

Evaluation of cleaning efficiency with a radioactive tracer and development of a microwave digestion method for semiconductor processes

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Abstract

A radioactive tracer technique was applied to investigate the effectiveness of various wet cleaning recipes in removing metallic impurities such as sodium, iron and cesium. The effects of solution temperatures and substrate types were studied. The mechanisms of the electrochemical segregation of metallic impurities between the substrate and cleaning solution were examined. The enthalpy of oxide formation and the effect of adsorption were the two reasons for the presence of surface metal impurities in the cleaning solutions. Our results indicated that SC2 and DHF can effectively remove the metallic impurities at 47 and 82°C, while SPM and BOE are only effective at 82°C. The gravimetric method was successfully implemented to evaluate the open-focused microwave digestion efficiency for anti-reflective coating and photoresist (PR) samples. By following the established microwave digestion method and inductively coupled plasma mass spectrometric determination, the detection limits (DLs) obtained for multi-elements were in the ng ml⁻¹ and sub-ng ml⁻¹ levels. Except for calcium, the spike recoveries of the metals were in the range 82–121% for the lithographic samples. The analytical results were found to be in reasonably good agreement with literature values, and the lithographic sample throughput can achieve up to 3.5 samples per hour for the analysis of 13 elements. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increasing complexity and miniaturization of modern integrated circuits demand a higher device yield, hence lower defect density in the active region

of silicon devices [1,2]. For a deep sub-micrometer device, a metal precipitate could cause a distortion of the resultant electrical properties, resulting in a faulty integrated circuit [3–8]. For example, metals can degrade the dielectric properties of a gate oxide, leading to premature breakdown. They can also diffuse into the bulk of the silicon substrate, resulting in increased junction leakage as well as reduced minority carrier lifetime after a high temperature process. Therefore, a

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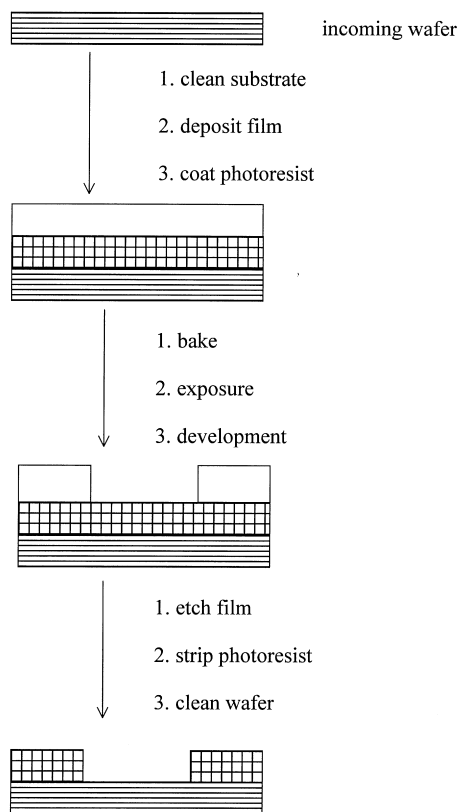


Fig. 1. Part of the process flow for patterning the semiconductor device.

more thorough understanding of the potential of metal diffusion into the silicon substrate during device fabrication is essential to reduce contamination and improve circuit yield [9].

The control of fabrication processes involved in device manufacturing has become increasingly crucial due to the growing complexity of materials and tools [3]. Fig. 1 depicts part of the process flow for patterning the device circuit. Basically, the incoming wafer needs to be clean prior to deposition of the film (such as silicon oxide, silicon nitride, polysilicon, dielectric or metal). The processes of bottom anti-reflective coating (BARC), photoresist (PR) coating, exposure, baking and development should be followed to pattern the deposition film [10]. After lithography, the wafer is etched. The area, protected by the PR, should be tolerant to the etching. After finishing the etching process, the PR is removed and the pattern is revealed. These processes are generally to be thought of as a

dirty procedure because many organic and inorganic contaminants can be transferred to the wafer surface during etching, especially in the energetic plasma etching process. Therefore, the cleaning process should succeed in ensuring reliability [3].

In Fig. 1, the wet chemical processes (e.g., cleaning and lithography) play a very important role because they are applied repeatedly to the wafer surface during device manufacturing. Contamination may come from the process materials, therefore material purity and cleaning efficiency are of extreme importance. In semiconductor fabrication, the well known RCA cleaning method [11], universally applied in wafer processing for removing the contaminant, was originally developed based on the radioactive tracer method by Kern and Puotinen in 1970. The effectiveness of the RCA cleaning method was established by deliberately contaminating the wafer surface with radioactive nuclides ^{64}Cu and ^{198}Au . Gamma radioactivity was recorded after and before RCA cleaning to monitor the cleaning efficiency. Wang et al. first [9] studied the diffusion of Mn and Zn out of lithographic materials into the underlying substrates, and also investigated the cleaning efficiency by using a radioactive tracer technique. They report that Mn and Zn in deep ultra-violet (DUV) PR may migrate into the substrates under various baking conditions. Fortunately, the presently used cleaning process is very effective for removing the Mn and Zn contamination. However, the cleaning efficiency for other metals, before and after lithography, needs further verification.

Today, the advanced semiconductor device manufacturers use graphite furnace atomic absorption spectrometry (GFAAS) to determine ultratrace elements in lithographic materials for assuring their quality. These materials include DUV PR (exposure wavelength = 248 nm) and i-LINE PR (exposure wavelength = 365 nm). In this method, the sample is digested in an acid mixture in a beaker on a hot-plate [12]. However, throughput and contamination are important issues with such a method. For this reason, it is inevitable that new analytical methods must be developed to meet the requirement of the industry. Plasma-based techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), possess the advantage of a simultaneous multi-element capability. However, they require a

rapid, efficient and reliable sample preparation technology to ensure their efficiency and capability. This is because the plasma-based instruments readily suffer from matrix induced spectral overlap problems and matrix induced signal intensity changes as a consequence of incomplete sample dissolution [13].

Numerous methods have been used for the destruction of organic samples [14–16]. The open-focused microwave digestion method, in comparison with the closed-vessel microwave method, shows the specific advantages of applicability to large samples (up to 10 g), operating in the ambient atmosphere, no accumulating pressure problem, and a relatively small irradiation zone. The drawback of the digestion method is the probability of contamination from ambient air, cross contamination between samples, and loss of analytes. To solve these problems, the use of a quartz chamber and reflux condenser can minimize the risk of contamination and loss of analytes.

In this work, a radioactive tracer technique was proposed to evaluate the cleaning efficiency for Na, Fe and Cs impurities by using currently used cleaning methods. The effects of the dipping temperatures and the types of substrates were tested. In addition, possible mechanisms involved in the metals' cleaning were discussed. Furthermore, the total dry residual solid method was proposed for evaluating the digestion efficiency of the lithographic samples (DUV BARC, DUV PR and i-LINE PR). A suitable digestion recipe was found, and was subsequently employed for matrix dissolution. The digestion solution after acid evaporation was analyzed by ICP-MS.

2. Experimental

2.1. Materials

Silicon (100) P-type wafers of 15 cm diameter were deposited with various films (polysilicon, silicon dioxide, silicon nitride), and non-deposited, bare silicon was used as a control. The wafers were cut into pieces, 2 cm by 2 cm, to serve as test samples. These test samples were subjected to radioactive tracer contamination onto the surface to study the cleaning efficiency. Carrier-free radioactive tracers from DAMRI (France) were used in this study. The composition

of tracers was $10 \mu\text{g g}^{-1}$ $^{22}\text{NaCl}$ (0.873 MBq g^{-1}), $24 \mu\text{g g}^{-1}$ $^{59}\text{FeCl}_3$ (0.93 MBq g^{-1}) and $10 \mu\text{g g}^{-1}$ $^{137}\text{CsCl}$ (0.747 MBq g^{-1}) in 0.1 M HCl.

Various popular wet cleaning recipes, including SC1, H₂O, SC2, DHF, SPM and BOE, were studied in this work. The chemical composition of SC1 solution was conc. ammonia, conc. hydrogen peroxide and water with a volume ratio of 1:1:5. The chemical composition of SC2 solution was conc. hydrochloric acid, conc. hydrogen peroxide and water with a volume ratio of 1:1:6. The chemical composition of DHF solution was conc. hydrofluoric acid and water with a volume ratio of 1:50. The chemical composition of SPM solution was conc. sulfuric acid and conc. hydrogen peroxide with a volume ratio of 4:1. The chemical composition for BOE solution was conc. hydrofluoric acid and conc. ammonium fluoride solution with a volume ratio of 1:6.

The lithographic materials used in this work were DUV BARC (AZ KrF-12, Clariant, Japan), DUV PR (SEPR-401H, Shin-Etsu Chemical, Japan), and i-LINE PR (IX-850G, Japan Synthesis Rubber, Japan).

All reagents used were of analytical or higher grade from Merck (Darmstadt, Germany). High-purity water, purified by demineralization, two-stage quartz distillation, and sub-boiling distillation, was used throughout. Nitric acid (Merck, Tracepure grade, further treated by in-house sub-boiling), sulfuric acid (Fisher Scientific, Pittsburgh, PA; Tracemetal grade), hydrogen peroxide and hydrochloric acid (both Merck) were used for digestion of the samples. Standard solutions of the analytes were freshly prepared by diluting the concentrated (1000 mg l^{-1}) stock solutions (Merck) with 1% nitric acid.

2.2. Film growing process

To prepare different underlying surfaces for this study, films of polysilicon, silicon oxide, and silicon nitride were deposited onto various starting silicon wafers by low-pressure chemical vapor deposition (LPCVD) in a quartz reactor. The polysilicon film was deposited with silane gas (SiH_4) at $60 \text{ cm}^3 \text{ min}^{-1}$ and 620°C . The silicon oxide layer was grown by wet oxidation with a gas mixture of hydrogen ($8000 \text{ cm}^3 \text{ min}^{-1}$) and oxygen ($4999 \text{ cm}^3 \text{ min}^{-1}$) at 978°C . The silicon nitride film was deposited with a

mixture of ammonia ($130 \text{ cm}^3 \text{ min}^{-1}$) and dichlorosilane (SiH_2Cl_2 , $30 \text{ cm}^3 \text{ min}^{-1}$) at 780°C . After deposition, the film thickness is characterized with a Nanospec monitor (Nanometrics, CA). The respective thicknesses of these films are 760, 1150 and 500 nm for polysilicon, silicon oxide and silicon nitride.

2.3. Radioactive tracer experimental procedure

To study the effectiveness of various wet cleaning recipes, 0.2 ml of diluted radioactive tracer (in 0.005 M HCl) solution was added onto the surfaces of test samples. The samples were dried on a hot-plate at 50°C . After solvent evaporation, the test samples were counted with the high resolution gamma-ray spectrometer. The counting system features an HPGe detector coupled with a multi-channel analyzer (CANBERRA AccuSpec, IL) and the usual electronics. The energy resolution of the system was 2.4 KeV at 1332 KeV. The intensities of the gamma rays for ^{22}Na ($t_{1/2} = 2.602\text{y}$), ^{59}Fe ($t_{1/2} = 45.1\text{d}$) and ^{137}Cs ($t_{1/2} = 30.15\text{y}$) were monitored at the peak energies of 1274.5, 1099.3 and 661.7 KeV, respectively. The radioactivity of the test samples was recorded by the gamma-ray counting system mentioned above. Subsequently, the test samples were immersed in the respective cleaning solutions, i.e., SC1, H_2O , SC2, DHF, SPM, and BOE, at various temperatures for 5 min, to dissolve or desorb the metals. Samples were taken out, immersed in room temperature water to rinse off the residual chemical, and then dried on a hot-plate. The radioactivity emitted from the radioactive tracers was again measured. The effectiveness of various wet cleaning recipes could thus be assessed based on the ratios of the radioactivities counted after and before wet cleaning.

2.4. Microwave decomposition and sample analysis

The open-focused microwave devices of Microdigest 3.6 (Prolabo, Paris) were composed of two PS-34 pumps, six microwave chambers, six temperature sensors, a fume-scrubbing unit and the controlling console. This system can automatically deliver the dissolution reagents (up to four reagents) without intermixing. The reagent volume can be introduced from 0 to 99.5 ml in 0.5 ml increments. As this digestion

system was operated at atmospheric pressure, the dissolution process was independently controlled at a given temperature setting by infrared-red monitoring from 100 to 400°C in each digestion chamber. The microwave energy (at 2450 MHz) is transferred to the solution contained in the quartz digestion vessel. The maximum power achieved for each chamber was 250 W, and can be adjustable in 1% increments from 10 to 100%, or at no power. The dissolution chamber and the reflux condenser were made of high purity quartz.

A lithographic sample (3 ml) was digested in the open-focused microwave system. Table 1 lists the different recipes of various digestion mixtures which were tested to find the best dissolution conditions. Upon completion of microwave digestion, the sample was cooled before transferring to another PTFE beaker. The sample solution was heated on

Table 1
Various digestion recipes used for dissolution of lithographic materials^a

| | Reagent volume | Temperature limit ($^\circ\text{C}$) | Power |
|-----------------|--|--|-------------|
| <i>Recipe 1</i> | | | |
| Step 1 | 10 ml HNO_3 3 ml H_2O_2 | 130 | 30% (75 W) |
| Step 2 | 5 ml HNO_3 5 ml H_2O_2 | 160 | 50% (125 W) |
| <i>Recipe 2</i> | | | |
| Step 1 | 5 ml HNO_3 5 ml H_2SO_4 3 ml H_2O_2 | 130 | 30% (75 W) |
| Step 2 | 5 ml HNO_3 5 ml H_2O_2 | 160 | 50% (125 W) |
| <i>Recipe 3</i> | | | |
| Step 1 | 9 ml HNO_3 3 ml HCl 3 ml H_2O_2 | 130 | 30% (75 W) |
| Step 2 | 5 ml HNO_3 5 ml H_2O_2 | 160 | 50% (125 W) |
| <i>Recipe 4</i> | | | |
| Step 1 | 3 ml HNO_3 9 ml HCl 3 ml H_2O_2 | 130 | 30% (75 W) |
| Step 2 | 5 ml HNO_3 5 ml H_2O_2 | 160 | 50% (125 W) |

^a All procedures take 30 min.

a quartz hot-plate in a clean container (class 100) to evaporate to incipient dryness, and subsequently adding 5 ml of nitric acid (1%). The solution was used for the determination of the metals by ICP-MS (Perkin–Elmer Sciex Elan 5000, Norwalk, CT) and ICP-AES (Perkin–Elmer, Optima 3000). To evaluate the completeness of the various digestion recipes, the solution after digestion was evaporated to dryness. The digestion efficiency was obtained from weighing the ratio of the total dry residual solid, after and before sample digestion and complete reagent evaporation.

3. Results and discussion

3.1. Behaviors of metallic impurities

As reported previously [9], metal impurities would migrate from the BARC and PR into the underlying substrates during the lithographic process. To achieve the best cleaning efficiency for Na, Fe, Zn and Cs, an understanding of the behavior of the surface metals and the reaction pathways is necessary.

It has been reported [17–19] that the electrochemical segregation of metal ions at the interface between cleaning solutions and silicon substrates includes the following three possible mechanisms. The first is related to electronegativity. In general, the differences of electronegativity between the atoms provide an indicator of the polarity and the ionic character for the chemical bond. The respective electronegativities [20] are 1.9, 0.93, 1.83, 1.65 and 0.79 for Si, Na, Fe, Zn and Cs. Na, Fe, Zn and Cs have a lower electronegativity than silicon. Due to the fact the metal contaminants (in the ionic form) can not attract electrons from the silicon substrate, electronegativity is ruled out as the segregation mechanism for the metals investigated in this work.

The second mechanism is related to the differences in the enthalpy of oxide formation for the metals and silicon. The mechanism is always to be considered because the cleaning processes of SC1 and SC2 have oxidation characteristics. The precipitation mechanism is that, during the formation of an oxide on the silicon surface, metal ions are included as metal oxides. Table 2 summarizes the standard molar enthalpies for the formation of metal fluoride and oxide compounds

Table 2
Standard molar enthalpy of oxide formation at 25°C in kJ mol⁻¹

| Formula | ΔH |
|----------------------------------|------------|
| NaF | -576.6 |
| Na ₂ SiO ₃ | -1554.9 |
| NaOH | -425.6 |
| FeF ₂ | -764.4 |
| Fe ₂ O ₃ | -824.2 |
| Fe ₃ O ₄ | -1118.4 |
| Fe ₂ SiO ₄ | -1479.9 |
| ZnF ₂ | -764.4 |
| ZnO | -350.5 |
| Zn ₂ SiO ₄ | -1636.7 |
| Zn(OH) ₂ | -641.9 |
| CsF | -553.5 |
| Cs ₂ O | -345.8 |
| CsOH | -417.2 |
| SiO ₂ | -910.7 |

[20]. A negative enthalpy indicates that oxide formation is a heat releasing process. This observation indicates that sodium metasilicate, iron(II, III) oxide, iron orthosilicate and zinc orthosilicate are possible structures because of their lower enthalpies than silicon dioxide.

The third mechanism considers the effect of adsorption of the metal ions. This effect is not only dependent on the concentration of the metals but also on the electrochemical potential and solution pH. The latter two mechanisms might be responsible as plausible surface reactions for Na, Fe, Zn and Cs in the cleaning solutions.

3.2. Evaluation of cleaning efficiency

Six wet cleaning processes, i.e., SC1, H₂O, SC2, DHF, SPM, and BOE, are commonly applied in wafer fabrication. Generally, the wet cleaning processes are used to overcome the contamination problem after pattern definition. Mixtures of HF and NH₄F, known as BOE, are used to etching silicon oxide film and can provide a constant etching rate. Removal or cleaning of heavy organic material, such as PR and its by-products, can be accomplished with SPM. However, the extents of residual metals after BOE and SPM cleanings should still be carefully evaluated. It is beneficial for the understanding of the residual metal

levels after the standard cleaning process. The cleaning sequence DHF–H₂O–SC1–H₂O–SC2–H₂O, modified from the conventional RCA clean, is well accepted because it shows better cleaning performance on light organic, particulate, and metal species [21]. In this work, various wet processes were tested against its removal efficiency for metal impurities by a radioactive tracer technique. Among the prominent factors affecting the impurity removal efficiency, the substrate types and the cleaning temperatures were studied.

Tables 3–5 list the (percentage) remaining ratios of radioactive tracers for Na, Fe, Zn and Cs after 5 min of treatment in various cleaning recipes at temperatures of 25, 47 and 82°C. It can be seen that Na and Cs impurities are not found for any substrates and temperatures after SC1 cleaning. This observation indicates that alkali metal ions can effectively be removed by SC1 cleaning. However, Fe shows more significant retention (>45%) than Zn (<5%), regardless of substrate type and solution temperature. What are the reasons for these different behaviors? According to the behaviors of metallic impurities mentioned in Section 3.1, the effects of the enthalpy of oxide formation and adsorption are the two major reasons. This finding could be explained from Table 2 that, during SC1 cleaning, iron(II, III) oxide and iron orthosilicate were included

Table 3

Residual ratios of radioactive tracers after 5 min of dipping in various cleaning recipes at 25°C

| Substrate | Element | SC1 (%) | H ₂ O (%) | SPM (%) | BOE (%) |
|-----------------|-----------------|---------|----------------------|---------|---------|
| Bare Si | Na | 0 | 0 | 0 | 0 |
| | Fe | 95.5 | 84.7 | 1.6 | 0.3 |
| | Zn ^a | 4.3 | 10.3 | 0 | 0 |
| | Cs | 0 | 1.6 | 0 | 0 |
| Poly Si | Na | 0 | 0 | 0 | 0 |
| | Fe | 92.1 | 72.0 | 1.1 | 0.7 |
| | Zn ^a | 0.3 | 0 | 0 | 0 |
| | Cs | 0 | 0.6 | 0 | 0 |
| Silicon oxide | Na | 0 | 0 | 0 | 0 |
| | Fe | 86.6 | 87.9 | 0 | 0 |
| | Zn ^a | 2.7 | 0 | 0 | 5.0 |
| | Cs | 0 | 0 | 0 | 0 |
| Silicon nitride | Na | 0 | 0 | 1.4 | 0 |
| | Fe | 93.9 | 93.1 | 0 | 0.8 |
| | Zn ^a | 2.1 | 0 | 1.8 | 0.9 |
| | Cs | 0 | 0 | 1.4 | 0 |

^a [9].

Table 4

Residual ratios of radioactive tracers after 5 min of dipping in various cleaning recipes at 47°C

| Substrate | Element | SC1 (%) | H ₂ O (%) | SPM (%) | BOE (%) |
|-----------------|-----------------|---------|----------------------|---------|---------|
| Bare Si | Na | 0 | 0 | 0 | 0 |
| | Fe | 75.2 | 64.1 | 0.5 | 0.2 |
| | Zn ^a | 0.5 | 20 | 0 | 0.9 |
| | Cs | 0 | 0.3 | 0 | 0 |
| Poly Si | Na | 0 | 0 | 0 | 0 |
| | Fe | 84.7 | 71.5 | 0.7 | 0.2 |
| | Zn ^a | 0 | 17.4 | 0 | 0.8 |
| | Cs | 0 | 1.3 | 0 | 0 |
| Silicon oxide | Na | 0 | 0 | 0 | 0 |
| | Fe | 73.8 | 60 | 0 | 0 |
| | Zn ^a | 0 | 0 | 0 | 0 |
| | Cs | 0 | 0 | 0 | 0 |
| Silicon nitride | Na | 0 | 0 | 0 | 0 |
| | Fe | 76.4 | 88.8 | 0 | 0.2 |
| | Zn ^a | 0 | 0 | 0 | 0 |
| | Cs | 0 | 0 | 0 | 0 |

^a [9]. Ratios were all 0% for SC2 and DHF.

in the grown silicon oxide, while zinc oxide can not exist on the surface due to the unfavorable enthalpy.

Comparing Table 3 (25°C) with Table 4 (47°C), the residual metallic impurities after SC1 treatment generally decrease with increasing with temperature,

Table 5

Residual ratios of radioactive tracers after 5 min of dipping in various cleaning recipes at 82°C

| Substrate | Element | SC1 (%) | H ₂ O (%) |
|-----------------|-----------------|---------|----------------------|
| Bare Si | Na | 0 | 0 |
| | Fe | 81.0 | 65.4 |
| | Zn ^a | 1.9 | 0 |
| | Cs | 0 | 0 |
| Poly Si | Na | 0 | 0 |
| | Fe | 73.8 | 83.9 |
| | Zn ^a | 0 | 0 |
| | Cs | 0 | 0 |
| Silicon oxide | Na | 0 | 0 |
| | Fe | 69.9 | 45.0 |
| | Zn ^a | 0 | 0 |
| | Cs | 0 | 0 |
| Silicon nitride | Na | 0 | 0 |
| | Fe | 48.1 | 36.7 |
| | Zn ^a | 0 | 0 |
| | Cs | 0 | 0 |

^a [9]. Ratios were all 0% for SC2, DHF, SPM and BOE.

suggesting that the diffusion of metals between substrates and SC1 solution is becoming significant on elevating the temperature. However, from Table 5, the cleaning efficiency at 82°C is not temperature dependent. This tendency could be explained on the basis of the bath life of the cleaning solution as a consequence of the change of chemical composition. The temperature strongly affects the lifetime (i.e., bath life) of SC1 solution, especially at higher temperatures. It has been reported that hydrogen peroxide is thermally unstable and ammonia is easily evaporated at higher temperatures [22]. For SC1 reactions, hydrogen peroxide serves as an oxidant, while ammonia serves to etch away the grown silicon oxide. The etching rates increase with temperature by using SC1 solution. But taking the bath life into consideration, the etching rates could be lowered with increasing temperature.

Water is generally used to rinse off chemicals from the previous cleaning step in wet wafer processes. It is found that the remaining ratios of Na, Zn and Cs become 0 for all underlying substrates at 82°C. This observation indicates that hot water immersion is very effective for dissolving Na, Zn and Cs from the wafer surface. Also, this finding suggests that the diffusion lengths of these metals are very shallow, and the wafer can easily be cleaned by hot water. However, it should be cautioned that this observation may be true only for Na, Zn and Cs; Fe is still present after hot water dipping (at 82°C). This may be attributed to either strong adsorption, or the formation of the oxide in hot water dipping.

SC2 solution is found to be satisfactory as a cleaning agent for removing Na, Fe, Zn and Cs impurities. Our results clearly show that Na, Fe, Zn and Cs impurities can be fully removed at higher temperatures (47 and 82°C) from any substrate. This occurs because its strong acid (H^+) composition effectively replaces the metal ions (i.e., Na^+ , Fe^{3+} , Zn^{2+} , Cs^+) on the wafer surface. Similar behavior is also apparent for cleaning with DHF solution. This result is apparently consistent with that of Anttila et al., who predicted that the contaminant Zn should be removed in DHF [23], despite the fact that thousands of particles may be added to the wafer surface. The SPM solution also has a strong acid composition, therefore the results are similar to those for SC2 and DHF. No retention effects can be seen at a cleaning temperature of 82°C, regardless of the substrate type. The cleaning efficiency of BOE solution

is only significant at 82°C for these metals. At room temperature and 42°C, a proportion of the radioactive metals is counted on the wafer. From these results, we have demonstrated that the metal impurities are initially trapped in the grown native oxide, while BOE dipping at the higher temperature can etch away the whole grown native oxide and remove the tracers.

3.3. Evaluation of digestion efficiency

The previous paper mentions that metal impurities might migrate from lithographic materials into the underlying substrate [9]. To prevent the contamination problem, the most effective method is to control the impurity levels in the original BARC and PR. However, it is not easy to determine trace metals in such samples. If using direct instrumental determination, the complex and viscous character of such materials can severely clog the sample loop or the interface to the measuring instrument, thus affecting the analytical reliability. For routine quality control, it is necessary to develop analytical methods which take less time, provide a quick response and a reasonable throughput for the processes. Taking reliability and throughput into consideration, it is necessary to develop the appropriate pretreatment method for trace metals determination. Destruction of the organic matrix with an open-focused microwave system has been used for trace and ultratrace analysis [15,16]. However, to what extent the matrix is destroyed by specific decomposition conditions has so far seldom been evaluated quantitatively. Conventionally, when clear and colorless solutions are obtained, or when total recovery of some elements is obtained, it is assumed that oxidation of the organic matter has been completed for all practical purposes. However, such assumptions are not necessarily reliable in all cases. More conclusive and direct information as to the amount of resultant residual material is beneficial for choosing the best digestion recipe.

In this study, a gravimetric method was tested for its applicability to evaluate the completeness of sample matrix destruction with various digestion recipes. Table 6 lists the digestion recipe and the digestion efficiency for DUV BARC, DUV PR and i-LINE PR. Prior to the sample analysis, the sample sizes were optimized to achieve the best detection limits (DLs)

Table 6
Effects of digestion efficiency on lithographic materials after open-focused microwave digestion for various recipes^a

| Sample | DUV BARC (%) | DUV PR (%) | i-LINE PR (%) |
|-----------------------|--------------|------------|---------------|
| Recipe 1 | 99.8 | 99.6 | 96.3 |
| Recipe 1 ^b | 96.5 | 97.2 | 73.0 |
| Recipe 2 | 97.9 | 95.9 | 95.6 |
| Recipe 3 | 99.8 | 96.7 | 87.7 |
| Recipe 4 | 97.0 | 78.7 | 80.1 |

^a Sample volume is 3 ml.

^b Digestion only with the first step of Recipe 1.

and fit the scale of the digestion vessel. If a 5 ml sample is used, the abrupt effervescence produced in the first minutes led to the ascent of the digestion solution through the vessel, causing spillover. Such an unsuitable sample volume should influence the method reliability. It can be noted that too large a sample volume increases the reaction (digestion) rate, and produces more effervescence. After testing different amounts of lithographic samples, the upper limit of the sample size is 3 ml. To minimize the dissolution time, the microwave power of the first step was elevated to 50%. However, the same problem arose, the digestion solution immediately bubbling out of the vessel, especially for BARC. The working power for the first step should be limited to 30% to assure digestion reliability. Likewise, the upper temperature limit, the power and the time for the first step of digestion are found to be 130°C, 30% and 30 min, respectively, while 160°C, 50% and 30 min are recommended for the second step.

The recipes in Table 6 are all effective for DUV BARC digestion, which indicates that the various recipes can easily destroy the matrix with the proposed open-focused microwave digestion program. For the DUV PR sample, Recipe 4 is less effective. The further question is how Recipe 3 can better dissolve the DUV PR sample than Recipe 4 by only changing the aqua regia for 'reverse' aqua regia in the first step. This observation shows that nitric acid is more beneficial for the digestion of lithographic samples than hydrochloric acid. A large nitric acid volume (9 ml) enhances the oxidizing ability and facilitates the digestion. This observation also confirms the digestion efficiency of Recipe 2, which uses only 5 ml of nitric acid. The presence of 5 ml of sulfuric acid in addition to the 5 ml of nitric acid also exerts powerful oxidation at temperatures above 100°C. Similar to

Recipes 1 and 3, Recipe 2 can also maintain better digestion efficiency.

For the i-LINE PR, Table 6 indicates that only the Recipes 1 and 2 can achieve better digestion efficiency than the other recipes. The use of only the first step of Recipe 1 is not satisfactory to destroy the matrix. However, the following with the second step with 5 ml of nitric acid and hydrogen peroxide can achieve and ensure higher digestion efficiency (from 73.0 to 96.3%). Although Recipes 1 and 2 are found to be appropriate for the digestion of lithographic samples, there are two drawbacks when using sulfuric acid for digestion. The first is the high boiling point of sulfuric acid, which requires a long time for reagent evaporation after digestion and prior to instrumental analysis. The second is that the incomplete evaporation of the sulfuric acid can induce troublesome mass spectroscopic interference in the ICP-MS determination. From these viewpoints, Recipe 1 has been chosen as the best means of decomposing lithographic samples.

3.4. Analysis of lithographic materials

The analytical performance of the open-focused microwave digestion and instrumental determination method were evaluated in terms of detection limit, spike recovery and accuracy. The detection limits of this method are defined as the analyte concentrations that give signal intensities three times the standard deviation of the procedure blank ($n=6$). It was estimated that the detection limits were in the ng ml^{-1} and sub-ng ml^{-1} levels for ICP-MS analysis, and ng ml^{-1} level for ICP-AES analysis. As shown in Table 7, Na and Al have poor detection limits for both ICP-MS and ICP-AES analysis. This observation can be attributed to the digestion process being operated in an open environment, leading to contamination problems for Na and Al. Except for Al, Ca and Fe, the detection limits for ICP-MS are better than those for ICP-AES. In ICP-MS detection, the consideration of mass spectroscopic interferences is necessary. The background of ^{27}Al is elevated by the intense signal at the neighboring peak of $m/z=28$ (from N_2^+ and Si^+). ^{44}Ca is generally affected by the polyatomic effect at $m/z=44$ from $^{12}\text{C}^{16}\text{O}_2^+$, and ^{57}Fe from $^{40}\text{Ar}^{16}\text{O}^+\text{H}^+$. For this reason, the detection limits of Al, Ca and Fe are degraded.

Table 7

Detection limits (DLs) for elements in lithographic materials digested by an open-focused microwave method, followed with ICP-MS or ICP-AES analysis^a

| Element | ICP-MS | | ICP-AES | |
|---------|--------|---------------------------|-----------------|---------------------------|
| | Mass | DL (ng ml ⁻¹) | Wavelength (nm) | DL (ng ml ⁻¹) |
| Na | 23 | 84 | 589.6 | 126 |
| Al | 27 | 20 | 396.2 | 15.9 |
| Ca | 44 | 45 | 396.8 | 4.5 |
| Cr | 52 | 0.74 | 267.7 | 1.2 |
| Fe | 57 | 10.2 | 259.9 | 3.9 |
| Ni | 60 | 0.39 | 231.6 | 2.4 |
| Cu | 65 | 0.39 | 324.8 | 2.4 |
| Zn | 66 | 1.28 | 213.9 | 4.8 |
| Au | 197 | 0.57 | 242.8 | 3.6 |
| Pb | 208 | 0.22 | 220.4 | 4.1 |
| Sn | 118 | 4.04 | 235.5 | 14.2 |
| Pt | 195 | 0.28 | 214.4 | 5.7 |
| Cs | 133 | 0.1 | – | – |

^a The detection limits are based on three times the standard deviation of the procedure blank ($n = 6$).

Recovery tests were performed by spiking equivalent amounts of 5 ng ml⁻¹ metals into the open-focused digestion reactor, followed by the use of digestion recipe (Recipe 1, see Table 1) and ICP-MS determination. The results of the spike recovery tests for these metals are shown in Table 8. As can be seen, the spike recoveries for all the analytes except Ca were in the ranges 82–119, 88–121 and 82–112% for DUV BARC, DUV PR and i-LINE PR, respectively. The recovery of Ca was not acceptable due to

Table 8

Spike recoveries (%) for lithographic samples digested by open-focused microwave digestion, followed by ICP-MS analysis

| Element | DUV BARC | DUV PR | i-LINE PR |
|---------|----------|--------|-----------|
| Na | 102 | 118 | 109 |
| Al | 119 | 121 | 112 |
| Ca | 125 | 146 | 131 |
| Cr | 110 | 97 | 82 |
| Fe | 99 | 92 | 95 |
| Ni | 82 | 100 | 109 |
| Cu | 87 | 101 | 100 |
| Zn | 100 | 103 | 110 |
| Au | 99 | 88 | 112 |
| Pb | 113 | 92 | 98 |
| Sn | 91 | 108 | 101 |
| Pt | 90 | 97 | 102 |
| Cs | 104 | 100 | 96 |

Table 9

Analytical results for lithographic samples digested by open-focused microwave, followed by ICP-MS analysis

| Element | DUV BARC | | DUV PR | | i-LINE PR | |
|-----------------|---------------------|---------|---------------------|---------|---------------------|---------|
| | ng ml ⁻¹ | RSD (%) | ng ml ⁻¹ | RSD (%) | ng ml ⁻¹ | RSD (%) |
| Na | 155 | 9.0 | 343 | 2.9 | 246 | 1.6 |
| Na ^a | 146 | 11.6 | 387 | 9.8 | – | – |
| Al | 172 | 35.5 | 3.63 | 9.9 | 49.1 | 0.6 |
| Al ^a | 178 | 35.4 | ND | – | – | – |
| Ca | 292 | 5.8 | 192 | 31.3 | 207 | 15.9 |
| Cr | 1.90 | 17.9 | 8.7 | 12.6 | 8.62 | 1.39 |
| Fe | ND ^b | – | ND | – | ND | – |
| Ni | 0.64 | 10.9 | 1.07 | 25.2 | 1.70 | 21.8 |
| Cu | 1.65 | 25.5 | 3.27 | 6.7 | 12.9 | 2.3 |
| Zn | 4.50 | 34.7 | 2.20 | 6.8 | 6.20 | 1.9 |
| Au | 5.38 | 12.3 | 13.2 | 24.2 | 1.45 | 12.5 |
| Pb | ND | – | ND | – | 1.14 | 4.4 |
| Sn | ND | – | 6.14 | 22.1 | ND | – |
| Pt | ND | – | ND | – | ND | – |
| Cs | ND | – | ND | – | ND | – |

^a Analysis by ICP-AES; RSD: relative standard deviation ($n = 3$).

^b ND: not detected.

the polyatomic interference from CO₂⁺ in ICP-MS detection. The results of spike recoveries indicate the feasibility by applying the open-focused microwave digestion method and ICP-MS multi-elements determination method for lithographic samples.

The proposed method has already been applied to the determination of metals in semiconductor lithographic samples. Table 9 shows the results. The relative standard deviations (RSDs) for DUV BARC, DUV PR and i-LINE PR are within 35.5, 31.3 and 21.8%, revealing that the results all have fairly good precision. Despite no commercial certified reference samples being available for these samples, the literature reports [24], obtained from closed-vessel microwave digestion and ICP-MS analysis, are all in good agreement with this study. In addition, the results for Na and Al by ICP-AES determination also demonstrate the accuracy of the proposed method.

The sample throughput of this method is up to 3.5 h⁻¹ for analysis of 13 elements. The conventional method using GFAAS, as proposed in the literature [12], is estimated to accommodate only 0.4 h⁻¹ for 13 elements. Therefore, the proposed method is very suitable for metals determination in lithographic

samples. The analytical throughput of the present method is eight times greater than the conventional GFAAS method.

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