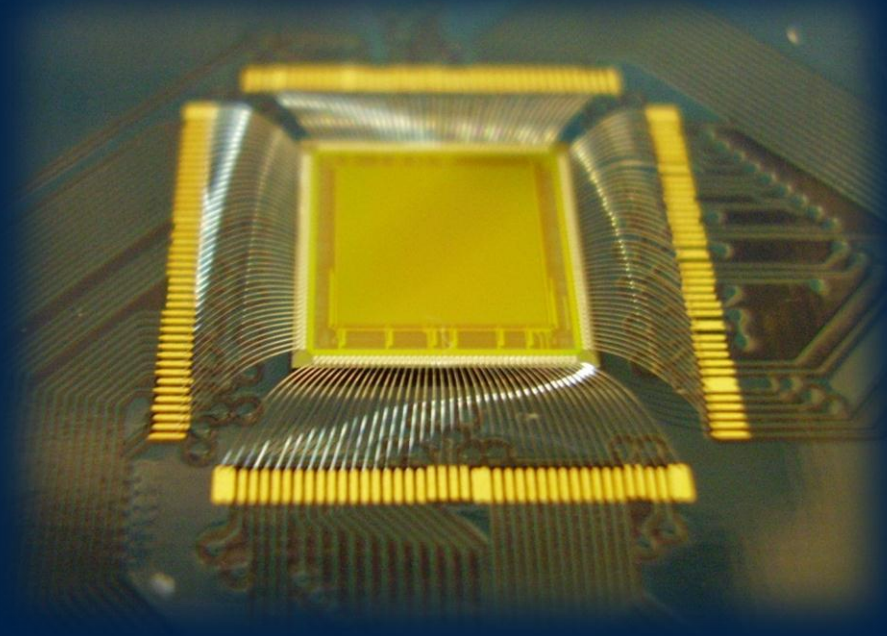


# PImMS

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

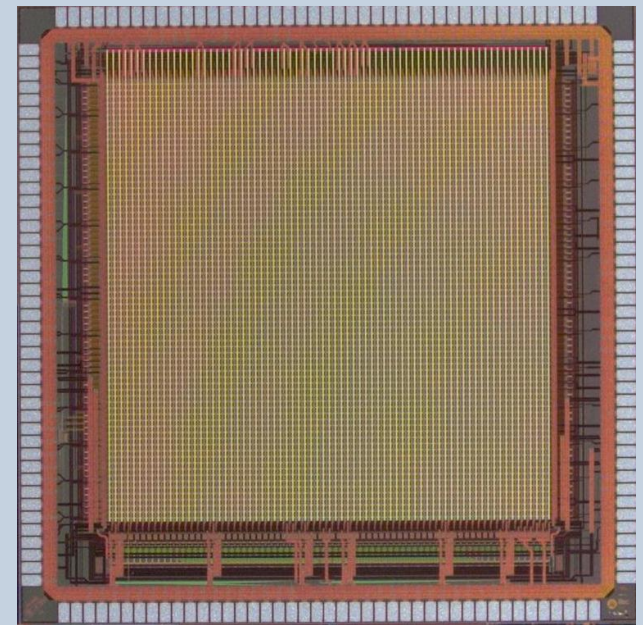


Jaya John John, on behalf of the PImMS Collaboration  
6 September 2012, PIXEL2012, Inawashiro

# Outline

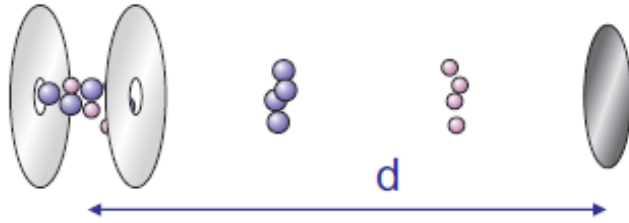
- Context and requirements for PImMS sensors
- PImMS1 and PImMS2 sensors
  - Specifications, design and operation
  - Project timeline and status
  - PImMS1 characterisation
  - PImMS1 application results
- Summary and future work

*PImMS 1*



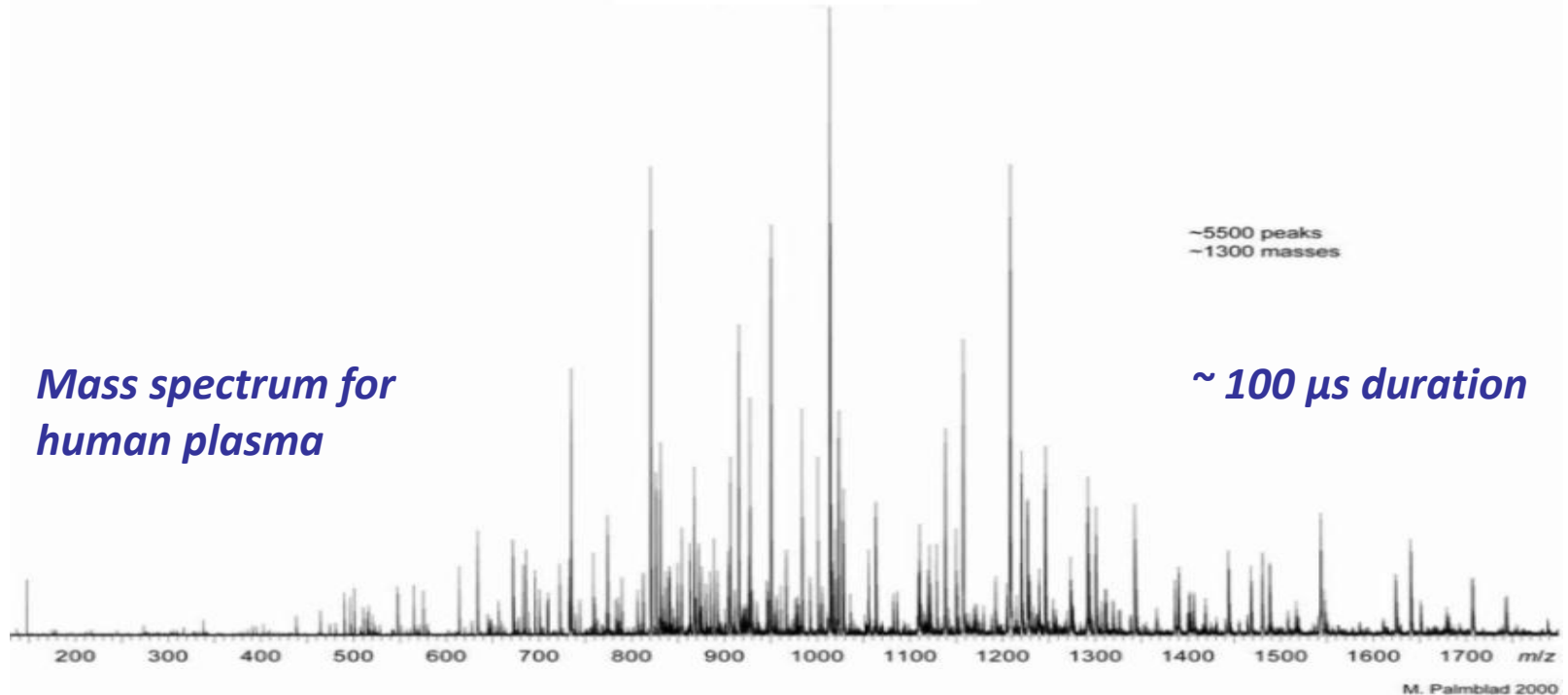
7.2 mm

# Context: time of flight mass spectrometry



$$E = zV = \frac{1}{2}mv^2$$

$$t = d / v \propto (m/z)^{1/2}$$

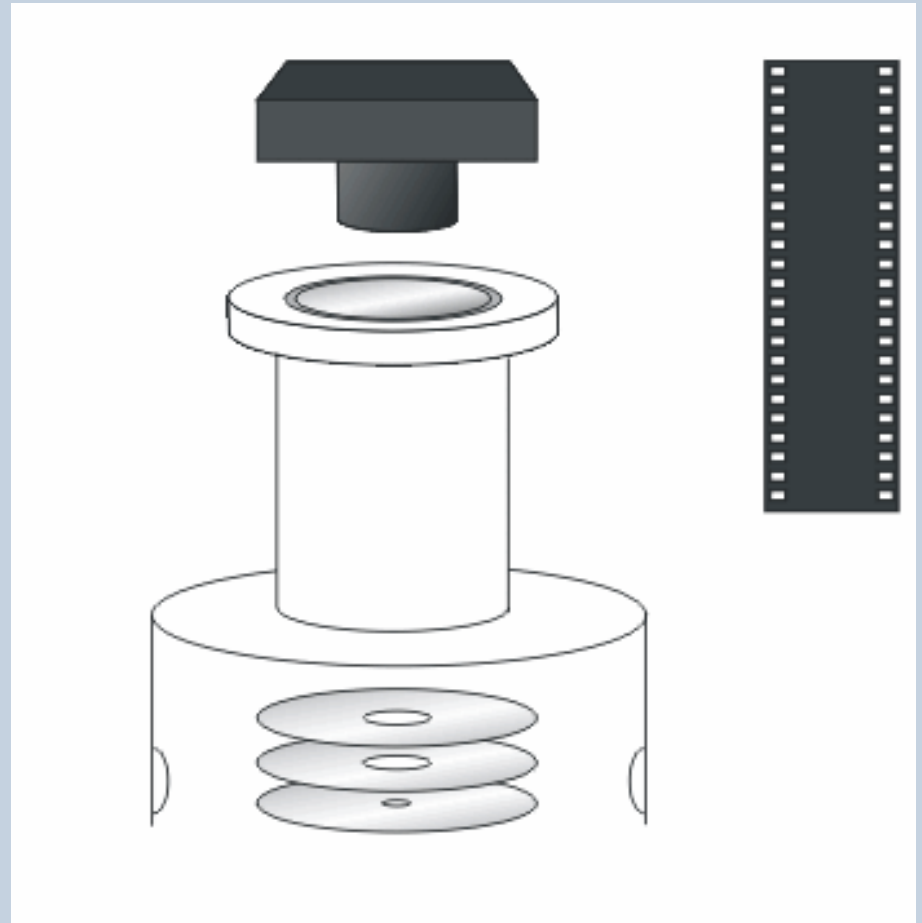


# Pixel Imaging Mass Spectrometry

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

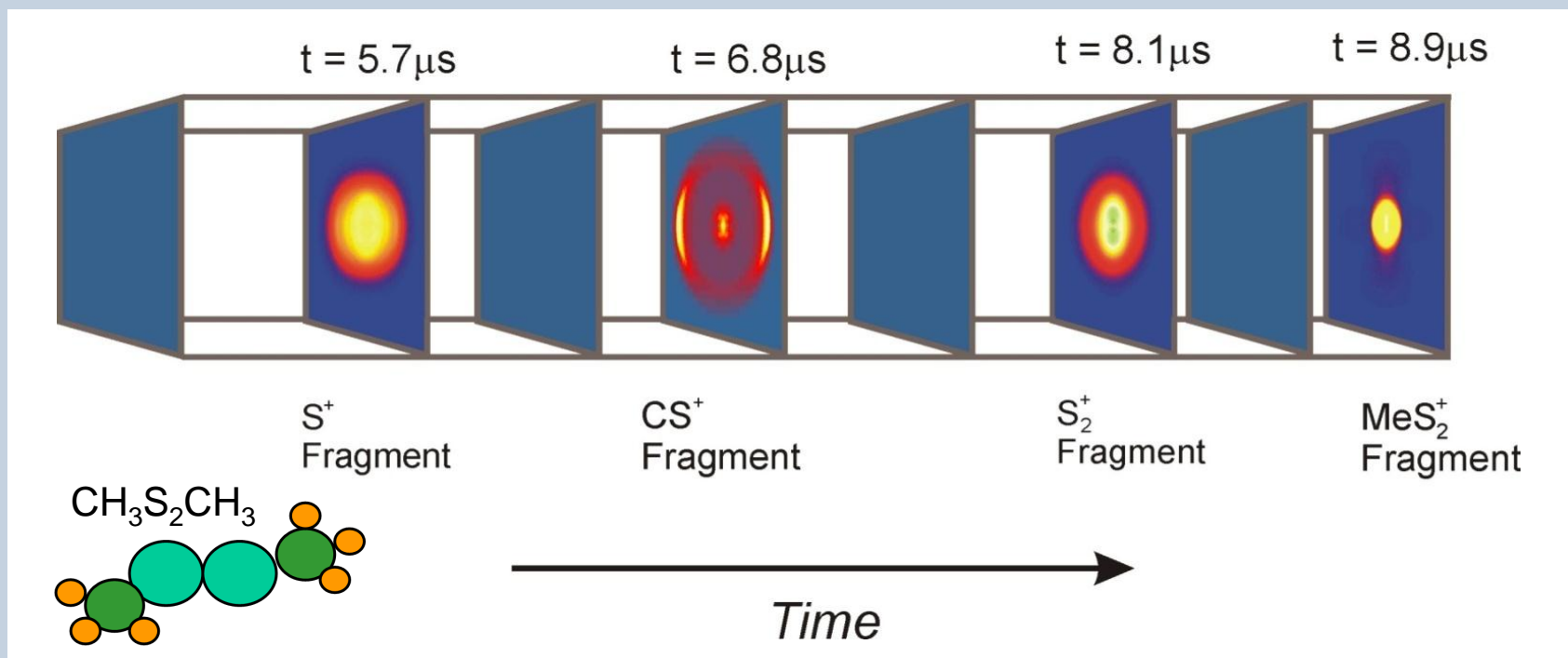
We can image:

- 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 dimethyldisulfide (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.

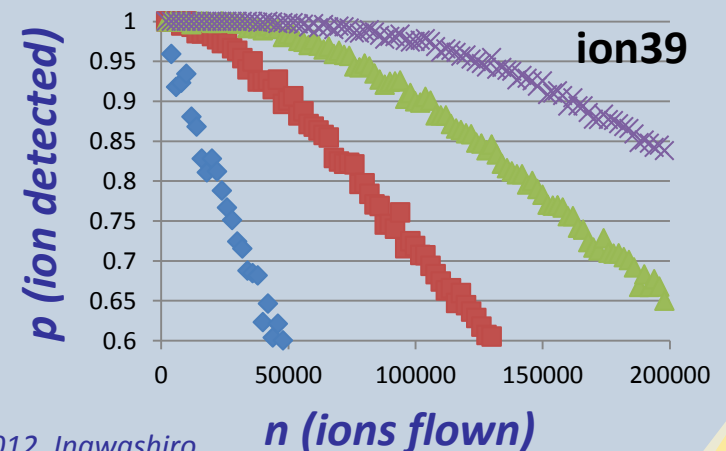
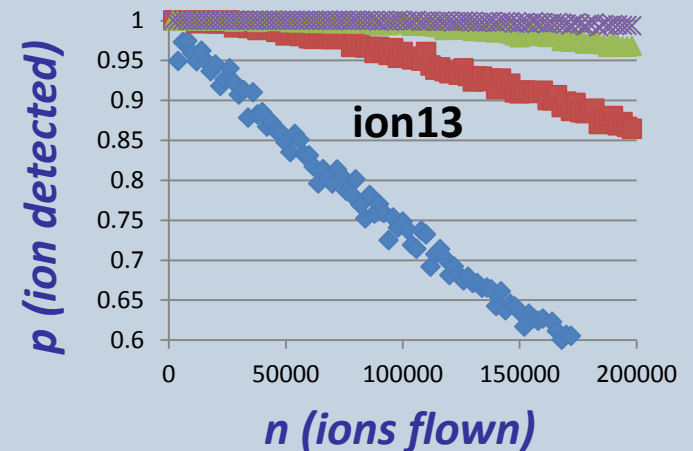
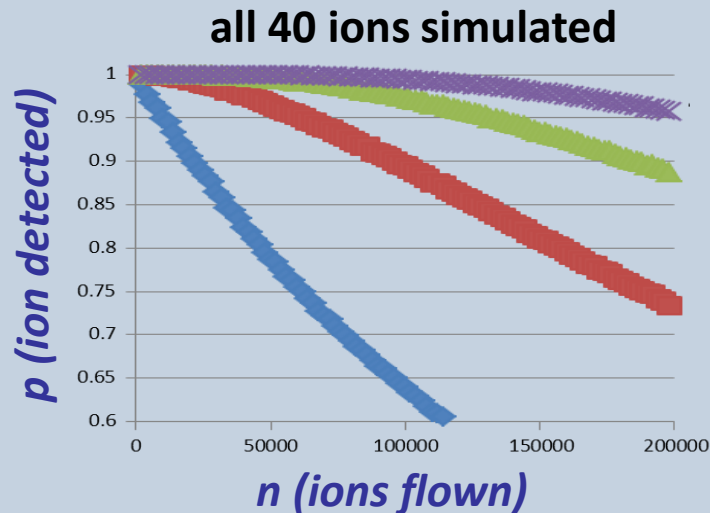


M. Brouard, E.K. Campbell, A.J. Johnsen, C. Vallance, W.H. Yuen, and A. Nomerotski, *Rev. Sci. Instrum.* 79, 123115, (2008)

# Requirements: multiple timestamps

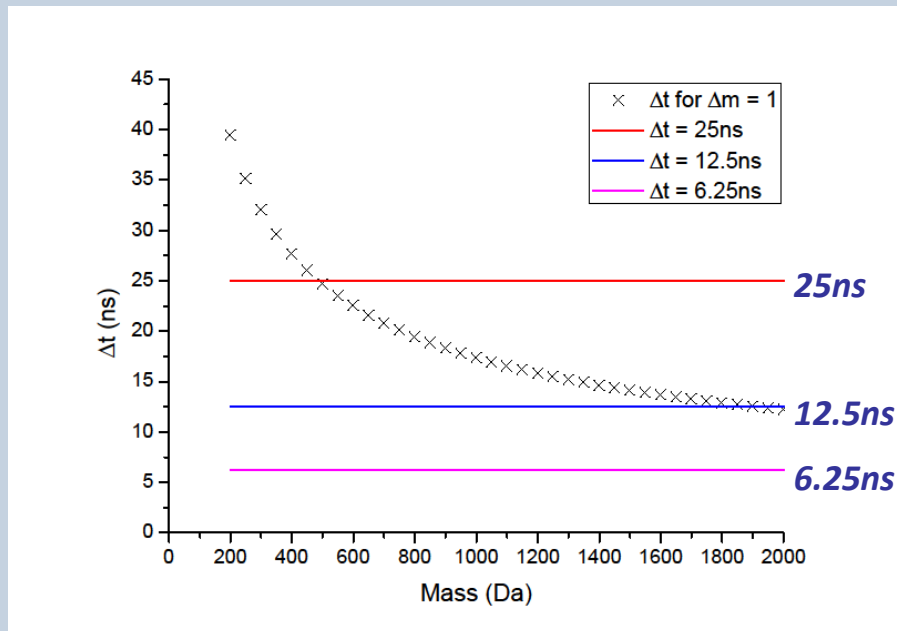
- Want a fast sensor, flexible to analyse any mass spectrum
- Sparse events → consider time-stamping approach
- To record both early and late ions, need multiple memories. How many? Simulate:

- ◆ 1 register
- 2 registers
- ▲ 3 registers
- × 4 registers



# 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  $\Delta m = 1$ :

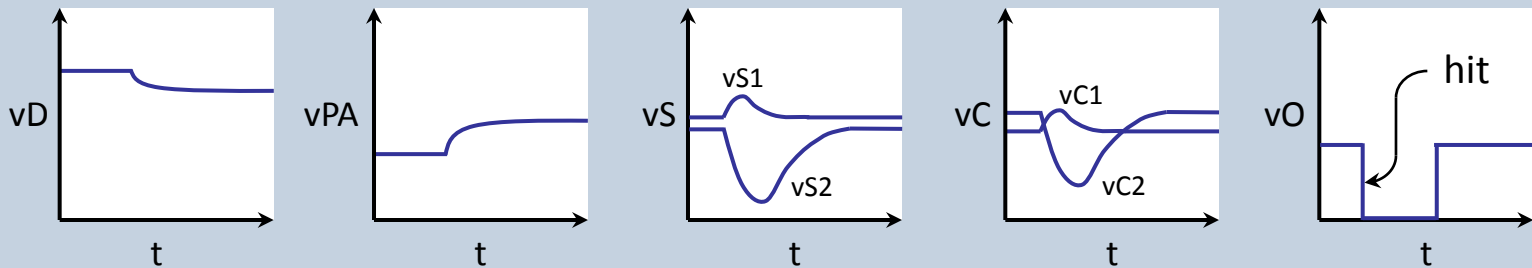
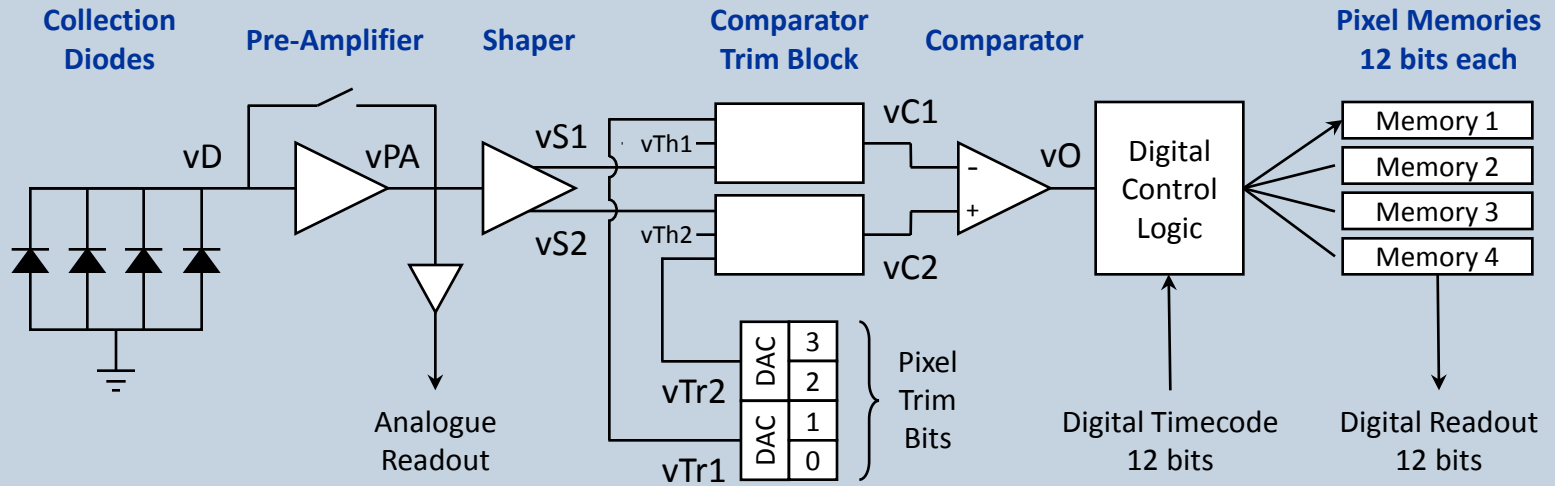
- $m/\Delta m \approx t/2\Delta t$
- $\Delta t = t/2m$

# PImMS sensors: specifications

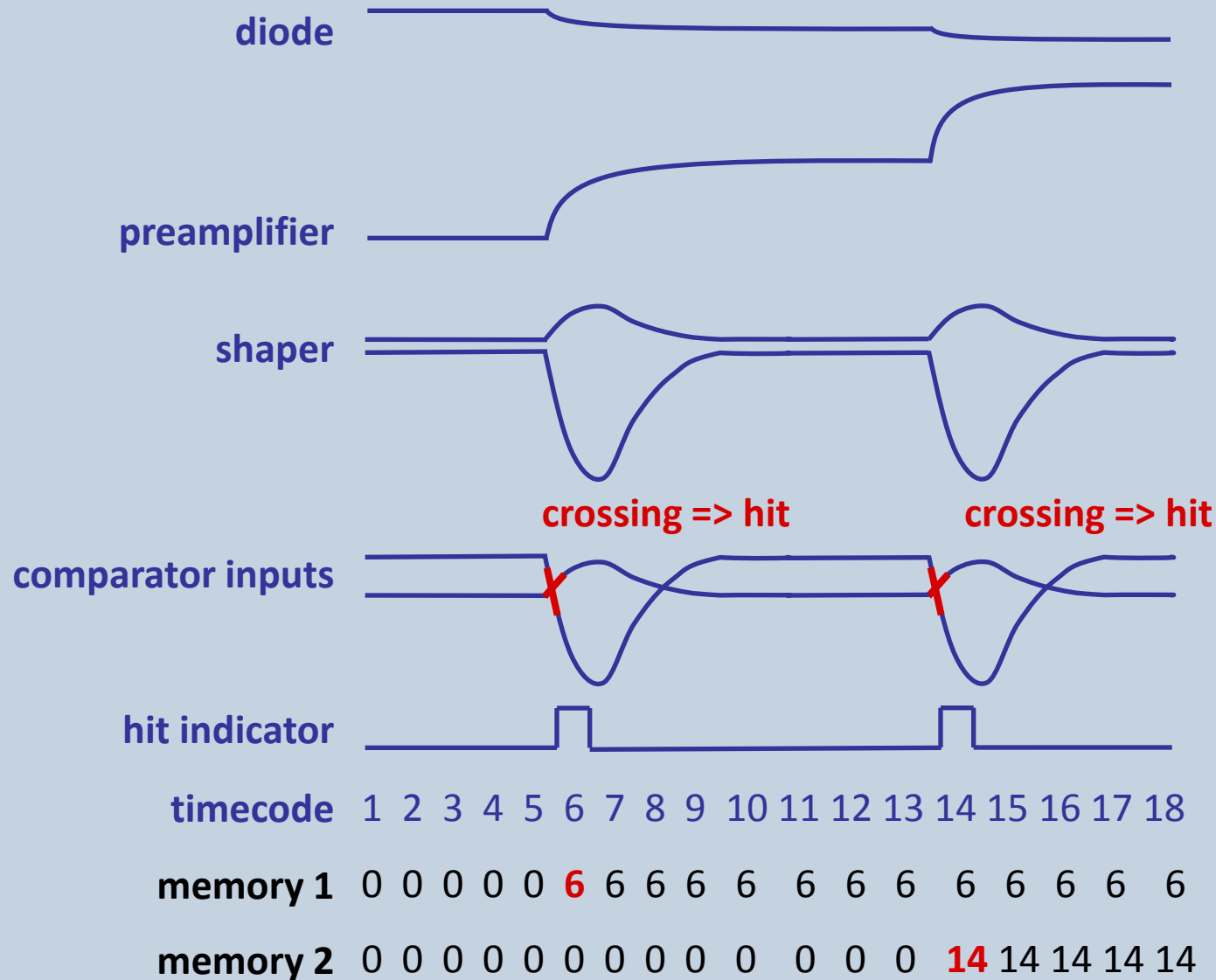
Spec	PImMS1	PImMS2
Array size	72 x 72 pixels	324 x 324 pixels
Active area	5mm x 5mm	22.7mm x 22.7mm
Sensor size	7mm x 7mm	25.4mm x 26.1mm
Pixel size	70 $\mu$ m x 70 $\mu$ m	
Pixel threshold trim	4 trim bits + 1 masking bit per pixel	
Timestamp storage	Four 12-bit registers per pixel	
Test pixel	1 test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



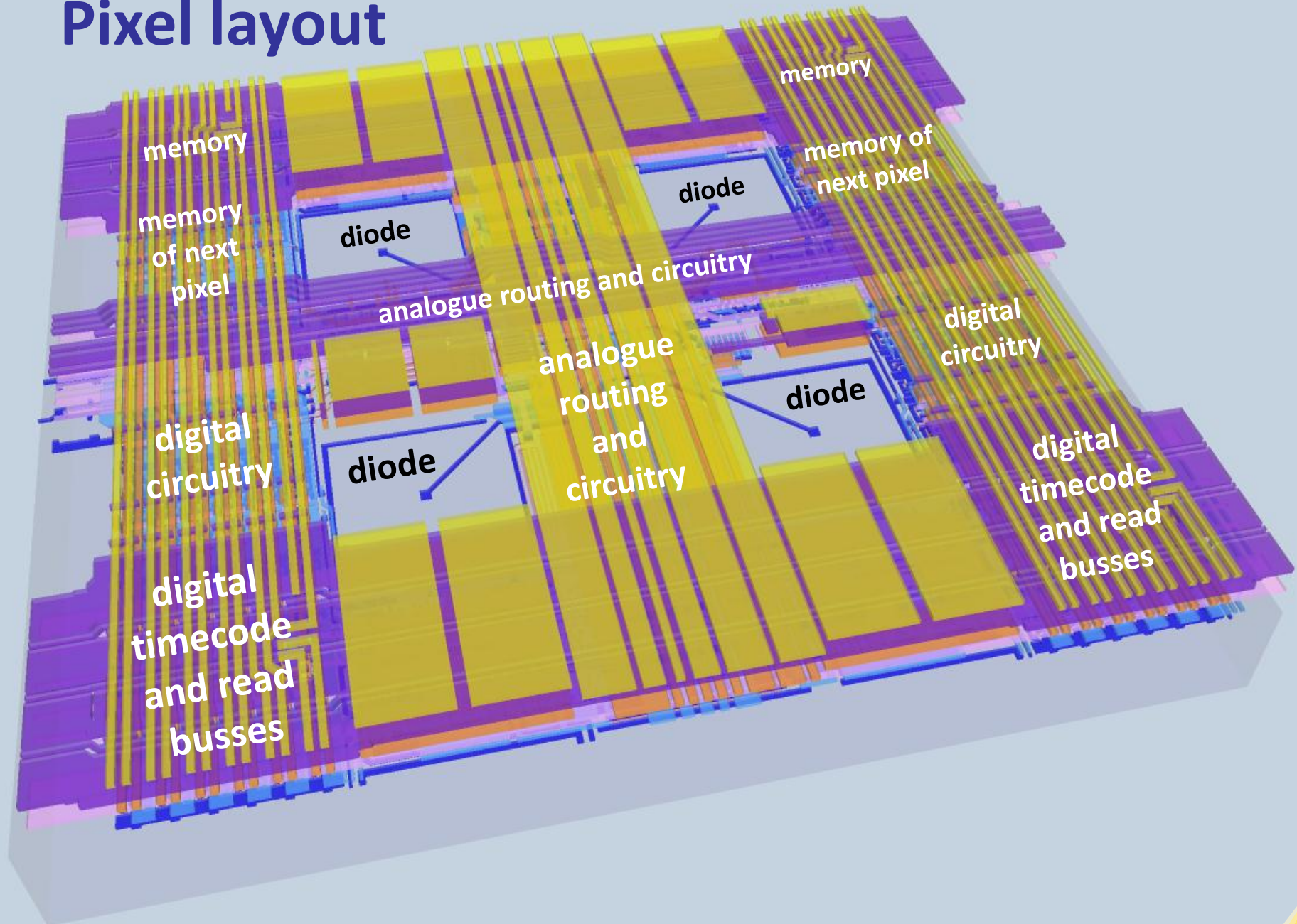
# PIImMS pixel



# Pixel operation

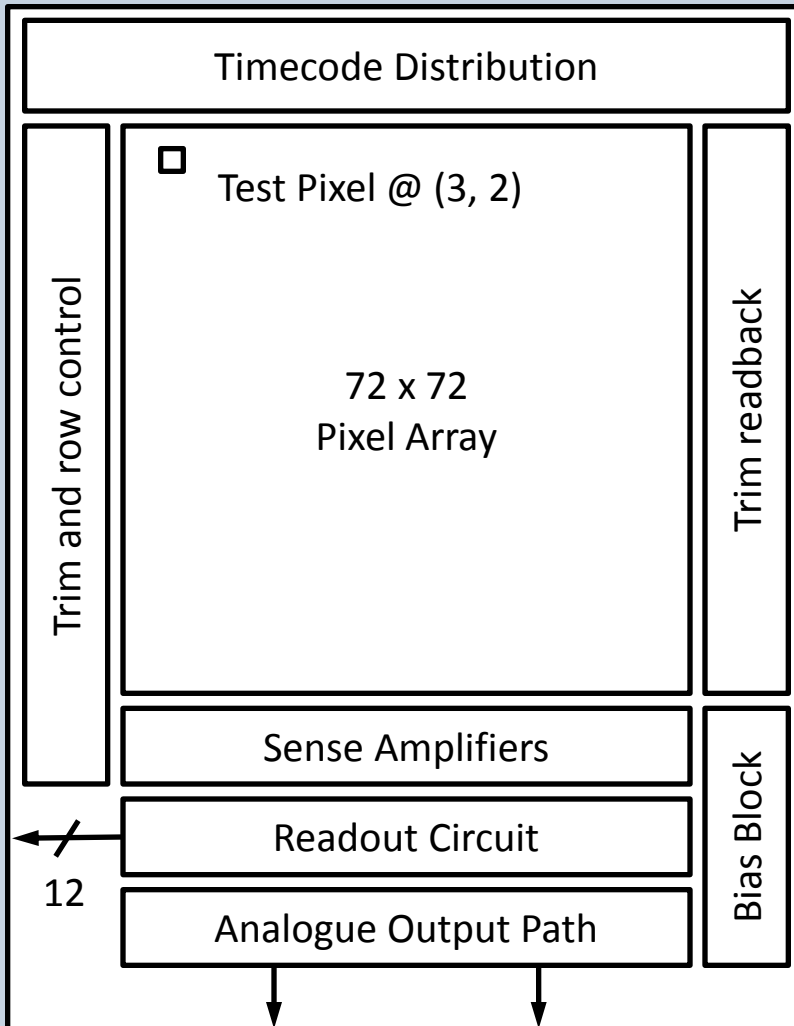


# Pixel layout

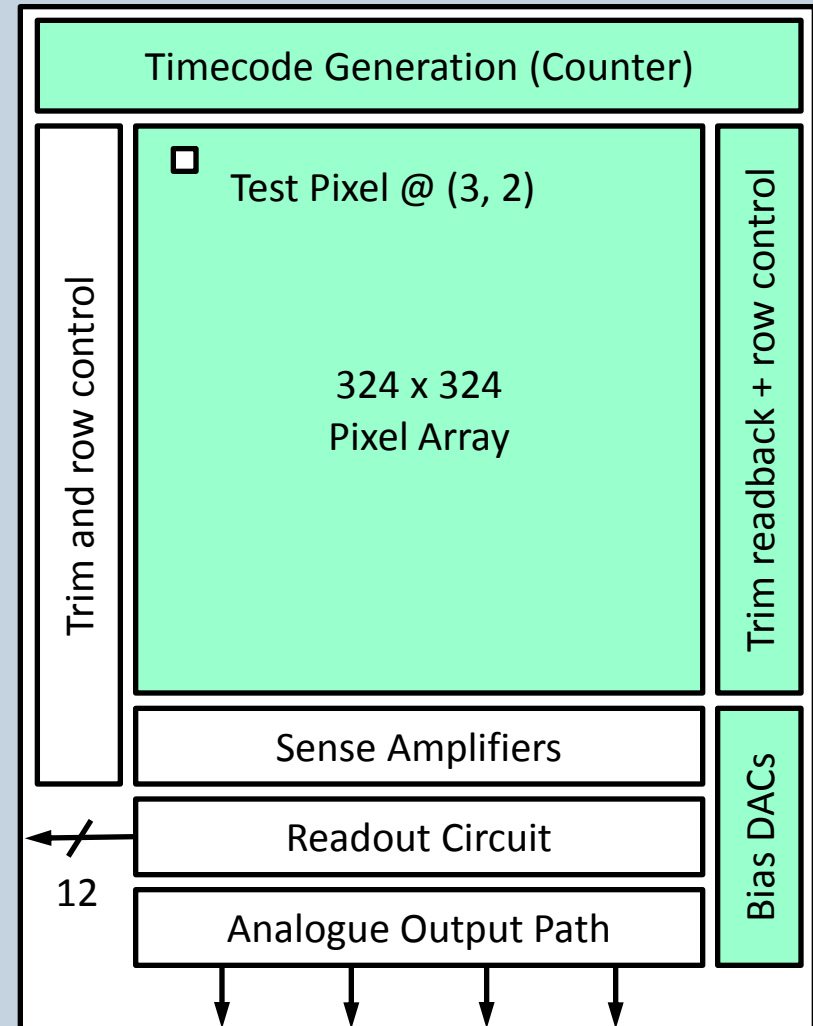


# PlmMS sensors: overview

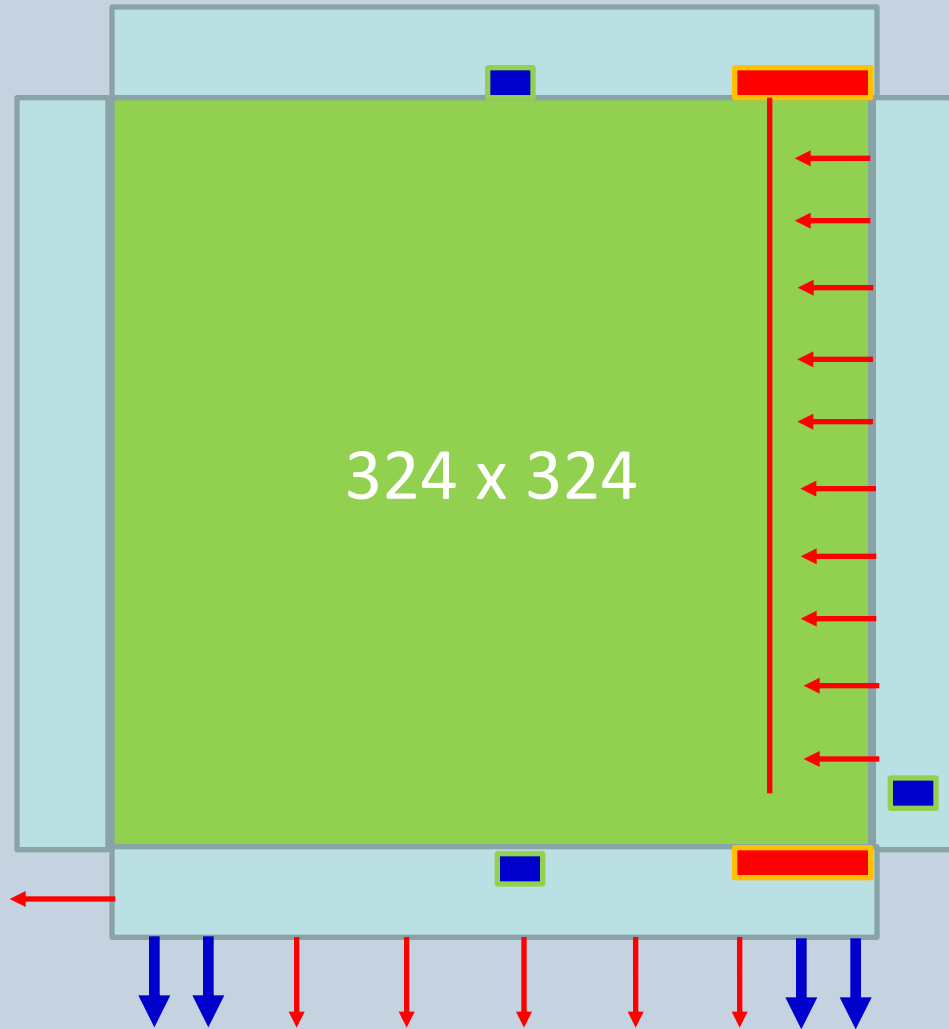
## PlmMS1



## PlmMS2



# PImMS1 to PImMS2:



## New features:

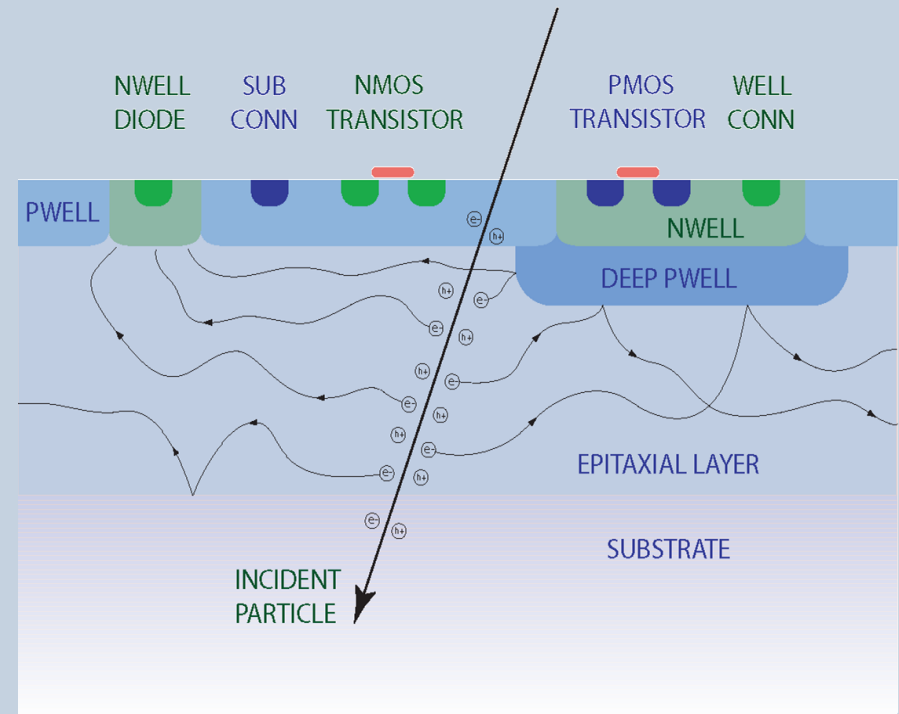
- Array size increased to 324x324
- Additional digital output taps
- Additional analogue outputs
- Extra counters
- Right hand side driver circuitry for row control signals
- Internal bias generator
- Extra pixel trim bias

# PIImMS sensors: technology

- 0.18 $\mu\text{m}$  CMOS fabrication
- INMAPS process developed at the Rutherford Lab:

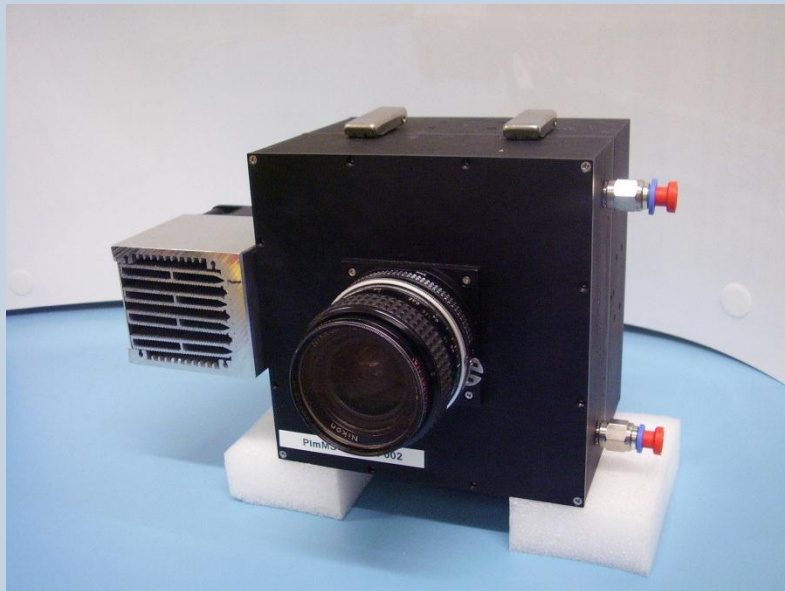
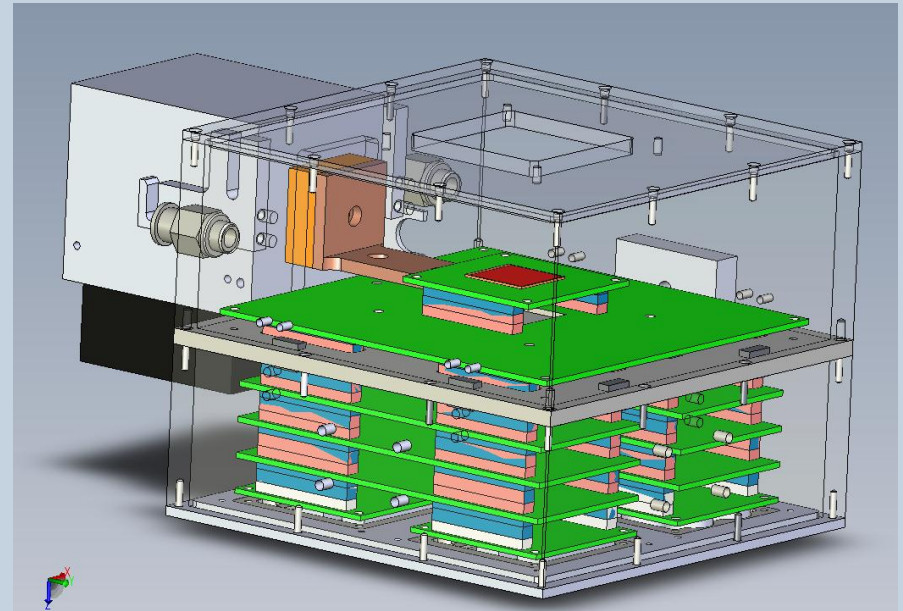
## *Isolated N-well Monolithic Active Pixel Sensors*

- PIImMS pixel: 615 transistors per pixel
- over 3 million transistors in total for PIImMS1



# 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

Milestone	Date
Start of PImMS project	July 2009
PImMS1 sensor received and first light	December 2010
PImMS2 design start	March 2011
PImMS1 first mass spectrometry results	April 2011
Resolution of several PImMS1 camera (DAQ) issues	January 2012
PImMS1 25ns timecodes verified	April 2012
PImMS2 design submitted	February 2012
PImMS1 12.5ns timecodes verified	Last week
PImMS2 current status: wafers are being diced	This week
Next steps: wirebonding then initial tests of PImMS2	Second half of September



# PIImMS1 characterisation: timing resolution

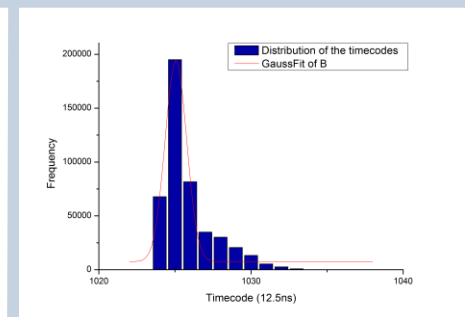
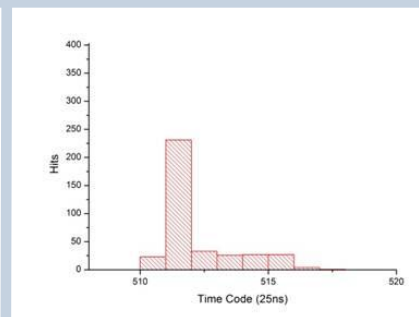
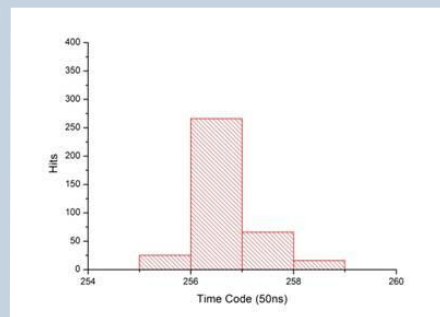
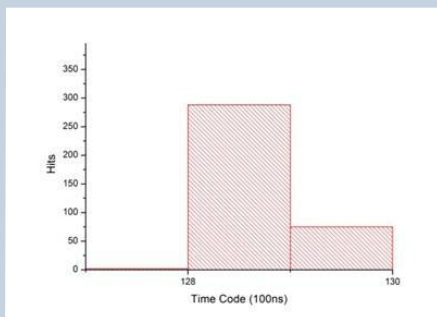
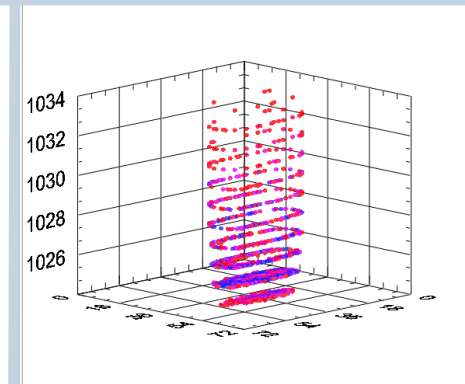
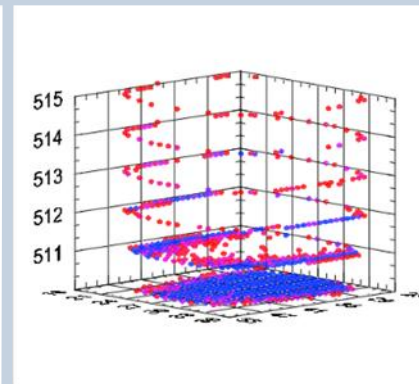
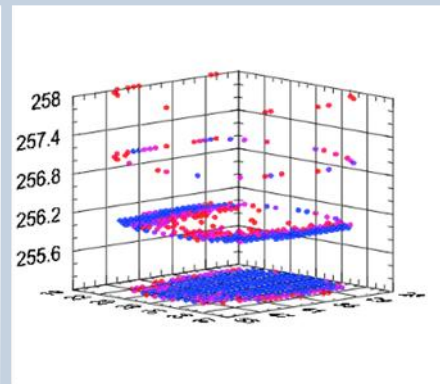
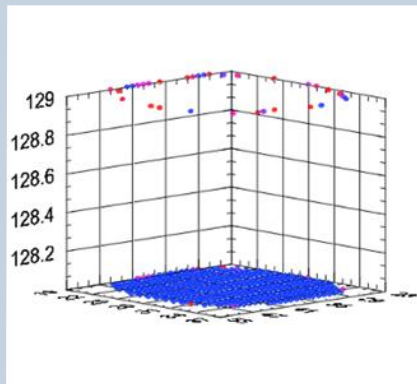
- Testing with timecodes at increasing speeds, using a low-power laser pulse generator
- The edges of the laser spot have progressively lower intensity, showing the degree of timewalk,  $\sim 125\text{ns}$

**100ns**

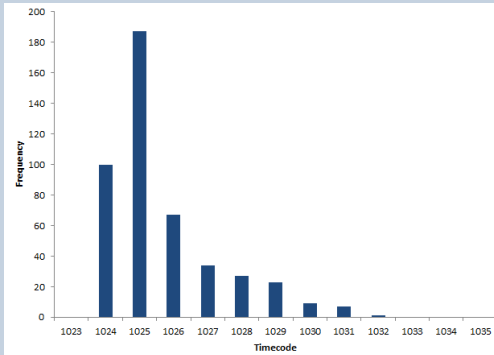
**50ns**

**25ns**

**12.5ns**

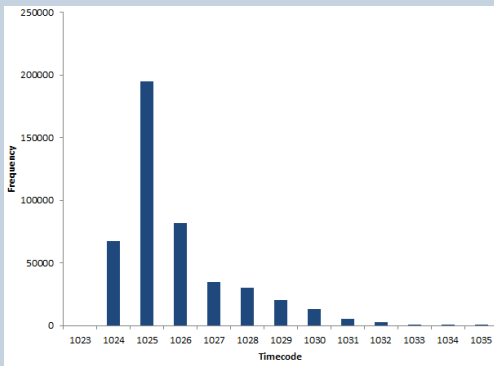


# Timing resolution, continued



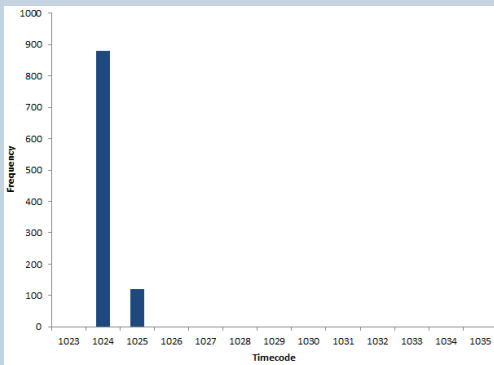
Timecodes present in one frame only:

- sigma 1.65
- time resolution 20.6ns



Timecodes present in all frames:

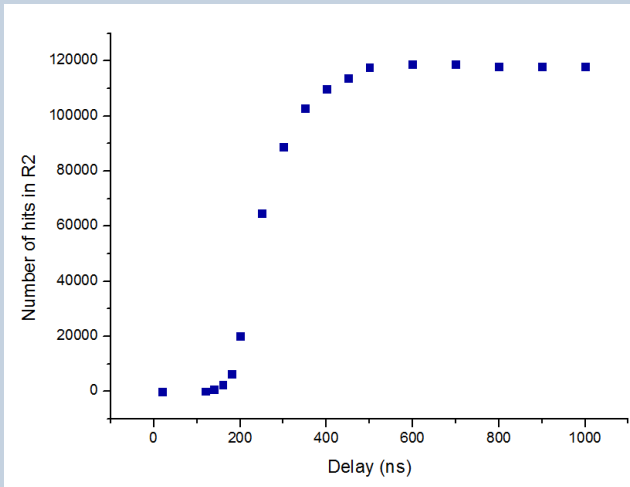
- sigma 1.68
- time resolution 21ns



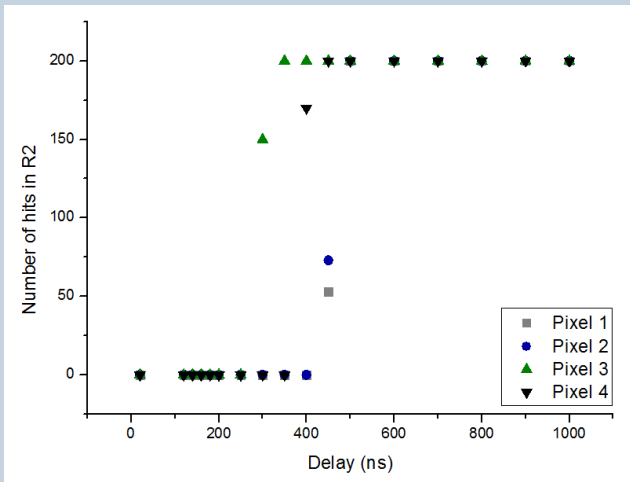
Timecodes present for a single pixel:

- sigma 0.33
- time resolution 4.1ns

# PIImMS1 characterisation: dead time

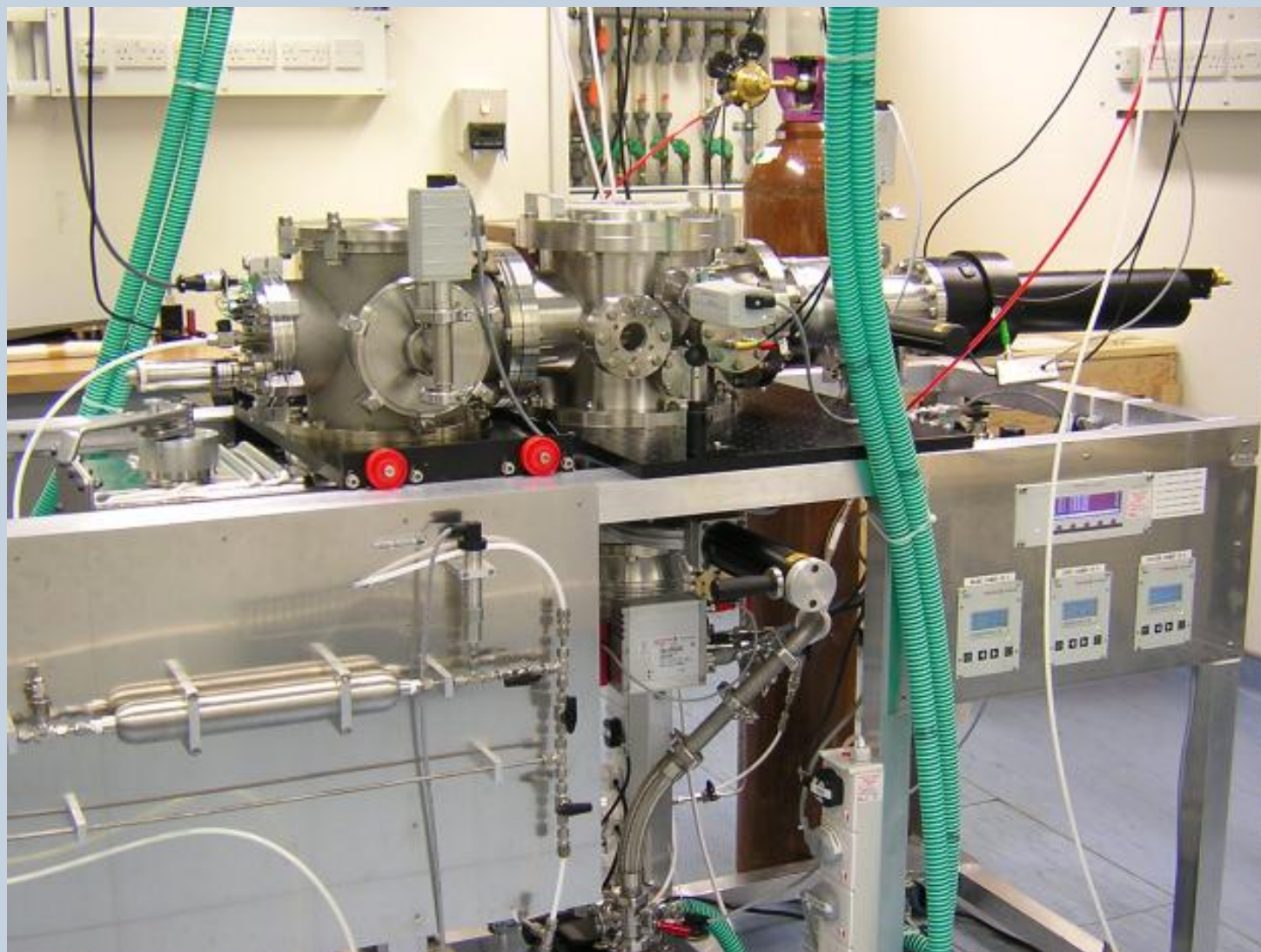


Results for firing two lasers at the same set of pixels, varying the delay between the lasers. If the second laser occurs within the dead time, no pulse will be recorded in the second register.



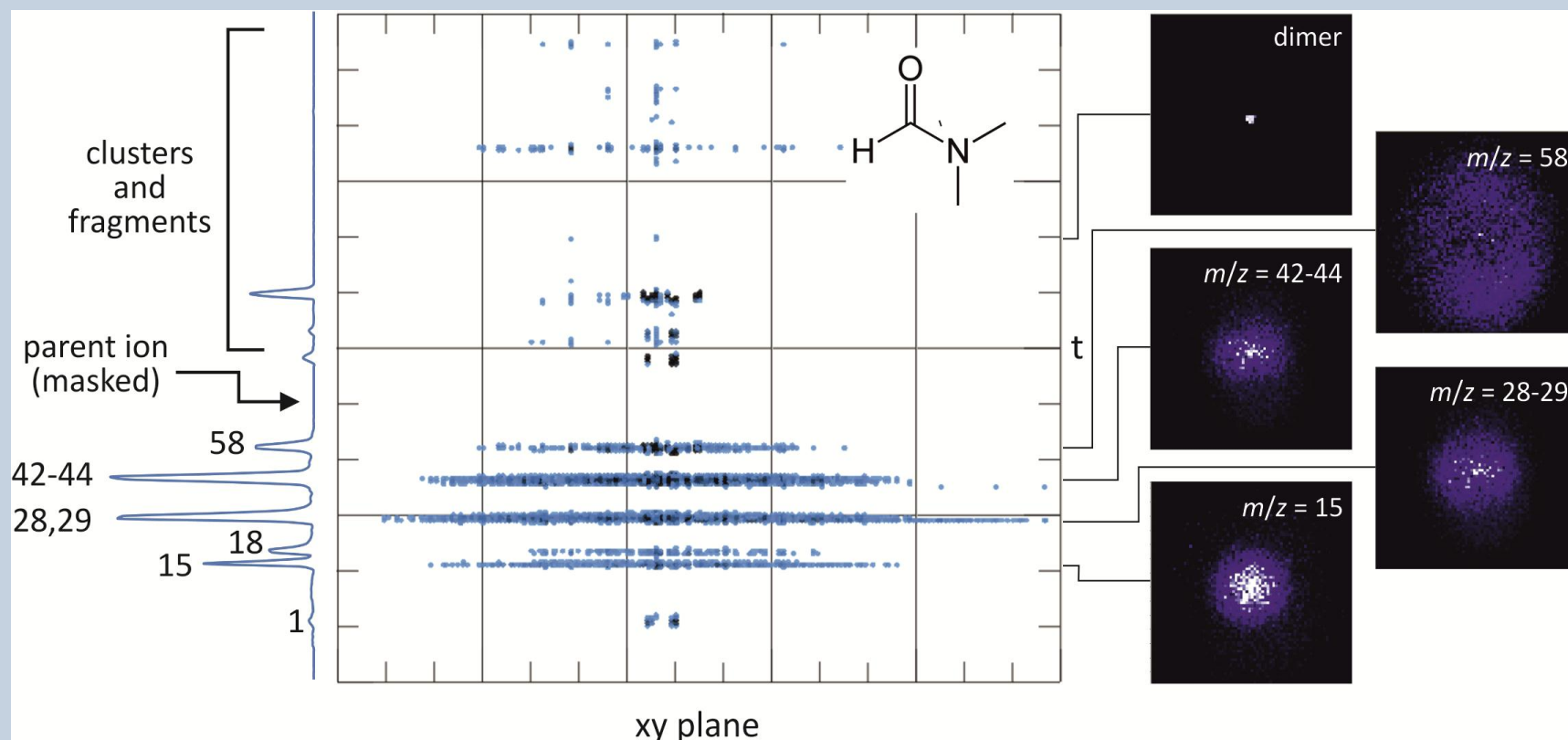
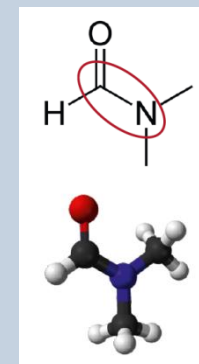
Results for 4 individual pixels, showing the range of responses.

# Application results



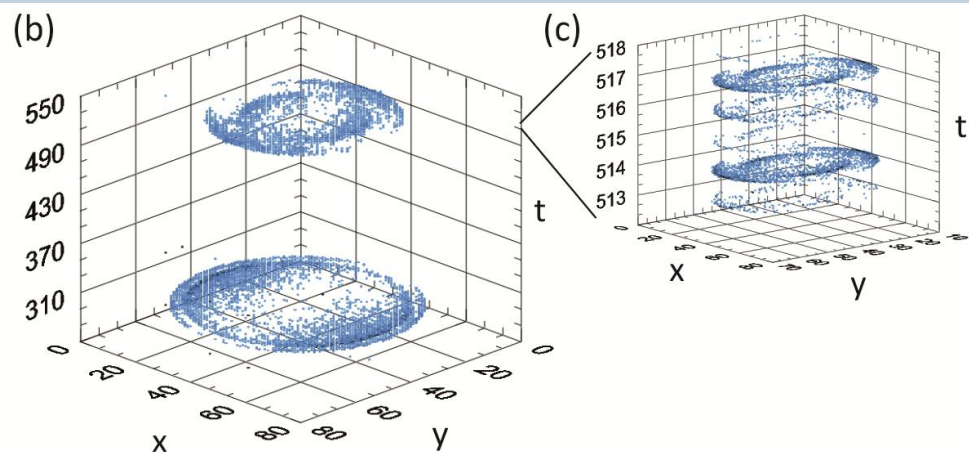
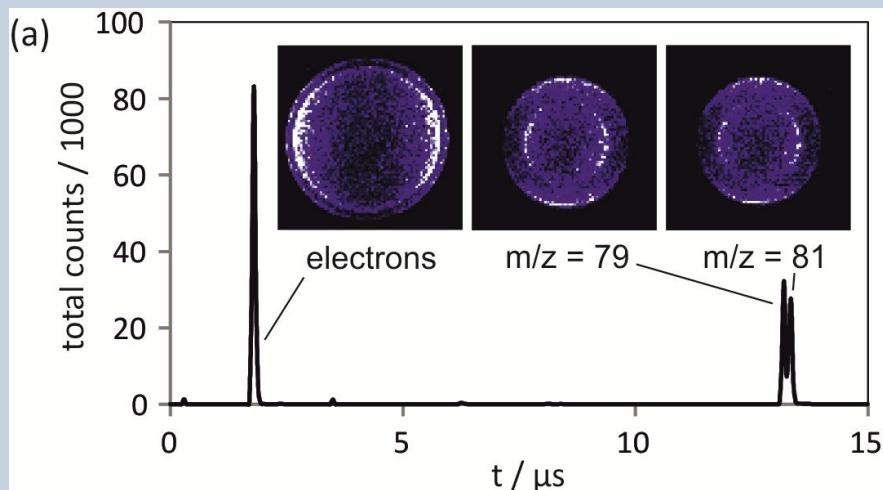
# Applications: velocity map imaging

- 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.

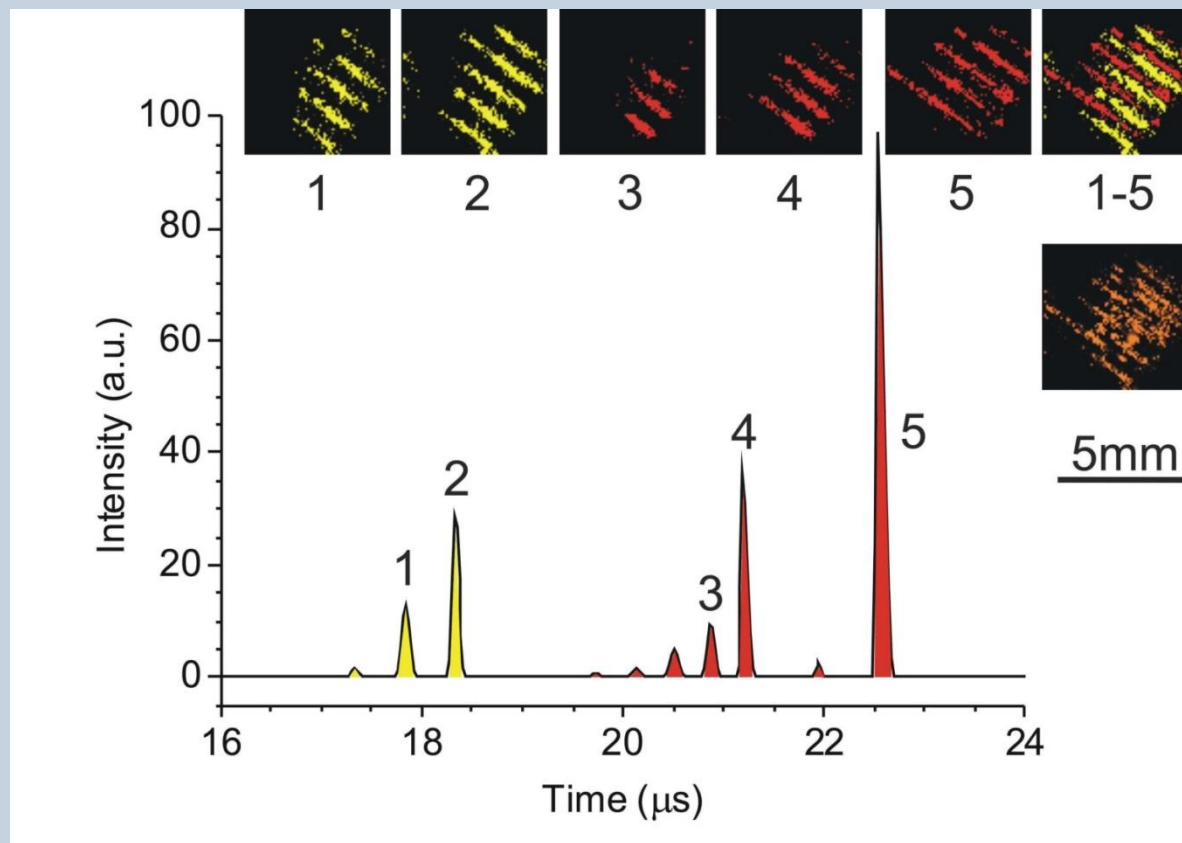


# Applications: coincidence imaging

- Here bromine gas ( $\text{Br}_2$ ) is dissociated. By switching the polarity of the ion optics, first the electrons are imaged, then the ions.
- (a) shows the mass spectrum including  $^{79}\text{Br}^+$  and  $^{81}\text{Br}^+$
- (b) shows the mass intersections for the electrons and Br ions
- (c) zooms in on the two isotopes,  $^{79}\text{Br}^+$  and  $^{81}\text{Br}^+$



# Applications: spatial imaging

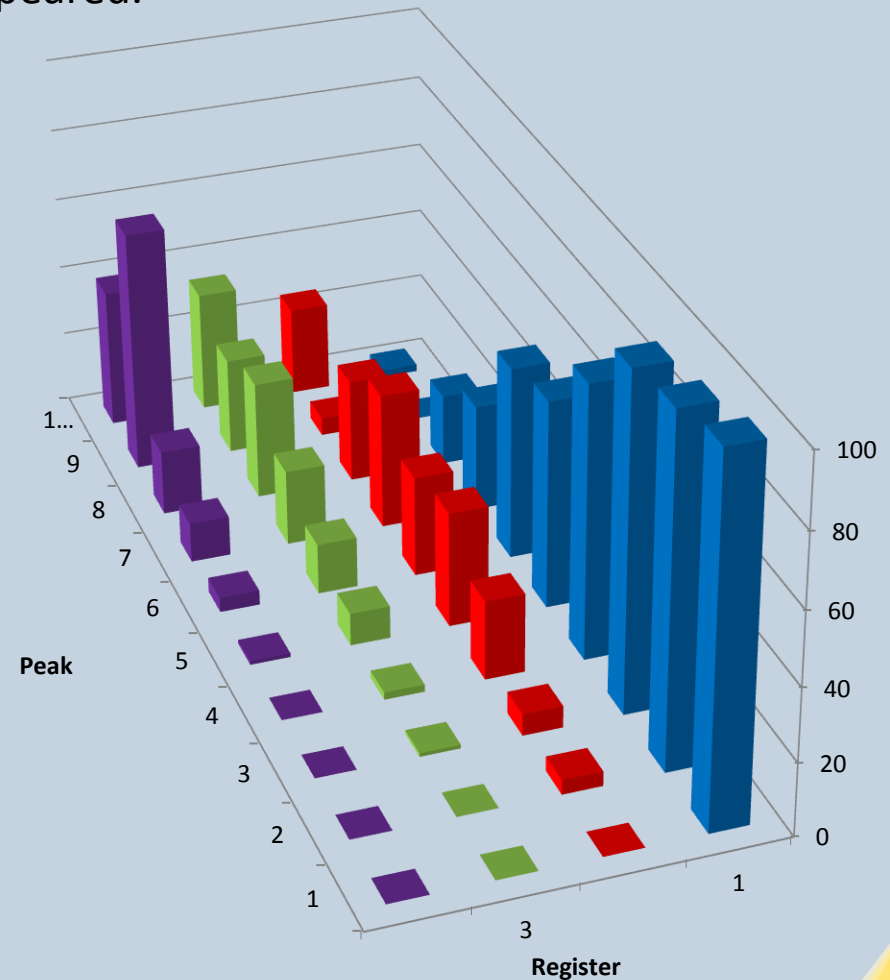
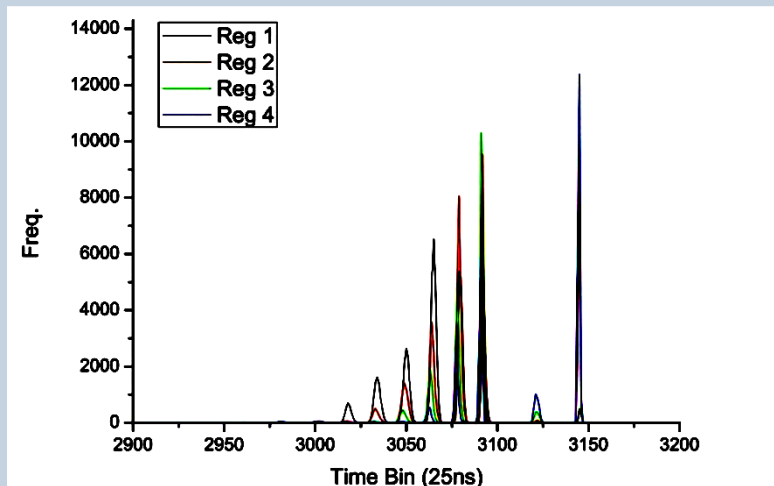
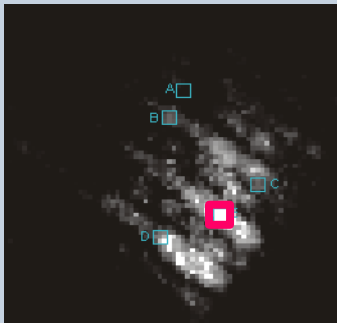


- This is imaging the mass spectrum over a 2D surface.
- Materials used: lines of Auramine O (yellow) and Rhodamine 590 (red)
- The samples produced 10 mass peaks in all. 5 are highlighted here.
- Data taken at 25ns time resolution
- Demonstrates multi-mass imaging

# Spatial imaging, continued

For an intense area of the image, we investigated:

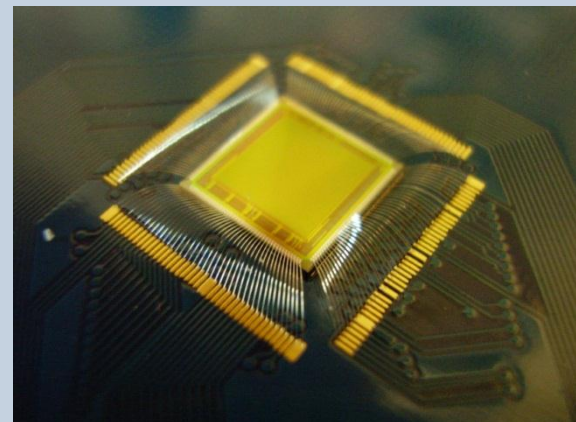
- the proportion of each mass peak seen
- in which pixel register the mass peaks appeared.





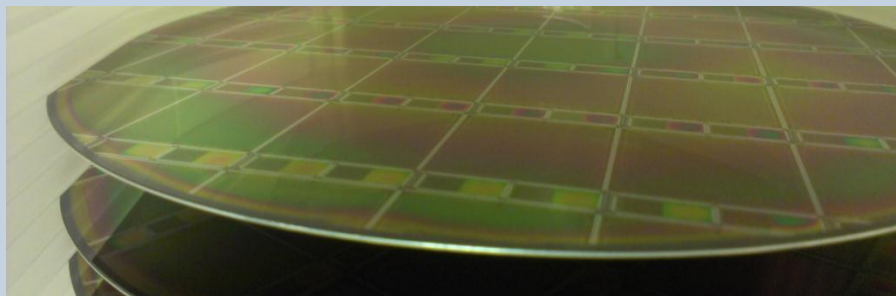
# Summary and future work

- 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?

*PIImMS2  
wafer:*



## The PIImMS Collaboration

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