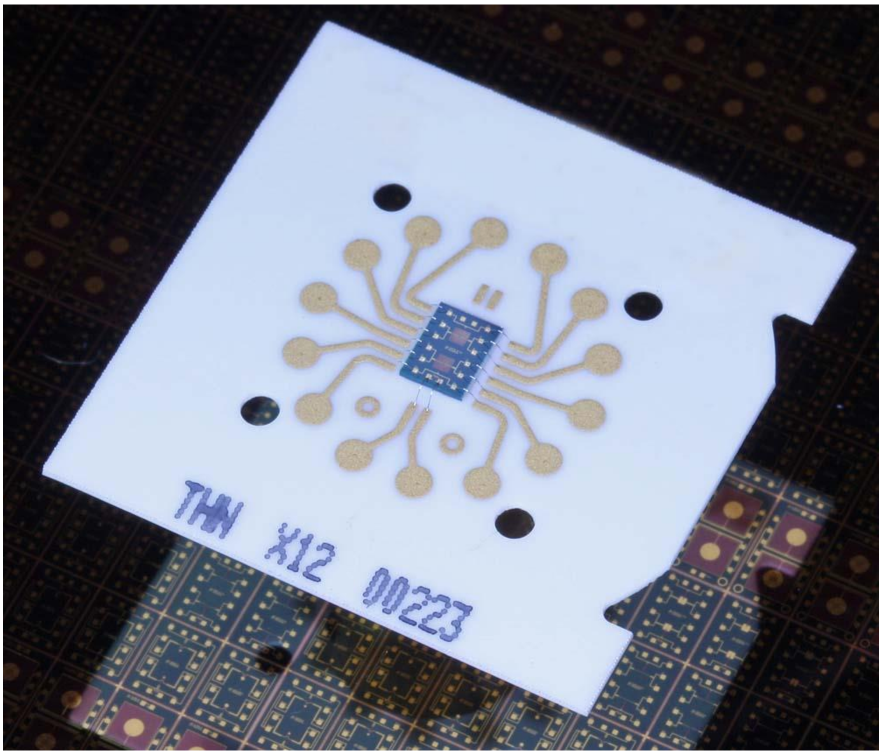

close up of nanogascalorimeter chip on XEN-40002 ceramic housing

Inhoud

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1 Introduction

1.1 About this Application Note

This Application Note is intended to help the users of Xensor's Thin Film Calorimeter chips for use in gases and interface electronics with the set-up and execution of their experiments. It will give some theoretical background information, practical guidelines, specific applications and references to the work of other users.
The Application Note is by no means exhaustive. This means, that if you miss something and have questions, or if you have useful information or interesting applications that you want to share, we highly appreciate your contribution to improving this note.

1.2 Short description

There are two types of nanocalorimeter chips available from Xensor, those based on thicker monocrystalline silicon membranes and those based on thin silicon-nitride membranes.
The first types have low thermal isolation, but are very robust, they are well suited for use in liquid and slow applications (XEN-LCM2506, XEN-LCMquad, XEN-NCM9924). They are described in the "nanogas3939" document.
The types based on SiN membranes of about 1 μm thickness are described in this document. They are fragile but very well isolated and fast, and therefore more suited for application in gaseous environments and for fast measurements, such as Fast Scanning Calorimetry.

The *Gold series* described in this document are made with gold interconnections, enabling them to go higher in temperature than the 3939?-series, which has aluminum interconnections.

All the chips described in this document have outside dimensions of 3.75×2.85 mm, and are 0.3 mm thick.

These sensors are currently not supported by Mettler-Toledo.

Below we will first give some background information on the thin film calorimeter chips and Fast Scanning Calorimetry. Then we will give technical data on the various devices available, and give photos and some details on the devices.

2 Background information

2.1 Introduction

The science of Calorimetry, that observes the heat flows resulting when samples are heated and cooled, is more than 200 years old. Since the early days, many calorimetric instruments have been devised and refined. In the last decades, improving technology has been enabling, but also demanding, that calorimetry becomes smaller, faster, more accurate.

For the analysis of very thin films and particles, measured in micrometers and even nanometers, weighed in micrograms or nanograms, even the most refined DSC instruments simply are not adequate anymore. The same holds for the high-speed calorimetric analysis. The speed of production processes is ever increasing to reduce costs. The speed of calorimetric analysis has to keep up, and where DSC rate of heating and cooling is measured in K/min, some applications really require speeds expressed in kK/s.
The silicon technology used to make computer chips also makes it possible to make different chips, that will actually work as calorimeters, measuring nanogram samples at speeds up to 10 MK/s. The secret is to make everything small, especially the heated volumes. This makes it easier to examine minute samples, and to heat and cool at incredible rates.

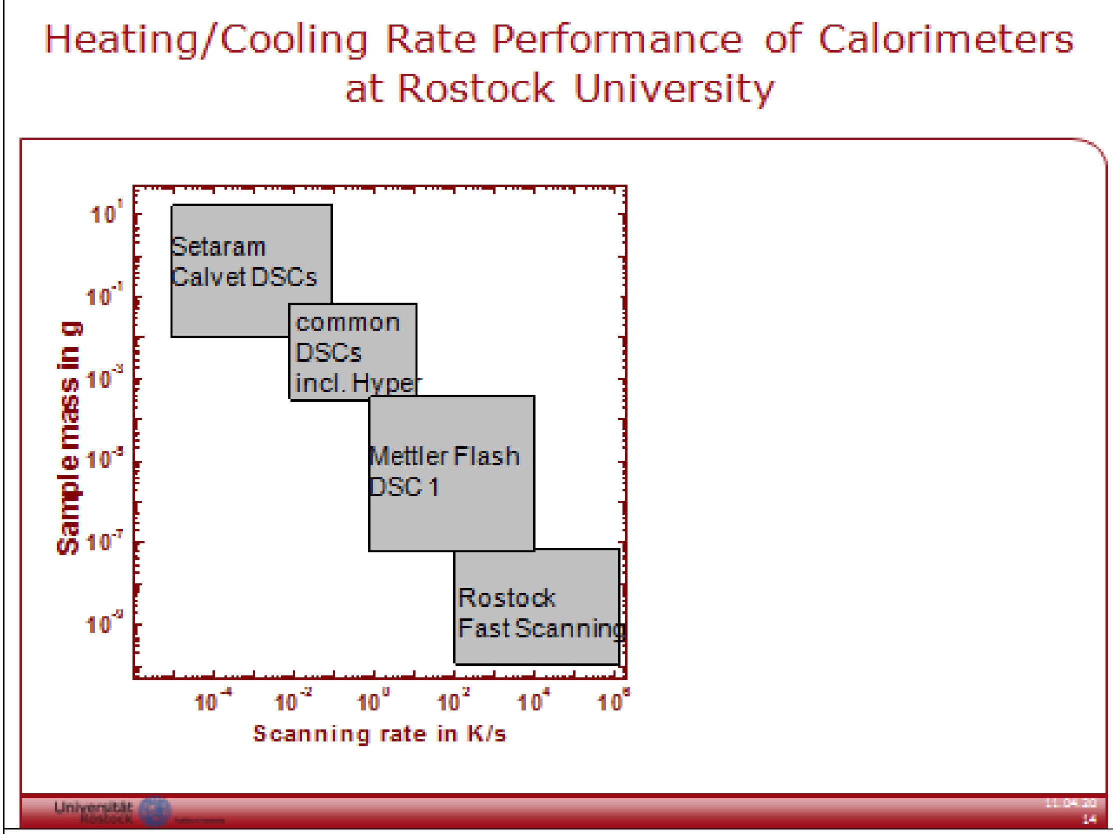
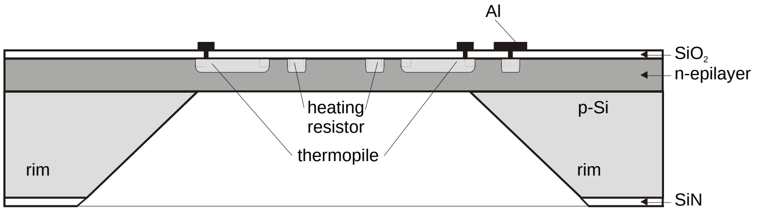


Figure 2.1 Scan rates and sample masses for traditional DSC instruments, the Flash DSC1 of Mettler-Toledo, and fast calorimeter chips.

2.2 Technology

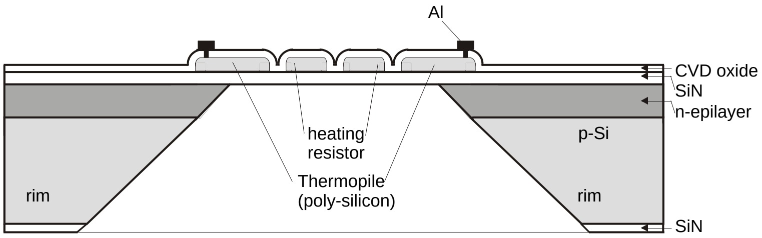
While a lot of work has been done on chip calorimeters with mono-crystalline silicon membranes (technological cross-section shown in Fig. 2.2a), more work has been done on chip calorimeters with dielectric membranes. Here, a membrane based on a low-stress silicon-nitride (SiN) layer is preferred, because of the excellent mechanical properties of such a layer and its relatively low thermal conductivity. The technology of such a device is shown in Fig. 2.2b. The low thermal conductivity of the SiN, together with its smaller thickness, makes that the membrane thermal resistance between the center and the silicon frame is now routinely of the order of 5-50 kK/W in vacuum, compared to a few hundred K/W for the mono-Si closed membranes. This enables us to detect much smaller heat effects.
However, in order not to spoil the high thermal resistance, thermopiles are usually less sensitive in these devices at 1-5 mV/K. So, the overall sensitivity in air is then of the order of 10-100 V/W, about one order of magnitude higher than for silicon-membrane chips.

Figure 2.2 Some technologies to fabricate chip calorimeters:



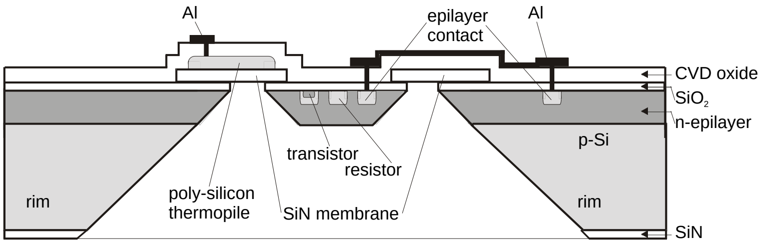
(a)

a) mono-crystalline Si membrane (6-40 μm thick) with mono-Si heating resistors and mono-Si/Al thermopile;



(b)

b) SiN membrane with poly-Si heater and thermopile (1-2 μm thick);



(c)

c) combined mono-Si/SiN membrane process, with poly-Si thermopiles and heaters, and heaters, diodes and transistors in the mono-Si island.

Xensor also offers thin-film-membrane chips for liquid applications, please see the data sheet for this device ("nanoliq-xen-39400"), that will fit on the Flash DESC1 from Mettler-Toledo. For dry applications, the thin dielectric membranes are especially suitable. There are many dry applications, for chemical sensing, for measurement of the thermal and thermoelectric properties of CMOS-process layers, for materials research and magnetic properties of thin films, and, for high-speed scanning calorimetric applications in general.
In the past the design XI-200 / XEN-TCG3880 has been widely used for calorimetry. This chip was designed for quite another application, the measurement of the thermal conductivity of a gas. Therefore, some features were optimized for that application, which has an adverse effect on the calorimetric performance.

2.3 (Ultra)-Fast Scanning Calorimetry

After the feasibility of the fast Calorimetry had been shown using the XEN-TCG3880, a number of new designs were made especially for the Calorimetry application. The XEN-3939? Series is the current series of thin-film fast calorimeter chips offered by Xensor.
Now, new chips are available that offer even higher scanning rates and higher operational temperatures, as the metallization is now gold (melting point 1064 ºC) instead of aluminum (melting point 660 ºC).

As mentioned above, the silicon-nitride membrane chips, which are characterized by a high thermal resistance to the ambient, have a very small time constant. This makes these sensors particularly suited for measurements in gaseous environments on small samples with high temperature scanning rates.
Temperature scan rates (cooling as well as heating) of about 10 MK/s have been obtained by the group of Prof. Schick at Rostock University with the XEN-39394, see Fig. 2.3.
Thus, in some milliseconds, a complete measurement is carried out. Here typical temperature ranges are from 4 K up to 450 K for the frame, while the membrane center, with the sample, can go up to 800 K for very short periods of time. The maximum temperature difference between frame and center of the membrane has to be limited, though, as the thermal expansion may cause mechanical problems. A difference of 500 K is usually the maximum that can be tolerated. Thus, the range of these sensors comes closer to that of basic calorimeter instruments.

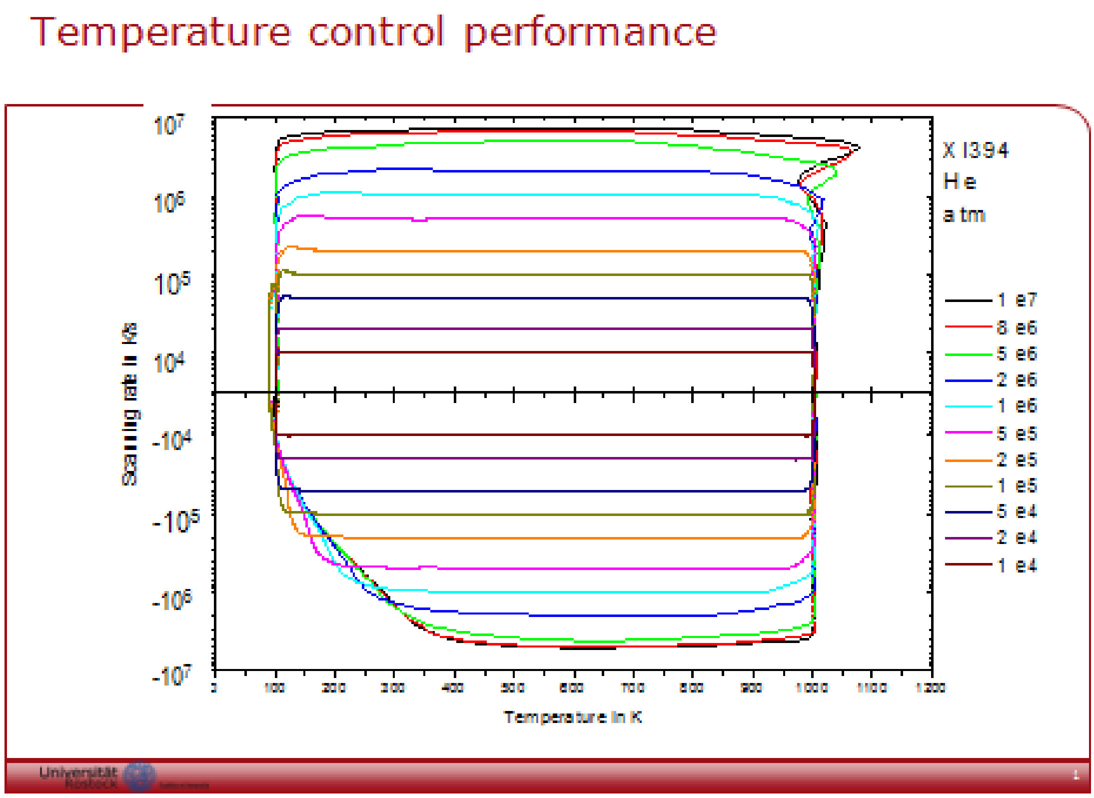


Figure 2.3 Scan rates achieved with the XEN-39394 in a helium atmosphere and the Rostock electronics. Graph courtesy of Prof. Schick, University of Rostock.

With the XEN-39473 high temperature sensor ultra high scan rates have been achieved by Rostock University (group of Prof. C.Schick). The cooling scan rates are well in excess of 100 MK/s (see Fig. 2.4). A cooling scan rate of 10 MK/s can be maintained down to 25 K above ambient temperature, as indicated in Fig. 2.4.

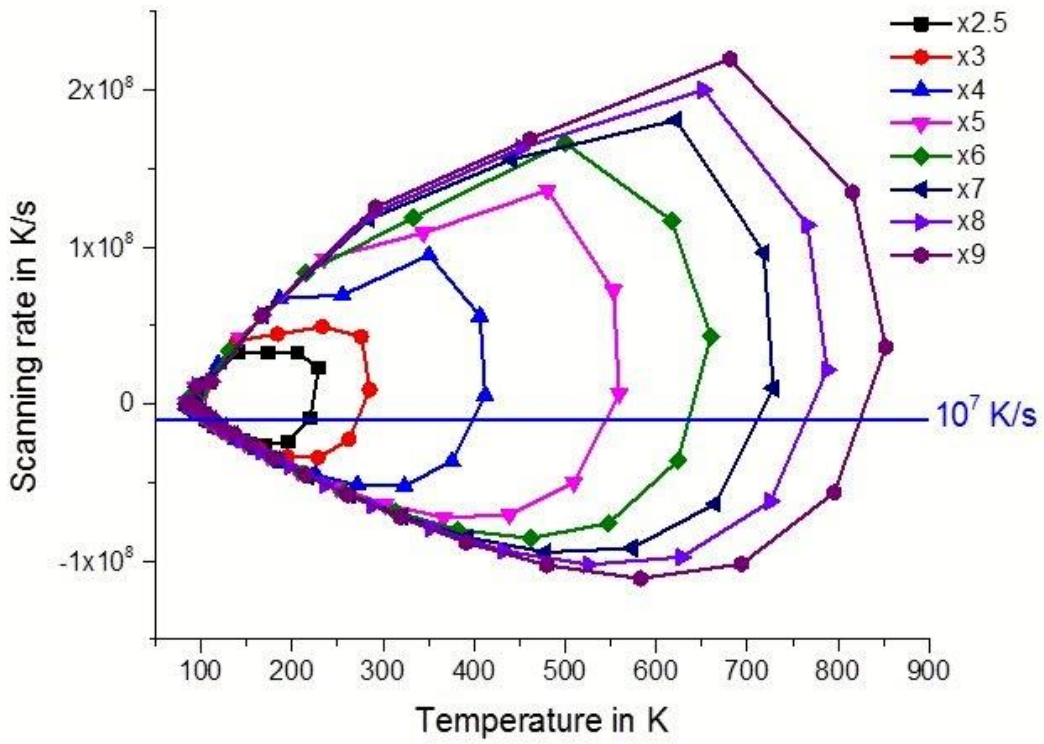


Figure 2.4 First high scan rates achieved with the XEN-39473 in a helium atmosphere and the Rostock electronics. Graph courtesy of Prof. Schick, University of Rostock.

3 Technical data

3.1 Specials

The chips described here are used extensively for scientific experiments. Many of our customers have special wishes for special experiments. Many of these wishes can be discussed, and often solutions are found enabling novel experiments. If you have an idea please contact us.

To give some examples, some specials are listed below.

- Mettler-Toledo Flash DSC1 compatible ceramic housing to use with spring-loaded contacts.
- Ceramic Housing XEN-40014 with holes to allow through-light, and placement of the sample at the back side (onto the SiN membrane).
- Non-magnetic LCC-20 housings for magnetic experiments.
- TO-5 10 pins housings.
- Special glues for extended temperature range, increased thermal conductivity or low outgassing.
- Naked die for mounting on your own housing.
- TO-5 sockets with (or without) small PCB for easy and convenient connection.

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3.2 Specifications (preliminary)

Table 3.1 Specifications (ambient temperature 22 ºC, air, 1013 mbar).

	XEN-39469	XEN-39470b	XEN-39471b	XEN-39472	XEN-39473b		
Parameter	*typ*	*typ*	*typ*	*typ*	*typ*	*unit*	*symbol*
Dimensions							
chip dimensions	→	→	3.75x2.85	←	←	mm^2	
chip thickness	→	→	0.3	←	←	mm	
membrane size	0.8×0.8	0.8×0.8	0.7×0.7	0.7×0.7	0.7×0.7	mm^2	
membrane thickness	→	→	1	←	←	µm	
Output	16	16	22	25	12	V/W	*S*
Time constant						ms	τ
Cooling rate						MK/s	τ
Effective Heat capacity						nJ/K	C (=τ/R_{th})
P-P-noise equiv. Power						nW	
Thermopile							
resistance	30	30	6.5	6.5	6.5	kΩ	R_{tp}
sensitivity*	*0.7*	*0.7*	*0.35*	*0.35*	*0.35*	mV/K	S_{tp}
temp coefficient	0.05	0.05	0.05	0.05	0.05	%/K	
Heater							
bias (inner) resistance	6.0	5.7	1.0	1.4	1.2	kΩ	R_{heat}
guard resistance	6.0	5.7	-	-	-	kΩ	R_{guard}
temperature coefficient	→	→	0.1	←	←	%/K	
Thermal resistance							R_{th} (=S/S_{tp})
membrane + gas	22	22	63	71	34	kK/W	
temperature coefficient	→	→	*-0.15*	←	←	%/K	
Maximum heating						V	U_{heat}
Sensor ambient temp							
minimum	→	→	*-40*	←	←	ºC	
maximum	→	→	*85*	←	←	ºC	
Heater max temp							
short term (seconds)	→	→	*800*	←	←	ºC	

Data in italics are estimated

- A preliminary approximation for the thermocouple sensitivity is 330 µV/K + 0.5×T µV/K (T in ºC, -50 ºC to +180 ºC). This value can be different for different designs.

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4 Overview of the devices

4.1 General overview

The use of Fast Scanning Calorimeter chips from Xensor started with Prof. Schick's group from the University of Rostock in fast calorimetry experiments with heating and cooling rates in excess of 10 kK/s using the XEN-TCG3880 on a TO-5 header. After this, new devices have been developed for the FSC application, enabling more accurate temperature measurement than the XEN-TCG3880 allows. Table 4.1 gives an overview of the currently available devices, some of the older devices, if not replaced by a new device, may still be available until sold out.

Table 4.1 Calorimeter chips with different hot spot areas.

Present Device	Replaces	Hot Spot (μm×μm)	Thermopile sensitivity (mV/K) estimated value at 300 K
	XEN-TCG3880	50×100	2.0
	XEN-39269	14×14	1.3
	XEN-39276 @	46×46	1.3
XEN-39390	XEN-39270, XEN-39320	30×30	2.0
	XEN-39277 @	62×62	2.0
XEN-39391	XEN-39271	60×60	2.0
	XEN-39278 @	92×92	2.0
XEN-39392	XEN-39272	100×100	2.0
XEN-39399℗	XEN-39279 @	100×100	2.0
XEN-39393	XEN-39292	8×14	0.35
(XEN-39394)	Sold out	8×10	0.35
XEN-39395	XI-240, XEN-39295	60×70	2.0
XEN-39397	XEN-39347	1000×1000	7.0
XEN-39398℗		250×250	2.0
XEN-39469©		150 Ø	0.7
XEN-39470b©		150 Ø	0.7
XEN-39471b	XEN-39394	8x11	0.35
XEN-39472		6x6	0.35
XEN-39473b		6x6	0.35

@ with aluminum-coated hot spot.
℗ with polysilicon-coated hot spot.
© with gold-coated hot spot.

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4.2 XEN-39469 + XEN-39470b: Large-area high temperature chips

These are two chips designed with large, circular hot spots on the membranes. Both chips have dual membranes. Each membrane has two, concentric heaters, with an outer diameter of 150 µm, and two thermocouples of n-type vs p-type poly-silicon. At high temperatures (800-900 ºC), the SiN membrane starts to electrically conduct, and electrically-conducting coatings can lead to short-circuits and the membrane cracks.
Therefore, in the XEN-39469, the center within the heaters is covered by gold to obtain a uniform temperature, but the heaters are not covered by gold. This should enable the XEN-39469 to survive higher temperatures than the XEN-39470b, in which also the heaters are coated with gold. Temperatures up to the silver point (962 °C) have been attained. Because of the risk of thermal runaway heating to such temperatures should be done carefully, preferably not from a pure voltage source.
The XEN-39470b is estimated to be somewhat more stable at high rates.
The chips are pin-compatible with the Flash DSC1 of Mettler-Toledo, but not yet electronically compatible.

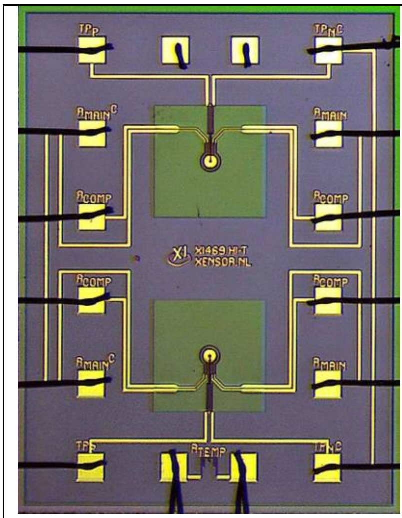

Figure 4.1 XEN-39469 chip, on XEN-40002 ceramic.

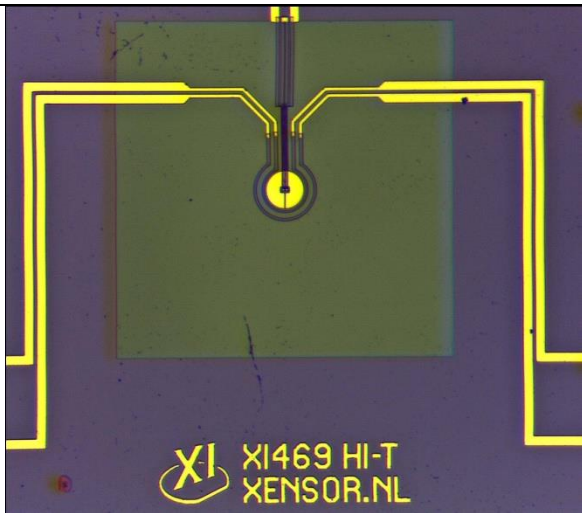

Figure 4.2 Close up of center of XEN-39469 chip.

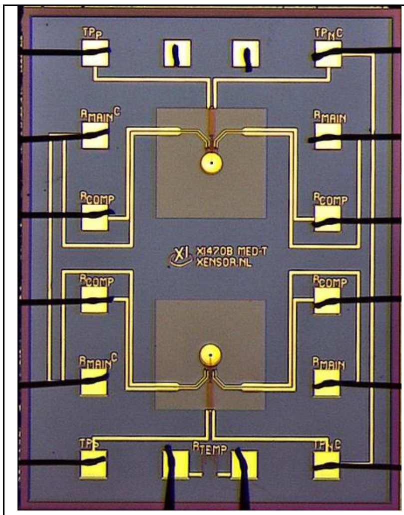

Figure 4.3 XEN-39470b chip, on XEN-40002

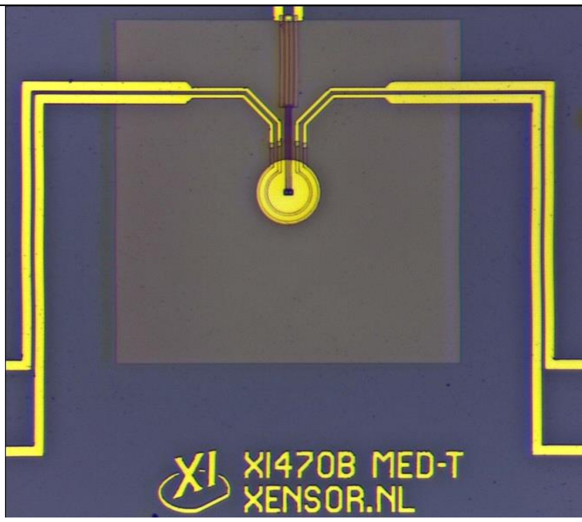

Figure 4.4 Close up of center of XEN-39470b chip.

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ceramic.		

4.3 XEN-39471b: Fast calorimeter chip replacing XEN-39394

This is a small-sized hot-spot-area nanocalorimeter chip, with a hot spot area of about 8×11 μm, with a single heater and a single thermocouple. It replaces the XEN-39394, and has dual membranes, in contrast to the XEN-39394 single membrane.

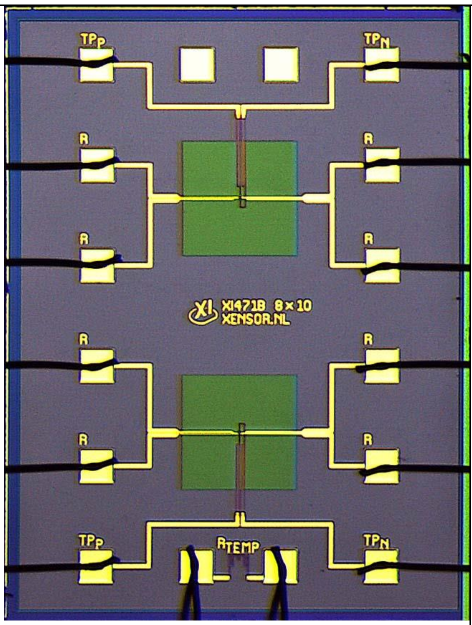		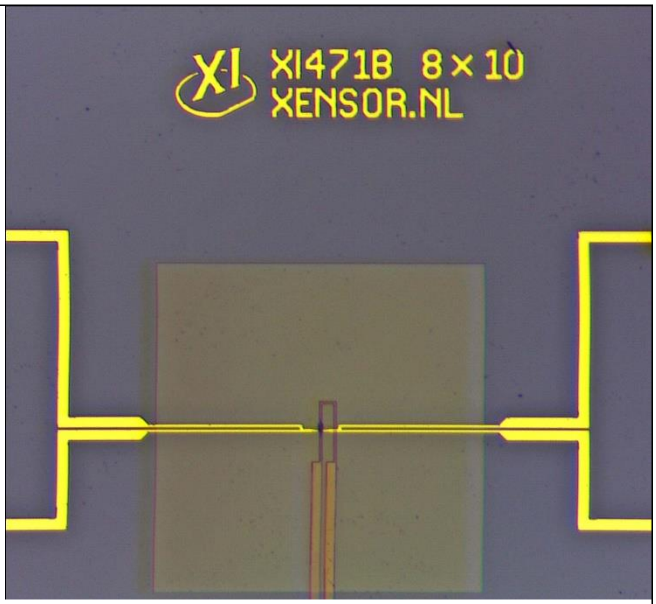
Figure 4.5 XEN-39471b chip, on XEN-40002 ceramic.		*Figure 4.6 Close up of center of XEN-39471b chip.*

4.4 XEN-39472 + XEN-39473b: Ultra-fast calorimeter chips

These two devices, which have dual membranes, have very small hot spots of about 6×6 μm, with a single heater and single thermocouple.
The small size of the hot spot is designed to make the devices very fast. In the XEN-39473b, an extra gold heat sink is created at 5 μm distance from the hot spot, so that cooling is even faster than in the XEN-39472. The transfer of the XEN-39473b is half as high as of the XEN-39472, as a result of this heat sink. For the XEN-39473 cooling scan rates in excess of 100 MK/s have been attained, see Par. 2.3.

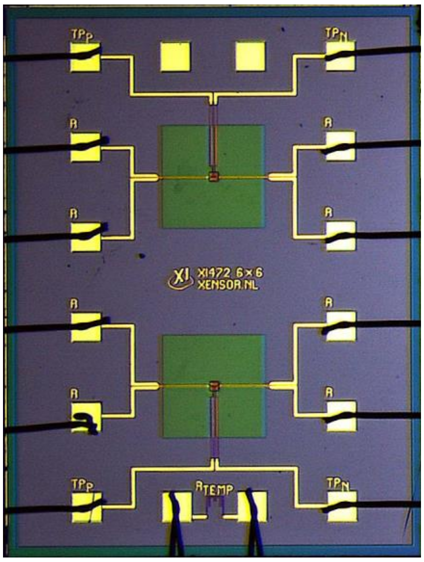

Figure 4.7 XEN-39472 chip, on XEN-40002 ceramic.

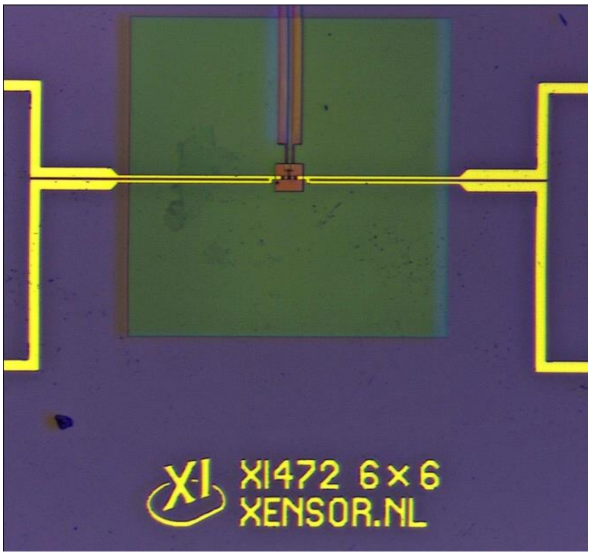

Figure 4.8 Close up of center of XEN-39472 chip.

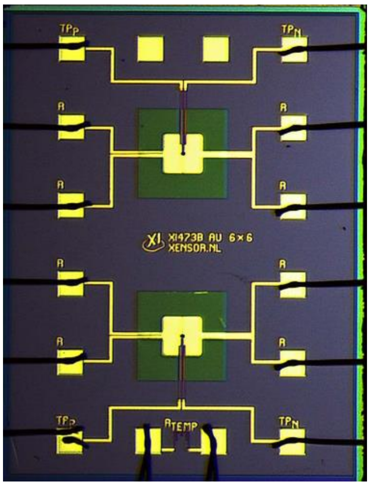

Figure 4.9 XEN-39473b chip, on XEN-40002 ceramic.

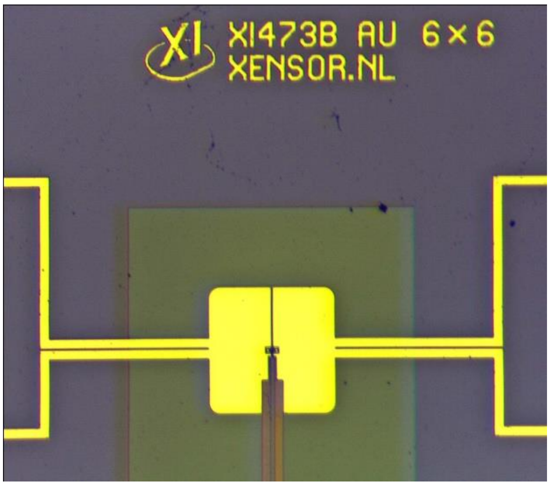

Figure 4.10 Close up of center of XEN-39473b chip.

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5 Housings and pinning

5.1 Housings

XEN-39471 on various available housings.

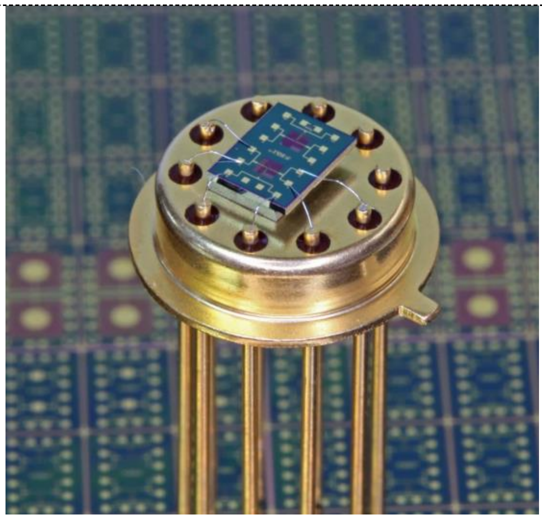

Figure 5.1 XEN-39471 on TO-5.

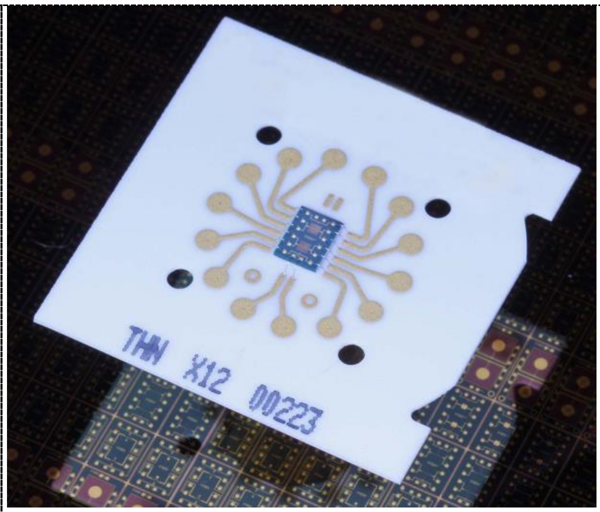

Figure 5.2 XEN-39471 on XEN-40002 ceramics. (24×24 mm).

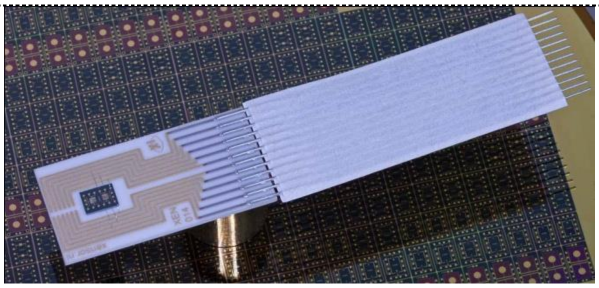

Figure 5.3: XEN-39471 on XEN-40014 ceramic (24×12 mm plus flex connector).

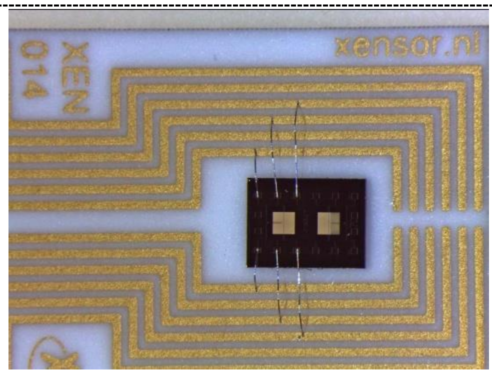

Figure 5.4: XEN-39471 on XEN-40014 ceramic (24×12 mm). Close up.

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5.2 Pinning

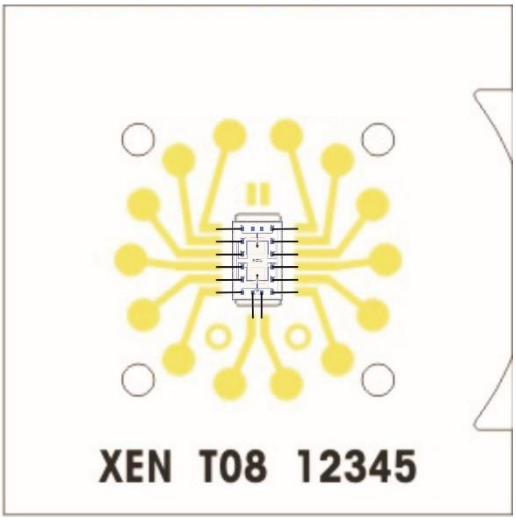

Figure 5.5 XEN-39469 on XEN-40002.

pin	(left top counter clockwise)
1	Out_{top} (+)
2	$R_{\text{main common}}$
3	$R_{\text{comp top}}$
4	$R_{\text{comp bottom}}$
5	$R_{\text{main common}}$
6	$\text{Out}_{\text{bottom}}$ (+)
7	R_{temp}
8	R_{temp}
9	$\text{Out}_{\text{common}}$
10	$R_{\text{main bottom}}$
11	$R_{\text{comp bottom}}$
12	$R_{\text{comp top}}$
13	$R_{\text{main top}}$
14	$\text{Out}_{\text{common}}$

Designs: XI-469 t/m XI-470b.

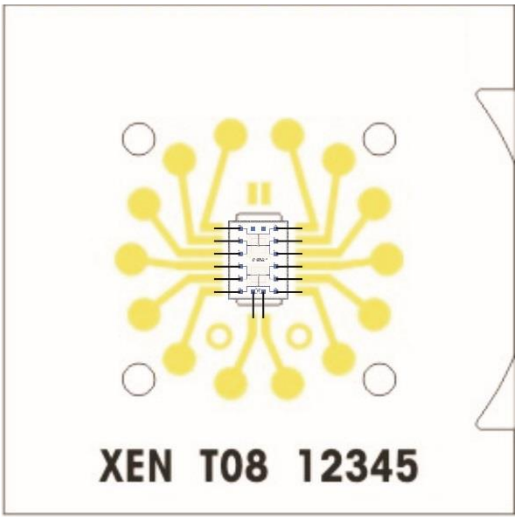

Figure 5.6 XEN-39471b on XEN-40002.

pin	(left top counter clockwise)
1	Out_{top} (+)
2	$R_{\text{heat top}}$ (+)
3	$R_{\text{heat top}}$ (+)
4	$R_{\text{heat bottom}}$ (+)
5	$R_{\text{heat bottom}}$ (+)
6	$\text{Out}_{\text{bottom}}$ (+)
7	R_{temp}
8	R_{temp}
9	$\text{Out}_{\text{bottom}}$ (-)
10	$R_{\text{heat bottom}}$ (-)
11	$R_{\text{heat bottom}}$ (-)
12	$R_{\text{heat top}}$ (-)
13	$R_{\text{heat top}}$ (-)
14	Out_{top} (-)

Designs: XI-471b t/m XI-473b.

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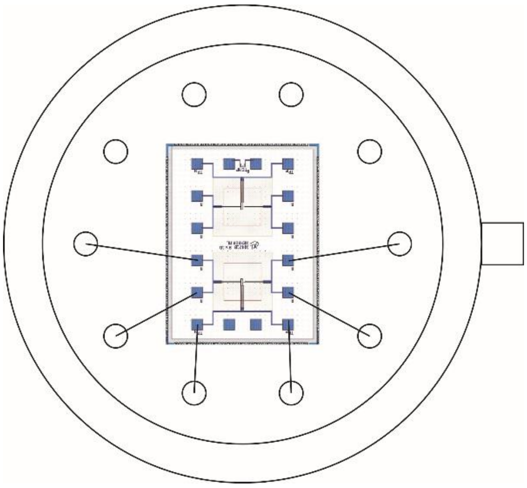
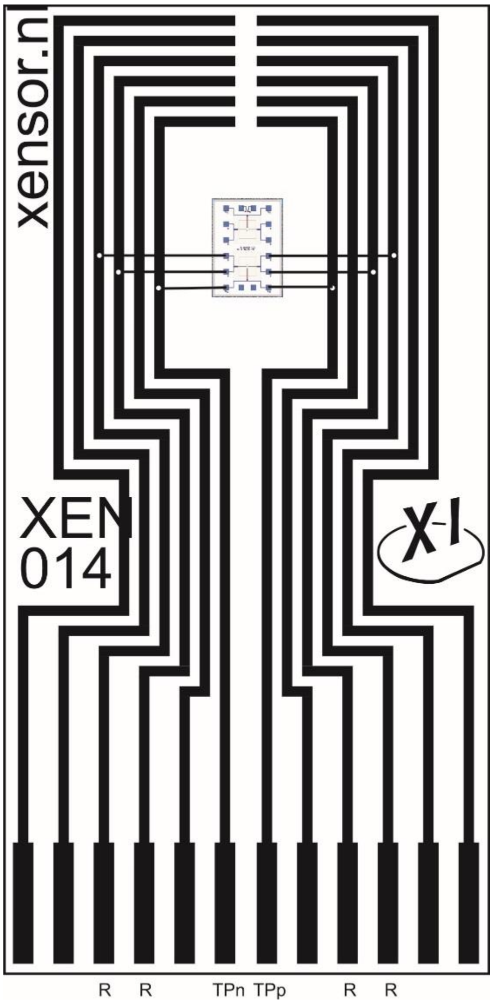


pin	(counter clockwise)
1	R_{heat} (+)
2	nc
3	nc
4	nc
5	nc
6	R_{heat} (-)
7	R_{heat} (-)
8	Out (-)
9	Out (+)
10	R_{heat} (+)

Figure 5.7 XEN-39471b 6 wires on TO-5 10 pin.

Designs: XI-471b t/m XI-473b.



pin	(left to right)
1	nc
2	nc
3	R_{heat} (-)
4	R_{heat} (-)
5	nc
6	Out (-)
7	Out (+)
8	nc
9	R_{heat} (+)
10	R_{heat} (+)
11	nc
12	nc

Figure 5.9 XEN-39471b on XEN-40014.

Designs: XI-393 t/m XI-395.

6 References

For articles on nanocalorimeters see our website:
www.xensor.nl/index.php/publications

In general for the work of the group of Prof. Schick, see their web site:
http://www.polymerphysik.uni-rostock.de/

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