Tin ions: Spectroscopy and Interactions

Ronnie Hoekstra
outline

introduction on lithography

advanced research center for nanolithography

Fundamental physics aspects of EUV generation

(propulsion and deformation of tin droplets)

tin ion spectroscopy for diagnostics

energetic-ion emission and plasma-wall interactions
number of transistors in *affordable* CPU doubles every two years!!!
.. driving miniaturization and innovation

wavelength: 193nm 13.5nm

feature size (nm)
Lithography is the step where a pattern is printed.

- Slicing
- Polishing
- Material deposition or modification
- Photoresist coating
- Exposure (step and scan)
- Developing and baking
- Packaging
- Separation
- Completed wafer
- Removing the photoresist
- Etching and ion implantation

Repeat 40 ~ 80 times to build 3 dimensional structure.
3 dimensional structure
elements of nanolithography tools
Moore’s second or Rock’s law

law 1: number of transistors in affordable CPU doubles every two years

law 2: costs of a semiconductor chip fabrication line double every 4 years

→ costs per transistor decrease

Samsung’s 2015 DRAM plant investment 14 B$
focus: fundamental and applied physics in the context of technologies for (nano)-lithography, primarily for the semiconductor industry

Concept: 2013 by ASML

Partners: ASML and FOM/NWO, UvA, VU

Start: Jan. 2014

Financial: M€ 7 /yr base funding; M€ 5 start up Amsterdam + Noord-Holland

Size: Currently 75 fte (84 ‘faces’); growing to ~100 fte

Location: Science Park, Amsterdam

Housing: temporary office + lab buildings – long-term housing now

Facilities/support: shared with AMOLF

www.arcnl.nl
arcnlsecretariaat@arcnl.nl

https://twitter.com/nanolithography
long-term housing: Matrix VII

January 2019
moved to new building
restart experiments April

from artist impression to realization =>
scientific program

SOURCE
EUV Plasma Processes
Ronnie Hoekstra, Wim Ubachs & Oscar Versolato
‘EUV Plasma Modeling’ vacancy

METROLOGY
EUV Generation & Imaging
Stefan Witte & Kjeld Eikema
EUV Targets
Paul Planken

SCANNER
Nanolayers
Joost Frenken
Contact Dynamics
Steve Franklin

PROCESSES
Nanophotochemistry
Fred Brouwer
EUV Photoresists
Sonia Castellanos

EXTRA
AMOLF-ARCNL Projects
Coord.: Huib Bakker
Accelerator-based EUV
Ronnie Hoekstra

Materials & Surface Science for EUVL vacancy

HHG and EUV Science Group
Peter Kraus

INTEGRATION
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A. Klein (University of Twente)
S. Reijers (University of Twente)
A. Ryabtsev (ISAN)
M. Basko (KIAM, ISAN)
D. Kim (ISAN)
A. Borschevsky (University of Groningen)
J. Berengut (UNSW Australia)
E. Kahl (UNSW Australia)
M. Bayraktar (University of Twente)
F. Bijkerk (University of Twente)
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J. Colgan (LANL)
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L. Mendez (UAM Madrid)
I. Rabada (UAM Madrid)

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Mart Johan Deuzeman (PhD)
Subam Rai (PhD)
Bo Liu (PhD)
Zoi Bouza (PhD)
Lucas Poirier (PhD)
Lars Behnke (PhD)
............ (2x PhD)
Alex Bayerle (postdoc)
Dmitry Kurilovich (postdoc)
............(postdoc)
John Sheil (postdoc/tenure track)
Laurens van Buuren (technician)
Wim Ubachs (group leader)
Oscar Versolato (group leader)
Ronnie Hoekstra (group leader)

ARCNL EUV G&I team:
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Randy Meijer (PhD)
Stefan Witte (group leader)

ASML team
Harry Kreuwel
Andrei Yakunin
Konstantin Tsigutkin
Alexandr Bratchenia
Adam Lassise
Wim van der Zande
Jayson Stewart
Andrew Laforge
Alex Schafgans
Rob Rafac
Igor Fomenkov ... a.o.

Research team
laser produced plasma for EUV sources

why tin? Sn ions (7-14+) all radiate around 13.5 nm

why 13.5 nm? EUV optics - MoSi mirrors
the plasma landscape

Plasma density \( n (m^{-3}) \)

Temperature (K)

solids, liquids and gases; too cool and dense for classical plasmas to exist

nebula

magnetic fusion reactor

inertial confinement fusion

solar core

aurora

neon sign

solar corona

lightning

plasma EUV source

flames

NEON

NEON

flames

lightning

plasma EUV source

solar core

magnetic fusion reactor

inertial confinement fusion

solar corona

neon sign

aurora

nebula

Plasma density \( m^{-3} \)

temperature (K)
Just do it, buy spectrometers and monitor the spectrum. But..

• most transitions in low-, medium charged tin ions (q<20+) are unknown.
• cross section / reaction rates for excitation are totally unknown.
• the dependence on the “environment” is unknown.
• ........

fundamental atomic data is called for!
optical spectra of low-charge state Sn
normalized, relative line intensity

$6s \ ^2S_{1/2} - 6p \ ^2P_{1/2}$

Intensity ($10^3$ counts)

- 0.5mJ
- 2mJ
- 10mJ
- 30mJ
- 100mJ
- 370mJ

Normalized intensity

Wavelength (nm)

420 421 422 423
line intensities

<table>
<thead>
<tr>
<th></th>
<th>Sn I</th>
<th>Sn II</th>
<th>Sn III</th>
<th>Sn IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mJ</td>
<td>5p² ¹S₀ – 5p6s ¹P₁</td>
<td>5d²D₅/₂ – 4f²F₇/₂</td>
<td>6s ¹S₀ – 6p ¹P₁</td>
<td>6s²S₁/₂ – 6p²P₁/₂</td>
</tr>
<tr>
<td>2 mJ</td>
<td>452</td>
<td>580</td>
<td>522</td>
<td>421</td>
</tr>
<tr>
<td>10 mJ</td>
<td>453</td>
<td>580</td>
<td>523</td>
<td>422</td>
</tr>
<tr>
<td>30 mJ</td>
<td>452</td>
<td>580</td>
<td>522</td>
<td>421</td>
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<td>100 mJ</td>
<td>453</td>
<td>580</td>
<td>523</td>
<td>422</td>
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<tr>
<td>370 mJ</td>
<td>452</td>
<td>580</td>
<td>522</td>
<td>421</td>
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Lines:

<table>
<thead>
<tr>
<th></th>
<th># lines</th>
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<tbody>
<tr>
<td>SnI</td>
<td>35</td>
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<tr>
<td>SnII</td>
<td>39</td>
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<tr>
<td>SnIII</td>
<td>76</td>
</tr>
<tr>
<td>SnIV</td>
<td>55</td>
</tr>
<tr>
<td>SnV</td>
<td>86</td>
</tr>
</tbody>
</table>
most simple tin ion
one electron outside a closed 4d^{10} shell

existing information:
NIST database: Moore 1958
ISAN EUV spectroscopy: Ryabtsev et al, 2006

4f^2F term most studied by theory
inverted, narrow fine structure
Ag, Cd, In, SnIV,
Sb, Te, I, Xe ... ....

[ground levels: j = l + \frac{1}{2} and j = l - \frac{1}{2} ]

of the 55 SnIV lines observed only 20 can be linked to the known levels
level predictions:
• COWAN code (Ryabtsev)
• FSCC - Fock Space CoupledCluster (Borschevsky)

“issue”: High-resolution in the optical

<table>
<thead>
<tr>
<th>uncertainty</th>
<th>$\Delta E$ cm$^{-1}$</th>
<th>$\Delta \lambda$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%</td>
<td>~250</td>
<td>~5</td>
</tr>
</tbody>
</table>

Quantum defect method (Edlen (1964)):

binding energy w.r.t. ionization level

$$E_{nl} = -R \frac{Z^2}{(n^*)^2} = -R \frac{Z^2}{(n - \delta_l)^2}$$

Taylor expansion:

$$\delta_l = a \left( \frac{1}{(n^*)^2} \right) + b \left( \frac{1}{(n^*)^2} \right)^2 + \ldots.$$
Quantum defect scaling

\[ \text{Sn}^{3+}: [\text{Kr}]4d^{10}nl \text{ core is } d^{10} \quad l_{\text{core}} = "d" \]

\[ l \leq l_{\text{core}} \]

\[ IP = 328920 \text{ cm}^{-1} \]
\[ IP_{\text{NIST}} = 328550 \text{ cm}^{-1} \]

\[ n = 5 \]
\[ n = 6 \]
\[ n = 7 \]

\[ n = 4 \]

\[ n = 5 \]

\[ n = 6 \]

\[ 1/n^2 \]

Graphs showing quantum defect scaling for different values of \( n \) and \( l \) levels.
mainly shift of $5d^2 D_{3/2}^{1/2}$ due to configuration interaction with $4d^9 5s^2 2D_{5/2}^{3/2} \sim 600 \text{ cm}^{-1}$

$$\Psi_{5d} = a \phi_{5d} + b \phi_{4d^9 5s^2}$$

<table>
<thead>
<tr>
<th>5d $^2 D_J$ fine structure</th>
<th>$\Delta E_{FS} \text{ [cm}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST database</td>
<td>106</td>
</tr>
<tr>
<td>RMBPT*</td>
<td>745</td>
</tr>
<tr>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>105</td>
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<tr>
<td>FSCC</td>
<td>735</td>
</tr>
<tr>
<td>(FSCC)+ MBPT – CI</td>
<td>120</td>
</tr>
</tbody>
</table>

### the inverted fine structure of nf $^2F$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{FS}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4f $^2F_j$</strong></td>
<td></td>
</tr>
<tr>
<td>NIST database</td>
<td>-61</td>
</tr>
<tr>
<td>RMBPT*</td>
<td>-74</td>
</tr>
<tr>
<td>RPTMP#</td>
<td>-60</td>
</tr>
<tr>
<td>MCDHF$\dagger$</td>
<td>-71</td>
</tr>
<tr>
<td>ARCNL experiment</td>
<td>-60</td>
</tr>
<tr>
<td>FSCC</td>
<td>-62</td>
</tr>
<tr>
<td>MBPT</td>
<td>-62</td>
</tr>
<tr>
<td><strong>5f $^2F_j$</strong></td>
<td></td>
</tr>
<tr>
<td>RMBPT*</td>
<td>-44</td>
</tr>
<tr>
<td>RPTMP#</td>
<td>-22</td>
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<tr>
<td>ARCNL experiment</td>
<td>-308</td>
</tr>
<tr>
<td>FSCC</td>
<td>-39</td>
</tr>
<tr>
<td>(FSCC)+ MBPT+CI</td>
<td>-412</td>
</tr>
</tbody>
</table>

# RPTMP: Ivanova, ANDT, 97, 1 (2011)
$\dagger$ MCDHF: Grumer et al, PRA 89, 062511 (2014)
EUV emission

LPP EUV spectrum

energetic out of band EUV
Sn^{15+} ................................ Sn^{8+}

13.5 nm in band EUV
Sn^{8-14+} ions
atomic origins of EUV light
detailed example: Sn^{10+} (SnXI)
EBIT group:
- J. Crespo López-Urrutia
- H. Bekker
- S. Dobrodey
- A. Windberger

electron impact excitation of trapped Sn ions in charge states 7 - 20+

**theory**

ISAN Troitsk
- A. Ryabtsev

School of Chemistry
- E. Eliav and U. Kaldor

Van Swinderen Institute
- A. Borschevsky

School of Physics
- J. Berengut and E. Kahl
charge state identification

the tin serendipidity

\[4p^6 \, 4d^m - 4p^6 \, 4d^{m-1} \, 5p + 4p^6 \, 4d^{m-1} \, 4f + 4p^5 \, 4d^{m+1}\]
“forbidden” transitions

EUV

ground level transitions

charge state specific ground level energies benchmarks to theory

EUV emission

LPP EUV spectrum

energetic out of band EUV
Sn$^{15+}$ .................. Sn$^{8+}$

13.5 nm in band EUV
Sn$^{8-14+}$ ions
Sn\textsuperscript{8+} ... Sn\textsuperscript{15+} transitions

energetic out-of-band radiation a diagnostics of in-band EUV emission

energetic ion ejection

energetic tin “bullets” damage plasma facing material
pragmatic solution: hydrogen stopping gas

Open Questions:
• what are the actual damage thresholds?
• what is the charge state distribution?
• what is the ionic-energy spectrum?
• what do the ions do to H$_2$ gas and vice versa?
• ..........
• how are the ions exactly generated?
### Sn Ion Detectors

<table>
<thead>
<tr>
<th>Open Faraday Cups</th>
<th>current measurement</th>
<th>energy distribution from ToF</th>
<th>no charge state resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retarding Field FC</td>
<td>current measurement</td>
<td>energy distribution from ToF</td>
<td>charge state information from retarding fields</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>charge state resolution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>grids in ion path</td>
<td></td>
</tr>
<tr>
<td>Electrostatic Analyser</td>
<td>direct energy measurement (E/q)</td>
<td>full charge state resolution via ToF</td>
<td></td>
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<tr>
<td></td>
<td>dynamic range - space charge effects</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ion detection efficiency</td>
<td>scan energy</td>
<td></td>
</tr>
<tr>
<td>Thomson Parabola</td>
<td>simultaneous energy and charge state measurement</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>absolute ion detection efficiencies</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ion trajectories</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
experimental layout of ion measurements

- $U_{ESA}/2$
- $-U_{ESA}/2$
- $A_{in}$
- $A_{out}$
- $A_{CEM}$
- $-2.1 \text{kV}$
- CEM signal

TOF Sn ion signals at different ESA voltages:

- 5+
- 4+
- 3+
- 2+
- 1+

H$_2$ 1064-nm laser, 10 ns

30-µm Sn droplet

Time →
detection of tin ions

Channel electron multiplier and channelplate efficiencies for detecting positive ions

M. Krames, J. Zirbel, M. Thomason, and R. D. Dubois
REVIEW OF SCIENTIFIC INSTRUMENTS 76, 095005 (2005)

Channeltron 2

Relative detection efficiency

Impact energy (eV)

Sn$^{Z+}$ ions

- Z = 1
- Z = 2
- Z = 3
- Z = 4

potential electron emission

Auger neutralization

Auger deexcitation

Sn ions on SiO$_2$

W $\sim$ 9 eV

$E_{ion}$

1+ - 7 eV $\gamma_{pot} = 0$

2+ - 14 eV $\gamma_{pot} = 0$

3+ - 28 eV $\gamma_{pot} = "small"$

order 0.1
comparison FC and ESA
effect of $\text{H}_2$ buffer gas on ion distribution

background $10^{-6}$ mbar

2$x10^{-4}$ mbar $\text{H}_2$
1 keV Sn ion charge state distributions

\[ \frac{dN_q}{dx} = \sigma_{q+1} n_{H_2} N_{q+1} - \sigma_q n_{H_2} N_q \]
overbarrier estimate of CX cross sections

\[ Sn^{q^+} + H_2 \rightarrow Sn^{(q-1)^+} + H_2^+ \]

\[ R_{capt} = \frac{1 + 2\sqrt{q}}{l} \]

\[ \sigma = \pi R_{capt}^2 \]

\[ E_{final} = l + \frac{(q-1)}{R_{capt}} \]

\[ l_{H_2} = 16.1 \text{ eV} \]

\[ A^{q^+} + B \rightarrow A^{(q-2)^{++}} + B^{2+} \rightarrow A^{(q-1)^{++}} + B^{2+} + e \]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Target</th>
<th>Quasi Molecule</th>
<th>Target</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(^{1+})</td>
<td>23</td>
<td>1</td>
<td>Sn(^{2+})</td>
<td>37</td>
</tr>
<tr>
<td>Sn(^{3+})</td>
<td>50</td>
<td></td>
<td>Sn(^{4+})</td>
<td>63</td>
</tr>
<tr>
<td>Sn(^{5+})</td>
<td>75</td>
<td></td>
<td>Sn(^{6+})</td>
<td>87</td>
</tr>
<tr>
<td>Sn(^{7+})</td>
<td>99</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>OvB</th>
<th>OvB adj</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-16} \text{ cm}^2</td>
<td></td>
</tr>
</tbody>
</table>

- \( q^+ \) is the ion
- \( (q-1)^+ \) is the quasi-molecule
- \( A^{(q-2)^{++}} + B^{2+} \rightarrow A^{(q-1)^{++}} + B^{2+} + e \)
Luis Mendez and Ismanuel Rabadan

\[ \sigma (\text{A}^2) \]

\[ \text{energy (keV)} \]

\[ \text{Sn}^{3+} + \text{H}_2 \rightarrow \text{Sn}^{2+} + \text{H}_2^+ \]

\[ \text{Sn}^{2+} + \text{H}_2 \rightarrow \text{Sn}^+ + \text{H}_2^+ \]
1 keV Sn ion charge state distributions

<table>
<thead>
<tr>
<th>OvB</th>
<th>adj.</th>
<th>M&amp;R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-16}$ cm$^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn$^{1+}$</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>Sn$^{2+}$</td>
<td>37</td>
<td>10</td>
</tr>
<tr>
<td>Sn$^{3+}$</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>Sn$^{4+}$</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>Sn$^{5+}$</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Sn$^{6+}$</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Sn$^{7+}$</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

- Background: $10^{-6}$ mbar
- 2x$10^{-5}$ mbar H$_2$
- 2x$10^{-4}$ mbar H$_2$
- 6x$10^{-4}$ mbar H$_2$
energy, mass and charge state selected Sn^{q+} ion beam facility with a full suite of auxiliary analysis equipment
type of interactions

Sn – Mo
SRIM stopping powers
electronic stopping
nuclear stopping

LPP-ejected tin ions
typical spectra 14 keV Sn$^{2+}$ - Mo

$\Phi$ = 5°

$\Theta = 10°$
$\Theta = 20°$
$\Theta = 30°$
$\Theta = 45°$

$\Psi = 5°$
$\Psi = 10°$
$\Psi = 25°$
$\Psi = 30°$

$\Phi$ = 30°
14 keV Sn\textsuperscript{2+} - Mo: SRIM vs experiment

![Graphs showing yield vs energy for different angles (15-30, 15-45, 30-60).]

- Single binary collision
- Quasi-single collision
- Quasi-double collision
## tests of “SRIM – experiment difference”

<table>
<thead>
<tr>
<th><strong>original experiment: 14 keV Sn(^{2+}) - Mo</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>incoming charge state</td>
</tr>
<tr>
<td>energy</td>
</tr>
<tr>
<td>ion species</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>outgoing charge state</td>
</tr>
<tr>
<td>target</td>
</tr>
</tbody>
</table>
first data 14 keV Sn$^{2+}$ - Ru

(a) $\varphi = 10^\circ$ and $\theta = 25^\circ$.

(b) $\varphi = 15^\circ$ and $\theta = 25^\circ$.

(c) $\varphi = 15^\circ$ and $\theta = 30^\circ$.

(d) $\varphi = 15^\circ$ and $\theta = 35^\circ$.

(e) $\varphi = 15^\circ$ and $\theta = 45^\circ$.

(f) $\varphi = 30^\circ$ and $\theta = 60^\circ$. 
scattering potentials

\[ U = \frac{Z_1 Z_2}{r} \chi \left( \frac{r}{a} \right) \]

Bohr
\[ \chi = e^{-r/a} \]
\[ a = \frac{1}{\left( \frac{Z_1^{2/3}}{3} + \frac{Z_2^{2/3}}{3} \right)^{1/2}} \]

TFM-F
\[ \chi = 0.35e^{-3r/a} \]
\[ + 0.55e^{-1.2r/a} \]
\[ + 0.1e^{-6r/a} \]
\[ a = \frac{0.8853}{\left( \frac{Z_1^{2/3}}{3} + \frac{Z_2^{2/3}}{3} \right)^{1/2}} \]

ZBL (SRIM)
\[ \chi = 0.1818e^{-3.2r/a} \]
\[ + 0.5099e^{-0.9423/a} \]
\[ + 0.2802e^{-0.4028r/a} \]
\[ + 0.2817e^{-0.2016r/a} \]
\[ a = \frac{0.8853}{Z_1^{0.23} + Z_2^{0.23}} \]

next step: SRIM → SDTrimSP-2D
“ARCNL’s” tin ion spectroscopy and interactions program

- EUV source plasma conditions and densities not to dissimilar from tokamaks
- **Spectroscopy:**
  - well underway
  - strong collaboration with theory (structure)/ opacity investigations starting
  - experiments on EUV source plasma and external facilities
- ZERNIKELEIF facility for energy, mass, and charge state selected beams of Sn ions operational
- **Interactions**
  - First scattering experiments on Mo and Ru surfaces hint at issues with SRIM
  - Set-up for CX in H2 is being commissioned