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14. ABSTRACT

This report results from a contract tasking Angstrom Aerospace Corporation as follows: This proposal offers to investigate in greater detail the properties between liquid metals and phase-change materials in nano-micro scale volumes on a fundamental level. Investigations of novel metal-alloy combinations and phase-change materials will be performed through three proposed phases, where the phases go from fundamental research to an experimental device. Properties of such as wetting, adhesion, surface deformation, tension, diffusion, in-stability (mixing) in the boundary interface will be studied. The research will focus on the properties between liquid metal-phase change materials where the melting point of the metal is below the phase change material.
A common feature of long hydrocarbon chains (Paraffin and similar) is the distinct volume increase during the phase change from solid to liquid, 15% or more is not unusual. The volume expansion is hydraulic or incompressible to its nature.
The metals to be tested are Low Melting Point alloys based on Bismuth/Tin/Indium compositions, but other alloys and even pure metals such as Mercury could beconsidered.
The wetting properties between a thin-film of solid metal and the boundary layer created between the LMP and the phase change material will also be investigated.

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THERMAL SWITCH

Fundamental investigation of interactions and behavior between phase change materials and liquid metals in nano-micro scale volumes

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1 Summary

A MEMS based thermal switch concept intended for active thermal control in aerospace or ground applications is investigated. The device uses paraffin as a phase changing actuator material and a low melting point alloy (LMP) as a heat/current transferring material. The fluid interface of these two materials is the focus of this study to ensure correct operation of the device as internal forces and effects turn out to be the dominant parameters influencing the behavior of the device.

Therefore the first part of this study includes observations about the interfaces of the involved materials on different surfaces like silicon, copper, aluminum, gold and nickel. This study includes the realization of a microstructured test environment and presents a generation of small structures under consideration of the final design concept. Fabrication and handling issues regarding the involved materials are addressed herein. Furthermore, the behavior and effect of various fluxes on a low melting point alloy in conjunction with several base metals are investigated along with possible flux-free methods of creating solder joints. Material configuration as well as pretreatment of the paraffin actuator as well as the LMP in order to enable device functionality.

Furthermore, the behavior and effect of de-oxidized low melting point alloy in conjunction with base metals used for soldering purposes are investigated along with the possibility to activate the LMP alloy utilizing diluted HCl or formic acid

Hereafter, we present a feasibility study of a thermal switch design entirely made of silicon and utilizing the phase change materials paraffin and LMP. The study includes the realization of microstructured test devices under consideration of design aspects which were derived from early phases. Fabrication and handling issues regarding the involved materials are addressed herein.

Prototypes have successfully been fabricated in silicon. They allow subsequent filling with the phase change materials and are operational after sealing off inlet and outlet. Finally, a successful proof-of-concept test showed the 10x10x1mm switch being able to handle 3W when actuated to contact with a heat sink, to compare to 1.3W when not (at 90 C).

In many devices, where substantial heat is generated, there is a need for active thermal control. This study is an investigation toward the realization of a micro mechanical thermal switch concept which is a crucial part of a complete thermal control system. The concept can potentially be used in either ground or aerospace applications and utilizes Micro Electro Mechanical Systems (MEMS) technology. The functionality of this switch concept is based on the interaction of a phase change paraffin actuator in conjunction with a low melting point alloy (LMP). The paraffin actuator is used in order to convert thermal energy into mechanical motion resulting in the deflection of a membrane, whereas the LMP enables improved transfer of heat and/or electrical current through the device.

This switch concept is based on the following operation principle. Upon heating, the phase change materials liquefy. As a result of the volume increase of the phase change actuator upon melting, the flexible membrane bends upwards. Accordingly, the liquid LMP is following this membrane movement and potentially stretches inside the cavity. While cooling down the paraffin solidifies slightly before the LMP and the membrane bends back to its initial position prior to the solidification of the LMP.

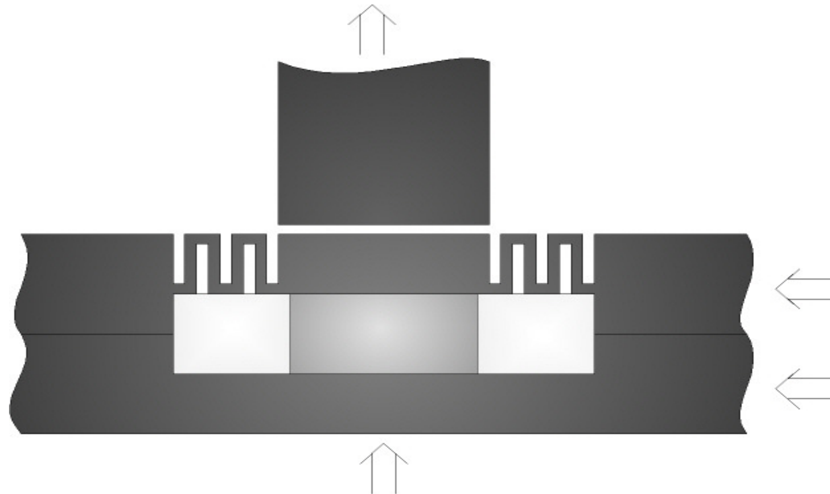


Figure 1: Thermal Switch Cross-section

The work is besides the fluid-to-fluid interface also divided into the fluid-to-substrate interface;

In fluid-to-fluid interface part studies, focus is on behavior of the fluid interface between liquid metals and paraffin. The interaction of the two materials in the liquid state is of great importance for the device to work properly and has to be investigated in detail. It is very important that the paraffin actuator and LMP remain separated during operation because potential mixing or switching of position of the materials inside the cavity could result in a device failure. Therefore, properties such as wetting, adhesion, surface deformation, tension, diffusion, in-stability (mixing) at the boundary interface will be studied in this investigation. Material properties and behavior have to be verified in the micro scale, where boundary effects can be determinant for the overall device functionality. Furthermore, the melting point of the LMP ought to be lower than the melting point of the paraffin actuator in order to let the membrane move freely upon the volume increase.

In the LMP / solder pad interface part studies, focus is on bonding metallic surfaces by means of a base metal and a metal alloy (solder). The temperature levels are just above the melting point of the applied metal alloy (generally regarded as soldering). At certain temperatures the metal alloy melts and begins to wet the base metal to form a bond between the two materials. Considering, e.g. a common Sn-based solder on copper, the molten solder reacts with copper to form a $Cu6Sn5$ intermetallic. This intermetallic layer links the solder and copper together resulting in a mechanical and electrical contact [1]. A drawback during this process is the generation of oxides during the temperature treatment. As a result, solders attach very poorly to such oxides, e.g. the various oxides of copper that are formed during the soldering process. Moreover, tin based solders for example are composed of several forms of tin oxides, which prevent the formation of good solder joints. To achieve high quality solder joints, these kinds of oxides must be prevented or removed by utilizing solder flux or other possible methods. However, the use of solder flux has several drawbacks, e.g. flux residues remain on the solder joint, containing ionic contaminants such as copper and tin ions as well as unused acidic species. The remaining residues in the system together with moisture could then, in its application, cause corrosion and therefore reduction of lifetime and stability. Therefore, in this study we look at different methods to remove oxides prior to soldering.

To achieve liable functionality, LMP should adhere well to solder pad but not to surrounding surface. It must also adhere stronger to the solder pad than to the paraffin to reduce the risk of paraffin contamination between LMP and solder pads. With paraffin having stronger bond to silicon surface than LMP, a layer of paraffin shall easily be created between silicon surface and the LMP, disconnecting the electrical and reducing the thermal contact of the switch.

During filling of the device, it must be able to have good control of membrane deflection, air entrapment, paraffin/LMP amount and location, therefore the final concept design is being considered during the whole work.

By membrane deflection measurements and thermal handling test, the functionality proofs to a “proof-of-concept” level.

3.1 Paraffin

Paraffin is mainly constituted of straight hydrocarbon chains with the composition C_nH_{2n+2} and its Latin name (*parum affinis*) means "lacking affinity" or "lacking reactivity" due to its property of not easily mixing with polar fluids as water; this feature is one of the reasons why it has been chosen for this application where mixing has to be avoided, but the second very important property is its considerable expansion when melted (10-15% of its volume) [2], which enables pushing of the silicon membrane and close the thermal switch when needed.

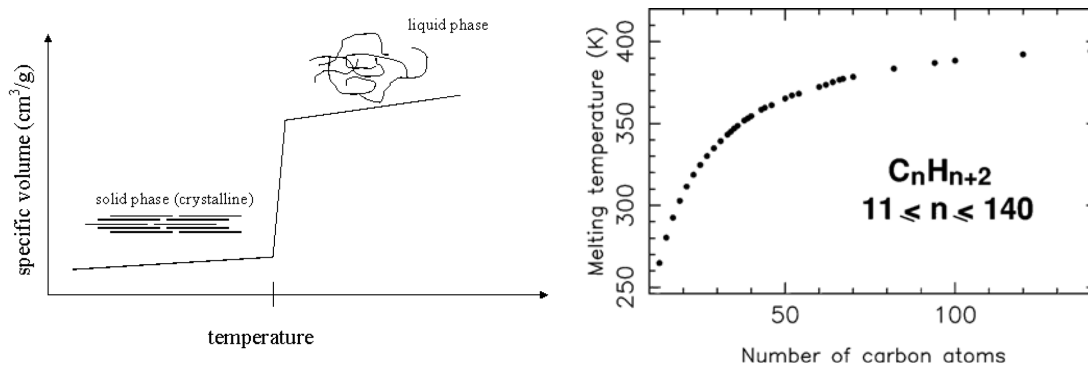


Figure 2: Left: Paraffin expansion [3], Right:Variation of melting temperature with number of carbon atoms [4]

Normal paraffins are named according to the number of carbon atoms in the chain. The large selection of paraffins with different chain lengths, hence different melting temperatures, makes them very attractive for different microactuator applications.

3.2 Low Melting Point Alloys (LMPs)

While the paraffin is acting as a phase-change actuator material in the thermal switch, a LMP is utilized as a conductor for heat and/or current transfer. One important characteristic of the LMP is a lower melting temperature than the one of the paraffin phase-change actuator, i.e. below ca. 70 degrees Celsius in this study. When the paraffin phase-change actuator starts its volume expansion, the metal should preferably be in its liquid state. Otherwise the LMP would remain soldered to the wafers and thus block the desired deflection of the membrane.

Furthermore, the surface tension of the LMP is supposed to be higher than the one of the paraffin actuator, in such a way that when the two liquids will be in contact, the metal's surface tension dominates demanding the paraffin to spread on its surface and not the opposite. Otherwise, there is a high risk that the paraffin would move inside the cavity and separate the LMP resulting in a device failure.

At the same time, considerations should be taken into account that a too high surface tension of the LMP would hinder its integration into the device in terms of bonding and soldering to the substrate, and thus resulting in device failure.

The results of these requirements, the two metal alloys that are going to be investigated are bismuth based LMP's which are commonly used as low-melting solders, low-melting casting metal and fire-melted valve elements in sprinkler systems.

The main properties of the two LMPs are shown in following table

Tabell 1: LMP properties

	MCP 58	**MCP 70 (Wood's Metal)**
Composition		
Bismuth	49%	50%
Tin	12%	13.3%
Lead	18%	26.7%
Cadmium	---	10%
Indium	21%	---
Melting Temperature	58°C	70°C
Electrical Resistivity	78.8μΩ.cm	48.0 μΩ.cm
Thermal Conductivity	0.100 $J.sec^{-1}.cm^{-1}.°C^{-1}$	0.180 $J.sec^{-1}.cm^{-1}.°C^{-1}$

3.2.1 LMP 70 and LMP 58 comparison

The previous results have been obtained using the LMP with lower melting temperature (58°C) but few other tests have been done on the other LMP with melting temperature around 70°C; the main parameter taken into account is still the contact angle, which gives information about the surface tension of the material. The following table contains a comparison between the two LMPs, considering their contact angles and some main parameters taken from literature (good properties in green and less good in red):

Tabell 2: LMP comparison

	MCP 58	**MCP 70**
Melting temperature	58°C	70°C
Contact angle on silicon	~ 90°	~ 60°
Contains Cadmium	No	Yes
Electrical Resistivity	78.8μΩ.cm	48.0 μΩ.cm
Thermal Conductivity	0.100 $J.sec^{-1}.cm^{-1}.°C^{-1}$	0.180 $J.sec^{-1}.cm^{-1}.°C^{-1}$

The last positive point of the MCP58 is that it doesn't contain cadmium which is a toxic element and should possibly be avoided.

On the other hand the MCP70 is not yet excluded as a possible LMP due to the fact that it has a better electrical and thermal conductivity which makes it a better conductor in this specific application. The initial tests will be conducted using the MCP58 which now is considered the more suitable, but in case it would turn out not to have the required performance, the MCP70 could be considered and its contact angle could be increased by adding some low surface tension materials on the silicon substrate to make the LMP not adhere on the area where just the paraffin should stay.

3.3 Interface behavior

The first step of the study is an observation about how the paraffin and the LMP wet the substrate, and how they behave together. An observation of the contact angle through the sessile-drop technique gives important information about the surface tension of the involved materials which is the main parameter that defines the macroscopic behavior of the device [5]. The experiments are executed with relatively small pieces (0.5-1mm) of paraffin and LMP with random shapes and dimensions; the materials are tested on a SiO_2 wafer on a hot plate in order to control the temperature. In normal air environment, two microscopes with attached CCD-camera are used to observe and simultaneously record the experiments from the top and from the side. Figure 3 and Figure 4 show the contact angle measurement for evaluation of wettability and examples of different wetting cases.

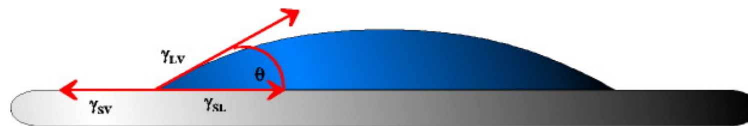


Figure 3: Contact angle measurement for evaluation of wettability

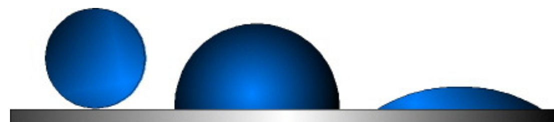


Figure 4: Different wetting cases

As it is desired achieving different LMP surface behavior on the solder pad than on the surrounding paraffin covered surface, suitable coating materials must be found to achieve each behavior. The most suitable coatings are thought to be Si/SiO2 or aluminum as wetting areas for the paraffin and copper, nickel or gold as wetting areas for the LMP, see Fel: Det gick inte att hitta referenskällan.

Tabell 3: Interfaces of interest for switch development

Surface material	Paraffin	LMP
Si / SiO2	X	X
Aluminum	X	X
Copper		X
Nickel		X
Gold		X

3.3.1 Paraffin on Si surface

The first experiments confirm the initial supposition that paraffin would have a very low surface tension (compared to the other materials involved); at the melting temperature paraffin totally spreads on the wafer surface in every kind of situation; according to the Young condition, a total wetting of the surface (contact angle equal to zero) means that the surface tension of the silicon-dioxide wafer is at least equal (most probably higher) than the sum of the liquid paraffin surface tension, and the interfacial tension between the solid and the liquid. In the system under investigation, the very low surface tension of the liquid paraffin implies that it will tend to spread within the available volumes, pushing on the surfaces in contact during its expansion, but adapting its shape to the one of the surrounding walls. When in liquid form, the paraffin is not stick to the wafer, but tends to move and spread like water in a glass, showing in this way its very low force of adhesion to the substrate when in liquid form; on the other hand, it sticks when solidifies, which is good because this means that it will keep its position when solid, but it is not a relevant information in this system where the solid phase, in a first analysis, doesn't seem to be a particular issue.

3.3.2 LMP on Si surface

A lower surface tension has been noticed in the MCP70, due to the fact that its contact angle on silicon substrate is around 60 degrees compared to the 90 degrees of the MCP58; this substantially means that its adhesion to the silicon is about 50% higher than the other LMP and this is the main reason why at the moment the choice of material is MCP58. It is very important that the LMP adheres very well to the metal pad and not too much to the rest of the substrate and therefore a high contact angle is needed in the area where just the paraffin has to lie. Another parameter that makes the MCP70 less desirable is the melting temperature that in this case is similar to the one of the paraffin; this can be a problem if the paraffin starts to expand while the LMP is still solid because the LMP would keep the structure stiff which could result in device failure. This could be a less important problem because a heavier paraffin could be used in order to have higher melting point than the metal.

LMP (MCP 58 and MCP 70) are tested on Silicon surface due to wetting. Contact angles are measured and shown to be ~90 deg resp. ~60 deg.

Having a look to this result and of what this implies for the current application, it is possible to think that, being the LMP commonly used for soldering applications, it could be possible to use some other kind of metals on which this alloy should spread in a better way and therefore adhere in more properly. The idea is that it could be possible to use a metal pad under the alloy and silicon under the paraffin, in a way that the LMP, adhering more to the metal would prefer it more than the silicon and would tend to solder to it and keep the position in which it is supposed to stay.

3.3.3 Paraffin / LMP wetting properties on aluminum surface

The aluminum is well known for being a metal to which it is very hard to adhere and is therefore not supposed to have a strong bonding to the LMP. Initial tests show that when the metal alloy is melted on top of an aluminum wafer, the contact angle in this case is very high (around 135 degrees) and the adhesion of the two materials is very weak and the LMP can be easily removed from the wafer manually with an external force showing that it has no soldering effect on aluminum.

The aluminum has good properties when it deals with having some surfaces to which the metal alloy doesn't have to attach. In case that just the silicon wouldn't guarantee good performances or another substrate material is used; The fact that also the paraffin doesn't adhere very well to aluminum is not relevant because it has this behavior even with other materials and the paraffin has to be free to move without problems inside the device's volume. Aluminum can be coated on top of the silicon in those areas where just the paraffin should lay.

3.3.4 Paraffin on aluminum surface

Figure 5 shows a measure of the paraffin sample before melting; after melting it totally spreads so we cannot have a good side-view picture.

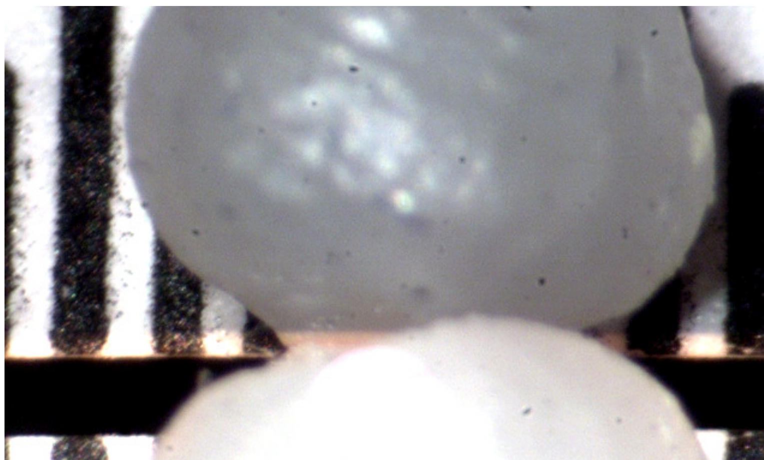


Figure 5: A 3mm piece of paraffin on aluminum surface before melting

The contact angle for LMP on aluminum surface is around 130 degrees, see Figure 6. One thing to comment is that we can see (both here on aluminum and on the silicon in the previous picture) that when a material spreads less and has a less contact angle, its shape is more flat (look for example the silicon side compared to the copper side in the previous picture). The fact that the sample has not a sphere shape but has a more flat one should be due to the fact that in the Young equation, no external forces are considered (like the gravitational force or air pressure). So, we can either notice a higher contact angle with aluminum, and either notices a more flat shape; the flatness could be another way to compare material because it seems to be connected to the contact angle.

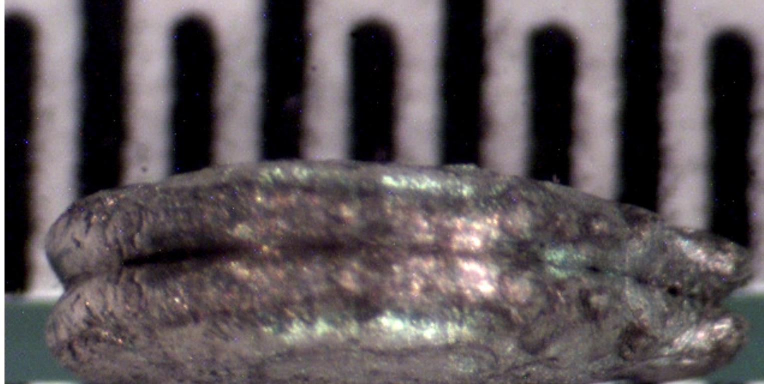


Figure 6: Molten LMP on aluminum surface, with a close up on the angle of contact, scale is 1mm.

3.3.5 Paraffin / LMP wetting properties on copper surface

A metal pad seems to be suitable for holding the LMP in the right position inside the device and a good material for this purpose needs to have the property of being well-wetted by the metal alloy. Considering that the LMPs taken into account, are often used for soldering applications as well, it is reasonable to adopt materials commonly used for soldering these metal alloys because those should be the ones which the LMPs should wet better and on which they should have a good adhesion. Copper is therefore chosen as the main candidate and is going to be tested for this purpose. The system, with, in this case, a copper pad is shown in Figure 7.

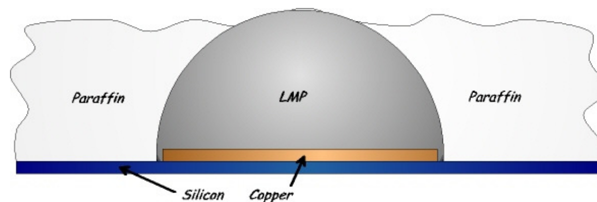


Figure 7: LMP centered on Copper pad and surrounded by paraffin

The conclusion of those observations is that the copper has a higher surface tension than the silicon and therefore it will force more the other materials on top of it to spread and cover its surface. At the same time we have the result that those materials (even paraffin) are going to adhere more to the copper, but this result is not influent in the case of paraffin that anyway remains still very fluid and free to move with no restriction; the important conclusion achieved is that the LMP is going to be more strongly connected to its position and definitely more force and pressure by the surroundings will be needed to push it away from there.

With LMP melted at 65 degrees so that the paraffin was still solid: the contact angle is around 70-75 degrees, see Figure 8 and the contact angle is noticed as much smaller after melting than before, see Figure 9 .

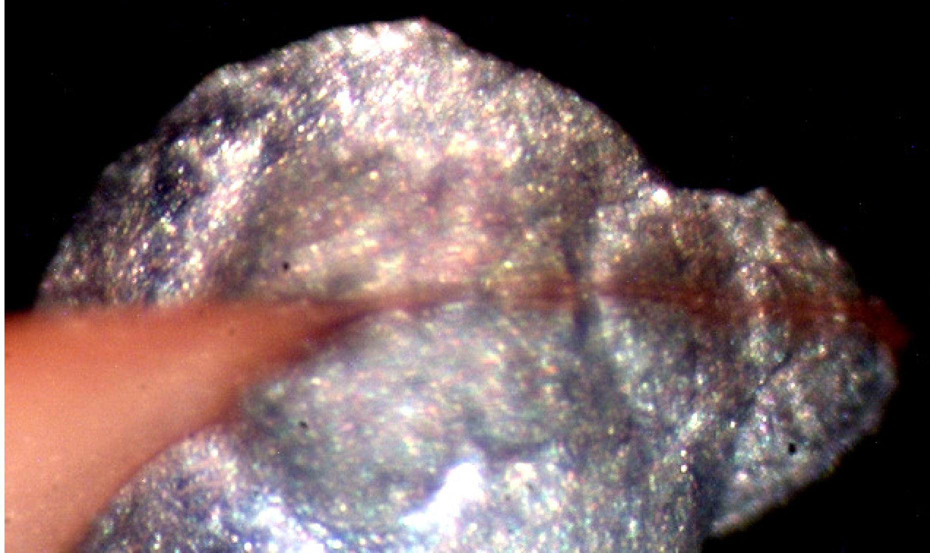


Figure 8: LMP melted at 65 degrees with the paraffin still in solid state

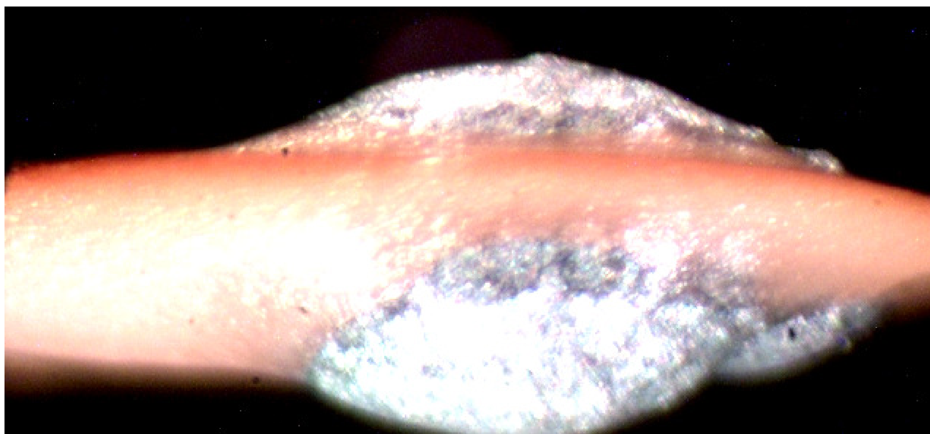


Figure 9: This is the same sample as before but after melting it at 80 degrees so that also the paraffin melted.

3.3.6 LMP on copper/silicon surface

A piece of LMP is placed on the border between silicon and copper (two different colors of the picture), so that in the same picture there is a comparison between the contact angle on copper and silicon. This picture is after melting and the size of this piece is around 4mm, see Figure 10.

Note! During this experiment, the surfaces may have surface oxide reducing solder-ability and wetting capabilities.

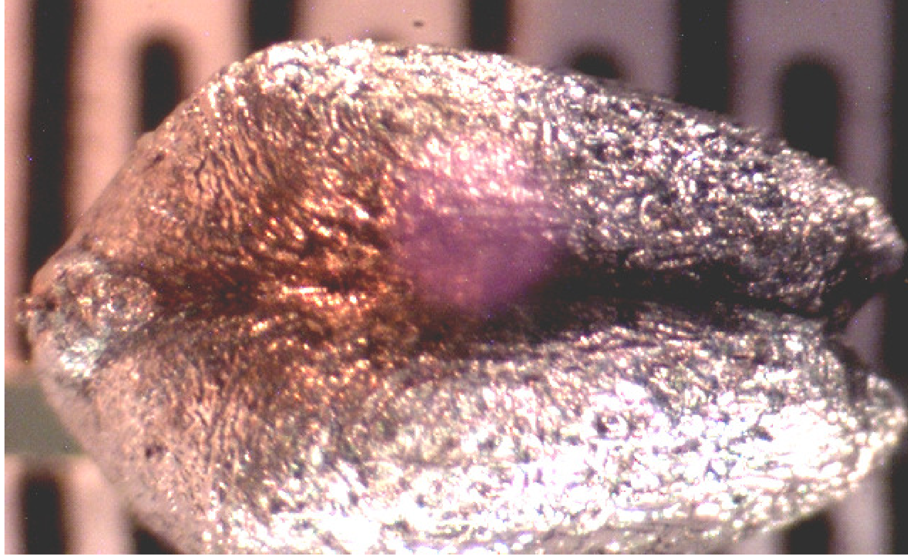


Figure 10: The contact angle on copper is about 40 degrees (left) and on silicon is more than 90 degrees in this case (right).

The picture after melting is from the top-view (second picture). The sample was situated on the Cu-Si interface so we can notice also how, when melting, it prefers to stay on copper than on silicon (copper has a higher surface tension) cause it spreads more on the copper side.

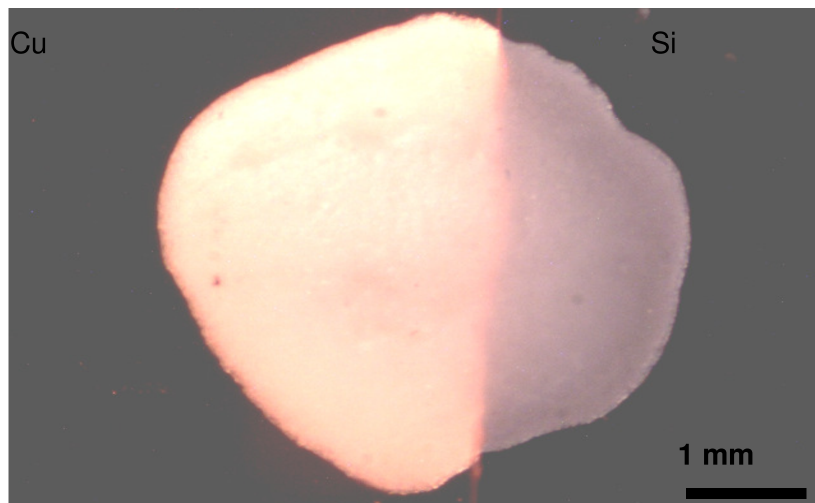


Figure 11: Melted paraffin situated on Cu surface to the left and on Si surface to the right.

After depositing a layer of copper on top of a silicon wafer and then etching away a part of it in order to have a silicon-copper interface, the same previous wetting experiments has been repeated and the contact angle observed; the obtained result is that the contact angle of the LMP on copper is around 20 degrees, which means, according to that there is an increase of about 90% of adhesion on copper compared to the adhesion on silicon. This contact angle has been observed testing the LMP on just copper and then has been confirmed testing it on the Silicon-Copper interface on which the different behavior between the two materials was more evident.

The same experiments have been executed with paraffin, with the result that also the paraffin prefers to spread on copper rather than on silicon.

3.4 Paraffin-LMP interface behavior

After testing separately how the materials behave with the different surfaces, which is important for the stability of the position of the metal alloy inside the device, it is relevant to test how the paraffin and the LMP interact with each other.

Therefore, for a preliminary observation of this interface, a preliminary layer of paraffin has been melted on top of the wafer (either on top of silicon, on top of copper or on the silicon/copper interface) and some samples of the chosen metal alloy have been deposited afterwards on the paraffin layer and then melted.

3.4.1 Solid paraffin - liquid LMP

The first observation has been done at a temperature of 65°C at which the paraffin layer is still solid and the LMP is in a liquid phase. One experiment done on the interface between copper and the paraffin layer shows a contact angle of about 70 degrees between LMP and solid paraffin, much higher than the contact angle of the LMP on copper and lower than the one between LMP and silicon.

Considering the contact angle as a property that gives some macroscopic information about the affinity of the involved materials, it is possible to obtain two other positive conclusions from this test; apparently indeed, the metal alloy adheres more to paraffin (solid) than to silicon but at the same time it "prefers" to stay more on copper than on paraffin. The consequence of this is that the copper pad is really needed in the system because on one side this result shows us that paraffin is a better substrate for the LMP than the silicon so that a layer of paraffin could be easily created between silicon and metal alloy, disconnecting then the electrical and thermal contact of the switch. This is positive in case the silicon is just a substrate for the paraffin, because in this way we can say that it is easier for the paraffin than for the LMP to lay on that substrate. At the same time, since the LMP lies better on copper than paraffin, it is considered that the system should be stable with this kind of solution due to the fact that a layer of paraffin between copper and metal alloy is a less physically favorable condition.

3.4.2 Liquid paraffin - liquid LMP

A second observation has been done at a temperature around 75°C at which both the paraffin and the metal alloy are in liquid phase; considering the temperature dependence of the surface tension (which decreases with a higher temperature), according to the Young condition we would expect to have a higher contact angle than the previous case, that is to say that the liquid metal alloy over the liquid paraffin is supposed to assume a more drop shape. The experiments showed instead that when the paraffin melts, the LMP spreads more on the surface with a lower contact angle (around 25 degrees) than the previous case. This is an unexpected behavior because it would change in a relevant way the behavior of the device. The presence of the oxygen in the test environment and inside the material is firstly thought to be the cause of this result because it is supposed that paraffin molecules reacting with oxygen could behave similar to a surfactant material which decreases the surface tension at the interface.

3.5 Micro-scale adaption

After gaining knowledge about the main material properties through the previous experiments, the next step is to focus more on micro-samples such as the ones that actually will be inside the final device. Even if the aim of the following test environment is to bring the analysis closer step after step to the real device, there is a relevant reason of testing the interface between the materials on a micro-scale: the surface tension is indeed dependent on the volume of the particle under test and mainly on its volume to surface ratio. Even if is stated in some studies conducted by H.M. Lu and Q. Jiang [6, 7] that a surface tension decrement is observed just on a nanometer scale and should therefore not be a relevant effect in our particular study, it will be observed with a new test environment which will compare samples up to 2.5mm and down to 100µm of ray.

3.5.1 The test environment

In order to fabricate and handle small particles due to the unusual nature of the two materials, the fabrication procedure turned out to be more complicated then expected and few issues had to be taken in consideration. The main idea is to etch a silicon wafer in order to fill it then with some structures of LMP surrounded by paraffin. One issue in the design is that a silicon thin structure has to be positioned between the LMP structure and the paraffin one to define and separate the two areas because otherwise the two materials will mix during the filling and will not occupy their right position in this test wafer.

Small volumes are created and handled with MEMS pieces fabricated using technologies similar to what is planned for the final switch fabrication. See Figure 12 for small sized copper surfaces.

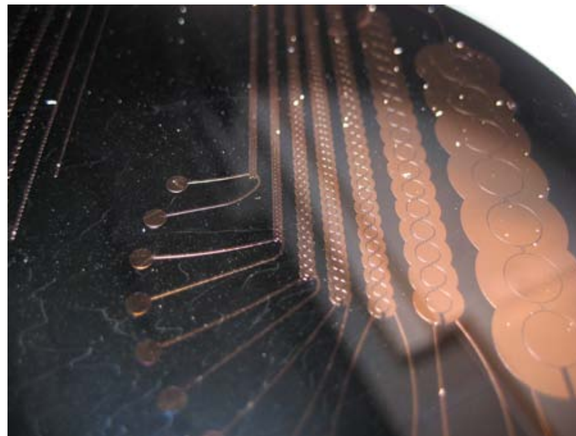


Figure 12: Silicon wafer with copper pads of different size,to be used with small volumes of LMP and paraffin

3.6 Wetting behavior and influence by flux

In order to conduct contact angle measurements, several LMP samples have been created using the earlier described approach. After LMP sample preparation, measurements have been conducted on different base materials, such as nickel, gold, silicon and copper. A contact angle measurement setup has been put in place, which included a precision hotplate as well as two microscopes with standard charged couple device (CCD) cameras attached to capture images for subsequent image analysis from both top and side

view. By means of visual image analysis, information regarding contact angle, corrosion, adhesion, defects, etc could be collected. These experiments revealed, the HCl treatment being the least affective one compared to e.g. the use of solder flux. Table 1 shows contact angles for various base materials used in this experiment. For each experiment a set of at least five LMP samples was used on the base material and subsequently evaluated. As expected the contact angle on silicon as a base material is very high, as silicon wafers with native oxide were used in this experiment. Furthermore, the LMP samples show best wetting toward copper as the base material. Therefore, copper has been one of the main base materials in this study.

Table 4: Typical result of a created LMP sample prior to usage in an experiment.

Base Material	Average contact angle /deg	Relative standard deviation / %
Nickel	39,13	12,95
Gold	46,78	13,11
Silicon	159,72	3,37
Copper	33,94	23,46

3.6.1 LMP on silicon

To evaluate the behavior of LMP samples on various materials, LMP samples have been placed on the substrate material of choice and a temperature treatment has been used to reflow the LMP sample. First, a bare silicon wafer with its native oxide layer has been used to study the LMP to substrate interaction, as the final device design suggests the use of silicon as the main device material. To study the LMP behavior on silicon dioxide several LMP samples have been melted using the earlier described deoxidation methods, such as solder flux, HCl and formic acid. In all cases, wetting of the LMP samples on the silicon surface could not be observed. The LMP samples took a spherical shape with a rather high contact angle (~160°) and did not adhere to the silicon surface whatsoever. This shows that there is no affinity between the two materials, even when using highly corrosive methods. To conclude this, silicon is well suited as the main device material and will be used in the future design. The previously suggested device design looks promising as it is straightforward by means of MEMS fabrication techniques to structure the silicon substrate and use surface micromachining techniques to add other materials (copper, nickel, etc) on top, which in turn can be structured to achieve areas that would form a reliable joint with the LMP. Proper paraffin to LMP interaction inside an enclosed silicon structure can be facilitated be optimizing the device design and using appropriate microfabrication techniques and materials.

3.6.2 LMP on copper

Due to its large use in electronics with outstanding electrical properties and its good soldering qualities, copper has been considered as the main choice for the anticipated application. Experiments have been conducted on unstructured copper surfaces with a thickness of ~1µm. The drawback with copper is that it spontaneously forms copper oxides when heated, which strongly influence the formation of a solder joint. This oxide can be removed by shortly dipping the copper surface in HCl solution prior to use. In order to achieve wetting of the LMP samples on the copper surface, we again utilize a diluted HCl solution during the experiment to assist the soldering process. This approach has been found to be the one least affecting the structures and therefore not compromising the device reliability as much. LMP to copper soldering has also been achieved using two different fluxes (Soft solder Flux No. 1S from JohnsonMatthey,

FluxX32-10i from Multicore), but with the effect of, visible and difficult to remove, residues remaining on the solder joint (Figure 13).

For life time purposes, the dissociation rate of copper (~30nm/sec at 200°C) has to be taken into account in the design, see Figure 14 where a thin layer of copper is dissociated into the LMP.

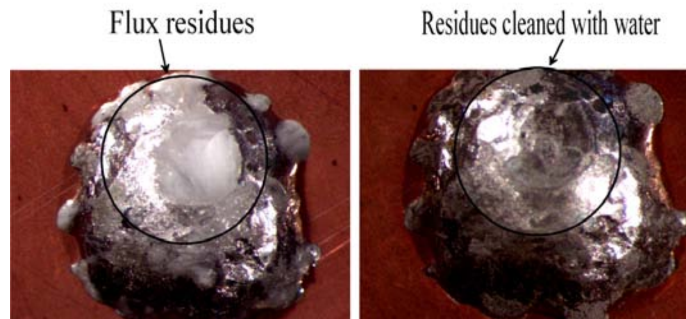


Figure 13: Photograph of a solder joint of LMP on copper assisted by flux leaving residues.

3.6.3 LMP on gold

Gold is a material widely used in the microelectronic industry and it shows some properties that make it very interesting for soldering, since gold does not spontaneously oxidize in ambient conditions [8]. In many applications gold coatings have been used as a substitute for soldering flux [9]. In this way many problems due to flux corrosion can be avoided and gold can be applied as a protective coating on top of a metal surface to be soldered. The gold will be removed during the soldering operation due to the fact that it will be dissociated by the solder. The dissociation rate of gold at ~200°C is about 1.5µm/sec. In contrast to the dissociation rate of copper being about 50 times slower and that of nickel being about 1000 times slower at this temperature, see Figure 14. This prevents the use of gold as the sole metal substrate for this application. A gold coating is easily wetted by most molten solders and it possesses other properties such as excellent corrosion resistance and high electrical conductivity. However, there are some problems associated to its use for soldering, such as susceptibility of joints to embrittlement. Such gold coating is considered to be useful in this application to substitute copper or as a protective coating on top of it. This solution could simplify the processing of the device in a way that the surface does not require treatment with flux, HCl, etc. However, the oxide layer on the LMP is seen as the major obstacle and deoxidation of this is necessary to achieve good soldering. In case the LMP could be treated separately in an inert environment to later make it solder to the gold surface.

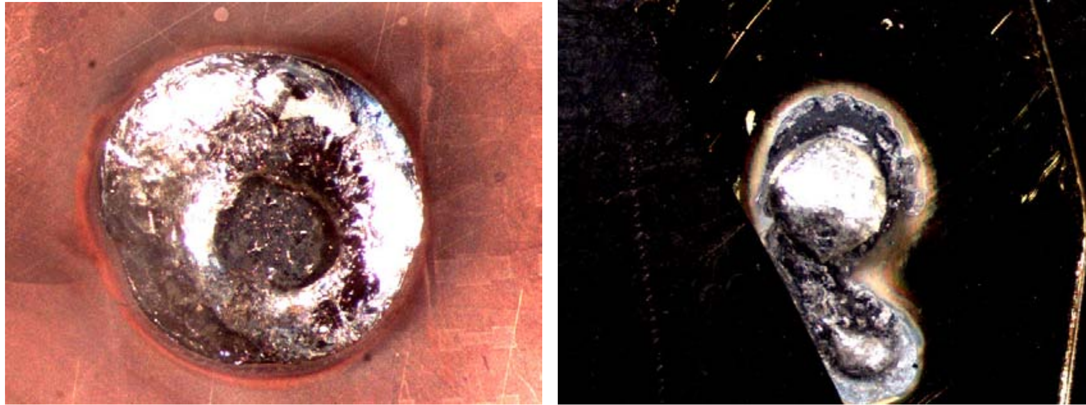


Figure 14: Photographs of dissociation of the metal surface into the LMP. Left: Dissociation of copper and, Right: Dissociation of gold into the LMP sample.

3.6.4 LMP on nickel

From the dissociation rate point of view, nickel is a very attractive material for this application and dissociated at just ~1nm/sec at 200°C. Figure 14 shows photographs where the base metal has been dissociated into the LMP solder. Nickel is also is widely used as metallization for solder joints in semiconductor devices and is straightforward to process. Moreover, it is strongly resistant to corrosion which makes it suitable for creating reliable solder joints. Nickel spontaneously and very quickly forms an oxide layer in air, which needs to be removed prior to soldering. To remove nickel oxide a special nickel flux needs to be applied, which is only available in the US. Nevertheless, the use of diluted HCl solution 0.05% works properly even to remove these kinds of nickel oxides. Figure 15 shows a photograph of an LMP sample soldered to a nickel surface.

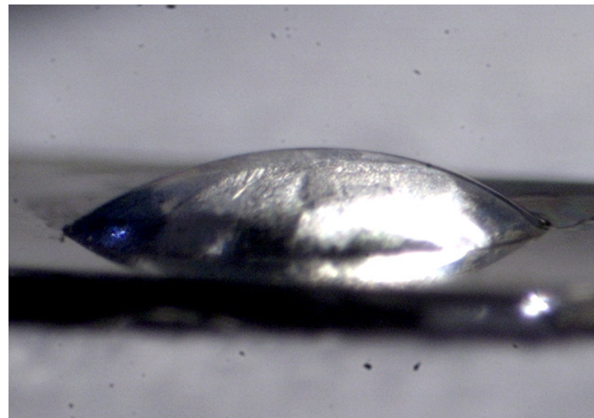


Figure 15: Photograph of LMP soldering after HCl treatment on a nickel surface.

3.7 Thermal Cycling

To evaluate the LMP/paraffin interaction at the boundary interface, an experiment has been conducted where the temperature on the chip has been changed continuously. This experiment aims at studying a change of properties, such as wetting, tension, surface deformation, adhesion, mixing, diffusion, etc, of a created LMP solder joint on a structured nickel surface which has been immersed in paraffin. The nickel has been structure by means of microfabrication techniques. LMP samples have been prepared and soldered on a nickel pattern using diluted HCl solution (0.15%). After the LMP has solidified, paraffin has been melted to surround and enclose the LMP samples. This approach leads to a quasi oxygen free environment during the thermo cycling. Prior to applying liquid paraffin to the LMP samples, it has been degassed in vacuum for 15 min in order to reduce the oxygen present in the paraffin. This experiment has been conducted for 15 hours during which the temperature has been cycled between 50°C and 80°C each 15 minutes in order reach the melting point of paraffin and LMP and reversely cool down, respectively. Simultaneously, pictures of the chip have been recorded every 2 minutes by means of a CCD camera.

Figure 16 shows a picture sequence of the experiment where each picture represents a 2h time progress. It can be seen that there is no substantial change in shape of the LMP.

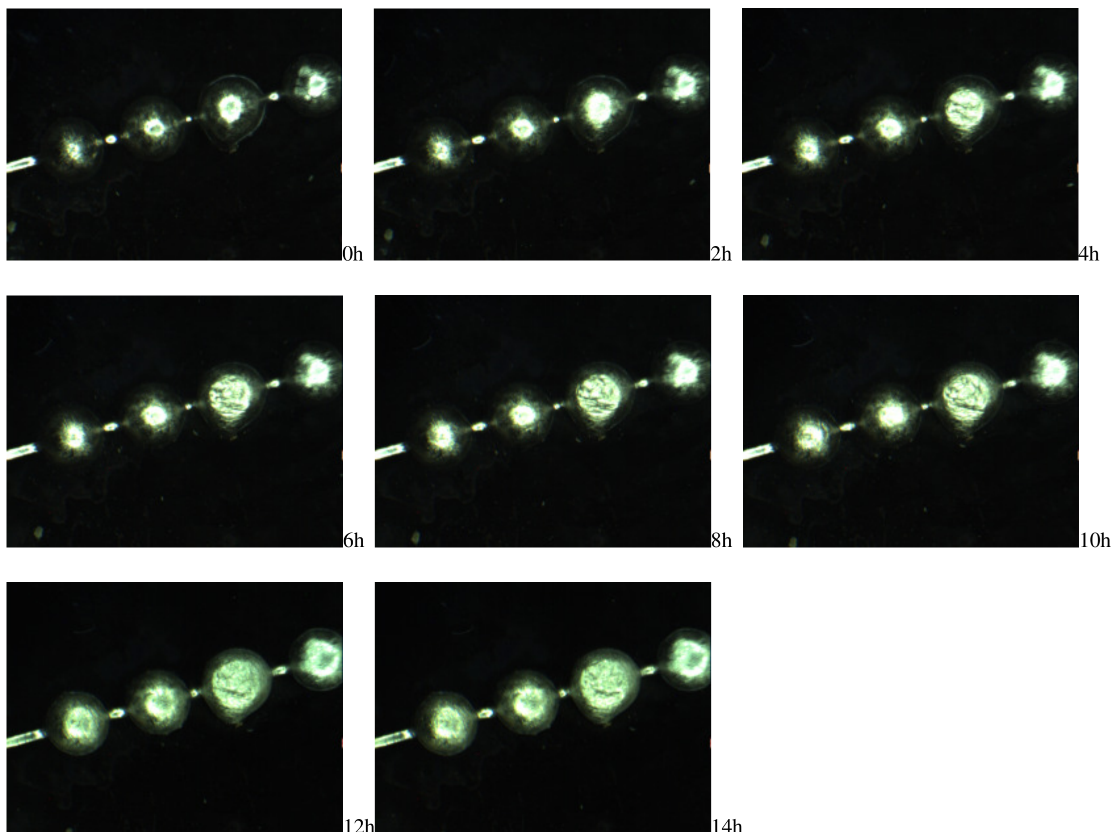


Figure 16: Picture sequence showing the behavior of the LMP soldered to a nickel surface inside paraffin under a constantly changing temperature. The first picture is recorded at T=0, whereas the last picture shows the structures after 14h temperature treatment.

Moreover the LMP samples do not move from the underlying nickel structures, which means that the adhesion is rather strong and the solder joint intact. Moreover, LMP and paraffin do not mix and there are no indications of one material diffusing into the other. No LMP defragmentation could be detected even after 15h. During visual observation through an optical microscope, strong paraffin movement could be

seen due to the heat treatment. The LMP samples remained unaffected by this paraffin movement. The picture sequence shows a change in surface roughness after several hours temperature cycling. This might be due to the formation of an oxide layer, which could occur in case oxygen is diffusing through the paraffin and the amount of oxygen atoms present inside the paraffin is increased. Note that the light conditions around the experimental setup have changed over the duration of the experiment, which could also influence the quality of the recorded pictures.

3.8 Vibration tests

In order to further investigate the LMP/paraffin boundary interface in terms of external forces, LMP samples have been prepared in a similar way as for the thermal cycling tests, i.e. soldered to a nickel structure and immersed into paraffin (Figure 17). A 80°C temperature treatment has been induced on the chip and the system has been put under vibration at a frequency of 20Hz with a sinusoidal waveform. For 30 minutes, the signal amplitude has been set to make the test chip accelerate periodically with 3.37G. Subsequently, the signal amplitude has been change in order to make the system vibrate at 4.49G and 6.73G for 30 minutes, respectively. Finally the temperature has been cycled periodically around the melting points of LMP and paraffin, respectively, to cause melting and solidifying of the materials under vibration at 6.73G acting on the test chip. A CCD camera attached to the experimental setup allowed recording pictures during the experiment. Figure 18 shows the picture sequence of the experiment.

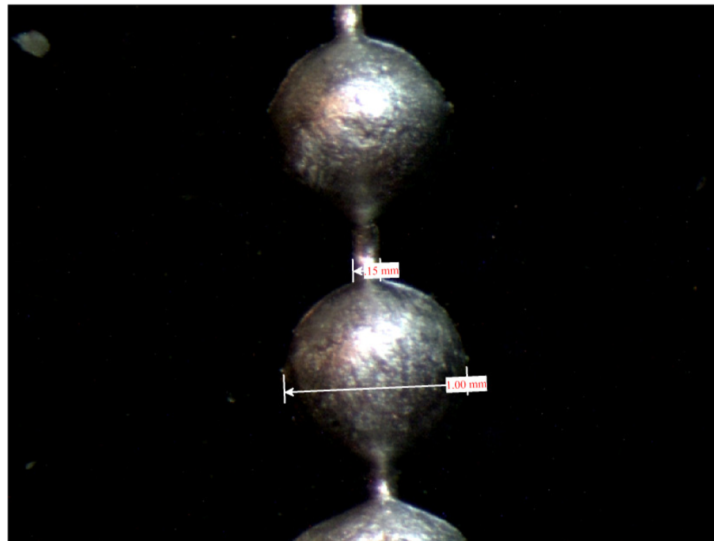


Figure 17: Close-up of an LMP sample soldered to an underlying nickel structure and immersed in liquid paraffin.

Every 10 minutes a picture has been recorded during the entire experiment. No substantial change in the LMP/paraffin boundary interface can be detected. The LMP remains on the structured nickel pattern even at strong acceleration with liquid paraffin flowing freely around the LMP. Slight deformation can be detected due to the strong acceleration during the experiment.

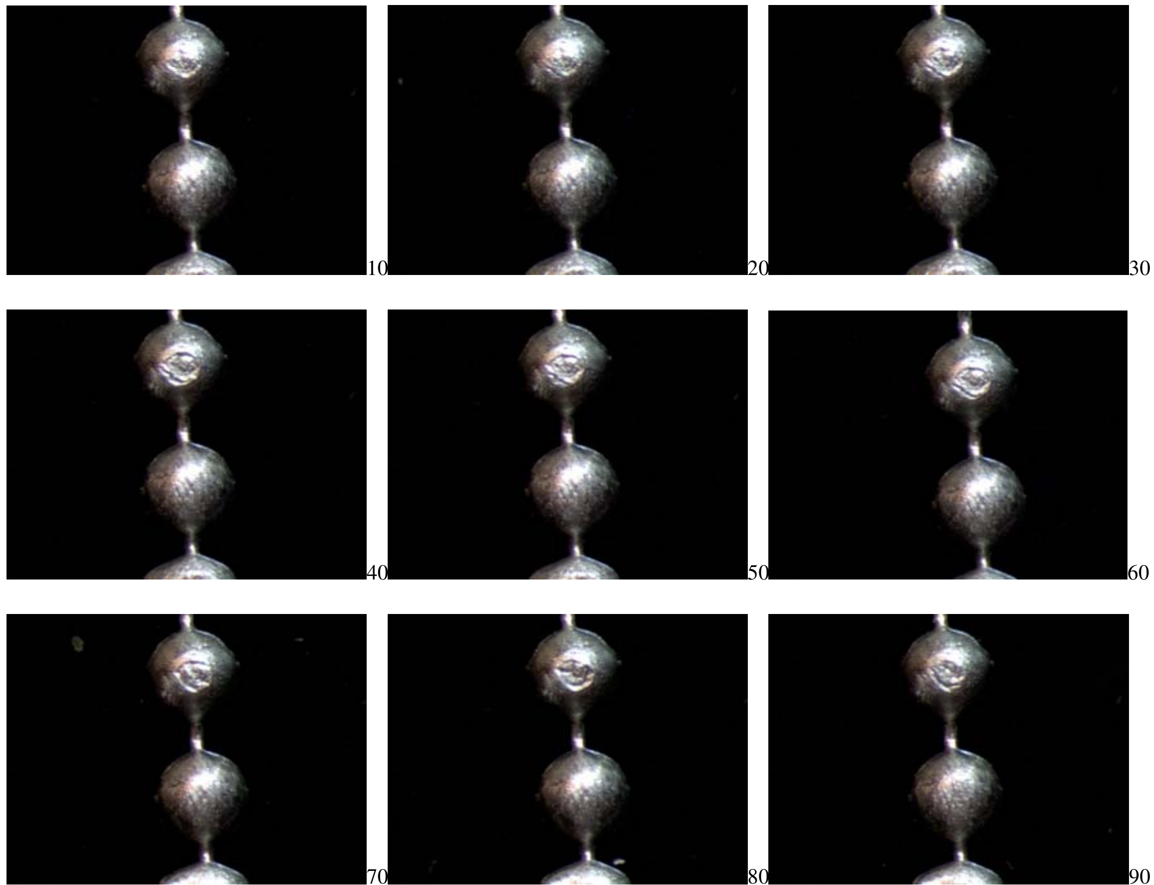


Figure 18: Picture sequence showing the behavior of the LMP soldered to a nickel surface inside paraffin under vibration and heated up to 80°C. Every 10minutes a picture has been recorded using a standard CCD camera attached to stereo microscope.

3.8.1 Fragmentizing of low melting point alloy

To be able to conduct experiments utilizing the low melting point alloy, the first problem that needs to be addressed is the generation of small LMP samples out of the LMP bar/ingot which have similar size and weight. In order to achieve an improvement when it comes to the handling of the LMP samples, a special technique of fragmentizing LMP and generating small spherical LMP samples has been applied. First, small fragments were chopped out the LMP bar. These fragments were then collected and scaled to achieve a certain weight. Subsequently, the LMP fragments were put in a Petri dish and a small amount of hydrochloric acid diluted in DI water was added, following a heat treatment until just the LMP's melting point is reached. As a consequence of this heat treatment and the hydrophobic nature if the Petri dish, together with the LMP's improved wetting characteristics due to the presence of HCl, the LMP fragments begin to recombine and form a spherically shaped sample. After reducing the temperature below the melting point, this spherical LMP sample in turn solidifies in its current state and can be used for further handling. Typical HCl concentrations used for this purpose are ~0.05% and below, in order not to leave residues on the created samples. Several other substances, besides HCl, can probably be used for this purpose, such as diluted Formic Acid, Formic Acid vapor, various commercially available solder fluxes, etc. The use of diluted HCl has shown not to affect the samples in a negative way and allows cleaning the samples after solidification leaving no noticed residues. Using this approach, it has been possible to

generate various LMP samples with similar size, weight and volume, which has been advantageous and very convenient when conducting further experiments. Figure 19 shows an LMP sample after such a treatment.

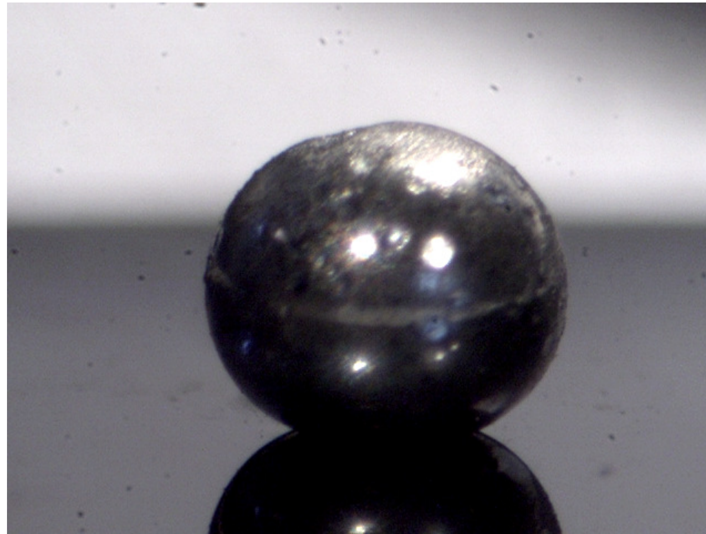


Figure 19: Typical result of a created LMP sample prior to usage in an experiment on Si surface.

3.9 Fluxless soldering

Despite the attempts to use no-clean solder fluxes, fluxless soldering techniques have in recent years gained increased attention since in many applications the use of solder flux is not possible for the various reasons. Some applications where fluxless soldering is required are in the IC industry as well as in Microelectromechanical Systems (MEMS) devices and sensors, biomedical applications, photonic applications, as well as some flip chip mounting of dies and wafer to wafer bonding applications. Such fluxless soldering approaches can be grouped in two main categories, one is using a chemical or RF plasma to convert or remove the oxide layer which is present on the solder or the base material surface, while the other one aims at removing the main cause, the solder oxidation itself. This is accomplished by producing the soldering materials in a controlled, non-oxidizing, atmosphere and instantly covering them with a barrier layer which prevents penetration of oxygen into the solder [1].

3.9.1 Soldering in controlled atmosphere environment

One promising approach of fluxless soldering is the use of formic acid in a controlled atmosphere. The formic acid eliminates the native oxide on the metal and creates a thin formiate layer on the surface that prevents reoxidation. However, the protection is only active for some hours wherefore the soldering must be done directly after the treatment. An alternative way is to do the activation and the soldering in the same chamber in one sequence. The approach utilizes a formic acid vapor which is highly reactive at typical soldering temperatures. The formic acid vapor further decomposes at the solder reflow temperatures and consequently does neither contaminate the solders nor the base material that are used to create a solder joint. A detailed description of the decomposition of formic acid vapor into carbon dioxide and hydrogen gas at elevated temperatures (> 150°C) can be found in [10]. A typical setup used for formic acid vapor assisted soldering is depicted in Figure 20. To achieve positive results it is critical to precisely control parameters such as the formic acid vapor concentration as well as the temperature inside the reaction chamber.

Figure 20: Lab setup for formic acid vapor soldering in controlled atmosphere.

The presence of oxygen in the soldering environment could cause quick reoxidation, which increases rapidly at the temperature levels used in soldering processes. As a result, this could prevent a high quality solder joint from being created. Therefore, an oxide free environment would assist the soldering process and at the same time protect the metal substrate from reoxidizing. Conducting the soldering process in reduced oxygen with an inert carrier gas or even in vacuum environment is highly recommended for the formation good quality solder joints.

Formic acid vapor soldering is conducted at the semiconductor laboratory (e-Lab) at the Royal Institute of Technology in Stockholm, Sweden. The setup offers computer controlled temperature regulation up to 400°C in a vacuum chamber, Nitrogen as the carrier gas for the formic acid vapor, flowmeters to control the flow speed and formic acid concentration as well as a microscope for visual inspection during the soldering process. The formation of good LMP solder joints via formic acid vapor soldering could be influenced due to the fact that the soldering temperatures of LMP are much lower than the decomposition temperatures of formic acid, see Figure 21.

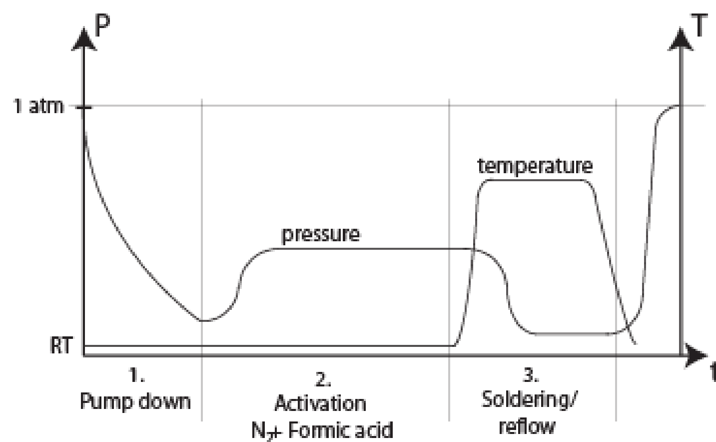


Figure 21: Graph illustrating an example of the different steps for flux-free soldering with formic acid treatment.

3.10 Formic acid vapor soldering

Experiments using a formic acid vapor soldering setup show that this process is influenced to by the set parameters during operation. The process of soldering LMP to Nickel assisted by formic acid vapor requires temperatures above 300˚C and precise control of the incoming gases. Below 300˚C the created solder joints between LMP and Nickel pads were intact (mechanically strong and electrically conducting) but the LMP did not wet the surface of the Nickel structures satisfactorily, it probably suffers from the limited stability of the formiate layer which prevents reoxidation. Furthermore, the simultaneous use of paraffin at these temperatures is not possible, e.g. to fill the final device in a single step. Figure 22 shows a photograph of LMP samples soldered to Nickel structures using this equipment, which results in wetting (>300˚C) and non wetting (<300˚C) solder joints. Figure 23 shows an attempt to solder LMP on Cu surface using formic acid activation with incorrect parameters.

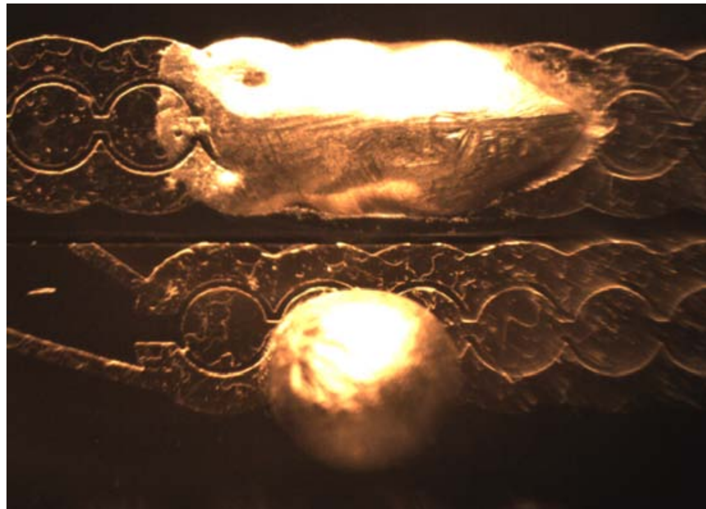


Figure 22: Photograph of formed solder joints between LMP and Nickel using formic acid vapor soldering technique. Top: LMP sample wets the Nickel structures during the process and spreads. Bottom: LMP sample does not wet the underlying Nickel structures.

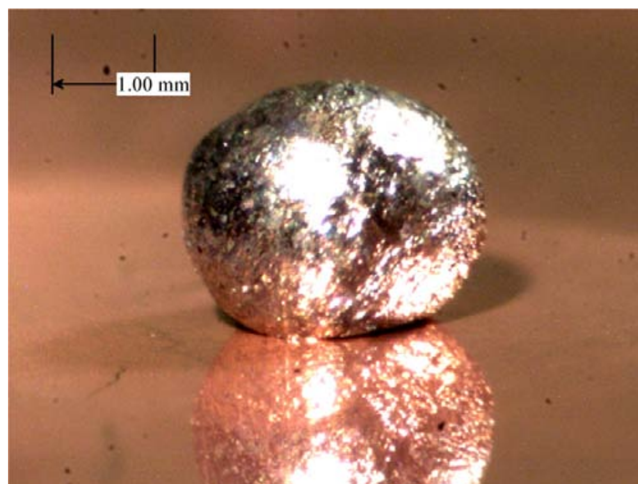


Figure 23: Photograph of an unsuccessful attempt of soldering LMP to copper surface using the incorrect parameters formic acid vapor activation equipment.

3.10.1 HCl assisted soldering

Similarly to the method of fragmentizing LMP by using diluted HCl in DI water and creating LMP samples of similar shape and volume, the method of using diluted HCl has been applied to create solder joints between LMP samples and a metal patterns. A similar approach has also been presented by others to fabricate MEMS based single-use micro-valves [11]. This approach of soldering LMP utilizes HCl in order to prevent both solder and metal surface from oxidizing. The method facilitates LMP deposition on wafer-scale and shows great potential for use in this study due to its versatile applicability and self-alignment capability as depicted in Figure 24. In this study, LMP samples are introduced to microstructures by placing samples on the inlet together with a drop of diluted HCL. Upon heating to the LMP's melting point, the LMP sample liquefies and can be aspirated into a microstructure by applying negative pressure at the outlet.

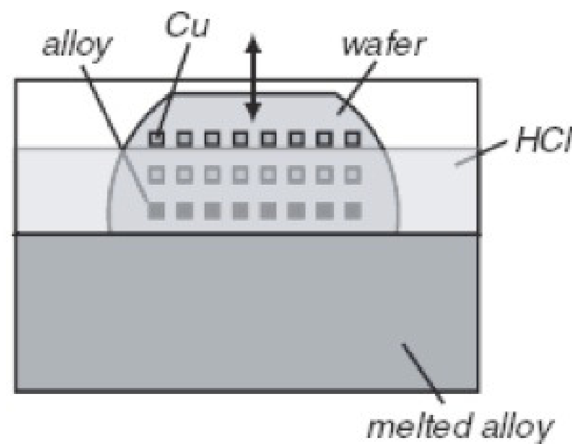


Figure 24: LMP coating on wafer-scale using HCl.

As described above, the method of immersing LMP samples in HCl, heating until the melting point of LMP and subsequently dipping the Silicon/Nickel chips, has shown good applicability and has been used herein. LMP samples have been soldered on nickel patterns using diluted HCl solution (0.15%) and manually dragging the LMP over the Nickel structures. The self-alignment capability of LMP on Nickel structures is shown in Figure 25 and could be very helpful for the filling of the final device, where LMP and paraffin are enclosed in a silicon cavity with a flexible membrane to enable device operation. This versatile technique can help to fill the structures after fabrication of the devices as the LMP can move freely in the carrier solution (HCl). Filling of devices and subsequently bonding of silicon is not a straightforward task. The method of HCl assisted soldering can even be applied in conjunction with paraffin which means that the application of LMP and paraffin could be achieved in a single sequence. Further studies will show how applicable this method is for this specific application.

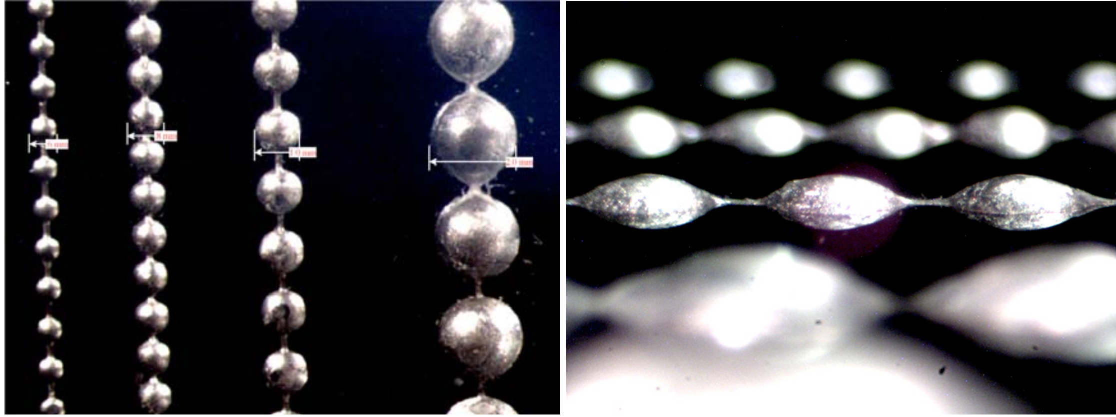


Figure 25: Photographs of top and side view of Nickel structures with self aligned LMP using HCl treatment.

3.11 Temperature cycling

Test structures have been fabricated in order to encapsulate LMP, paraffin or both inside a microstructure and separate it from the surrounding environment. Temperature cycling experiments have been conducted in order to evaluate the interaction and the behavior of the phase change materials inside an enclosed cavity. During the experiments the temperature has been changed continuously to mimic the switching cycles of the final device and gather information regarding fatigue at the interface due to the continuous melting and solidification process as well as the expansion of the paraffin. Prior to applying liquid paraffin to test structures, it has been degassed in vacuum for 15 min in order to reduce the oxygen present in the paraffin. All experiments have been conducted for at least 24h during which the temperature has been cycled between 50°C and 90°C each 15 minutes in order reach the melting point of paraffin and LMP and cool down, respectively. Simultaneously, pictures of the test structures have been recorded every 30 minutes by means of a CCD camera

3.11.1 Temperature cycling of LMP on Nickel structures

For this experiment a silicon chip with nickel structures has been prepared. LMP samples have been deposited using diluted HCl and the earlier described method of self alignment. Subsequently the LMP samples have been enclosed in a PDMS cavity. The picture sequence in Figure 26 depicts that the continuous melting and solidification process of LMP basically leaves the LMP structures unaffected.

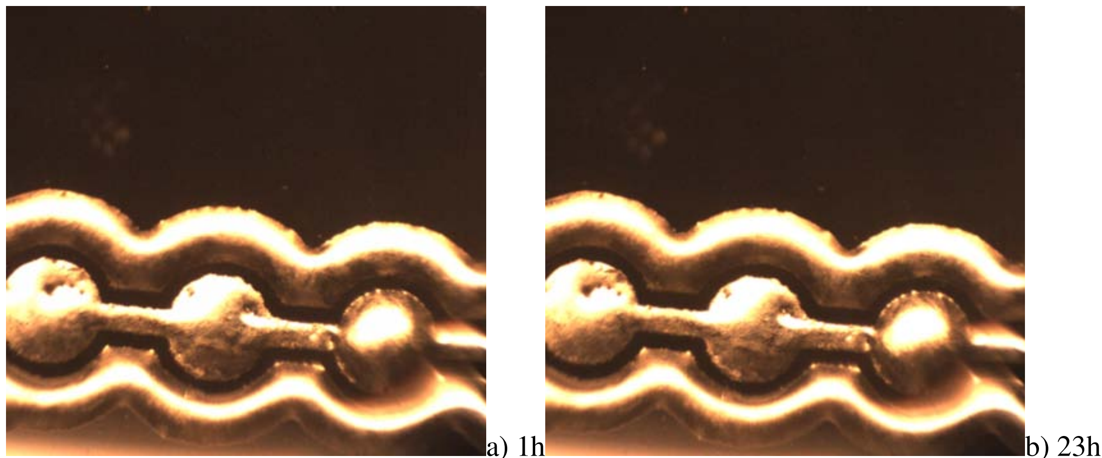

a) 1h b) 23h

Figure 26: Photographs of self-aligned LMP soldered to Nickel structures on a silicon chip and encapsulated in a PDMS cavity during thermal cycling. Picture a) and b) show the structures after start and before ending the experiment.

3.11.2 Temperature cycling of paraffin on silicon

For this experiment a bare silicon chip was used, paraffin deposited and encapsulated by PDMS. This experiment showed no change in structure of paraffin after melting and solidifying many times. The paraffin remains clear and transparent in the melted state and does not affect the silicon in any way. The experiments below show a release of gas, probably originating from paraffin. Supposedly, the reason why no gas release has been detected in this experiment is that the pictures have been taken very close to the edge of the paraffin at very high magnification. Most probably, gas has been released during this experiment as well, but accumulated at the center of the cavity with space to move freely instead of the narrow edge.

3.11.3 Temperature cycling of paraffin on nickel structures

For this experiment a silicon chip with nickel structures has been prepared. Paraffin has been deposited and enclosed in a PDMS cavity. The picture sequence in Figure 27 shows the release of gas inside the cavity and depicts the paraffin in it's *a)* solid state and *b)* liquid state when melted. Pictures *c)-d)* clearly show the accumulation of gas inside the liquid paraffin.

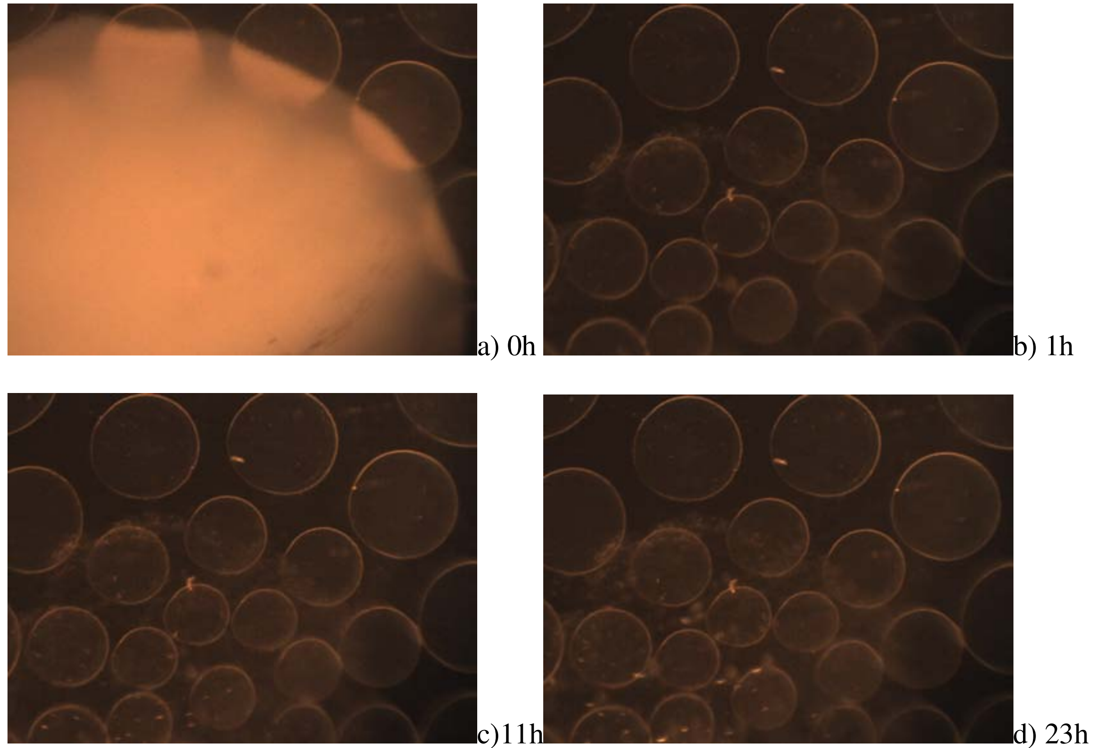


Figure 27: Photographs of Nickel structures on a silicon chip with paraffin encapsulated in a PDMS cavity during thermal cycling. Picture a) shows the paraffin in the solid state, b) melted state after 1h, c) 11h and, d) 23h.

3.11.4 Temperature cycling of paraffin/LMP on nickel structures

For this experiment a silicon chip with nickel structures has been prepared. LMP samples have been deposited using diluted HCl and the earlier described method of self alignment. Subsequently, paraffin has been deposited and the complete structures have been enclosed in a PDMS cavity. The picture sequence in Figure 14 shows the release of gas inside the cavity after the experiment has been ongoing and the oxidation of the LMP structures is clearly visible. The LMP structures deteriorate with increasing level of oxidation *a-d)* due to the accumulation of gas inside the enclosed cavity.

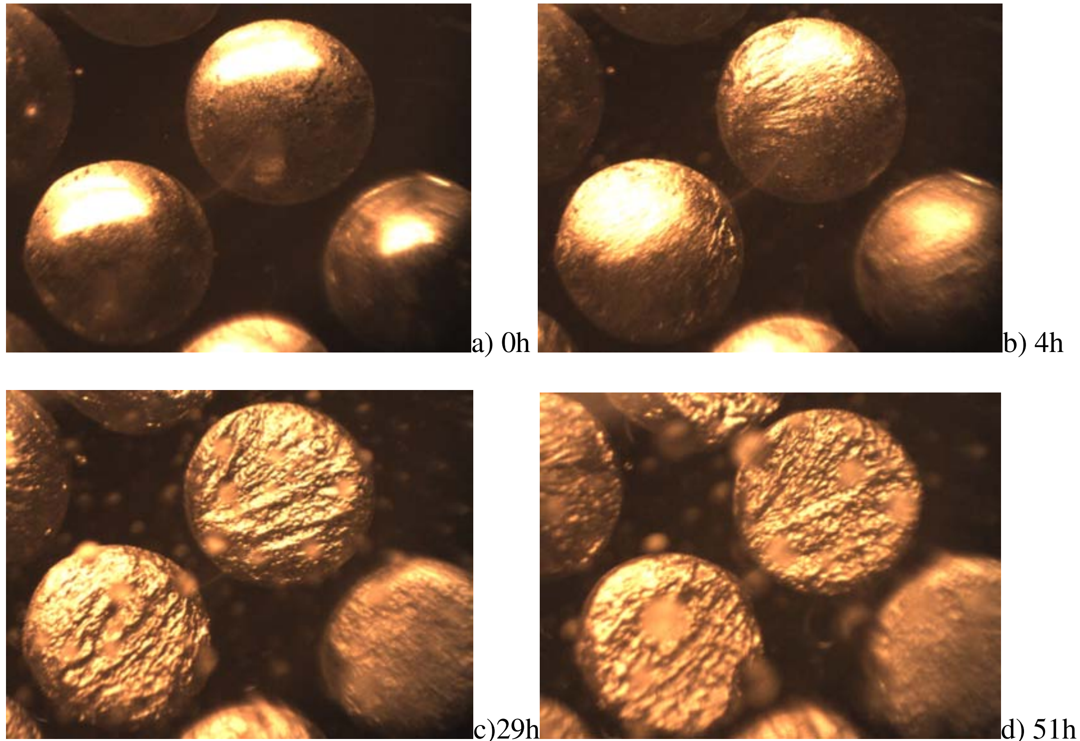


Figure 28: Photographs of LMP on Nickel structures surrounded by paraffin and encapsulated in a PDMS cavity during thermal cycling. Picture a) shows the LMP structures at start of the experiment. b)-d) pictures taken at progressing time during the experiment. It can be seen that the LMP structures oxidize due to gas being released during the ongoing experiment.

3.12 Fabrication of enclosed test devices in PDMS

In order to study the behavior of the phase change materials LMP as well as paraffin in simulated operational conditions and on various substrates, the LMP and paraffin are separated from the surrounding atmosphere by encapsulating them in cavities. The use of polydimethylsiloxane, (PDMS) (Sylgard184 Silicone Elastomer Kit, DowCorning) as an encapsulating material has several beneficial characteristics; it is transparent, durable, chemically inert, nontoxic and is rather straight forward to apply. Several test chips have been fabricated using microfabrication processes on silicon wafers and depositing nickel structures using the design suggested therein. After the application of either LMP, paraffin or both on silicon substrates, PDMS has been prepared in a 10:1 ratio, degassed in vacuum and applied on top of the test substrates. Subsequently, the test substrates have been cured at room temperature for at least 24h.

3.13 Design and fabrication of enclosed cavities in silicon

In order to study the behavior of the phase change materials LMP as well as paraffin in simulated operational conditions and on various substrates, the LMP and paraffin are separated from the surrounding atmosphere by encapsulating them in cavities. The use of polydimethylsiloxane, (PDMS, Sylgard184 Silicone Elastomer Kit, DowCorning) as an encapsulating material is one possible choice. However, experiments showed poor LMP stability inside a paraffin filled cavity for several reasons. One could have been the degassing step of paraffin prior to encapsulation in a cavity, which has been conducted incorrectly. Another reason might be the oxygenated nature of bulk PDMS material together with the fact that the material is gas-permeable. In order to circumvent these issues silicon based cavities have been designed, which enable filling and draining of paraffin, filling with LMP and simultaneous recording of the cavity. Test chips have been fabricated using standard microfabrication processes as depicted in Figure 29. First, an oxidized silicon wafer, used as the bottom substrate has been structured by standard photolithographic methods. Subsequently, the silicon wafer has been prepared in buffered hydrofluoric acid and then etched in 30% potassium hydroxide (KOH) at 60˚C.

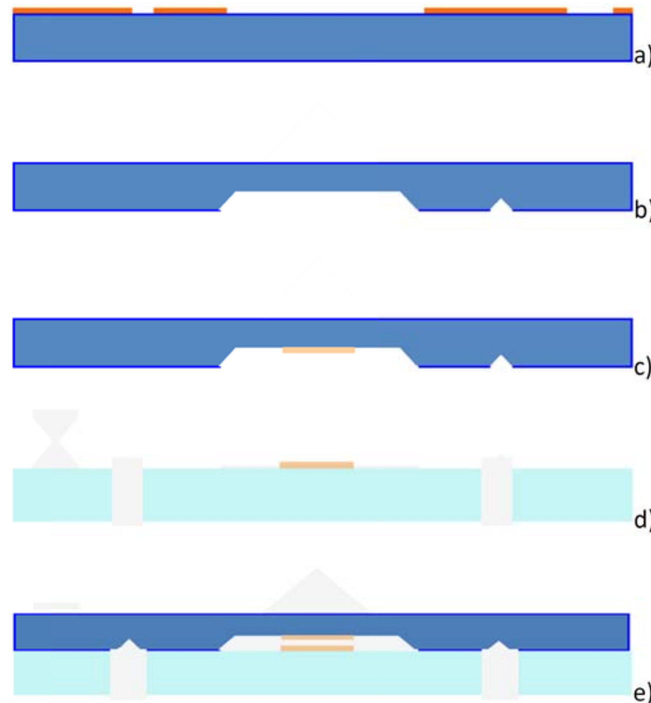


Figure 29: Fabrication sequence of test devices facilitating filling and draining features as well as visual inspection during operation. a) photolithographic patterning of oxidized standard 100 silicon wafer. b) wet etching of patterned silicon wafer using BHF and KOH. c) metal deposition and patterning on etched silicon wafer. d) metal deposition and patterning on drilled borosilicate glass wafer. e) anodic bonding of top and bottom wafer.

The cavity with inlet and outlet is etched using KOH wet etching, see also Figure 30. Afterwards, metal has been deposited using a combination of titanium tungsten (TiW), nickel (Ni), gold (Au) in sequence. Metal pads have been structured by standard photolithographic techniques and wet etching of the various metals. Borosilicate glass wafers have been prepared as top wafers prior to anodic bonding. Diamond drills have been used to drill holes in the borosilicate glass wafers in order to create an inlet and outlet. Similar to the bottom silicon wafers, metal pads have been structured on the borosilicate glass wafers by

depositing a combination of titanium tungsten, nickel, gold in sequence, which subsequently have been patterned by means of photolithographic methods and wet etching of the metal layers. To finalize the test structures, top and bottom wafers have been bonded by anodic bonding.

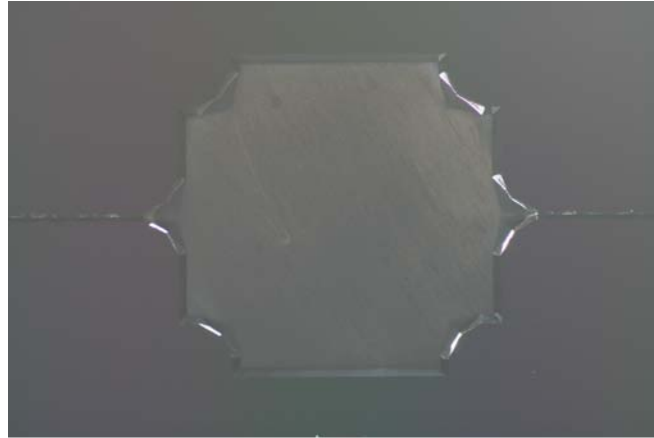


Figure 30: Photograph of the test substrate after KOH etching depicting the test cavity with inlet and outlet, respectively.

3.14 Filling of test structures

As described earlier, the method of HCl assisted soldering has shown good applicability and versatility and has been used in this study in order to fill test structures.Test structures have been filled with LMP samples and soldered to the integrated metal pads using diluted HCl solution (0.15%) as a carrier. First, an LMP sample and a drop of diluted HCl are placed at the inlet of a test device. Heating the test structure and aspirating the liquefied LMP and HCL solution enables filling of the test structures. While liquefied LMP and HCl pass through the test device and make contact to the integrated metal structures, the LMP adheres to the integrated metal pads and the test device is filled at designated positions (metal pad area) by self-alignment of LMP to the metal structures. The process of filling test structures via self-alignment of LMP to integrated metal pads is depicted in picture sequence of Figure 31. A close-up view of test cavities after filling with LMP is shown in Figure 32. Excessive HCl solution is rinsed by flushing the test devices subsequently with deionized water (DI water) and placing it in vacuum until the DI water is evaporated, i.e. only LMP present inside the device. In order to fill the test device with paraffin, liquid paraffin is applied at the inlet and as before aspirated into the devices by applying negative pressure at the outlet of the device. Subsequent vacuum treatment ensures that no air is present inside the test device prior to operation.

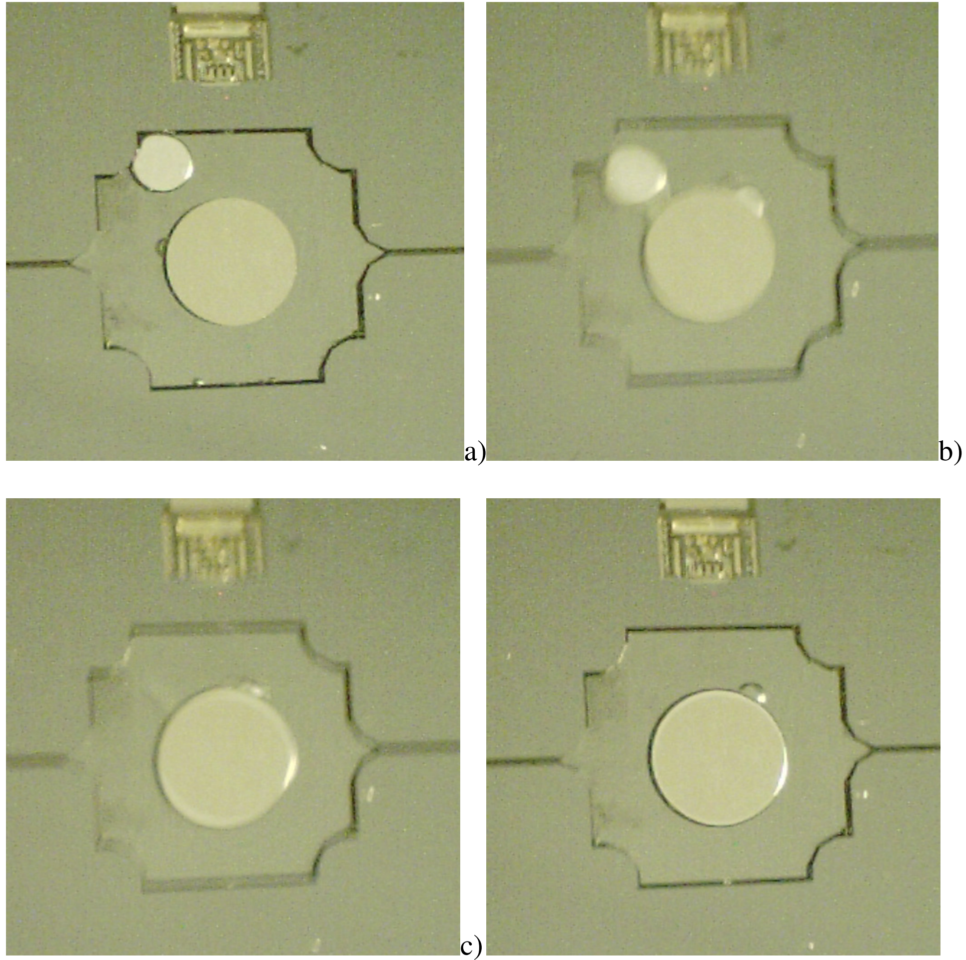


Figure 31: Picture sequence of self-alignment of liquefied LMP inside a test cavity. A) LMP structure is in upper corner of test cavity, b) upon slight vibration at 50Hz the LMP starts to move freely inside the test cavity, c) LMP is self-aligned to the metal pad in the center of the test cavity, d) LMP stays in place at the position of the metal pad and renders a similar shape.

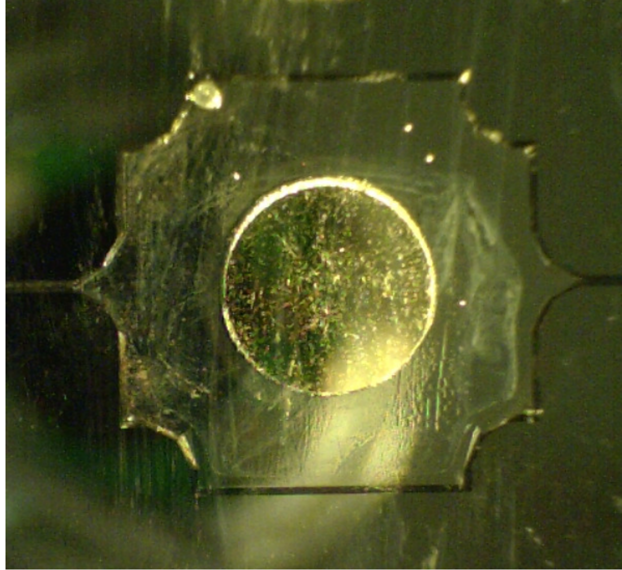


Figure 32: Close-up of a test cavity filled with LMP. Depicted is the metal pad in the center of the cavity which the LMP adheres to after filling. LMP excess is slightly visible at the edge of the metal pad.

To realize fully operational prototypes in silicon, conventional microfabrication techniques and materials are used. In order to circumvent the issue of filling the prototypes after fabrication, filling and draining channels have been integrated which enable sealing of the prototypes by using standard solder or silicone elastomer.

4.1 Design and fabrication of silicon based switch prototype

The fabrication process of the prototypes is depicted in Figure 33. First, an oxidized silicon wafer, used as the top substrate has been structured by standard photolithographic methods. Simultaneously, another silicon wafer has been structured as the bottom wafer by similar means (Figure 33 a). Next, the silicon wafers have been prepared in buffered hydrofluoric acid solution and then etched in 30% potassium hydroxide (KOH) at 80˚C (Figure 33 b). Afterwards, metal has been deposited on the wafer pairs using a combination of titanium tungsten (TiW), nickel (Ni) and gold (Au) in a sequence. The metal layers have been structured by standard photolithographic techniques and wet etching of the various metals (Figure 33 c). Finally, the prepared top and bottom wafers have been bonded eutectically to yield prototypes with enclosed cavities.

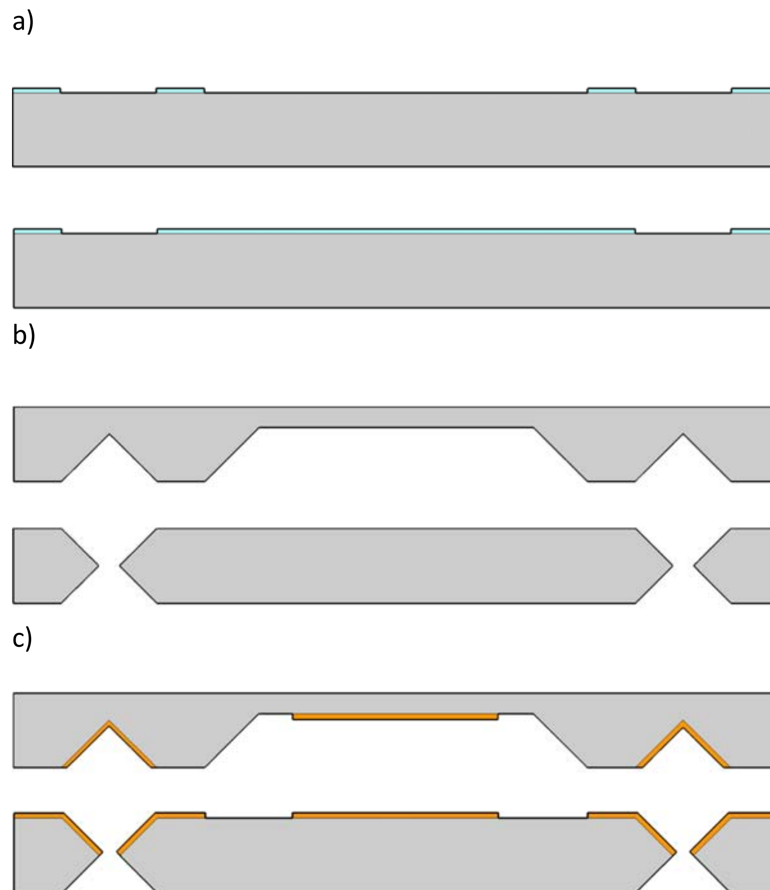


Figure 33: Fabrication sequence of test devices facilitating filling and draining features. a) photolithographic patterning of a oxidized standard 100 silicon wafer pair; b) wet etching of patterned silicon wafers using BHF and KOH. c) metal deposition and patterning on etched silicon wafer. Subsequently bonding of wafer pairs via eutectic bonding

4.2 Filling of prototypes

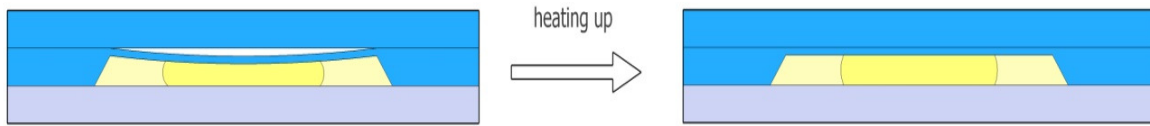
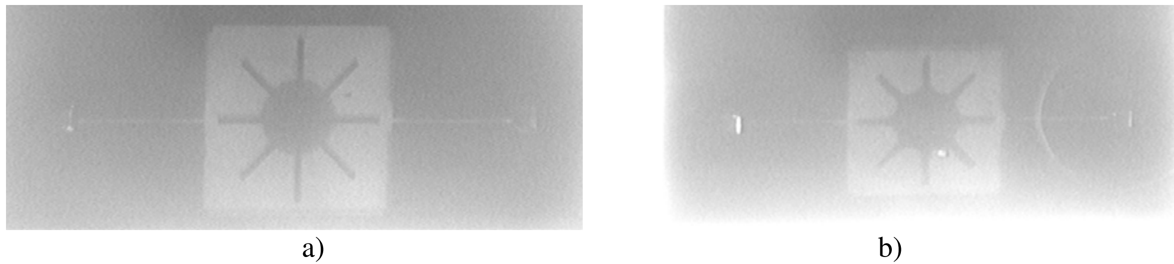


Figure 34: Schematic showing the thermal switch concept utilizing paraffin as a phase change actuator and LMP for heat conduction. Upon heating the paraffin expands and deflects a membrane. Depicted here is an initially negative membrane bending after filling due to the volume decrease after filling with liquid paraffin.

Fabricated prototypes can be filled with LMP and paraffin subsequently through the inlet and outlet channels. Figure 35 depicts such a device during the filling process with LMP. Filling of devices was conducted under an IR camera which reveals the inside of the prototypes with enclosed cavity, inlet and outlet as well as integrated metal pad. The picture shows the device after liquid LMP has been flushed through the cavity and soldered to the metal pad via a self-alignment process. LMP soldering is noted via the meniscus of the LMP between the various branches of the metal pad. The branches have been added to the design in order to improve the filling capabilities of the device. The branches are acting in a fashion to attract LMP inside the cavity which might be moving freely inside.

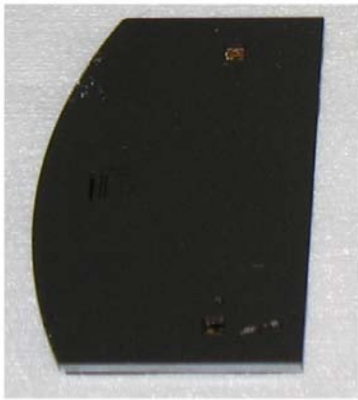


a) b)

Figure 35: IR-photograph of a prototype prior to filling with LMP under an IR camera (a). Clearly visible is the device cavity with inlet and outlet as well as the integrated metal pad. b) After filling through the inlet (right hand side), excess HCl solution is visible which is used as a carrier liquid for the liquefied LMP. The meniscus between the various metal branches depicts the presence of LMP at the metal pad.

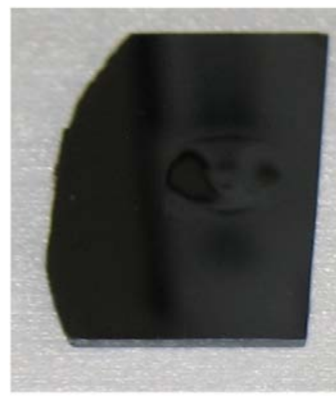
4.3 Sealing of filled prototypes

Fabricated prototypes are depicted in Figure 36 in its filled and unfilled state. The prototypes can be sealed by using silicone elastomer or a standard solder inside the inlet/outlet hole after the filling and cleaning procedure with LMP and paraffin. Clearly visible is the negative membrane bending after filling. This can potentially be counteracted by using a sloped temperature profile during the filling procedure.



a)

b)



c)

Figure 36: Photograph series of a prototypes prior to filling (a), after filling with LMP and paraffin through the inlet/outlet (b) and after filling with LMP and paraffin depicting the membrane side revealing the negative membrane bending after the filling process (c).

Deflection of switch membrane is monitored with a laser interferometer, see Figure 37. It shows a very stable behavior under the actuating temperature of ~60 C, above 60 C the membrane starts to move in a nearly linear way and at 90 C the deflection is ~60µm, see Figure 38.

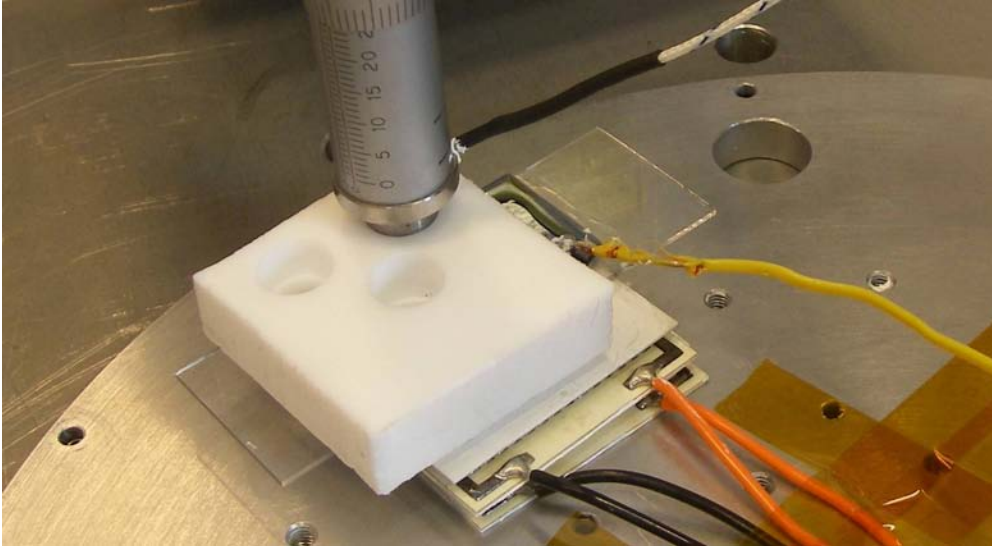


Figure 37: Set-up for temperature monitoring during proof-of-concept test of thermal switch.

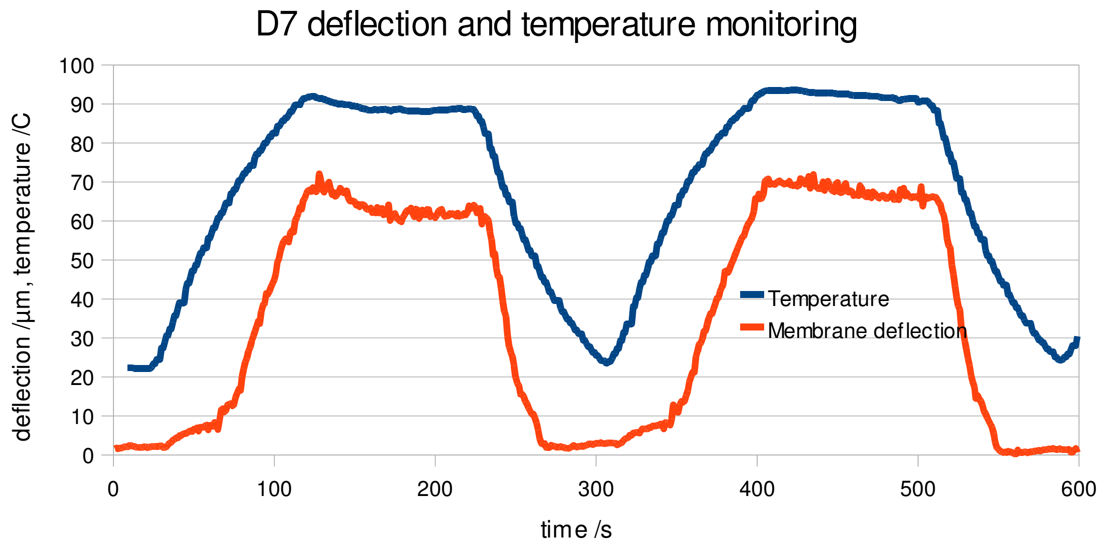


Figure 38: Monitored membrane deflection and temperature shows a deflection activation temperature of ~60 C and a ~60 µm deflection at 90 C.

Functionality testing of prototype is done using a 95 gram micrometer screw as heat sink with controllable distance to membrane, by monitoring temperature on the switch itself and on the heat sink during heating with a certain power and time (up to ~90 C) the switch showed a capacity of handling 1.3 W at off-mode (with 1µm distance to heat sink) and 3 W at on-mode (with a 50µm distance but after membrane deflection making contact with heat sink). Figure 39 show the temperature measurements during this experiment.

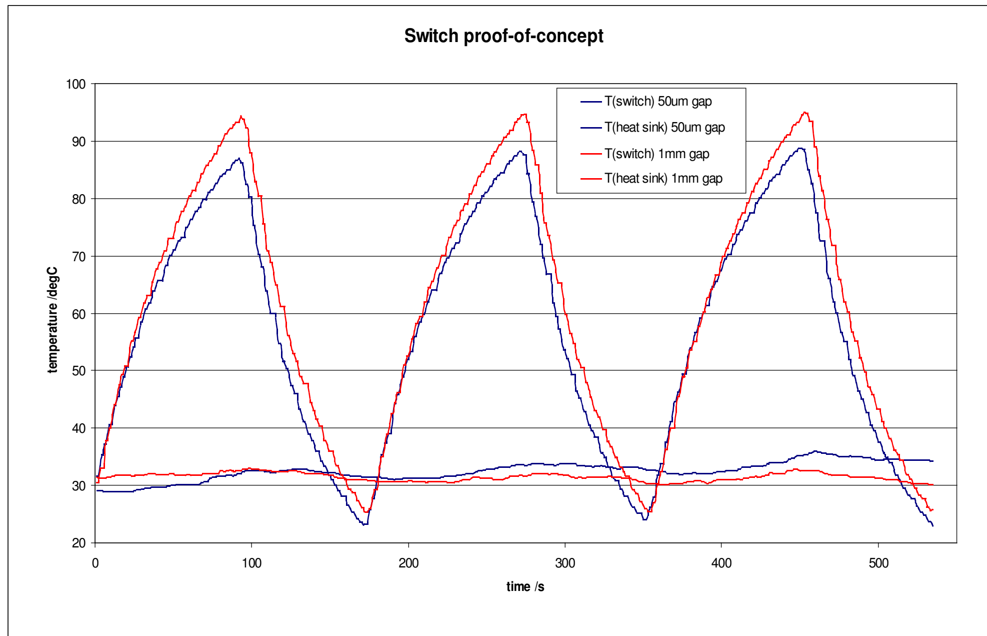


Figure 39: With a certain power generated to the system, proof-of-concept testing of the thermal switch show a temperature decrease from ~95 C to ~87 C. It corresponds to a capacity to handle 3 W of power instead of 1.3 W.

6 Discussion and conclusions

We have successfully shown the fabrication of a thermal switch which is entirely based on silicon and shows integrated filling/draining channels as well as flexible membrane deflection during operation. The filling of the fabricated prototypes has been shown by using a diluted HCl solution as a carrier liquid for LMP sample which enables the filling of prototypes via self-alignment of LMP to integrated metal pads. Furthermore, the fabricated devices have subsequently been filled with paraffin. Simultaneous IR-camera observation enables correct filling of test devices. Due to the volume decrease of paraffin upon cooling the filled devices show a negative membrane bending prior to sealing. Sealing has been accomplished by using a silicone elastomer (PDMS), but can potentially be conducted by applying standard solder to the inlet and outlet of the devices.

The tests have shown important results about the different interfaces, giving us a good description of their behavior; Copper is a suitable material to be used as a pad for the metal alloy, it has a good adhesion and should therefore have a good electric and thermal contact without allowing the paraffin top put itself in interface. Silicon is suitable to be a good substrate for the paraffin, but aluminium could also be adopted as well.

The use of formic acid vapor has shown very limited applicability in soldering LMP and is not compatible with filling of cavities with LMP. It is not compatible with paraffin or low temperature ranges used for melting LMP. Considering the fabrication process of a silicon based thermal switch the implementation of this technique together with paraffin seems unrealistic.

Temperature variations as well as vibration test show promising results where no diffusion, mixing and de-fragmentation could be detected after such treatment. It can be seen that LMP practically remains unaffected if kept in an oxygen free environment. But the experiments, where paraffin has been involved show that gas has been released during the experiments and as a result, e.g. LMP structures oxidized and collapsed inside the cavity. We assume that the degassing of paraffin prior to application on the test structures has been conducted incorrectly so that oxygen, dissolved inside the paraffin, has been released during the ongoing experiment.

7 Future work

To deeper understand the behavior and life time of this switch; thermal cycling, vibration, storage, vacuum and radiation testing is desired. Identifying the reason for the released gas and the oxidation of LMP mentioned in this report is of great importance. The switch also needs further simulations and shall be adapted to a system-perspective with suitable heat sink and external interfaces. Future work should as well aim to lower fabrication cost and raise yield.

8 Acknowledgement

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BGA = Ball Grid Array

CCD = Charged Coupled Device

HCl = Hydrochloric Acid

LMP = Low Melting Point alloy

MEMS = Micro Electro Mechanical Systems

PDMS = Poly(-dimethylsiloxane)

Si = Silicon

KOH = Potassium hydroxide

DI = deionized

IR = Infrared

TiW = Titanium tungsten

Ni = Nickel

Au = Gold