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Kern W & Puotinen D A. Cleaning solutions based on hydrogen peroxide for use in silicon semiconductor technology. *RCA Rev.* **31**:187-206, 1970.
[RCA Laboratories, Princeton, and RCA Solid-State Division, Somerville, NJ]

Clean silicon surfaces suitable for device fabrication have been prepared successfully for nearly 20 years by simple and safe sequential oxidative desorption at 75-85°C, first in H_2O_2-NH_4OH-H_2O to oxidize organics and to complex heavy metals, then in H_2O_2-HCl-H_2O to remove remaining inorganic contaminants. [The *SCI*® indicates that this paper has been cited in over 120 publications since 1970, making it the 4th most-cited paper ever published in this journal.]

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"The work published in our 1970 article originated in 1961 at the RCA Solid-State Division when it was realized that trace impurities on silicon can lead to detrimental effects on the electrical performance of devices. It became clear to me that a highly effective yet simple and hazard-free method was needed for purifying pre-cleaned silicon wafers, and that such a method should be based on first removing organics by oxidative breakdown, followed by removal of trace metals and chemisorbed ions by solubilization, complexing, and rinsing with high-purity water. In addition, a sensitive analytical technique was needed at that time for measuring the efficiency of cleaning processes.

"On the basis of reaction chemistry and reagent purity, water-diluted, unstabilized H_2O_2 at 75-85°C and at high pH, attained by adding NH_4OH solution, appeared to be the ideal reagent for removing organics by oxidative breakdown and heavy metal complexing. I selected diluted H_2O_2 at low pH by adding HCl solution for removing the remaining inorganics in the second step, again at 75-85°C. Deionized, distilled, and microfiltered water served as the diluent and rinsing agent. To prevent leaching of alkali and boron from Pyrexware during processing, I introduced beakers of fused quartz and wafer holders of Teflon. Concurrently, I investigated the origin and concentration of contaminants by adding trace quantities of ions of over one dozen types of radioactive elements to numerous etchant and reagent solutions. Radioactivity measurements, autoradiography, and gamma-ray spectroscopy of semiconductors treated with these tagged solutions allowed quantitization of specific impurities initially and after various cleaning steps with the mixtures noted.[1-7]

"By mid-1960, the peroxide cleaning technique (dubbed 'SC-1' and 'SC-2' to denote 'Standard Clean, Steps 1 and 2') was applied widely at RCA in the fabrication of silicon devices. In 1966, a process patent (US 3,281,915) that incorporated the desorption procedure was issued to RCA, and I received an RCA Outstanding Achievement Award, shared with James A. Amick and Arthur I. Stoller, 'for new technological advances for processing integrated circuits,' which included the peroxide method in conjunction with passivation and tungsten metallization processes. In 1970, I obtained permission to publish the radiochemical studies and the peroxide process; the latter incorporated the contributions of my coauthor, David A. Puotinen, who had studied in some detail several aspects of peroxide cleaning as applied to silicon device processing. Also, a brief optional etch in dilute HF solution to remove the thin native oxide layer on silicon was introduced after the first peroxide step.

"Several of my colleagues contributed to the success of this work, particularly Norman Goldsmith and Amick during the development and implementation over several years, and Alfred Mayer, who introduced megasonic peroxide cleaning at low temperature, effectively combining removal of particulates with desorption of adsorbed contaminants.

"This paper has been highly cited because extensive analytical and device reliability studies by independent researchers have confirmed the process to be the most effective cleaning method known for silicon. The process is safe and simple, has economic and ecological advantages, uses high-purity solid-free reagents, and has been used successfully in industry. The process is now so widely employed that most authors refer to it without citing our original work. I published a summary and literature reference update in 1978.[8] A recent review article[9] appeared in 1982."

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