



Analytical note

Analysis of metal ion impurity in tetraethyl orthosilicate by sector field inductively coupled plasma mass spectrometry

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ABSTRACT

A sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) method was developed to directly analyze metal ion impurity in tetraethyl orthosilicate (TEOS). As trace metal ion impurity in TEOS can cause a damaging effect on wafer-product-based electronic devices, it is necessary to develop an efficient analytical method for quantifying the trace metal ions in TEOS for semiconductor manufacturing. The low metal ion content (nanogram per liter level) in a TEOS solution is difficult to be analyzed directly by SF-ICP-MS. Pretreatment such as acidic digestion and direct dilution results in lower concentrations of the metal ions down to picogram per liter level which reaches the instrumental limitation and is not suitable for analysis. In this study, simple liquid–liquid extraction (LLE) was applied by adding isopropanol and deionized water to extract the metal ion in TEOS. The interfering compounds can be directly separated from the analyte by SF-ICP-MS with an appropriate resolution, thereby preventing any ambiguity in the identification of metal ions. The maximum concentration factor was 18.94. The applicability of the proposed method has also been validated by the analysis of three TEOS samples for different applications. The concentrations of metal ions with the range from nanogram per liter to microgram per liter can all be determined with good precision (RSD < 9.46%) and good accuracy (spike recoveries from 94% to 113%). This study demonstrates that SF-ICP-MS with LLE pretreatment is a promising approach for analyzing metal ion impurity in TEOS.

1. Introduction

Tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) has wide range of applications, such as a cross-linking agent in silicone polymers, a silica source for zeolite synthesis, and a precursor to silicon dioxide in the semiconductor industry [1–3]. The concentration of metal ions in TEOS is typically at the milligram per liter level. However, the specific requirements of TEOS depend on its use. For example, the metal ion impurity in TEOS used for silicon oxide thin films in chemical vapor deposition needs to be strictly controlled to prevent interference with the operation of electronic components on the wafer [4]. Being the main material of the dielectric layer in semiconductors, TEOS with trace amount of metal ions can result in the failure of electric devices, such as electrical instability (caused by alkaline), dielectric breakdown of gate oxides (caused by transition metals), threshold voltage shift (caused by inorganic dopants) and so on [4–6]. As the widths of semiconductor devices decreased down to the nanometer scale, it is critical that the allowed amount of metal ion impurity in processing chemicals must be at the microgram per liter to nanogram per liter level

[7].

Inductively coupled plasma mass spectrometry (ICP-MS) has been applied to determine trace metal ions in various samples, with great advantages, such as high sensitivity, low detection limit and rapid multi-element analysis [8–15]. In general, aqueous samples can be directly analyzed by ICP-MS. For organic solvents, high vapor pressure causes instability and even burnout of the ICP torch. Furthermore, the nebulizer and injector can be clogged by the carbon-rich matrix, and carbon can be deposited on the sampler cone and skimmer cone [16,17]. By digestion pretreatment employing thermal decomposition and acid addition, the organic sample can be transferred to the aqueous phase; this step eliminates interferences caused by carbon, thereby permitting analysis by ICP-MS [18]. Various improvements to the instrumentation for ICP-MS have been reported, such as a micronebulizer, which permits low sample injection volumes [19] and a cooling desolvator, which reduces solvent effects [20], as well as the introduction of oxygen gas into the torch, which enables complete sample combustion [21]. Thus, organic samples diluted with specific organic solvents can be directly introduced into ICP-MS systems and analyzed.

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However, the above approaches are not suitable to determine metal ion impurity in TEOS at a nanogram per liter level. Digestion pretreatment is a complicated, tedious process and is prone to contamination. Another serious problem with the pretreatment is the dilution factor. For digestion, approximately 5–10 times of acid are added with the sample, and the pretreated sample is then diluted by approximately 10 folds deionized water to minimize the acidic matrix effect prior to ICP-MS analysis. As a result of the digestion pretreatment, the sample is diluted by approximately 50–100 times which can affect the precision and accuracy due to the detection limit of the instrument [22]. Another issue is direct organic sampling for the ICP-MS system. Although organic samples can be homogenized by dissolving them in organic solvents, they typically require a dilution factor of 10. In addition, the intensity of ICP-MS signals for organic samples is weaker than that of signals for aqueous samples because of the lower sample injection volume and organic matrix effect [23]. For metal ion impurity in TEOS solution at the nanogram per liter level, 10 times dilution lowers the detection range for ICP-MS down to the sub-pico-gram per liter level, albeit with poor precision of analytical results. In this study, TEOS is concentrated by simple liquid–liquid extraction (LLE) and addition of a specific assisting agent. Here, the concentration factor can be adjusted by controlling the solvent ratios according to the sample requirements. The assisting agent contains isopropanol (IPA) and deionized water in a specific ratio with TEOS. The metal ion impurity in TEOS not only disperse to the homogenous solution but also remain in H₂O after vigorous stirring. Some IPA and ethanol (EtOH) are formed by the hydrolysis of TEOS, and all of H₂O in the above solution is extracted with vigorous stirring using an extracting agent containing H₂O. H₂O and TEOS phases are separated after centrifugation, and all of the metal ion impurity in TEOS is transferred into the aqueous phase. The concentration factor depends on the ratio of the amounts of TEOS to that of the aqueous phase in the final solution.

Spectral interference in ICP-MS is primarily generated from nebulizer gas, plasma and matrix components in the sample. Especially, the polyatomic interferences such as ²⁸Si¹⁶O with ⁴⁴Ca, ²⁸Si¹⁷O¹H with ⁴⁷Ti, ⁴⁰Ar²⁸Si with ⁶⁸Zn, ²⁸Si¹²C with ⁴⁰Ca are found in the ICP-MS determination. These interferences are often difficult to reduce, especially for low analyte concentration. Sector field ICP-MS (SF-ICP-MS) can directly separate the analyte from the interfering compounds by utilizing an appropriate resolution, thereby preventing any ambiguity in the identification of metal ions. [24–26]. To minimize the variations during quantitation, an internal standard is added to the samples and to the calibration standards; this method normalizes the background variation for the samples and standards. The concentrations of metal ions in TEOS are quantified by utilizing external calibration curves of the standard metal ions.

2. Experimental

2.1. Chemicals

Ultrapure selected grade IPA and nitric acid were obtained from BASF Taiwan (Taoyuan, Taiwan) and JT Baker (Avantor, PA, USA), respectively. A certified standard solution of metal ions (10 mg L⁻¹) and an internal standard Cs solution (1000 mg L⁻¹) were purchased from Merck KGaA (Darmstadt, Germany), and a second certified 10 mg L⁻¹ standard solution of metal ions was purchased from Ultra Scientific (North Kingstown, RI, USA). Deionized H₂O with a resistivity of 18.2 MΩ cm at 25 °C was obtained using a Milli-Q System (Millipore, Merck KGaA, Darmstadt, Germany). Standard solutions of metal ions in a 1.4% nitric acid solution were freshly prepared by diluting a concentrated multi-element standard solution. Various TEOS samples in this study were provided by Air Products and Chemicals (Allentown, PA, USA), Sigma-Aldrich (St. Louis, MO, USA), and Nanomate (Kaohsiung, Taiwan).

Table 1
Analytical parameter settings for SF-ICP-MS.

Parameter	
Nebulizer	Microflow
Nebulizer flow rate, μL min ⁻¹	100
Spray chamber	PFA
Injector	Sapphire
Sampler cone	Pt
Skimmer cone	Pt
Peristalsis pump speed, rpm	5.00
RF power, W	650 ^a & 1200 ^b
Plasma Ar flow rate, L min ⁻¹	17.00
Auxiliary Ar flow rate, L min ⁻¹	0.75
Sample Ar flow rate, L min ⁻¹	0.645
O ₂ flow rate, L min ⁻¹	0.12 ^a & 0.15 ^b
Extraction lens, V	-1980.0
Focus lens, V	-900.0
X-Deflection lens, V	2.32
Y-Deflection lens, V	3.42
Shape lens, V	120
Acquisition mode	Magnetic jump, electric scan
Number of scans	3 × 3
Sample time, sec.	0.01
Samples per peak	30
Resolution ^c	300, 4000, 10,000 (low, medium, high)

^a Cold plasma.

^b Hot plasma.

^c The analytical resolution (m/Δm) of SF-ICP-MS was 300 for ^{6,7}Li, ²³Na, ²⁴Mg, ²⁷Al, ^{69,71}Ga, ^{86,88}Sr, ^{90,91}Zr, ^{96,98}Mo, ^{107,109}Ag, ^{110,114}Cd, ^{118,120}Sn, ^{121,123}Sb, ¹³⁸Ba, ¹⁹⁷Au, ^{206,208}Pb, and ²⁰⁹Bi; 4000 for ⁹Be, ^{42,44}Ca, ^{48,50}Ti, ⁵¹V, ^{52,53}Cr, ⁵⁵Mn, ^{54,56}Fe, ⁵⁹Co, ^{58,60}Ni, ^{63,65}Cu, ^{66,68}Zn, and ⁷⁵As; 10,000 for ³⁹K.

2.2. Apparatus

The clean room for the experiment, which is in a Class 1000 environment, was maintained at 22 ± 1 °C and 50% humidity. The SF-ICP-MS instrument was a Element 2 system (Thermo Fish Scientific, Bremen, Germany). The purities of Ar and O₂ exceeded 99.995%. Table 1 summarizes the operating parameters of the SF-ICP-MS system for the TEOS sample. A Seta 90000-0 centrifuge (Heraeus Instrument, Hanau, Germany) and Kimax tubes (45240; Kimble-Chase, Vineland, NJ, USA) were used after calibration. PFA centrifuge tubes (Part 210-050-30; Saville, Eden Prairie, MN, USA) were used after rinsing.

3. Results and discussion

Water is a better solvent than TEOS for metal ions because of its high polarity [27]. Because of the hydrophobic nature of the ethoxy groups, TEOS and water are immiscible in all proportions [28]; therefore, water appears to be a suitable extracting agent. However, TEOS react with H₂O to form SiOH and EtOH upon mixing with water. The hydrolysis rate of TEOS is low in the absence of a catalyst. With short extraction time, excessive formation of EtOH can be avoided [29,30]. The rate of metal ion transfer between two homogeneous media is more rapid than that for transfer by dual-phase extraction [31,32]. IPA is miscible with both TEOS and water. IPA and water are mixed in a specific ratio to form the assisting agent, which is then mixed with a specific amount of TEOS to form a homogenous ternary phase. Metal ion disperses in the aqueous medium after vigorous stirring. With the addition of appropriate amounts of water to serve as the extracting agent, two phases separation can be obtained. The metal ions from the TEOS were extracted into water layer and can be quantified by ICP-MS analysis.

3.1. Analysis of metal ions by SF-ICP-MS

EtOH from TEOS hydrolysis or the cosolvent IPA is miscible with water. EtOH and IPA at certain proportions were dissolved in the final

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