PImMS
an event-triggered time-stamping sensor with storage of multiple timestamps

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6 September 2012, PIXEL2012, Inawashiro
Outline

- Context and requirements for PlmMS sensors
- PlmMS1 and PlmMS2 sensors
  - Specifications, design and operation
  - Project timeline and status
  - PlmMS1 characterisation
  - PlmMS1 application results
- Summary and future work
Context: time of flight mass spectrometry

\[ E = zV = \frac{1}{2}mv^2 \]
\[ t = \frac{d}{v} \propto (m/z)^{1/2} \]

Mass spectrum for human plasma

~ 100 µs duration
Pixel Imaging Mass Spectrometry

Combines time-of-flight MS with 2D ion imaging.

We can image:

- the velocities of the ions at their point of formation -- giving info on fragmentation dynamics, or

- the positions of the ions at their point of formation – used in surface imaging or parallel acquisition of multiple mass spectra from an array of samples
Requirements: self-triggering

- Proof of concept experiments with a fast-framing camera: multiphoton fragmentation of dimethyl disulfide (images recorded in 2008 using a Dalsa Zenith CCD camera).
- Required prior knowledge of timing of mass peaks, programming the framing for the known time of arrival of each peak.

Requirements: multiple timestamps

- Want a fast sensor, flexible to analyse any mass spectrum
- Sparse events → consider time-stamping approach
- To record both early and late ions, need multiple memories. How many? Simulate:
Requirements: timing resolution

- Initial spec for time resolution: 50ns
- Updated spec, based on our significant progress in mass spectrometer timing, is to distinguish ions with a mass difference of 1 Dalton over a wide range of masses.
- This yields a new target spec of 12.5ns (see results later)

**Time Resolution for $\Delta m = 1$**

If we want $\Delta m = 1$:
- $m/\Delta m \approx t/2\Delta t$
- $\Delta t = t/2m$
## PImMS sensors: specifications

<table>
<thead>
<tr>
<th>Spec</th>
<th>PImMS1</th>
<th>PImMS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Array size</td>
<td>72 x 72 pixels</td>
<td>324 x 324 pixels</td>
</tr>
<tr>
<td>Active area</td>
<td>5mm x 5mm</td>
<td>22.7mm x 22.7mm</td>
</tr>
<tr>
<td>Sensor size</td>
<td>7mm x 7mm</td>
<td>25.4mm x 26.1mm</td>
</tr>
<tr>
<td>Pixel size</td>
<td></td>
<td>70µm x 70µm</td>
</tr>
<tr>
<td>Pixel threshold trim</td>
<td></td>
<td>4 trim bits + 1 masking bit per pixel</td>
</tr>
<tr>
<td>Timestamp storage</td>
<td></td>
<td>Four 12-bit registers per pixel</td>
</tr>
<tr>
<td>Test pixel</td>
<td>1 test pixel with access to inner analogue nodes</td>
<td></td>
</tr>
<tr>
<td>Time resolution</td>
<td>Initial spec: 50ns; simulation target: 25ns</td>
<td>Updated spec: 12.5ns</td>
</tr>
<tr>
<td>Current performance</td>
<td>12.5ns verified</td>
<td>(will be tested in future)</td>
</tr>
<tr>
<td>Substrate</td>
<td>5µm epi</td>
<td>5µm epi</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18µm high-resistivity epi</td>
</tr>
</tbody>
</table>
PlmMS pixel

Collection Diodes → Pre-Amplifier → Shaper → Comparator Trim Block → Comparator → Digital Control Logic → Pixel Memories 12 bits each

- Collection Diodes
- Pre-Amplifier
- Shaper
- Comparator Trim Block
- Comparator
- Digital Control Logic
- Pixel Memories 12 bits each

Analogue Readout

Digital Readout 12 bits

Digital Timecode 12 bits

Graphs:
- vD vs. t
- vPA vs. t
- vS vs. t
- vS1 vs. vS2 vs. t
- vC1 vs. vC2 vs. t
- vO vs. hit vs. t
Pixel operation

diode

preamplifier

shaper

crossing => hit
crossing => hit

comparator inputs

hit indicator

timecode 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

memory 1 0 0 0 0 0 6 6 6 6 6 6 6 6 6 6 6 6

memory 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 14 14 14 14 14

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Pixel layout

- Memory
- Memory of next pixel
- Diode
- Analogue routing and circuitry
- Digital circuitry
- Digital timecode and read busses
- Memory of next pixel
- Digital circuitry
PlmMS sensors: overview

**PlmMS1**
- Timecode Distribution
- Trim and row control
- Test Pixel @ (3, 2)
- 72 x 72 Pixel Array
- Sense Amplifiers
- Readout Circuit
- Analogue Output Path

**PlmMS2**
- Timecode Generation (Counter)
- Trim and row control
- Test Pixel @ (3, 2)
- 324 x 324 Pixel Array
- Sense Amplifiers
- Readout Circuit
- Analogue Output Path
- Bias DACs
**New features:**

- Array size increased to 324x324
- Additional digital output taps
- Additional analogue outputs
- Extra counters
- Right hand side driver circuitry for row control signals
- Internal bias generator
- Extra pixel trim bias
PImMS sensors: technology

- 0.18µm CMOS fabrication
- INMAPS process developed at the Rutherford Lab:
  
  *Isolated N-well Monolithic Active Pixel Sensors*

- PImMS pixel: 615 transistors per pixel
- over 3 million transistors in total for PImMS1
Readout: camera

- USB control and readout
- F-mount SLR lens
- C-mount SLR lens also possible – delivers more light to sensor

- Cooling system based on copper finger and Peltier device
- Connection for nitrogen/dry air flushing
## Project timeline and status

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start of PlmMS project</td>
<td>July 2009</td>
</tr>
<tr>
<td>PlmMS1 sensor received and first light</td>
<td>December 2010</td>
</tr>
<tr>
<td>PlmMS2 design start</td>
<td>March 2011</td>
</tr>
<tr>
<td>PlmMS1 first mass spectrometry results</td>
<td>April 2011</td>
</tr>
<tr>
<td>Resolution of several PlmMS1 camera (DAQ) issues</td>
<td>January 2012</td>
</tr>
<tr>
<td>PlmMS1 25ns timecodes verified</td>
<td>April 2012</td>
</tr>
<tr>
<td>PlmMS2 design submitted</td>
<td>February 2012</td>
</tr>
<tr>
<td>PlmMS1 12.5ns timecodes verified</td>
<td>Last week</td>
</tr>
<tr>
<td>PlmMS2 current status: wafers are being diced</td>
<td>This week</td>
</tr>
<tr>
<td>Next steps: wirebonding then initial tests of PlmMS2</td>
<td>Second half of September</td>
</tr>
</tbody>
</table>
PImMS1 characterisation: timing resolution

- Testing with timecodes at increasing speeds, using a low-power laser pulse generator
- The edges of the laser spot have progressively lower intensity, showing the degree of timewalk, ~125ns
Timing resolution, continued

Timecodes present in one frame only:
- $\sigma = 1.65$
- time resolution $20.6 \text{ns}$

Timecodes present in all frames:
- $\sigma = 1.68$
- time resolution $21 \text{ns}$

Timecodes present for a single pixel:
- $\sigma = 0.33$
- time resolution $4.1 \text{ns}$
PlmMS1 characterisation: dead time

Results for firing two lasers at the same set of pixels, varying the delay between the lasers. If the second laser occurs within the dead time, no pulse will be recorded in the second register.

Results for 4 individual pixels, showing the range of responses.
Application results
Applications: velocity map imaging

- N,N-dimethylformamide (DMF) is a prototype molecule for studying peptide bond cleavage.
- PlmMS data on the 193 nm photolysis of DMF is shown below.
Applications: coincidence imaging

- Here bromine gas (Br₂) is dissociated. By switching the polarity of the ion optics, first the electrons are imaged, then the ions.

- (a) shows the mass spectrum including ⁷⁹Br⁺ and ⁸¹Br⁺

- (b) shows the mass intersections for the electrons and Br ions

- (c) zooms in on the two isotopes, ⁷⁹Br⁺ and ⁸¹Br⁺
Applications: spatial imaging

- This is imaging the mass spectrum over a 2D surface.
- Materials used: lines of Auramine O (yellow) and Rhodamine 590 (red)
- The samples produced 10 mass peaks in all. 5 are highlighted here.
- Data taken at 25ns time resolution
- Demonstrates multi-mass imaging
Spatial imaging, continued

For an intense area of the image, we investigated:

- the proportion of each mass peak seen
- in which pixel register the mass peaks appeared.
Summary and future work

- PImMS is both a new technique in mass spectrometry and a self-triggered time-stamping sensor.
- PImMS1 has been proven for mass spectrometry, operating at 12.5ns timecode rates (4x initial spec)
- Multiple memories record various events within one experimental cycle.
- Taking a wider view, PImMS also suits other applications generating step changes of signal.
- PImMS2 testing will begin in the second half of September, promising improved spatial resolution, with its larger pixel array.
Thank you for your attention. Questions?

The PImMS Collaboration

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The support of the STFC, ICONIC, EPSRC, ERC, RC-UK and ISIS Innovation Ltd. are gratefully acknowledged.