AQUEOUS FOAM
DRYING AND CLEANING OF
SEMICONDUCTOR WAFERS
INTRODUCTION:

Business
Slides
References
Information
Philosophy
Surface Treatment of Semiconductor Substrates
U.S. Patent 6,090,217 [drying]
U.S. Patent 6,296,715 [cleaning]
U.S. Patent 6,439,247 [equipment]
plus additional continuations

Taiwan Patent 131,360

Hong Kong Patent, filed, pending

WIPO Patent, filed, pending
(Germany, Great Britain, France, Austria Switzerland, Netherlands)

Aquafoam Inc.
SEMICONDUCTOR WAFER PRODUCTION

Multi-step Chemical Process
Surface Chemistry
Low Chemical Consumption
High Purity Materials
System Delivered Contamination

Opportunities for Improvement

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FOAM PARAMETERS
Expansion Ratio (E/R): 10 to 20
Drain Time = Decomposition Time

FOAM CHARACTERISTICS
Metastable
Immediate Draining - Providing a Liquid Phase Delivery Medium
Collapsing Bubbles Provide Energy Transfer Thixotropic Flow Properties

FOAM ADVANTAGES $\sim 1.0/(E/R)$
Reduce Liquid Phase Volume
Reduce Chemical Usage
Reduce Impurity Exposure
Reduce Costs

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DRYING
Heated rinsing fluid.
Wafers are heated to drying fluid temperature.
Drying vapor is purged by introducing a dry, inert, non-condensable gas (nitrogen) after replacement of rinsing fluid.
Drying vapor is water miscible, saturated, superheated - isopropanol.
Drying fluid forms a minimum boiling water azeotrope.
Drying vapor, non-reactive organic compound, bp < 140°C.
METHOD FOR REMOVING IN A CENTRIFUGE A LIQUID FROM A SURFACE OF A SUBSTRATE

The substrate is brought into contact with a vapor which yields a mixture having a reduced surface tension.

It is PRESUMED that the Marangoni effect applies.

Many alcohols, glycols, aldehydes, esters and ketones can produce a clean surface.
Case A: Polar organic compound is specified.  
Carrier gas is $O_2$, $N_2$, argon, or mixtures.  
Drying fluid, $N_2$, @ $T > 75^\circ C$.

Case B: No polar organic compound.  
Carrier gas is $O_2$, $N_2$, argon, or mixtures.  
Drying fluid, $N_2$, @ $T > 70^\circ C$
Surface Tension of H_2O

From: Handbook of Chemistry & Physics

YIELDUP

\[
\frac{S}{T} = -0.1665(T) + 75.987 \\
R^2 = 0.9981
\]

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WATER MARKS

\[ \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \]
\[ [K = 10^{-14}] \]

\[ \text{Si} + 6\text{OH}^- = \text{SiO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \]
\[ [E_0 = +1.73v] \]
METHOD TO MINIMIZE WATERMARKS ON SILICON SUBSTRATES

Pre-rinse with an organic solvent
Long chain alcohol suggested
PROCESS FOR FABRICATING A SEMICONDUCTOR DEVICE USING RE-IONIZED RINSE WATER

Add carbon dioxide to the rinse water
Post-photoresist strip/immersion
C.S. Pustilnik & G.E. Shannon
Honeywell, Inc.

A PROCESS FOR REMOVING CORROSIVE BY-PRODUCTS FROM A CIRCUIT ASSEMBLY

Add carbon dioxide to the rinse water
Solder flux residues
SEMICONDUCTOR WAFER CLEANING AND RINSING TECHNIQUES USING RE-IONIZED WATER AND TANK OVERFLOW

Add carbon dioxide to the rinse water
Photoresist stripper
CARBON DIOXIDE

Carbon dioxide is a symmetrical linear triatomic molecule. The structure is:

\[ \text{O} = \text{C} = \text{O} \]


At 5-wt. % concentration, for instance, the surface tensions of aqueous carbon dioxide and aqueous isopropyl alcohol are equal: 50 dynes/cm.
CO$_2$ - H$_2$O Solubility

From: Handbook of Chemistry & Physics

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Surface Tension - CO₂ + H₂O

(45°C): \( \frac{S}{T} = -0.0303(P) + 68.427 \)

(25°C): \( \frac{S}{T} = -0.0401(P) + 70.621 \)

(11°C): \( \frac{S}{T} = -0.0549(P) + 73.494 \)

YIELDUP


Surface Tension (dynes/cm)

CO₂ Pressure (psi)

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CARBON DIOXIDE REFERENCES


“Vapor Phase Composition of Carbon Dioxide-Water Mixtures at Various Temperatures and Pressures to 700 Atmospheres.”

“The Binary System Carbon Dioxide-Water Under Pressure.”

“Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide, and Ethane. Evidence for Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase.”

“Structure and Internal Rotation of H₂O-CO₂, HDO-CO₂, and D₂O-CO₂ van der Waals Complexes.”
CARBON DIOXIDE DRYING

REFERENCES

Klaus F. Sylla
Kohlensaeurwerk Deutschland GmbH, Germany
“Process for Drying of Plant or Animal Material”


T.G. Jones and J.C.F. Walker,
“Decompression Drying of Pinus Radiata Sapwood Chips,”

Aquafoam Inc.
Carbon dioxide was shown to be an efficient drying medium for electrical cables – better than dry air.


Nitrous oxide has been used also:

Kenneth L. Miles
US Patent 3,511,671, May 12, 1970
“Process for Dehydration of Foodstuff”
Coan & King, 1971 -

\[ \text{H}_2\text{O}_(g) + \text{CO}_2(g) = \text{Complex}_g \]

Complex is \( \text{H}_2\text{O}:\text{CO}_2 \)

\( \text{CO}_2 \) can remove 5X \( \text{H}_2\text{O} \) vs \( \text{N}_2 \)
PROCESS REQUIREMENT

Remove the complex
- then -
Vent to atmosphere
- or else –
Generate aerosol
WE KNOW

Carbon dioxide dries wafers
Pressure is required
Process sequence is important
CHEMICAL CLEANING

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WASHING METHOD FOR SEMICONDUCTOR DEVICE

Introduction of small bubbles
METHOD OF REMOVING UNDESIRABLE PARTICLES FROM A SURFACE OF A SUBSTRATE

Particles “on” surfaces
Advancing/Retracting Surface Tension Gradients
Effective “zero” Surface Tension
Slow Interface Movement
Bubble Interface Cleans
Patent Example 6 – remember for CMP
SYSTEM FOR SURFACE AND FLUID CLEANING

Explosive decompression.
Japanese Patent 3-30329(A)
February 8, 1991

A. Washitani
Mitsubishi Electric Corp.

SEMICONDUCTOR WAFER CLEANING APPARATUS

Depressurization bubble formation

Aquafoam Inc.
U.S. Patent 5,000,795
March 19, 1991 (Filed 6/89)

B.C. Chung, et al
AT&T Bell Laboratories

SEMICONDUCTOR WAFER CLEANING
METHOD AND APPARATUS

Bubbles – inert gas injection

Aquafoam Inc.
Japanese Patent 3-94428(A)
April 19, 1991

A. Washitani
Mitsubishi Electric Corp.

CLEANING OF
SEMICONDUCTOR WAFER

Depressurization bubble formation

Aquafoam Inc.
Japanese Patent 4-171724A
June 18, 1992

J. Yoshigami (Yugami)
Hitachi Ltd.

METHOD AND APPARATUS
FOR WASHING
SEMICONDUCTOR SUBSTRATE

Introduction of small bubbles

Aquafoam Inc.
U.S. Patent 5,904,156
May 18, 1999 (Filed 9/97)

G.G. Advocate, et al
IBM

DRY FILM RESIST REMOVAL IN THE
PRESENCE OF ELECTROPLATED C4’S

Bubbles, again – inert gas injection
CHEMICAL CLEANING
“T” WAFERS
EXPERIMENTAL
EKC 640
NCW601A
ROOM TEMPERATURE
20 MINUTES
EKC640+3%NCW601A
RT 20 min
BEAKER
Unprocessed
CHEMICAL CLEANING "S" WAFERS
EKC 640
NCW601
ROOM TEMPERATURE
30 MINUTES
EKC 640D
DDBSA(Na⁺)
ROOM TEMPERATURE
5 MINUTES
RINSE
5 MINUTES
EKC640D+3%DDBSA(Na+)
RT 5+rinse+5 min

BEAKER
EKC BHX
DDBSA(Na⁺)
ROOM TEMPERATURE
10 MINUTES
RINSE
10 MINUTES
EKC BHX + 0.5% DDBSA (Na+)
RT 10 + rinse + 10 min

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CONCLUSIONS

Foam:

Delivers liquid phase chemistry to the wafer surface

Provides cleaning equivalent to the liquid phase

Transports displaced material away from wafer
PLEASE NOTE:
This concept applies to all chemical treatments
NON-CHEMICAL CLEANING
MEGASONIC CLEANING

Cavitation ~ Mechanism~ Bubble Formation

Higher Temperatures ~ Lower Surface Tension ~ Better Cleaning

Slow Movement ~ Better Cleaning

Energetics Delivered to Substrate
Foam is Equivalent to Megasonics
MEGASONICS

\[ \text{Work} = 4\pi r^2 \gamma \text{ (ergs)} \]

Monodisperse, \( r = 0.003 \text{ cm} \) & 50 dynes/cm

\[ \text{Work} = 0.0057 \text{ ergs} \]

Assume, 300 mm wafer, 10 minute treatment,
50% drain time = 10 minutes

125,000,000 bubbles

0.071 Joules

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BREAKING BUBBLES

Force = $4\pi r \gamma$ (dynes)

same parameters

Force = 1.88 dynes/bubble

Force = 235,000,000 dynes/wafer

Force = 529 pounds/wafer

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Megasonics @ 300W
Acceleration $\sim 2.5 \times 10^8 \text{ cm/sec}^2$
[Menon, Microcontamination, 8, 29-34(1990)]

Foam
Mass $= \pi r^2 \delta \rho$
$F = MA$

Acceleration $= \frac{\text{Force}}{\text{Mass}} = \frac{4 \gamma}{r \delta \rho}$
[$\gamma = 50 \text{ dynes/cm}, r = 0.003 \text{ cm}, \delta = 0.001 \text{ cm}, \rho = 1.0 \text{ gm/cm}^3$]

$Acceleration = 0.66 \times 10^8 \text{ cm/sec}^2$
Ohio State has developed an ultrasonic ceramic water filter cleaning technique efficient enough to replace chemical cleaning. Ultrasound causes the formation of bubbles in water, which release energy when they burst, leading to the formation of small, powerful jets of water that clean the filters quickly and cheaply.

Chemical Week, May 29, 2002, page 26
A NOVEL CAVITATION PROBE DESIGN AND SOME PRELIMINARY MEASUREMENTS OF ITS APPLICATION TO MEGASONIC CLEANING

G.W. Ferrell, L.A. Crum

Gas injection improves megasonics
NO CLEANING CHEMICAL
DDBSA(Na⁺)+NCW601A
ROOM TEMPERATURE
10 MINUTES
RINSE
10 MINUTES
Surfactants only
RT 10+rinse+10 min
BEAKER
REPEATED
INDEPENDENTLY
NO CLEANING CHEMICAL
ROOM TEMPERATURE
10 MINUTES DDBSA(Na⁺)
RINSE
10 MINUTES NCW601A
“S” WAFER

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CONCLUSION

Collapsing bubble action ONLY can degrade and remove photoresist residue

Surfactant independent
WE KNOW:

Foam bubble interfaces clean
Foam bubbles alone clean
Foam “chemical” bubbles clean

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TWO KINDS OF FOAM
WHAT DOES FOAM REQUIRE?

Fluid, generally water
Reduced surface tension - surfactant
Expansion gas

A TERNARY MIXTURE
CONSIDER CARBON DIOXIDE

Soluble in water
Reduces the surface tension
Produces foam upon depressurization

BINARY MIXTURE

INTERESTING CONCEPT:
Cleaning wafers with only CO₂ and H₂O? Followed directly by drying?

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VIAS & TRENCHES
VIAS & TRENCHES
(decompression cleaning)

Diameter = 0.07µ, Length = 0.7µ, L/D = 10
Volume = \( \frac{3.14}{4} \times 0.07 \times 0.07 \times 0.7 \times 10^{-12} \) cm\(^3\)
Volume = 2.69x10\(^{-15}\) cm\(^3\) or grams (H\(_2\)O)

Gas to fill = 2.69x10\(^{-15}\) / 22400 = 1.20x10\(^{-19}\) moles
CO\(_2\) weight = 44 x 1.20x10\(^{-19}\) = 52.8x10\(^{-19}\) grams

Weight % CO\(_2\) = 100 x 52.8x10\(^{-19}\) / 2.69x10\(^{-15}\)
= 0.528x10\(^{-15}\) / 2.69x10\(^{-15}\)
= 0.2% or 2000 ppm

At T = 25°C, 75 psig, [CO\(_2\)] in H\(_2\)O is 8500 ppm

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METHOD OR REMOVING DEPOSITS FROM SURFACES WITH A GAS AGITATED CLEANING LIQUID

Low boiling organic liquid

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POST ETCH RESIDUE REMOVAL:
NOVEL DRY CLEAN TECHNOLOGY
USING DENSIFIED FLUID CLEANING

D. Beery, K. Reinhardt, et al

IITC, Burlingame, CA
June, 1999

Liquid NH$_3$, 20 dynes/cm, 25 atm
Applied megasonics, also.
WE KNOW:

Decompression cleaning works with:
Ammonia, S/C CO$_2$, Solvents
Pressure not critical

Therefore:
Binary foam decompression
USING AN IMMERSION-TYPE BEOL CLEANER WITH HYDROXYLAMINE AND FLUORINE CHEMISTRIES

J.I. Song and Richard Novak

Micro, April, 2003, pp. 31-36

Uses CO$_2$ injection & megasonics
DIELECTRICS
Organic and/or Porous Cleaning and/or Drying

Aquafoam Inc.
FAB EQUIPMENT CLEANING
KNOWN
Drying with carbon dioxide
Cleaning using a chemical foam medium
Megasonics and foam are equivalent
Cleaning via bubble collapse

PROBABLE
Binary cleaning using CO₂ and H₂O
Soluble expansion gas decompression cleaning
WHAT’S POSSIBLE?

Multiple Applications
Chemical Usage Reduction
Water Usage Reduction
Waste Treatment Reduction
Process Simplifications

Cost Improvement

Aquafoam Inc.
THANK YOU
THE END