Monitoring metal ion contamination onset in hydrofluoric acid using silicon–diamond and dual silicon sensing electrode assembly

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Potentiometric detection of trace levels of metallic contamination onset in hydrofluoric acid using a silicon-based sensor in conjunction with two non-contaminating reference electrode systems is presented in this paper. In the first case, conductive diamond was used as a non-contaminating reference electrode. Cyclic voltammetry and open-circuit potential experiments demonstrated the feasibility of using a conductive diamond film electrode as a quasi-reference electrode in the HF solution. In the second case, a dual silicon electrode system was used with one of the silicon-based electrodes protected with an anion permeable membrane behaving as the quasi-reference electrode. The dual silicon sensing electrode system possessed an additional operational advantage of being unaffected by the solution acidity. Though both sensing configurations were able to detect the metal ion contamination onsets at the parts-per-trillion to parts-per-billion levels, the dual silicon electrode design showed a greater compatibility for the on-line detection of metallic impurities in HF etching baths commonly used in semiconductor processing.

Introduction

The purity of the silicon wafer surface is an essential prerequisite for the successful fabrication of ultra-large-scale integrated silicon circuits. Many wafer-cleaning methodologies have been developed to remove trace impurities such as, ions, metals and particles from the silicon surface prior to high temperature processing (thermal oxidation, epitaxial growth, and diffusion). The chemistry based on sequential hydrogen peroxide chemical oxidation, chloride complexation and hydrofluoric acid (HF) etching is generally the most utilized cleaning approach for silicon wafers before metallization. To ensure the optimal device fabrication yield, the impurities in various chemical cleaning baths were carefully monitored by periodic sampling off the production line.

We previously reported a new class of silicon-based sensors, which can sensitively detect parts-per-billion (ppb) to parts-per-trillion (ppt) levels of ionic impurities in hydrofluoric acid, alkaline hydrogen peroxide solution and ultra-pure water. In NH₄OH–H₂O₂ solutions, adsorption of ion impurities such as, Fe³⁺ and Cu²⁺ into a thin sub-oxide layer results in a large positive shift of silicon open-circuit potential. In HF solutions, metal ion impurities such as, Ag⁺, Cu²⁺, Au³⁺, Pt²⁺ and Pd²⁺ can readily be reduced and deposited as zero-valence metal particles on HF-etched silicon surfaces. The nanoscale metal deposition shifts the silicon potential more positively to afford below ppb detection sensitivity. The silicon-based sensor can be used in integration circuit (IC) device fabrication processes to detect the critical contamination onset and ensure the device fabrication yield. However, a non-contaminating stable reference electrode is needed to accompany the potentiometric silicon-based sensor in a practical on-line monitoring application.

Conventional calomel and Ag/AgCl reference electrodes with free flow capillary or leaky ceramic junctions are suitable for general potentiometric analyses, but will cause detrimental contamination in the ultrapure chemical baths used in the fabrication of IC devices. Based on reported literature, to avoid the leakage problem the internal liquid electrolyte is generally protected by a polymeric membrane layer or replaced by embedding the electrolyte in a polymer membrane matrix.

In another interesting approach, the reference electrode is made from two separate anion and cation conductive membranes coated on Ag/AgCl electrodes connected in parallel. However, the chemical stability of Ag/AgCl based solid-state reference electrodes can be compromised in corrosive environments, such as HF acid baths. In this work, we report two different approaches for the preparation of a non-contaminating quasi-reference electrode for the silicon sensor assembly. First, we use a conductive diamond electrode as a non-contaminating quasi-reference electrode. Cyclic voltammetric studies with a standard redox couple indicated that the conductive diamond material is suitable for functioning as a quasi-reference electrode. In another approach, an additional silicon electrode protected by an anion permeable membrane was used as the quasi-reference electrode. The latter approach allows both sensing and reference electrodes to be derived solely from the silicon wafer and has a greater potential to be applied in the online monitoring application for IC chemical processing.

Experimental

Silicon electrode preparation

Two different configurations were used for the silicon electrode assembly. In the first case the silicon chip derived from single crystal n-Si arsenic doped wafers was encapsulated in a perfluoroalkoxy (PFA) polymer electrode body as previously described. In the second case n-Si arsenic doped wafer was first cut to size (3 cm × 1 cm) and then subjected to standard silicon wafer cleanings (HF, NH₄OH–H₂O₂, HCl–H₂O₂). The silicon chip was held by a specially designed clamp, which was covered with a gold foil to ensure proper electrical contact. The Ag⁺–HF solutions were prepared by dissolving Ag₂SO₄ (99.999%, Puratronic, Aesar) in electronic grade HF (Hashimoto) solution. All PFA labware was cleaned by boiling in 10% HNO₃ three times followed by an ultrapure water (R > 18.2 MΩ) rinse prior to running the experiments.
Diamond electrode preparation

Polycrystalline diamond films (ATM Inc.) were grown on Si (100) (p-type, 0.01 Ω cm) substrates in a hot-tungsten filament assisted chemical vapor deposition system. The diamond coated wafers were cut into (1 cm × 1 cm) chips, which were then treated with 10% HNO₃ for 10 min, etched in 4.9% HF for 5 min followed by ultrapure water rinsing. The electrical contact was made to the back side of the diamond chip using Ga-In eutectic (99.99%, AESAR). The diamond chip was then encapsulated in a custom-made PFA electrode body, which allowed solution contact only to the front side of the diamond chip.⁶

Pre-treatment of anion membrane

Anion selective membranes provided by Millipore Corporation were used for the experiments. These membranes were designed to be selectively permeable to F⁻ ion. The membranes were conditioned (after cutting to 2 cm × 2 cm dimensions) by soaking in hot ultrapure water (80 °C) for 15 min. For the purpose of cleaning they were soaked in 10% HCl for 1 h followed by rinsing in ultrapure water. This cleaning process was carried out three times after which the membranes were soaked in a 0.01% HF solution for a minimum of 24 h before being used in experiments. The pre-treated membranes were sealed in a specially designed PFA tube during the course of the experiment.

Instrumentation

The open-circuit potential of the sensing electrodes was measured with respect to a double junction standard Ag/AgCl reference electrode (Orion, Model 900200) using a computer interfaced high input impedance potentiometer (Accumet 50, Fisher Scientific) under normal room light conditions. The outer body of the reference electrode was thoroughly rinsed with ultrapure water and the outer junction solution (10% KNO₃) replenished prior to each experiment. Cyclic voltammetry experiments were performed using an EG&G 273 potentiostat in a standard three-electrode cell with a glassy carbon working electrode, a platinum counter electrode and a diamond thin-film quasi-reference electrode. Inductively coupled plasma mass spectroscopy ICP-MS (Fisons, Model PQS) and graphite furnace atomic absorption spectroscopy (GFAAS, Varian SpectraAA 330/400) were used to analyze the purity of the sample solutions. An atomic force microscope (AFM, Nanoscope III, Digital Instruments) operated in tapping mode was used to image the silicon sensor surface. Scanning electron microscopy (SEM) was performed with a JEOL JSM-T300 electron microscope and energy dispersive X-ray (EDX) analysis was carried out using a Tracor Northern TN–5500 analyzer.

Results and discussion

Fig. 1 depicts the time dependent potentiometric response of a silicon-sensing electrode with respect to a double junction Ag/AgCl reference electrode in 0.01% HF solution. The hydrogen terminated silicon electrode was previously shown to hold a stable potential in pure HF solution.¹¹ It has been suggested that the hydrogen abstraction from a hydrogen-terminated silicon surface is a reversible step during the open-circuit potential conditions.¹³ Thus the observed stable background potential could be due to the proton exchange reactions on the silicon-sensing electrode when immersed in HF solution. As observed in Fig. 1, the silicon potential remains stable for only ca. 15 h, after which there was an abrupt positive shift of the silicon potential indicating that the silicon electrode was contaminated. AFM analysis of the silicon sensor electrode confirmed that nanometer-sized deposits were present on the silicon surface.¹² For a reference electrode to function optimally there has to be a steady flow (3–30 µl h⁻¹) of the filling electrolyte through liquid junctions into the test solution.¹⁴ The observed abrupt change in the open-circuit potential of the silicon-sensing electrode is caused by the leakage of silver containing electrolyte into HF solution from the inner body of the Ag/AgCl reference electrode. To delay the onset of reference electrode contamination, we employed a double junction configuration to initially contain the electrolyte leakage in the outer junction KNO₃ solution. However, a non-contaminating reference electrode is clearly needed for the silicon-based sensor to be effectively operated in a continual operation mode like monitoring HF etching baths for IC processing.

Diamond as a quasi-reference electrode

The essential characteristics of suitable reference electrodes for the silicon-based sensor are that they should be non-contaminating, stable and chemically inert especially in the highly corrosive chemical environments prevalent in semiconductor processing. Most of the junction-free reference electrodes reported in the literature cannot meet all of the above requirements.¹⁵ The growth of polycrystalline diamond thin films by chemical vapor deposition has been well established.¹⁶ The synthetic diamond thin films possess several technologically important properties: hardness, corrosion resistance, high thermal conductivity, chemical inertness, dimensional stability and a conductive nature due to doping. Also, there is a growing interest in electrochemical and electroanalytical studies using conductive boron-doped diamond thin film electrodes.¹⁷ Our approach is to take advantage of the unique properties of the diamond thin film electrode and utilize it as a quasi-reference electrode.

To verify the chemical inertness of the diamond electrode in HF solution, we placed a diamond sample in pure HF solution for 24 h and then analyzed the solution with ICP-MS and GFAAS. The analysis indicated that no metallic contaminants were present above the detection limits (ca. 1 ppt) of the instruments. To further verify the chemical inertness of diamond, we placed a free-standing diamond film in a 1 ppm Ag⁺–HF solution for 1 h. No Ag deposits were observed on the diamond surface under SEM and EDX analyses. Separate measurements were also carried out to evaluate the potentiometric responses of the diamond electrode in HF solution in the presence of 1 ppb to 1 ppm Ag⁺. No apparent change of

![Fig. 1 Time dependent potential response of a silicon-sensing electrode in 0.01% HF with respect to Ag/AgCl reference electrode.](image-url)
diamond potential was observed even in the 1 ppm Ag⁺-HF solution. Therefore, diamond is chemically inert and exhibits stable potential in the HF solution containing metal ions.

To evaluate the effectiveness of the diamond reference electrode we carried out potential controlled experiments using a ferro-/ferri-cyanide redox couple. Fig. 2 shows a set of cyclic voltammograms of Fe(CN)₆³⁻/⁴⁻ redox couple for different scan rates using diamond as a quasi-reference electrode and glassy carbon as a working electrode. The cyclic voltammograms indicate that the formal reduction potential of Fe(CN)₆³⁻/⁴⁻ redox couple is stable with various scan rates and the plot of peak current versus (scan rate)²/₃ gives a linear response as expected for a fast reversible electron transfer system. This further validates the assertion that diamond does possess favorable qualities to be used as a quasi-reference electrode.

Fig. 3 shows the time dependent potential response of a silicon-sensing electrode with respect to a diamond quasi-reference electrode. As can be seen, a relatively stable background (±8 mV) can be maintained for at least 57 h when a diamond quasi-reference electrode was used. At the end of 57 h, 10 ppb of Ag⁺ was intentionally added to the HF solution to simulate an actual onset of metal ion contamination. The observed abrupt potential jump indicated that the silicon-based sensor retains its sensing capacity to detect trace amounts of metallic contaminants after 57 h of continual operation.

Although diamond has the above-mentioned favorable properties as a reference electrode, it has its drawbacks. In addition to the diamond film being fairly expensive, the potential of the diamond quasi-reference electrode can be changed by the pH of its contacting solution. The diamond films used in our study were hydrogen-terminated as previously prepared. We postulate that the potential of the diamond electrode is held by some equilibrium reactions between the hydrogen-terminated diamond surface and the protons in the solution. The change in the proton concentration will then cause a shift in the diamond potential. For example, our experimental data indicates that there was a potential difference of ~45 mV in the diamond baseline potential in 0.049% and 0.0049% HF solutions. However, for an IC HF etching bath with strictly controlled pH, the diamond quasi-reference electrode should perform well with the silicon-based sensor. Another useful observation is that the diamond quasi-reference potential drift due to the solution pH change was a slower process in comparison with the abrupt potential increase caused by metal ion contamination on the silicon sensor electrode. In principle, with proper analysis of the potential dynamic responses, the onset can be identified of the more detrimental metal ion contamination.

Quasi-reference electrode based on silicon/anion membrane configuration

Although the diamond quasi-reference electrode is a good candidate for solving the contamination problems originating from the leaky conventional reference electrode, it would be ideal if the reference electrode could be derived from the silicon wafer as well to maximize compatibility. Liu and co-workers previously reported a dual ion-selective electrode-flow injection system that does not contain a conventional reference electrode and no liquid junction is present. The system was successfully applied to simultaneously determine fluoride–nitrate, sodium–potassium and nitrate–potassium in natural waters. The operational requirement is that no cross-contamination should occur between two ion-selective electrodes that are operated in parallel. Our strategy is to use a dual silicon electrode system and protect one of the silicon electrodes by an anion permeable membrane to function as a quasi-reference electrode. The anion permeable membrane is designed to block the flow of metal cation contaminants from reaching the silicon reference electrode thereby maintaining a constant potential.

To verify the effectiveness of the membrane, the potential of a silicon-based sensor was monitored with respect to a Ag/AgCl reference electrode that was isolated from a silicon-based sensor with an anion permeable membrane. As previously demonstrated in Fig. 1, the leakage of the Ag/AgCl reference electrode will contaminate the silicon sensor within 15 h. With the protection of the anion membrane, the silicon potential can remain stable for several days without contamination. For instance, Fig. 4 shows the silicon sensor can sensitively detect a simulated contamination onset of 500 ppt Ag⁺ via a rapid increase of silicon potential deviation from a stable silicon potential background after 67 h of non-stop monitoring. The fact that a stable potential is maintained for such a long duration indicates that the anion membrane is effective in preventing the effusing metallic species from reaching the silicon sensing electrode surface. Another important point is that the anion permeable membrane was shown to be chemically stable in the corrosive HF acid environment and did not curtail the detection sensitivity of the silicon-based sensor.

Once the effectiveness of the anion specific membrane was established, we proceeded to test the dual silicon electrode and anion permeable membrane configuration. As shown in Fig. 5, the silicon electrode behaving as the reference electrode was sealed within the PFA tube with the anion specific membrane. Fig. 5 shows that the silicon sensor response in the silicon/
membrane/silicon configuration is stable for over 30 h and on the addition of just 100 ppt of Ag⁺ there is a shift in potential of over 100 mV in the positive direction. On addition of higher concentrations of Ag⁺ a more positive silicon potential shift is observed. In addition to Ag⁺, other metal ions including Cu²⁺, Au⁺, Pt²⁺ and Pd²⁺ can also be sensitively detected by the new dual silicon electrode–membrane configuration. The results indicated that the new silicon-based sensor assembly could effectively detect trace metal ion impurities down to the parts-per-trillion level, which is the sensitivity requirement for state-of-the-art IC processing control. Another important observation is that the sensor response from the dual silicon electrode system is practically independent of the solution acidity. Since the new sensor assembly derives both the sensing and the reference electrodes from the silicon wafer, any difference in potential is nullified. Our experimental data showed that there was a difference of only 6 mV in the silicon potential background in 0.01% and 0.49% HF solutions using the dual silicon electrode system.

In summary, two types of non-contaminating reference electrode systems were developed in this work to assist the silicon-based potentiometric sensor for detecting trace levels of metallic contamination onset in HF under simulated long term monitoring conditions. Both the diamond quasi-reference electrode and the dual silicon electrode–membrane configurations possess the essential characteristics of a suitable reference system. They are non-contaminating, stable and chemically inert especially in the highly corrosive chemical environments for semiconductor processing. Our data demonstrated that the dual silicon electrode design has two additional advantages, i.e. excellent compatibility and independence of solution acidity, and can thus be used in the on-line detection of metallic contaminants in HF baths for microelectronics applications.

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