CONTAMINATION CONTROL OF PREDIFFUSION WET CHEMISTRIES

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Introduction

The efficiency of a solar cell can be broken down into four key elements:

- Maximizing the collection of light
- Maximizing the number of p–n junction carriers and their lifetime
- Reducing the forward bias dark current
- Efficient current transfer from the cell to the module

Metallic contamination on a silicon wafer can have a large effect on carrier lifetimes and cell performance.[1,2] Contaminants can be present in the silicon bulk or introduced to the wafer during exposure to contaminated process baths.

As a means to improve the carrier's lifetime and improve cell efficiency, it is critical to eliminate contamination from the prediffusion wet chemical systems. Contamination in these baths can result in:

- Nonuniform or under-etched wafers
- Reduction in etching efficiency
- Reduction in cleaning effectiveness
- Contamination carryover from one bath to the next
- Increased water and chemical consumption

Purpose

- This research looks at several fluid handling materials as sources of contamination for the prediffusion chemistries and their theoretical contamination contribution to a chemical bath.
- Utilizing techniques and theories to measure the residual thickness, along with the liquid contamination level on a wafer, it is possible to quantify the contamination level increase as a result of the impurities in a liquid bath.
- Using actual extractable data from various wetted materials,[3] along with the amount of fluid in contact with these materials, the amount of contamination was calculated for a theoretical piping system.
- The research then studies methods to reduce the level of contaminants introduced from chemicals and components in recirculation baths.
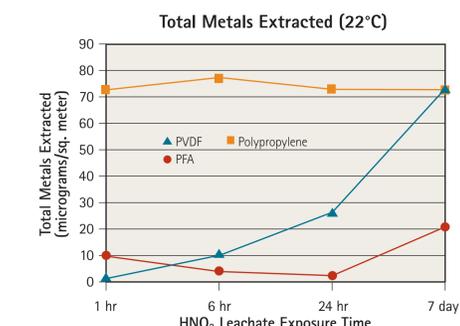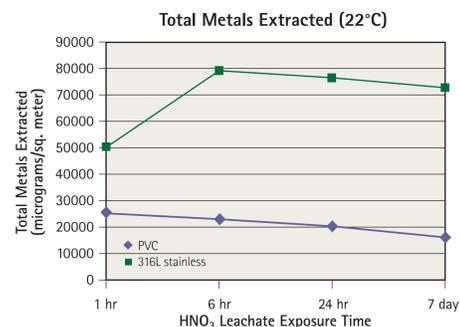
Sources of Contamination

- Materials of construction of the wet processing system
  - Tubing, hoses, pipe, valves, fittings, flow meters, containers and filters
- Chemical and silicon used in wafer processing
- The wrong filter can introduce contamination due to chemical, temperature or flow incompatibilities
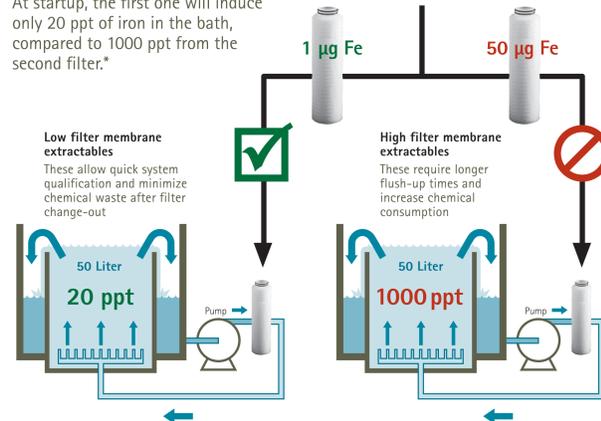
Manufacturing cleanliness yields cleaner components. Extensive cleaning of the wet process is necessary to achieve ultra-clean products.

Contaminants Extracted from Piping Materials

The following graphs compare extractable levels of contamination from various materials used as wetted surfaces in prediffusion process piping. The data are based on the amount of contaminant in micrograms/square meter of wetted surface. This information will later be used to generate potential levels of various contaminants in a theoretical process piping system.

Total Metals Extracted (22°C)
PVC; 316L stainless
HNO₃ Leachate Exposure Time: 1 hr, 6 hr, 24 hr, 7 day

Total Metals Extracted (22°C)
PVDF; Polypropylene; PFA
HNO₃ Leachate Exposure Time: 1 hr, 6 hr, 24 hr, 7 day

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In a recirculation bath, any new element introduced is likely to affect the system's cleanliness. The initial cleanliness of that new element will determine the system's recovery time and the amount of chemical that might be wasted at startup. Below are two examples of filters installed into a 50 liter recirculated system. The first filter contains only 1 µg of extractable iron and the second filter contains 50 µg of extractable iron.

At startup, the first one will induce only 20 ppt of iron in the bath, compared to 1000 ppt from the second filter.*

1 µg Fe — **Low filter membrane extractables** These allow quick system qualification and minimize chemical waste after filter change-out — **20 ppt** — 50 Liter

50 µg Fe — **High filter membrane extractables** These require longer flush-up times and increase chemical consumption — **1000 ppt** — 50 Liter

For comparison purposes only. Actual bath contamination level will vary based on temperature, type of chemical and other sources of contaminants.

The chart below shows three examples of filter membrane materials and the impact the filter material can have on the system's ionic contamination.


18 Megohm-cm feed
Philic UPE; PSO membrane; PES membrane
Resistivity (Megohm-cm) vs Time (Minutes)
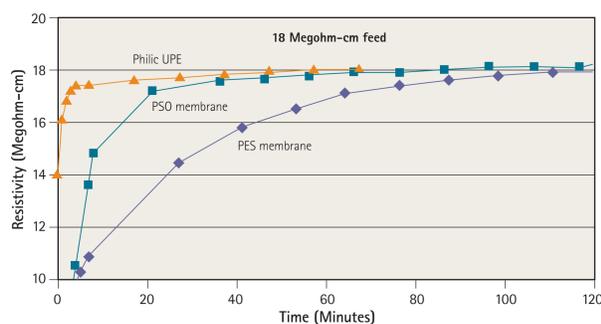
UPE = Ultra-high molecular weight Polyethylene; PSO = Polysulfone; PES = Polyethersulfone

Calculating Contaminants on Silicon Wafers

Using the residual thickness along with the liquid contamination level, it is possible to quantify the contamination level increase on a wafer as a result of the impurities in the liquid bath. The liquid layer thickness (h) is determined using the Landau–Levich equation, commonly used in dip coating processes, where V is the withdrawal velocity of silicon substrate, g is the acceleration due to gravity and γ, ρ and η are the surface tension, density and viscosity of the liquid.

$$h = 0.946 \left(\frac{\gamma}{\rho g} \right)^{1/2} \left(\frac{\eta V}{\gamma} \right)^{2/3}$$
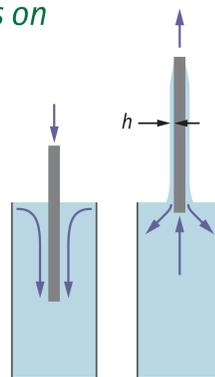
The amount of contamination remaining on the silicon wafer (Γ) after submersion and removal from a contaminated bath is proportional to the liquid film layer (h) remaining on the wafer and the bulk contamination concentration (c) in the liquid.[4]

$$\Gamma = hc$$

Example Piping System Contamination Analysis

Using actual extractable data from various wetted materials,[3] along with the amount of fluid in contact with these materials, the amount of contamination was calculated for a theoretical piping system.
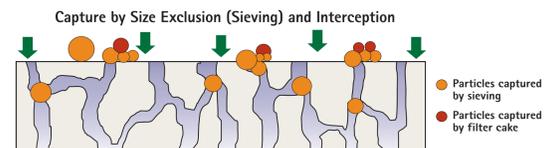
- 25.4 mm nominal line size
- 365.76 meters of equivalent tubing
- 25.5 square meters of wetted surface area
- 142.0 liters of fluid

Piping Material	Total Metals Extracted (microgram/sq. meter)[3]	Metal Contamination in System (micrograms)	Metal Concentration (ppm or mg/L)
PFA	20	510	0.0036
PVDF	73	1,861	0.0131
PP	73	1,861	0.0131
PVC	17,378	443,139	3.12
304 SST	72,122	1,839,111	12.95

Contamination Removal

Membrane Retention Mechanisms

Capture by Size Exclusion (Sieving) and Interception

Particles captured by sieving; Particles captured by filter cake

- Dominant form of retention in liquids
- Capture occurs at membrane surface and within pores
- Particles larger than pore size are retained at the surface
- Smaller pore diameters in membrane interior retain smaller particles

Capture by Adhesion/Adsorption
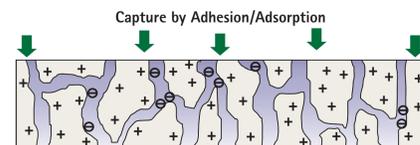
- Very small particles in liquids have a negative charge and can be captured by attraction to a positive charge in a filter
- Changes in pH can affect this retention mechanism
- Adsorption of particles can be by hydrophobic interactions
- Capture through:
  - van der Waals forces
  - Electrostatic forces
- Require transport to the membrane wall:
  - Impaction (Brownian motion)
  - Interception (flow lines)
  - Diffusion
 - Electrostatic attraction

Contamination in Wet Benches

A concern over contamination is compounded in wet benches where chemical baths are often recirculated without the use of filtration, causing the contamination levels to grow over time. If wafer lots are timed too closely together, the wafers will be processed in a contaminated bath. A higher flow provides a quicker turnover and lots can be processed more rapidly.

Particles (a.u.) vs Turnover
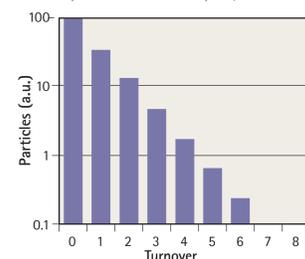
- 1 turnover = system volume/system flow
- The graph shows the reduction in particles in a typical recirculation bath using a filter with a typical retention of 99.00–99.99%
- Based on the exact retention of the filter, it may take between 5 and 8 turnovers to divide the particle concentration in the bath by a factor of 100
- Recirculation baths need high chemical flow and high particle retention to maximize the removal of contaminants, ultimately leading to increased carrier lifetimes and cell performance

Contamination Removal Using Filtration

Particles generated during processing should be removed from the bath by filtration before the next lot is placed in the bath.

Silicon Test Wafers
Dunked Si wafers; >0.1 µm
Counts per mL vs Time
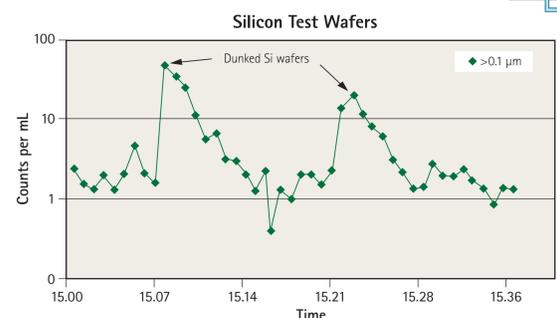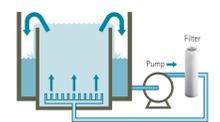
- An OPC (optical particle counter) was used to count particles over time
  - Unit is particles >0.1 µm per mL
- Lots are appropriately spaced to return to the baseline of approximately 1 particle/mL

Conclusion

It has been shown that particle and ionic contamination on a silicon wafer can degrade the performance of photovoltaic solar cells by reducing the minority carrier lifetime. The source of contamination can be found in the bulk silicon as well as the chemical delivery system that manages high-purity chemicals used in the prediffusion texture etch and clean steps.

Contamination will be extracted from the wetted surfaces of fittings, tubing, valves, filters and containers by process chemicals. These contaminants are then present in the fluid media and ultimately end up on the wafer surface .

The amount of contaminants remaining on the wafer surface is dependant upon several factors including fluid viscosity, rate of removal from the chemical and bath temperature. Though the greatest contributor to extractable contaminants remaining on a wafer is the concentration of contaminants found in the chemical.

This fact makes the selection of materials for fluid handling components extremely important. The data presented show the wide range of contamination levels that can be found in a chemical distribution system, depending upon the materials used. Of the materials evaluated, the system using PFA had the lowest contamination concentration factor in the fluid at a level of 0.0036 ppm. Consequently, by using this high-purity material, the level of contamination contributed by the fluid handling system will be minimized.

Additionally, by identifying proper filtration techniques, including filter material selection as well as recirculating bath design and operation, it is possible to further reduce the amount of contaminants present in the chemical delivery systems and recirculating baths.

References

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2. Smith, A.L., "Transition Metal Gettering Studies and Simulation for the Optimization Silicon Photovoltaic Device Processing, *Ph.D. Thesis, MIT*, May, 2002.
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