averaged value obtained from silver atomic spectrum at 328.068 nm. In figure 10, the intensities are averaged value obtained from silver atomic spectrum at 338.289 nm. The error bars represent minimum and maximum values of peak intensity obtained each experiments.

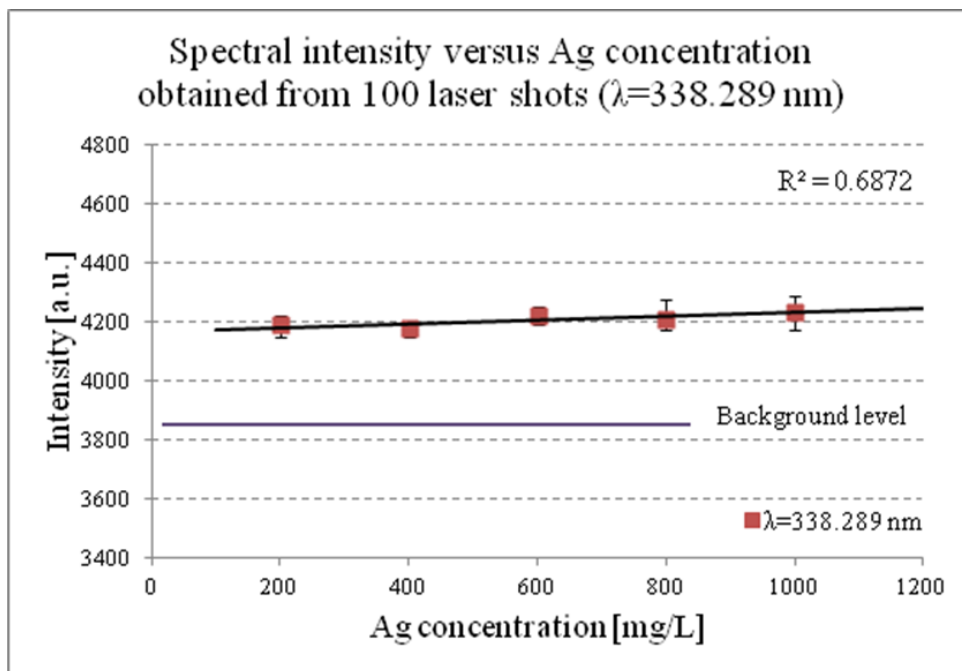


Figure 10. Calibration curve of spectral intensity versus silver concentration performed using silver atomic spectrum measurements at 338.289 nm obtained from 100 laser pulse shots

B. COPPER NANOPARTICLE INK

Figures 11 to 15 show a part of the experimental data for the copper nanoparticle ink. These measurements were carried out using typical element-specific radiation emanating from copper at wavelengths of 324.754 nm and 327.396 nm. The intensity of the signal was based on the data obtained for 100 laser pulse shots from three measurements.

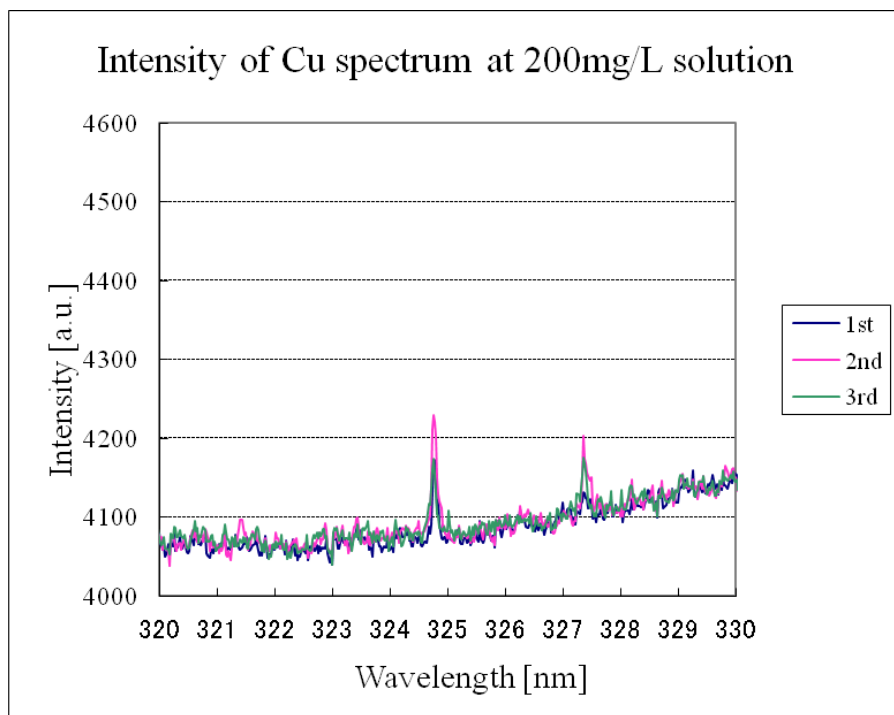


Figure 11. Variation in the Cu emission intensity from three measurements of 200-mg/L solution

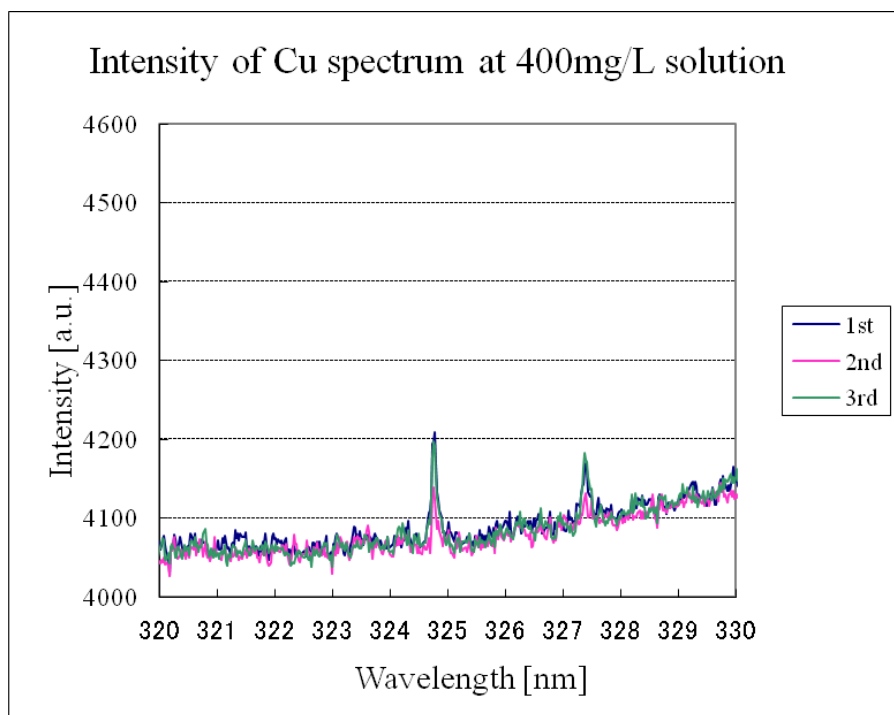


Figure 12. Variation in the Cu emission intensity from three measurements of 400-mg/L solution

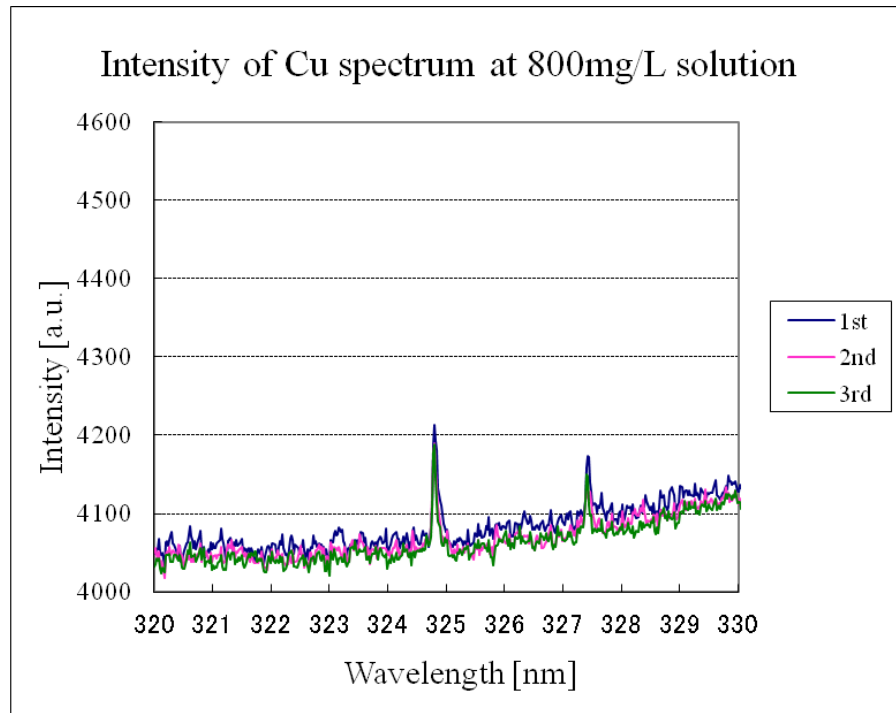


Figure 13. Variation in the Cu emission intensity from three measurements of 800-mg/L solution

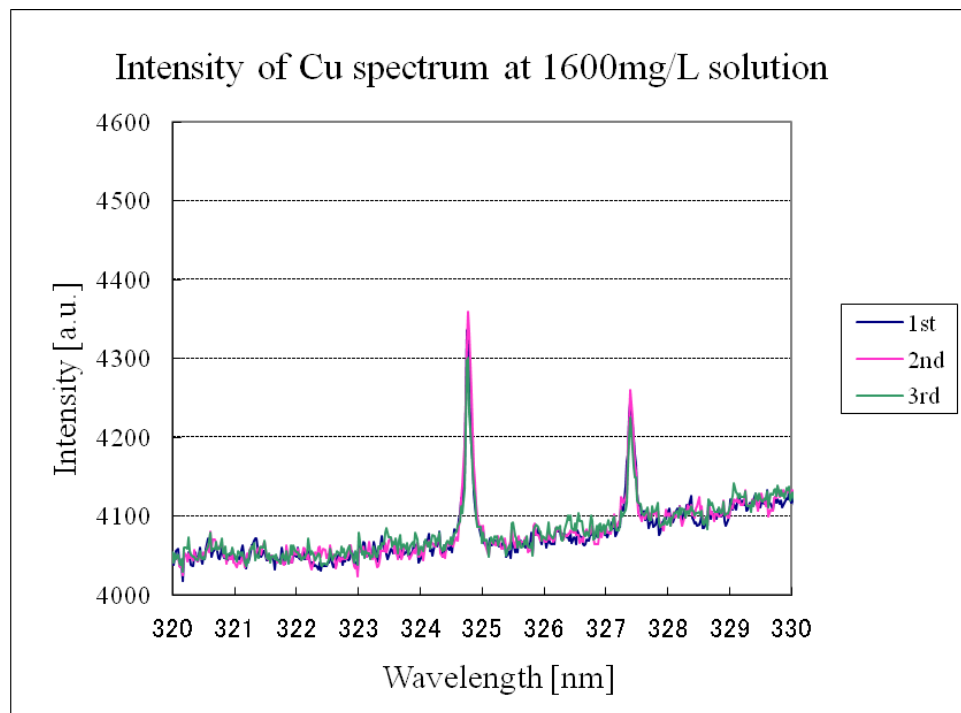


Figure 14. Variation in the Cu emission intensity from three measurements of 1600-mg/L solution

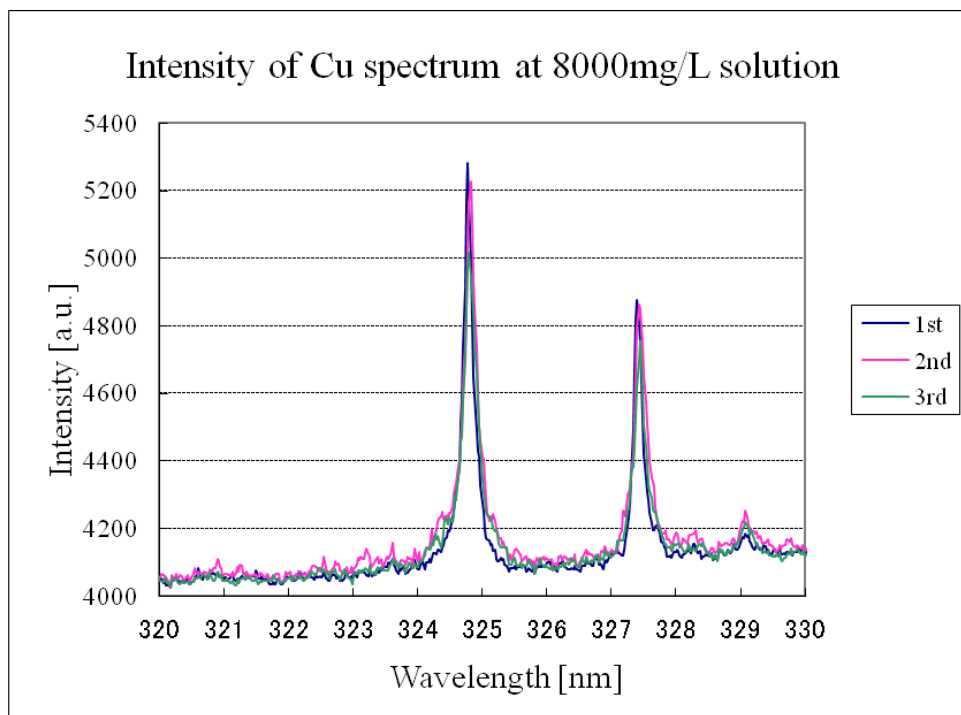


Figure 15. Variation in the Cu emission intensity from three measurements of 8000-mg/L solution

Figures 16 and 17 show that calibration curves obtained using the spectra for 200-mg/L to 1600-mg/L Cu nanoparticle solution samples used as ink-jet with argon ambient gas assist system. In figure 16, the intensity values are averaged value obtained from copper atomic spectrum at 324.754 nm. In figure 17, the intensities are averaged value obtained from copper atomic spectrum at 327.396 nm. The error bars represent minimum and maximum values of peak intensity obtained each experiments.

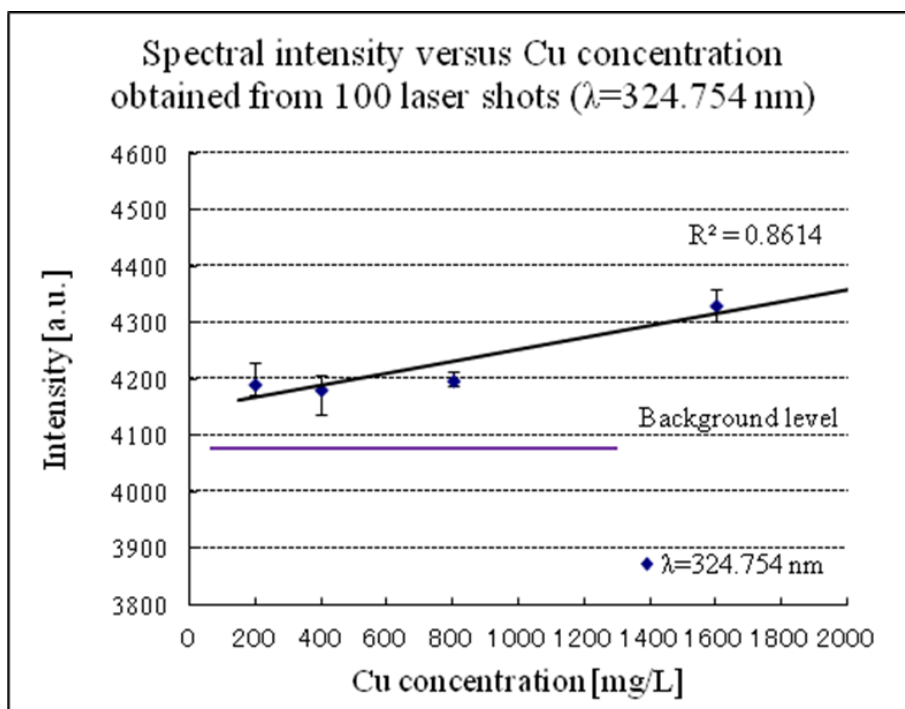


Figure 16. Calibration curve of spectral intensity versus copper concentration performed using copper atomic spectrum measurements at 324.754 nm obtained from 100 laser pulse shots

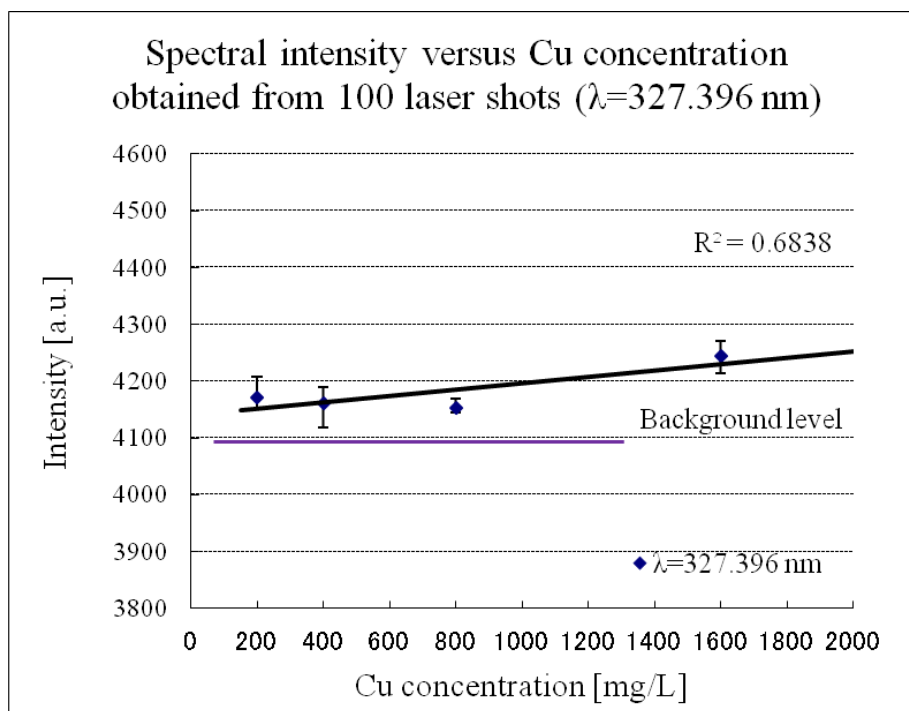


Figure 16. Calibration curve of spectral intensity versus copper concentration performed using copper atomic spectrum measurements at 327.396 nm obtained from 100 laser pulse shots

VI. CONCLUSIONS

Semi-quantitative analysis of silver and copper nanoparticle ink was successfully carried out using laser-induced breakdown spectroscopy (LIBS). During silver material detection, good spectral peak resolutions were obtained when the spectra were recorded at wavelengths of 328.068 nm and 338.289 nm. These spectra were used for quantitative calibration. The LIBS system with ink-jets and an argon gas assist system were used for the quantitative detection of silver nanoparticles in the oil-based ink. Argon as an ambient gas increased the sensitivity of the LIBS system and protected the equipment from the chemical reaction between the flammable solvent (n-tetradecane) and oxygen in the air. The intensity of dispersion for quantitative analysis still remains a big issue. LIBS quantitative measurement for copper nanoparticle ink plays an important role for the environmental monitoring of copper particles in a clean room. Some of contaminated matter were carbonaceous particles that could have come from outside; the others were copper particles that could have originated in the clean room. The origin of copper particles is not well understood at present. It is speculated that they come from the motor brushes in the clean room or are generated during the sputtering or reflow processes during the fabrication of MEMS devices. To clarify the origin of copper particles, an LIBS measurement of fine metal particles is effective. Controlling nanoparticle contamination with the help of chemical component information used by LIBS system significantly enhances the production yield rate.

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