J. J. Thompson’s Ghost: Modern SIMS developments enable interface engineering at the technology forefront

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How can SIMS analyze very small features?
Diffusion of Implanted Cr in Si

as-implanted

after anneal

SIMS

TEM

H. Francois
St. Cyr, et al.
Univ. Central Florida

CAMECA IMS-3f (60µm analyzed diameter)
Nonuniform Distribution

Cr after anneal at 0.2µm on previous slide is uniform on 60µm scale (variations <1µm)

Species not uniformly distributed
Semiconductor Technology Analyses

Technology Calendar
2014 14nm
2017 10nm
2018 7nm
2020 5nm (15 – 20 atoms)
Average over repeating structure

- FinFET too small to analyze directly, but present in large array
- Planarize with poly-Si or SiO$_2$ and include large number of FinFETs in analysis area.
- Use TEM analysis to measure geometry and make it possible to quantify the results.
Scary Thought: Quantification of Organic Materials by Ion Implantation

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Quantification Using Ion Implantation

- Quantification of multiple elements in semiconductors

- Quantification of periodic table for variety of matrices

- BF$_2$ in photoresist

- >40 elements in polymethylmethacrylate, polyimide, epoxy
Implants in PMMA

Quantify Organic Species in Organic Substrate

- Can organic species be quantified in organic material?
- Cannot ion implant the species – will disintegrate at surface
- If organic species contains element not present in substrate, may be possible to quantify with ion implant of that element
- Insecticides used on mosquito netting used as example
Mosquito on Mosquito Net

- Live mosquito (*Anopheles gambiae*, female) on mosquito net
- Insecticide on the fiber surface is available for uptake by mosquitoes

Photo by James Gathany, CDC
Mosquito Nets and Insecticide

- Over 1 billion mosquito nets deployed: primary factor in prevention of malaria deaths

- Insecticide typically incorporated in the netting but no satisfactory method to measure insecticide on the netting

- Standard chemical analysis with solvent extraction and chromatography can measure total insecticide but not bioavailable fraction (A. Tami, et al., Malaria Journal 3, 19 (2004))

- Mosquito bioassays measure ability of netting to kill mosquitoes. Measurements are error prone, time consuming, and require rearing facility to produce mosquitoes. (WHO Cone Bioassays, World Health Organization (2013) p. 8)
Successful Method with ToF-SIMS Analysis

- Quantification of Permethrin insecticide incorporated in fiber
- Chemical mapping of insecticide on net surface

Insecticide: Permethrin
C$_{21}$H$_{20}$Cl$_2$O$_3$

Olyset net: HDPE (High Density Polyethylene)

TOF SIMS Surface Spectrum of Net Fiber

- High intensity of Cl observed from Olyset fiber surface
- C$_3$H$_2^-$ and C$_4$H$_3^-$ are fragments ions of polyethylene
SIMS depth profile of $^{35}$Cl Ion Implants

$^{35}$Cl 140 keV 5x10$^{15}$ atoms/cm$^2$  
Cs$^+$ sputter beam

Cl concentration (atoms/cm$^3$)

Depth (nm)

HDPE (thin sheet)

35Cl implanted Olyset Net Fiber

- 3:1 ratio of Cl to 37Cl in the bulk of the fiber due to Cl natural abundance
- Detection limit of Cl in Olyset net: 3E19 atoms/cm³
- Matrix signal and Cl peak concentration similar to thick HDPE
- Discontinuity of matrix species C_7^- at implant penetration range: Implant probably changes HDPE structure and affects secondary ion yield

Low and High Surface Insecticide

**Olyset mosquito netting**

- Cl concentration in bulk is very similar for both high and low surface insecticide area
- Aggregation of insecticide appears to be in first 2 µm from surface.
Br Based Insecticide Deltamethrin

C$_{22}$H$_{19}$Br$_2$NO$_3$

Successful quantification of deltamethrin on netting with Br ion implant

SIMS Depth Profiles of Br Ion Implants

$^{79}$Br 180 keV $2 \times 10^{15}$ atoms/cm$^2$ into Si and sheet HDPE

Deltamethrin incorporated in HDPE NetProtect netting

Depth Profiles in Unimplanted Netprotect Fibers

a) Br conc. vs. depth       b) Deltamethrin wt% vs. depth

Pyriproxifen Chemical Structure

Pyriproxifen used as insect growth inhibitor

\[ \text{C}_{20}\text{H}_{19}\text{NO}_3 \]

N not present in mosquito netting

Mosquitoes developing resistance to permethrin
Study in progress to combine pyriproxifen and permethrin
## SIMS Analysis Conditions

ION-TOF TOF-SIMS V

<table>
<thead>
<tr>
<th></th>
<th>Beam</th>
<th>Current</th>
<th>Energy</th>
<th>Raster (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter</td>
<td>Cs⁺</td>
<td>20nA</td>
<td>10keV</td>
<td>120 x 120</td>
</tr>
<tr>
<td>Analyze</td>
<td>Bi₃⁺</td>
<td>0.3pA</td>
<td>25keV</td>
<td>50 x 50</td>
</tr>
</tbody>
</table>
Pyriproxifen Negative Ion Mass Spectrum

Pyriproxifen

\[ \text{Bi}_3^+ \text{ analysis} \]

\[ \begin{align*}
26, & \text{CN}^- \\
42, & \text{CNO}^- \\
50, & \text{C}_3\text{N}^- \\
93, & \text{C}_6\text{H}_5\text{O}^- \\
108, & \text{C}_6\text{H}_4\text{O}_2^- \\
185, & \text{C}_{12}\text{H}_9\text{O}_2^- \\
\end{align*} \]
N Ion Implants in Si used to Check Dose

$^{14}\text{N} \ 25\text{keV} \ 4 \times 10^{15} \ \text{atoms/cm}^2$

$^{14}\text{N} \ 50\text{keV} \ 5 \times 10^{15} \ \text{atoms/cm}^2$

Implanted at same time as netting

Used to check dose: RSFs within 4%
Depth Profile of N Implanted in HDPE

$^{14}\text{N}$ 25keV $4 \times 10^{15}$ atoms/cm$^2$

Only about 1 order magnitude dynamic range

Suspect some N present in HDPE

Need to use molecular species to analyze N

Detection limit $\sim 2 \times 10^{19}$ atoms/cm$^3$
## Detection Limit vs. Insecticide Concentration

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>Amount in Netting (wt%)</th>
<th>HDPE Detection limit (at/cm³)</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permethrin</td>
<td>2</td>
<td>$1 \times 10^{18}$</td>
<td>0.05</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>0.2</td>
<td>$1 \times 10^{18}$</td>
<td>0.05</td>
</tr>
<tr>
<td>Pyriproxifen</td>
<td>1</td>
<td>$2 \times 10^{19}$</td>
<td>1</td>
</tr>
</tbody>
</table>

N detection limit ~ amount expected in netting
Quantify N in Si Using Rare Isotope

$^{15}\text{N}$ 150keV $2 \times 10^{15}$ atoms/cm$^2$

Detection limit $\sim 2 \times 10^{17}$ atoms/cm$^3$

Unless insecticide made with $^{15}\text{N}$
effective detection limit factor
of 100 higher

$^{14}\text{N}$ 99.63%  
$^{15}\text{N}$ 0.37%
Apply Method to a Medication: Amiodarone

Amiodarone
Chemical Structure

NanoSIMS 50 and BSE images

Can we implant $^{127}$I to quantify?

Cs and Ar GCIB sputtering of Cl implanted HDPE

$^{35}\text{Cl}$ 140keV 5x10$^{15}$ atoms/cm$^2$

Matrix changes in implanted region complicate Ar GCIB results
Summary

• Ion implantation quantification of organic species successful for Cl and Br based insecticides used in mosquito netting

• N ion implantation needs improved detection limit to quantify pyriproxifen insecticide

• Implant damage affects Ar GCIB secondary ion yields but unimplanted samples show useful results.

• May be able to apply quantification with Cs+ sputter beam to analysis with Ar GCIB. Need constant level in substrate to create secondary standard.