# On-site Determination of Trace Nickel in Liquid Samples for Semiconductor Manufacturing by Highly Sensitive Solid-phase Colorimetry with $\alpha$-Furil Dioxime

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A new, highly sensitive colorimetry for trace $Ni^{II}$ at the parts per billion level has been developed. The method is based on effective adsorption of the orange-colored $Ni^{II}$ chelate with $\alpha$-furil dioxime to a membrane filter. There was superior tolerance to coexistence of high concentration of salts such as sodium nitrate in the trace $Ni^{II}$ analysis. The proposed method was successfully applied to the NaOH solutions used for the silicon wafer processing and enabled on-site $Ni^{II}$ analysis which has been urgently needed in the semiconductor manufacturing.

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In the recent semiconductor manufacturing, nickel contamination on the processing of silicon wafers or the making process of semiconductor devices is one of the most serious problems because the remarkable degradation of device performance is caused by fast-diffusion of $Ni^{II}$ in silicon wafers. Although the $Ni^{II}$ concentration in the liquid samples such as sodium hydroxide solutions used for silicon wafer etching is preferably below $20\,\mu g\,L^{-1}$, or more preferably $5\,\mu g\,L^{-1}$ or less,[1] even the electronic industrial grade solutions of NaOH contains nickel impurities of several hundreds of parts per billion. Various techniques of purification of the alkaline etching solutions have also been investigated.[1] Therefore, it is very important to develop a simple analytical method which enables on-site analysis of $Ni^{II}$ with high sensitivity and selectivity.

Nickel determination techniques, including inductively coupled plasma with atomic emission spectrometry or mass spectrometry, graphite furnace atomic absorption spectrometry, and neutron activation analysis are highly developed. However, a determination method which is simple, relatively inexpensive, and applicable to on-site analysis with high sensitivity is still lacking. Although solvent extraction spectrometry has also been used for a long time, these methods have many disadvantages from a practical view point. Furthermore, simple analytical methods which have the tolerance to the coexistence of a severe matrix such as the 48% NaOH are hardly known.

This paper reports an on-site determination method for trace $Ni^{II}$ with high sensitivity and selectivity based on solid-phase concentration of the orange-colored $Ni^{II}$ chelate with $\alpha$-furil dioxime ($\alpha$-FD) to a membrane filter. Over the past decades, a significant amount of effort has been expended towards the development of solid-phase extraction systems using membrane filters,[2] which are very useful media for preconcentration of various analytical techniques and are also an appropriate tool for field works.[3,4] It is well known that $\alpha$-dioximes, such as $\alpha$-FD and dimethylglyoxime (DMG), form $M(HL)_2$ type water-insoluble chelates with $Ni^{II}$, and the water solubilities of these chelates are $6.3 \times 10^{-7}$ and $9.8 \times 10^{-7}\,mol\,dm^{-3}$, respectively.[5] Although there was an approach to a sensitive determination of $Ni^{II}$ by collecting the precipitate of the $Ni^{II}$–DMG complex, the lower limit of detection was $0.47\,mg\,L^{-1}$.[6]

In the discussion below it is shown that a specific interaction between the $Ni^{II}$–$\alpha$-FD complex and a membrane filter brings about not only a highly sensitive determination of $Ni^{II}$ at the parts per billion level but also a superior tolerance to the coexistence of high concentration of salts, such as sodium nitrate, which is caused by neutralization of concd acid or alkaline solutions. The detection limit was $2 \times 10^{-8}\,mol\,dm^{-3}$ ($1\,\mu g\,L^{-1}$) in 50 mL of the sample solution. The proposed method has been successfully applied to the 48% NaOH solutions used for etching of silicon wafers.

Nickel(II) standard solution, $1000\,mg\,L^{-1}$, was from Kanto Chemical Co., Inc. (Tokyo, Japan) and intermediate solutions were prepared by appropriate dilution of the stock solution. The solution (0.1 wt %) of the reagent, $\alpha$-furil dioxime (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), was prepared by dissolving it in ethanol. The pH buffer solution used was $0.2\,mol\,dm^{-3}$ of *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS)–NaOH (pH 9.0). All other reagents used were of guaranteed reagent grade. The membrane filter (25 mm in a diameter) made of cellulose acetate (pore size 0.20 µm) was purchased from Advantec Toyo Kaisha, Ltd. (Tokyo, Japan).

Reflection spectrometric measurements were carried out with a tristimulus colorimeter (model NF-777, Nippon Denshoku, Tokyo, Japan), which was calibrated with a white standard reference plate. For the inductively coupled plasma mass spectrometry (ICP-MS), a model SPQ-9500 (SII Nano-Technology Inc., Tokyo, Japan) was used. An Advantec KG-13A filter holder was used under suction (0.03 MPa) with an aspirator. A cellulose acetate type membrane filter, which was set on the glass filter holder, was conditioned prior to filtration procedure by rinsing with the buffer solution.

A typical procedure is as follows: To 10 mL of the sample solution containing $Ni^{II}$ ion, 2 mL of $\alpha$-FD solution and 3.0 mL of pH buffer solution were added, and the mixture was diluted to 50 mL with water. This solution was filtered under suction through a cellulose acetate type membrane filter which was conditioned as noted above. The filter paper on which an orange-colored circular fleck retained was dried at room temperature for 10 min. The $Ni^{II}$ concentration was determined by visual comparison with a standard series previously prepared. Reflection spectrometric measurement was also carried out at 480 nm to estimate the color intensity.

In this study, it was found that the orange-colored $Ni^{II}$ chelate with $\alpha$-FD was adsorbed effectively from the parts per billion level solutions to a membrane filter made of cellulose acetate, mixed cellulose ester, cellulose nitrate, PTFE, and polycarbonate. A cellulose acetate type membrane filter was chosen because the highest color intensity was obtained under the same experimental condition. On the other hand, the $Ni^{II}$–DMG chelate was not collected with the membrane filters tested in this

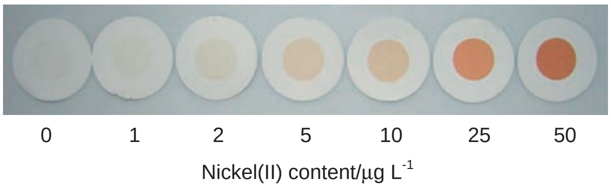

**Figure 1.** The color transition of the membrane filter with relation to Ni$^{\mathrm{II}}$ content. The volume of the sample solution was 50 mL.

study when the Ni$^{\mathrm{II}}$ concentration was below $0.2\,\mathrm{mg\,L^{-1}}$. It should be noted that the adsorption of the Ni$^{\mathrm{II}}$–$\alpha$-FD complex was occurred when the concentration of the chelate was even below the water solubility. We also confirmed that the filter coloration was observed when 500 mL of the sample solution containing $2 \times 10^{-9}\,\mathrm{mol\,dm^{-3}}$ of Ni$^{\mathrm{II}}$–$\alpha$-FD complex was filtered. Furthermore, the particles that were much smaller than the pore were was confirmed on the filter fiber by the SEM observations, and the amount of the particles was increased as the Ni$^{\mathrm{II}}$ concentration was rose. The appropriate pH region of the mixture when filtering it was between 7 and 12. The formation of the Ni$^{\mathrm{II}}$–$\alpha$-FD complex was fast enough, and the complex solution was filtered at once after the preparation. The color intensity of the filter was decreased as the flow rate, pore size or temperature of the complex solution was increased. The difference of the color intensity was within 5% when the flow rate was between 0.03 and $0.1\,\mathrm{mL\,s^{-1}}$. The membrane filter with the pore size 0.20 µm, which was the minimum size in the filters made of cellulose acetate, was used in this study. We confirmed that more than 98% of Ni$^{\mathrm{II}}$ was collected on the filter under the appropriate condition with $20\,\mathrm{\mu g\,L^{-1}}$ of Ni$^{\mathrm{II}}$.

The color transition of the membrane filters with relation to Ni$^{\mathrm{II}}$ content was shown in Figure 1. The Ni$^{\mathrm{II}}$ concentration was determined at the parts per billion level by visual comparison of the filter color. The visual detection limit was $2\,\mathrm{\mu g\,L^{-1}}$, defined as the minimum concentration which was visually distinguishable against the reagent blank. The calibration curve assessed with the reflection spectrometric measurement was linear over the concentration range up to $25\,\mathrm{\mu g\,L^{-1}}$ ($r = 0.998$). The RSD for reflection absorbance at $5.0\,\mathrm{\mu g\,L^{-1}}$ was 6.5% ($n = 5$), and the detection limit on this occasion was $1\,\mathrm{\mu g\,L^{-1}}$.

The effect of commonly occurring foreign ions on the determination of $10\,\mathrm{\mu g\,L^{-1}}$ of Ni$^{\mathrm{II}}$ in 25 mL of the mixture solution was investigated. In this study, the tolerance limit was set as the amount which caused an error of ±10% in the recovery of Ni$^{\mathrm{II}}$. This value is appropriate for satisfying the needs from the viewpoint of regarding both rapidity and simplicity. The concentrations of Ba$^{\mathrm{II}}$, V$^{\mathrm{V}}$, $\mathrm{NH_4}^+$, $\mathrm{Cl}^-$, and $\mathrm{SO_4}^{2-}$ below 10000 fold of molar ratio, those of Mg$^{\mathrm{II}}$, Ca$^{\mathrm{II}}$, Zn$^{\mathrm{II}}$, and Sn$^{\mathrm{II}}$ below 1000 fold of molar ratio, those of Al$^{\mathrm{III}}$ below 500 fold of molar ratio, and those of Fe$^{\mathrm{III}}$ below 100 fold of molar ratio did not interfere. The tolerable amounts of Co$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ were below 10-fold molar ratio. However, those of Co$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ were increased to 100- and 500-fold molar ratio by adding $0.05\,\mathrm{mol\,dm^{-3}}$ of sodium thiosulfate. It should be noted that coexistence of below $4.8\,\mathrm{mol\,dm^{-3}}$ of sodium nitrate was not interfered. The masking effect of sodium thiosulfate was obtained even in the sodium nitrate solution. On the other hand, the temperature influence as noted above was suppressed by the coexistence of the sodium nitrate. With $4.8\,\mathrm{mol\,dm^{-3}}$ of sodium nitrate, the difference of the color intensity was below 5%, when the temperature of the complex solution changed at 20–50 °C. These results suggest that proposed method should be suitable for the determination of Ni$^{\mathrm{II}}$ in the solution that neutralized concd acid or alkaline solutions. In this study, the application to the 48% NaOH solutions for the silicon wafer etching was demonstrated. The 48% NaOH solutions were diluted to five times by preparing the final solutions. The analytical results were summarized in Table 1. There was good agreement between the results for the 48% NaOH solutions used for silicon wafer etching by the proposed method and those by ICP-MS.

**Table 1.** Analytical results

| Sample[a] | Ni$^{\mathrm{II}}$ found/µg L$^{-1}$ | | |
|---|---|---|---|
| | Proposed method | | ICP-MS |
| | Visual method | Reflection spectrometry | |
| A | <10 | <5 | N.D.[c] |
| B | <10 | <5 | 1.1 |
| C | 25 | 23 ± 2[b] | 31 |
| D | 50 | 67 ± 5[b] | 71 |
| E | 25 | 21 ± 3[b] | 15 |
| F | <10 | <5 | 2.0 |

[a] The 48% NaOH solutions which were provided from a semiconductor manufacturing factory. [b] Three replicate analyses. [c] Not detected.

In conclusion, a very sensitive and simple method for the determination of Ni$^{\mathrm{II}}$ ion at the parts per billion level has been demonstrated and successfully applied to the neutralized sample of the 48% NaOH solution. The proposed method will become a useful technique for the monitoring of trace Ni$^{\mathrm{II}}$, which has been urgent demand in the semiconductor manufacturing.

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