SPWCC 2007 PROCEEDINGS

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THOMAS J. MOSEMAN, NXP SEMICONDUCTORS

In-coming chemical quality has been left to the chemical suppliers. Semiconductor fabricators have very limited or no capability to detect problems with process chemistries from their suppliers. This is to say that poor chemical quality is discovered through in-line test data or poor e-sort performance. Chemical quality is assumed to be what has been sent from the supplier and is typically documented through a certificate of analysis. Changes than can and do occur during in-house handling are disregarded and not monitored

Historically speaking, the risk from suppliers is low. Documented mishaps for out of specification material shipments are rare. In fact the semiconductor industry in general insists on suppliers with a superior quality history and a robust quality program. Once the chemical has been containerized and shipped there is very little quality control. However, these quality programs are not perfect and there have been isolated events. Events that resulted from human error within the fabrication facility are not very well documented, but those that have been have resulted in significant losses in product, production time and in some cases process equipment damage.

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EUGENE SHALYT, ECI TECHNOLOGY

Modern trends in wet processing requires real-time control of highly diluted multicomponent solutions. This presentation illustrates the capability of NIR analysis. Ultra low noise level in combination with multivariate signal from diode-array spectrometer allows effective compensation for temperature and bubble-induced interferences, as well as selective determination of multiple components present in wide concentration range from ppm level to almost 100%.

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PRANATHI PERATI, DIONEX CORPORATION

This paper describes a new and improved method for determining trace anions in water-miscible organic solvents by ion chromatography (IC).

Introduction

In the manufacture of semiconductor materials, a great deal of attention is focused on minimizing sources of contamination. Yield and reliability can be significantly compromised by ionic contamination. Of particular interest are those chemicals that come into contact with microelectronic circuitry, such as isopropyl alcohol, acetone, and N-methyl-2-pyrrolidone.

Analysis of trace anions in solvents by wet chemical methods is laborious and time consuming. Procedures have, in the past, involved evaporation of a large volume of sample for several hours on a hot plate.[1] Anions are determined by either colorimetric or turbidimetric methods, and each anion must be determined separately. This paper describes a new and improved method for determining trace anions in water-miscible organic solvents by ion chromatography.

In a prior method[2], anions are removed from the solvent matrix and concentrated on a 4-mm IonPac® AG9-HC column. These concentrated anions are then eluted to a 2-mm IonPac AS9-HC analytical column set, where separation occurs. Method detection limits (MDLs) for chloride, sulfate, phosphate, and nitrate are less than 1 µg/L. The procedure is automated and yields an analysis for the four anions in less than 45 min. See Figure 1 example chromatogram.

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JUNICHI TAKAHASHI, AGILENT TECHNOLOGIES, INC.

In order to get the full performance of ICP-MS, sample introduction device, plasma parameters and ion lens parameters must be optimized for each sample type. Actually ultra pure water or clean hydrogen peroxide analysis requires the lower detection limit. In this case the sample introduction device is chosen so that the higher sample uptake rate can be applied. On the other hand, for high matrix sample analysis the sample uptake rate must be reduced and the ion lens conditions must be optimized to minimize signal drift and matrix interference. Typical example is the bulk silicon wafer analysis. The various tuning sets of analytical condition and the choice of sample introduction device were shown and discussed for ultra pure water, bulk silicon wafer and isopropyl alcohol as example.

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MIKE QUILLEN, EASTMAN CHEMICAL COMPANY

Wafer cleaning challenges at the integration level are time consuming and resource intensive. In fact, many processes are qualified based upon achieving trade-offs between throughput and material integrity, such as in Cu/low-K integration where dielectric damage by plasma etch or CMP is weighed in against moisture uptake and residue [1-4]. Many of these applications may be modeled at the laboratory scale to rapidly generate a high volume of data [5]. This paper discusses the modeling of surface sensitive processes such as the Marangoni tool design [6] and introduces the use of alternative solvents and their mixtures to pure IPA in removing ionics, moisture, and particles using immersion bench-chemistry models of various processes. Method development and confirmation use in-situ analytical methods based upon ICP-MS, moisture outgas/titrimetry, and particle detection by laser interference. Physical properties were monitored to include contact angle by the Wilhemy technique to model surface effects. Methyl acetate (MA) [7] has been observed to provide >25% relative improvement in ionic and moisture capture and may further provide up to 60% improvement as compared to the industry standard, isopropanol (IPA). Unlike many of the cleaning processes which use IPA, we believe the advantages of MA go beyond what the physical properties may offer. Particle removal benefits were identified, however, the values were found to be method dependent using various deposition approaches. A description of the chemistries investigated, modeling, analytical equipment, and statistical analysis using Q-test are given.

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VLADIMIR DOZORTSEV, TRACEDETECT, INC.

The control of metal ion contamination during wet-chemical cleaning processes is critical to the fabrication of next generation of high density semiconductor devices. Moreover, continuous monitoring of the different cleaning sites contributes to better understanding of both contamination sources and mechanisms.

In this paper robust online analyzer for trace metal ion monitoring based on novel voltammetric detector has been presented. The analyzer is characterized by both high performance and versatility: 20 + metal and some nonmetal ions (Cu, Fe, Ni, Co, halogens etc.) can be determined at wide concentration range (µg/l to g/l). Robust and chemically inert design of the detector is compatible with electronic grade chemicals including HF, as well as with different process and waste waters. Long term overall system stability has been evaluated using continuous measuring of synthetic sample containing lead and copper ions: over 3000 consecutive measurements have been performed with high accuracy without any system maintenance. Characteristics of the detector have been demonstrated through analysis of nickel, cobalt, copper, and chromium at concentrations ranging fom 0.1ug/l through 125mg/l in synthetic samples.

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PING JIANG, ATMI

As semiconductor device geometries continue to shrink, wafer cleaning and surface preparation become some of the most important operations in device fabrication. Metal contamination during the wafer cleaning process is a critical issue. Current wafer cleaning solutions cannot effectively prevent metal redeposition without sacrificing cleaning efficiency and surface quality of the substrate. In this paper, we present a new generation of cleans, HF-R, developed to prevent metal contamination and redeposition during surface cleaning of silicon wafers. Electrochemical open circuit potential (OCP) measurements are used to investigate the effects of new cleaning solutions and different additives in the solution on Cu contamination during wafer cleaning processes. The ability of the HF-R solution to prevent/suppress copper deposition is compared with the traditional cleaning chemistries of dilute HF (DHF) and SC2 ($HCl:H_2O_2:H_2O$). The silicon wafers were further characterized by EDS, ICP-MS, SEM and AFM to determine surface quality and contamination levels after processing. In addition, the cleaning efficiency of copper films on silicon wafers using our novel cleaning chemistry was also investigated.

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DREW SINHA, SUMCO USA

The Impact of aluminum contamination on gate oxide quality and growth rate of gate oxide has increased interest in the reduction of aluminum contamination from the silicon surface. High segregation co-efficient of aluminum for silicon results into relatively higher level of aluminum precipitation, compared to other metals, on silicon wafer from SC1 solution of RCA based wet cleaning of silicon wafer. A number of physical properties including solution chemistry and thermodynamic properties influence the precipitation of its hydroxide on silicon surface or near silicon oxide interface. This results into inclusion of aluminum in chemical and/or native oxide grown during wet cleaning of silicon wafer. Hydrochloric acid is found be effective in removing the surface aluminum and prevents re-deposition whereas a mixture of hydrochloric acid and hydrofluoric, at room temperature is found to be effective in removing both the surface and oxide-included aluminum from silicon wafer. Kinetics of aluminum de-sorption from contaminated silicon wafer is obtained with hydrochloric acid alone at room temperature and at 68 C. De-sorption of aluminum is found to be significantly enhanced by addition of hydrofluoric acid. Desorption of aluminum is evaluated with a mixture of hydrochloric acid and varied concentrations of hydrofluoric acid. Measurement of native oxide thickness revealed progressively lower aluminum level away from the surface following mixed acid treatment. However, optimum concentration of hydrofluoric acid is required in order to maintain residual chemical oxide on the wafer front side necessary for a hydrophilic wafer surface. Furthermore, low-metal containing chelating agent is found to effective in reducing aluminum precipitation on the wafer from SC1 solution and increase the process capability for reduction of aluminum contamination further during subsequent acid treatment.

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HAIZHENG ZHANG, ENTEGRIS, INC.

As the number of interconnect layers in ICs has increased, the planarization of dielectric and metals layers has become more critical. Chemical mechanical polishing (CMP), mechanical polishing assisted by chemical action, produces such selective material removal, which makes the global planarization of both delectric and metal layers possible.

Post CMP wafer cleaning does never like in the past, which was a simple DI water rinse for removal of slurry particles. Additives now are added into the solution to make unique chemistries to remove trace levels of metallic residues and ions. Additives are also added to modify the adhesion force of the slurry particles to the metal films surface and to make the residue slurry particles easy to be removed. These additives in the post CMP cleaning solution offers unique challenges for the analytical laboratory. To measure the trace level metals in these solutions, traditionally, sample preparation is necessary to remove the organic contents.

In this article, an analytical method was developed to measure trace level metals in post CMP cleaning solutions without sample preparation. Using an Octopole Reaction Cell system inductively coupled plasma mass spectrometer (ORS-ICPMS), 25 elements can be analyzed directly in these post CMP cleaning solutions. The detection limits for these elements are in sub ppb level.

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Mark R. Litchy, CT Associates, Inc.

Delivery systems used to supply slurry to CMP planarization tools can damage slurry. In this experiment, four slurries were circulated in a simulated slurry delivery loop at a fixed flow rate and pressure using a variety of pumps (bellows, diaphragm, and magnetically levitated centrifugal) to determine the effect of circulation on the slurry health. During each test, a number of slurry health parameters were monitored including the size distribution of the particles in the slurry. Most slurry health parameters were unaffected during the tests. However, significant changes in the large particle tail (particles $\geq 0.5\ \mu m$) of the slurry particle size distributions (PSD) were observed. Both the pump and slurry type played important roles in the magnitude of the change. In some slurries, large increases in the large particle concentrations were observed during circulation with diaphragm and bellows pumps, while in other slurries increases were not observed. With the magnetically levitated centrifugal pumps, minimal changes were observed, regardless of the type of slurry tested.

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Jiaxiang (Jason) Ren, EGC Plastics

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Russell Holmes, RASIRC

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Zhao Lu, Hach Ultra Analytics

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S.H. Liu, Taiwan Semiconductor Manufacturing Company, Ltd.

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Shu. Fan. Chen, Taiwan Semiconductor Manufacturing Company, Ltd.

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Chia-Ching Wan, Taiwan Semiconductor Manufacturing Company, Ltd.

A sensitive air sampling method has been developed for the determination of phosphine in semiconductor clean room environment. Samples are collected with personal sampling pumps through sampling cassettes containing a silver nitrate-treated Teflon membrane filter and then acid trapped with nitric acid, analyzed by ICP-MS. The very low blank and high sensitivity provide low detection limit 8.0 pptv by 120min sampling time with a flow rate 2.0L/min, which is enough to monitor PH_3 contaminants in semiconductor manufacture environment. The collection efficiency was

estimated 90%. Demonstrated that high selectivity for phosphine without adsorptive interference of triethyl phosphate (TEP) and trimethyl phosphate (TMP), commonly existing in Fab environment. To minimize spectral interference from $^{19}F^{12}C$ molecular, using a higher resolution of 4000 mdm^{-1} of inductively coupled plasma mass spectrometer with sector field (ICP-SFMS) to determinate phosphine concentration. We use this method to detect the phosphine emitted from implanter tool during the PM period and reducing the phosphine level by local house vacuum treatment.

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IQBAL (IZZY) BANSAL, M/A-COM, A TYCO ELECTRONICS COMPANY

Silicon-to-silicon direct wafer bonding (DWB) is a 3-step sequence consisting of surface preparation, contacting and thermal annealing. The contacting is an operation of ultra-fine alignment and face-to-face joining of "handle" and "device" silicon wafers. Prior to ambient temperature Si-o-Si bonding, each silicon wafer surface is hydrophobic with minimal surface contaminations.

An in-situ hydrophobic technique is employed for simultaneously processing of both "handle" and device" wafers through an ultra-dilute oxide etchant for complete removal of chemical and native oxide films. The oxide etching step is immediately followed by a drying step. The contact angle averages between 65° and 70° for a "hydrogen-terminated" hydrophilic silicon surface.

Prior to joining operation, a laser beam Surfscan is employed to directly measure haze and light point defects (LPD's) on the surfaces of each silicon wafer. The sub-micron LPD's counts must be minimal in order to reduce density of voided or "disbonded" regions. A scanning acoustic microscope is used to quantatively detect the presence of micro-voids, delamination and other defects with an interface layer of a bonded wafer.

Detailed product throughput and yield data in terms of voided density are presented in this technical paper. Since 2000, over 8,600 annealed pairs have been manufactured with an overall voided "pass" yield measured in excess of 94%. These bonded silicon wafers are successfully utilized in fabrication of RF microwave products.

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HIROSHI TOMITA, TOSHIBA CORPORATION

Recently, copper and low-k dielectric materials have been used in the back-end-of-line (BEOL). These materials are very "soft" and "weak", so the use of organic solvents is well established in BEOL manufacturing. But, the organic residues and organometallic residues formed after dry etching are difficult to remove using historical one step chemical cleans without "self-induced-damage". Thus, special blend organic chemicals have been used by each device maker. Generally, the organic solvent processes are used in re-circulated chemical systems in single wafer clean machines, so resist and polymer residues accumulate in the chemical over time. Thus, particle counts and size on the wafer treated by a re-circulated chemical would depend on the sieving (or pore) size and volume of recirculation filters. The point of use type (POU) cleaning is a major system in batch wet benches, and it would be advantageous to introduce POU cleaning in single wafer. This study focused on the effectiveness of the single wafer POU cleans (one pass type) in the BEOL.

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SAMEER MADANSHETTY, UNCOPIERS, INC.

A new method based on constructively controlled microcavitation is being developed for resist stripping from wafers. Controlled microcavitation implosions are able to concentrate mechanical energy at surface points of interest to bring about desired local delamination, which in the present application is the removal of resist. Tests indicate that post processed resist can be removed precisely and completely without any collateral damage. Further, the method is entirely chemical free and environmentally friendly because only clean water and silent sound are used to implement microcavitation. Also, since the removed resist is still in solid phase it can be filtered out and the water can be reprocessed and reused, thus conserving the valuable resource. Most significantly, since no chemicals other than clean water are used and all unwanted resist is removed in one step, a further cleaning step is not needed. This article describes the energetics of controlled microcavitation, its implementation, and its instantiation in the stripping of variously processed resists.