

## Determination of Na and Al Ions in Semiconductor Cleaning Solution Using Capillary Electrophoresis

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Received September 19, 2003*

**Key Words :** Cleaning solution, Metal ion, Capillary electrophoresis, Semiconductor

As the scale of integration for semiconductor device has continued increasing, the purity of process chemicals has to be carefully controlled for device reliability by monitoring trace levels of ionic contaminants and particulates.<sup>1,2</sup> The most common process chemical used in the manufacturing process is a standard cleaning (SC) solution, a mixture of ammonia and hydrogen peroxide in deionized water. Since the purity of the SC solution used in the process has been required to the level of sub-ppb range, accurate and reliable determination of ionic contaminants becomes increasingly difficult. In order to satisfy the requirement of impurity control, inductively coupled plasma-mass spectrometer (ICP-MS), graphite furnace atomic absorption spectrometer (GFAAS), and ion chromatography (IC) are currently the most common analytical instruments used in the process.<sup>3</sup> However, those instruments are not designed for on-line monitoring but rather for off-line analysis.

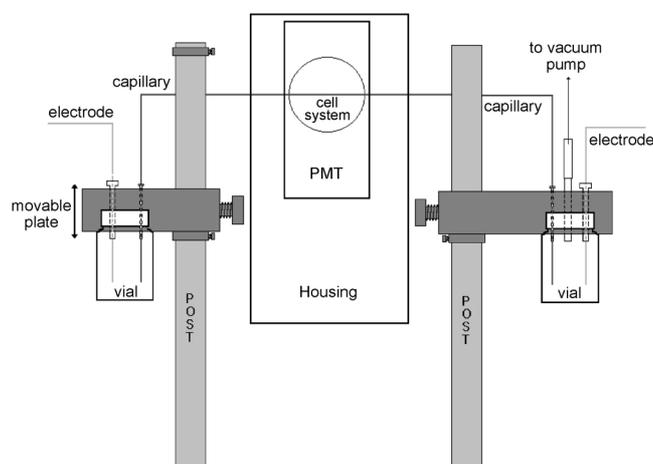
Recently, separation and detection of various particles, such as cells and nanoparticles, with capillary electrophoresis (CE) was reported, although the application of CE has been mostly limited to organic or biological samples.<sup>4-6</sup> Capillary electrophoresis has been emerging as an alternative to ICP-AES and AAS for trace metal analysis. In CE, some analytes such as inorganic cations and anions do not absorb at all or only very weakly absorb the light in the UV range. Therefore, an indirect UV absorption technique, in which the analyte displaces a mobile phase additive in the eluted band, has been used successfully in capillary electrophoresis.<sup>7-13</sup> The displacement causes a decrease in the absorption or fluorescence signal, because the concentration of the mobile-phase additive is lower in the eluted bands when compared with its steady-state concentration.

Recently, separation and detection of various kinds of metal ions, including, alkali, alkaline earth, transition metals, and even lanthanide ions by CE in the presence of UV absorbing complexing agent were reported.<sup>14-18</sup> For semiconductor application, method development and applications of capillary electrophoresis for determination of cations in the highest purity grades of hydrogen peroxides that has been utilized widely in critical wafer processing steps were reported.<sup>3</sup> However, no article for the determination of trace metals in SC solution was reported so far. In this work, a lab-made CE with a movable pinhole for optical adjustment was

built and demonstrated for the determination of Na and Al ions in SC solution for semiconductor application.

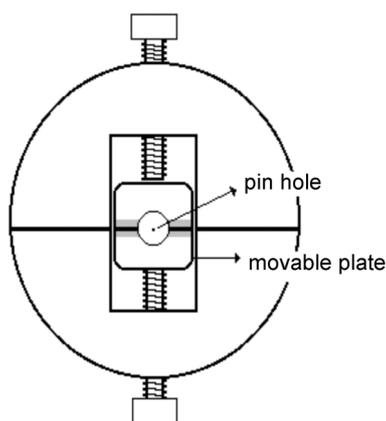
### Experimental Section

**Developed Capillary Electrophoresis System.** The laboratory-made capillary electrophoresis system with an on-column UV-VIS detector has been described in the previous papers<sup>19,20</sup> and the schematic diagram is shown in Figure 1. A fused silica capillary (70 cm  $\times$  75  $\mu$ m i.d., Polymicro Technologies Inc., USA) was used as separation column. The effective capillary length was 52 cm and operating voltage of CE was -20 kV. A high voltage power supply (0-30 kV DC, Spellman High Voltage Electronics Corp., NY, USA) was used to drive the electrophoresis process across the capillary. Detection was carried out by on-column measurements of UV absorption. For the UV detector, light from D<sub>2</sub> lamp (Hamamatsu, model L613) of 30 W passed through an interference filter (Optical Corp. of America, Model 4TFN, 255 nm center, 12 nm bandpath) and was focused into the capillary column through a 100  $\mu$ m diameter pinhole by a ball lens (Yunam Hitech Inc., Korea). The absorption light was collected with a single UV transparent optical fiber (Oriel, model 77573, 0.8 mm diameter). A Hamamatsu PMT power supply (Hamamatsu, model C3830, Japan) operated a photomultiplier tube (Hamamatsu,



**Figure 1.** Schematic diagram of a lab-made capillary electrophoresis system: -20 kV, 75  $\mu$ m i.d. capillary, sample injection with a vacuum pump.

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**Figure 2.** Movable pinhole for optical alignment in capillary electrophoresis; bottom screw for pinhole adjustment to the capillary, top screw for guide.

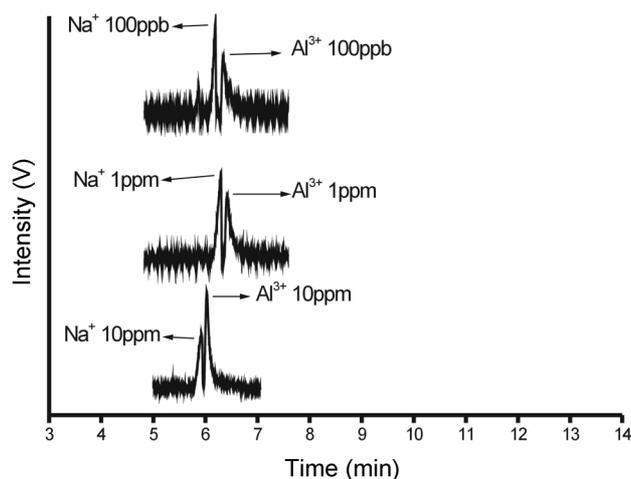
model R212) with a locally-constructed housing. The output of the photomultiplier tube was fed to the current pre-amplifier (Oriel, model 70710) and transferred to a data acquisition board. The data acquisition system consisted of an I/O interface with A/D converter and a computer with locally made graphic software.

For better sensitivity and selectivity in a lab-made CE, good alignment is required. In this system a movable pinhole system was newly designed to make alignment easy, as shown in Figure 2. As shown in Figure 2, the position of the pinhole can be movable by adjusting the screw for the best sensitivity. For sample introduction, electrokinetic sample injection method was used. This electromigration sampling can provide sufficient sensitivity for the measurement of trace contaminants in this indirect UV-CE. For easy capillary cleaning, vacuum suction system was built as well.

**Chemicals used.** All solutions, electrolytes, and standard working solutions were prepared using doubly distilled deionized water. The standard solutions of  $\text{Na}^+$  and  $\text{Al}^{3+}$  were purchased from Aldrich (Sigma-Aldrich, A.C.S. reagent). Imidazole buffer (Fluka, Chemika reagent) of 5 mM prepared from 250 mM stock solution was adjusted to pH 3 by adding 0.1 M HCl (Dongwoo Fine Chem., semiconductor grade, Korea). For calibration, standard addition was employed in this experiment.

## Results and Discussion

A standard cleaning (SC) solution was prepared by mixing ammonia, hydrogen peroxide, in D.I. water with the volume ratio of 1 : 4 : 20. Since the lab-made capillary electrophoresis system and analytical method were not optimized and no clean room was employed, sensitivity was not good enough to detect metal ions of sub-ppb range for semiconductor purpose. However, the ability to analyze processing chemicals directly is essential for the reliable determination of alkali, alkaline earth cations,  $\text{Al}^{3+}$ , and some transition metals, such as Fe, Cu, Ni, and Zn. For the demonstration of analytical application of capillary electrophoresis, 100 ppb

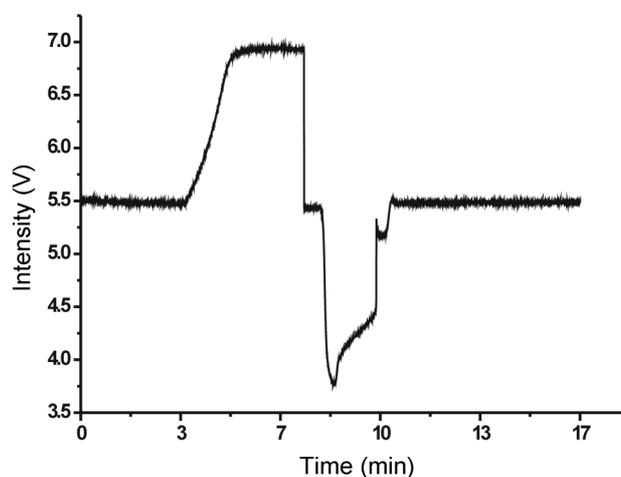


**Figure 3.** Electropherogram of  $\text{Na}^+$  and  $\text{Al}^{3+}$  in hydrogen peroxide; -20 kV, indirect UV absorption (255 nm), 5 mM imidazole buffer.

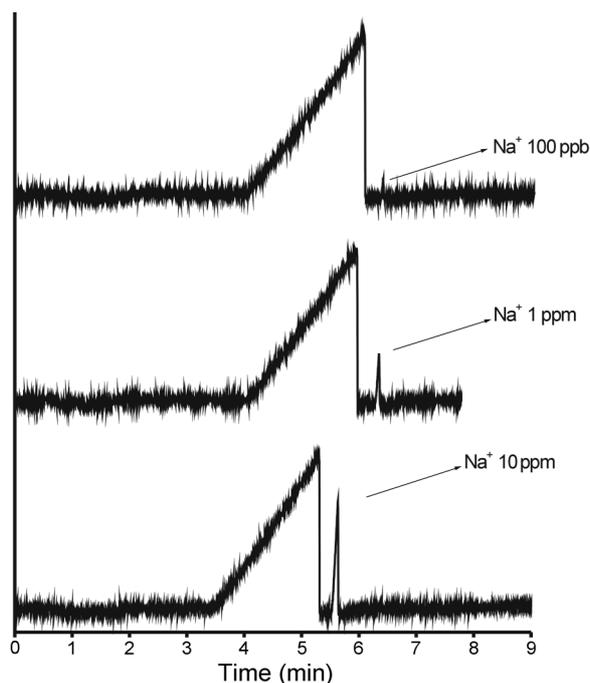
to 10 ppm of Al and Na in the standard cleaning solution were prepared and determined in this experiment.

At first a hydrogen peroxide solution containing 100 ppb of Al and Na was prepared and run in the system. Figure 3 is showing the electropherogram separated  $\text{Na}^+$  from  $\text{Al}^{3+}$ . As shown in Figure 3, there was no baseline drift observed, and it seemed that the peroxide samples could be analyzed directly without the catalytic decomposition step usually employed prior to CE analysis of anions. Calibration curve for each ion showed regression coefficient better than 0.997. Limits of detection of 63 and 24 ppb for  $\text{Na}^+$  and  $\text{Al}^{3+}$ , respectively, were obtained by four measurements with relative standard deviations of 2.0% for  $\text{Na}^+$  and 8.9% for  $\text{Al}^{3+}$ .

For the SC solution, tiny bubbles were continuously produced from the mixture, so that the determination of metal ions was almost impossible using the CE system, as shown in Figure 4, an electropherogram of  $\text{Na}^+$ . In order to eliminate the bubbles, the solution was heated to 85 °C for 30 min before injection. After heating, the solution was



**Figure 4.** Electropherogram of  $\text{Na}^+$  in standard cleaning solution without pretreatment; -20 kV, indirect UV absorption (255 nm), 5 mM imidazole buffer.



**Figure 5.** Electropherogram of  $\text{Na}^+$  in standard cleaning solution; 85 °C, 30 min heating before sample injection; -20 kV, indirect UV absorption (255 nm), 5 mM imidazole buffer.

injected into the capillary by electrokinetic method, and the electropherogram was shown in Figure 5. As shown in the figure, peak of 1 ppm  $\text{Na}^+$  was separated from the gigantic peak of ammonium ion matrix. Linear regression coefficient was obtained to be 0.946, poorer than for the hydrogen peroxide solution only.

**Acknowledgement.** The present research was conducted by the research fund of Dankook University in 2003.

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