Characterization of Ionic Liquid Ion Sources for Focused Ion Beam Applications

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Outline

Motivation
- Focused Ion Beam (FIB) Technology Overview
- Current technologies
- Motivation for Ionic Liquid Ion Sources (ILIS) and previous work

Research Approach: properties of ILIS relevant for FIB

Results
- Emission Characterization via Beam Visualization
- Neutral Particle Population

Summary and Conclusions
Future Work
Focused Ion Beam Technology (FIB) and its applications

In FIB, a beam of ions is focused to nanometer dimensions (probe size).

Applications in semiconductor industry, MEMS and biological studies:
- Localized milling
- Spectrometry
- Microscopy

Integrated circuit connections exposed by FIB erosion [2]

Intel Atom Processor [1]
Ion sources for FIB: requirements

- **Require high brightness**
  \[ \beta = \frac{4I_b}{(\pi \alpha_0 D)^2} \]
  - Current \( I_b \)
  - Aperture \( \alpha_0 \)
  - Source size \( D \)
  - \( \beta > 10^6 \text{ A cm}^{-2} \text{ sr}^{-1} \)

- **Require pure ionic emission**  
  (no neutrals, no droplets)

- **Require lifetimes > 100 hours**

- **Require beams with energy spreads < 10 eV for focusing**

- **Require stable beam production; single beam emission easier to focus.**

- **Chromatic aberrations (Uneven focusing)**

This research aims to characterize properties of a new ion source, ILIS, required for its implementation in a FIB system.
The big picture: focusable charged particle sources
(Literature Review)

- Positively Charged Particles
  - Solid Electrolytes
    - Escher et. al [12]
  - Plasma Sources
    - Smith et al. [13]
    - Scipioni et al. [14]
  - Liquid Metal Ion Sources (LMIS) [15,16,17]
  - Gas Field Ionization Sources
    - Ward et al. [18]

- Negatively Charged Particles
  - Plasma H⁻
    - Guharay et. al [3]
  - Ionic Liquid Ion Sources
    - Lozano [5,6,7]
    - Zorzos [8]
    - Perez [9,10,11]
  - Electrons [4]
    - Thermionic Schottky

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January 2013
The big picture: focusable charged particle sources

Positively Charged Particles

Solid Electrolytes
Escher et. al [12]

Plasma Sources
Smith et al. [13]
Scipioni et al. [14]

Liquid Metal Ion Sources (LMIS) [15,16,17]

Ionic Liquid Ion Sources
Lozano [5,6,7]
Zorzos [8]
Perez [9,10,11]

Plasma H⁺
Guharay et. al [3]

Electrons [4]
Thermionic Schottky

Negatively Charged Particles

• Produce: Ga⁺, Au⁺, Sb⁺, Si⁺, Bi⁺ [15]
• β = 10⁶ A cm⁻² sr⁻¹ (Ga)
• ΔE ≈ 5 eV [16]
• Minimum probe size ≈ 5 nm [16]
• LIMITATION: contamination
The big picture: focusable charged particle sources

- **Positively Charged Particles**
  - **Solid Electrolytes**
    - Escher et. al [12]
  - **Plasma Sources**
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  - **Liquid Metal Ion Sources (LMIS)** [15,16,17]
  - **Gas Field Ionization Sources**
    - Ward et al. [18]

- **Negatively Charged Particles**
  - **Plasma H⁺**
    - Guharay et. al [3]
  - **Electrons** [4]
    - Thermionic Schottky

**产销**: He⁺ [18], Ne⁺ [19]
- $\beta = 10^9$ A cm⁻² sr⁻¹, $\Delta E \approx 0.5$ eV
- Minimum probe size $\approx 0.25$ nm
- **LIMITATION: throughput**
The big picture: focusable charged particle sources

Positively Charged Particles

- **Solid Electrolytes**
  - Escher et. al [12]

- **Plasma Sources**
  - Smith et al. [13]
  - Scipioni et al. [14]

- **Liquid Metal Ion Sources (LMIS)** [15,16,17]

- **Gas Field Ionization Sources**
  - Ward et al. [18]

Negatively Charged Particles

- **Plasma H⁻**
  - Guharay et. al [3]

- **Electrons** [4]
  - Thermionic Schottky

**Ionic Liquid Ion Sources**

- Lozano [5,6,7]
- Zorzos [8]
- **Perez [9,10,11]**

Why do we care about negative ions?

CHARGING [21]

- Beam
- Secondary electrons
- Dielectric target
Ionic Liquid Ion Sources could be used for FIB

Rely on field evaporation from ionic liquids
- Room-temperature molten-salt
- Mixture of complex organic and inorganic ions

EMI-BF$_4$
(C$_6$N$_2$H$_{11}$ BF$_4$)

ILIS for FIB:
- Brightness estimated $> 10^6$ A cm$^{-2}$ sr$^{-1}$
- Small energy spreads [7]
- Room temperature operation
- Positive and negative ions
- High mass ions and reactive species

ILIS have enhanced etching rate compared to Ga LMIS due to ion REACTIVITY.
*Perez-Martinez et. al, [9]*

Mask Pattern Transfer to Si wafer by EMI-BF$_4$ irradiation.
Previous efforts towards an ILIS-based FIB

**Lozano:** *fraction* of the beam has $\Delta E \sim 6-8$ eV (EMI-Im [6], EMI-BF$_4$ [7])

**Zorzos and Lozano** [8]:
- Probe size estimation, assuming $\Delta E = 7$ eV:

$$
d^2 = I^3 \frac{C_s^2}{\pi M^2 \left( \frac{dI}{d\Omega} \right)^3} + I \left( \frac{\Delta W_{1/2}}{W} \right)^2 \frac{C_c^2}{\pi M^2 \left( \frac{dI}{d\Omega} \right)} + M^2 D^2
$$

- Could focus EMI-BF$_4$ ILIS beam to **30 μm** with single lens
  → Limited by chromatic aberrations (full beam, not monochromatic)

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**For FIB implementation, need to understand energy characteristics of full beam, its emission stability and its long-lifetime behavior.**

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*Carla Perez-Martinez*

January 2013
RESEARCH GOAL
Characterize ILIS properties to recommend strategies for implementation in a FIB column and other applications in micro and nanofabrication.

Relevant property
- Require single, stable beam for focusing. Is ILIS emission single or multiple beam?
- Require no neutrals. How many and where are they? Can we eliminate them?
- What is the lifetime of ILIS? (in progress)

Characterization Method
- Beam Visualization System (BVS)
- Retarding Potential Analyzer (RPA) + Beam Visualization System
- Spectrometry, RPA and BVS
(1) Contribution: Emission characterization via beam visualization

- **Experimental Setup:**

  - ILIS
  - Extractor
  - Attenuating grids
  - Microchannel plate
  - Phosphor screen
  - Ion beam
  - CCD camera

- **Beam impacts for alternating polarity at 0.1 Hz**

  - (a) \( V_{\text{app}} = -2.75 \text{ kV} \)
  - (b) \( V_{\text{app}} = +2.75 \text{ kV} \)

  - Parabolic profiles consistent with previous data [5]

Sample Beam Impact: basic trajectory information

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<table>
<thead>
<tr>
<th>x (mm)</th>
<th>y (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

\( V_{MCP} \) and \( V_P \) represent the potential differences in the microchannel plate and phosphor screen, respectively.

Max. signal captured

No signal
Emission Characterization: multiple beam emission as $V_{\text{app}}$ increased

Increasing $E$ field at tip, can sustain multiple Taylor cones:

FIB implications: cannot operate in multiple beam regime.
Current work involves shape optimization of ILIS to avoid multiple beamlets.
(2) Contribution: Neutral Characterization

- The beams from ILIS contain several ion species [5]:

  Ionic liquid $C^+ A^-$, e.g. EMI$^+$ BF$_4^-$

  $V_{app} > 0$: $(AC)_n C^+$
  
  $V_{app} < 0$: $(AC)_n A^-$

  $n=0,1,2$ is the degree of solvation

- Heavy ions may break up in flight, and yield an ion and neutral clusters.

  n=1 to n=0:
  (dimer to monomer)

  How many neutrals are produced? Where are they within the beam?

  ILIS

- Neutrals detrimental for FIB.
- Fragmentation affects energy properties
Neutral particle beam fraction via Retarding Potential Analysis

- Ideal RPA signal: monochromatic beam with no break-up
  \[ K_n = qV_{app} \]

- Break-up after acceleration
  \[ n \rightarrow m : K_m = q \frac{m_m}{m_n} V_{app} \]

- Break-up in acceleration zone
  \[ K_m = q \frac{m_m}{m_n} |V_{app} - V_b| + qV_b \]

Extractor
ILIS
\[ V_{app} \]
Retarding grids
\[ V_{RP} \]
Faraday cup
\[ -15 \text{ V} \]

\[ \frac{1}{I/I_{\text{max}}} \]
\[ \frac{1}{V_{RP}/V_{app}} \]

\[ \frac{1}{I/I_{\text{max}}} \]
\[ \frac{1}{V_{RP}/V_{app}} \]

\[ \frac{1}{I/I_{\text{max}}} \]
\[ \frac{1}{V_{RP}/V_{app}} \]
Neutral population is located at the center of the beam

FIB Implication: to avoid neutrals, deflect the beam using an E×B filter and select most energetic monomers for focusing.
(3) Current work: long-lifetime behavior and source optimization

- Require source lifetimes > 100 hours
- Until recently, ILIS DC operation for more than a few minutes impractical due to electrochemical decomposition; had to use voltage alternation [22].
- Distal Electrode configuration (Brikner and Lozano [23]) limits electrochemical decay

Brikner and Lozano: fired stably for 76 hours

Perform long-lifetime tests, monitoring
- Current fluctuations
- Beam-composition
- Energy via RPA
- Beam Visualization

Need to improve emitter surface to ensure single beam emission and continuous liquid supply
## Conclusions

### RESEARCH GOAL
Characterize ILIS properties to recommend strategies for implementation in a FIB column and other applications in micro and nanofabrication.

### Relevant property

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Implication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Require single beam for focusing. Is ILIS emission single or multiple beam?</td>
<td>Single beam emission at voltages close to start-up voltage, increase voltage to transition to multiple beam. Need to improve source geometry.</td>
</tr>
<tr>
<td>Require no neutrals in the beam. How many and where are they? Can we eliminate them?</td>
<td>Neutrals located at the center of the beam. To eliminate neutrals, select MONOCHROMATIC monomers using an E×B filter.</td>
</tr>
<tr>
<td>What is the lifetime of ILIS?</td>
<td>Still need to characterize long-lifetime behavior, determine maximum operation time.</td>
</tr>
</tbody>
</table>
Future Work: road to an ILIS-based FIB

Path to thesis:

1. Achieve **repeatable source geometry**, with uniform roughing that enables flow to tip and limits emission to one beam.

2. **Long-lifetime**: study beam composition, energy and trajectories with distal configurations over prolonged emission.

3. **Filter monoenergetic monomers** and measure energy distribution, to estimate ultimate probe size.

4. Implement distal-electrode configuration and filtering in an optics column, and **measure probe sizes attainable**.

5. Study interactions with other materials: GaN, SiGe, graphene

6. Determine ILIS capabilities in specific applications: localized etching, secondary ion mass spectrometry, ion implantation.
Thank you for your attention

Q/A?
References

[1] Image retrieved from Intel.
Supplemental Slides:

ILIS basic physics
Taylor Cone Formation

- Assume emitter surface is parabolic
- Solve Laplace equation to find potential
- B. C.: (1) Emitter at $V_{\text{app}}$ (2) extractor at ground (ignore space charge effects)
- Balance electric pressure to surface tension at the metal surface

\[
\frac{1}{2} \varepsilon_0 E^2_{\text{tip}} = \frac{2\gamma}{r_c}
\]

\[
V_{\text{min}} = \sqrt{\frac{\gamma r_c}{\varepsilon_0}} \ln \left(4 \frac{d}{r_c}\right)
\]

$\gamma = 0.052$ N/m, $r_c = 10$ um, $d = 0.5$ mm, $V_{\text{min}} = 1.5$ kV

- Liquid evolves into Taylor Cone when electric pressure balances surface tension
- Singularity at tip apex

\[
E_n = \sqrt{\frac{2\gamma \cot \theta_T}{\varepsilon_0 r}}
\]
Schottky Model of Ion Evaporation

Why does the current increase with the applied electric field?

- An electric field lowers the energy barrier required for ion evaporation.
- Schottky model of emitted current:
  \[ j = \frac{\sigma k T}{h} \exp\left( -\frac{1}{kT} \left( \Delta G - \sqrt{\frac{e^3 E}{4\pi \varepsilon_0}} \right) \right) \]

- Critical field for ion emission is:
  \[ E > E^* = \frac{4\pi \varepsilon_0}{e^3} \Delta G^2 = 1.6 \cdot 10^9 V / m \]

- Why does the E field reduces the energy barrier?
  \[ W = \int_x^{\infty} (qE - \frac{q^2}{16\pi \varepsilon_0 x^2})dx = -qEx - \frac{q^2}{16\pi \varepsilon_0 x} \]

- The amount of work that the electric field prevents us from doing is
  \[ W(x_c) = -\sqrt{\frac{q^3 E}{4\pi \varepsilon_0}} \]
Relaxation time (liquid conductivity \( \kappa \), dielectric constant \( \varepsilon \))

The relaxation time tells us how long it takes to the liquid to become like a conductor, with all free charges at the surface and zero electric field inside.

\[
\begin{align*}
\vec{E}_{\text{in}} & \rightarrow \vec{E}_0 \\
\kappa, \sigma & \quad \text{Liquid} \\
& \quad \text{Vacuum}
\end{align*}
\]

From Gauss Law:
\[
\vec{n} \cdot (\vec{D}_{\text{out}} - \vec{D}_{\text{in}}) = \sigma_{\text{surf}}
\]

\[
\varepsilon_0 E_{\text{out}} - \varepsilon \varepsilon_0 E_{\text{in}} = \sigma_{\text{surf}}
\]

From Ohm’s Law
\[
j = \frac{d\sigma_{\text{surf}}}{dt} = \kappa E_{\text{in}}
\]

Then, we have:
\[
\frac{d\sigma_{\text{surf}}}{dt} - \kappa E_{\text{in}} = 0 \implies \frac{d\sigma_{\text{surf}}}{dt} - \kappa \left( E_0 - \frac{\sigma_{\text{surf}}}{\varepsilon_0} \right) = 0 \implies \frac{d\sigma_{\text{surf}}}{dt} - \frac{\kappa \sigma_{\text{surf}}}{\varepsilon \varepsilon_0} = \frac{\kappa E}{\varepsilon}
\]

\[
\sigma_{\text{surf}} = \varepsilon E_0 \left( 1 - e^{-t/\tau} \right)
\]

\[
\tau = \frac{\varepsilon \varepsilon_0}{\kappa}
\]

For EMI-BF\(_4\):
K=1.3 Si/m, \( \varepsilon \approx 10, \tau = 70 \) ps
Estimation of the source size and ILIS brightness

What is the size of the emission site? D=2r*

- **At emission site, Taylor cone solution is no longer valid as charges are REMOVED.**
- Can estimate size of emission site using stress balance in unrelaxed liquid

\[
\frac{1}{2} \varepsilon_0 E^*^2 - \frac{1}{2} \varepsilon_0 \varepsilon \left( \frac{E^*}{\varepsilon} \right)^2 = \frac{2\gamma}{r^*}
\]

\[
\Rightarrow r^* = \frac{4\gamma}{\varepsilon_0 E^*^2} \left( \frac{\varepsilon}{\varepsilon - 1} \right)
\]

Source size \( r^* \approx 10 \text{ nm} \)

Liquid dielectric constant \( \varepsilon \approx 10 \)

Now can compute brightness:

\[
\beta = \frac{4I_b}{(\pi \alpha_0 D)^2}
\]

\( \alpha_0 = 18^\circ, D = 20 \text{ nm}, I_b = 600 \text{ nA}: \beta = 6 \times 10^6 \text{ A cm}^{-2} \text{ sr}^{-1} \)
Advantage for FIB: ILIS operate stably at low currents

For FIB, the probe size $d$ should be minimized:

$$d^2 = I^3 \left( \frac{C_s}{\pi M^2 \left( \frac{dI}{d\Omega} \right)^3} + I \left( \frac{\Delta W_{1/2}}{W} \right)^2 \frac{C_c^2}{\pi M^2 \left( \frac{dI}{d\Omega} \right)} + M^2 D^2 \right)$$

$I$ current, $\Omega$ solid angle
$W$ energy, $D$ source size
$M$ Magnification factor
$C_s$ spherical aberration
$C_c$ chromatic aberration


Currents of ILIS (10-1000 nA) improve the probe size compared to LMIS:

**Ga LMIS I-V**

Currents of ILIS (10-1000 nA) improve the probe size compared to LMIS:

**Ga LMIS I-V**

**EMI-BF$_4$ ILIS I-V:**

P. Lozano and M. Martinez-Sanchez, J. Colloid Interface Sci. 280, 149 (2004)
ILIS have small energy spreads and energy deficits

For FIB, the probe size should be minimized:

\[ d^2 = I^3 \frac{C_s}{\pi M^2 \left(\frac{dl}{d\Omega}\right)^3} + I \left(\frac{\Delta W_{1/2}}{W}\right)^2 \frac{C_c^2}{\pi M^2 \left(\frac{dl}{d\Omega}\right)} + M^2 D^2 \]

Retarding Potential Analyzer curves (EMI-Im)

- Deficit comes from energy to evaporate some ions
- Energy spread from monochromatic part comes from the finite source size; emission site is not an equipotential as liquid is not completely relaxed.

Source Optimization

• Tried to replicate results from Brikner and Lozano (Appl. Phys. Lett. 101, 193504, 2012)
• Tested distal electrode source, and obtained stable emission for a few hours
• Problems with liquid supply to the emitter.

Short term goals:
• Understand electrochemical etching process to find a repeatable fabrication technique
• Explore smaller wire diameters
Source Fabrication Process

1. Start with 0.5 mm DIA W wire
2. Electrochemical etch in NaOH (1 N), 10 $V_{\text{RMS}}$ (60 Hz) 10 s to activate surface
3. Electrochemical etch in NaOH (1 N), 50 V D.C. to cut into sharp apex
4. Electrochemical etch in NaOH (1 N), 20 V D.C. to smooth surface
   (Alternative 20 V A.C. alternative gives too rough a surface)
5. Microroughening treatment in hot NaOH (1 N) and $K_3Fe(CN)_6$ solution

IN PROGRESS: Trying to integrate post-roughing ETCH to achieve a smooth tip.
Supplemental Slides

Interactions with materials
Interactions of ILIS beams with materials

- Compare ILIS to other high brightness sources by understanding sputtering yields.
- Irradiate masked Si wafer with 15 keV EMI-BF$_4$ beam for 30 min.

**Figure of Merit:**
Sputtering Yield $Y = \frac{\# \text{ Si atoms removed}}{\# \text{ Incident ions}}$

<table>
<thead>
<tr>
<th></th>
<th>Ga (10 keV)</th>
<th>He (10 keV)</th>
<th>ILIS (15 keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y$</td>
<td>2.22 [20]</td>
<td>0.12 [20]</td>
<td>5 to 35</td>
</tr>
</tbody>
</table>

Mask pattern transferred to Si Carved depth: ~15 nm
Explaining substrate-ion beam interaction

Masked Pattern transferred by EMI-BF$_4$ ($C_6N_2H_{11}BF_4$) irradiation

X-ray Photoelectron Spectroscopy:
- Creation of Si-C and Si-N bonds on etched surfaces.
- Ratio of F to B is 1.5 instead of 4.

⇒ EMI-BF$_4$ ions break upon impact: free radicals.
- C, N react with surface
- F, B create volatile compounds

LMIS and GFIS: material removal is mechanical:

Introduce reactive gas assistance to speed up LMIS/GFIS etching:

FIB (and GENERAL APPLICATIONS): use ionic liquids with reactive species. No chemical assistance.
Supplemental Slides

Other ion/electron sources
High-brightness ion sources for FIB: LMIS and GFIS

(1) Liquid Metal Ion Source (LMIS)
Field evaporation from liquid metals

- Produce: Ga\(^+\), Au\(^+\), Sb\(^+\), Si\(^+\), Bi\(^+\)
- $\beta = 10^6$ A cm\(^{-2}\) sr\(^{-1}\) (Ga), $\Delta E \approx 5$ eV
- Minimum probe size $\approx 5$ nm
- **LIMITATION:** contamination

(2) Gas Field Ionization Sources (GFIS)
Ionization of noble gases

- Produce: He\(^+\), Ne\(^+\)
- $\beta = 10^9$ A cm\(^{-2}\) sr\(^{-1}\), $\Delta E \approx 0.5$ eV
- Minimum probe size $\approx 0.25$ nm
- **LIMITATION:** writing speeds

**LIMITED TO A FEW POSITIVE SPECIES**

References found on literature review slides
## Other high-brightness ion sources

<table>
<thead>
<tr>
<th>Source</th>
<th>Source Size (μm)</th>
<th>Angular Intensity</th>
<th>Brightness (Acm⁻²sr⁻¹)</th>
<th>ΔE (eV)</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inductively Coupled Plasma Source (Smith et. al)</td>
<td>15 (Ar+) 9.5 (Xe+)</td>
<td>10 mAs⁻¹</td>
<td>4590 @ 8.5 kV 10500 @ 11.5 kV</td>
<td>7 10</td>
<td>Larger mill rates than Ga LMIS FIB Excellent beam purity, lifetime</td>
<td>Can be focused to sub-100 nm, but not as high resolution as Ga FIB</td>
</tr>
<tr>
<td>Commercial: FEI VION</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multicusp Plasma Source (Scipioni et. al)</td>
<td>16.9 (Kr+) 23 (Ne+) 40 (He+)</td>
<td>12 μAs⁻¹ 8.2 μAs⁻¹ 12 μAs⁻¹</td>
<td>1650 @ 30 kV 590 @ 30 kV 300 @ 30 kV</td>
<td>N.A. N.A.</td>
<td>Large mill rates. No contamination of Kr in photomask applications.</td>
<td>Low brightness. Smith mentions cathodic element has limited lifetime.</td>
</tr>
<tr>
<td>Solid Electrolytes (Escher et. al) (AgI)₀.₅(AgPO₃)₀.₅ → Ag⁺</td>
<td>&lt; 1, although could improve</td>
<td>Current ranges in a few μA</td>
<td>N.A.</td>
<td>N.A.</td>
<td>Potentially provide many species, Cu+ Stable current for several days.</td>
<td>Not well developed. Many emission sites.</td>
</tr>
<tr>
<td>Penning surface plasma source (H-) (Guharay et al.)</td>
<td>10</td>
<td>40 mAs⁻¹</td>
<td>5·10⁵ @ 7 kV</td>
<td>&lt;3</td>
<td>Negative beams!</td>
<td>Pulsed operation.</td>
</tr>
</tbody>
</table>

References found on list at end of main presentation
# Electron Sources

From 6.781 Course Notes, 2012:

<table>
<thead>
<tr>
<th>Source</th>
<th>Lifetime (h)</th>
<th>B @ 25 kV (A cm⁻²sr⁻¹) @ Temperature</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W (Thermionic)</td>
<td>100</td>
<td>2·10⁵ @ 2900 K</td>
<td>2-3</td>
</tr>
<tr>
<td>LaB₆ (Thermionic)</td>
<td>1000</td>
<td>10⁶ @ 2000 K</td>
<td>2-3</td>
</tr>
<tr>
<td>W, cold (Field Emission)</td>
<td>&gt;1000</td>
<td>5·10⁸ - 10⁹</td>
<td>0.5</td>
</tr>
<tr>
<td>ZrO/W Thermal + Field Emission</td>
<td>&gt;1000</td>
<td>2·10⁸ @ 1800 K</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Supplemental Slides

ILIS electrochemical issues
ILIS operation creates a double layer in the electrode/liquid interface

(1) Positive ions leaving emitter due to applied electric field

(2) Electrons flow towards the power supply to maintain the current, leaving electrode positively charged

(3) Negative ions are attracted towards the electrode

At the electrode-liquid interface, we have the formation of a double layer
If the charge accumulated at the double layer is too high, reactions can occur

The width $\delta$ of the double layer is very small (of the order of the ion size) $\rightarrow$ a small potential difference due to charge accumulation generates a strong electric field.

At some point, electron transfer can occur between the electrode and the liquid, leading to undesired reactions. The point where this transfer occurs is when we exceed the *electrochemical window* $V_w$ of the ionic liquid ($V_w \approx 4-6$ volts for EMI-BF$_4$)

Model the double layer as a CAPACITOR: charge accumulates as current is transmitted. It is a parallel plate capacitor, with area $A$ (liquid-electrode contact area) and separation $\delta$.

When the capacitor fills, reactions occur. The reactions will corrode the electrode and the liquid, and we get emission degradation.

Solution: alternate polarity of the source

- Discharge the capacitor before reactions take place.
- By switching to the other polarity, electrons are supplied/removed to the electrode, start forming the opposite double layer.
- Lozano and Martínez-Sánchez: double layer charging time is in the order of 10 s for externally wetted configuration, so using a 1 Hz alternating frequency prevents electrochemical degradation.

Supplemental Slides

Beam Visualization
Deflector Assembly for Neutral Visualization Experiments

- Installed two deflector plates 7 mm downstream of the extractor exit.
- The deflector act over $l=12.7$ mm along the path of the beam. The plates are separated by $d=20$ mm.
- Using a $V_{\text{def}}=1.5$ kV, a 1.4 keV EMI+ should be deflected 25 mm when it hits the MCP.

\[
y = \frac{V_{\text{def}} d^2}{4 l V_{\text{app}}}
\]
How do the neutrals from negative mode look like?

- $V_{\text{app}} = \pm 1.16$ kV, 10 s period 50% symmetry squarewave. The extractor is grounded. Current is 4.6 and -3.2 nA in positive and negative polarity.
- We apply deflection, using a 2 kV bias. The deflectors is always turned on.
- Each image is the average of 20 frames, taken every 0.2 seconds.

- In negative mode, have an intermediate signal between neutral signal and deflected beam. Reasons? (1) Break-up occurring in deflector; negative regime different from positive regime (2) Lack of symmetry of detector, maybe negative ions hit detector and produce secondary electrons (unlikely though)
Supplemental Slides

Ion filtering/optics
A magnetic filter in the ion path can separate ion species

Create a uniform magnetic field in ion path: Lorentz Force

\[
\theta_{dev} = \sin^{-1}\left(\frac{lqB}{mu_0}\right)
\]

\[
u_0 = \sqrt{2qV_{app}/m}
\]

l length where B acts
q ion charge
B magnetic field strength
m ion mass
\(u_0\) ion velocity

Constructive filter has B=0.3 T
Ion Magnetic Filtering + Retarding Potential Analyzer

**Issue:** collected signal too small. (less than 0.5 nA)
- Signal-to noise ratio is not acceptable.
- Test at $V_{\text{app}} = -2.7$ kV, with lens at -2.9 kV
- Captured Fragments
How does an Einzel Lens work?

- Symmetric so beam energy is unchanged
- Particle trajectories go from diverging to converging
- Smallest disc or trajectories after the lens – circle of less confusion

Supplemental Slides

Potential FIB Applications
Focused Ion Beams can be applied in a wide range of applications

1) Scanning Ion Microscopy
2) Secondary Ion Mass Spectroscopy
3) Ion Implantation in Integrated Circuit (IC) Industry
4) Micromachining (TEM Sample Preparation)
5) Material Deposition
(1) Nanoimaging: Scanning Ion Microscopy

- Ion beam scans a sample and sputters particles (electrons, ions)
- Secondary e-s can be used to create sample image.
- Highest resolution is 5-10 nm (< 10X less than SEM); destructive.
- High contrast in crystalline materials due to ion channeling.

Cr coated steel wire, showing contrast due to different grain orientations (FEI Company)

ILIS Potential Advantage
- Avoid charging issues by using alternating polarity.
- Can use light ions to avoid sample sputtering.

(2) Secondary Ion Mass Spectroscopy

- Send sputtered ions to a time-of-flight detector.
- Mill away the surface to get data about **depth profile**

**ILIS Potential Advantage:** can choose interacting ions with the sample (avoid contamination). ILIS have large ion species available that increase sputtered material and give larger signals for TOF-SIMS
(3) Implantation: ions from ILIS could dope silicon and other semiconductors

- IC manufacturing uses a collimated but broad beam of ions to implant dopants
- The energy of the incoming ions is adjusted to control the depth of the implant
- FIB too slow for production, but resolution of interest as devices shrink

ILIS Potential Advantages:
- Liquids with doping species (e.g. EMI-BF₄)
- Can perform low energy (<2 kV) implants for ultra shallow junctions
(4) Micromachining

- Nanopores permitted by FIB resolution

Applicable to DNA separation.

Schiedt B et al., Sub-5 nm FIB direct patterning of nanopores, *Proceedings of MRS Symposium*, San Francisco USA, 2009

- 3D Milling possible


T. Fujii et al., *J. of Micromech. and Microeng.*, 15, 10, 2005
(4) Micromachining

- Popular use of FIB is TEM sample preparation

Source: FEI company

(5) FIB can be used for material deposition

- Similar to reactive ion etching, but instead of reactive gas we use a precursor gas
- W, Au, Al, Pt Si (with Ga impurities)

**ILIS Potential Advantage:** select ions that will not contaminate


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