Reclamation of Water and Treatment of Hazardous Materials in Silicon Processing

by Viven Krygier, Ph.D.
Rolf Berndt, Prof. Dr.-Ing.

Pall Microelectronics

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PV Industry has

- Experienced tremendous growth over the past few years
- Brought hundreds of new production facilities on line
- Hired thousands of workers interfacing with complex and potentially dangerous systems

PV Industry struggles with Environmental, Health and Safety (EHS) Challenges

Some of these challenges are linked to waste materials generated in the production of intermediate goods and components for PV wafers and cells.
Reasons for treating waste generated in PV production are:

- To meet local and legal discharge limits
- To preserve nature and conserve natural resources
- To ensure the sustainability and the green reputation of PV industry
- To reduce manufacturing costs by re-using valuable waste components
- To ensure product quality and operational safety by controlled modification and containment of critical waste components

“Defensive” position; costs increase

“Offensive” position; costs reduced
Question:

How to treat waste so that the treatment is self-financing through better utilization of resources and improved product quality?

Answer:

By early separation of waste streams into components that either can be re-used or modified for risk-free disposal.
PV: Examples of Waste Treatment

Example 1: Water/Silicon Reclamation in Ingot Shaping

Example 2: Treatment of Slicing Slurry

Example 3: Puller Exhaust Gas Dust Abatement

mc-Si

exhaust gas

Crystal Growing

Ar

water

wastewater (Si + water)

slurry

spent slurry (SiC, PEG, Si,...)

Slicing

WAFERS

pc-Si

exhaust gas

Casting

Ar

water
Example 1: Water/Silicon Reclamation in Shaping Operations

Shaping of ingots includes cropping, cutting, squaring, chamfering, surface grinding/polishing →

Manufacturing of 1 MWp wafer capacity requires
≥ 1,000 m³ or 264,000 gal of feed water for saws and grinders
→ more than 1,000 m³ w/water is generated if not reclaimed!

At typical wafer manufacturers, water consumption in the shaping area ranges from 10 - 40 m³/h or 44 – 176 gpm. Silicon losses due to pre-shaping are 3 to 5% of ingot volume.

→ Strong incentive to re-use water and to consider Si reclamation
Basics
1. Pre-shaping of silicon ingots prior to wafering comprises (for example)
   • Cropping
   • Squaring
   • Top & Tail Cutting

2. Sawing/grinding tools are typically:
   blades or discs or bands, armed with diamonds

3. Water is used for cooling the hot surfaces, as a lubricant, and to carry the abraded silicon particles away

4. Water traditionally used in PV industry:
   **TAP WATER** with or **without** recycling
Critical Issues
a) water quality
b) incomplete solids removal
c) settling / concretion
### Critical Issues

- **a)** water quality
- **b)** incomplete solids removal
- **c)** settling / concretion

### Questions

- **How does water quality influence the sawing/grinding operation?**
- **Are centrifuges and settling tanks capable in removing all silicon particles?**
  - Are there better technologies?
- **Are there ways to avoid or to limit uncontrolled settling of silicon particles and concretion of sediments on tools, in pipes or channels?**
Studies show that

Well-controlled, low-conductivity cooling water results in

- higher *sawing speed*
- better *grinding quality*
- easier *cleaning* of machine tools
- less uncontrolled *settling and concretion* or solidification in tools, piping and drains.

Why?

- Less coating of edges and surfaces by minerals and colloids
- Less aggregation of silicon particles
“Coating of edges and surfaces by minerals” means

There are high temperatures up to some 1000 °C on the rupture front in a zone of some nm in size

- Flash Evaporation of cooling water
- Dissolved minerals remain as coating on diamond edges and silicon surfaces and are not completely re-dissolved which is certainly not good for further disintegration
a) after sawing with tap water
net of many white lines

b) after sawing with recycled water (low ionic strength)
   nearly no white lines

With drinking water (~600 µS/cm) and recycling water (~5 µS/cm):

- White lines are pits – poor surface quality
- Contaminants can deposit in the pits
- Findings support observations in the field: Cooling with tap water results in lower surface quality and increases coating of Si surfaces by minerals

$\Rightarrow$ Tap water not suitable for cutting and grinding!
“Aggregation of Si particles” results in uncontrolled sedimentation of matter and concretion in pipes and drains. Colloid stability in the spent process water is desirable on its way to the sewer or recycling process. The DLVO theory\(^1\) explains how to achieve colloid stability:

1. Silicon particles in water have a surface charge compensated by strongly adsorbed counter-ions and an outer, diffuse ion layer.
2. Colloid stability is controlled by the balance of London – van der Waals attraction and electrostatic repulsion due to similar surface charge.
3. If the similar surface charge is large compared to the v.d. Waals attraction, the particles cannot approach each other \(\rightarrow\) STABLE SUSPENSION.

\(^1\) Derjagin/ Landay/ Verwey/ Overbeek
Si particles in DI water form **stable** colloidal dispersion since:
- same surface charge on all particles
- strong electrostatic repulsion
- single particles too small for significant sedimentation

Si particles in tap water form **unstable** colloidal dispersion since:
- reduced or zero surface charge
- weak or no electrostatic repulsion
- particles form agglomerates which settle fast and form solid deposits

\[\text{I don't like all these guys. They all have the same charge}\\\]

sediment (concretion!)
Primary Aspect for Water Reclamation

1. Sawing/grinding water should be free from particles and colloids, and at low ionic strength!
2. De-ionized, filtered water is too expensive to be used only once, and too aggressive!

Water reclamation has to assure perfect removal of particles and colloids and controlled, low ionic strength in the reclaimed water!

Further targets are

• Re-use of water at reasonable recovery rate and acceptable Cost of Ownership
• Reduction of waste discharge volume
• Control of chemical hazards due to hydrogen
1. Example for Waste Treatment

PALL’s process design based on experience with 32 Pall systems for Si/water separation since 1995

- Water Recovery & Redistribution System
- Dynamic Membrane Filtration Unit
- Optional facility units

Diagram:
- Collection tanks
- BUFFER TANK
- MF UNIT
- HOLDING TANK
- WATER SUPPLY PUMPS
- DE-WATERING
- DI WATER UNIT
- DI Water Make-Up
- Spent water
- Process Feed Water
- Tap Water
- Concentrate
- Si Sludge
- W/water
- Gas
- Permeate

Options:
- DI WATER UNIT
- IEx
- OPTIONS
The heart of Pall‘s technology is a dynamic membrane filtration based on PVDF hollow fibre membranes with pore sizes \(< 0.1 \mu m\) → physical barrier against particles and colloids

The membranes are arranged in compact modules with up to 50 m² membrane area, with the feed port towards the bottom of the module.
Dynamic Membrane Filtration

(Outside-in mode with Cross-Flow, periodic Reverse Filtration and periodic Air Scrubbing)

The clear filtrate is collected in the hollow fibres and leaves the module on its top.

The particles are typically collected on the outer surface of the hollow fibre, and removed from the membrane by cross-flow effects and other dynamic fluid flow mechanisms.
Typical PALL Grinding/Sawing Water Reclaim System

Dynamic membrane filtration system, fully automated

140 gpm (32 m³/h) water capacity

Start-up 2007

2 x 75% architecture for safe process water supply

Automated process feed water distribution unit

Process feed water supply

PLC control & Operator interface

Membrane Modules

CIP Unit

Filtration. Separation. Solution. SM
Benefits of Pall’s automated separation systems for water/ silicon sludge reclaim:

- **up to 90 % re-use of spent process water as high quality water**
- **reduce wastewater discharge volume**
- **reduce chemical hazards** due to silicon-water interaction by controlled pre-treatment of spent process water
- **collect silicon** debris with low chemical contamination as feedstock for future silicon re-use
- **improve sawing/grinding performance** (surface quality, operational speed) by means of controlled process water specifications
- **reduce machine fouling and uncontrolled sedimentation** in pipes, tanks and sinks

1) RoI due to water re-use typically 0.8 to 2 years
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Crystal Growing

Casting

Shaping

Slicing

WAFERS

mc-Si

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Ar

exhaust gas

exhaust gas

water

slurry

wastewater

(Si + water)

spent slurry

(SiC, PEG, Si,...)
Example 2: Slicing Slurry Treatment

Wafering is slicing of ingots by means of smooth wires in combination with abrasive slurries.

Slicing slurries are typically composed of SiC grains dispersed in polyethylene glycol (PEG).

The slurry is degraded during the operation, accumulating abraded Si fines and thus, must periodically be replaced.

→ slurry is discarded or (better yet) regenerated
Slurry Treatment -- State of the Art

a) **External regeneration**: Phase separation, solids classification, PEG polishing, re-mixing → **high freight charges, sophisticated logistics**

b) **Internal regeneration**: Two-stage classifying solid-liquid separation by centrifuges, re-mixing → **limited regeneration effect, poor PEG clarification, sophisticated control**

c) **Hybrid method**: On-site phase separation, external solids regeneration, on-site PEG clarification → **PEG clarification again critical**

**General problem: Viscosity of PEG (about 50 cP@20°C)**

Pall developed a technology for clarification of spent PEG based on Crossflow Microfiltration, either as a single on-site operation or in combination with SiC/Si classification (patent pending).
PALL Crossflow Membrane Filtration System

PEG filtered  PEG spent
1. PV production should aspire to the **highest environmental standards**.

2. **Proper treatment of waste** is necessary to meet environmental regulations and to limit hazards to health, environment and equipment.

3. The most efficient and economic waste treatment is to avoid waste or to reduce its volume by **converting** its components **into reusable materials**. Water recycling makes **high water quality** affordable.

4. A well-designed **waste treatment** system often pays for itself. Reuse of water, silicon carbide and PEG and – in near future - reuse of silicon are typical examples.

5. Waste should be separated and converted/modified close to where it is generated. Therefore, proper **waste treatment** must be taken into account **early in the factory planning phase**.
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Filtration is needed to retain abrasive, reactive Si/SiO dust
- to protect operators and environment
- to convert waste for acceptable disposal
- to extend vacuum pump life
Conventional Filters:

- Cartridges typically made from thin, pleated fibrous material
- **Oxidizing** Si, SiO grains **burn holes** into filter material
- Frequent loss of filter integrity

→ operators, environment and equipment are no longer protected

- Filters are regenerated off-line (mechanically, manually)

→ manpower needed, filter up-time limited, replacement units necessary, risk to environment and operators
Better solution: Blowback Filtration

Features of the Pall PV Blowback Filtration Unit:

- extremely robust PSS® stainless steel filter elements and housings
- oxidation Si → SiO → SiO₂ contained in filter vessel
- quick cleaning after each cycle by blowback operation
- semi-automated or fully automated as desired
- several years operation without filter change-out

1) CoO model shows RoI in a one to two years

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**Regeneration of Filter**

- Close valve before crystal processing
- Quick opening valve
- Close valves after crystal processing
- Open valve for dust removal

monocrystalline

Filtration. Separation. Solution. SM
With Blow Back Technology the filter cartridge does not need to be changed; it's cleaned automatically or semi-automatically.
FIGURE 3. DIFFERENTIAL PRESSURE VS. TIME

- Reverse Flow Initiation $\Delta P$
- $\Delta P$ Permanent Cake
- Initial $\Delta P$
- Equilibrium $\Delta P$
BLOWBACK - Operation

- Clean cartridge
- Cake formation
- Gas Blowback
- Fines removal
• Large areas of filter cake sometimes slough off at the end of the process.
• Cartridges after process without blowback
Thank you for your kind attention!