9950-498

DRL Line Item No. 5

DOE/JPL-955342-79/2
Distribution Category UC-63

DEVELOPMENT OF MEGASONIC CLEANING FOR SILICON WAFERS

A. Mayer
RCA Corporation
Solid State Division
Somerville, New Jersey 08876
RCA Laboratories
Princeton, New Jersey 08540

FINAL REPORT

Subcontract under NASA Contract NAS7-100
Task Order No. RD-152

September 1980

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

Prepared under Contract No. 955342 for

CALIFORNIA INSTITUTE OF TECHNOLOGY
JET PROPULSION LABORATORY
Pasadena, California 91103

DRL Line Item No. 5

DOE/JPL-955342-79/2
Distribution Category UC-63

DEVELOPMENT OF MEGASONIC CLEANING FOR SILICON WAFERS

A. Mayer
RCA Corporation
Solid State Division
Somerville, New Jersey 08876
RCA Laboratories
Princeton, New Jersey 08540

FINAL REPORT

Subcontract under NASA Contract NAS7-100
Task Order No. RD-152

September 1980

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

Prepared under Contract No. 955342 for

CALIFORNIA INSTITUTE OF TECHNOLOGY
JET PROPULSION LABORATORY
Pasadena, California 91103

PREFACE

This program depended on the willing help of many coworkers, but special thanks are due to A. Firester, R. D'Aiello, and R. Daniels for their critiques and help with fabrication and evaluation of the solar cells; R. Rayeskie, D. Krawitz, P. Britt, and S. Shwartzman for making the system work; and U. Roundtree for his liaison and administrative help.

ABSTRACT

The major contract goals to develop a cleaning and drying system for processing at least 2500 three-in.-diameter wafers per hour and to reduce the process cost were achieved.

The new system consists of an ammonia-hydrogen peroxide bath in which both surfaces of 3/32-in.-spaced, ion-implanted wafers are cleaned in quartz carriers moved on a belt past two pairs of Megasonic transducers. The wafers are dried in the novel room-temperature, high-velocity air dryer in the same carriers used for annealing. A new laser scanner was used effectively to monitor the cleaning ability on a sampling basis.

The following factors contribute to the improved effectiveness of the process: (1) Recirculation and filtration of the cleaning solution permit it to be used for at least 100,000 wafers with only a relatively small amount of chemical make-up before discarding. (2) Uniform cleanliness is achieved because both sides of the wafer are Megasonically scrubbed to remove particulate impurities, the wafer carriers are cleaned simultaneously, and the chemistry of the solution ensures removal of soluble impurities. (3) The novel dryer permits wafers to be dried in a high-velocity room-temperature air stream on a moving belt in their quartz carriers. Thus, cleanliness is maintained and the loss due to wafer breakage by handling is reduced because no transfers are needed from plastic to quartz carriers prior to the high-temperature anneal. (4) The personnel safety of such a system is excellent and waste disposal has no adverse ecological impact.

With the addition of mechanical transfer arms, two systems like the one developed here will produce enough cleaned wafers for a 30-MW/year production facility. A projected scale-up well within the existing technology would permit a system to be assembled that produces about 12,745 wafers per hour; about 11 such systems, each occupying about 110 square feet, would be needed for each cleaning stage of a 500-MW/year production facility.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

SECTION I

INTRODUCTION

RCA has been an active contributor to the evaluation of processes used in the manufacture of flat-plate photovoltaic solar-cell arrays. A number of sequences had been investigated for the processing of silicon wafers to finished cells. One of the more promising ones consists of ion-implanting phosphorus into 3-in.-diameter sliced and etched substrates, cleaning these substrates by first scrubbing (optional), then using system "Z" which consists of sulfuric acid-hydrogen peroxide at 80°C, spin-drying, transferring to quartz carriers and annealing at about 850°C prior to the metallization processes. The estimated cost per watt when the present contract was initiated was $3.87/Wp in a 15-MW year manufacturing facility, assuming 0.5 W per sheet, i.e., 3-in.-diameter cell.

The purpose of the program was to develop Megasonic cleaning and air-drying as an improved cleaning and handling method in order to reduce the cost substantially.

Savings derive essentially from the following sources:

(1) Reduced consumption of chemicals by about a factor of 10 because the cleaning solution is not heated and does not decompose and, with continuous filtration, can be used for many more cycles than is customary; the amount of power required per sheet in room-temperature air drying is about a factor of 10 lower than either for hot air or spin-drying.

(2) The uniformity of cleaning is improved because the wafers are scrubbed on both sides, the carriers used for diffusion are cleaned simultaneously, and the wafers, once loaded after ion implantation, need not be transferred until they are ready to be metallized. Improved cleanliness is expected to result in longer carrier diffusion length and hence in a reduction of cells with low conversion efficiency, i.e., the average cell efficiency is increased. This can be a major cost improvement factor.

(3) The new system is compact, relatively inexpensive and has a high throughput. This means that amortization and overhead costs are low. While this program demonstrated the effectiveness of the

design and permitted evaluation of chemicals utilization, it did not evaluate a fully automated and optimized total system. Such a system is discussed in subsection II.E.4. Here, we suggest that the addition of another two pairs of transducers, lengthening the tank and rinse system, and additional dryer tracks could readily increase the throughput to 12,745 wafers per hour with a small investment increase. This also requires the addition of automatic transfer arms from Megasonic tank to rinse, and into the dryer. Transfer equipment is commercially available, but its adaptation to our system and evaluation was outside the scope of this development program.

(4) Other cost improvement factors are clearly inherent:

(a) Savings in the treatment of waste chemicals, both in the amount of chemicals needed and the area of the treatment facility. Use of a "water saver" will be cost effective in a larger facility.

(b) There are few heavily stressed moving parts and the solutions used are not nearly as corrosive as acid-based systems, leading to improved maintenance costs. The personnel safety hazard is also minimized.

(c) With full mechanization it is expected that the amount of wafer breakage will be significantly reduced.

(d) A laser scanner was introduced that permits the effectiveness of the cleaning operation to be monitored with almost instant feedback. It produces a digital count of scattering centers, usually particulate impurities, and a display on a scope screen of the location of these centers. This allows the quick diagnosis of the cause of a cleaning problem and can prevent a major yield loss in a full-scale manufacturing operation. Such a problem would normally not be spotted until the final device was tested.

As will be described in the technical discussion, all these factors were examined in the laboratory pilot operation at the Somerville location. After the system had been debugged, it was shipped to the Power Device manufacturing plant of the RCA Solid State Division in Mountaintop, PA. Here it was reinstalled and used to test the engineering soundness under three-shift processing-plant operation.

Operators were trained, and maintenance personnel were instructed in troubleshooting and repairs. The Megasonic cleaning system, rinse tank, and laser scanner worked well, but a problem developed with the recirculation pump that had been operating most reliably in Somerville. In addition, the belt drive for the air dryer was found to be too flimsy to withstand continuous operation and the adjustments required were too difficult and time-consuming to be tolerated in a production environment.

All-in-all, no serious problem remains to be solved for the Megasonic cleaning and drying system to become a reliable production machine. The progress from drawing board through concept testing to production has been remarkably rapid considering that several completely new concepts were introduced. Although the present study is too small to permit an accurate assessment of all factors, the program has successfully demonstrated the cost effectiveness of the Megasonic cleaning and air-drying system pioneered by RCA.

SECTION II

TECHNICAL DISCUSSION

A. MEGASONIC STATION

1. Background

For the production of silicon-photovoltaic cells, at least one cleaning step is required. The cheapest existing method, based on mechanical scrubbing (optional) and the use of sulphuric acid-hydrogen peroxide at 80 to 100°C, known as system "Z," is the most developed and, prior to this program, the least expensive per unit. (A unit equals one 3-in.-diameter slice with a nominal peak output of 0.5 W.) Whether scrubbing to remove particles from both wafer surfaces is cost effective (i.e., improves the average yield of high-efficiency cells sufficiently to warrant its use) had never been demonstrated but the present work confirmed it is.

The only system that can chemically clean and remove particles simultaneously is RCA's Megasonic System [1,2]. This system uses high-frequency ultrasonic energy and a solution of ammonium hydroxide-hydrogen peroxide at room temperature, i.e., with no heat added. The system used before work on this contract began is described in Appendix A. Its introduction by RCA into the Solid State Power Device Line in Mountaintop, PA in 1976 was immediately successful, not only because of the cleanliness achieved on both sides of the slice at the same time, but also because the consumption of chemicals dropped to less than 10%, and waste disposal was even further unburdened. It is a batch system with a throughput capability of about 600 wafers per hour. The wafers are then dried in a high-velocity, hot-air dryer in the same carriers.

2. Design Objectives

A major goal of this contract, to increase the rate to 2500 wafers per hour, was achieved. Several companies have been licensed by RCA to build

1. A. Mayer and S. Shwartsman, U. S. Pat. 3,893,868 (assigned to RCA Corp.), July 8, 1975.
2. A. Mayer and S. Shwartzmawn, "Megasonic Cleaning: A New Cleaning and Drying System for Use in Semiconductor Processing," J. Elect. Mat. 8 885 (1979), Appendix I.

Megasonic systems but only Fluorocarbon Co.* chose to manufacture. In collaboration with the Fluorocarbon Co., RCA developed a new design using two pairs of transducers on the sides of the cleaning tank. Three carriers with wafers are loaded on each platen and platens are moved through the tank on a belt. The following tasks were necessary to make this part of the system useful for solar-cell manufacture:

(1) Design, build, and operate machinery allowing wafers to be cleaned, and relate throughput to cleaning ability, ultrasonic power, belt speed, carrier geometry, wafer spacing, and chemical composition.

(2) Design, construct, and test a circulation-filtration system for SC-1, the standard RCA cleaning solution of ammonium hydroxide, hydrogen peroxide, and water [3]. The purpose of this was to ensure that no build-up of particles would occur, thus extending the life of the solution. It then became necessary to determine the limiting concentrations of the chemicals and to learn how to minimize their consumption.

(3) Evaluate a rinsing system using filtered, deionized (DI) water.

(4) Perform tests to ensure that all materials used were compatible and did not corrode or contaminate the wafers.

3. Description

a. Megasonic Cleaning Tank and Hood

A system for the continuous cleaning of solar-cell wafers was designed and built by the Fluorocarbon Process Systems Division of Fluorocarbon Co. Figure 1 shows the new unit being installed in May 1979. Only minor modifications have been made since then. The system fits into a standard 6-ft Domnier station.**

The design was based on the concept of moving carriers with wafers past pairs of transducers. Since the largest commercially available piezoelectric ceramic capable of being driven at about 1 MHz, which is about 1.8 mm thick,

*Process Systems Div., Anaheim, CA.
**Thermco Products Corp., Orange, CA.

3. W. Kern and D. A. Puotinen, "Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology," RCA Rev. 31(2), 198 (1970).

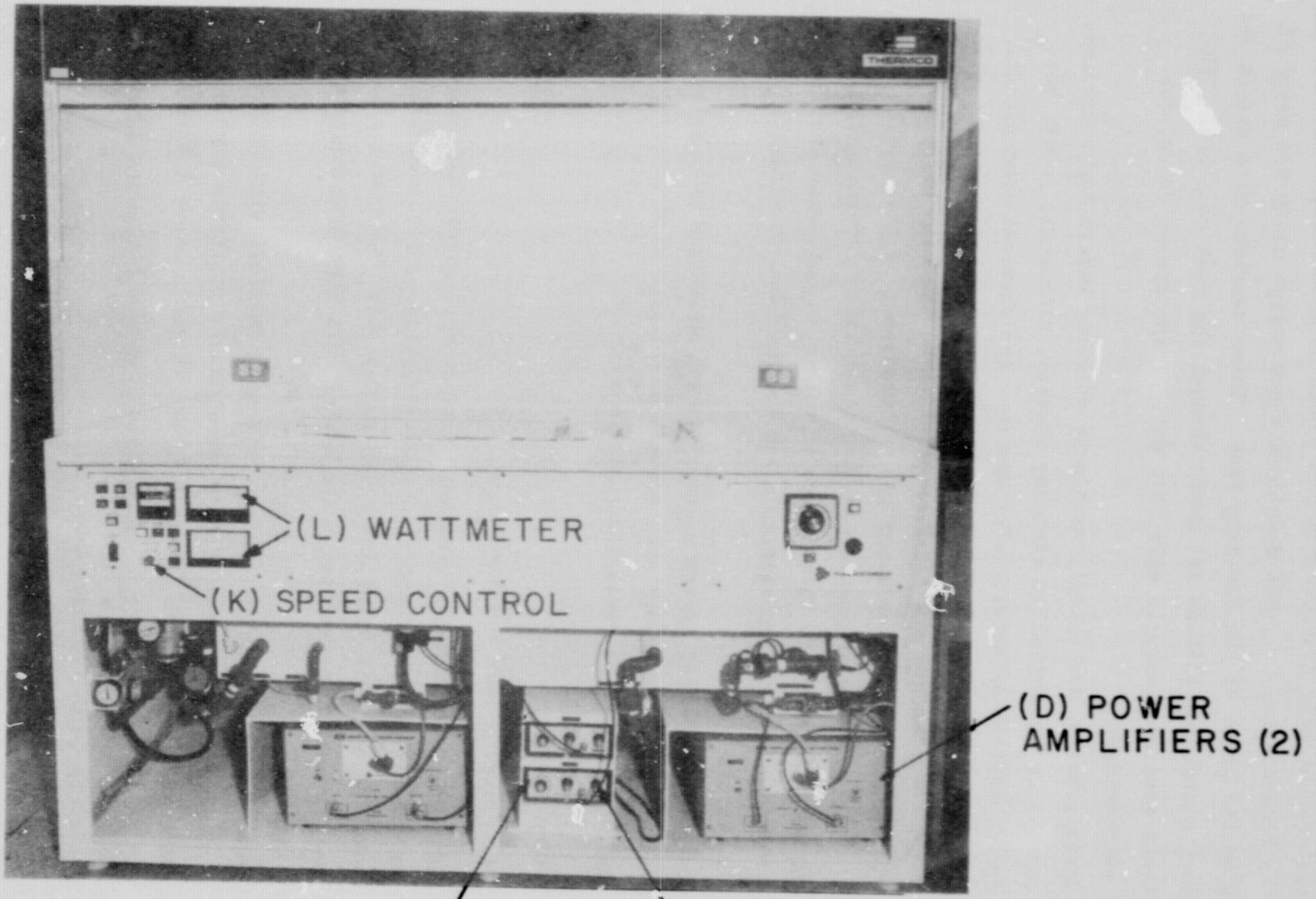


Figure 1. Megasonic unit.

has only a 63-mm diameter, two pieces that are offset have to be used to cover 76-mm-diameter or 100-mm-diameter wafers. Construction as well as repair is then quite simple if modules of such pairs are fabricated; one of these can be seen with cover removed (Fig. 2). When two such pairs, A and B, are incorporated (Fig. 3), they must be staggered (i.e., not opposite each other) to avoid interference of the sonic beam. In the new design, a quartz reflector, C, is set into the wall opposite each transducer pair. Note that this modular construction permits the system to be scaled up either by adding a third transducer or by additional offset modules.

The wafers, D, are held in carriers, E, on the platen, F. The platen hangs from rod, G, which engages on and is carried by a polypropylene continuous chain drive, H. The speed can be controlled linearly between 0 and 65 cm/min and set by knob, K (Fig. 1). When the platen reaches the magnetic switch, I (Fig. 3), the drive is stopped. The operator will then manually transfer the three carriers on a platen to the overflow rinse tank, J (Fig. 4). An automatic transfer arm, which is standard equipment with chemical processing stations, can be incorporated. The transducers can be powered only when the drive is moving. This is to avoid excessive exposure of a plastic carrier if the drive is stopped while a carrier is exposed to the sonic beam. The solid-state power supplies, O (Fig. 1) are stored underneath the plenum; each is driven by a signal generator, P (Fig. 1). The input power can be read on the wattmeter, L, and the supplies can be adjusted by the power control, M. The power amplifiers (D) and signal generators (P) are kept under constant nitrogen purge to avoid corrosion. With careful enclosure design, the nitrogen purge can be as little as 10 liters/hour. The power supplies are interlocked through a level detector that shuts the power off if the liquid level falls below the level of the detector. If the transducers were exposed to air, i.e, not cooled, they would rapidly overheat and fail. The top level detector has to be covered before the unit can be powered.

A more detailed layout of the top left part of the control panel is shown in Fig. 5.

b. Recirculation and Rinsing System

During Megasonic cleaning, particles are removed from the wafers and carriers. In our experience, the build-up in the old production system, which processed about 2000 wafers per shift with no filtration, necessitated changing the cleaning solution once each shift. Based on experience, clean control

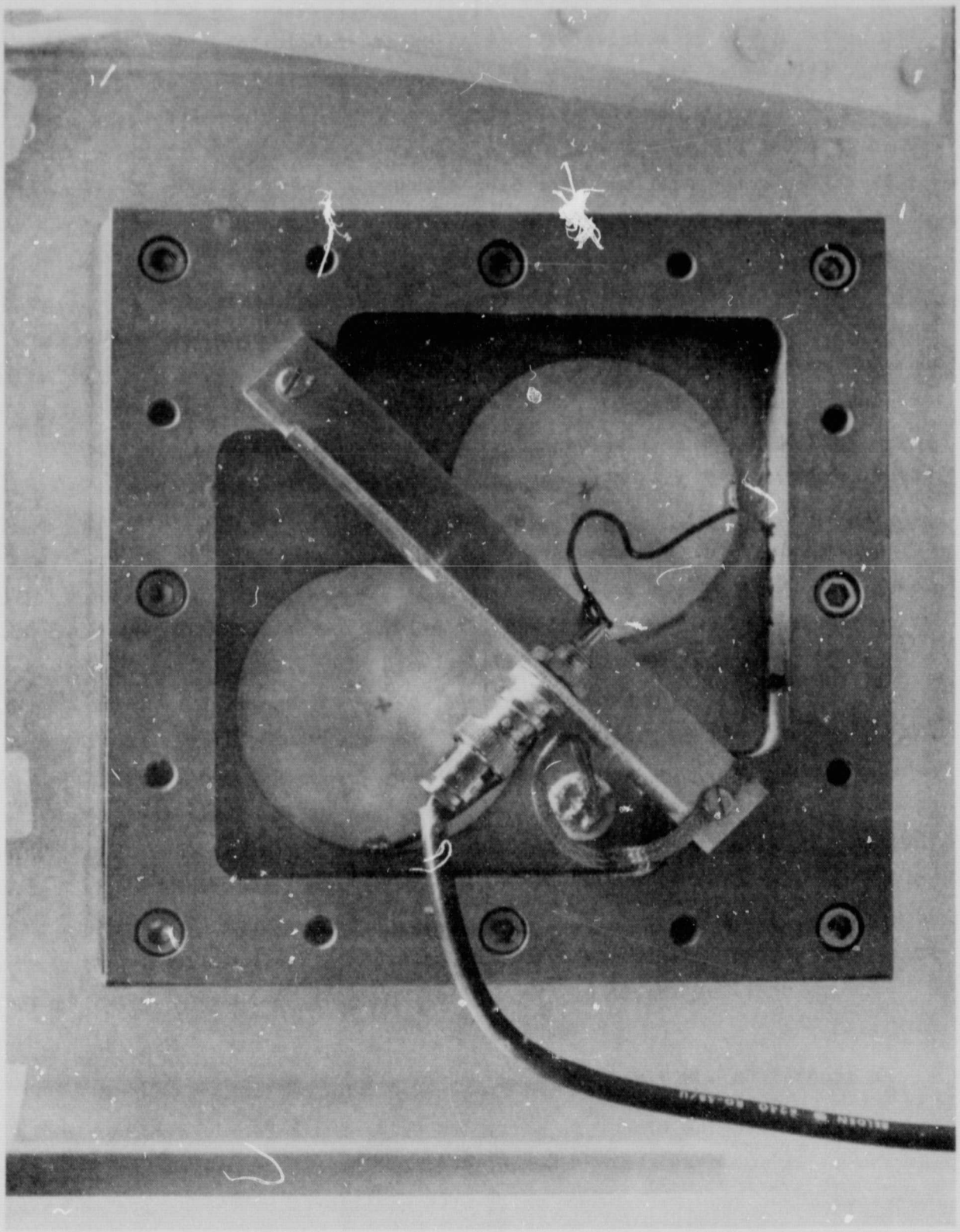


Figure 2. Transducer.

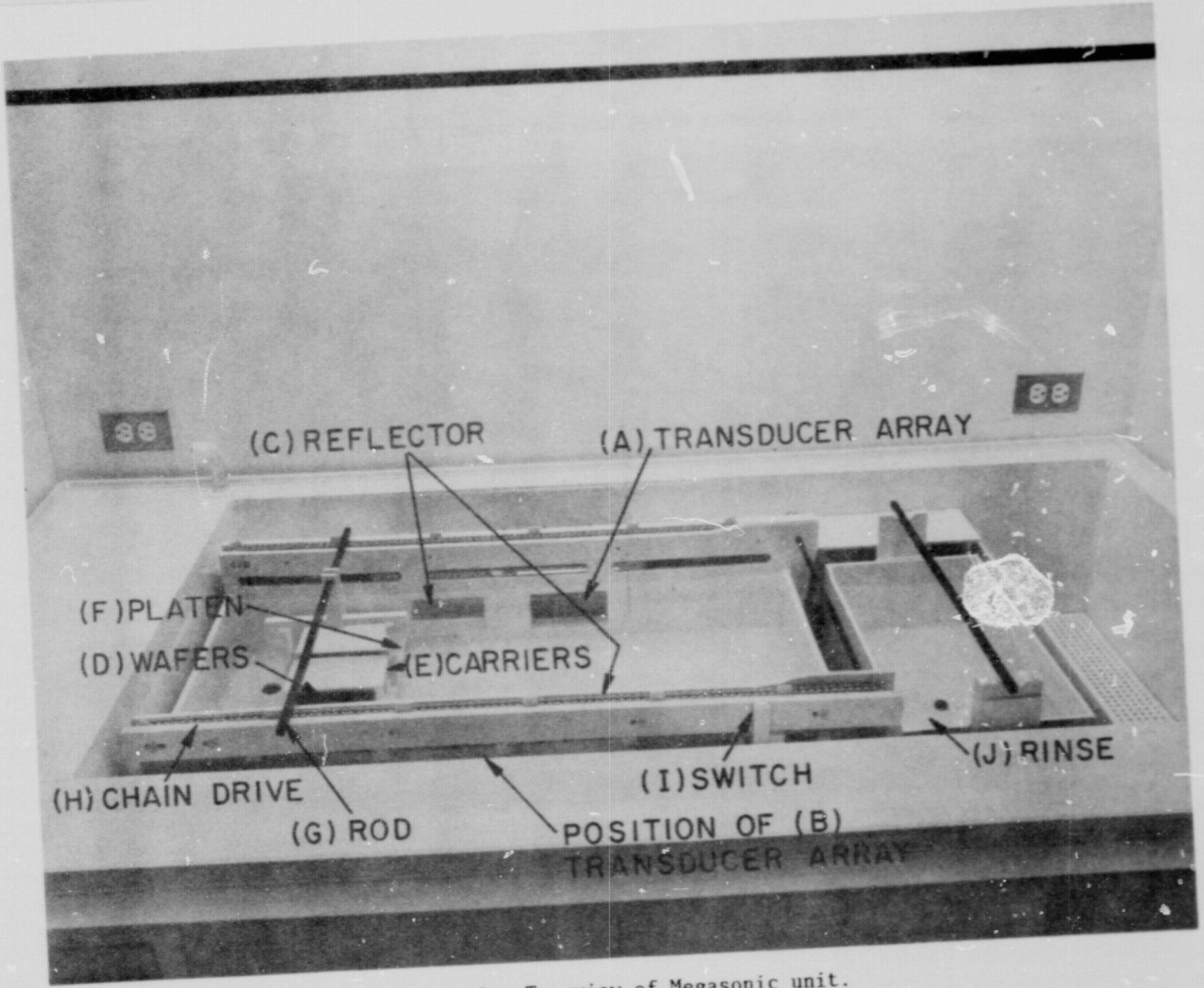


Figure 3. Top view of Megasonic unit.

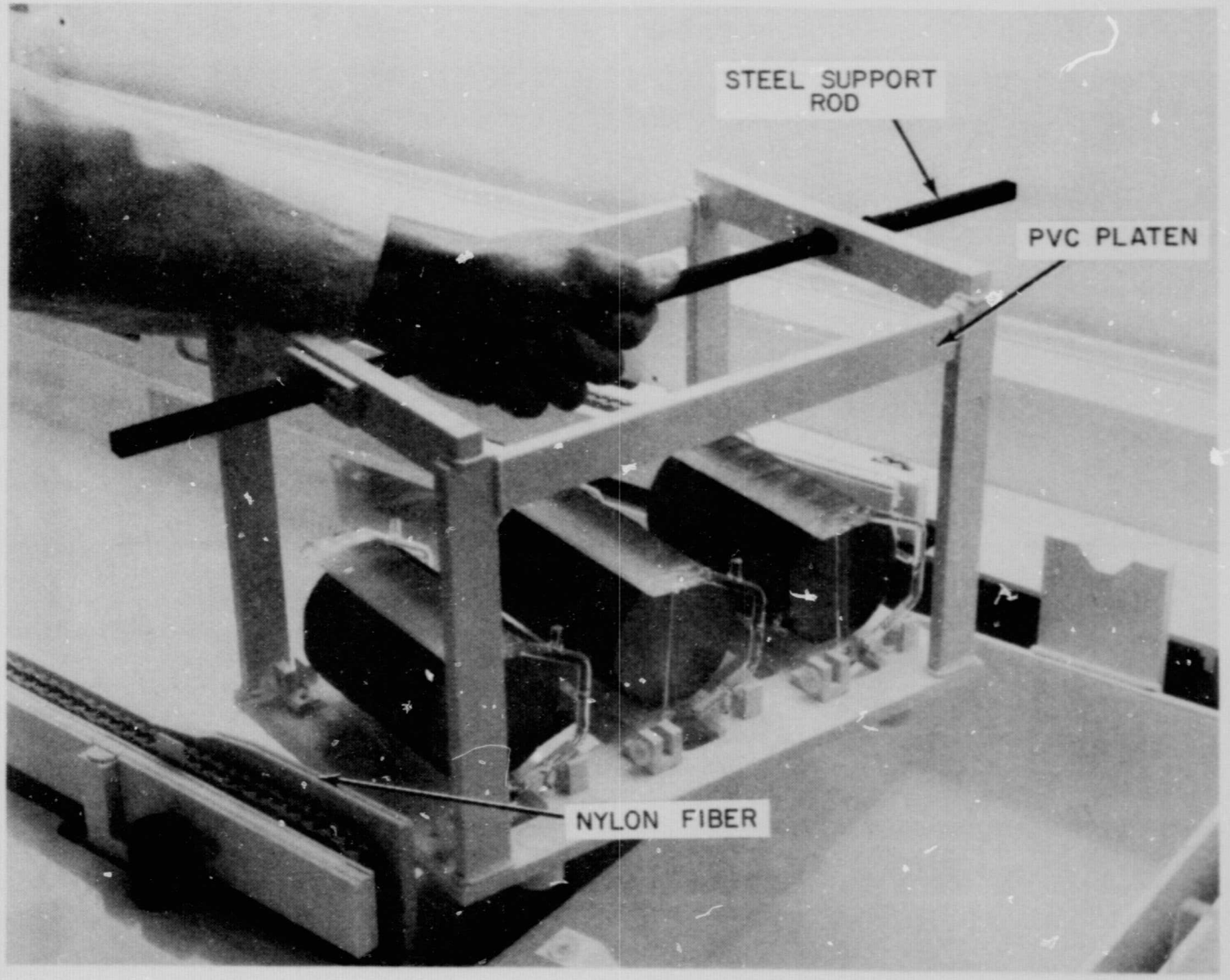


Figure 4. Platen and three loaded carriers being transferred to the rinse tank.

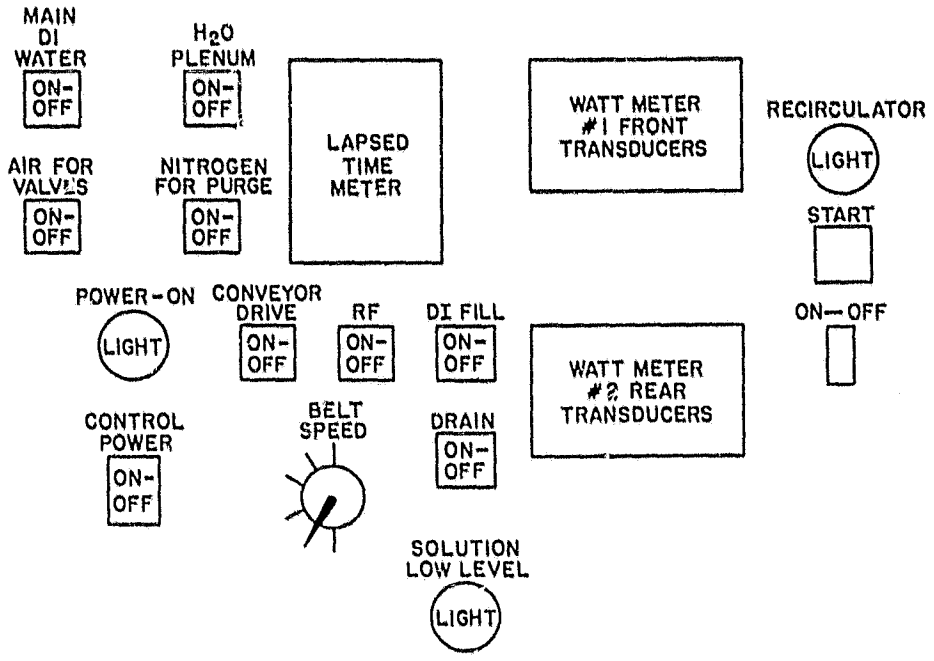


Figure 5. Detailed layout, top left of control panel.

wafers would pick up a small but statistically significant number of particles when exposed to the system. Therefore, we thought that continuous filtration would extend the life of the solution significantly. This was confirmed. The major questions to be answered were whether existing construction materials, especially the filter, could stand up to the SC-1 solution and a pump could be found capable of reliably circulating SC-1 in spite of the tendency for that solution to generate gas bubbles. These problems were solved and the corrosion tests are described in the next subsection.

Figure 6 shows the final system and also indicates what components were used. The only addition made to the commercial system was a floating magnet, encased in polytetrafluoroethylene (PTFE) which was inserted into a 1/2-in. polyvinyl chloride (PVC) standpipe connected to the tank so that the magnet reflected the liquid level. A pair of magnetic reed switches attached to the outside of the pipe react to the level of the magnet by opening and closing a relay, which then starts and stops the circulation pump. The schematic is shown in Fig. 7.

In practice, the SC-1 solution, when first prepared, tended to give particle counts on control wafers that were only slightly greater than the optimum obtainable, i.e., counts in the order of 30 to 50, instead of less than 30.

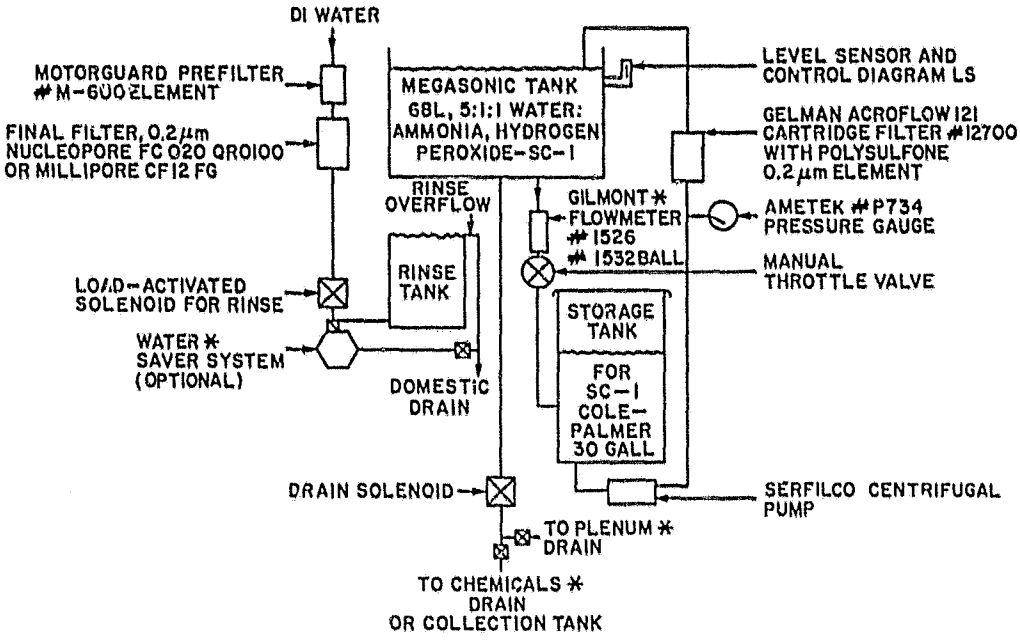


Figure 6. SC-1 recirculation and rinse system schematic.

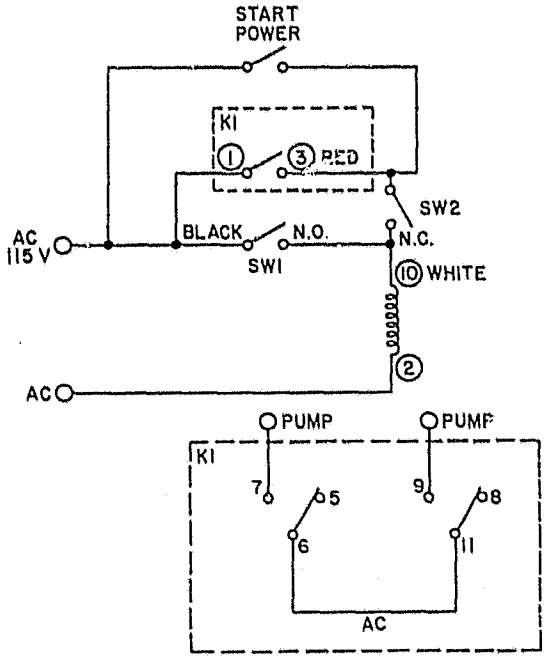


Figure 7. Level sensor/pump switch schematic.

Higher counts were found when new platens or carriers were introduced, even when these had been scrubbed with detergent, rinsed, and wiped with lint-free cloth. However, after continued recirculation for several hours at a rate of about 2 L/min, the SC-1 solution appeared to be cleaner and optimum counts on control wafers were again obtained.

In use, the 0.2-μm pore size filter did not appreciably increase the resistance to flow and the pressure required to pump the solution remained between 1.5 and 5 psi for several months. The Ametek* pressure gage is coupled to the system via a PTFE diaphragm and is glycerin-filled. After about 3 months use, the gage ceased to function due to a screw coming loose. This was repaired, a somewhat larger orifice was inserted, and the gage housing was also filled with glycerin. This seemed to cure the problem, but an oil leak developed later and required the refilling of the diaphragm-to-gage portion. No corrosion was observed. Initially, a Vanton** pump which had been in use caused considerable pressure fluctuations during each cycle and probably caused loosening of the screw. This pump ceased to function when the Megasonic system was transferred to the RCA Mountaintop facility and was replaced by a Serfilco† centrifugal pump which causes much less vibration. This pumps well for a few hours but then has to be stopped and restarted.

Due to an oversight during the assembly of the tank, the solenoid-driven outlet valve had been improperly assembled, exposing some stainless steel to the SC-1 solution. This caused excessive catalytic decomposition of the hydrogen peroxide, but was completely rectified when properly assembled. The rinse tank is also shown schematically in Fig. 5. This is a single-stage overflow tank of about 12 L capacity. The recommended flow during rinsing is 15 L/min. Rinsing for 2 minutes is usually sufficient. The plant deionized water is supplied at about 30 psi. This is filtered through a Motorguard†† depth filter and a Millipore 0.2-μm cartridge filter. The rinse mode fast flow is activated by the steel bar of the platen switching a magnetic relay in the yoke on which it rests in the rinse tank. When not in the rinse mode, i.e., when the timer has switched to low flow, a steady stream of about 2 L/min is maintained. The system functioned as designed. However, during the

*Truesdell Co., Skillman, NJ.
**Vanton Pump and Equipment Corp., Hillside, NJ
†Serfilco, Glenview, IL.
††Motorguard Corp., Medham, NJ.

laboratory trials, a brown-red shadow developed on the overflow side of the tank. This was identified as ferric hydroxide. It was observed only during a 1-month period. During the same period the Millipore filter had to be replaced several times because it plugged rapidly. Investigation showed that in all probability, colloidal ferrous iron in the raw water supply caused the problem. Careful analysis of rinse water and SC-1 subsequently, using atomic absorption analysis, failed to detect iron in amounts above the detection limit. The water flow returned to "normal" in the course of 3 to 4 weeks and no further problems were observed.

c. Choice of Materials and Parts and Corrosion Testing

(1) General. The following materials had already been use-tested in the older type of Megasonic system employed at RCA for the past 6 years: polypropylene, polyethylene, polytetrafluoroethylene (PTFE), polychlorofluoroethylene, polyvinyl chloride (PVC), silicone rubber, quartz, tantalum, and zirconium.

For the recirculation system, the use of the gray, asbestos-filled PVC was held to a minimum to avoid a possible source of contamination. The major piping system chosen was made of polypropylene, and all valves, pumps, and connectors were chosen so that no stainless-steel parts or metals other than tantalum were exposed to SC-1, because hydrogen peroxide decomposes catalytically on such metals as nickel, iron, and platinum, and because SC-1 attacks copper and titanium and pits aluminum. A few fittings such as pipe size adapters were obtainable only in the gray PVC.

It should be noted that a 2- to 3-second exposure of PTFE to the sonic beam in SC-1 causes no damage, but that polypropylene melts locally during prolonged exposure, leaving a pinhole pattern. This is the reason for covering the wall of the tank opposite the transducers with a quartz reflector plate inclined so that the reflected beam is guided to the surface.

While the intent was to use quartz carriers for cleaning solar cells, it was expedient on occasion to clean in plastic carriers. PTFE was the first choice. It stands up well to insonation in SC-1, although it eventually shows some surface deterioration, becoming powdery and shedding particles.

(2) Polysulfone. Polysulfone, an inert material with a high-temperature tolerance, is used for filter membranes. Since it can be molded and has good

engineering properties, we also decided to test it for use in the recirculation system and as a possible carrier construction material. Accordingly, corrosion tests were run first on solid sections of polysulfone. No change in appearance, brittleness, or weight change was observed after immersion for 300 hours. Gelman Sciences Co. of Ann Arbor, Michigan, offers a wettable polysulfone membrane filter in a polypropylene housing. The filter is attached to the acetal copolymer core with polyurethane, and gaskets are either of neoprene or polyfluorochloroethylene.

Another test was made on the Gelman ASC 121 Acroflow cartridge. This was exposed in SC-1 for 35 h at 50°C, for 85 h at 23°C, and for 2 h at 75°C. It showed no change except for a slight yellowing, and was sent to Gelman for detailed examination. The membrane was extracted from the filter and tested* for water flow and bubble point integrity. Gelman's Quality Department reported no change in properties, compared with those of a new filter. This means that the 0.2-μm filtering ability was not affected.

Although several filter manufacturers recommended PTFE membranes for use with SC-1, it was found that one manufacturer had problems sealing these membranes to the headers, while another warned about the danger of not prewetting them before use, preferably in alcohol, because otherwise they might rupture when water is first admitted. Further, at about $300 each, these cartridges are quite expensive. The polysulfone cartridges, on the other hand, cost about $90 each, have the same filtration area as the PTFE ones, and require no special handling at installation because they are wettable - good reasons to test these further in the recirculation system.

The second of the chosen Gelman polysulfone filters remained in use for 3 months and was removed to be examined even though it was filtering well. A third filter then continued to serve for the remaining operating time in Somerville. No deterioration was observed in spite of the excessive load placed on it by the introduction of 0.3-μm alumina which was used to deliberately contaminate wafers during the evaluation of the cleaning ability of the Megasonic system.

Polysulfone, because of its wetting properties, was also a likely candidate material for a carrier. It performed well in corrosion tests with SC-1. Three carriers were purchased that had been fabricated from machined parts. These were assembled with threads and screws and had a groove width of 0.06

*In accordance with ASTM 316-70.

in. (1.5 mm). The manufacturer reported that the material was difficult to machine and that the grooves were rough-textured. Shot blasting improved this slightly. In view of the relatively slight advantage of polysulfone over PTFE (polytetrafluoroethylene) in terms of wettability and possibly ease of molding, the major expenditure of purchasing a mold at this stage seems unjustified. In addition, the material is attacked by many solvents so that carriers can be used in degreasing or photoresist operations only after careful selection of the solvents to be employed. It was therefore decided not to experiment any further with this material.

(3) Polyphenyl Sulfide. A suggestion was made by a company that specializes in the experimental molding of plastics to use the polyphenyl sulfide plastic Ryton made by Phillips Petroleum Co., Chemicals Division, Bartlesville, OK. This is thought to be chemically more inert than polysulfone. Accordingly, some test pieces of Ryton 4 and 10 were corrosion tested. These did not hold up in a warm sulfuric acid-hydrogen peroxide solution, as used in system "Z" cleaning. In SC-1 at about 50°C for 89 h, the test pieces showed a slight weight gain of approximately 0.1% and no physical signs of attack.

The test solution was then analyzed and found to contain levels of calcium, magnesium, sodium, aluminum, boron, and silicon significantly greater than the blank solution treated similarly but without test pieces. As Ryton is glass-filled, the data suggest that this filling is leachable. In a recirculating solution, as used in the Megasonic system, this would lead to an undesirable buildup of soluble ions. No further studies were made.

(4) Platen Carrier and Storage Tank Materials. Platens were fabricated from polypropylene and polyvinyl chloride (PVC) and the steel support rods were PTFE coated. In addition, nylon* cord was used as a guard, strung across the platen to prevent wafers from rolling out when the carriers were laid on their sides, ready to be cleaned in this position in the Megasonic tank (Fig. 4).

All these materials have now been exposed to SC-1 in the Megasonic tank while the sonic beams were operating at full power for several months with no apparent degradation.

All the carriers used for the actual fabrication of solar cells, and for the development and testing of the air dryer, were made of quartz. However,

*E. I. du Pont de Nemours & Co., Inc., Wilmington, DE.

the carriers used in the production test were made of PTFE because not enough quartz carriers could be procured in time for the test. Also they cost about four times as much as the PTFE carriers actually used. The disadvantage of the PTFE carriers is that the wafers have to be dried at about half the rate for that of quartz. This will be discussed in subsection II.B.e.

Other carrier materials like polyethylene, polypropylene, or PVC are less desirable because they tend to float in SC-1 unless loaded fully with silicon wafers; for some tests, and even in production, it is not always possible to wait until a carrier is fully loaded.

The storage tank is made from unfilled polypropylene.

(5) Piping and Meters. Almost all the pipes were black polypropylene; a few fittings were made from white PVC and some gray-filled PVC fitting had to be used because others were obtainable only on a very long delivery schedule. None of these showed any signs of deterioration. In addition, chemical analysis of solutions that had been circulating in the system for up to 4 weeks showed no major buildup of sodium, copper, or iron as measured by atomic absorption analysis with detection limits of 0.025 µg/L for sodium and 0.1 µg/L for copper and iron. The Gilmont* flowmeter tube is clear methacrylate and the float is tungsten carbide. It was originally designed to indicate the SC-1 return flow from the tank to the reservoir, but for space reasons could not be fitted. It proved to be valuable for the DI water flow measurement.

Back pressure was judged by the Ametek pressure gage. This gage has a PTFE diaphragm and transmits pressure via oil to a dial gage which has continued to read between 1.5 and 5 psi. The dial gage was sent to the manufacturer for repairing a loose screw and then for refilling when a loss of oil to the outside occurred; it has functioned well since then.

(6) Circulation Pumps. The pump originally installed was a Vanton "Flexiliner" CCAMT 60A with "Viton," a chlorofluorocarbon elastomer, as the liner of this magnetically driven, PTFE-covered rotor. This pump delivered the required 12 L/min for 9 months in Somerville, NJ, with no problem other than an occasional airlock that could be readily bled. Yet, when installed at

*Gilmont Instruments, Inc., Great Neck, NY.

the Mountaintop, PA, location it could not be made to work on SC-1. (It pumped well with water.) It remained gas-locked even when the entire system was leak checked, the liner was replaced, and the new bearings were fitted.

It was finally replaced by a magnetically coupled, seal-less centrifugal pump, part #CPP 3450BL made by Serfilco; this too at first did not pump SC-1 but pumped water very well. At the manufacturer's suggestion, the output line of the pump was then throttled back and as soon as the pressure rose, the pump functioned well with SC-1 for a few hours, then had to be stopped and re-started. The only explanation that we have for this problem is that the change in altitude of about 2000 ft changed the relationship between the partial pressure of ammonia and dissolved oxygen in the SC-1 solution to the atmospheric pressure sufficiently to cause the evolution of gas by the impeller suction at the intake port to cause the gas lock.

d. Comments and Conclusions

In operation over several hundred hours, one power supply (still under warranty) lost output power and was repaired. After two transducer assemblies failed because of a poorly constructed ground connection, Fluorocarbon redesigned the supply connection; so far it seems to perform as designed, operating at a maximum of 320-W power input to each module at 0.92 MHz in continuous operation. As will be detailed in subsections II.D.3 and II.D.5, the belt speed gives adequate control in the operating region of about 15 cm/min. There is room for three platens of our design in the tank at the same time. However, these have not been optimized for minimum width design, and with attention to this point and a closer spacing on the driving vanes on the belt, four platens can probably be accommodated.

No acceptable method could be worked out to measure the power output of each transducer. Polypropylene vanes pivoted in the tank opposite the transducers attracted oxygen bubbles that changed the buoyancy unpredictably. A strip of the piezoelectric transducer resonant at about 0.9 MHz was coated with polytetrafluoroethylene (PTFE) and inserted into the tank opposite the transducer. It did produce a voltage output but was found to be insensitive to power changes; another strip of piezoelectric material, resonant at about 2.4 MHz, behaved similarly. From the operating data it seems clear that the power input to the transducers is quite steady and any deviation is sufficient warning to check the system out.

The ambient atmosphere in the laminar flow enclosure for the Megasonic cleaning tank can be adequately maintained by paying attention to the manufacturer's recommendation for balancing the exhaust and air supplies so that the curtain air flow into the plenum is maintained without dragging room air into the unit. This adjustment, combined with care to avoid major perturbances of the laminar flow by operators reaching in or objects obtruding, permits the maintenance of ambient air with a particle count of a few tens of particles of 0.3-μm diameter and close to zero of 1-μm-diameter particles.

We conclude that the design objectives have been met regarding physical layout and functionality of the Megasonic cleaning tank and the rinse and recirculation system. It is also clear that for use in a full-scale plant, it will be necessary to incorporate mechanical means to transfer the carriers from the Megasonic tank to the rinse tank and then to the dryer. The Fluorocarbon Co. already has some options for sale; these can be adapted to the needs outlined above, but that is outside the scope of the present work.

B. DRYING STATION

1. Background

It is customary in the semiconductor industry to dry silicon wafers by spinning them in a centrifuge. This has a number of disadvantages: The construction material of the carrier cannot be quartz because quartz is not strong enough. This implies that the wafers must be cleaned and dried in a plastic carrier and then transferred to quartz (which has to be cleaned separately) before annealing, diffusion, or oxidation. Another problem is that centrifuging is essentially a batch operation and does not fit in well with continuous processing; also, the downtime of a centrifuge is relatively great because, like all highly stressed mechanical systems, it requires maintenance and is difficult to clean if it gets contaminated by insertion of an improperly handled dirty carrier, by the inevitable breakage of a wafer that showers debris, or by particle-laden air being dragged into the chamber.

The Megasonic systems in current use at RCA rely on a high-speed air dryer to first remove all the large water drops from the surface, then raise the temperature to about 100°C to ensure complete removal. This takes about 3 minutes and requires about 6 kW for heating the filtered air needed to dry one

carrier with twenty-five 76-mm-diameter wafers. The details of this system are fully described in Ref. 2. It should be noted that no streaks develop if the water used in rinsing is clean; conversely, if streaks are visible, it is immediately clear that the water supply is dirty and needs attention. This self-indicating feature is most valuable in detecting a problem long before device electrical tests would show that it exists.

The best utilization achieved before this program was the drying within 5 minutes of the contents of two or three carriers, each holding 25 wafers. Conceivably, the number of wafers could be doubled by closer spacing, but even so, hot-air drying would require 5 to 6 watt-hours per wafer plus the cost of the high-velocity air. Another problem to be solved is the disposal of the heated air that is vented into the plant.

An alternative appeared to be to increase the airflow sufficiently to achieve drying with room-temperature air by physical displacement of the surface water and evaporation of the few surface layers of adsorbed water.* This implies that drop formation should be avoided, i.e., that the surface energy of the water should be smaller than that of the wafers so that the drops can spread. As SC-1 naturally makes the wafer surface hydrophilic, the water can be displaced in a relatively mild air stream. However, experimental work was required to determine how fast this stream must be. Preliminary experiments had indicated that a room-temperature air stream with a velocity of over about 12 m/s (27 mph) was sufficient.

2. Design Objectives

The major goal was to design a system that permitted carriers with wafers to be dried in a continuous manner at a rate compatible with the Megasonic cleaning rate, i.e., over 2500 wafers/h. As this was essentially a new field, the study did not include design of a mechanism for the automatic loading of carriers onto the belt drive, or its unloading and transport to the next processing station.

We anticipated that the nature of the wet surfaces of the carriers and the wafers, geometry of the retaining groove of the carrier, and wafer spacing would play a major part, in addition to the air-flow pattern and velocity. It was also clearly essential to ensure that the cost of generating an air stream at high velocity would be low.

*Patent applied for by RCA.

Finally, we intended to construct a machine in such a way that its capacity could be increased readily either by doubling, i.e., constructing a second module in parallel, or extending the active length of the drying zone.

The following tasks were therefore before us:

(1) Design and test a prototype system for drying 3-in. silicon wafers in their carriers with a room-temperature filtered air stream.

(2) Optimize the airflow patterns in relation to the carrier geometries.

(3) Design and test a system for moving the carriers through the drying, evaluate, and optimize its performance.

3. Description

a. Dryer Duct and Air Supply

An experimental air dryer was designed by RCA and constructed and delivered by Atmos-Tech Industries of Eatontown, NJ. It is capable of delivering air filtered through a 2-ft by 3-ft HEPA (high-efficiency particulate air) filter rated 99.9% efficient for particles down to 0.3-μm diameter. The maximum velocity was designed to be about 23 m/s. This unit is shown in Fig. 8. It consists of the HEPA filter underneath a plenum chamber. Air is supplied by a 3/4-hp squirrel-cage fan regulated by a speed control mounted on the side. The air is delivered through an opening that is just wide enough for one and long enough for two carriers, i.e., 100 mm x 355 mm. A duct with a moving belt connects the laminar flow station, the dryer, and the inspection station. The latter consists of another laminar flow station and the laser scanner used for process control.

Most experimental work on drying ability and geometry was carried out with the dryer funnel terminating in an opening of a clear plastic (Lucite) tunnel. Initially, the carriers with the wafers were moved through by hand. As can be seen in Fig. 9, the funnel mouth is wide enough for one carrier and long enough for two. A cutout in the tunnel floor, which is about 1 cm larger in all dimensions than the top opening, permits the air to exit freely. An oblique plastic sheet under the tunnel deflects the air to the back of the unit, away from an operator. The design criteria were to make the flow as close to laminar as possible and to force virtually all the air to pass through the carrier with wafers. The purpose is to ensure that the resistance to flow is uniform to avoid dead spots and "short circuits" that might divert a large fraction of the flow to areas where no wafers were. The HEPA filters are DOP (dioctyl phthalate) rated at 99.97%. Actual particle counts later

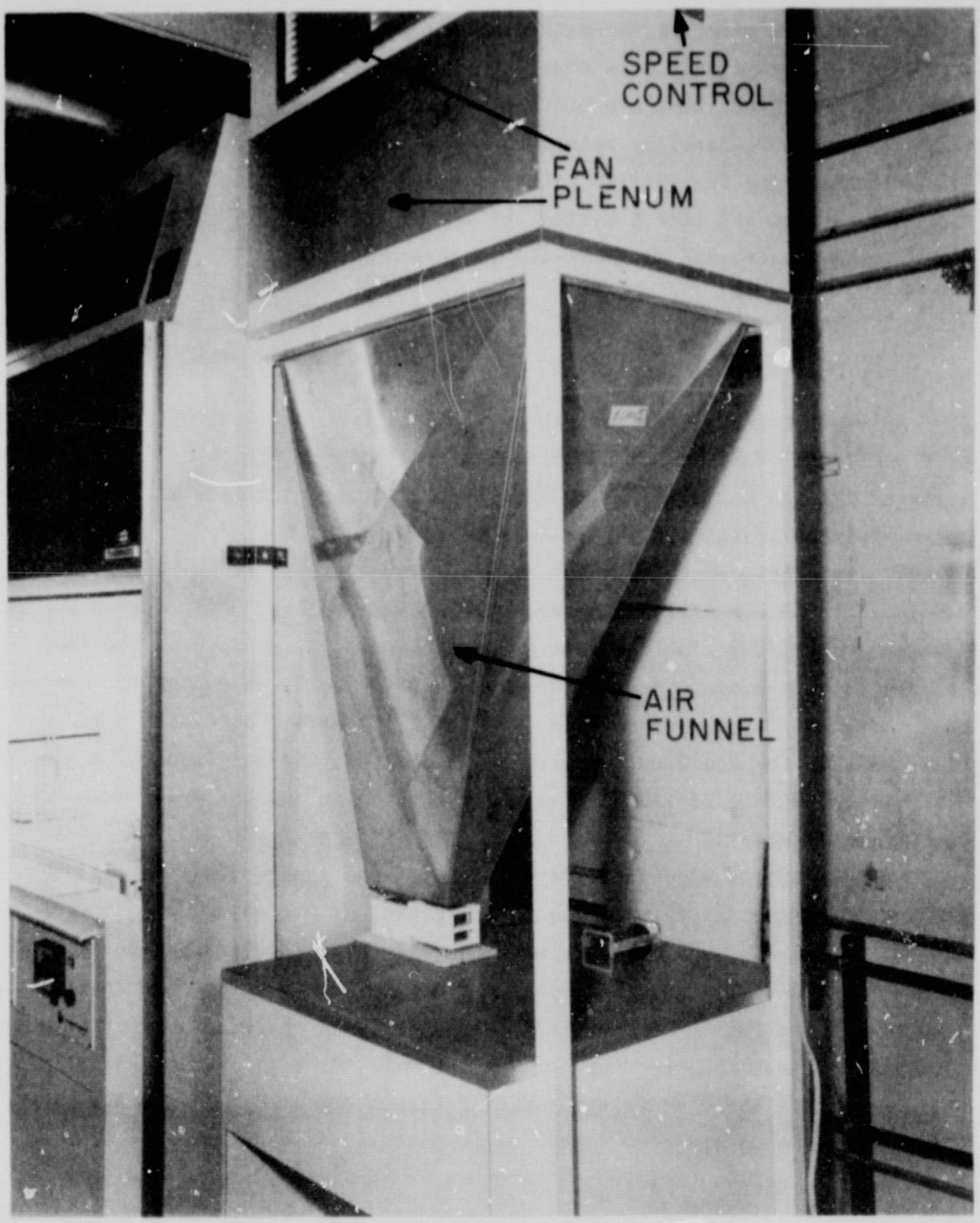


Figure 8. Cold-air dryer, as delivered.

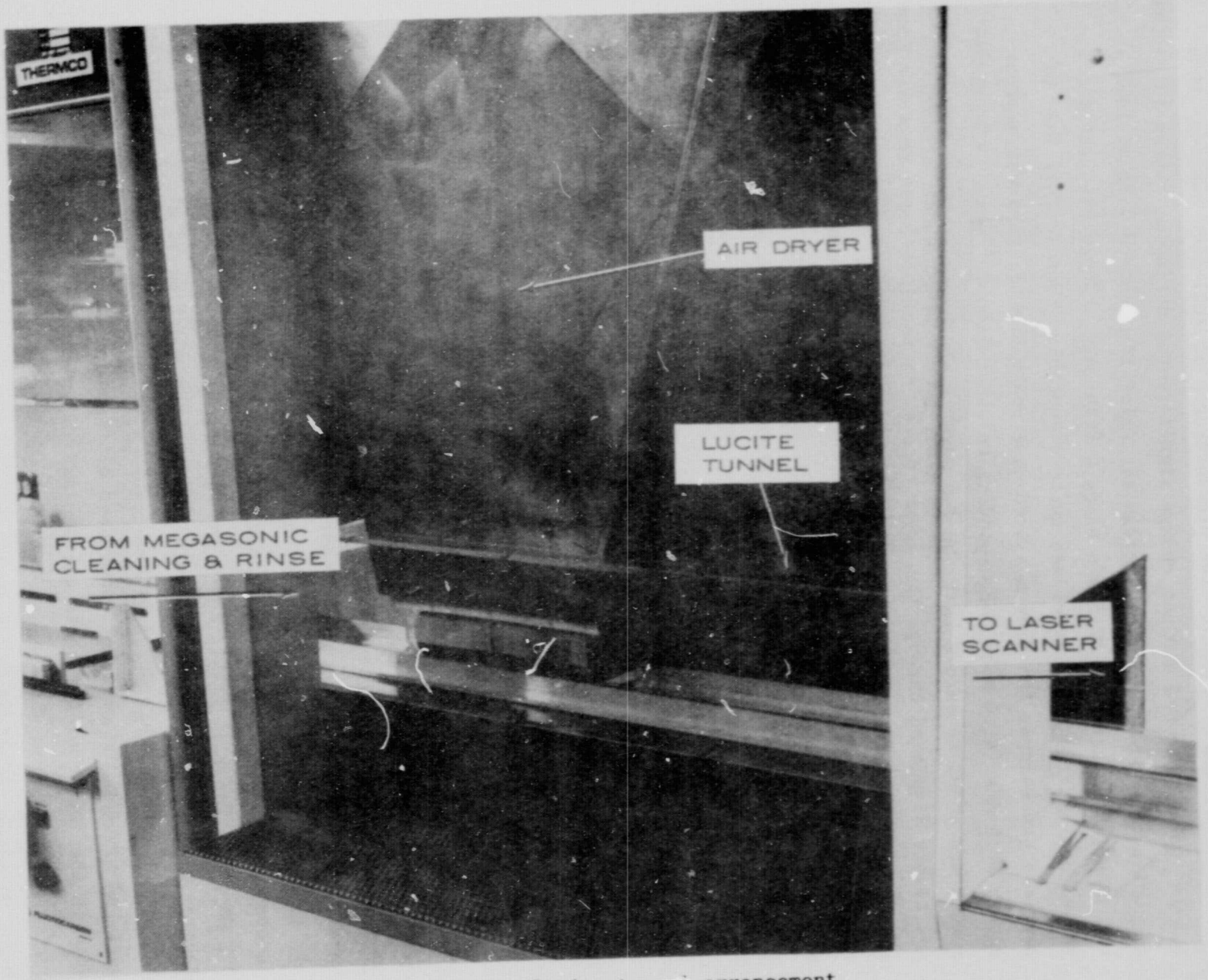


Figure 9. Drying-tunnel arrangement.

showed that there were no statistically significant particles in the air in the funnel 0.3 μm or larger. The pressure drop at full flow was less than 0.4-in. water gage and did not change significantly during more than 12 months of continuous operation. The average air velocity measured with no load at the funnel mounth was 25 ±2.5 m/s using a Peto gage. There was little turbulence and the noise level was quite acceptable. With a full load of carriers and wafers, the flow measured underneath the carriers was approximately 18.8 m/s (41.4 mph) corresponding to about 1400 ft^3/min. A high-low switch was added to ensure that the fan never stopped and air was always positively displaced through the dryer to prevent particle-laden room air from intruding. The experimental work showed the importance of ensuring that the resistance to airflow over the wafers in the carrier was kept reasonably constant. For example, the clearance between the wafer and the carrier-groove wall had to be at least 25 mil, i.e., a groove width of 36 mil when 11-mil-thick wafers were used. In addition, means had to be found to ensure that two wafers did not lean toward each other; with the wide-groove spacing this meant that they would touch and effectively cut off the airflow between them.

That problem was solved by inserting a roof-shaped deflector over the carriers at the start of their movement through the dryer. The deflector was arranged at right angles to the direction of travel and diverted the air stream so that it deflected the wafers first to lean in the direction of travel and then in the opposite way; this also separated them effectively. We found later that an even better arrangement is to insert two air or nitrogen jets positioned again at the dryer mouth, one jet on each side of the carrier just above the grooves, at a slight angle. In addition to separating the wafers, this also blew out the occasional water drop that may have lodged in the groove; it ensures more consistent drying and he[illegible] a faster drying rate. In our experiments we used compressed nitrogen at 25 psi, filtered through a 0.2-μm-pore size flat filter and a jet opening of about 0.75 mm. In future Megasonic cleaning systems, we would advocate the addition of a clean air source as part of the cold air dryer system. This would neglibly increase the system cost and obviate the need for compressed nitrogen.

In the course of the tests carried out in Somerville, the laboratory temperature ranged from about 65 to 76°F and the relative humidity from about 20 to 76%. No major effect on the drying rates was observed, but it has to be borne in mind that most of the tests were made before the belt dryer was available. Since

the wafers were pushed through manually, the reproducibility and statistical validity is questionable. Also, the system did not yet have to perform under the most adverse conditions of really high relative humidity as might occur during wet spring weather. At worst, a dehumidifier would have to be installed in the room. We calculate that about 6 gallons of water per day would be released by drying 2500 wafers/h.

b. Belt Drive

The requirements were to design a system that allowed quartz and standard PTFE carriers to be used, to be able to vary the belt speed deliberately and reproducibly, to ensure that the air could ex.. from the chamber freely, and to enclose the entire system in a tunnel that would not permit particle-laden room air to intrude. The basic design is shown in Figs. 10 and 11. Note that the broken line in Fig. 10 indicates the cross section of the dryer funnel.

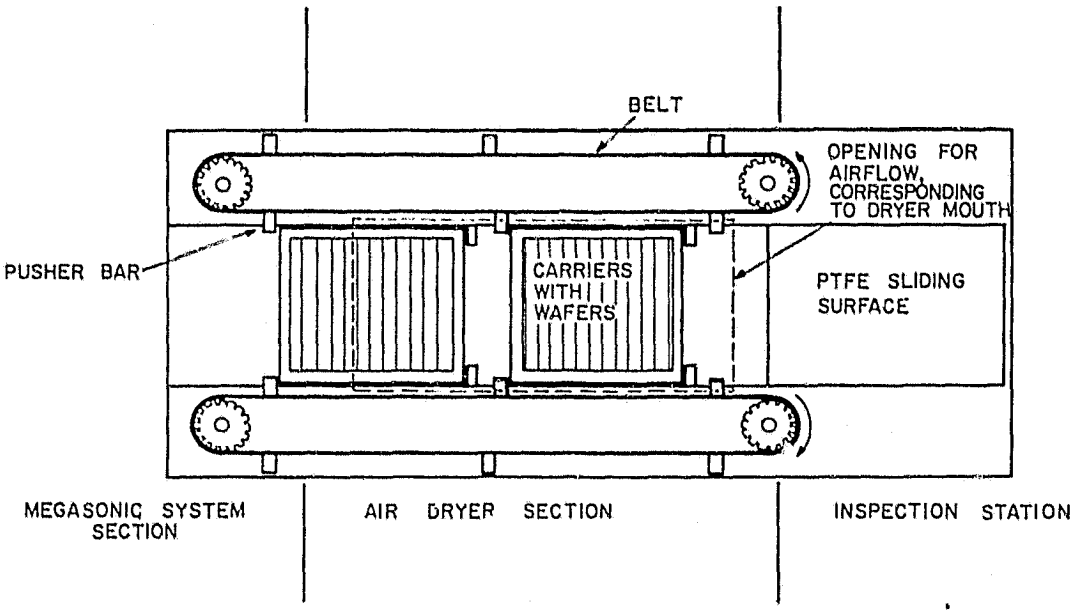


Figure 10. Top view of conveyor (concept).

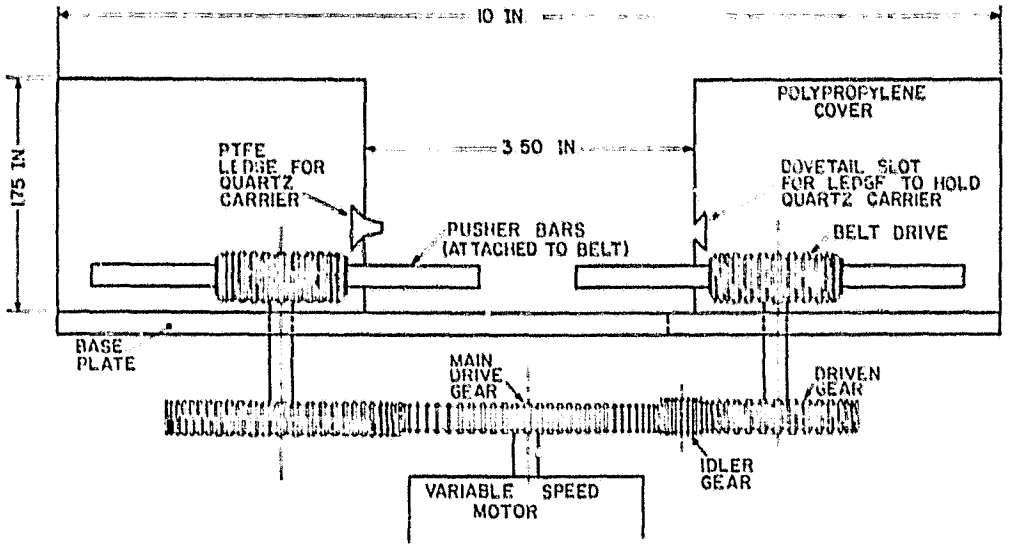


Figure 11. Cross section of conveyor (concept).

A major design problem turned out to be the limitation of having available only a 101-mm i.d. diffusion tube that had been fully characterized for making solar cells. It was necessary to use this tube to obtain valid comparison between Megasonically cleaned and standard "Z" cleaned cells. The standard Megasonic carrier has a square cross section, but the quartz carriers had to have the corners removed. This meant that they could not ride on the same channel as the PTFE carriers. The problem was solved by making provisions to insert strips of PTFE with a T cross section (Fig. 11) that could provide a ledge for the short quartz support ears provided on the carriers and shown in Fig. 12. Pusher bars on the belt drive then had to be made long enough to engage the center portion of the quartz carriers. The design and preliminary trials were time-consuming, but the basic system that was finally commissioned and built at Fluorocarbon was usable in the laboratory. All the data pertaining

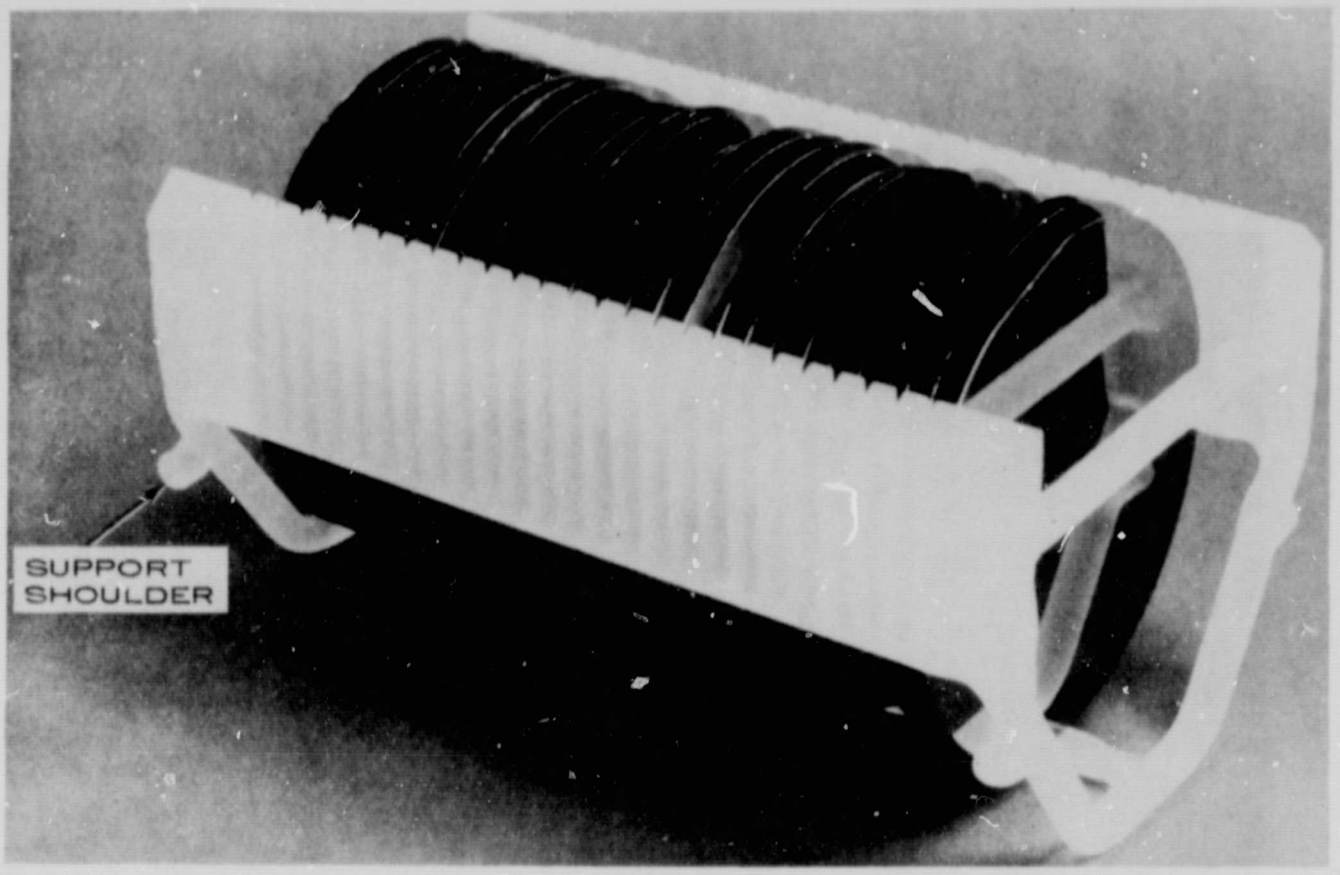


Figure 12. Quartz wafer carrier.

to drying rate in relation to carrier geometry, belt speed, cleanliness, and deflection devices were obtained with that system. It is shown in Figs. 13, 14 and 15, as installed in the Mountaintop plant.

In practice, the design of the belt and pushers did not stand up to the rigors of 24-h shift operation. The pusher tabs were too weak and tended to break off. When a stoppage occurred, the belts were thrown out of synchronism and insufficient adjustment was provided to permit maintenance when the belt stretched.

A new design was made but had not been installed by the close of this project. However, the Fluorocarbon belt system functioned for long enough periods (3 to 4 days and nights at a time) to verify that the basic concepts are sound.

c. Choice of Materials

The body of the air duct, plenum chamber, and deflector vane were made from aluminum; the only other metal in contact with the air stream is stainless steel in a few bolts. It is believed that stainless steel sheet could have been used with equal satisfaction, but aluminum was easier to form and less expensive.

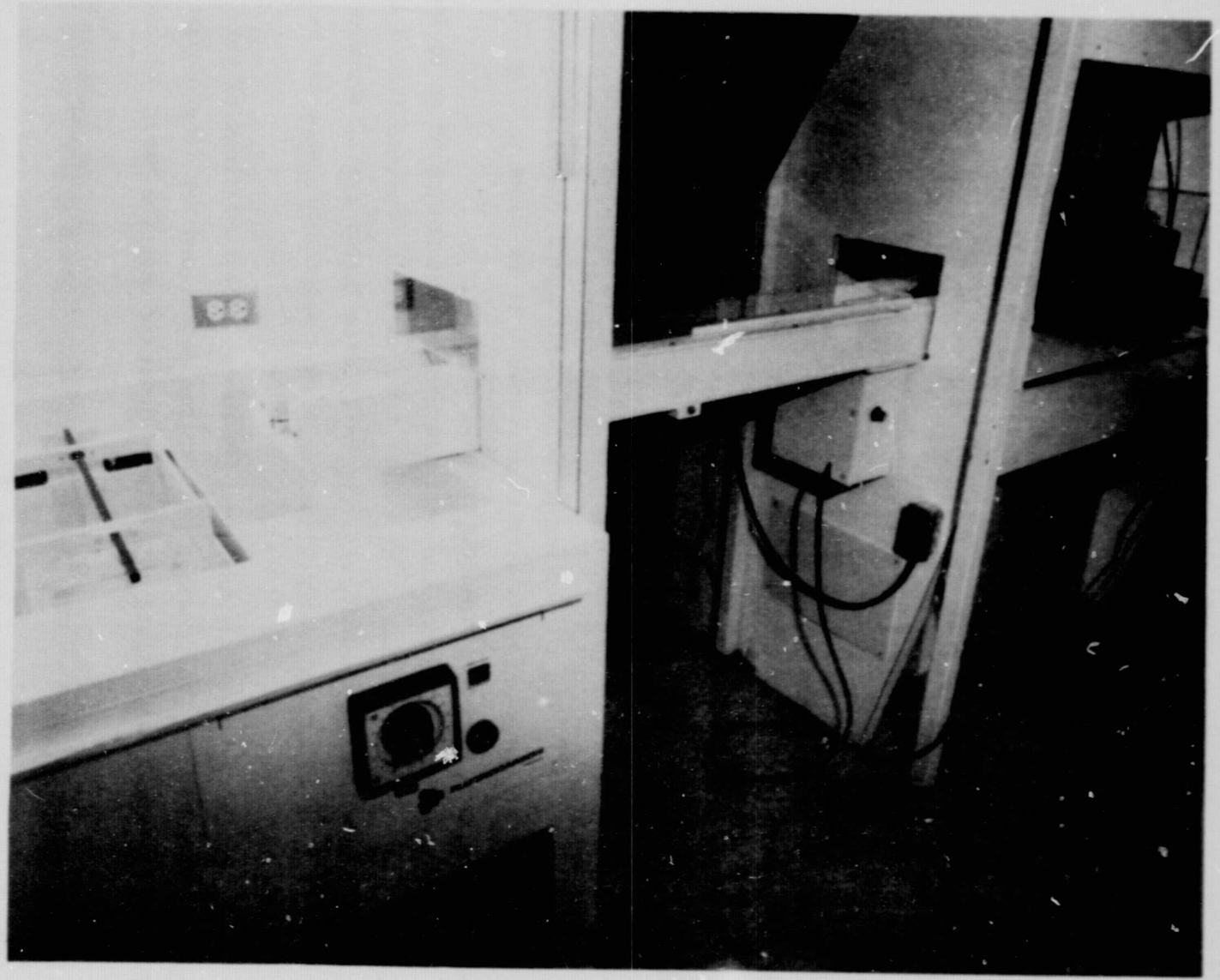


Figure 13. Megasonic cleaning system with Megasonic cleaning and rinse station (left), dryer (center), and laser scanner inspection (right).

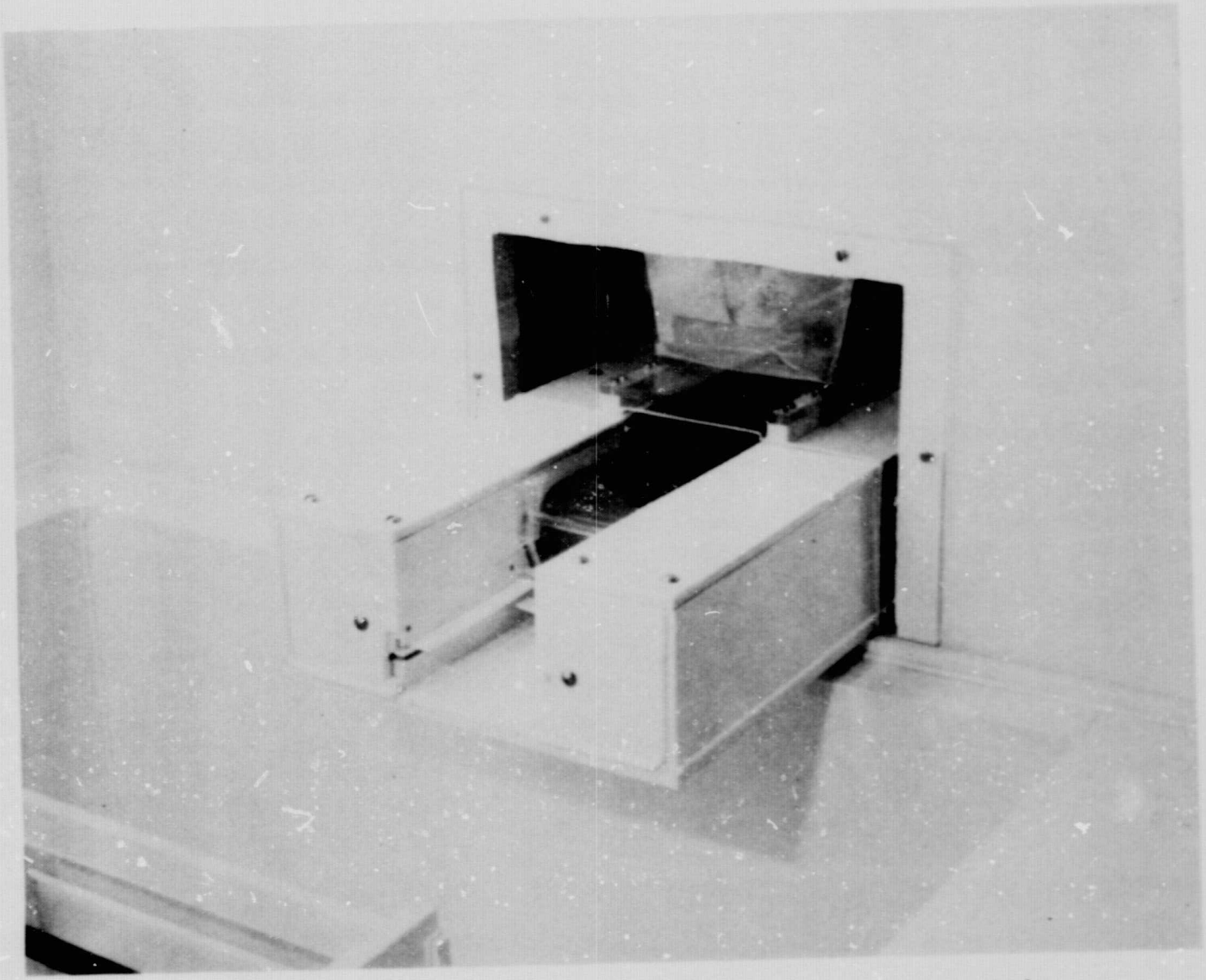


Figure 14. Quartz carrier with silicon wafers being carried into the drying section by the belt drive.

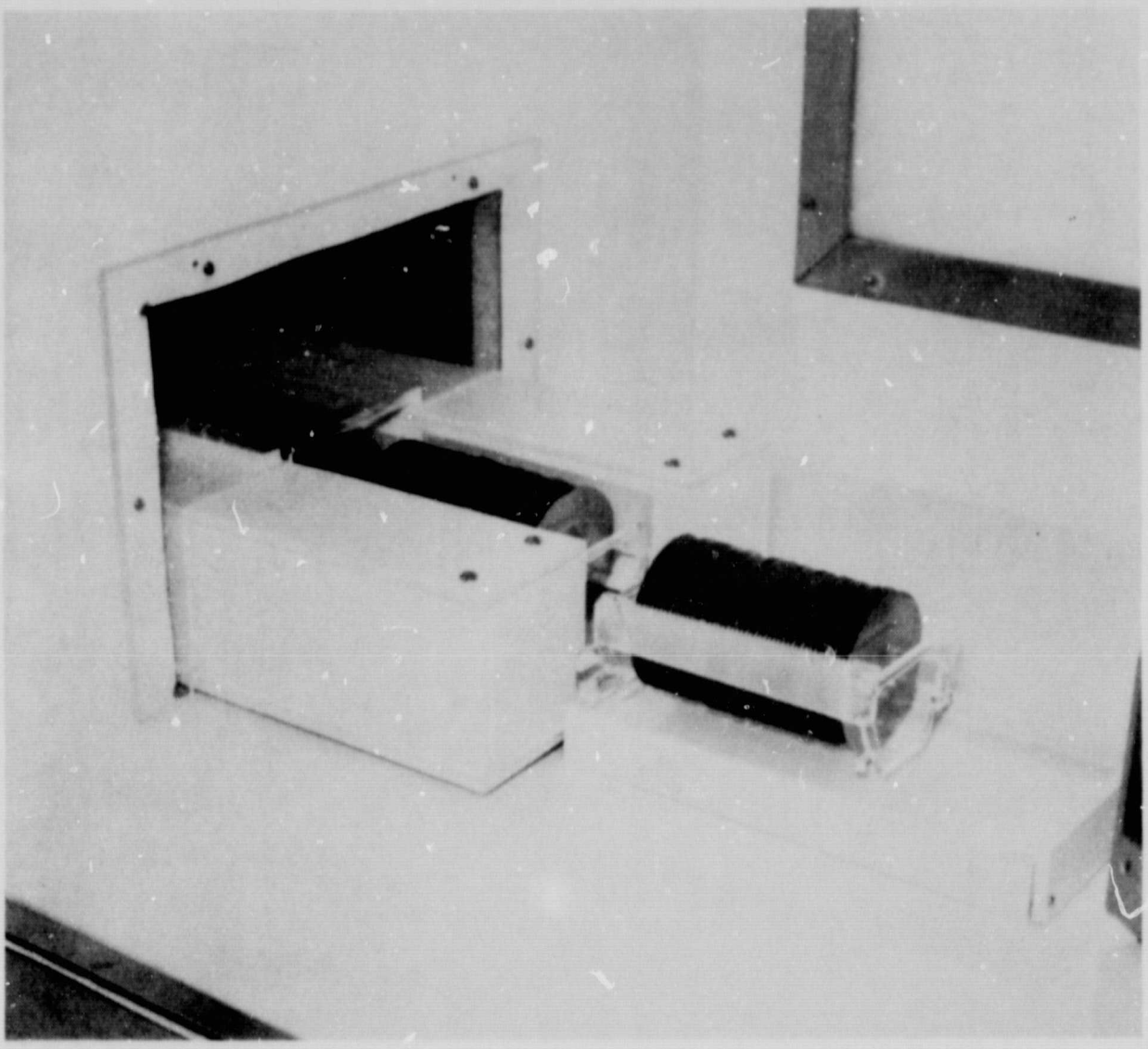


Figure 15. Dried wafers being pushed out into the inspection station by the belt mechanism.

The tunnel for the belt drive was made from transparent methacrylic plastic (Lucite), primarily to permit observation during the experimental phase. Later the belt drive base was constructed of PVC and polypropylene. All these materials gave satisfactory service.

The majority of carriers were the standard PTFE ones, used regularly in the semiconductor industry, as indeed the quartz carriers are. In addition,

some carriers were made from polysulfone; they too gave satisfactory results, once they had been cleaned of machining debris that was very hard to remove.

The quartz carriers were loaded onto aluminum sleds during the initial phase of testing the drying system when the carriers were moved through manually. These had to be replaced by sleds made of polypropylene because aluminum was found to corrode, presumably from the water thrown onto it during the initial drying cycle. The aluminum corrosion products contaminated the wafers (Fig. 16).

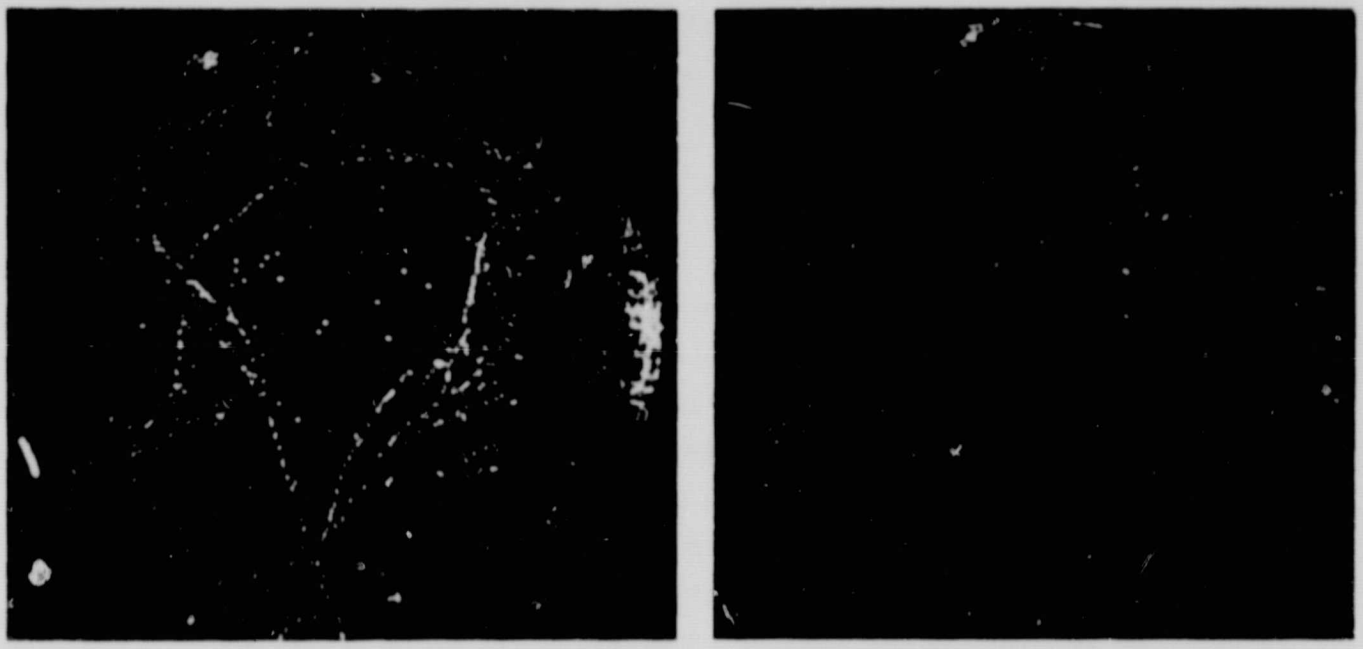


Figure 16. Comparison of surface cleanliness, aluminum and polypropylene sleds.

d. Comments and Conclusions

It was indeed gratifying that the room-temperature air drying concept was functional and the basic design considerations were correct, i.e., that a near-laminar, relatively high, flow system could be built that could dry wafers on both sides very rapidly without breaking them. The blower-HEPA

filter combination was viable and gave us trouble-free operation for over a year.

It can also be seen that another basic concept of design was realized, namely, that doubling the throughput rate is readily achievable by either parallel tracking of similar systems, or by using two blowers, doubling the filter surface and lengthening the funnel mouth. The addition of the air or nitrogen jets helped to improve the drying rate significantly. The overall design has very few moving parts, appears to be rugged, and requires little maintenance, with the exception of the belt drive. The latter is unsatisfactory for factory operation and had to be redesigned. As will be shown in subsection II.D.1, the drying rate, using 3/32-in.-spaced quartz carriers, is somewhat in excess of the design goal of 2500 wafers/h.

C. LASER SCANNER

1. Background

A significant parameter for solar-cell efficiency is the carrier lifetime. Previous work at RCA had shown that particles left on the surface of silicon slices can be a major source of lifetime killers. This occurs because chemical cleaning leaches out heavy metals only from the immediate surface of particles. But during high-temperature annealing or diffusion, the metallic impurities can diffuse fast enough to reach the slice surface and interior. Megasonic cleaning is the only "stand-alone" method capable of removing particles from both surfaces, in addition to cleaning the surface chemically. It is customary in the semiconductor industry to inspect the surface of cleaned wafers under a bright light, either with the unaided eye or, often under dark field illumination, using a suitable microscope. This is a tedious procedure, especially when one is looking for only a few hundred or less particles on each slice; further, these particles can be clustered and thus are easily missed by the usual inspection plan that looks at three or five spots.

The introduction of RCA's proprietary laser scanner* has greatly improved such measurements by scanning the entire wafer and permitting the count to be

*Patent applied for by E. F. Steigmeier, assigned to RCA.

registered of discrete scattering sites within 12 seconds of insertion into the scanner.

The RCA scanner is a more robust and versatile instrument than those described by Oswald and Munro [4] or Patrick and Patzner [5].

We proposed to evaluate the use of the laser scanner to provide rapid feedback on the cleaning ability of the Megasonic system under a variety of operating conditions to permit optimizing them, and to determine whether the laser scanner could be used as a process control instrument in a production plant.

The tasks to be performed consisted of:

(a) Integrating the laser scanner into the cleaning system and determining its utility as an indicator of cleanliness.

(b) Establishing calibration procedures and determining the reproducibility of the instrument.

(c) Working out conditions that would permit the Megasonic cleaning ability to be measured.

(d) Examining the laser scanner as a diagnostic tool.

2. Description

The scanner is shown in Fig. 17. The instrument consists of a stage that rotates and translates a silicon wafer under a HeNe laser beam. The specularly reflected light is rejected, but scattered light is detected by photodetectors and the intensity modulates the display on the storage oscilloscope. In addition, each event is counted and the total counts are displayed separately.

The operation consists of opening the drawer which is interlocked so that the laser beam cannot be activated when it is open. The wafer to be measured is placed on the vacuum chuck which applies a vacuum as soon as the drawer is closed. A pushbutton starts the wafer rotation; its translation and illumination is started by another pushbutton. The scattered light signals are

4. D. R. Oswald and D. F. Munro, J. Elect. Mat. 3, 225 (1979).
5. N. J. Patrick and E. J. Patzner, "Semiconductor Silicon," Proc. of 2nd Int. Symposium on Silicon Materials Science and Technology, Chicago, 1973, p. 482. Edited by H. R. Huff and R. R. Burger, Electrochem. Soc.

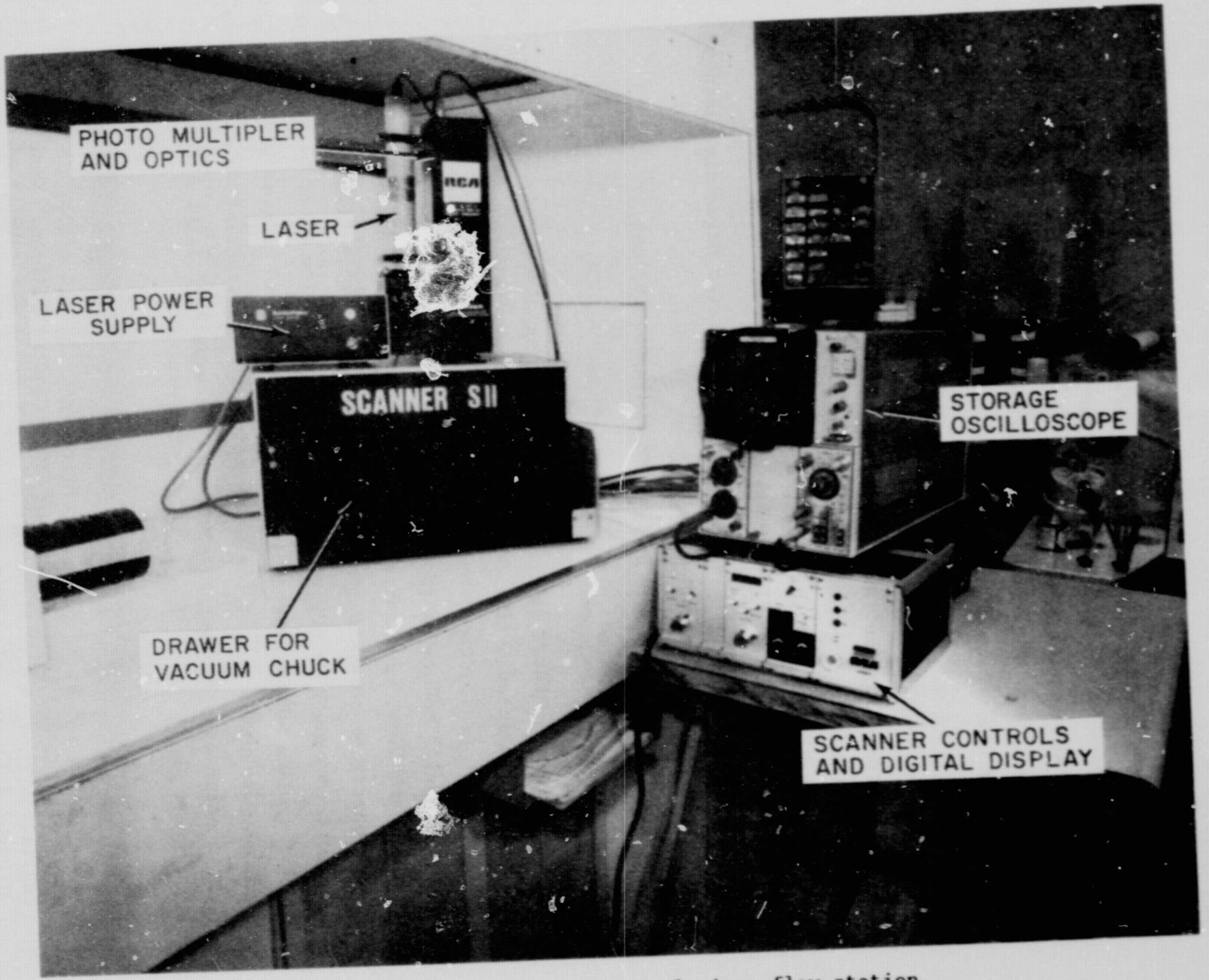


Figure 17. Laser scanner in laminar flow station.

displayed on the storage scope as the scan proceeds and the stage returns to its original position in 12 seconds. A repeat scan can then be initiated. To remove the wafer, the rotary vacuum chuck has to be switched off. The vacuum chuck is synchronized so that the storage scope image always presents the wafer in its real orientation; when the wafer flat is placed against the color-coded stop, it appears at the top of the image. Total cycle time is 25 to 30 seconds. Table 1 shows the specifications for the instrument.

3. Utilization

a. Typical Product Scan and Calibration

The objective was to determine meaningfulness of the display and the reproducibility of the count of scattering centers.

It became immediately obvious that not only particles but any geometrical irregularities in the wafer surface caused scattering and a corresponding "count." The instrument cannot be used to determine particulate scattering on lapped or chemically etched surfaces. All data reported below were taken on chemically-mechanically polished wafers; these were used as controls in all the tests, usually placed to represent various positions in a carrier and on a platen.

The scanner was set at its optimum sensitivity which for our instrument was a setting of the intensity amplifier at 6.5 and the display amplifier at 0.5. At a setting greater than 6.7, the instrument noise was excessive and the display was swamped. The best wafers were those delivered by the major suppliers of silicon wafers to the semiconductor industry. These ranged from counts of 0 to about 50. Most of the time, the wafer center counts were less than about 5 and the scattering centers at the edges tended to be clustered. We ascribe this to handling problems.

Normal product, after exposure to routine plant conditions of implantation, transfers, and cleaning other than Megasonic, produces counts that range from 200 to 1500. Routine inspection of such wafers under bright light as, for example, described in the testing procedure "Unaided Visual Inspection of Polished Silicon Slices," F 523-79, American Society for Testing Materials, part 43, 1979, normally would not detect any major problem on such slices. Similarly, inspection under dark field microscopy at 100X magnification, sampling five areas on each wafer, would normally pass wafers that show scatter counts of 250 to 500. The allowed limits differ somewhat for various

TABLE 1. SPECIFICATIONS FOR LASER SCANNER

GENERAL		
Wafer size	:	3 in. standard; 4 in. max. possible
Scan time	:	6 s (for 3-in. wafer) and 6 s to return to start
Laser spot size	:	250 μm
Scan spiral pitch	:	200 μm
Spot overlap	:	50 μm
Scan spiral length	:	21.5 m (for 3-in. wafer)
POWER		
Supply	:	115 V, 60 Hz
Turntable motor speed	:	1800 r/min
Scan motor speed	:	300 r/min
OPERATING MODES		
Auto	:	Automatic scanning from center to edge, return with beam off to center
Manual	:	Manual scanning with switches IN/OUT, BEAM ON/OFF
INTENSITY AMPLIFIER		
Gain	:	1700
Bandwidth	:	dc to 600 kHz
Threshold	:	Adjustable sensitivity
Invert/Noninvert	:	Intensity modulation positive/negative
Test	:	Test pattern displayed, of 6-μs optical square-wave pulses; to be used with laser turned off
DISPLAY		
Counting	:	9999 events max
Threshold	:	Adjustable sensitivity (up to a maximum value given by setting of intensity amplifier threshold)
Invert/Noninvert	:	Intensity modulation positive/negative

TABLE 1. SPECIFICATIONS FOR LASER SCANNER (Continued)

COORDINATE TRANSFORMATION POLAR TO RECTANGULAR

Arranged so that picture of wafer on storage oscilloscope appears upright to permit 1:1 correspondence.

LASER (incorporated in system)

HeNe Spectrophysics Model 145 P 2 mW or Equivalent

Power Supply 248

STORAGE OSCILLOSCOPE

Tektronix 5115 Storage Scope or Equivalent

Frequency range (intensity): dc to 1 MHz (Note: Square pulse of 2 V and length of 1 μs can turn storage on)

External intensity input (at back): Positive, i.e., +5 V turns display ON from OFF level

Setting: X : 0.5 V/div dc calibrated
Y : 0.5 V/div dc calibrated
Beam intensity: Vertical position
Enhance : OFF
Brightness : min
Storage : ON

VACUUM PUMP (proposed model)

Membrane pump Reciprotor 506 R or Equivalent

Specifications: Endvacuum - 240 Torr
0.5 m^3/h at 360 Torr
0.9 m^3/h at 460 Torr
Power typically: 50 W

semiconductor product lines but are in the order of one or two clusters of three particles in each of the five fields.

A more difficult problem is presented by the question of particle size represented by a scattering center. Clearly, much of the ability of a particle to scatter light depends not only on its reflectivity but also on its geometry. A cleaved particle is likely to reflect differently from one with a conchoidal fracture or a hydrated colloid such as a clay particle. Detailed study of

these problems is beyond the scope of this work, we confined our work to obtaining reproducibility of laser scanner sensitivity.

Only statistically meaningful data collected over a reasonable time from an operating plant will make it possible to determine the significance of the counts on solar-cell efficiency. All we know at present is that the cells fabricated with Megasonic cleaning show slightly improved efficiency over ones cleaned by the routine "Z" technique. (See subsection II.E.1.) A rough guide to the particle size detectable by the scanner was obtained by deliberately contaminating the surface of a clean wafer with a suspension of 2.5 g/L of nominally 0.3-μm-diam alumina and 0.5 g/L of 0.03-μm-diam alumina in water and rinsing and drying it. Such wafers generally gave counts in excess of 20,000 and 2,000 to 5,000, respectively. When examined under 750X magnification under phase contrast, the apparent particle size measured from photomicrographs was 1.5 to 3.5 μm. Presumably, the alumina particles nearly always clump together.

M. Leahy, at the RCA Laboratories, Princeton, NJ, made available silicon wafers with grid patterns consisting of etched lines and dots. Under any standard conditions, the laser scanner normally could just detect lines and dots in the 3- to 5-μm range. There is considerable discussion about how to compare such measurements to scatter center counts. In a recent private communication by the inventor of the laser scanner, it was pointed out that the optical properties of most scattering centers are such that the scattering power of small particles is at least 10 to 80 times greater than that of the etched lines. From the contamination studies in which we used 0.3- and 0.03-μm-diam alumina on the silicon wafers, it would appear that we can readily see clumps of particles having a diameter of 1 to 1.5 μm, as measured by phase-contrast microscopy.

From a practical viewpoint, it is more important to know how reproducible the data are. Tests carried out using the grid pattern indicated that resetting the amplifier could produce counts within ±10% in the range of 50 to 1000 counts. In addition, photographs were taken of surfaces of wafers that were cycled many times as controls, with deliberate contamination and subsequent Megasonic cleaning when the cleaning ability of the unit was evaluated. It was gratifying to find that the same spots were found reproducibly; often these were later diagnosed as small surface defects by oxidation and differential etching. Finally, when the unit was optimized, wafers could be cleaned reproducibly to levels of 30 to 100 counts.

The overall evaluation of the laser scanner, in our experience, is that it is a reliable tool and can guide the operator in judging how the Megasonic cleaning system is performing.

b. Use as Diagnostic and Control Tool

In routine operation, a number of different patterns can be observed when the laser scanner is used to inspect Megasonically cleaned and air-dried polished control wafers. These range from just a few scattering centers on a clean wafer surface to streaks, clusters, edge smears, and whorl-like patterns. In addition, crystal defects such as slip or lineage and scratches can be seen.

Typical patterns can be seen in Fig. 18 which clearly indicates tweezer marks, a scratch, and water spots; the latter only appear when the rinse water is of poor quality or when an outside contamination source of particles is present which accumulate in the carrier groove because it is the last place on the wafer to dry. Poor rinse water also can show up as long streaks. As pointed out earlier and shown in Fig. 16, the aluminum sled used at one time to support the carriers was found to cause contamination which was diagnosed through its scanner pattern. Other examples will be seen in subsection II.D.2.

Finally, and most importantly, the performance of the Megasonic cleaning step can be monitored by the technique of deliberately contaminating a control wafer with 2.5 g/L of 0.3-μm-diam alumina suspended in water. After rinsing and drying, these wafers have a count of >20,000 and should clean up to less than a scattering count of 100. If one of the transducers is not emitting full power, either the top or the bottom half of the control wafer shows a higher contamination level than background. Once alerted to this possibility by the scanner pattern, it is usually easy to determine which it is by the input power reading and by holding a silicon wafer with tweezers at a 45-degree angle to the sonic beam so that it is reflected to the surface. When properly tuned, and at full power, a solution spout will be clearly visible from a good, but not from a bad, transducer.

c. Comments and Conclusions

The most important comment is that the program on development of Megasonic cleaning could not have been completed in the alloted time frame without the

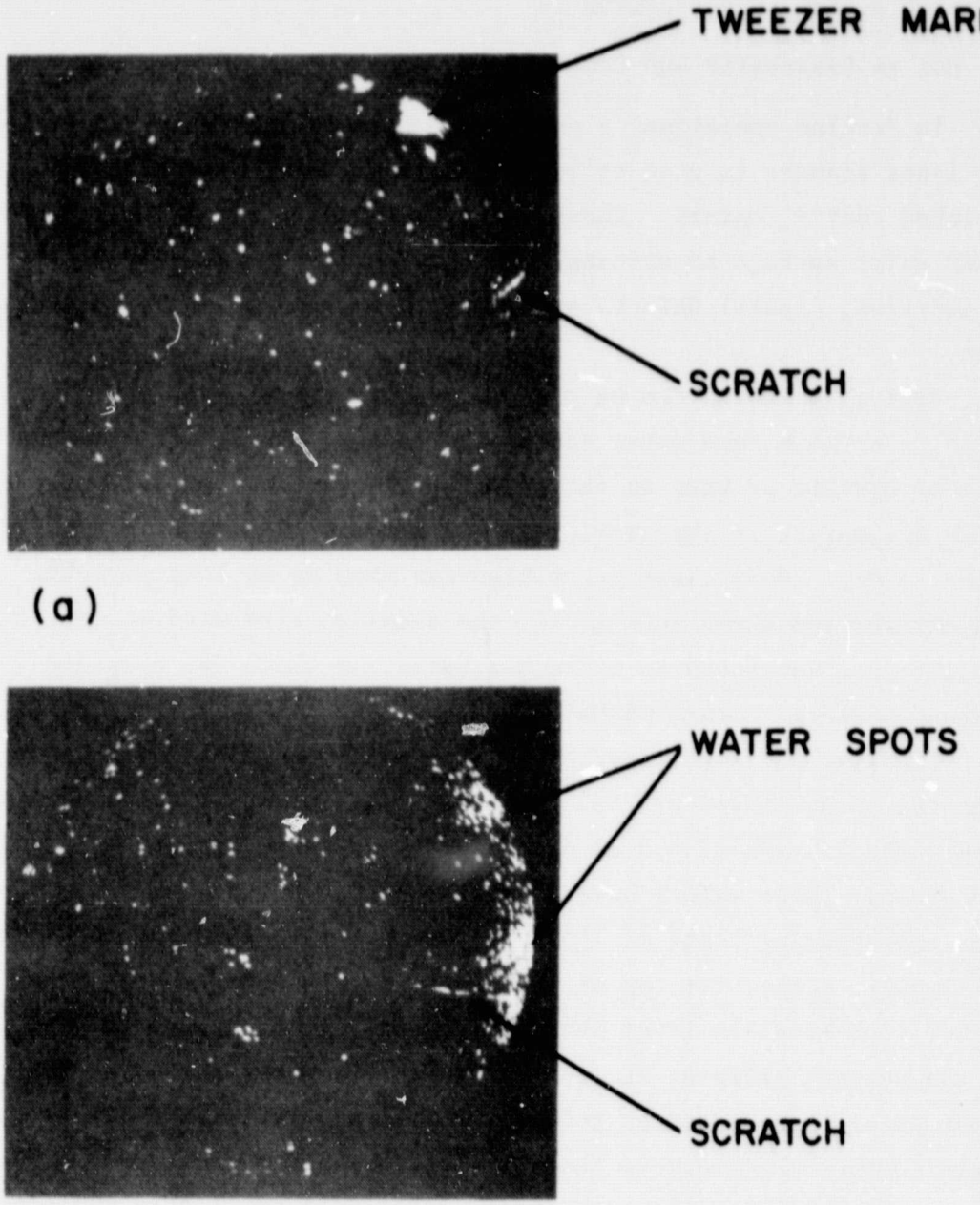


Figure 18. Silicon wafer (3 in.); typical scatter-point count = 100.

rapid feedback made possible by the laser scanner. The ability to immediately "see" how much and where contaminants were on a wafer surface permitted us to quantitatively evaluate a succession of experiments such as the effect of belt speed, power density, and chemical composition with a minimum of delay. Note that the usual method of evaluation is a judgment of a visual, naked eye inspection, or sampling a number of areas by dark field microscopy, a very time-consuming process not easily adapted to detecting nonuniform contamination. By placing deliberately contaminated wafers in strategic positions in the carriers, we found that the laser scanner can be used effectively as a process-control tool. This facilitated early detection of cleaning or rinsing problems. For most solar-cell fabrication tests, we sampled at the rate of 4%, i.e., two control wafers per 50 wafers, and these were recycled.

Some improvements to the sensitivity controls of the apparatus would be useful in a production control model, as would be cassette-to-cassette operation. Apart from one power supply failing and requiring transistor replacement, the unit was found to be reliable and easily serviced.

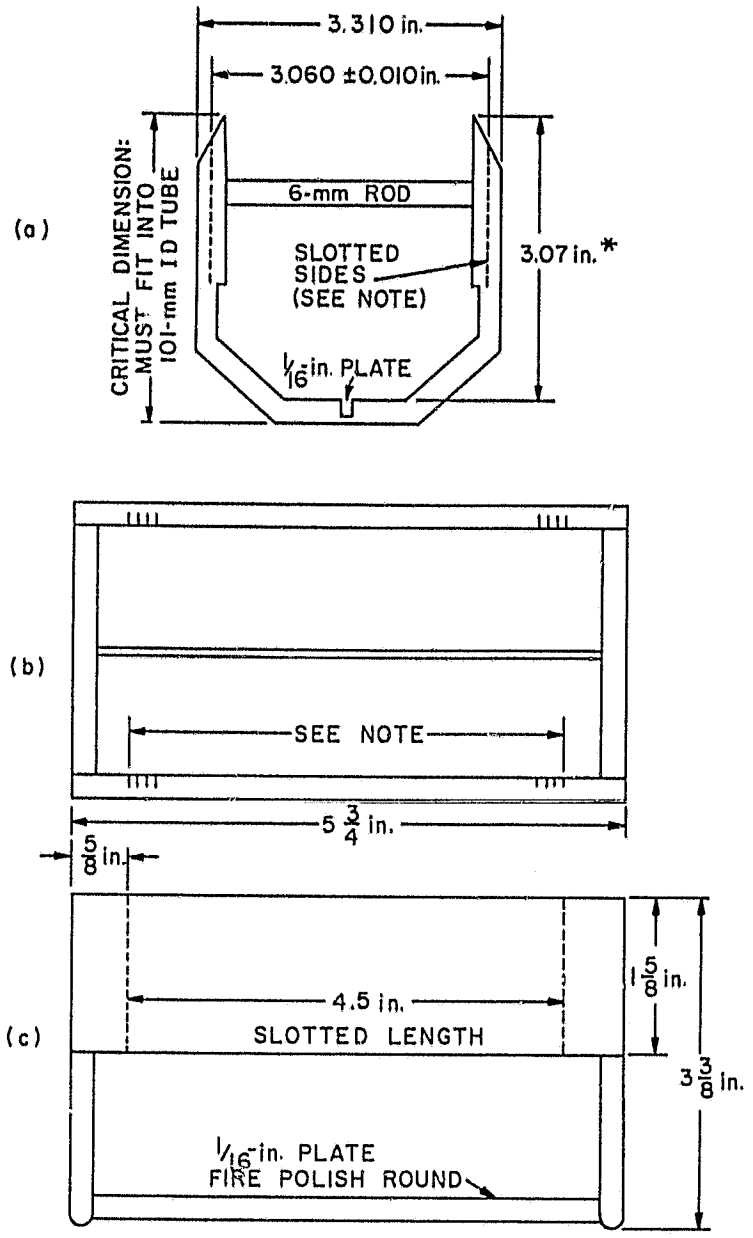
We conclude that, because of the rapid feedback, the RCA laser scanner is a most useful instrument for keeping the cleaning station downtime to a minimum.

D. CLEANING ABILITY AND DRYING RATE

1. Wafer Carriers and Platens

a. Wafer Carriers

The design of wafer carriers is of critical importance because the wafers have to be held during the cleaning operation in a way that presents the minimum shadowing to the sonic beam during cleaning and permits the maximum airflow, as uniformly as possible, during drying. This is accomplished by using straight-sided carriers with wide grooves in which the wafers are supported by a crossbar running the length of the carrier. The design of the quartz carriers is shown in Figs. 12 and 19. Note that these carriers are laid on the side during cleaning so that the open top faces the transducer assemblies, as shown in Fig. 4. This also shows how the carriers are held in the platen. The wafers are retained by a nylon cord on the platen.



NOTE:

NO.	SLOT SPACING
1	25 SLOTS AT 0.1875 in. = 4.50 in.
2	50 SLOTS AT 0.09375 in. = 4.50 in.

*THE SIDES WERE SHORTENED TO 2.75 TO IMPROVE THE REMOVAL OF WATER DROPLETS IN THE GROOVES.

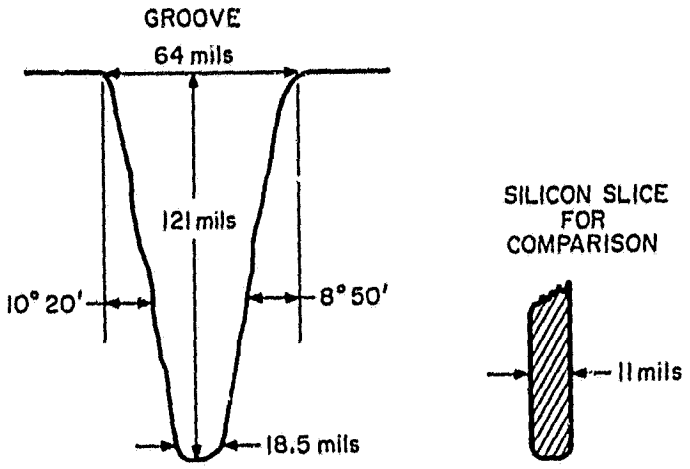
Figure 19. Quartz carrier construction.

As was explained in subsection II.A.3, the specific configuration of the quartz carrier was determined by the 101-mm diam of the diffusion tube qualified for the fabrication of solar cells. The removal of the corners required that quartz support ears be added to enable the dryer belt pushers to engage properly.

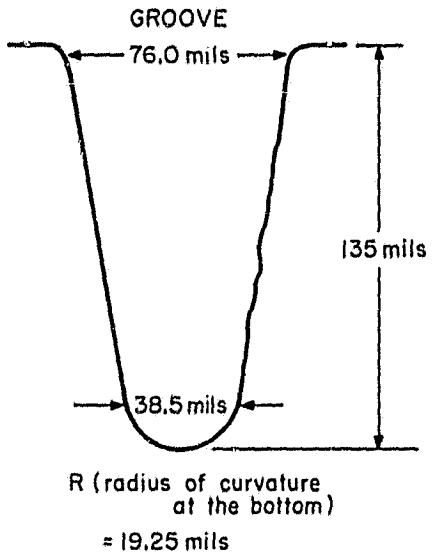
Standard PTFE carriers were used for all the tests prior to the receipt of the quartz carriers and also during the production test in Mountaintop. These carriers were purchased from Emerson Plastronics, Inc., Bronx, NY, as were the experimental polysulfone ones of the same configuration. The only change was to the nylon cord to support the wafers instead of the more commonly used PTFE-covered stainless steel rod. The latter tends to develop discoloration due to SC-1 penetrating through some pinhole or crack; this would be highly undesirable. The nylon cord worked very well and also prevented some breakage during loading of the wafers by being less rigid than the steel rod. The grooves in the PTFE and the polysulfone carriers were spaced 3/16-in. apart and had the cross section shown in Figs. 20(e) and 20(f). No difficulties were found in the use of these carriers during the cleaning step.

Much detailed experimental work was required to determine the best groove shape for air drying in quartz carriers. The first set of carriers made by U.S. Fused Quartz Co., Fairfield, NJ, had grooves that did not conform to the design. They were measured on a shadowgraph comparator and are shown in Fig. 20(a). On the assumption that there was insufficient clearance between the wafer and the groove wall, we etched these carriers in hydrofluoric acid. This produced the grooves shown in Fig. 20(b) and after firepolishing in Fig. 20(c). A new set of quartz carriers was then ordered and great care was taken to keep the cutting tool sharp to ensure a square-ended groove shape. This was achieved and is shown in Fig. 20(d).

The drying tests with the various carriers were made as follows: The carriers were loaded with 11-mil-thick, 3-in.-diam slices, cleaned Megasonically in SC-1, and rinsed; then each carrier was dried between dummies loaded with wafers to ensure equal airflow distribution. Each wafer was inspected for dryness, and the state of the carrier was also noted. The temperature was 65°F and the relative humidity, 20%. The results are given in Table 2.

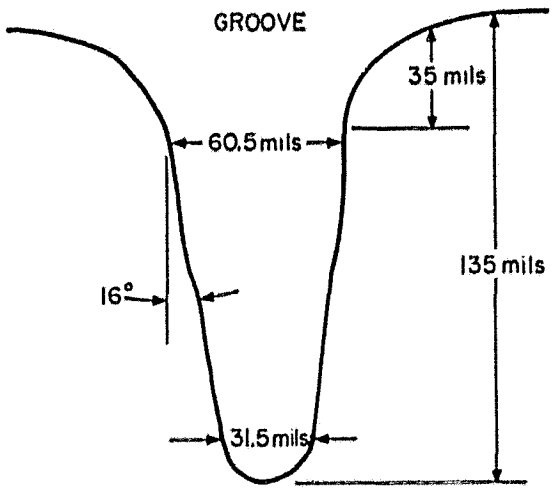


(a) With 3/16-in. spacing; as received.

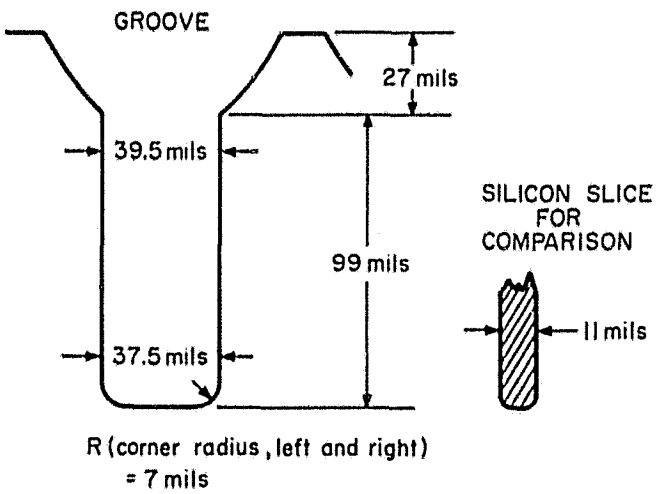


(b) With 3/16-in. spacing, etched for 2 h in HF.

Figure 20. Shadowgraphs of carrier grooves.

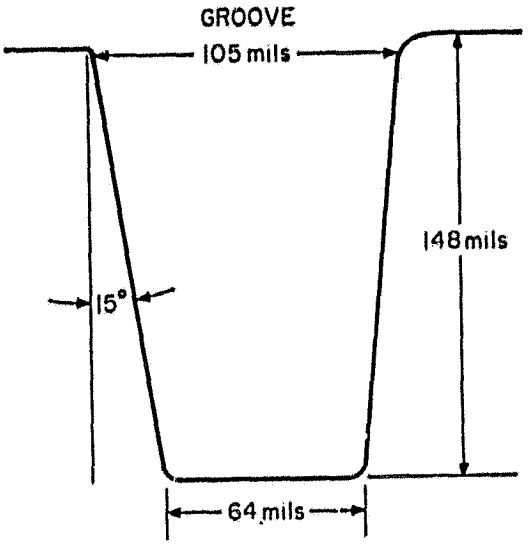


(c) With 3/16-in. spacing; etched as (b), but then fire-polished.

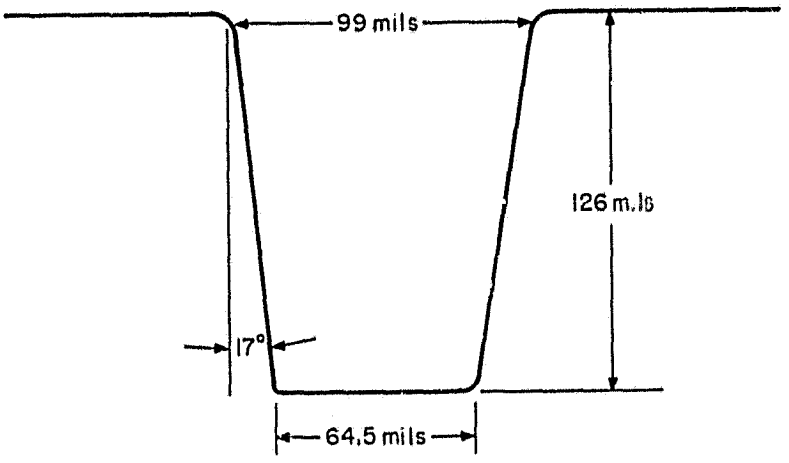


(d) With 3/32-in. spacing; as received.

Figure 20. (Continued).



(e) PTFE carrier.



(f) Polysulfone carrier.

Figure 20. (Continued).

TABLE 2. COMPARISON OF DRYING TIMES WITH DIFFERENT CARRIERS

Material	Figure	Slice Spacing	Groove Shape	Groove Width	Groove Surface Condition	Drying* Time (min)	Comments		Equivalent Drying Rate (slices/h)
							Slice	Groove	
Quartz	1(d)	3/32	Square	0.0395-0375	Diamond Ground	4	Dry	Dry	2500
Quartz	1(d)	3/16	Square	0.0395-0375	Diamond Ground	4	Dry	Dry	1250
Quartz	1(d)	3/32	Square	0.0395-0375	Diamond Ground	3	Dry	Dry	3300
Quartz	1(d)	3/16	Square	0.0395-0375	Diamond Ground	3	Dry	Dry	1650
Quartz	1(d)	3/32	Square	0.0395-0375	Diamond Ground	2 1/2	24/25 Dry	24/25 Dry	~4000
Quartz	1(d)	3/16	Square	0.0395-0375	Diamond Ground	2 1/2	12/13 Dry	12/13 Dry	~2000
Quartz	1(a)	3/16	Taper	0.064-0.018	Diamond Ground	4	Wet	Wet	<1250
Quartz	1(b)	3/16	Taper	0.076-0.0385	HF	4	Wet	Wet	<1250
Quartz	1(c)	3/16	Taper	>0.075-0.0315	HF and Firepolish	4	Wet	Wet	<1250
PTFE	1(e)	3/16	Square Taper	0.105-0.064	Machined	4	Dry	Some Wet	<1250
PTFE Repeat	1(e)	3/16	Square Taper	0.105-0.064	Machined	4	Dry	Dry	1250
PTFE Repeat	1(e)	3/16	Square Taper	0.105-0.064	Machined	4	Dry	24/25 Dry	~1250
Polysulfone	1(f)	3/16	Square Taper	0.099-0.0645	Machined	4	Dry	Dry	1250
Polysulfone	1(f)	3/16	Square Taper	0.099-0.0645	Machined	3 1/2	24/25 Dry	Few Wet	1430
Polysulfone	1(f)	3/16	Square Taper	0.099-0.645	Machined	3	Wet	Wet	<1650

*Drying time = Entry of first slice to exit of last slice in each carrier into air delivery duct region.
HF = Etched in 48% hydrofluoric acid for two hours.

The only difference between the 3/16-in. and the 3/32-in.-spaced quartz carriers, as received, is the groove shape. Clearly, the tapered, round-ended groove leaves too little clearance between the wall and the slice for the force of the air to overcome the capillary force that holds water in this region. The square groove of the 3/32-in. carrier dries out most rapidly. In fact, as can be seen from Table 2, the drying time can be reduced to about 3 min.

A comparison between the quartz carriers, Figs. 20(a) through 20(d), shows that merely widening the groove is not decisive, but that the square shape is. This indicates that the contact between the rim of the slice and the end of the groove must be minimized to reduce the capillarity in that region to a minimum and to allow as much access of air as possible. This is further borne out by the observation that drying in the square-grooved PTFE and polysulfone carriers is achievable in 4 minutes. However, it must be noted that these carriers have even wider (approximately 0.060-in.) grooves. PTFE can be seen to have retained some water in the grooves after 4 minutes, even though the slices were dry. The maximum actual drying rate obtained using quartz carriers with 3/32-in. spacing was 2600 wafers/h, corresponding to about an 18-cm/min belt speed.

b. Platens

The PVC platens were designed to accommodate quartz and PTFE carriers. Conversion from one use to the other is simple and requires only the removal of the screws that hold the six pedestals in place. As can be seen in Fig. 4, the carriers are placed on their sides and the wafers are prevented from rolling out by a nylon cord stretched across the platen in front of each carrier. The platens are suspended from a PTFE-coated steel rod which rests on the polypropylene chain drive of the conveyor. No problems were encountered with these platens.

2. Environmental Cleanliness

As was pointed out in earlier sections, problems which cause high scattering-site counts derive from sources that include poor rinse water, the use of aluminum supports for quartz carriers, and turbulence of the air stream. In addition, scratches, handling-tool marks, and subsurface defects also show

up as high counts under the laser scanner. Most of these are readily diagnosable by the patterns seen on the storage scope screen.

However, high counts in the range of 200 to 600 per wafer were observed on occasion. The Climet II* particle counter was used to search for the cause of these sporadic contaminant sources. It was known from previous work that a linear relationship exists between the logarithms of particle concentration and their diameter, similar to that observed in liquids. The latter serves as the basis of classification in ASTM Standard F 575-78.** If this relationship holds for the laboratory where these tests were made, then it is necessary to count the particles of only one diameter; the concentration of particles with other diameters is predictable. This is shown in Fig. 21 for room air. The next line shows the distribution in the laser scanner hood: although this has a much lower particle concentration, the relationship still holds and the two slopes are similar.

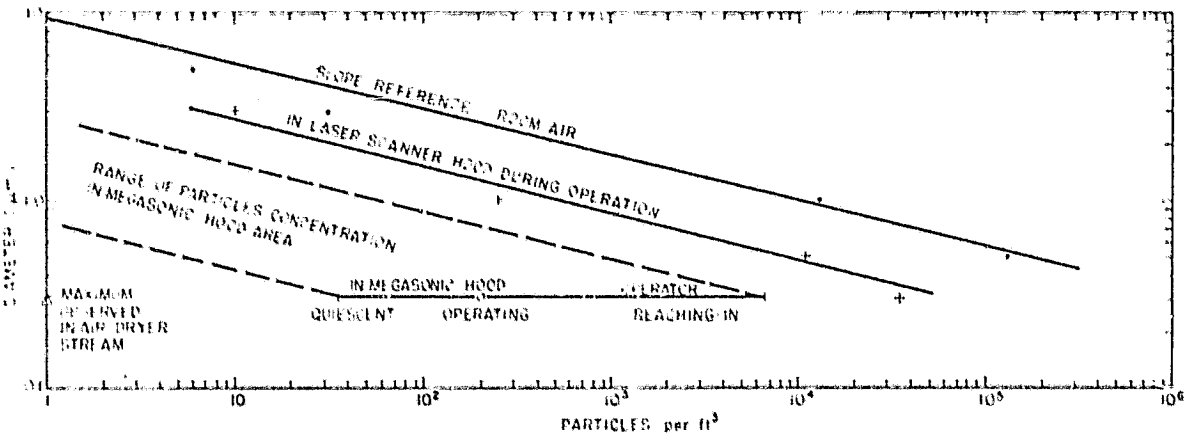


Figure 21. Dust particle distribution.

*Climet Instruments Co., Redlands, CA.

**F 575-78, "Particle Concentration in Liquids," 1979 Annual Book of ASTM Standards 43, 1015, American Society for Testing and Materials, Philadelphia, PA.

The area between dotted lines, assumed to follow the same shape, indicates the particle concentration encountered in the Megasonic station when it is quiescent (lower boundary) and during maximum activity (upper boundary). This shows how critical careful fixturing is in avoiding the introduction of room air through turbulence. Note also that the air in the dryer is extremely clean.

3. Megasonic Cleaning Ability

As discussed in subsection II.C.3, slices deliberately contaminated with aqueous alumina suspensions could be cleaned, and the particle count on the wafer surface then reverted to that found before contamination.

Wafers also were deliberately contaminated with 2.5 g/L of 0.3-μm-diam alumina suspended in 1,1,1-trichloroethane (1-1-1 TCE) containing 10 g/L of "Liquid Mounting Wax" (Semimetals Corp., Mountainview, CA) used to mount silicon wafers during polishing. The wafers were dipped into this solution, rinsed with 1-1-1 TCE, dried, rinsed with water, and spun dry before Megasonic cleaning. Other sets of wafers were contaminated with a suspension of 2.5 g/L of 0.3-μm-diam alumina in water, followed by rinsing and drying. In all cases, these contaminated wafers showed particle counts of about 20,000 and could be cleaned to background levels of less than 200. A few wafers could not be cleaned to counts of less than 500. There was no difference between the aqueous or wax-solvent contaminated wafers.

It seems that the removal of major contaminants such as the alumina mentioned above, even when the contaminants are allowed to dry overnight, can be carried out at belt speeds between 4 and 15 cm/min under maximum available power from over 20,000 counts to a few hundred.

By connecting one power supply to each transducer, it was possible to double the power density. To ensure complete exposure of all wafers, the platen was turned around after it passed the tranducer pair powered in the above-described way and was passed through it again. This simulated the normal condition of cleaning with two transducer pairs. The wafers were contaminated with alumina and dried for various times up to 20 h. Rates up to 20 cm/min and power levels of 160, 220, and 300 W per transducer were examined by scanning the cleaned wafers and taking photographs of the distributions.

A rate of 15 cm/min is marginally better than a rate of 20 cm/min. However, the results obtained at 15 cm/min, at the various power levels, were

not markedly different. Figure 22 illustrates a typical test result that shows that at a belt speed of 15 cm/min, the deliberately contaminated wafer can be cleaned. This speed corresponds to a throughput rate of 4500 wafers per hour. Figure 23 shows a somewhat scratched wafer which, before each cleaning step, was contaminated with alumina. It was then cleaned in the Megasonic unit at 160, 220, and 300 W per transducer. As virtually the same final scattering-center count was reached, we conclude that an input of 160 W per transducer provides adequate power density.

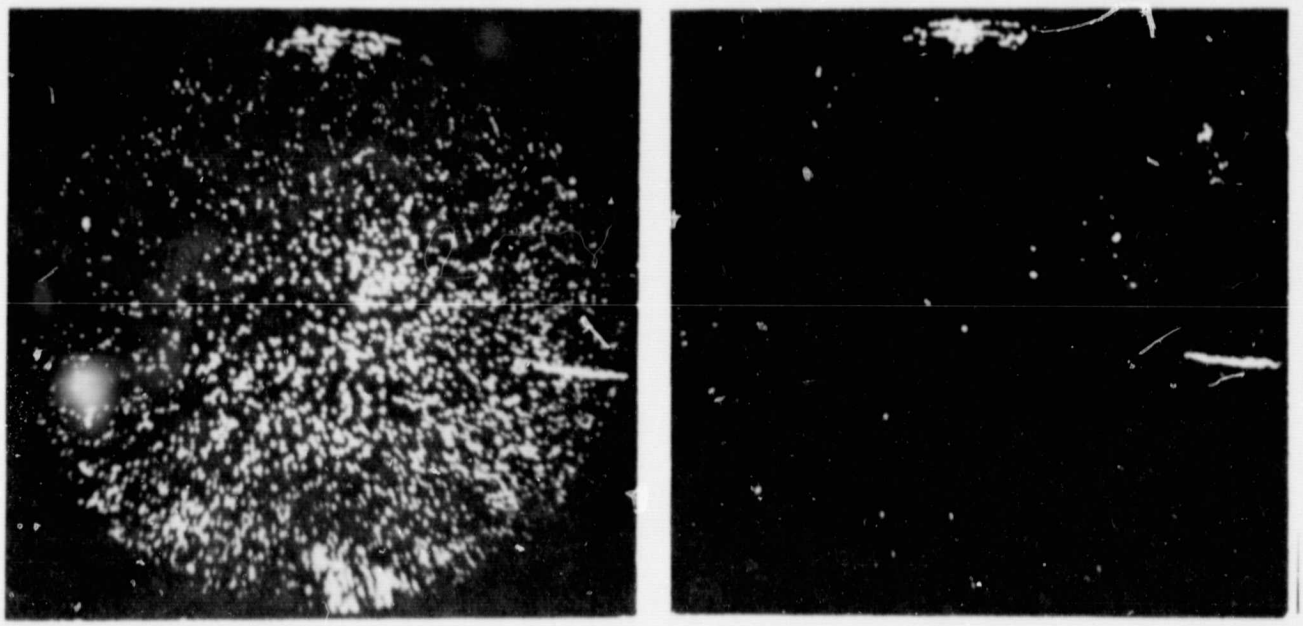


Figure 22. Megasonic cleaning at belt speed of 15 cm/min (equivalent to 4500 wafers/h).

We also conclude that the power supplies now being used are adequate for the existing system and the designed rate. Only long-term device-related and

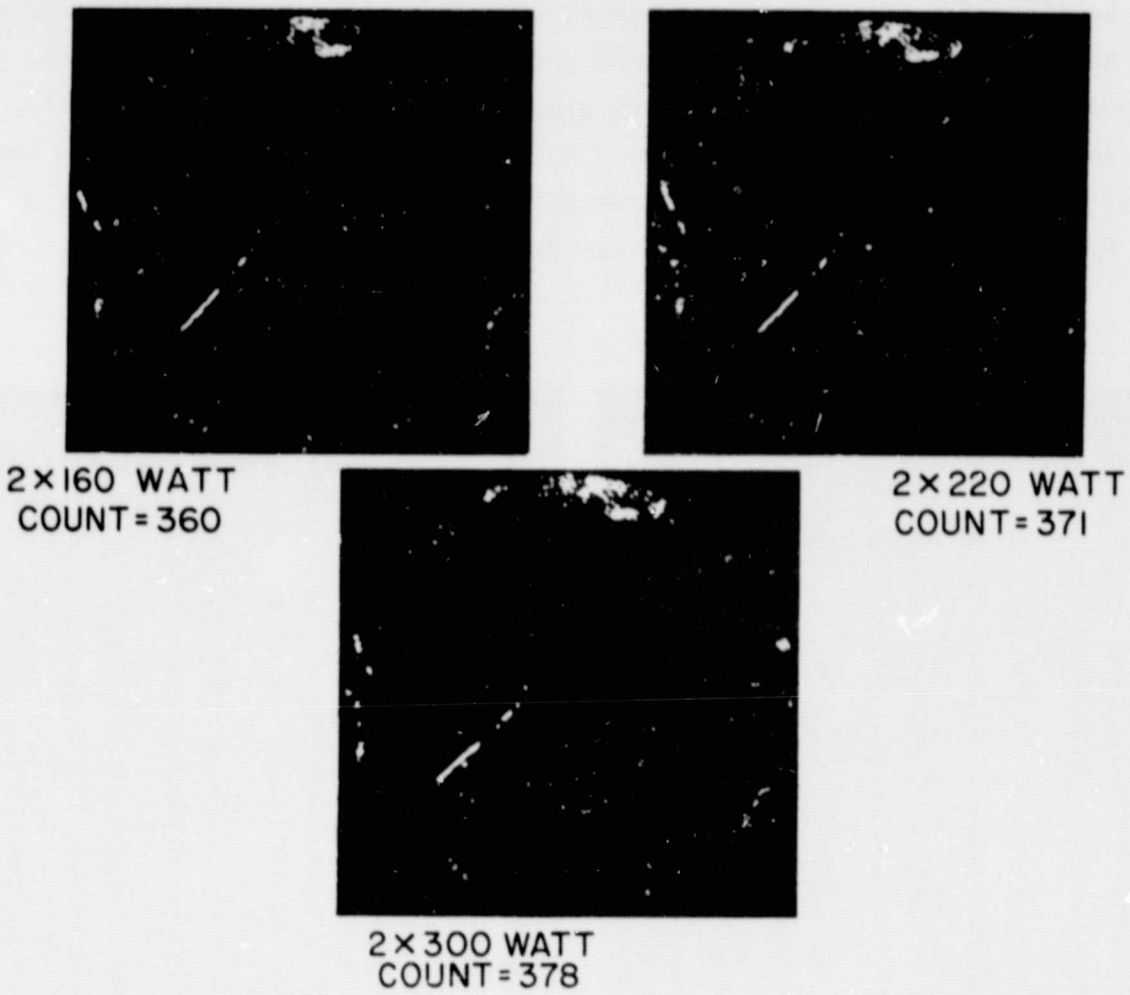


Figure 23. Transducer power vs cleaning ability.

statistically significant tests could show whether larger power supplies would be cost effective for cleaning solar cells in mass production.

4. Standard Cleaning Solution (SC-1), Chemicals, and Water Utilization

Our experience over many years has taught us that the composition of SC-1 may vary considerably without impairing its ability to clean. The usual composition range is 4 to 7 parts of water to 1 part of 30% hydrogen peroxide solution and 1 part of (29.7% nominal) ammonium hydroxide solution. Actual analyses of the starting SC-1 solution in the Megasonic system during the laboratory phase averaged 28 g/L of ammonia and 37 g/L of hydrogen peroxide.

Analytical data on the solution (Appendix B), even without Megasonic power use, made it clear that the ammonia volatilizes relatively quickly over the first 20 h to about half the initial concentration, then more slowly to about 10 g/L in a little over 80 h.

In the initial design, a considerable amount of air from the dryer swept into the Megasonic hood area and contributed to the loss of ammonia. In the final version, the dryer tunnel mouth was kept covered or blocked by full carriers to minimize this loss. This was shown to be effective in the large-scale test. There, the loss of liquid due to drag-out and volatilization was such that to maintain an ammonia level of 5 to 15 g/L, it was sufficient to add 2 L of concentrated ammonia solution per 8-hour shift.

The function of the hydrogen peroxide is to maintain a redox potential high enough to oxidize the thin organic surface films usually acquired on solar-cell wafers during handling and storage, and to prevent the attack of ammonia on silicon. In the absence of peroxide, silicon is pitted rapidly and unpredictably by ammonia; even small concentrations of peroxide, however, on the order of 2 g/L, are sufficient to inhibit this effect. When the hydrogen peroxide solution is allowed to stand in the system without circulation and in the absence of power, it drops from the 40 g/L to the 10 g/L level in about 60 h.

A test was run with power on continuously for 6 hours; in that time the concentration of peroxide dropped to 35 g/L. With power on for 7.5 out of 24 h, the peroxide dropped to 22 g/L, but in the large-scale test it dropped from 28 to 5 g/L during an 8-hour period of continuous use. It is calculated that the addition of 4 L of 30% hydrogen peroxide every 8 hours will suffice to maintain the safe level of 5 to 15 g/L of H_2O_2. The amount of water lost by evaporation and drag-out was 13 L for approximately 10,000 wafers.

As was pointed out before, the SC-1 solution is continuously filtered to remove particles. In our experience a circulation rate between one and two tank changes per hour is sufficient to avoid a major build-up in particles as judged by the scattering center count of Megasonically cleaned control wafers. The limit to the number of times an SC-1 solution can be replenished with ammonia and hydrogen peroxide in the long run depends on how fast undesirable impurities build up. In our tests, sodium, copper, and iron were monitored by atomic absorption analysis. In all cases, copper was found to be less than 0.1 ppm and, with the exception of two analyses, the iron content was in the

same range; the exceptions were 0.25 ppm and 0.15 ppm iron. The sodium content of a freely prepared SC-1 solution, i.e., the amount introduced by the reagents, was usually on the order of 0.3 to 0.6 ppm. In the most extended test performed, in which over 10,000 wafers were put through the solution (through several recycles) during 8 hours, the sodium built up to about 30 ppm. The solar cells fabricated from wafers cleaned at that time showed no unusual features. It may be concluded that at least at that level the build-up of soluble impurities does not limit the life of the SC-1 solution. Information on the ultimate limits can best be obtained by monitoring a production plant over a long period of time. Our best judgment is that a bath can probably be kept for cleaning 100,000 wafers. This was used in the cost estimates for this program. In summary, Fig. 24 shows the plot of the analytical data obtained during the large-scale test, when 10,200 wafers were processed in one shift. Based on these figures and the assumption that with replenishment, the solution will require replacement after 100,000 wafers, the total requirements come to 3860 g of NH_3 and 26.4 L of H_2O_2 (30% nom). The amount of water lost by evaporation and by drag-out amounted to 0.0017 L per wafer, which is small compared to the rinse water consumption of 0.132 L/wafer.

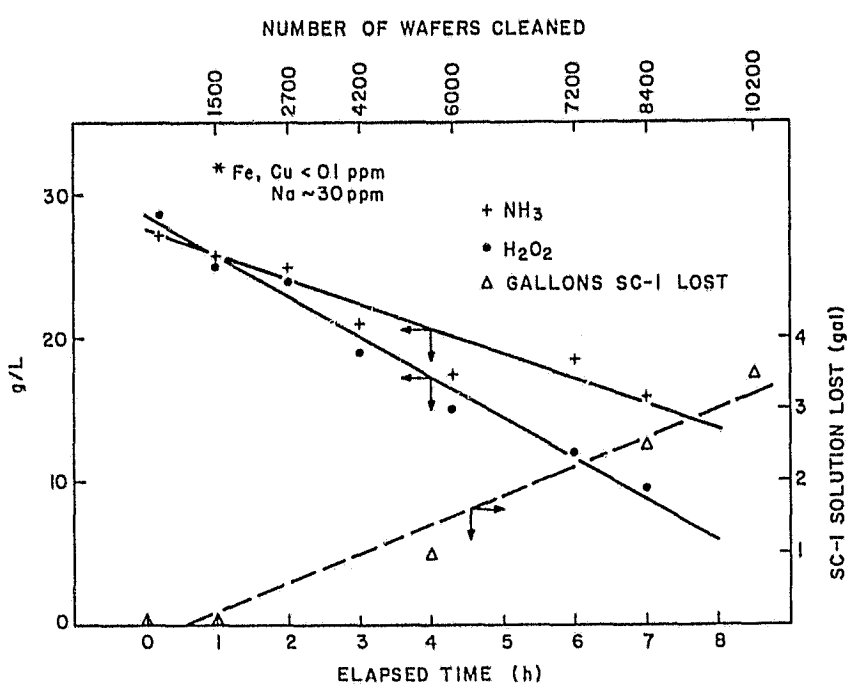


Figure 24. Chemical usage and analysis in large-scale test.

It should be noted that the water consumption can be further reduced in a large scale plant by means of a commercially available "Water Saver." That system consists of a monitor which controls a valve that permits only the initial rinse water with high conductivity to pass into the drain, but which recycles the major portion through ion exchange columns and returns it to storage for reuse. The cost effectiveness of such a system must be evaluated in the context of the plant capacity, but can lead to as much as 70% water conservation.

5. Safety, Waste Treatment, and Ecological Impact

a. Safety

A major advantage of the SC-1 system is that it is relatively safe compared with any hot concentrated nitric acid or sulfuric-peroxide system. The ammonia may be an irritant but it is not toxic when breathed in or contacted over long periods. Hydrogen peroxide, similarly, is nontoxic in the concentrations used, but skin contact can lead to local oxidation. This is generally not painful. However, when exposure to SC-1 occurs, it is best to wash it with water within the next few minutes. Note that hydrogen peroxide is used as a disinfectant for wounds and ammonia is an antidote for insect stings and a household detergent.

The only precaution against corrosion we found to be desirable when SC-1 is used, is to arrange for a nitrogen purge of the power supplies.

Sulfuric acid, hydrogen peroxide, and nitric acid are always used hot and concentrated and are very strong oxidizing agents that can cause severe burns and charring when a worker is exposed to them. Very strict safety precautions are required to guard against splash, spray, spillage, or contact. Also, the fumes and inevitable acid residues from spillage present hazards to electrical equipment, switches, and measurement apparatus, causing corrosion and short circuits.

b. Waste Treatment and Ecological Impact

Since the ammonia is quite volatile and the hydrogen peroxide decomposes readily, the waste from the cleaning operation requires no special treatment other than allowing it to decompose in air. The spent solution should contain just a few grams per liter of NH_3 and H_2O_2 and amounts to only about 120 liters per 100,000 wafers.

Surfuric acid, on the other hand, requires a neutralization facility usually based on lime, and an area for dumping the calcium sulfate. About 4.9 kg of limestone are required for the neutralization of 1 L of sulfuric acid; this produces about 5.8 kg of hydrated calcium sulphate that needs to be dumped. Other than finding an appropriate site for it, this does not present an ecological hazard either.

6. Rate Optimization

In subsection II.D.1 we discussed the maximum throughput rates sustainable separately in the Megasonic cleaning and rinse station and in the air dryer. The former is capable of sustaining a throughput of about 4600 wafers per hour using the 3/32-in. quartz carriers and a belt speed of 15 cm/min. With a statistically slightly worse cleaning ability, the belt can be speeded up to 20 cm/min corresponding to just over 6000 wafers per hour.

In order to cope with the increased rate, it will be necessary to add more rinse capacity. We suggest that this can best be achieved by mechanizing the transfer from the Megasonic tank to at least two rinse tanks and an extension of the belt conveyor. Transfer arms are commercially available that permit such a system to be integrated.

The maximum drying capacity is about 2700 wafers per hour, using the satin finish, square-grooved quartz carriers and a belt speed of 18 cm/min. This is based on the data given in Table 2 and on subsequent experience in routine operation, and corresponds to a rate of insertion of a 50-wafer carrier about every 67 seconds, compared with a maximum arrival rate of a carrier about every 59 seconds from the rinse station handling 4600 wafers per hour.

Therefore, using two tracks of the dryer, i.e., doubling the system, is sufficient to cope with that rate. The main unsolved problem in an attempt to optimize the capacity of the system remains the transfer from the rinse to the dryer. This involves unloading the carriers from the platen and loading them onto the dryer belt.

In Fig. 25, the rates between various cleaning and drying conditions are compared. It is clear that quartz carriers are superior to PTFE carriers, mainly because the former have a hydrophilic surface, allowing the water to spread; the latter have a hydrophobic surface that induces water drops to ball up.

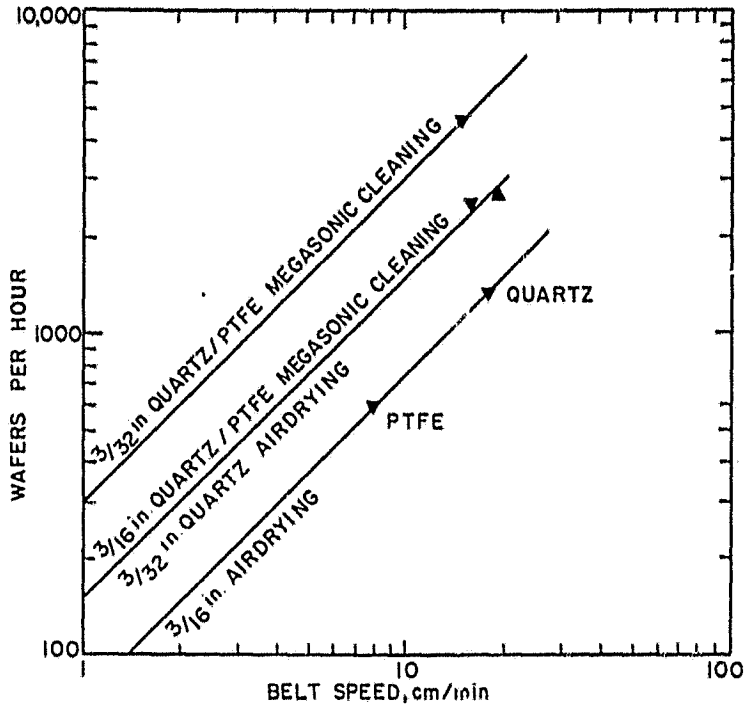


Figure 25. Cleaning and drying rates at various belt speeds.

In practice, the maximum rates were achieved only for each section separately because transfers from Megasonic to rinse to dryer were manual.

E. OPERATIONAL EVALUATION AND SOLAR CELLS

1. Laboratory Evaluation

When the Megasonic system had been assembled and became operational in Somerville, it could be used for the evaluation of the cleaning ability as a function of SC-1 composition, power, belt speed, and for the impact of ambient cleanliness. After the establishment of the laser scanner and the control test conditions involving the contamination of clean wafers with alumina, numerical data of scattering point counts were established. We determined that wafers dipped into a suspension of alumina deliberately contaminated with wax could also be cleaned. During this period, the air dryer was operated by pushing carriers through manually. Several improvements were made then, such as the use of nylon cord to retain wafers in the carriers, covering the control panel with a hinged shield to prevent accidental shutdown, changes to the dryer tunnel mouth to prevent excessive air from sweeping ammonia out of the hood, a high-low switch to assure that air would always flow in the dryer, and the addition of a microswitch that stops the dryer belt when more than three carriers arrive at the end of the Lucite tunnel.

An unforeseen problem was the appearance of the ferric hydroxide precipitate, later tracked to colloidal-iron contamination of the deionized water. This appears to have been a unique situation. We believed at the time that the water was clean, judged by the appearance of control wafers using the laser scanner and by the conductivity readings of the rinse water. According to work done at the Millipore Corporation, Bedford, MA, the 0.2-μm-diam absolute filter would remove up to 80 in. of colloidal iron. Conceivably, the remaining traces of iron could have caused that contamination; being colloidal, it would not register as a conductivity change.

No major problems occurred in the operation of the station. The dryer belt arrived just before the unit was to be shipped to Mountaintop and required extensive engineering and machine shop work. It functioned briefly in the laboratory, but when re-installed in the production area, was found to be unreliable and underwent several more changes. A new design was eventually made but not fabricated.

The laboratory facility was also used to familiarize technicians, service personnel, and supervisors with the new concepts and machinery. Further, the facility was used to clean solar-cell wafers between implantation and anneal-diffusion. This test will be discussed below.

2. Production Facility

When all the parts functioned, the Megasonic system worked effectively in the production facility. It was used to clean wafers on a routine basis by the usual plant shift personnel. The large-scale trial was run during one full shift, cleaning 10,200 wafers. Not a single wafer was broken in this period. Because not enough quartz carriers were available, the trial was run using PTFE carriers. Because there were not enough wafers available, the wafers were recycled. The main purpose of the test was to determine the amount of decomposition and loss of SC-1 in continuous operation. The data obtained were discussed earlier and are considered sound. At the same time, another batch of ion-implanted wafers was cleaned, diffused, and made into solar cells as described below.

The data obtained during the regular production, which consisted of 2 to 4 days operation at a time, on 24-h shifts, indicated that at least 24 h were needed initially for the system to clean itself up by continuous filtration.

It is believed that the main cause of this slow clean-up was the fine machining debris left on the PTFE carriers that had never been used before.

The operators had no problem learning to operate and control the system and they especially liked the ability to examine the degree of cleanliness achieved by means of the laser scanner. It became obvious that such a monitoring system is very useful in detecting problems at earlier stages in the production of silicon wafers, such as poor handling, contaminated tools, scratches, polishing difficulties, and poor rinse water. It spite of the problems mentioned earlier (the circulation pump being inadequate and the dryer belt breaking down frequently), it is clear that the system is a very useful addition to the production machinery available to the manufacturer of semiconductor devices.

Before the system was accepted by the production department, a spare parts list and kit were required. These parts were to be kept in stock at all times:

Megasonic Rinse Tank and Recirculation System: 2 transducer modules, 1 power supply, 1 amplifier, 1 output meter, 1 circulation pump and 1 motor, 4 magnetic reed switches for level control, 2 solenoid and 1 air-operated valve, control relays for the pump motor, motor and control of Megasonic tank chain drive, spare chain, 1-in.-i.d. flexible tubing, 3 filter cartridges, for each recirculation and rinse system, 1 sensor for rinse tank and timer. HEPA and prefilters for laminar flow station.

Dryer: HEPA filters, 1 motor and 1 controller for chain drive, 1 spare chain.

Laser Scanner: 1 spare laser, 1 power supply, 1 filter for the laminar flow station.

3. Solar Cells

a. Processing

The cell processing used to test and compare Megasonic cleaning to a standard cleaning method was selected from those evaluted by RCA for the LSA program. This sequence, shown in Fig. 26, contains many potentially low-cost process steps likely to be used in near-term photovoltaic manufacturing. For the Megasonic versus "Z" clean test, the use of an ion-implant junction was preferred to that of a diffused-junction process because the latter process

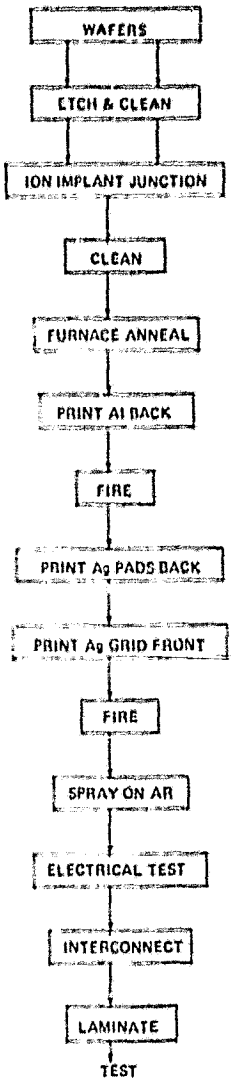


Figure 26. LSI production sequence.

introduces the possibility of gettering [7] impurities which might be left on the wafer after cleaning and thus remove, in an uncertain way, some of the differences we are seeking to detect.

In the application of the process sequence of Fig. 26 to this test, several precautions were taken after the cleaning step to ensure equal treatment

7. E. C. Douglas and R. V. D'Aiello, "A Study of the Factors which Control the Efficiency of Ion-Implant Silicon Solar Cells," IEEE Trans. Electron. Devices ED-27, 792 (1980).

to the wafers and to prevent possible contamination. First, the diffusion boats were designed to serve as the carriers during both cleaning processes so that no transfer of wafers was required. Also, after cleaning, these boats were placed in clean, dust-free boxes for transfer to the diffusion-anneal area for the furnace anneal. In each case, wafers cleaned by both methods were annealed together and during all subsequent processing the wafers received equal treatment.

b. Evaluation

The laboratory system was used to clean wafers that were fabricated into solar cells at the RCA Laboratories, Princeton, NJ. During March 1980, 24 test and 18 control cells were measured. A summary of the data is given in Figs. 23 and 27. The Megasonically cleaned cells average 8.46% efficiency (not AR coated) and ranged from 7.3 to 9.3%, while the "Z" cleaned cells averaged 8.2% and ranged from 7.1 to 9.1%. It appears that three cells, about 17%, of the Z-cleaned cells are considerably poorer than the rest. If these are excluded, the distribution of the remaining cells is indistinguishable from that of the Megasonically cleaned ones, as seen in Fig. 28. This seemed to confirm the original hypothesis that Megasonic cleaning would tend to reduce the number of poor-efficiency cells and produce a tighter population of the higher-efficiency ones compared with Z-cleaned cells. However, statistical analysis of the data showed that the number of cells measured is insufficient to make a positive statement.

Another batch of cells was prepared, this time with the production system at the Mountaintop facility but using the same procedures as before.[1] Fourteen Megasonically cleaned and 17 Z-cleaned cells were measured with the following results:

	Megasonic	Z-clean
Average Efficiency	7.59%	7.55%
Standard Deviation	0.16%	0.18%

As these data showed a normal distribution, a t-test was applied. This showed that the null hypothesis, both means being equal, could not be rejected. The same applied when the two groups were combined statistically. It was calculated that to detect a 5% difference (considered of minimum significance)

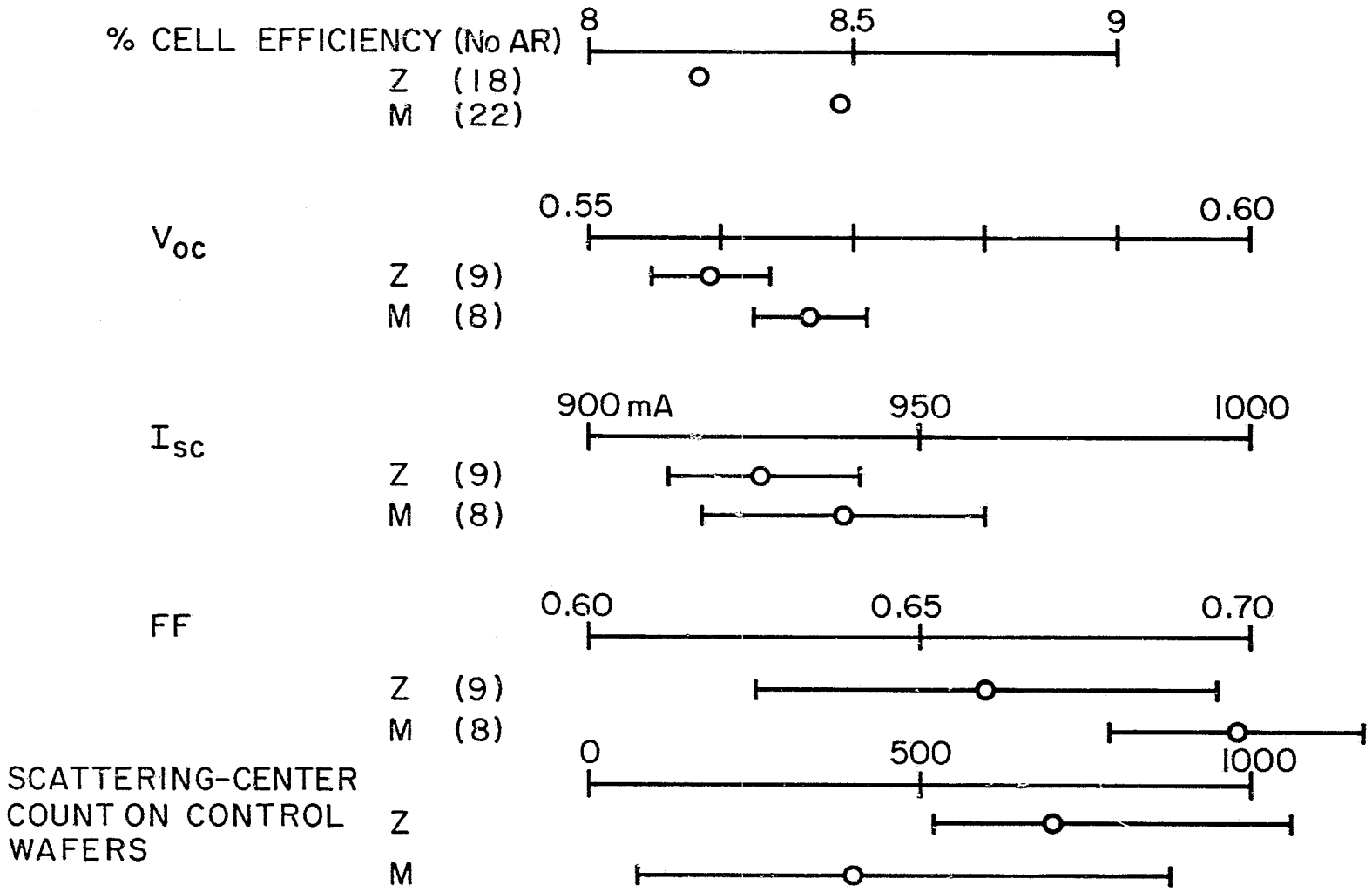


Figure 27. Preliminary solar-cell data.

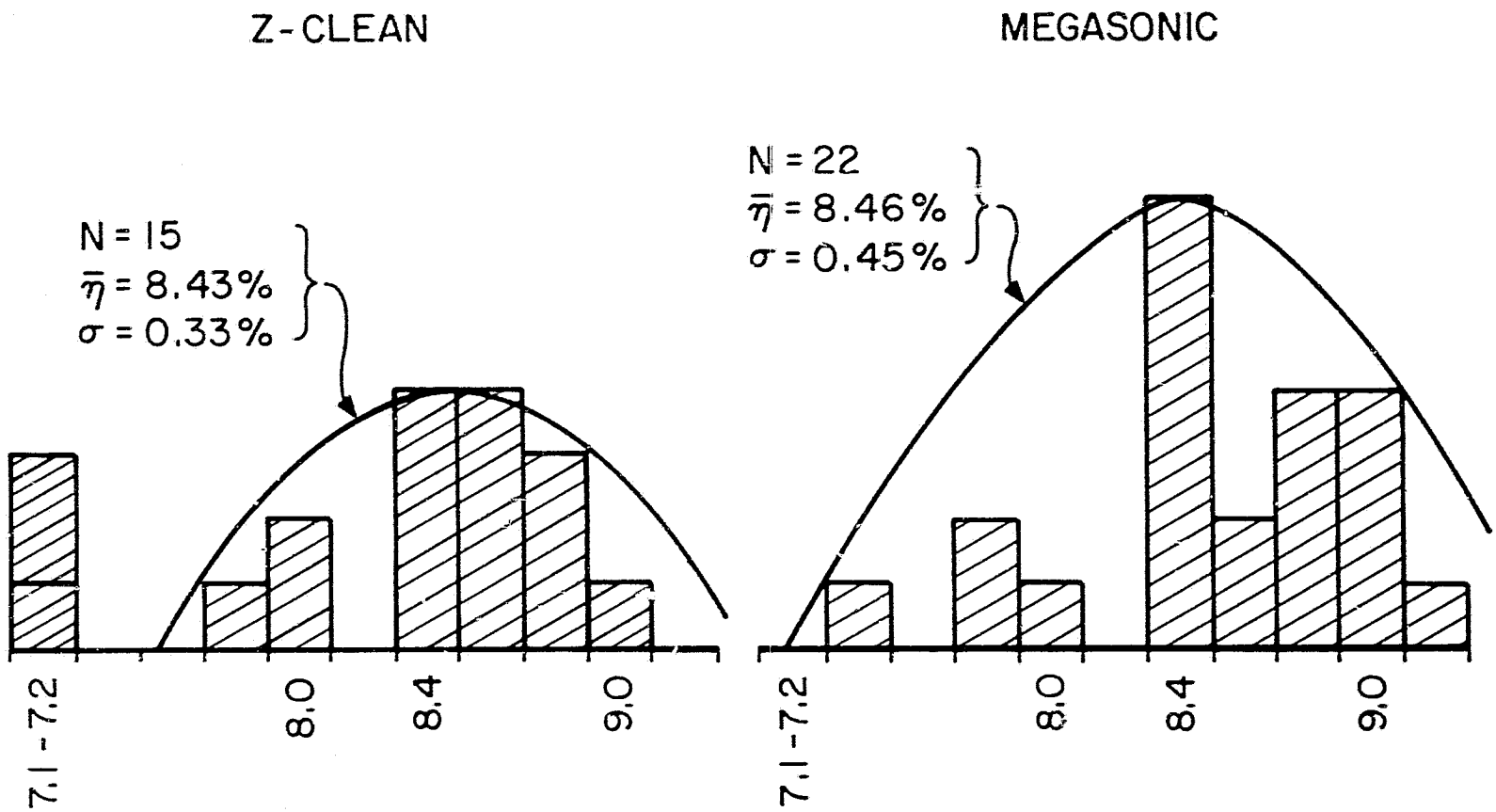


Figure 28. Solar-cell efficiency.

a sample size of about 160 cells would be needed. From the histograms, it appears that some cells show a much lower efficiency, as if there were a bimodal distribution. However, a hypergeometric test of proportion on the sample distribution also proved to be inconclusive. A histogram of this second set of solar cells is given in Fig. 29.

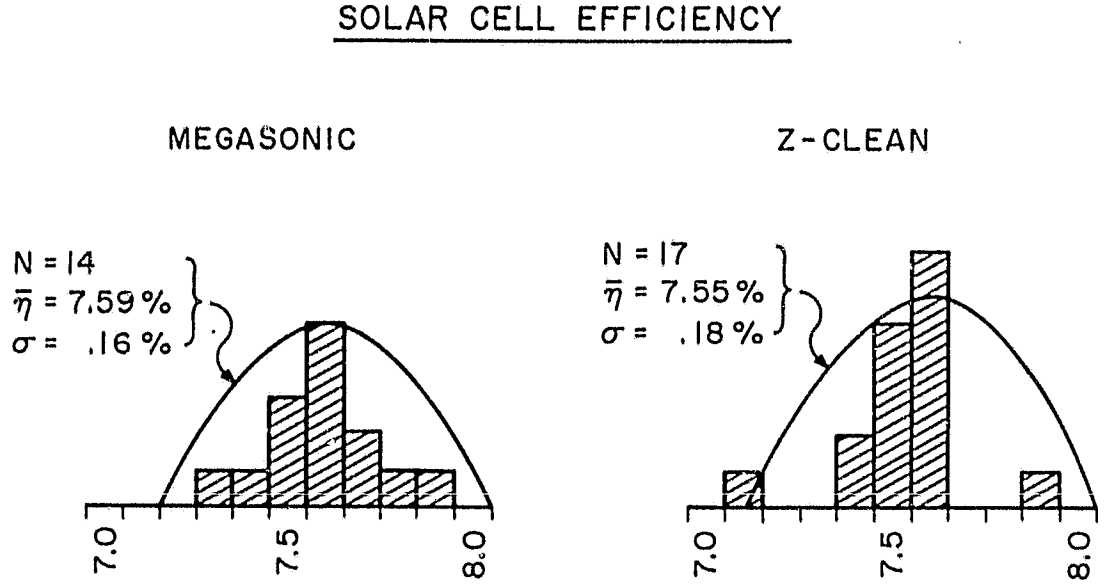


Figure 29. Comparison of Megasonically and Z-cleaned solar-cell efficiencies.

In order to highlight differences between Megasonically cleaned wafers and Z-cleaned wafers, processed solar cells were measured to determine the minority carrier diffusion lengths of cells cleaned by both processes. We measured the quantum efficiency as a function of incident radiation wavelength and fit this data to a solar-cell model in which the variable parameter is the minority carrier diffusion length. These measurements are made at relatively low light levels, and in order to verify their accuracy and relevance to actual solar-cell operation, a short-circuit current for the solar cell under AM1 solar irradiance is calculated based upon these measurements. This calculated short-circuit current is then compared to the experimental short-circuit current for

that cell using a calibrated Xenon solar simulator. If the two are in reasonable agreement, we assume that the derived minority carrier diffusion length is valid under AM1 irradiance conditions. Data for cells Megasonically cleaned at the production facility and Z-cleaned cells prepared at the same time are shown below:

	Average Minority Carrier Diffusion Length	Standard Deviation
Z-Clean	75 μm	16 μm
Megasonic Clean	90 μm	11 μm

Measurements of minority carrier diffusion length of the first batch of cells Megasonically cleaned at the laboratory facility, as well as the reference Z-cleaned cells, resulted in ambiguous data. At low light levels the Megasonically cleaned cells had diffusion lengths averaging 250 μm compared with diffusion lengths of only 150 μm for the Z-cleaned cells. However, a comparison of the calculated AM1 short-circuit currents with the actual AM1 short-circuit currents for both of these cell batches showed large discrepancies. Furthermore, under measurement conditions using higher light intensities, the respective diffusion lengths became closer to equal.

In conclusion, we can state that the evaluation of solar cells only qualitatively agreed with the hypothesis that Megasonic cleaning is more consistent than Z-cleaning, as there were not enough data points to make a statistically valid, quantitative statement.

A much larger production run is needed to be confident in the measurement of the amount of improvement in efficiency to be expected consistently. As discussed in this report, there are, of course, a number of good reasons why the Megasonic cleaning system is superior, based on handling, chemicals, usage, breakage, etc.

4. Recommendations for Large-Scale Production Facility

The system as presently arranged, but with the addition of mechanical transfers between Megasonic cleaning, rinsing, and drying and a second dryer track, is capable of a sustained production rate of about 4600 clean wafers per hour, making allowance for eventually sampling only 5% of the cleaned

wafers for control purposes. A 90% yield, including recycle, will produce 3.4×10^7 cleaned wafers per year, equivalent to a 15.7-MW/year facility or about two systems are needed for a 30-MW/year facility. For a 500-MW/year production facility, 1.15×10^9 wafers are required as the input. Therefore, 34 such Megasonic cleaning systems would be needed for one cleaning cycle.

In order to stay within reasonable bounds of scaling the unit, we suggest that doubling the number of transducer modules would permit an increase of a factor of about 2.5, with a belt speed of about 35 cm/min; this is equivalent to running the existing belt at 17.5 cm/min, i.e., slightly faster than the present 15 cm/min. It is also proposed to improve the platen design to accommodate four carriers per platen. Such a unit would also require a series of three rinse tanks or a longer cascade rinse and a platform to unload the platens and stage the carriers for loading into the dryer tracks, but the same or only slightly larger power supplies. The above assumption will produce a unit with an output of about 12,745 wafers per hour, or 1.06×10^8 wafer per year (yielded), thus requiring 11 systems, a reasonable number for such a large plant.

The air dryer can be scaled up by lengthening the funnel opening to 2.5 times the present length, increasing the HEPA filter area by the same factor, and adding another fan; then, a second such system in parallel with the first will produce a total output of 13,250 wafers per hour with a belt speed of 45 cm/min. With sampling 0.5%, the laser scanner would need to read 64 wafers per hour, easily within its present capability.

The layout of such a cleaning system can be visualized as a Megasonic sink, rinse, and deck unit about 13 ft long and a dryer and inspection section about 6 ft long, all about 2.5 ft wide. With additional floor space for an SC-1 storage tank, pumps, reagent storage, and filters, the total area would be approximately 110 ft^2, a very compact and high-efficiency layout for a system with such a large throughput.

F. COST ANALYSIS

Based upon our development of the Megasonic cleaning process and upon the experiments performed during the course of this program, an analysis was made of the Megasonic cleaning process costs. This analysis is summarized in

Appendix C, which contains the Solar Array Manufacturing Industry Cost Standard (SAMICS) Format A Process Description and a set of accompanying engineering notes to clarify the cost components required by Format A Process Description. An IPEG analysis of the process costs based upon these data inputs is included for clarification in this section. This IPEG analysis is based upon the following equation:

$$P' = C(1)*EQPT + C(2)*SQFT + C(3)*DLAB + C(4)*MATS + C(5)*UTIL,$$

where P is the process cost in 1980$ for an entire year of operation, EQPT is the cost of the captial equipment in 1980$, SQFT is the total required floor space in square feet, DLAB is the cost in 1980$ of direct labor, maintenance and quality control, MATS is the cost in 1980$ for the expendable materials required for one year, and UTIL is the cost in 1980$ of the utilities required for one year of operation.

The coefficients used in this equation were as follows:

C(1)=0.54

C(2)=111,

C(3)=2.14,

C(4)=1.23, and

C(5)=1.23.

Assuming 40 hours per shift per week and 345 days per year and running the process continuously with the costs and requirements described in the SAMICS Format A, we find that the annual cost of operating the process is $196,000. Furthermore, assuming the output rate and the machine usage fraction of 41.7 slices per operating minute and 0.9 operating minutes per minute, respectively, and 0.57 W per slice (3.0-in.-diameter slice, 13% efficient) results in an annual output of 10.6 MWp/Year. Thus the IPEG process costs per peak watt are $0.18/Wp. Table 3 illustrates the IPEG cost breakdown for these calculations.

TABLE 3. MEGASONIC IPEG PROCESS COSTS
(2500 slices/hour; 90% operating time)

Equipment Costs	0.00236 $/Wp
Floor Space	0.00052
Direct Labor	0.00627
Deionized H_2O	0.00330
NH_4OH	0.00448
H_2O_2, Filters, Transducer Sets, Electricity	0.00118
N_2	0.00003
TOTAL	0.018 $/Wp

F. CONCLUSIONS

The continuous Megasonic cleaning process for silicon wafers having a diameter of 3 in. or larger was developed and demonstrated. The designed and fabricated system has a continuous capability of cleaning wafers at a rate of more than 2,500 per hour more effectively and more economically than is possible with previously existing Megasonic cleaning equipment for solid-state power devices. The overall objective of this effort has been to provide proven technology and hardware that will be capable of achieving significant reduction in the cost of cleaning silicon wafers and that will also contribute to the improvement in the energy conversion efficiency of solar cells made from such wafers. The specific goals to be achieved were:

(1) Cleaning system throughput of 2,500 wafers per hour with the yield of 99.5%;
(2) Projected solar cell efficiency of 12.5%; and
(3) Projected cost reduction of 16.2¢/W at the module level.

Two novel concepts, Megasonic cleaning and room-temperature air drying, were harnessed to make an efficient, compact, and fast system for cleaning solar-cell wafers, at least as well as by any other method.

The design goal was exceeded when we demonstrated that at least 2600 wafers per hour could be cleaned and dried in such a system. In a test run of 10,200 wafers, no wafers were broken.

It was calculated that with only slight changes in geometry and the addition of automatic transfer machinery between the cleaning tank, the rinse tank, and the dryer, a system could be assembled from existing components with a capacity of 12,745, 3-in.-diam wafers per hour. Again, minor changes would permit this to be adapted up to at least 5-in.-diam wafers.

Improved cleanliness and less breakage can be expected because wafers are cleaned on both sides simultaneously with the quartz carrier used for annealing them. Thus, there is only one handling stage, with consequent improved cleanliness and less breakage. It was shown that the consumption of chemicals can be substantially improved and that the choice of ammonia-hydrogen peroxide is advantageous from the point of cost, safety, and ecology of waste disposal.

The second design goal of a 12.5% efficient solar-cell structure was met by some of the Megasonically cleaned solar cells but not by the average device. In the data shown in Fig. 28, 23% of the Megasonically cleaned cells had efficiency greater or equal to 12.5% compared with only 6% of the Z-cleaned cells (assuming an efficiency increase of 1.4 times with an antireflection coating).

It could not be shown unequivocally that the solar cells fabricated using this cleaning process were superior to those made by sulfuric acid-hydrogen peroxide Z-cleaning; the energy-efficiency and diffusion-length data do not contradict the hypothesis that Megasonic cleaning reduced the percentage of cells with lower than optimum efficiency compared to Z-cleaning, but there were insufficient data points to confirm this statistically. On the other hand, the data depicted in Fig. 28 does suggest that Megasonic cleaning is more efficient in the removal of particulates which can significantly degrade the solar devices. Consistent with the data of Fig. 28 we can assume that a fraction of the Z-cleaned cells will be significantly lower in efficiency than the average. For example, if the mean efficiency without antireflection coating is 8.46%, then some small fraction of the devices will have efficiencies more than 3 standard deviations lower such as at 7.1% efficiency. If we further assume that the current cost of the average efficiency solar device is $8.00/Wp at the module level, then if only 13% of these devices have a 7.1% efficiency, the increased cost will be slightly greater than $0.162/Wp at the module level. In comparison, the data in Fig. 28 shows that 23% of the Z-cleaned cells had this low an efficiency. Thus, our results are consistent with a savings of $0.162/Wp at the module level. A significantly larger data base is necessary to confirm this result with statistical certitude.

In addition to the specific achievement goals of the program, a major achievement was the design, assembly, debugging, construction, and operation of a practical, high-capacity cleaning and drying system, a revolutionary design from components that are now commercially available.

REFERENCES

1. A. Mayer and S. Shwartzman, U.S. Pat. 3,893,868 (assigned to RCA Corp.), July 8, 1975.
2. A. Mayer and S. Shwartzman, "Megasonic Cleaning: A New Cleaning and Drying System for Use in Semiconductor Processing," J. Elect. Mat. 8, 885 (1979), Appendix I.
3. W. Kern and D. A. Puotinen, "Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology," RCA Rev. 31(2), 187 (1970).
4. D. R. Oswald and D. F. Munro, J. Elect. Mat. 3, 225 (1979).
5. N. J. Patrick and E. J. Patzner, "Semiconductor Silicon," Proc. of 2nd Int. Symposium on Silicon Materials Science and Technology, Chicago, 1973, p. 482. Edited by H. R. Huff and R. R. Burger, Electrochem. Soc.
6. R. V. D'Aiello, "Automated Array Assembly, Phase II," Quarterly Report No. 5, DOE/JPL-954868-79/2, March 1979.
7. E. C. Douglas and R. V. D'Aiello, "A Study of the Factors which Control the Efficiency of Ion-Implant Silicon Solar Cells", IEEE Trans. Electron. Devices ED-27, 792 (1980).

APPENDIX A

Journal of Electronic Materials, Vol. 8, No. 6, 1979

MEGASONIC CLEANING: A NEW CLEANING AND DRYING SYSTEM FOR USE IN SEMICONDUCTOR PROCESSING*

A. Mayer and S. Shwartzman

RCA Solid State Division
Somerville, N.J. 08876

(Received December 20, 1978; revised April 17, 1979)

A compact system for cleaning wafers in all stages of device manufacture has been developed which uses high frequency (0.8 to 1 MHZ) ultrasonic energy (hence, the term "Megasonic") and a standard chemical solution which is not heated. The patented process effectively removes particles down to approximately 0.3 μm diameter simultaneously from the front and back surfaces, thin organic films, and many ionic impurities. After a brief water rinse, the wafers are dried in a hot air stream. The total cycle time is approximately 15 minutes, and at least 100 wafers can be cleaned in quartz or plastic carriers at the same time and without the need for loading or unloading.

Megasonic cleaning has been applied to silicon wafers, ceramics, and photomasks, and has been used for photo-

Key words: Ultrasonic cleaning, Megasonic cleaning, semiconductor processing and cleaning.

*Paper presented at 20th Annual Electronic Materials Conference, University of California at Santa Barbara, CA, June 30, 1978.

0361-5235/79/1100-0855$03.00/1

resist removal, dewaxing, and degreasing by using different solvents and stripping solutions. The outstanding system advantages are major savings in chemicals, superior wafer cleanliness, especially as regards particles, ability to clean and dry both sides of the wafer simultaneously, and less wafer handling. Several systems have been in production use for more than two years.

Introduction

The Megasonic Cleaning System is a brushless scrubbing system [1] with no moving parts. It removes particles from the front and back surfaces of at least 100 wafers simultaneously with a chemically clean solution. The scrubbing action is provided by piezoelectric transducers producing a 0.8 MHz sonic wave of about 1.5 mm length. The name "Megasonic" was coined to distinguish the system from the 20- to 80-kHz ultrasonic cleaners, which were found to be quite ineffective for particle removal, even when used at high enough power densities to produce crystal damage. Reference is made to the Megasonic System because it is designed so that cleaning, rinsing, drying and storage steps are compatible. If desired, the wafers can be cleaned and dried in the same quartz carriers, then stored for up to six weeks and inserted with no further cleaning into the next processing operation.

Reason for System Development

Why develop a new cleaning system? First, the removal of particles is essential for the production of large-scale integrated circuits, which now include approximately 50,000 active elements per chip and which have critical line widths in the order of 4 μm. This line width is expected to become 2 μm in the next 3 to 4 years, which means that particles down to at least 0.5 μm diameter should be removed following the rule of thumb that defects greater than 25% of line width are significantly harmful statistically. At the same time, the substrate surface must be made chemically clean. As most dirt particles are made up of silicons or organic matter and are insoluble

in the cleaning agents, they are usually removed by means of mechanical scrubbers. However, these scrubbers, built to be used with aqueous neutral detergent solutions, leave thin films of nylon behind and corrode rapidly when used with chemically active cleaning solutions. Therefore, one is forced to follow the mechanical scrubbing with a chemical cleaning step that, by observation, almost inevitably introduces additional particles; even the filtered reagents available commercially contain particles up to 5 μm in diameter.

A second problem is the maintenance of scrubbers. The brushes load up with dirt particles, and periodically a wafer is chipped or broken, showering debris over the brushes. If the brushes are not replaced quickly they become a source of scratches and particle contamination.

Thirdly, scrubbers are sequential in operation and have to be loaded and unloaded, one wafer at a time. Many machines scrub only the front of the wafer and leave the back surface wet.

Finally, conventional chemical cleaning based on the use of hydrogen peroxide is relatively slow and requires a large amount of the chemical since the peroxide decomposes rapidly in the hot solution. Therefore, because the solution can be used only once, the conventional method is wasteful of energy and chemicals.

One must then conclude that a need exists for a highly reliable cleaning system, compatible with current wafer-handling technology, that can remove particles down to at least 0.5 μm and chemically clean both surfaces and leave them dry. These design goals have been achieved in the Megasonic Cleaning System.

Megasonic Cleaning System

Cleaning

Fig. 1 shows one of the Megasonic Cleaning Systems now in use. It consists of a tank with a transducer array at one end. The tank can hold four 25-wafer carriers in series; the carriers are immersed in ammonium hydroxide-hydrogen peroxide solution.[2] Note that the wafers are

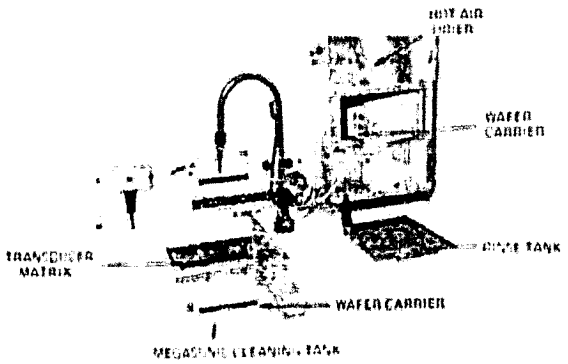


Fig. 1 Megasonic cleaning and drying station.

placed edge-on into the beam. Power supplies drive the transducer matrix, which consists of an array of 8 hexagonal lead zirconate titanate discs. A sequencer energizes two transducers at a time every few seconds. The sonic beam shows little divergence, as measured by profiling with a small piezoelectric transducer probe. A large cross-sectional area can be covered economically by having each tube-type power supply drive one transducer, and by sequencing, so that each transducer is on 25% of the time. A solid-state power supply is now under test.

The beam is barely attenuated when the wafers are placed edge-on, so that at least four carriers full with wafers (up to 3 inches in diameter) at their normal 1/8 or 3/16-inch spacing can be cleaned in series. At this spacing there is room between wafers for approximately two to three bundles of wave trains.

The acoustic power delivered at the ceramic-liquid interface is 10 to 15 W/cm^2. The solution heats up to approximately 35°C during normal operation when each wafer is exposed for 2.5 minutes to the energy beam. No heating of the chemical solution is required, even for pre-oxidation cleaning. The build-up of particles in the solution is normally slow, and they are not re-adsorbed as the carrier is removed. For cleaning very dirty wafers, e.g., after sawing or lapping, it is preferable to circulate the cleaning solution through a filter continuously. After cleaning, the substrates are rinsed in a simple overflow tank with DI water and inserted into the hot-air dryer.

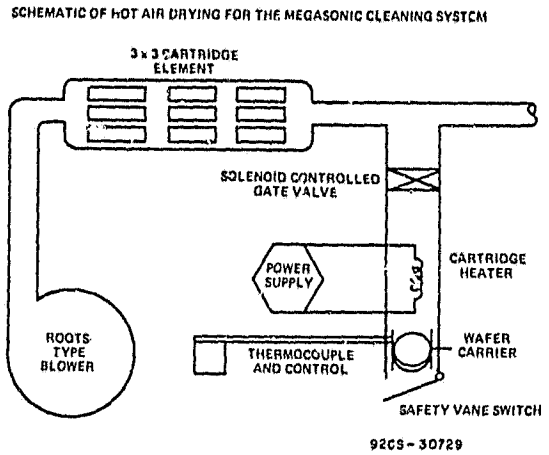


Fig. 2 Schematic diagram of hot-air drying station.

Drying

The drying system is shown schematically in Fig. 2. The wafer carrier is inserted into a chamber, and for the first minute cold air at 500 ft/min is blown through it to remove most of the water. The air is supplied by a Roots-type blower and filtered through a 3 x 3 series-parallel arrangement of cartridge filters that retain 100% of particles over 0.2 μm in size. After one minute, the air is heated by a cartridge heater to about 100°C; drying is complete in two to three minutes.

Air drying systems have not been popular in the past because they allegedly leave streaks. After cleaning in ammoniacal hydrogen peroxide, the bare silicon wafers invariably have a hydrophyllic surface, and dry cleanly provided the rinse water has been filtered through a 0.2μm or finer filter. Streaks have occurred with air drying only when the filter has burst or was badly seated and when the water supply contained collodial or bacterial debris. Note that such contamination does not show up as a change in conductivity and would not be visible on a wafer dried by spinning. This ability to determine water quality by the appearance of streaks is a valuable diagnostic feature of the drying system.

Maintenance

A Megasonic cleaning station has been on two shift

operation since December 1975; its maintenance record has been excellent after an initial break-in period. The most vulnerable parts of the system are the tubes of the power supply and the transducer matrix, which can be damaged by pinholing of the protective metal foil followed by local arcing and thermal- shock damage. Each matrix has an average life expectancy of approximately 1500 duty hours. While its replacement in the system is simple, its construction requires skill and experience.

Application and Results

The Megasonic System was first used to clean silicon substrates before depositing epitaxial layers. There is an urgent need to remove particles in this case because they act as nucleation centers and cause spikes to grow out of the epitaxial surface. Before the introduction of Megasonic cleaning, the substrates were scrubbed and then cleaned chemically.

The conservative judgement is that substrates that are cleaned by use of the Megasonic System have epi layers with as few or fewer spikes than those prepared by mechanical scrubbing. The substrates are inspected visually under controlled lighting conditions by the ASTM Method F 523-77 and cross checked using dark-field microscopy at about 150x magnification. This inspection should show up particles with an effective diameter greater than 0.3 μm.

The results indicate that Megasonic cleaning is at least as good as scrubbing. Wafer breakage is virtually nil. The throughput for the same investment is about four times greater for Megasonic cleaning than for scrubbing and chemical cleaning. In addition, the amount of chemicals used is down to about 1/8 of that used in chemical cleaning. This reduction, in turn, reduces the amount of chemical waste and effluent treatment required.

In addition to cleaning silicon substrates during processing, it is also possible to clean finished, metallized devices, either in chip form, on headers, or in packages, by special fixturing. Military specifications do not permit the use of low-frequency ultrasonics to remove debris because device reliability tends to deteriorate.

Indications from a few tests on metallized chips contaminated with scribe dust are that Megasonic cleaning is effective in removing the dust and, judging from electrical test data, may be less severe than other methods; it could, perhaps, be used as a clean-up prior to sealing.

Discussion

The success of the Megasonic System is undoubtedly due as much to the attention paid to the total system concept -- choice of solvent, cleaning fixtures, rinsing, drying, storage and handling -- as to the high-frequency insonation. Why then is it not possible to obtain anything like this cleaning action with a 20 to 80-kHz system used in the same way even at 10 times the power density?

The authors believe that, in contrast to low-frequency insonation, Megasonic cleaning does not take place mainly by cavitation. The reasoning is as follows: Cavitation depends on the formation of shock waves and their impact on particles that stick to the surface. Cavitation bubbles are formed by the successive high-pressure and low-pressure components of the acoustic wave; i.e., the wave activity causes a hole or cavity to form in the liquid. The cavity implodes when the walls can no longer sustain the tensile forces. Gas bubbles or particles are nucleation centers that cause the cavities to collapse before they fully develop. That is why it is customary to degas solutions to obtain maximum cavitation in low-frequency ultrasonic cleaning.

Observations of the effectiveness of Megasonic cleaning indicate that gas bubbles are no detriment. The best cleaning action has been observed to take place when the cleaning solution can wet the substrate and particle surface, hence the use of ammoniacal hydrogen peroxide as the medium. The hydrogen peroxide evolves oxygen freely even in the cold solution. The cleaning action is excellent as measured on silicon substrates deliberately contaminated with 0.3 μm alumina or with "standard" fingerprints made with a saturated hydrocarbon grease. Calculations based on a transfer of 7.5 W/cm^2 to the wafer surface suggest that the water molecules move only about 0.1 μm in each cycle, but that their

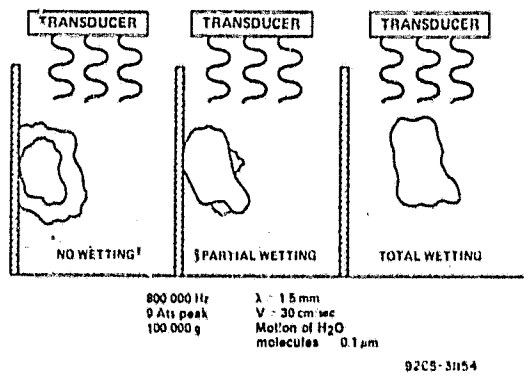


Fig. 3 Model of Megasonic action on a particle held on a silicon wafer surface.

acceleration is in the order of 100,000g. The maximum instantaneous velocity is about 30 cm/s. It is believed that the time between pulses, 1.25 μs, is too short for the formation of cavitation bubbles but that the scrubbing action derives from the high-pressure wave which pushes and tugs at particles 800,000 times a second. The peak pressure is about nine atmospheres. It is not difficult to imagine that the particles move sufficiently to permit solvent to diffuse rapidly into the interface between the substrate surface and the particle, and to hydrate the surface, provided it is wettable. The liquid film acts as a wedge and progressively reduces the contact area between particle and surface until the particle is free to move. It's re-adsorption is prevented by the liquid film. This sequence is shown schematically in Fig. 3.

The main features of high-frequency insonation are the local action, the large pressure of the pulse and its frequency, the dimensional match between wave and particle, and the wetting action of the medium.

Depending on the nature of the bond between the particle and the substrate, it may be necessary to select other chemicals than ammoniacal hydrogen peroxide. For photoresist stripping, the usual chemicals can be used and need not be heated. If the

contaminants are physically incorporated in the surface, as can happen after excessive polishing pressure, not even Megasonic cleaning will remove them. Again, once an impurity, such as polishing slurry, has been allowed to dry on the surface, much longer exposure or a higher power density may be required to hydrate the interface and float the particle off.

System Disadvantages

- The solvent system must be adapted to the nature of the contaminant-substrate bonding.
- The transducer matrix is not a commercial item.
- The system cannot be used with cleaning agents that attack the metal foil that protects the piezoelectric transducers (e.g., strong hydrofluoric acid).
- Substrate carriers must be somewhat redesigned to minimize obstruction to the megasonic beam.

System Advantages

- Scrubs and chemically cleans both sides of all wafers in several carriers simultaneously.
- Reduces normal chemical usage by 80%.
- Three to four times higher productivity than scrubbing plus chemical cleaning plus drying and at equal or lower investment cost.
- Low maintenance because there are no moving parts; simple to automate. Replacement of the transducer matrix is simple.
- Designed so that substrates can be cleaned, rinsed, and dried in the carriers used for high-temperature processing and stored ready for use weeks later.
- Virtually no breakage, chipping, or scratches incurred because substrates are not transferred or subjected to any mechanical stress.
- Hot-air drying is compatible with quartz boats and shows rinse-water problems instantly.
- Adaptable to many applications other than silicon-wafer cleaning.

References

1. A. Mayer and S. Shwartzman U.S. Patent 3,893,869, July 8, (1975); assigned to RCA Corporation. The following companies are licensed by RCA to build cleaning systems:

Fluorocarbon
P.O. Box 3640
1432 South Allec St.
Anaheim, California 92803

Interlab Inc.
Precision Rd
Danbury, Ct. 06810

Southern Scientific Associates, Inc.
304 Cynthia Lane
Indian Harbour Beach, Florida 32935

2. W. Kern and D.A. Puotinen, RCA Review 31, 187, (1970).

APPENDIX B

ANALYSIS OF STANDARD CLEAN SOLUTION (SC-1) OUTLINE OF METHODS

The ammonia (NH_3) is titrated with hydrochloric acid (HCl) using Methyl Purple* as the indicator.

The hydrogen peroxide (H_2O_2) is titrated with potassium permanganate ($KMnO_4$) using manganous sulfate ($MnSO_4 \cdot 2\ H_2O$) as the catalyst and after acidification of the solution with sulfuric acid (H_2SO_4).

Sampling

Rinse out a clean 250-ml Erlenmeyer flask with a little of the SC-1 solution to be assayed, withdraw about 200 ml with that flask, and keep it stoppered until it has been analysed, but not more than 1 hour.

Ammonia

Into a clean 250-ml Erlenmeyer flask, pipette a suitable aliquot portion of SC-1; 25 ml for a freshly prepared solution and up to 100 ml for a nearly spent solution. Add two drops of Methyl Purple solution and titrate with 1 N HCl standardized solution to a purple endpoint. Toward the end of the titration, it may be necessary to add 2 more drops of the indicator. Note that Methyl Red cannot be used as it is oxidized too readily. The HCl solution can be standardized in the usual manner against 1 N sodium hydroxide solution, previously standardized against potassium hydrogen phthalate.

Calculation

$$g/L\ NH_3 = \frac{ml\ HCl \times 0.01703 \times N_a \times 1000}{ml\ of\ aliquot\ taken}$$

N_a = normality of standardized HCl.

Hydrogen Peroxide

Pipette a suitable aliquot portion into a clean 250-ml Erlenmeyer flask; 5 ml for a freshly prepared solution and up to 25 ml for a spent solution. Rinse the walls and dilute to about 50 ml with distilled water. Add about 1.5 ml of sulfuric acid and several milligrams, a spatula tipful, of manganous

*Fleisher Chemical Co., Washington, DC.

sulfate. Swirl to dissolve, then slowly titrate with 0.1 N potassium permanganate solution to a permanent pink endpoint. The permanganate is best standardized in the usual way against sodium oxalate. The endpoint is taken when the pink tinge first persists for more than a few seconds.

Calculation

$$g/L\ H_2O_2 = \frac{ml\ KMnO_4 \times 0.0170 \times N_b \times 1000}{ml\ of\ aliquot\ taken}$$

N_b = normality of standardized $KMnO_4$ solution.

Sodium, Copper, Iron

Any atomic absorption equipment may be used that is capable of analysing in the concentration range of 0.1 to 10 µg/mL. We used a Perkin Elmer PE 403. Calibrate against standard solution. Sodium and copper can be determined on the solution as sampled, but for iron analysis, it is necessary to acidify first to avoid the coagulation of ferric hydroxide.

APPENDIX C

SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

FORMAT A

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Dr. / Pasadena, Calif. 91103

PROCESS DESCRIPTION

Note: Names given in brackets [ ] are the names of process attributes requested by the SAMIS III computer program.

A1 Process [Referent] MSCLN

A2 [Descriptive Name] Megasonic Cleaning: Advanced System

PART 1 – PRODUCT DESCRIPTION

A3 [Product Referent] CLNWF

A4 Descriptive Name [Product Name] Clean Wafer

A5 Unit Of Measure [Product Units] Slice

PART 2 – PROCESS CHARACTERISTICS

A6 [Output Rate] (Not Thruput) 41.7 Units (given on line A5) Per Operating Minute

A7 Average Time at Station [Processing Time] 10 Calendar Minutes (Used only to compute in-process inventory)

A8 Machine "Up" Time Fraction [Usage Fraction] .9 Operating Minutes Per Minute

PART 3 – EQUIPMENT COST FACTORS [Machine Description]

A9	Component [Referent]	MSYS		
A9a	Component [Descriptive Name] (Optional)	Megasonic Cleaning System		
A10	Base Year For Equipment Prices [Price Year]	1979		
A11	Purchase Price ($ Per Component) [Purchase Cost]	47000		
A12	Anticipated Useful Life (Years) [Useful Life]	7		
A13	[Salvage Value] ($ Per Component)	0		
A14	[Removal and Installation Cost] ($/Component)	0		

Note: The SAMIS III computer program also prompts for the [payment float interval], the [inflation rate table], the [equipment tax depreciation method], and the [equipment book depreciation method]. In the LSA SAMICS context, use 0.0, (1975, 6.0), DDB, and SL.

Format A: Process Description (Continued)

A15 Process Referent (From Page 1 Line A1) MSCLN

PART 4 -- DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)
[Facilities and Personnel Requirements]

A16 Catalog Number [Expense Item Referent]	A18 Amount Required Per Machine (Per Shift) [Amount per Machine]	A19 Units	A17 Requirement Description
A2080D	50	Sq. Ft.	Manuf. Space (Type B)
B3096D	.5	Prsn. yrs.	Semicond. Assemb.
B3688D	.1	Prsn. yrs.	Elec. Maint. Man

PART 5 -- DIRECT REQUIREMENTS PER MACHINE PER MINUTE
[Byproduct Outputs] and [Utilities and Commodities Requirements]

A20 Catalog Number [Expense Item Referent]	A22 Amount Required Per Machine Per Minute [Amount per Cycle]	A23 Units	A21 Requirement Description
C1032B	8.5×10^{-2}	Kw hr.	Elec. Power
C1144D	2.56×10^{-1}	Cu. ft.	Deionized water
E1110D	8.3×10^{-2}	Cu. ft.	Ammonium hydroxide
E1336D	2.28×10^{-2}	lbs.	Hydrogen Peroxide
E1282D	2.75×10^{-3}	Dollars	Filters
ERTRD	2.22×10^{-5}	Sets	Tranducer sets
E1780D	5.9×10^{-3}	Cu. ft.	Nitrogen gas, high pressure

PART 6 -- INTRA-INDUSTRY PRODUCT(S) REQUIRED [Required Products]

A24 [Product Reference]	A28 [Yield]* (%)	A26 [Ideal Ratio]** Of Units Out/Units In	A27 Units Of A26***	A25 Product Name
	99.5	1.0	slice / slice	
			/	
			/	

Prepared by R.E. Daniel Date 8/22/80

* 100% minus percentage of required product lost.
** Assume 100% yield here.
*** Examples: Modules/Cell or Cells/Wafer.

REVERSE SIDE JPL 3037--S R 10/78

DIRECT REQUIREMENTS PER MACHINE PER MINUTE

C1032B Elec. Power

Cleaning Unit	4.5 kWh	$5.1 \div 60 = 8.5 \times 10^{-2}$ kWh
Dryer	0.6 kWh	
	5.1 kWh	

E110D Ammonium Hydroxide

Initial Solution	1950 g
Losses over 5, 8-h shifts. At this time the initial solution is replaced. (Will clean 105 wafers.)	2328
	4278 g

$$\frac{4278 \text{ g} \times 22.4 \text{ L/mole}}{17 \text{ g/mole}} = 5636.9 \text{ L } (NH_3)$$

$$\frac{5636.9 \text{ L}}{28.32 \text{ L/cu.ft}} = 199.18 \text{ cu.ft } (NH_3) \quad 8.3 \times 10^{-2} \text{ cu.ft/min}$$

Lasts for 40 h

E1536D Hydrogen Peroxide

Initial Solution	6.4 L
Losses over 5, 8-h shifts. At this time initial solution is replaced. (Will clean 105 wafers.)	16.0 L
	22.4 L

sp. g 1.11 g/cm^3 2.48 x 104 g

$2.48 \times 104 \text{ g} \times 2.2 \times 10^{-3}$ lb/g = 54.7 lb (H_2O_2)

lasts for 40 h 2.28×10^{-2} lb/min

E1282D Filters

12 filters/yr	$80 each	= 960
6	36	= 216
6	10	= 60

Cost per yr for filters $1236

Approx 4.5×10^5 min of machine operating time per year. $\$2.75 \times 10^{-3}$/min

C1144D Water Deionized

Initial plus losses

Lasts 40 h	160 L	2.35×10^{-3} cu.ft/min
Rinse water	1.9 gal/min	0.254 cu.ft/min
		0.256 cu.ft/min

ERTRD Transducer Sets

Two per machine

Lasts 1500 h 2.22×10^{-5} sets/min

Cost $365 per set

E1780D Nitrogen Gas

Constant purge of power amplifiers and signal generators - approx. 4.5×10^5 machine operating minutes per year 5.9×10^{-3} cu.ft/min