Sensitive Quantitative Analysis of Strontium in Microdroplet by Surface-enhanced Laser-induced Breakdown Spectroscopy Using Porous Silicon

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Surface-enhanced laser-induced breakdown spectroscopy (SELIBS) is a promising method for microanalysis of liquid samples. We previously demonstrated that the SELIBS signal was significantly enhanced by using porous silicon (Si) instead of flat Si. In this work, we dried aqueous droplets containing 1 – 200 ppb strontium (Sr) on porous Si substrates and evaluated the quantitative performance by analyzing the dry residues. A linear calibration curve for the Sr quantification ($R^2 = 0.998$) was obtained and an LOD was 0.67 ppb.

Keywords Surface-enhanced LIBS, microanalysis, metal-assisted chemical etching, porous silicon

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Introduction

Laser-induced breakdown spectroscopy (LIBS) has attracted attention as one of elemental analysis methods. In LIBS, elements of samples can be identified by measuring the emission spectra of plasma generated by laser ablation. LIBS enables one to perform the rapid analysis of samples under various environments. Recently, a fiber-optic LIBS system was developed for the remote analysis of nuclear fuel debris in the decommissioning site of the Fukushima Daiichi nuclear power plant. This system will accelerate the decommissioning work. However, it is specialized in the analysis of solid samples. In the decommissioning work, the monitoring of contaminated water is also required to understand the situation of damaged nuclear reactors. In this context, surface-enhanced LIBS (SELIBS) is a promising method for liquid analysis. In SELIBS, a sample solution is dropped on a solid substrate, and subsequently the dry residue is analyzed by LIBS. By using a single droplet, the amount of sample solution can be minimized. This is suitable for the analysis of liquid samples containing radioactive materials. Recently, various substrates have been proposed for improving the sensitivity and precision of SELIBS. In previous work, we applied porous silicon (Si) as a substrate of SELIBS in analyzing a strontium chloride (SrCl₂) aqueous solution for the purpose of detecting a fission product in the contaminated water. We demonstrated that the Sr signal intensity was significantly enhanced by using porous Si instead of flat Si, and investigated the effect of the pore depth of porous Si on the signal intensity. We also demonstrated that the position-to-position signal fluctuation was suppressed owing to an uniform distribution of the dry residue on porous Si. Although we focused on the effect of the porous structure on the signal intensity and the signal stability, the quantitative performance of this technique has not been evaluated. In this work, we analyzed aqueous solutions containing different concentrations of Sr, and evaluated the quantitative performance using a calibration curve method.

Experimental

A Si substrate with a porous layer on its top surface (porous Si substrate) was produced by metal-assisted etching using gold (Au) nanoparticles as catalysts. Details of the substrate preparation can be found in Ref. 14. The Au nanoparticles were deposited on an n-Si (100) substrate by immersing in a tetrachloroauric(III) acid aqueous solution containing hydrofluoric acid (HF) for 120 s. To produce the porous layer, the Au-nanoparticle-deposited Si was immersed in a HF aqueous solution containing hydrogen peroxide for 60 s. In this work, the Au nanoparticles were removed by immersing the porous Si substrate in aqua regia at 298 K for 15 min so as to avoid overlapping between the Sr I resonance line at 460.73 nm and the Au I line at 460.75 nm, although the Au nanoparticles can be one of the factors to enhance the LIBS signal. Figure 1 shows a cross-sectional scanning electron microscopy (SEM) image of the porous Si substrate. We can see straight pores with a depth of about 180 nm. For hydrophilization, the porous Si substrate was immersed in a 60% nitric acid solution at 363 K for 10 min. The porous Si substrate was mounted on a holder with a polytetrafluoroethylene washer (inner diameter of 4.5 mm) and put on a heater set to 373 K. Sample solutions containing different concentrations of Sr were prepared by using a standard solution of Sr (Sr: 1000 ppm (mg/L), SrCO₃ in 0.15 M HCl aq.) to ensure the accuracy of the concentration. In order to suppress the inhomogeneous distribution of the dry residue, a standard solution of sodium (Na: 1000 ppm, NaCl aq.) was added so that the Na concentration was 25 ppm, although the effect of the additive is unclear under the present circumstances. A 7.0-μL single droplet of the sample solution was dropped on the porous Si substrate. We can see straight pores with a depth of about 180 nm.
Si substrate. After confirming that the sample solution was completely dried, the substrate was detached from the holder. We prepared seven substrates on which 1, 5, 10, 20, 50, 100, and 200 ppb (μg/L) Sr solutions were dried, respectively. Note that one droplet was dropped on one substrate. The dry residue on the porous Si substrate was analyzed by LIBS. Details of the LIBS setup can be found in Ref. 14. A Nd:YAG pulsed laser (1064 nm, 6 ns) was used. The irradiation energy was adjusted to 2.5 mJ/pulse on the substrate. Emission spectroscopy was performed using a Czerny–Turner spectrometer equipped with an ICCD camera. The slit width of the spectrometer was set to 100 μm. The delay time, the gate width, and the gain of the ICCD camera were set to 1 μs, 5 μs, and 200, respectively. The substrate was put on a manual stage and the irradiation position was changed shot-by-shot within the dried area of the sample solution (diameter: 4.5 mm). The step width was 0.2 mm so as to avoid overlapping of the irradiation positions. We obtained an average spectrum from 10 shots and measured the average spectrum five times for each substrate.

Results and Discussion

Figure 2 shows emission spectra obtained without and with the dry residue from a sample solution containing 200 ppb Sr. As shown in Fig. 2a, in the absence of the dry residue, emission lines that originated in the porous Si substrate were not observed at around 460.73 nm where the Sr I resonance line was observed. Note that we observed a very small Au I line at 479.26 nm, indicating that Au was not completely removed by the aqua regia. Figure 2b shows that Sr I emission lines originating in the dry residue were observed. This indicates that the dry residue on the porous Si substrate could be detected without spectral interferences from the substrate in this wavelength range. To evaluate the quantitative performance, we plotted the peak height of the Sr I resonance line at 460.73 nm as a function of the Sr concentration of a sample solution from 1 to 200 ppb. The circles and the error bars correspond to the average values and the standard deviations of five replicate measurements, respectively. The best-fit linear function passing through the origin is shown as a solid line.

![Cross-sectional SEM image of the porous Si substrate.](image)

![Emission spectra obtained (a) without and (b) with the dry residue from a sample solution containing 200 ppb Sr.](image)

![Intensity of the Sr I resonance line at 460.73 nm as a function of the Sr concentration of a sample solution from 1 to 200 ppb.](image)

that the detection sensitivity can be improved by a simple pretreatment, i.e. droplet drying on the porous Si substrate.

In order to evaluate the quantitative performance for a higher concentration range, we analyzed solutions containing 0.5 – 5 ppm Sr, and added the results to Fig. 3 (Fig. 4). The Sr signal intensity tended to be saturated in the high concentration range, which declines the performance of the quantitative analysis using a calibration curve method. As a factor of saturation, the self-absorption of the Sr resonance line can be considered (the self-absorption can be significant in the case of a resonance line...
Therefore, we used a Sr I non-resonance line at 483.21 nm (the lower energy level is not the ground state) instead of the resonance line to make a calibration curve in the concentration range from 0.2 to 5 ppm (Fig. 5). As a result, a linear calibration curve was obtained with $R^2 = 0.997$. This suggests that quantitative analysis can be achieved over a wide concentration range by properly selecting emission lines in response to the concentration.

Conclusions

In this work, we analyzed aqueous droplet containing different concentration of Sr by SELIBS combined with porous Si. By using the Sr I resonance line, the linear calibration curve was obtained in the Sr concentration range from 1 to 200 ppb and the LOD was 0.67 ppb. The result indicates that this technique has a capability for the sensitive quantitative analysis of a single droplet (7.0 μL) with a low laser energy (2.5 mJ).

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