Effect Of Organic Contaminants On The Quality Of Ultra-Thin Silicon Oxide Films

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Presentation Outline

- Significance of Organic Contamination
- Research Objectives
- Experimental Approach
- Results and Discussion
  I a. BHT interactions at wafer and effect of moisture
  II Effect on Thin-Gate Oxidation
     a. Effect of Pre-Oxidation Cleans
     b. Effect of Organic Concentration
     c. Effect of Ramp Ambient
- Conclusions and Future work
Ultra-Thin Oxides

Higher speed $\rightarrow$ Higher device density $\rightarrow$ Smaller structures

For transistors:
$I = C_{ox} (V_g - V_{th})^2$
$C_{ox} = e_{ox} A/t_{ox}$
Effects at Low Dielectric Thicknesses

Oxide Thickness

- 5.6 nm
- 3.5 nm
- 3.0 nm
- 2.5 nm

Leakage/Power Increasing Rapidly

Gate Voltage (V)

Gate Current (A/cm²)

Standby Power Consumption (W)
Critical Contaminants

- Particles
- Metals
- Substrate Roughness
- Organics
**Organics and their Consequences**

**Sources**
- Solvents
- Volatiles & Polymers
- Paints, Filters

**Effects**
- Haze Formation
- Hydrophobicity
- Gate Oxide Degradation
- Epitaxial growth deterioration

**Scheme**
- Desorption
- Removal by Reaction
- Incorporation
- Substrate
## Typical Organics and their End-Effects

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Probable Source</th>
<th>Potential Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibutyl Phthalate, Butyl Hydroxy Toluene, DOP</td>
<td>Polymeric materials, filters, paints, floor tiles</td>
<td>Gate oxide degradation</td>
</tr>
<tr>
<td>Amines, Amides</td>
<td>Cleaning solutions, CMP, humidity controllers, epoxies</td>
<td>Affect DUV lithography, increase linewidths</td>
</tr>
<tr>
<td>Organophosphates</td>
<td>HEPA/ULPA filters</td>
<td>Counter doping, voltage shifts</td>
</tr>
<tr>
<td>Silicones</td>
<td>Sealants, caulks</td>
<td>Hydrophobicity, particle formation</td>
</tr>
<tr>
<td>Cresols</td>
<td>Photoresists</td>
<td>Corrosion, hydrophobicity</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Polymers, tubes</td>
<td>Negative effect on wet and dry processes</td>
</tr>
</tbody>
</table>

Ref: [www.balazs.com](http://www.balazs.com)
## Typical Organics on Wafer Surface

<table>
<thead>
<tr>
<th>Low boiling organics</th>
<th>High boiling organics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl Acetate</td>
<td>Caprolactam</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Dodecanoic ester</td>
</tr>
<tr>
<td>2-Ethyl-hexanol</td>
<td>Tris (2-chloroethyl) phosphate</td>
</tr>
<tr>
<td>1-(1-Methylethoxy), 2-propanol</td>
<td>N-butyl benzene sulfonamide</td>
</tr>
<tr>
<td>1,6-Hexanediol</td>
<td>Dibutyl Phthalate</td>
</tr>
</tbody>
</table>

### Trends:

- Low boiling organics adsorb immediately and decrease with time.
- High boiling organics generally increase with time.
Reported Literature On Organics

Kasi et al (IBM) : HF last surface prone to HC contamination, Annealing causes SiC formation and dielectric degradation.

Saga and Hattori (Sony) : $Q_{bd}$ improves by $O_2$ addition. Residual F increases BHT and DBP uptake on HF last.

Guan, Gale and Bennett (Sematech) : C contamination at oxide-poly interface correlates with post-cleaning C on surface.

M. Verghese et al (U of Arizona): $H_2O$ increases IPA uptake on silicon oxide and leads to chemisorption.
Research Objectives

Fundamental study of the fate and the effects of organic contamination

- How organics adhere to surface of wafer?
- What happens to them in high temperature processes?
- What are the consequences?
Model Organics

Iso Propyl Alcohol (IPA)

Used as solvent, drying agent
M.Wt : 60.10
B.P : 83 0C
$\mu$ : 1.84 Debye

Butyl Hydroxy Toluene (BHT)

An antioxidant outgassing from polymeric materials such as plastic wafer carriers, storage boxes, bottles etc
M.Wt : 220.35
B.P : 265.2 0C
$\mu$ : 1.48 Debye
Experimental Setup - I

- All Metal MFCs
- EPSS Tubing, 7 RA
- No Dead Volumes
- Research Grade Gases
- Isotopic Labeling Studies

Detection Capabilities
- Single digit ppt levels !!
- Numerous dedicated analyzers
- Surface Analysis such as Auger

Diagram:
- QMS
- APIMS
- Test Reactor
- Challenge System
- Vent
- Organic/H₂O
- N₂
- O₂
Reactor for Kinetic Studies

Pyrex Reactor

Thermal Well

Wafer Coupons
Experimental Procedure

- Pre-purge & bake: Prepare fresh surface
- Challenge Step 1: H₂O Adsorption
  Equilibrate surface w/ Moisture
- Challenge Step 2: BHT Adsorption
  Equilibrate surface w/ BHT Gas
- Desorption & bake: Determine kinetics & amount adsorbed
BHT Desorption Profiles

- Reactor 154.5 °C and purged at 300 ccm
- Reactor 43 °C and purged at 300 ccm
- Reactor 53 °C and purged at 300 ccm
- Reactor 53 °C and purged at 200 ccm

Graph showing BHT concentration (ppm) over time (min).
Effect of Moisture on BHT adsorption

- 28 ppm BHT at 43 °C in presence of preadsorbed 32 ppb H₂O
- 28 ppm at 43 °C in absence of moisture
## Organic Loading on Surface

<table>
<thead>
<tr>
<th>BHT ppm</th>
<th>H$_2$O ppb</th>
<th>Temp. $^\circ$C</th>
<th># BHT/cm$^2$</th>
<th># H$_2$O/cm$^2$</th>
<th># BHT per H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>0</td>
<td>43</td>
<td>3.4 E14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>32</td>
<td>43</td>
<td>5.0 E14</td>
<td>3.5 E13</td>
<td>2.3</td>
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<tr>
<td>28</td>
<td>0</td>
<td>105</td>
<td>2.5 E14</td>
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<tr>
<td>28</td>
<td>32</td>
<td>105</td>
<td>3.7 E14</td>
<td>2.5 E13</td>
<td>2.3</td>
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<tr>
<td>28</td>
<td>0</td>
<td>150</td>
<td>2.1E14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>32</td>
<td>150</td>
<td>3.0 E14</td>
<td>2.1 E13</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Experimental Procedure

- **Pre-Oxidation**
- **Cleaning**
- **Pre-Purge**
- **And Bake**
- **Adsorption**
- **Desorption**

T = 20 °C
Ramp 20 °C/min
Oxidation 800 °C
Ramp Down 5 °C/min
Experimental Response

75 ppm IPA challenge, Ramp up to 800 °C at 20 °C/min in N₂

**Adsorption**

- HF last
- SC1 last (hydrophilic surface)

**Desorption**

- SC1 last
- HF last (hydrophobic surface)
50 ppm IPA Challenge on SC1 last wafers
Effect of Cleans and Organic Concentration

Carbon Atoms/cm² x 10¹⁵

- Adsorbed
- Retained

SC1  HF  SC1  HF  SC1  HF

Last Clean
IPA Conc.

- 25 ppm
- 50 ppm
- 75 ppm
Effect of Oxygen during Ramp-Up

![Graph showing the effect of oxygen during ramp-up. The x-axis represents different cleaning procedures (SC1, SC1 HF, HF, HF) and the y-axis represents carbon atoms/cm² x 10^15. The graph compares adsorbed and retained carbon under ambient conditions with N₂ and O₂ at 0.5% concentrations.]

- **Adsorbed**
  - N₂
  - O₂ 0.5%

- **Retained**

**Carbon**

**Adsorbed**

**Retained**

**Last Clean**

IPD Concentration

- 50 ppm
- 75 ppm
Carbon Incorporation in Substrate

% of Adsorbed Carbon Retained in Surface

IPA Concentration (ppm)

25 50 75

Last Clean
Ambient

HF
N₂

SC1
N₂

HF
0.5 %O₂

SC1
0.5 %O₂
Effect on Gate Oxide Integrity

Defect Density cm$^{-2}$

- N$_2$ ambient
- 1% O$_2$ ambient

Contamination:
- None
- BHT
- HF

Last Clean:
- SPM
- None

Results show a significant effect on gate oxide integrity under different conditions.
Model for Oxidation/Incorporation of Organics

Species
- Gas Phase Organic ($C_{org}$)
- Adsorbed Organic (R)
- Oxygen ($O_2$)
- Oxidation Product (P)
- Incorporated Carbon (I)

Reactions

$$C_{org} + X \xrightleftharpoons[k_d]{k_a} R$$

$$R + O_2 \xrightarrow{k_{ox}} P + X$$

$$R \xrightarrow{k_{inc}} I$$
Fit of Model to Data

![Graph showing the fit of a model to data with dimensionless concentration and dimensionless time axes. The graph compares data points to model values for nitrogen ambient (N₂ ambient).]
<table>
<thead>
<tr>
<th>Process</th>
<th>Parameter</th>
<th>Symbol</th>
<th>N&lt;sub&gt;2&lt;/sub&gt; ambient Ramp</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; ambient Ramp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Rate constant @ 20ºC</td>
<td>k&lt;sub&gt;a&lt;/sub&gt; (cm/min)</td>
<td>5.8E-02</td>
<td>3.7E-03</td>
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<tr>
<td></td>
<td>Activation energy</td>
<td>E&lt;sub&gt;a&lt;/sub&gt; (kJ/mol)</td>
<td>18.9</td>
<td>18.9</td>
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<tr>
<td>Desorption</td>
<td>Rate constant @ 20ºC</td>
<td>k&lt;sub&gt;d&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>1.5E-01</td>
<td>1.7E-02</td>
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<tr>
<td></td>
<td>Activation energy</td>
<td>E&lt;sub&gt;d&lt;/sub&gt; (kJ/mol)</td>
<td>6.2</td>
<td>6.2</td>
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<tr>
<td>Incorporation</td>
<td>Rate constant @ 700ºC</td>
<td>k&lt;sub&gt;inc&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>4.4E-02</td>
<td>1.5E-02</td>
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<tr>
<td></td>
<td>Activation energy</td>
<td>E&lt;sub&gt;inc&lt;/sub&gt; (kJ/mol)</td>
<td>77.9</td>
<td>77.9</td>
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<tr>
<td>Surface oxidation</td>
<td>Rate constant @ 20ºC</td>
<td>k&lt;sub&gt;s&lt;/sub&gt; (cm/min)</td>
<td>1.2E-14</td>
<td></td>
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<tr>
<td></td>
<td>Activation energy</td>
<td>E&lt;sub&gt;s&lt;/sub&gt; (kJ/mol)</td>
<td>88.4</td>
<td></td>
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</table>
CONCLUSIONS

• Organic contamination affects interfacial and thin film properties in gate oxidation and epitaxial growth.

• Moisture enhances adsorption of polar organics such as BHT, IPA and forms chemisorbed species at high temperatures.

• A novel method is developed to detect the kinetics and mechanism of the removal/retention of trace organic contamination.

• SC1 last (hydrophilic) surface adsorbs greater amounts of IPA compared with HF last (hydrophobic) surface. However, a greater fraction of the adsorbed organic gets incorporated in the hydrophobic surface.
CONCLUSIONS (cont.)

• As IPA concentration increases, carbon incorporation in the substrate increases.

• Oxygen in ramp-up decreases the amount of carbon incorporation and the resulting defects; however, it appears to cause other defects, possibly due to immobilization of certain inorganic impurities.

• A model is developed and validated to simulate the simultaneous removal and incorporation of organic impurities during desorption or thermal oxidation.
Future Work

- Study other factors in oxidation
- Complete experiments with BHT
- Investigate effects of DOP
- Continue refining the models
- Organics on promising Alternate Gate Dielectrics