identifying imperfections in silicon and silicon dioxide layers. The issue concludes with two papers on special technologies, one concerns selective electroless plating from aqueous media and the other, a spin-off from silicon processing, describes glass-to-metal seals made possible by the use of a silicon nitride barrier layer.

The processing techniques described in these 19 papers are drawn from the classical disciplines of chemistry, physics, ceramics, metallurgy and electrical engineering. The contributions of each discipline are so commingled, however, that the processes may more aptly be described as derived from materials science. Though trained in one or another of the classical sciences, the authors have acquired broadened perspective by interacting with individuals representing other disciplines. The stimulation resulting from this contact leads to increased ingenuity and imagination in the solution of scientific problems, and is a principal factor in the development of the new technology that continues to revolutionize the electronics industry.

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Cleaning Solutions Based on Hydrogen Peroxide for use in Silicon Semiconductor Technology

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Abstract—Hydrogen peroxide solutions at high pH are particularly effective for removing organic contaminants by oxidation; at low pH they are effective for desorbing metal contaminants primarily by complexing. The stability of these mixtures during usage and the effects of hydrogen peroxide depletion on the etching of silicon were measured as functions of resistivity type and doping concentration. These solutions are effective and simple to use, and have wide applications to the cleaning and preparation of silicon device wafers, quartz tubes, and implements employed in semiconductor processing.

1. Introduction

The increased demands on performance and reliability of silicon semiconductor devices and microcircuits in recent years have required the development of improved processing techniques. One key advance in modern solid-state technology is clean processing; contamination of sensitive device surfaces is minimized so that stability and reproducibility of device characteristics are greatly improved.

Hydrogen-peroxide-containing reagents have long been used to clean electron tube components,[1] but their use has not previously been described for the processing of semiconductor devices. The advantages and limitations of hydrogen-peroxide-containing solutions for silicon technology are pointed out, and their efficiency for removing contaminants has been determined by radioactive tracer[2,3] and MOS capacitance measurements.*

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* Parts of this work were performed and reported under U. S. Government Contract AD-36-039-SC-86729 (ref. 4).

2. Types, Sources, and Effects of Surface Contaminants

Surface contaminants can be classified broadly as molecular, ionic, or atomic.

Typical molecular contaminants are natural and synthetic waxes, resins, and oils. These are typically present after the mechanical grinding, lapping, and polishing operations of wafers. They may also include grease from fingers and greasy films that are deposited when surfaces are exposed to room air or stored in plastic containers. Photoresists and organic solvent residues also fall into this category. Layers of such molecular impurities in contact with the substrate surface are usually held by weak electrostatic forces. Organic contaminants on silicon devices, especially on surface-sensitive MOS structures, may cause polarization[5] and ionic drift[6] due to the transport of protons.[7] Water-insoluble organic compounds tend to make semiconductor and oxide surfaces hydrophobic, thus preventing the effective removal of adsorbed ionic or metallic impurities. The elimination of molecular contaminants should therefore be considered the first step in a cleaning process.

Ionic contaminants are present after etching of wafers in HF-containing etchants or in caustic solutions, even after extensive rinsing in deionized water.[2] They may deposit on the silicon surface by physical adsorption or by chemisorption. The removal of chemisorbed ions is much more difficult than the removal of ions attached to the surface by physical forces, and a chemical reaction must generally be used to achieve desorption. Of the ionic contaminants, alkali ions are particularly harmful in that they may move under the influence of electric fields or at elevated temperatures, causing inversion layers, surface leakage, drifts during device operation, and other instabilities.[8] In the growth of epitaxial silicon layers, visible ionic and molecular residues from improper cleaning are reported to give rise to twinning, dislocations, stacking faults, and other crystal defects.[9]

Atomic contaminants present on silicon surfaces include heavy metals such as gold, silver, and copper. They originate from acid silicon etchants and are usually plated out in the form of metallic deposits.[2] The removal of this type of contaminant generally requires reactive agents that dissolve the metal and complex the ionic form to prevent redeposition from the solution. Atomic impurities, especially the heavy metals, can seriously affect minority-carrier lifetime, surface conduction, and other device parameters governing stability of the devices.[10-12]

Since a contaminated surface is likely to contain all three types of impurities, it is necessary to first remove the gross organic residues masking the surface, then the residual organic materials, and finally the residual ionic and atomic contaminants. The gross organic residues from materials used in wafer-polishing operations may be removed by treatment with an organic solvent.*

3. New Cleaning Procedure

Two solutions, used sequentially, have been devised to remove any organic and inorganic contaminants remaining after solvent rinsing. Both solutions contain volatile reagents diluted with pure water. The exact compositions are not critical; some of the work discussed was done using slightly different compositions. However, the recommended compositions afford greater freedom in their application.

The first solution, typically 5-1-1 to 7-2-1 parts by volume of H_2O^*-$H_2O_2^\dagger$-$NH_4OH^\ddagger$, was designed to remove organic contaminants that are attacked by both the solvating action of the ammonium hydroxide and the powerful oxidizing action of the peroxide. The ammonium hydroxide also serves to complex some group I and II metals such as Cu, Ag, Ni, Co and Cd.

The second solution consist of H_2O^*-$H_2O_2^\dagger$-$HCl^{\dagger\dagger}$ in the typical proportions 6-1-1 to 8-2-1 by volume and was chosen to remove heavy metals and to prevent displacement replating from solution by forming soluble complexes with the resulting ions. The reagents used in these two solutions were chosen over other possible combinations because they are completely volatile. The cleaning action of the dilute HCl-H_2O_2 solution is similar to that of concentrated H_2SO_4-H_2O_2, or that of chromic–sulfuric acid mixtures, but is not as hazardous and presents no disposal problems.

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* Rinses in hot trichloroethylene are most generally used and yield satisfactory results if overheating is avoided so that thermal decomposition of the solvent is minimized. Triethyl amine is commonly added to trichloroethylene as a stabilizer, i.e., it reacts with the hydrochloric acid formed by thermal decomposition of the solvent. The resultant triethyl amine hydrochloride may remain as a residue on the surface following a rinse in trichloroethylene. As much as 140 mg of residue has been isolated from 1000 ml of a typical batch of electronic grade trichloroethylene. Tetrachloroethylene stabilized with ethyl alcohol does not have this disadvantage and is a more effective degreasing solvent. Hot xylene is one of the most effective degreasing solvents; even halocarbon grease residues are readily removed from silicon wafers. However, it has the disadvantage of being flammable and toxic. Freon fluorocarbon solvents are also satisfactory, especially if vapor degreasing or carefully controlled ultrasonic agitation techniques are employed.

* filtered DI or quartz distilled H_2O

† 30% unstabilized H_2O_2

‡ 27% NH_4OH

†† 37% HCl

The hydrogen peroxide used in the cleaning solutions should be the unstabilized, electronic grade. Stabilized peroxide may contain nonvolatile sodium phosphate and sodium stannate or amine derivatives as stabilizers. As mentioned, the compositions are not critical but the solutions of the approximate proportions given above have been found to be reliable, as well as simple to prepare and use.

Cleaning in either mixture is carried out at 75°C to 85°C for time periods of 10 minutes to 20 minutes, followed by a quench and rinse in running DI or quartz distilled water. As a final step, the wafers are "spun" dry and immediately transferred to an enclosure flushed with prefiltered inert gas. *Caution:* As both solutions are vigorous oxidizing agents and can evolve large quantities of gas even when cold, they must be kept in vented containers, or, preferably, mixed just before use.

4. Effectiveness of Contaminant Removal

Mechanically polished and precleaned bare and thermally oxidized silicon wafers were deliberately contaminated with typical organic water-insoluble materials, such as Apiezon wax, stearic acid, etc. They were rinsed with organic solvents and then cleaned with the ammonia–hydrogen peroxide solution only. Water spray tests[13] indicated that less than 1/10 monomolecular layer of hydrophobic organic contaminant remained.

The presence of surface contaminants, including water soluble organic compounds that can not be detected by the water spray test, can be determined by the more sensitive Capacitance-Voltage Bias Temperature Test (CVBT) on Metal-Oxide-Semiconductor (MOS) capacitors.*[8,14,15] The capacitor is formed by thermally growing a thin oxide layer on a silicon wafer to be tested, then evaporating a metal contact. The CVBT characteristics of the capacitor are measured in an inert atmosphere using a biasing stress of 10^6 V/cm and a bias temperature of 300°C. The lateral displacement of the characteristic CV curve provides a measure of the mobile charge (a shift of 1.0 volt is equivalent to 2.1×10^{11} mobile charges/cm^2 for an SiO_2 thickness of 1000Å). The use of MOS capacitors as detectors for both organic and inorganic contaminants is fully established[7,14,15] by correlation of CV measurements with radiotracer analysis of deliberately contaminated MOS devices. The CVBT method as described was therefore utilized to test the effectiveness of our cleaning procedure for removing deliberately introduced organic contaminants on MOS devices. These results are summarized in Section 5.

For inorganic contamination studies, silicon wafers and fused quartz samples were immersed in various solutions or etchants containing known quantities of specific ionic impurities "labeled" with radioactive ions of the same type. The quantities of radioactive impurities deposited and the amounts subsequently removed by cleaning treatments were determined by monitoring the radioactivity.[2,3] The efficiency of various acid hydrogen peroxide solutions for removing atomic contaminants including copper, gold, and chromium from silicon wafers and quartz surfaces is illustrated by the desorption curves presented in Figs. 1-4. For comparison, rinse curves for water, diluted hydrogen peroxide without acid, and diluted acid without hydrogen peroxide are also shown. These data were obtained by gamma-radioactivity measurements using Au^{198}, Cu^{64}, and Cr^{51} as radioactive tracers.

Curve A in Fig. 1 shows the results obtained with silicon wafers that had been etched in a HNO_3-HF mixture containing Au^{198}. The surface concentration on the etched silicon after quenching with deionized water followed by a 30-second water rinse was 7.3×10^{13} Au atoms/cm^2. Desorption at 90°C with an HCl-H_2O_2-H_2O mixture removed 97.4% of the gold in 15 minutes. For comparison, a solution consisting of 1 vol HCO_2H (formic acid),** 1 vol 30% H_2O_2, and 8 vol distilled H_2O removed 86% of the gold in the same time period. Used separately, the reagent components (diluted H_2O_2, diluted HCO_2H, distilled H_2O) removed only negligible quantities of the gold.

Silicon immersed in diluted HF had initially 2×10^{15} Au atoms/cm^2. After 15 minutes desorption in HCl-H_2O_2-H_2O, similar percentages of gold removed were found as for acid-etched silicon (Curve B, Fig. 1). Curve C in Fig. 1 shows the desorption for silicon previously etched in iodine-containing HF-HNO_3 etchant, resulting in an initial gold surface concentration of 3×10^{15} atoms/cm^2. In this case, the formic acid–hydrogen peroxide was more effective (98.8% removal) than the HCl-H_2O_2-H_2O mixture.

Fused quartz contaminated with Au^{198} from HNO_3, HCl, HF, and aqua regia, to an initial surface concentration of 10^{11} to 10^{12} Au atoms/cm^2 was decontaminated effectively with acid H_2O_2. A typical desorption curve is presented in Fig. 2. Similar results were obtained with quartz that had been immersed in the same acids but contained Cu^{64}.

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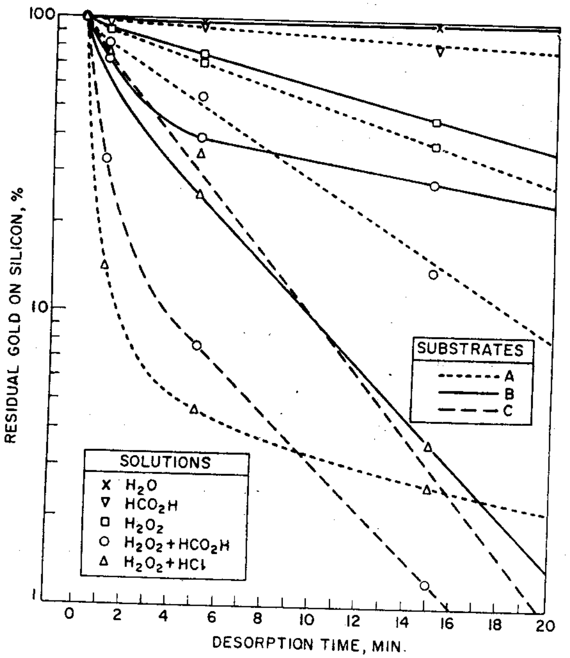
* For example, Hofstein[7,14] demonstrated by CVBT techniques that contamination of MOS devices with alcohols can cause proton drift instability. Similar drifts caused by other organic contaminants were also observed by CVBT tests.[6]

** Formic acid can be used[3] instead of hydrochloric acid to lower the *p*H of the solution to attain metal complexing action; however, this system is generally less effective, partly because of consumption of hydrogen peroxide in the oxidative breakdown of the formic acid.

As seen from Fig. 3, acid hydrogen peroxide is very effective for desorbing copper from silicon. Over 99% is removed within the first 2 minutes of rinsing. Over 30 different desorption treatments involving combinations of complexing, chelating, and oxidizing agents have been tested for copper removal.[3] None was as effective as the acidic hydrogen peroxide. Water or hydrogen peroxide without added acid were quite ineffective.



<u>Substrates:</u>

Curve A (dotted line)—Si etched in $HNO_3 + HF + Au^{198}$; 100% $= 7.3 \times 10^{13}$ Au atoms/cm^2

Curve B (solid line)—Si immersed in 49% $HF + Au^{198}$; 100% $= 2.2 \times 10^{15}$ Au atoms/cm^2

Curve C—(dashed line)—Si etched in $HF + HNO_3 + I_2 + CH_3CO_2H + Au^{198}$; 100% $= 3.0 \times 10^{15}$ Au atoms/cm^2

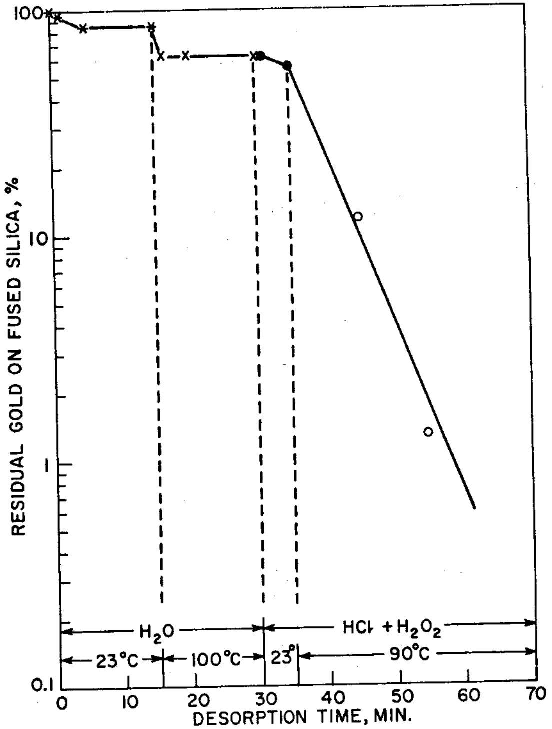
<u>Solutions:</u>

× Deionized and distilled H_2O, 100°C
▽ 1 vol 90% HCO_2H + 9 vol H_2O, 90°C
□ 1 vol 30% H_2O_2 (unstabilized) + 9 vol H_2O, 90°C
○ 1 vol 30% H_2O_2 + 1 vol 90% HCO_2H + 8 vol H_2O, 90°C
△ 1 vol 30% H_2O_2 + 1 vol 1N HCl + 8 vol H_2O, 90°C

Fig. 1—Desorption efficiency for gold labeled with Au^{198} from silicon surfaces with various solutions at 90°C.

Similar desorption curves for chromium on silicon are presented in Fig. 4. Diluted formic acid-H_2O_2 mixture at 90°C removed 93% of the chromium in 5 minutes. Less dilute solutions were more effective; HCl-H_2O_2 was not tested, but can be expected to be even better because of the high solubility of chromium in HCl.

The desorption of sodium was previously studied with Na^{22} and Na^{24} as tracers for the sodium ions. Aqueous solutions containing HCl were demonstrated to be highly effective in removing physically and chemically adsorbed sodium ions from silicon surfaces.[2]



<u>Substrates:</u>

Fused quartz etched in 49% $HF + Au^{198}$; 100% $= 1.56 \times 10^{12}$ Au atoms/cm^2

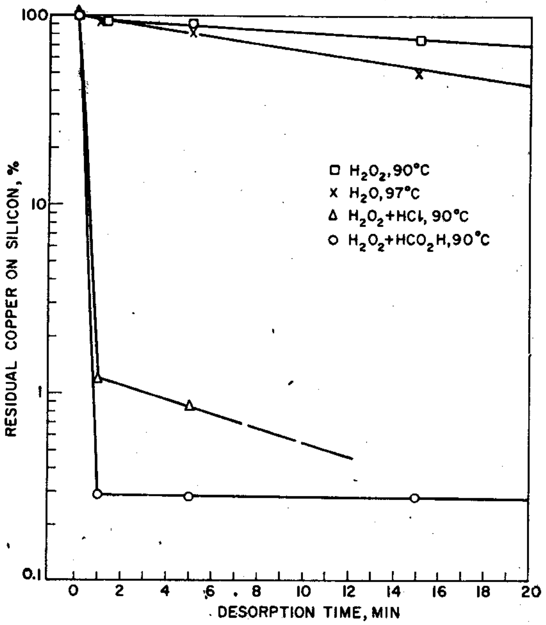
<u>Solutions:</u>

* Deionized distilled H_2O, 23°C
× Deionized and distilled H_2O, 100°C
● 1 vol 30% H_2O_2 + 1 vol 1N HCl + 8 vol H_2O, 23°C
○ 1 vol 30% H_2O_2 + 1 vol 1N HCl + 8 vol H_2O, 90°C

Fig. 2—Desorption efficiency for gold labeled with Au^{198} from fused quartz under various conditions.

Considerably higher concentrations of the metals on silicon were used in these desorption studies than are normally present in silicon processing in order to determine the effectiveness of the cleaning mixtures. Although the rates of desorption are different for different metals, the following generalizations can be made on the basis of the results obtained. (1) Each of the single components (H_2O, H_2O_2, HCl, HCO_2H) used separately, regardless of the temperature, is relatively ineffective. (2) Elevated temperatures increase the oxidation potential of the acidic hydrogen peroxide system and the efficiency of desorption.

Radioactive-tracer studies have also demonstrated the importance of the acidic hydrogen peroxide treatment following an oxide removal step in aqueous HF or buffered HF. Heavy metal impurities are readsorbed by the silicon where it becomes exposed to these reagents, but can be effectively removed in the acid peroxide medium.



Substrates:

Si immersed in 49% HF + Cu^{64}; 100% = 1.5×10^{17} Cu atoms/cm^2 for □, ×, ○; for Δ, 100% = 3.3×10^{16} Cu atoms/cm^2

Solutions:

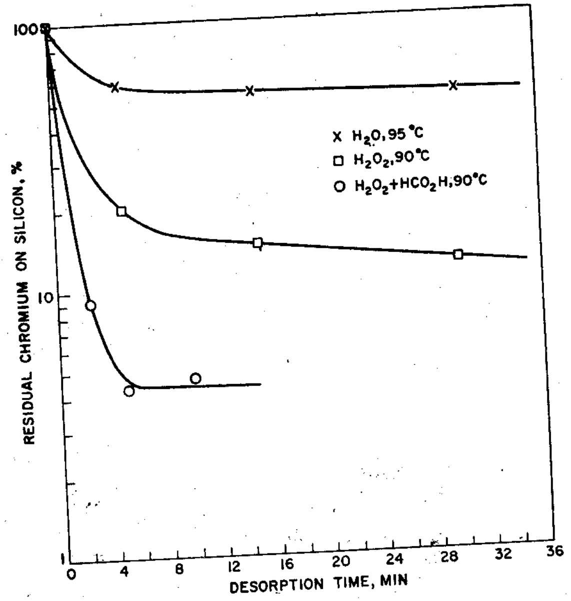
Explanations as for Fig. 1, except that H_2O temperature was 97°C

Fig. 3—Desorption efficiency for copper labeled with Cu^{64} from silicon with various solutions at 90°C.

The behavior of a number of other metals in acidic hydrogen peroxide can be predicted from data in the literature. The following metals are known to dissolve: silver,[16] nickel,[16] cobalt,[17] lead,[18,19] magnesium,[16] niobium,[20] tellurium,[21] and tungsten.[16]

It should be noted that the cleaning solutions are effective for surface contaminants only. If the contaminant is already distributed within an oxide layer, an etch back with dilute HF followed by cleaning in the acidic hydrogen peroxide mixture may be required to remove it. In a more pragmatic sense, silicon wafers that have undergone this cleaning treatment can be used for the routine growth of silicon epitaxial layers free from hillocks, bumps, spikes, etc. Furthermore, vapor-deposited SiO_2 layers deposit uniformly on the wafers, a fact previously correlated with surface cleanliness.[22]

Ellipsometry[23-25] was used to determine the oxide thickness of clean



Substrate:

Si immersed in 49% HF + Cr^{51}; 100% = 2.2×10^{14} Cr atoms/cm^2

Solutions:

Explanations as for Fig. 1 except that H_2O temperature was 95°C.

Fig. 4—Desorption efficiency for chromium labeled with Cr^{51} from silicon at 90°C.

Si surface.* Chemically/mechanically polished (111)-oriented silicon wafers (1-10 ohm-cm p-type) had an initial film thickness of 21 Å. After the cleaning treatment in the ammonia–hydrogen peroxide solution, the film thickness was 18 ± 1 Å; this thickness changed only slightly to 16 ± 1 Å on the subsequent acid-hydrogen peroxide treatment.[26] It can be concluded that no excessive surface oxidation takes place during these cleaning treatments.**

5. Experiments in the Electrical Performance of Devices

The effectiveness of the cleaning procedure was evaluated using MOS capacitors fabricated using these cleaning treatments.

CVBT tests on silicon wafers deliberately contaminated with methanol and cleaned in these solutions prior to metallization showed flat-band voltages and driftable charge levels identical to those of uncontaminated control samples.[27]

A statistical evaluation of MOS capacitors fabricated on reference ingot wafers cleaned with these solutions was also performed using CVBT testing. Over a nine-month test period, a 1100 and a 1200°C furnace was found to result in flat-band shifts arising from driftable charge of (average $\pm 1\sigma$ limit) 0.20 ± 0.07 volt, and 0.18 ± 0.09 volt, respectively.

6. Chemistry of Hydrogen Peroxide Solutions

6.1 General

The chemistry of hydrogen peroxide has been extensively studied.[16,28,29] It is a powerful oxidizing agent in both acidic and basic solutions. Dilute solutions at 50°C are most stable at a pH in the vicinity of 4.5 to 5.0, and are least stable at high pH's, decomposing to water and oxygen. Decomposition is catalized by traces of most heavy metals.

As cleaning agents, hot formic acid and hydrogen peroxide,[1] hot hydrogen peroxide and hydrochloric acid,[13] and cold hydrogen peroxide and ammonium hydroxide[30,31] have been used in a variety of applications. In all of these mixtures, the chemistry is considerably complicated by changes in the reagent concentration with time, and by the complexing nature of both the chloride and ammonium ions. For example, nickel and cobalt each form six different amines;[32] copper and zinc also form amine complexes. The potential–pH diagram shown in Fig. 5 is thus highly idealized, but it illustrates the relative oxidizing powers of the cleaning solutions at room temperature. The measured pH ranges for the alkaline peroxide and acid peroxide solutions described in this paper are indicated.

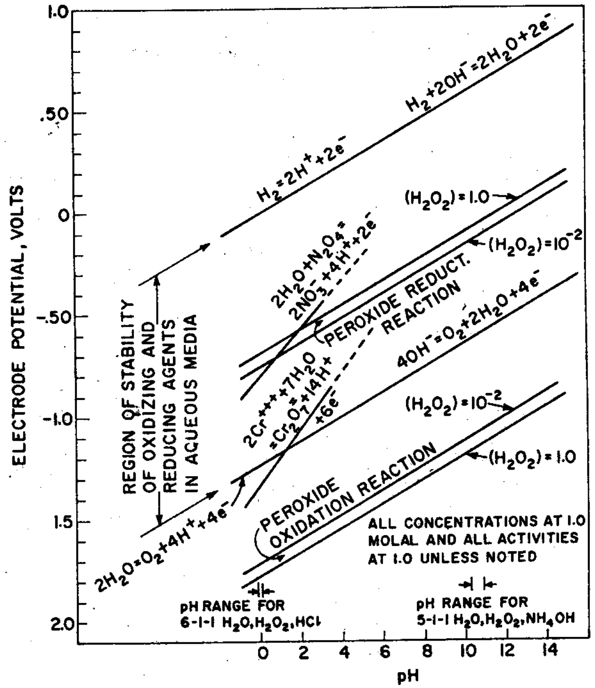


Fig. 5—Potential versus pH diagram for hydrogen peroxide solutions at 25°C.

Within the limits of solution stability and peroxide depletion (Section 6.2) the exact concentrations of reagents are not critical. However, if excess peroxide is used, the solutions tend to froth and overflow the container from the too rapid evolution of oxygen.

6.2 Stability of Hydrogen Peroxide Mixtures

These hydrogen peroxide solutions gradually decompose, losing their cleaning effectiveness. Their decomposition rates were determined by titration with a standard potassium permanganate solution. Half-lives of the alkaline and acidic solution[33] at room temperature are, respectively, 11 hours and 50 hours (Fig. 6); these half-lives decrease rapidly with increasing temperature. The relative hydrogen peroxide content

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* The refractive index of SiO_2 (1.48) was assumed for all films.

** For comparison, immersing the cleaned wafers in HF solution followed by water rinsing reduced the film thickness to 7 ± 1 Å; subsequent boiling for 15 or 30 minutes in deionized and distilled water led to a limiting film thickness of 31 ± 1 Å.[26]

of the acidic solution was found to decrease by 98% in 30 minutes, and by 99.95% in 60 minutes, after the solution reached the operating temperature of 80°C.†

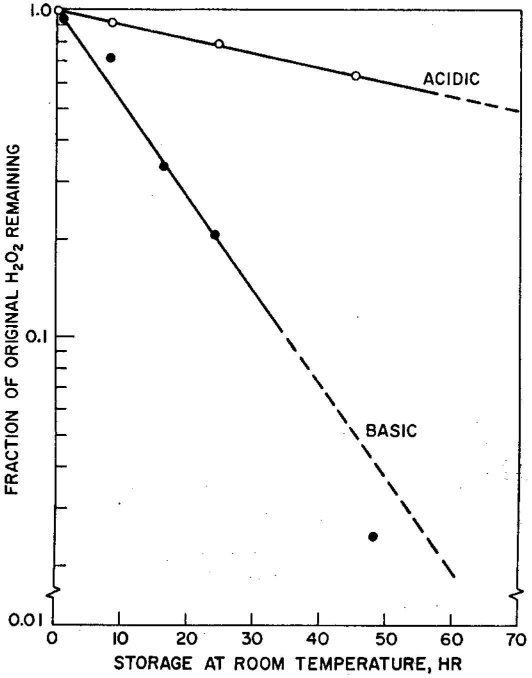

Fig. 6—Rate of decomposition of acidic and alkaline hydrogen peroxide as a function of storage time at 23°C.

To determine more precisely the shape of the decomposition curve during typical processing conditions, the peroxide content in 405 ml of alkaline solution heated in a beaker on a hot plate was monitored. After the beaker was placed on the hotplate the amount of peroxide remaining was determined as a function of time (Fig. 7). The half-life of the solution at 88-90°C was approximately 5 minutes, and the time for the concentration of peroxide to be reduced to the etching threshold* level for (111)-oriented silicon was approximately 40 minutes after the solution reached temperature. Since the recommended cleaning time is 10 to 20 minutes at 75-80°C, there is an adequate margin of safety if the initial peroxide concentration is at the recommended level.

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† It should be realized that the rates of decomposition can be affected by the presence of trace impurities.

* This is the etching threshold under the conditions recommended for cleaning silicon.

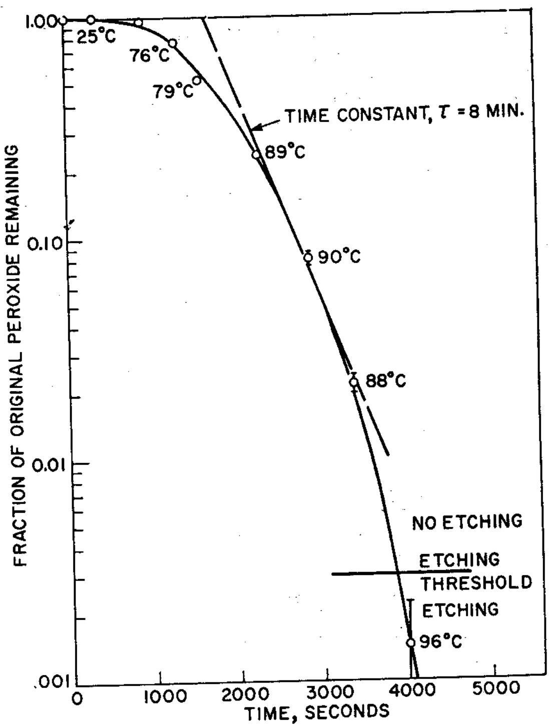

Fig. 7—Fraction of hydrogen peroxide remaining as a function of use time in H_2O_2-NH_4OH-H_2O cleaning solution (etching threshold indicated by horizontal line is for (111) and (100)-oriented silicon; value is approximate).

6.3 Effects of Hydrogen Peroxide Depletion

A bare silicon surface is readily attacked by even a weak base, such as ammonium hydroxide. However, when hydrogen peroxide is present, the surface is immediately passivated, presumably by the formation of a thin (<50 Å) continuous layer of hydrous oxide. This oxide layer is very resistant to chemical attack by ammonium hydroxide at the temperatures and concentrations used for cleaning.*

The etch rate of n- and p-type (111)-oriented chemically polished silicon has been determined in hydrogen-peroxide-free ammonium hydroxide solutions. Resistivity and types used were 0.25 ohm-cm and 20 ohm-cm p-type; 1 ohm-cm and 15 ohm-cm n-type. Etching was conducted in a Pyrex chamber immersed in a constant-temperature bath

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* A complete equilibrium potential-pH diagram for the Si-H_2O system is given in Ref. [34].

and capped with a stoppered, water-cooled condenser to minimize loss of ammonia. Wafers were prepared for etching by growing 5000 Å of oxide in steam at 1000°C, by defining and etching a 1-cm-wide stripe along a diameter to expose a bare silicon surface, and by cleaning in H_2O-H_2O_2-NH_4OH solution. Each wafer was then given a 5 second dip in 5% HF, rinsed in distilled water, quartered, and transferred to the etching apparatus. This procedure was adopted to ensure that the bare silicon surface was covered by no more than a thin film of freshly formed hydrous oxide when the wafer quarters were placed in the etching solution. The samples were removed from the etch at prescribed time intervals and the oxide was stripped in buffered HF etch.

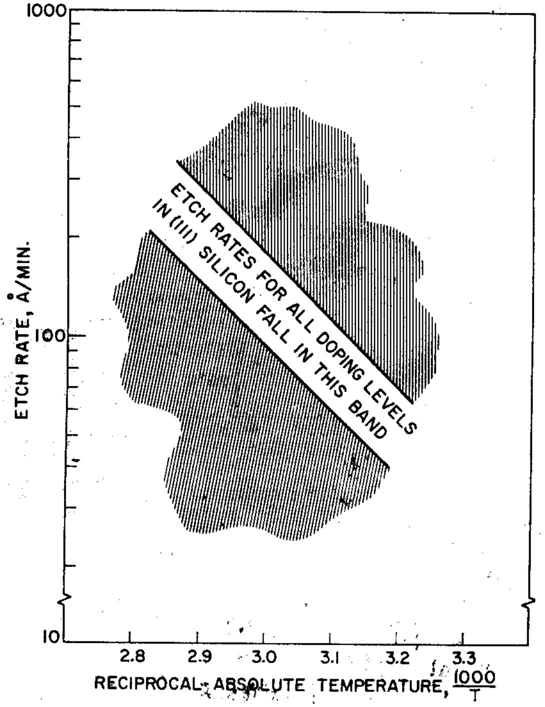

Fig. 8—Etch rate of (111)-oriented silicon in ammonium hydroxide solutions as a function of temperature.

The depth of step formed in the silicon as a result of localized etching was measured with a Talysurf** surface profilemeter with an accuracy of better than ±2%. This technique was also used to determine the thickness of the oxide films by measuring the step height formed from the top of the film to the substrate surface.

The observed etch rate values for 2N to 6N NH_4OH solutions fall into the broad band shown in Fig. 8 where the etch rate is plotted as a function of reciprocal temperature. Despite the precautions used to obtain an oxide-free surface, plots of step height versus time showed considerable scatter even on the four quadrants of the same wafer. These results may indicate that the oxide formed at room temperature offers some barrier to the attack of ammonium hydroxide on silicon, or that the chemical polishing had not completely removed the work-damaged surface and that the etch-rate variations reflect this. Within the limits of the experiment, there was no difference between the etch rates of n- and p-type silicon. There was no discernable etching of the oxide mask at any concentration or temperature used in this experiment. It should be noted that ammonium hydroxide etching of silicon is orientation sensitive; (100)-oriented material etches more rapidly than (111)-oriented material. As expected, no silicon etching effects have been observed in aqueous HCl or in the acidic peroxide solution.

6.4 Effects Of Fluoride Ion Additive

A common semiconductor processing operation is to either completely strip the surface oxide or to conduct limited etch-back in HF or buffered HF. A large number of fluoride ions are adsorbed during this kind of treatment.[2] If rinsing is inadequate, these fluoride ions could transfer to the ammoniacal cleaning solution producing a silicon etch.[35] As an extreme test of this type of contamination, the etch rates of both n- and p-type (111)-oriented epitaxial silicon in H_2O-NH_4F-H_2O_2 solutions were determined over a five-decade range in fluoride ion concentration. The solutions were prepared by adding aliquot amounts of aqueous ammonium fluoride solution (40% NH_4F by weight) to 5 ml of 30% unstabilized H_2O_2 and diluting with distilled water to a total volume of 30 ml. Each test solution was preheated on a hotplate for five minutes to bring the temperature to 75 ±2°C, the wafer was added, and heating continued for 10 minutes to a final temperature of 80°C. The wafer preparation procedure was similar to that described in the previous section except that the HF dip was omitted. The thickness of the remaining oxide was measured, the oxide was then stripped in buffered etch, and the silicon etch-step height was measured on the Talysurf.

The observed variation of silicon and silicon dioxide etch rate with fluoride ion concentration are shown in Figs. 9 and 10. The silicon etch-rate curve has two distinct regions, one for low fluoride ion con-

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** Talysurf Model 4, Rank Taylor Hobson, Leicester, England.

centration and one at higher concentrations where the etch rate increases quite rapidly with increasing fluoride ion concentration. While the different regions are of considerable interest in the interpretation of the etching mechanism, the immediate practical significance of this curve is that peroxide solutions containing fluoride ion concentration at the level that might be found by casual contamination during normal handling and processing have very low etch rates. This means that trace contamination of the H_2O_2-NH_4OH cleaning solutions with fluoride ion will not be a cause of etching of (111) oriented silicon wafers. A similar conclusion applies to (100) wafers. It follows that any fluoride ion that might be leached out of Teflon workholders will not cause any significant amount of etching. The oxide etch rate becomes appreciable only at the highest fluoride concentrations and is essentially zero at concentrations below 0.1 ml NH_4F per 30 ml solution.

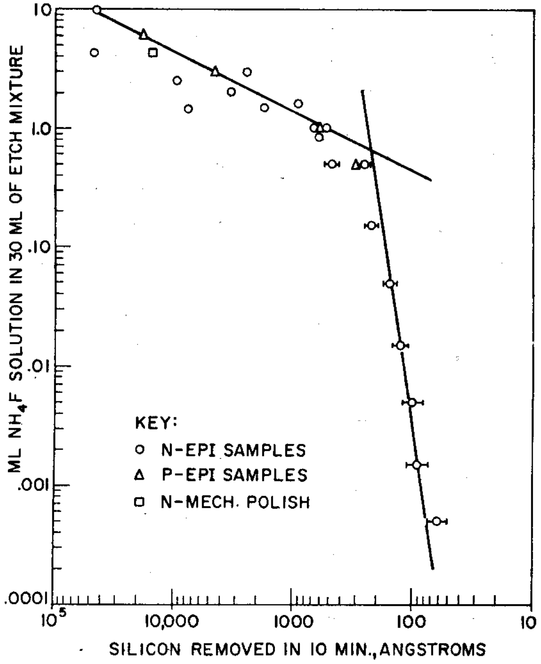

Fig. 9—Etch rate of (111)-oriented silicon in ammonium fluoride solutions (solution composition: 5 ml 30% H_2O_2, aliquot 40 wt % NH_4F solution, diluted with H_2O to total volume of 30 ml).

A feature of both the ammonium hydroxide and the ammonium fluoride-hydrogen-peroxide solutions is that, although physically isolated samples of n-type and p-type (111) oriented silicon will etch at nearly the same rate, adjacent n and p regions will etch at different rates. This differential etch rate may be illustrated by the change in relative heights shown in Fig. 11. This figure shows the surface levels before and after a 10-minute etch at 80°C in a 5-1 H_2O_2-NH_4OH solution; in Fig. 12 levels for treatment in 5-1-1 H_2O-H_2O_2-NH_4F solution are displayed.

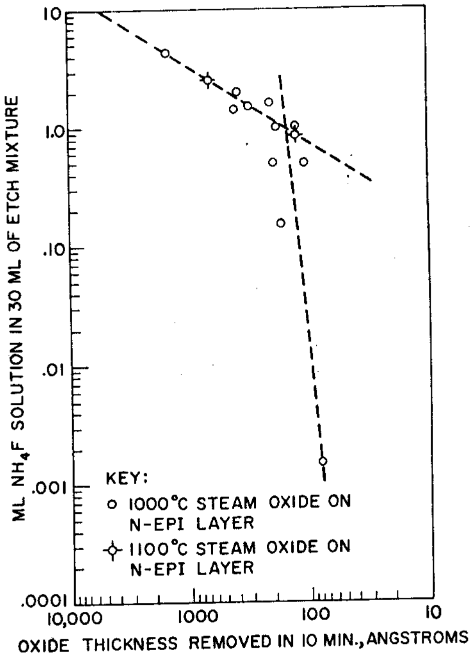

Fig. 10—Etch rate of thermally grown silicon dioxide in ammonium fluoride solutions (solution composition: same as for Fig. 9).

7. Summary and Conclusions

Two sequential cleaning solutions (H_2O-H_2O_2-NH_4OH, and H_2O-H_2O_2-HCl) have been devised for cleaning silicon surfaces to reduce organic and inorganic contaminants to the very low levels required for silicon device fabrication.

The solutions do not attack either silicon or silicon dioxide as long as sufficient hydrogen peroxide is present. If the hydrogen peroxide is depleted or if gross fluoride ion contamination is present, etching can occur.

The hydrogen peroxide depletion rate and the concentration de-

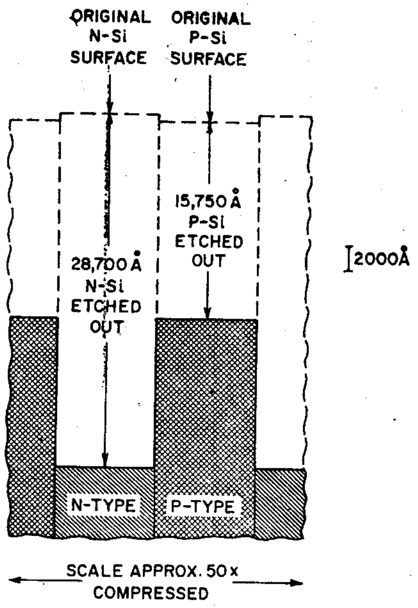

Fig. 11—Surface profiles of n- and p-type silicon regions before and after etching in ammonium hydroxide (conditions: 1 vol 27% NH_4OH + 5 vol H_2O, 10 min at 80°C).

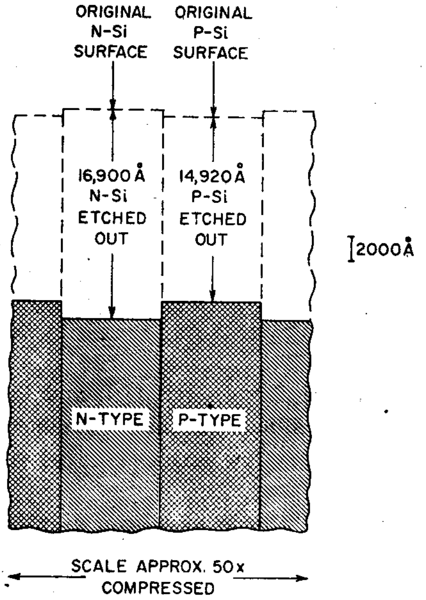

Fig. 12—Surface profiles of n- and p-type silicon regions before and after etching in fluoride hydrogen peroxide etch (conditions: 1 vol 40 wt % NH_4F + 1 vol 30% H_2O_2 + 5 vol H_2O, 10 min at 80°C).

pendence of the silicon etch rate in depleted hydrogen peroxide solutions or in fluoride ion contaminated solutions have been determined and found safe for the recommended cleaning conditions.

The chemical effectiveness of these solutions has been demonstrated by water spray tests and radiotracer analyses. Moreover, the ability of the cleaning procedure to remove electrically active impurities has been verified using CVBT measurements on MOS capacitors.

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Radiochemical Study of Semiconductor Surface Contamination

I. Adsorption of Reagent Components

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Abstract—The adsorption of reagent components on semiconductor surfaces was measured by radioactive tracer methods to assess the extent of surface contamination from typical reagent solutions used in solid-state-device processing. Substrates used were primarily silicon and germanium. Reagent solutions include NaOH, HF, HCl, HF-HNO_3-CH_3CO_2H mixtures, iodine-containing semiconductor etchants, and chromic-sulfuric acid. Radionuclides used as tracer ions are Na^{22}, Na^{24}, F^{18}, Cl^{36}, and I^{131}.

Adsorption of Na^+ ions by Si slices from dilute NaOH at 25°C was predominantly physical, Si increasing slowly with increasing NaOH concentration. In 0.1% NaOH, adsorption equilibrium was established in 1 hour, leading to 4×10^{13} Na^+/cm^2. An initial 60-second rinsing treatment in cold H_2O removed 63%, but continued rinsing desorbed Na^+ at decreasing rates. Hot water desorbed 99.5% within 2 minutes, lowering the surface concentration to below 0.004 monoionic layer.

Etching of Si wafers in 5% NaOH at 100°C led to 1×10^{14} Na^+/cm^2. Desorption with HCl reduced this layer to less than 0.0002 of one monolayer of Na^+ ions. In contrast to thermal SiO_2, pyrolytic SiO_2 sorbed large quantities of Na^+, probably due to its porous nature. On immersing in diluted HF, Si and Ge wafers adsorbed on the order of 10^{16} to 10^{17} F^-/cm^2. The major portion was desorbable by rinsing with cold water, but a fluoride residue of several monolayers remained. Fluoride in Si volatilized only partly at 1250°C. Etching of Si and Ge wafers in strong HF-containing etchants led to concentrations in the 10^{16} F^-/cm^2 range. Desorption of etched and water-rinsed wafers with acetone was extremely effective, reducing the adsorbate to a residual concentration of 10^{14} F^-/cm^2 in 30 seconds. Si etched in hot NaOH followed by immersion in dilute radioactive HCl adsorbed 1×10^{14} Cl^-/cm^2. Ge immersed directly in the HCl acquired 3×10^{14} Cl^-/cm^2. Metal surfaces adsorbed larger quantities, especially indium (10^{17} Cl^-/cm^2). Iodine from CP-4 type etch mixture contaminated both Si and Ge surfaces with 10^{13} to 10^{14} I_2 molecules/cm^2. The adsorbate on Ge could be desorbed readily with aqueous solutions, but Si required hot EDTA solution to lower the residue to 3% of the initial value in 5 minutes. A special etch containing only 1.9 mg/liter NaI led to uniformly adsorbed 10^{11} I_2/cm^2 on Si and 10^{12} I_2/cm^2 on Ge. Iodide ions from 1N NaI led to 10^{14} I^- ions/cm^2 Si or SiO_2. Treatments of Si in hot chromic-sulfuric acid, followed by cold water rinsing, resulted in absorbed chromium concentrations of less than 10^{14} atoms/cm^2.