Ag-In transient liquid phase bonding for high temperature stainless steel micro actuators

Martin Andersson
Abstract

**Ag-In transient liquid phase bonding for high temperature stainless steel micro actuators**

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A stainless steel, high temperature, phase change micro actuator has been demonstrated using the solid-liquid phase transition of mannitol at 168°C and Ag-In transient liquid phase diffusion bonding. Joints created with this bonding technique can sustain temperatures up to 695°C, while being bonded at only 180°C, and have thicknesses between 1.4 to 6.0 µm. Physical vapour deposition, inkjet printing and electroplating have been evaluated as deposition methods for bond layers. For actuation, cavities were filled with mannitol and when heated, the expansion was used to deflect a 10 µm thick stainless steel membrane. Bond strengths of the joints are found to be in the region of 0.51 to 2.53 MPa and pressurised cavities sustained pressures of up to 30 bar. Bond strength is limited by the bond contact area and the surface roughness of the bonding layers.
Populärvetenskaplig sammanfattning

Många av dagens högteknologiska uppfinningar är konstruerade till att användas i miljöer där temperaturen inte överstiger 70°C. Vid miljöer där högre temperaturer kan påträffas, så som i krävande industriapplikationer och rymdmiljö, kan detta utgöra en begränsning. Det kan dessutom vara fördelaktigt för viss teknik att arbeta vid högre temperaturer, men då inte alla delkomponenter i systemet klarar av detta hindras i många fall sådana landvinningar. I detta arbete beskrivs hur en sådan komponent, en mikroaktuator, kan utvecklas för att fungera vid en högre arbetstemperatur.

Mikroaktuatorer är en typ av mekanisk mikrokomponent, av storleksordningen µm till mm, som skapar rörelse och kan användas för att utföra en mängd olika uppgifter så som att draiva en mikropump eller ett elektromekaniskt relä. Denna komponent kan sedan vara del i ett integrerat system inom högteknologiska tillämpningar, så som analys av kemiska ämnen och styrning av optik. Vid avdelningen för mikrosystemteknik, Uppsala Universitet, har en mikroaktuator tidigare utvecklats som är konstruerad av rostfritt stål. För att skapa rörelse utnyttjas den expansion som sker när materialet paraffin smälter och expanderar, vilket får ett membran att böja. Mikroaktuatorn är konstruerad för att arbeta kring rumstemperatur, och detta begränsas dels av paraffin samt också den plastbaserade fogningsteknik som används för att bygga komponenten.


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1 Introduction

Much of everyday technology utilise some form of actuation, the creation of movement. Whether it is the pumps in a chemical process plant, the motor of a car, or the compressor of a refrigerator, an actuator will provide force and work. Miniaturisation of actuators hope to offer similar benefits as the electronic industry has seen in regard to increased efficiency, cost reduction and portability in applications such as microvalves, pumps for analytical systems and highly reliable electromechanical switches. However, these systems are often limited by the service temperature for which they are designed to operate, and for high temperature applications, only a limited number of micro actuators are applicable.

One approach for creating actuators is to use phase change materials, PCM:s. For a PCM, the solid-liquid phase transition is often associated with a significant volumetric increase, which can be used for actuators, i.e. by pushing on a deflecting membrane. By this method, designs can be made simple and compatible with micro system fabrication processes. Such a system has been demonstrated by the division of microsystems technology, Uppsala University, where PCM micro actuators have been developed and then further implemented for microfluidic tasks. These PCM micro actuators are designed to operate at room temperature, however, by changing PCM in the design and bonding technology, these actuators are anticipated to be able to work also at higher temperatures.

1.1 High temperature actuators

Several different approaches have been demonstrated to create high temperature micro actuators. In one design, a 130 by 128 mm electromagnetic linear actuator, provides a force of 300 N at temperatures up to 800°C [1]. Shape memory alloys with a transformation temperature in the range of 100 to 1000°C have also been used for actuation [2]. Around 350°C, Ni-Ti-Zr and Ni-Ti-Hf alloys are used and for higher temperatures, Ni-Pd-Ti alloy has its transformation temperature at 1000°C [2]. Also, carbon nanotubes have been used for super elastic muscles which can withstand high temperatures [3].

1.2 Stainless steel micro actuators

PCM micro actuators developed at the division of microsystem technology, Uppsala University, use paraffin as a PCM [4]. The paraffin goes from solid to liquid at 44°C to 48°C, and expands about 15% by volume when melted. It is enclosed in a cavity by a membrane. The actuator is made out of stacked stainless steel grade 304 stencils, forming the main structure of the design. The membrane is made out of stainless spring steel grade 301 to allow for the higher stresses associated with membrane deflection. The corrosion resistance provided by stainless steel allows the actuator to be used in applications where
Si-components could possibly degrade, such as hot water fluidics and corrosive solution handling. To keep all the parts together, the steel stencils are thermocopressively bonded at 240°C using parylene C, a chemically vapour deposited polymer commonly used in the electronics industry.

For usage at high temperatures, there are two main restrictions on the service temperature of this actuator:

- There does not exist any paraffin with a melting point above 100°C.
- The glass transition temperature of parylene C is 50°C. Above this temperature, the mechanical properties starts to degrade [5].

To develop a high temperature PCM micro actuator it is therefore necessary to change both the PCM material and the bonding technology.

### 1.3 High temperature phase change material

A PCM suitable for actuation at elevated temperatures needs to comply with several conditions. First, it needs to have a phase transition slightly higher than the service temperature of the actuator. Secondly, this phase transition must yield a volumetric expansion of interest. The degree of expansion needed depends on the actuator design, but in general an expansion in the region of ten percent is desirable. Thirdly, the PCM must be stable and show repeatability in its transitions.

Much of the research on high temperature PCM is found in the field of energy storage, as phase transitions provide latent energy, stored in the enthalpy of fusion. Salts offer a broad range of melting temperatures, where nitrates are found in the region 240°C to 700°C and fluorides are in the range of 850°C to 1500°C [6]. Corrosion of the structural materials encapsulating the salts is a problem, and inorganic salts with a melting point of less than 200°C is not found in pure compositions. Sugar alcohols, such as mannitol, galactitol and erythritol offer an alternative in this temperature region and the melting points are 168, 188 and 121°C, respectively. The sugar alcohols do not react with metals and the melting points or other properties do not alter during extended thermal cycling [7]. Sugar alcohols are organic compounds containing several hydroxyl groups and are commonly used in the food industry as artificial sweeteners.

### 1.4 Metal bonding

The main method of bonding stainless steel for industrial applications is welding. By melting the contact area between two parts and adding more melted material, followed by rapidly cooling, the parts are joined together. This produces a joint that can become as
strong and heat resistant as the bulk material. To create a melt of the stainless steel joint area and filler material, temperatures needs to exceed 1400°C. This requires a great deal of energy added, and is done by e.g. electric arch, lasers or friction. Welding may be a feasible bonding method for microsystems, but sets a high demand on fabrication methods and process designs, as microsystems often have complex bonding sequences, and have heat sensitive components and structures.

In soldering, a filler material of lower melting point than the materials to be bonded is used [8]. The solder is dispensed to the surfaces before they are put in contact with each other, and the stack is heated to the point where the solder will become a liquid. The liquid will flow out and fill irregularities in the bond area, and therefore lessens substrate flatness requirements. Also, the solder material will generally have lower mechanical properties than the bulk material. The element composition of the filler material is often chosen so that it melts at an eutectic point, to completely melt at a single temperature. Solder materials are often divided into soft and hard solders. Soft solders have melting points less than 400°C and hard solders melts at higher temperatures. Hard solders, are often based on Au, Ag or Cu alloys, and at the high temperatures used, they alloy with the substrates and create stronger joints than soft solders do. To implement soldering for microsystem bonding, the filler material is often deposited as a thin films. To create the proper melting composition, layers of different elements can be added that form an eutectic system. Upon heating, solid state diffusion into each of the layers causes mixing so an eutectic composition will be reached and a liquid melt will form. An example of such bonding methods are \( Al - Ge \) eutectic bonding [9].

Solders near their melting point become mechanically weak. For example, a common high temperature soft solder, eutectic \( Sn - Ag - Cu \), has a melting point of 217°C, but can not be used for service operations higher than 180°C or the joint risks mechanical failure [10]. As the process temperature used for bonding is above the melting point of the solder, there exists a correlation between the highest process temperature the device can withstand, and the solders high temperature joint reliability. To implement a PCM into the process scheme, the solid-liquid phase transition sets an upper limit on the process temperature once added, as the volume expansion can break the structure. Hence, a joint must be produced that can withstand a higher temperature than it originally was produced at to be able to encapsulate the PCM. Transient liquid phase diffusion bonding, TLP, is such a soldering method and utilises a low melting point material to form a melt that starts to react with a high melting point material, and through diffusion forms a solid high temperature joint. The low melting point material is often \( Sn \) or \( In \), while the high melting point materials can be \( Ni, Cu, Ag \) or \( Au \) [11].

The \( Ag - In \) TLP joints developed have mainly been thick, for example a 40 \( \mu \)m joint has been developed for flip chip connections [12]. One thin high temperature \( Ag - In \) TLP joint is 7 \( \mu \)m and was used to bond \( Si \) substrates [13]. For a stainless steel micro actuator,
this joint is an interesting replacement for the Parylene C joints. However, the previously presented thin, high temperature $Ag-In$ TLP joint, is made on flat Si-substrates and not on rough stainless steel. Therefore, this thesis faces a challenge to implement the bonding technology on stainless steel.

1.5 Main objectives

- Design, fabrication, and evaluation of a thin, high temperature, $Ag-In$ TLP joint for stainless steel microsystems.
- Evaluation of mannitol as a potential high temperature PCM.
- Build a proof-of-concept high temperature PCM micro actuator.
2 Theory

2.1 Transient liquid phase diffusion bonding

TLP bonding consists of three main layers. First, there is a metal layer of low melting point, here denoted solder layer. Secondly, there is an oxidation protective layer of a different material deposited on top of the low melting point solder layer. This layer protects against oxidation of the solder layer prior to bonding, as many low melting point metals have stable native oxides in ambient conditions that will stay solid if the solder material is melted, hence hinder bonding. Thirdly, the joint consists of a diffusion layer that is made from a material with a higher melting point than that of the low melting point solder layer. To create a joint between two substrates, one of substrates must have the solder layer. Located on either both or one of the substrates are the diffusion layers, placed closest to the substrate interfaces. By stacking the substrates together under pressure and heat, the solder layer will melt creating a joint. After the initial solder layer bond is created, the low temperature material can diffuse into the diffusion layer of high melting point. If this changes the composition of the joint to a large enough extent, then the mechanical characteristics of the bond will be represented of the high melting point material rather than that of the low melting point material.

TLP bonding can be implemented with the binary $Ag-In$ system. To help in the following discussion, the phase diagram of $Ag-In$ can be viewed in figure 1. $In$ has a low melting point.
point of 156.6 °C as oppose to Ag which has a high melting point of 961.9°C. Ag shows a solid solution of up to 20% (at.) In in Ag and in the span between 20% and 66.7% (at.) In, several intermetallic phases exist such as the AgIn\(_2\)-phase and \(\gamma\)-phase. The \(\gamma\)-phase has a variable composition between 31% to 33.5% (at.) and is located next to Ag\(_2\)In. The solubility of Ag in In is small. At 96% (at.) In, the system has an eutectic with a melting point of 144°C. The liquid phase line has a steep angle as the ratio of Ag increases, being at 144 °C at the eutectic and 695°C at 20% (at.) In in solid solution of Ag. This is further extended to the melting point of pure Ag.

If a thin In solder layer is deposited onto a Ag diffusion layer and heated, the interface of In and Ag will first form AgIn\(_2\). In will start to melt at the interface at 144°C, the temperature of the eutectic, and melt throughout the solder layer at 156.6°C. At this stage, the melted In solder can flow and fill out surface irregularities between substrates. As temperature reaches between 166°C and 205 °C, AgIn\(_2\) will decompose in a peritectic reaction, and a mixture of In-rich melt and \(\gamma\)-phase grains will start to form. Diffusion of In into Ag at the interface causes the Ag to be released into the melt, increasing the content in the melt continuously. This will drive the reaction and precipitate more \(\gamma\)-phase grains until all of the In-rich melt has reacted and solidified. After the reaction is completed, the composition has changed to between 31% and 33.3% (at.) In. Parts of the Ag diffusion layer will be left as not all of the layer is consumed during the reaction.

The phase transformations were experientially studied with in-situ x-ray diffraction [15]. The studied samples had electrodeposited films of 4 \(\mu\)m Ag and 2 \(\mu\)m In laid over a Ni adhesion layer, and were heated to 500°C at 10°C/min with diffraction data recorded throughout the heating process. At 144°C In melts and AgIn\(_2\) reflections are seen. When the temperature reaches 166°C, the AgIn\(_2\) reflections change to Ag\(_9\)In\(_4\)-reflections, indicating the peritectic reaction where AgIn\(_2\) decomposes, forming the \(\gamma\)-phase. Above 205°C, the \(\gamma\)-phase starts to disappear and \(\zeta\)-phase start to form.

The \(\gamma\)-phase is an intermetallic, that is mechanically weak, and is stable up to 312°C from where it starts to decompose into \(\zeta\)-phase. For higher bond strengths and high temperature resistance, it is much more favourable to have a joint made out of Ag with In in solid solution. Therefore, the joint is annealed, at temperatures similar to that of bonding, for some period of time to diffuse In into Ag yielding an overall total composition of less than 20% (at.) In. No mechanical strength evaluations of TLP In – Ag joints are known, but for a perfectly adherent joint to the substrates, the mechanical properties for the joint should be close to that of Ag, having a yield strength of 170 MPa [16].

### 2.1.1 Oxides and Flux

For all metal bonding methods, oxidation of metal in the interface is a main concern. Solder will not wet and adhere to oxide layers and produced joints will be weak. For a lot
of applications, the bonding surface and solder is treated with an oxide removal material, flux [8]. These materials reduce metal oxides to metal and protect the melted solder from oxidising during bonding, and can partially remove surface oxides from metal substrates. Flux is easy to employ on simple bonding operations, but is also troublesome as it is often organic and corrosive, and needs to be removed prior to the completion of the bond. Making layered structures where the bond area is concealed is not ideal for the removal of flux. Instead, for large joints, other oxide protection methods are used. For example, solder material can be coated with Au which lack a stable native oxide and then the bonding process can be preformed in an inert environments such as in vacuum, nitrogen or argon. Sometimes a gas reducing agent can be added, such as hydrogen. When Ag is deposited over In, a reaction immediately takes place where AgIn$_2$ is formed at the layer interface [17]. The fluxless ability of an In – Ag TLP bond principle comes from the fact that the phase AgIn$_2$ is stable in ambient oxygen rich environments [18].

### 2.1.2 Diffusion processes

TLP is controlled by diffusion processes and it is important to give an overview of how this affects bonding designs and methods. The diffusion of In and Ag affects storage of unbonded samples, the amount of liquid melt, and the annealing of bonded joints to create high temperature mechanically strong joints.

Two diffusion mechanisms dominate the In – Ag binary system [17]. Ag can dissolve into In by interstitial diffusion with an activation energy of 0.55 eV and diffusion coefficient of $0.52 \times 10^{-4} m^2 s^{-1}$. In diffuses into Ag through grain boundaries with an activation energy of 0.42 eV and a diffusion coefficient of $2.4 \times 10^{-12} m^2 s^{-1}$, as measured on unanneled evaporated samples. Despite that the interstitial diffusion is fast, the solubility of Ag in In is very small and the activation energy of grain boundary diffusion is lower. Therefore, the dominating mechanism is the grain boundary diffusion of In in Ag.

This will affect the storage life of the AgIn$_2$ oxide protective layer as underlying In can diffuse up and be exposed to air, where it will form oxides and hinder bonding. To estimate the storage time, the semi-infinite solution to Flick’s law, for a constant surface concentration, can approximatively be used. This model does not fully fit the description of the diffusion situation as surface concentration varies, films are not semi-infinite and that the diffusion properties may be different in the AgIn$_2$ phase. However, it provides a good insight in the diffusion speeds of the In grain boundary diffusion into Ag and can be used to roughly estimate the thickness of the oxidation protective layer. The storage time, at 25°C, can be related to figure 2(a) and shows that an In content below 66.7% (at.), AgIn$_2$, can be held for about 4 days for a 150 nm thick Ag film. For a description of the calculation, see appendix 8.2.

Controlling the grain size of Ag yields better bond interfaces [19, 20]. During bonding, the
liquid In rich melt reacts with Ag to produce γ-phase, and as mentioned, this process is controlled by grain diffusion of In into Ag. A vital feature is the ability of the melt to flow and fill out the uneven surface structures to form a void free bond interface. If the diffusion and corresponding production of γ-phase is too fast, the melt will solidify before the entire bond gap is filled, which makes the joint porous and hence weak. To control the grain boundary diffusion, the Ag layers can be annealed to increase grain size and lower the diffusion rate.

The grain size of Ag layers is dependent of the deposition method, film thickness, substrate and annealing conditions. Electroplated Ag on commonly used Au coated substrates such as Si and alumina show a grain size between 10-30 nm [20]. Ag grain sizes on sputtered films have been reported to be larger, 100 to 200 nm [21], and for thermally evaporated films the grains are of a similar size. It has been shown that annealing Ag films can increase the grain size up to several μm. For a 85 μm thick Ag film on Cu substrates, the Ag grains could be grown from 9.3 nm to more than 2 μm by annealing at 450°C for 3h in air environment [19]. Onto stainless steel with Ni as an adhesion layer, electroplated 10to 50 μm thick Ag films with a grain size less then 200 nm annealed at 250°C for 40 h, produced grains larger than 2 μm [22]. These layers were used to produce void free joints with In using TLP bonding. For sputtered films the grain growth is similar, but different grain growth behaviours are seen as the film thickness is increased. Ag films, 0.6 μm thick annealed for 30 min at 400°C, yielded an average grain growth of 1 to 2 μm where Ag films of 2.4 μm followed an abnormal grain growth mechanism producing islands of mm-sized Ag grains at the same annealing conditions [21]. These mm-sized Ag grains completely

Figure 2: (a) Diffusion during storage for 240 h, 10 days. Each line represent the concentration gradient for every 24 h period at 24°C. (b) Diffusion during post bonding annealing for 144 h, 6 days. Each line represent the concentration gradient for every 24 h period at 180°C.
covered of the film after 120 min.

The post bonding annealing step where \( \gamma \)-phase is transformed to solid solution of \( In \) in \( Ag \) can be done at temperatures similar to those of the bonding temperature. As shown in figure 2(b) annealing joints for 24 h at 180\(^\circ\)C will diffuse \( In \) several \( \mu m \). This is an idealised case, as the diffusion rate data does not correspond to either \( \mu m \)-sized \( Ag \) grains or the presence of intermetallic phases. However, this method has been demonstrated to work with annealing conditions ranging from 26 to 40 h and temperatures between 130 to 145\(^\circ\)C [23, 13]. These conditions can be modified to meet the desired application limits, where a higher annealing temperature can be traded for a shorter annealing time.

2.2 Metal deposition

2.2.1 Evaporation

Physical vapour deposition, PVD, is a technique to deposit thin films on a variety of substrates such as tubing, foil, tools and circuit boards. Film thicknesses deposited by PVD ranges from a few Å up to several \( \mu m \). The substrates are placed above an evaporation source, that is melted and vaporised by resistive heating or an electron beam, and are under high vacuum. Because of the high vacuum, vaporised atoms will move almost without collisions and condensate on the colder substrates in a line of sight fashion. The thickness control of these systems can be monitored by the gain of weight of the deposited surfaces. To do this, a quarts crystal oscillator with a frequency dependent mass is placed close to the substrate and the frequency of the crystal will change as materials is being deposited. This deposition rate can then be used to control the power output of the evaporation source [24].

2.2.2 Electroplating

Electroplating is an electrolysis process where a substrate is submerged in an electrolyte solution containing ions of a depositing material. The substrate is used as a cathode, and a counter electrode, preferably made of the deposition material, is used as an anode [25]. By driving a current though the circuit, ions of the material to be deposited are reduced and plated onto the substrate.

2.2.3 Inkjet

Inkjet printers eject dispersed nanoparticles of the material to be deposited. When cured by heating, solvents evaporate and the dispersion polymers are burned off. Further heating
causes the material to sinter. Being a drop-on-demand technique, structured metal films can be made without masking and together with the usually low curing temperatures for the nanoparticles, the range of substrates possible to use goes beyond what is possible with conventional techniques such as thick-film technologies.

2.3 Adhesion layer

Stainless steel of grade 304 has a high Cr content, 18% (wt.), and stable Cr₂O₃ formed on the surface gives the material corrosion resistant properties. Noble metals such as Ag or Au show a low degree of interaction to oxides and do not adhere well to the oxide surface of stainless steel. Therefore it is necessary to use an adhesion layer between the deposited metal and the stainless steel substrate.

For films to adhere to a substrates, there must be valence forces or interlocking forces holding the layers and substrates together [26]. For a chemical bond to be made, several interactions can take place such as a metallic bond where atoms share orbital electrons, electrostatic bonds where ions are formed with an exchange of electrons or due to Van der Waals interaction from polarisation of molecules [27]. Adhesion layers with strong chemical bonds to the substrate can often be made by evaporating a metal that form stable bonds with the native oxide found on surfaces. The bonding energy of the adhesion layer will then be related to the formation energy of the metal-oxide bond of the deposited metal [27]. Common adhesion metals are Cr and Ti, which form the stable oxides Cr₂O₃ and TiO₂. Both these oxides have a high formation energy and hence Cr and Ti create strong metal oxide bonds to well oxidised surfaces, which in turn create strong adhesion. As the adhesion metals are evaporated under vacuum, they will leave an oxide free surface where noble metals can be deposited and adhere, creating a metal bond.

Electroplating Ni on stainless steel is another surface treatment that can promote adhesion of metal films. By the use of a Woods Ni Strike, an acid Ni bath containing a high degree of Cl⁻ ions, the Cr₂O₃ layer of stainless steel can be dissolved and Ni-film can be deposited.

Inkjet Ag will not adhere to the Cr₂O₃ surface of stainless steel. Therefore, a thin film of Ag or Au can be evaporated, as described above, to give a surface capable to adhere inkjet depositions.

2.4 Mannitol for actuation

Mannitiol undergoes a gradual melting process that starts at 162.15°C, peaks at 167.8°C and has an enthalpy of fusion of 326.8 J/g [7]. It is a sugar alcohol with 6 hydroxyl groups, as shown in figure 3. The solid material is brittle, hard and behaves much like table sugar.
Figure 3: Structural formula of mannitol.

Figure 4: Volumetric expansion measurements of mannitol as determined by Netzsch Applications Laboratory. The measurement data show a transformation of mannitol with volumetric loss, at around 170°C. This is followed by a large increase in volume. It is indicated that the measurement was not done correctly, as mannitol first shows a negative expansion and then a positive. It is believed that the sample was in powder form during measurement, which resulted in a false expansion profile.
Mannitol is thermally stable up to 300.15°C where it starts pyrolysis and loses mass. The volumetric expansion of melting mannitol has not been determined, but is around 10% for the chemically similar Erythritol [28]. To determine the volumetric expansion of mannitol, samples were sent to Netzsch Applications Laboratory for evaluation. However, the results were inconclusive as testing was done on mannitol in powder form, which lost a great deal of volume during the first melting cycle, seen in figure 4.
3 Design

3.1 TLP joints

3.2 Design requirements

The layer thickness of a high temperature $Ag - In$ TLP joint is controlled by the following requirements:

1. The oxidation protective layer must be thick enough to protect $In$ from oxidation for a practical time period.
2. The liquid melt created during bonding must be thick enough to fill out surface irregularities on the top substrate to create a void free joint.
3. The total content of $In$ in the joint must be less than 21\% (wt.) after bonding to reach solid solution of $In$ in $Ag$.

The amount of liquid melt is not only dependent on the $In$ solder layer thickness, but as well of adjacent $Ag$. The oxide protective layer first increases the thickness of the melt by adding more $Ag$ to the melt. However, if too much $Ag$ diffuses into the $In$ solder layer and a composition of less than 68.0\% (wt.) $In$ is reached in the solder layer, a melt will not be produced during bonding. The material in the joint that can melt is the $AgIn_2$ and $In_{-phases}$.

The surface roughness of the stainless steel stencils, which are the test substrates used for all samples in evaluating $In - Ag$ TLP bonding, is composed of line hills and valleys from the hot rolling manufacturing of the stainless steel. These formations have a peak to valley difference of 1.6 $\mu$m and are found in a parallel configuration. The average roughness, with the hill formations excluded, is 104 nm.

3.3 Bond designs

The $Ag - In$ TLP bond layer structures, figure 5(a) and 5(b), all have a top substrate with a $Ag$ diffusion layer, deposited onto an adhesion layer of either $Cr$ or $Ni$. The bottom substrate utilises the same type of adhesion layers and holds an $In$ solder layer protected by a thin layer of $Ag$, the oxide protection layer. The $Ag$ diffusion layers are annealed prior to further processing to increase grain size and hinder diffusion on all samples except for a few specific samples, made to evaluate the effect of $Ag$ grain growth annealing.

The bond designs have been made to evaluate the conditions that result in a joint that is as thin as possible but still holds a sufficiently thick meltable solder layer and also has a total $In$ composition that is less than 21\% (wt.). The low $In$ composition is essential.
Figure 5: (a) Bond layer structure with single Ag diffusion layer. (b) Bond structure with Ag diffusion layers on both top and bottom substrates.

as solid solution of In in Ag can be reacted in the final joint, creating the reliability at high temperatures and high mechanical properties. There are 7 different bond designs, and their deposition methods and thicknesses can be found in table 1. Table 2 shows the phase characteristics of the bond designs, where the total composition of In in the joint is given, as well as the concentration of the meltable phases In and AgIn$_2$ in the bottom substrate. The deposition method used to create the Ag diffusion layer is the main variable among these 7 different designs and is denoted in the design name by PVD for evaporation, INK for inkjet and EL for electroplating. Within each deposition type, other variations have been made such as creating a thinner joint, PVD-Thin, adding a Ni adhesion promoter, INK-CrNi, or having two diffusion layers, PVD-2Diff.

PVD-2Diff follow the two side diffusion layer structure as depicted in figure 5(b). With this layer structure, the interface between the joint layer and the substrates is the same on both sides. Because of the extra Ag diffusion layer, the concentration of meltable phases is affected. During deposition and prior to bonding, the extra Ag can diffusion into the In solder layer to an extent where $\gamma$-phase can form and deplete the content of meltable In and AgIn$_2$ phases. As the diffusion conditions during evaporations are unknown, the level of $\gamma$-phase formation is unknown and hence this bond design evaluates if the diffusion prior to bonding is low enough to still allow for a meltable solder layer. To slow diffusion, the extra Ag diffusion layer is annealed to increase grain size prior to the deposition of the In solder layer.
Table 1: Layer thicknesses and deposition method for bond designs. The first and second column denotes design name and the total joint thicknesses. The third and fourth column show thicknesses, in nm, and deposition methods for each layer on top and bottom substrates. The deposition methods are denoted by (ink) for inkjet, (el) for electroplating and if not otherwise stated, evaporation. Unknown thickness is denoted (un).

<table>
<thead>
<tr>
<th>Design</th>
<th>Total</th>
<th>Top Description</th>
<th>Bottom Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>INK-Cr</td>
<td>5500</td>
<td>100 Cr, 150 Ag, 3600 Ag (ink)</td>
<td>100 Cr, 1400 In, 150 Ag</td>
</tr>
<tr>
<td>INK-CrNi</td>
<td>6000</td>
<td>100 Cr, 150 Ag, 3600 Ag (ink)</td>
<td>500 Ni (el), 100 Cr, 1400 In, 150 Ag</td>
</tr>
<tr>
<td>PVD-Thin</td>
<td>1370</td>
<td>100 Cr, 800 Ag</td>
<td>100 Cr, 300 In, 70 Ag</td>
</tr>
<tr>
<td>PVD-2Diff</td>
<td>2550</td>
<td>100 Cr, 800 Ag</td>
<td>100 Cr, 800 Ag, 600 In, 150 Ag</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>3850</td>
<td>100 Cr, 2500 Ag</td>
<td>100 Cr, 1000 In, 150 Ag</td>
</tr>
<tr>
<td>EL-Thick</td>
<td>4350</td>
<td>Ni (un, el), 3000 Ag (el)</td>
<td>100 Cr, 1000 In, 150 Ag</td>
</tr>
<tr>
<td>EL-InLow</td>
<td>4050</td>
<td>Ni (un, el), 3000 Ag (el)</td>
<td>100 Cr, 700 In, 150 Ag</td>
</tr>
</tbody>
</table>

Table 2: Concentration of meltable $In$- and $AgIn_2$-phases (wt. %), in bottom substrate prior to bonding for all of bond designs. Total composition of $In$ in joint after bonding (wt. %). All figures are based on complete mixing between layers.

<table>
<thead>
<tr>
<th>Design</th>
<th>Bottom substrate $In$</th>
<th>Bottom substrate $AgIn_2$</th>
<th>Total $In$</th>
</tr>
</thead>
<tbody>
<tr>
<td>INK-Cr</td>
<td>58.3</td>
<td>41.7</td>
<td>20.0</td>
</tr>
<tr>
<td>INK-CrNi</td>
<td>58.3</td>
<td>41.7</td>
<td>20.0</td>
</tr>
<tr>
<td>PVD-Thin</td>
<td>21.5</td>
<td>78.5</td>
<td>19.4</td>
</tr>
<tr>
<td>PVD-2Diff</td>
<td>0</td>
<td>0</td>
<td>19.3</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>44.6</td>
<td>55.4</td>
<td>20.8</td>
</tr>
<tr>
<td>EL-Thick</td>
<td>44.6</td>
<td>55.4</td>
<td>18.1</td>
</tr>
<tr>
<td>EL-InLow</td>
<td>13.4</td>
<td>76.5</td>
<td>13.4</td>
</tr>
</tbody>
</table>

3.4 Actuator design

The actuator is mainly composed from three stacked 100 $\mu$m thick stainless steel grade 304 stencils and a cross section of the device is seen in figure 6. A structured cavity of 50 $\mu$m depth and 1 mm radius is located at the centre. Filling inlet and outlet holes are located 3 mm from the cavity centre on the back side and is connected to the cavity by a 250 $\mu$m wide inlet channel and a 150 $\mu$m wide outlet channel. A stainless steel grade 301 10 $\mu$m thick foil is bonded against the top side of the cavity stencil. The cavity is filled from the back side with mannitol which then is enclosed by bonding another stainless steel stencil at the back. A supporting stencil, with a 1 mm radius hole in the middle, is bonded onto
Figure 6: Cross-section sketch of the mannitol-filled actuator. On top is the supporting stencil (1), followed by a stainless steel membrane (2). Below is the cavity stencil (3) filled with mannitol through a filling channel enclosed by a backside stencil at the bottom (4). The filling inlet and outlet channels (5.) connect with the actuator cavity (6.).

The cavity and channel volume of the device is 0.149 \( \mu \text{L} \) and a volumetric expansion of the mannitol phase transition of 5% yields a membrane deflection of 4 \( \mu \text{m} \). An expansion of 10% yields a deflection of 9 \( \mu \text{m} \). The highest deflection that the membrane can withstand before stresses causes yielding of the membrane is 14 \( \mu \text{m} \). The deflection calculations can be found in appendix 8.1. The membrane foil is joined with \( Ag-In \) TLP joints. With bond design \textit{EL-Thick}, the cavity stencil acts as the top substrate holding the \( Ag \) diffusion layer and the foil acts as the bottom \( In \) substrate. The supporting stencil is bonded with bond design \textit{EL-InLow}, with the foil being the bottom \( In \) substrate. The back side stencil is bonded with epoxy glue after filling the cavity with mannitol. The choice of using epoxy glue introduces a non high temperature reliable joint into the design, but also lowers the risk of the actuator breaking during fabrication, as the phase transformation and volumetric expansion of mannitol can be evaded during the back side stencil bonding.
4 Experimental

4.1 TLP

4.1.1 Evaporated Ag films

Ag thin films were made with physical vapour deposition using a Lesker PVD 75. First, the SS 304 substrates were cleaned in an alkaline cleaning solution for 5 min in an ultrasonic bath at 60°C. The cleaning solution was prepared with 40 ml of UPON 5800, Henkel, cleaning concentrate in 1 L of deionized water. After washing in deionized water, the substrates were further cleaned in ultrasonic bath for 5 min in ethanol and dried with nitrogen gas. Just prior to deposition, the substrate surface was further cleaned and partially chemically activated by plasma etching (18 sccm Ar, 2 sccm O₂) for 5 min, PT-100 Plasma Etch.

The first 100 nm thick Cr adhesion layer deposited on the stainless steel substrates were conducted by e-beem evaporation at a rate of 1.5 nm/s in a vacuum below $5 \times 10^{-6}$ torr. This was directly followed by resistively evaporated Ag to the appropriate thickness corresponding to the bond designs, at the rate of 0.4 to 1 nm/s without breaking the vacuum.

The Ag films were utilised as either adhesion layers to inkjet Ag or as a diffusion layers for TLP bonding. For the use as a diffusion layer, the films was annealed to increase grain growth at 400 °C for 15, 30, 60 and 200 min in order to find the proper process parameters for for a TLP bond in air environment with a Entech MF 2/15 high temperature oven.

Tape adhesion tests were done on the deposited surfaces using Scotch 3M clear tape. The tape was first mounted on the surface and then pulled away. To pass the test, the tape must then be free of deposited material, as determined by visual inspection.

4.1.2 Inkjet Ag films

Inkjet Ag layers were created with inkjet printing on the evaporated Ag films. The printing, curing, sintering and grain growth annealing were done by 4 different methods to evaluate if µm-sized grains, a layer thickness of more than 3.6 µm and a uniform surface roughness could be produced. A total of 7 layers were printed, either in one or two sequences. After each sequence, a curing step was done, at 130°C for 15 min, to evaporate solvents and bind the ink together. When all the layers had been deposited and cured, heat treatments were done to burn off polymers, sinter the particles, and grow the grains. The methods are denoted A, B, C and D and the process order is described in table 3. For method A, B and C, the heat treatment was done by first heating samples to 150°C for 1 h followed by 190°C for 24 h. For method B, C and D, an annealing step was added to further grow
Table 3: Description of process order for method A, B, C and D.

<table>
<thead>
<tr>
<th>Step</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Print 4 layers</td>
<td>Print 4 layers</td>
<td>Print 4 layers</td>
<td>Print 7 layers</td>
</tr>
<tr>
<td>2.</td>
<td>Cure ink</td>
<td>Cure ink</td>
<td>Cure ink</td>
<td>Cure ink</td>
</tr>
<tr>
<td>3.</td>
<td>Print 3 layers</td>
<td>Print 3 layers</td>
<td>Print 3 layers</td>
<td>Annealing 450°C</td>
</tr>
<tr>
<td>4.</td>
<td>Cure ink</td>
<td>Cure ink</td>
<td>Cure ink</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Sinter</td>
<td>Sinter</td>
<td>Sinter</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Annealing 240°C</td>
<td>Annealing 450°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

the grains. It is done for 5 h and at 240°C for method B and 450°C for method C and D.

4.1.3 In films

The stainless steel substrates were first cleaned and plasma etched as described in 4.1.1. A Cr adhesion layer was first deposited with e-beem at 1.5 nm/s directly followed by an In deposition using e-beem at the rate of 0.4 nm/s. This was followed by a resistively evaporated Ag layer at a rate of 0.4 to 1 nm/s. All depositions were done below $5 \times 10^{-6}$ torr without breaking the vacuum. Also, to lower the contamination of In into the PVD equipment, sides and shutters were covered in aluminium foil. These samples were then stored in a N$_2$ purged $10^{-3}$ bar vacuum oven from Salvis Lab to hinder oxidation of In, and prolong the storage life of the films.

4.1.4 Electroplating

Stainless steel 304 grade substrates were sent for electrodeposition of a 3 $\mu$m thick Ag film to a commercial vendor, Fintlings ytbehandlingsfabrik AB, Sweden. In their plating procedure, a Ni adhesion layer was used to adhere the Ag to the substrate. The annealing of these films were done as described in 4.1.1.

Electroplating of Ni as an adhesion promoter for evaporations was done in-house. It was done with a Woods Ni strike solution, and used a current controlled setup of 0.21 A cm$^{-2}$.

4.1.5 Bonding

The TLP bonding was preformed in either in a rapid heating solder oven, Protoflow S LPKF, or in a $10^{-3}$ bar vacuum oven, VO-400 Memmert. The substrates were held together
Figure 7: (a) Pressure disk spring fixture (1.) The metal housing for the pressure disk springs and cylinder. (2.) The pressure distribution plates. The sample is located between these plates. (b) Clamp fixture with corresponding clamp. The sample is located between the to fixture plates.

by metal fixtures, where the contact pressure was achieved either with a pressure disk spring fixture, figure 7(a) or by a clamping fixture, figure 7(b). The disk springs were mounted in a metal housing, giving a well defined pressure of 0.4 MPa on a 6 mm radius cylinder forcing down on a 5 mm thick pressure distribution plate. The clamp fixture had an undefined, but higher pressure. Polyimide films were placed between the fixture parts and the substrates to further even out pressure.

The bonding in the solder oven was done in air-environment with a 5 min ramp up to 195°C, with a 5 min dwell. This was followed by a cooling step, where the oven hatch opens and fans cool down the fixtures to room temperatures within 5 min.

For bonding in the vaccum oven, the oven was preheated to 160°C before the fixtures were loaded into the oven. This was immediately followed by pumping down a $10^{-3}$ bar vacuum and raising the temperature to 180°C. The fixtures were covered in aluminium foil to allow good thermal connectivity to the heated oven base plate. After 60 min, heating was turned off and the oven was allowed to cool down to 100°C before removing the fixture.

After bonding, samples were removed from the fixtures and moved to a UPF-400 Memmert oven for the post bonding annealing step. The annealing was done at 175°C between 48 h and 144h in ambient atmosphere.
Figure 8: (a) PCM filling fixture with weight rod (1.) on top. Underneath there are vertical inlet and outlet channels (2.) on the top part (3.) of the fixture. A bottom metal plate (4.) holds the sample in place. (b) Cross section of the fixture with mounted sample. Mannitol crystals are placed in the vertical inlet channel and flows down into the cavity when melted.

4.2 Actuator

4.2.1 Mannitol filling

Mannitol was filled using a fixture, figure 8(a), designed and manufactured with regards to difficulties seen in filling high temperature PCM materials into actuator cavities. Samples with cavities are placed on a bottom metal plate with screws holding the sample in place. A top part of the fixture with two vertical channels placed above the inlet and outlet of the fluid channel leading to the actuator cavity. At the fixture and sample interface, vecron sealing rings keep the fixture leak proof.

Before filling, fine mannitol powder is melted and recrystallised in a vacuum oven, Salvis Lab, at $10^{-3}$ bar over night to drive out moisture and yield larger crystals. With this, air trapped in the powder can be drawn out and thereby lessens the risk of air cavities in actuator.

Filling starts by mounting the actuator into the fixture and adding about 0.5 cm$^3$ of recrystallised mannitol grains to the vertical inlet channel of the fixture, figure 8(b), and mounting the weight rod on top. The fixture is then put in a vacuum oven which is pumped down to $10^{-3}$ bar to let trapped air out. After 1 h, the temperature is raised to 190°C. This causes the mannitol to melt, and with the help of gravity and the weight rod, mannitol
flows through the cavity and out through the outlet vertical channel in the fixture. As the temperature is lowered to room temperature, trapped mannitol solidifies inside the cavity.

4.2.2 Mannitol encapsulation

As the temperatures of $Ag-In$ TLP bonding is in the same region as the phase transformation of mannitol, encapsulation of mannitol with this method can cause the mannitol to melt during bonding. Therefore, to not risk breaking the actuator during bonding, the actuators inlet and outlet filling holes were closed off by epoxy gluing the back side stencil. The glue was a 2-component Power Epoxy from Loctite.

Tests of encapsulating mannitol with a TLP joint was however done on other samples. Bond design $EL$-$Thick$ was used, with the cavity stencil being the top $Ag$ substrate and the back side stencil being the bottom $In$ substrate. To deal with melted mannitol leaking out to the bond area from the filling inlet and outlet holes, these were plugged with a small amount of epoxy glue that was allowed to cure while both the back side and actuator stencils were mounted in the bonding fixture.

4.3 Evaluation

4.3.1 Tape adhesion test

Tape adhesion tests were done on the deposited films using Scotch 3M clear tape. The tape was first mounted on the surface and then pulled away. To pass the test, the tape must then be free of deposited material, as determined by visual inspection.

4.3.2 Tensile strength test

The bond strength was evaluated with tensile strength tests. The bonded samples were glued at centre of aluminium studs having a cross section area of $2.25 \text{ cm}^2$. The glue was a 2-component Power Epoxy from Loctite. The total cross section of the bond area was $4.5 \text{ cm}^2$. The studs were then connected to a metal loop with several twined steel wires clamped to a tensile strength testing machine, AGS-X from Shimadzu. The straining speed was set to $1 \text{ mm/min}$.

As the test setup contains several joints and materials, the test only evaluates the ultimate tensile strength of the weakest component in the set up. The main restriction is the epoxy joint, that has a ultimate tensile strength of between $12$ and $30 \text{ MPa}$.
The standard conditions for the measured samples consist of annealing the Ag diffusion layer, bonding with a pressure disk fixture and using vacuum oven. The post bond annealing is set for 2 days.

### 4.3.3 Pressure test

Bonded samples with 1 mm radius cavities were used to evaluated the leak resistance and pressure tolerance. Samples were fitted in a fixture that provided support to fluid connectors while in the same time not tightening the area underneath the cavity. This setup allowed the substrate to deform around the cavity and cause strain on the TLP joint. Water pressure was provided with a binary HPLC 5100 Waters pump running at 100 µl/min and pressure was measured with a pressure sensor, Keller PA-11.

Three samples were used for pressure test, E-2D, E-6D and E-NG. All samples use bond design *EL-Thick*. E-2D follow the standard bonding conditions; annealing the Ag diffusion layer, bonding with a pressure disk fixture and using the vacuum oven. The post bond annealing is set for 2 days. E-6D use the same bonding conditions, except for the post bond annealing that is done for 6 days instead of 2, as for E-2D. E-NG is bonded without annealing the Ag diffusion layer prior to bonding.

### 4.3.4 Actuator measurements

The actuator was mounted in a fixture with resistive heating wires and water cooling. The fixture hinders the actuator from bending and bulking during heating. The expansion of the membrane was measured with a laser displacement sensor located 3 cm above the fixture and the fixture temperature was monitored with a K-type thermocouple. For each test run, temperature was slowly raised by increasing the voltage of the heating wire by 1 V/min reaching a temperature of 180°C corresponding to a rate of 32°C/min. This was followed by lowering the voltage at the same rate back to room temperature. The range and temperature data was recorded throughout the measurements. 4 measurements were done on the actuator membrane and 2 measurements were done on the sides of the membrane for reference. The laser point location, while measuring on the membrane, was about 0.5 mm away from the middle on the 2 mm diameter membrane, and right next to the membrane, while measuring the reference.
4.4 Imaging

4.4.1 Scanning electron microscope

Scanning electron microscope, SEM, imaging was done with 4 different instruments. ESEM XL30 from FEI, SEM LEO 1550 from Zeiss, FIB-SEM DB235 from Strata and SEM Merlin from Zeiss. FIB etching was done with a Ga-beam and depositions of Pt film was used to protect sample area. The SEM Merlin was also fitted with an energy dispersive spectrometer, EDS, which was used for element detection on fracture surfaces.

4.4.2 Optical profilometer

Height profiles was done with a NT1100 WYKO operating at VSI mode. The threshold was set to 3%.

4.4.3 Light optical microscope

The light optical microscope, LOM, was from Olympus AX70.

4.4.4 X-ray inspection station

The X-ray inspection station was from Nikon, model XT V 130.
5 Results

5.1 TLP

5.1.1 Film deposition of In

Cr/In/Ag films were deposited successfully for all thicknesses and bond designs and showed good adhesion, as confirmed with tape adhesion tests. The surfaces of the In films, for bond designs INK-Cr/CrNi, EL-Thick, PVD-Thick and PVD-Thin, had agglomerated grain formations. Between these formations, a thinner film was observed. Figure 9(a) and 9(b) shows In films, of thickness 1000 nm and 1400 nm resp. The area ratio between grain formation and thin film changed as thickness increased, with the 1400 nm In films almost completely covered with grain formations, and the 1000 nm In films having more of the thin film areas. For 300 nm In films, bond design PVD-Thin, the grain formations are only seen as scattered islands and the thin film type surface dominated, see the border areas of figure 10(a). To further study the In surface, FIB etching was done to give side profiles, on the 300 nm In film. The surface before FIB etching is shown in figure 10(a) and the side profile of the film, etch out by FIB, is shown in figure 10(b). Whiskers are also seen on the 300 nm In films, looking like long rods.

The In film for bond design PVD-2Diff, seen in figure 11(a) and 11(b) looks different.
Figure 10: Bottom substrate for bond design *PVD-Thin*, In 300 nm followed by 70 nm Ag. Wiskers, grain formations and thinner film regions are seen in (a). The line, marked FIB etch cut in (a), shows the etched side profile of the substrate in (b). Images captured with FIB-SEM, (a) (SED, 10 kV) and (b) (TLD-S, 10 kV).

Figure 11: (a) Bottom substrate for bond design *PVD-2Diff*, Annealed 800 nm Ag, followed by deposition of 600 nm In and 150 nm Ag. (b) Close-up of the same surface, grain formation with pores. Images captures with SEM LEO (InLens, 10 kV)
than for the other In films. The grain formations are smaller and porous channels are
seen around them. The visible colour of the film was much darker. The film was not
able to create a joint, with a corresponding Ag top substrate. Because of this, a melting
test was preformed under microscope, but no melting was seen. This indicates that the
In solder layer has diffused into the Ag diffusion layer during evaporation to an extent so
that the content of In and AgIn phases on the surface is too low. It therefore follows
the assumptions of how much meltable phases that can be present in the bottom substrate
prior to bonding, as seen in table 2.

5.1.2 Film deposition of Ag

Both the PVD films, figure 12(a), and the electroplated films, figure 12(b), had a very
uniform surface and did not show any defects. The grain size of the Ag PVD films were
about 100 nm and large formations are seen on the electroplated surface. The visual look
of both electroplated and evaporated films were bright and shiny. Most of the Ag films
deposited by PVD resulted in adherent films, confirmed by tape adhesion tests, and was
used for bonding. However, some evaporation trials resulted in poor adhesion, all having
spherical shaped Ag hills with heights of tens of µm, scattered over the surface. An example
of this can be seen in figure 13(b).

The inkjet Ag films deposited on the evaporated Cr – Ag adhesion layer adhered good, ac-
ccording to tape tests. However, the surfaces suffered from uneven topography. Line defects
could be related to the inkjet deposition, where droplet ejection periodically stopped, resulting in locally thinner Ag film. Along the borders of the samples, more Ag was localised. This resulted in a height difference between the structured edges and the flat middle area. This height difference varied over different samples and locations but could in some parts be as high as 6 µm.

5.1.3 Ag grain growth

The annealing methods of inkjet Ag, table 3, showed differences, in figure 14(a) and 14(b), the annealing of method A at 190°C and method B at 240°C did not result in grain growth. When a temperature of 450 °C was used, as in method C and D, Ag grains of around 1 to 6 µm were formed. The surfaces of method C and D were not uniform and voids were present in the films. For method C, figure 15(a), the void formations end with exposing more Ag grains further down in the layer. For method D, figure 15(b), the voids expose the substrate and the underlying Cr adhesion film.

The annealing of evaporated and electroplated Ag films, done at 400°C, showed that after 5 min, the films started to change visual appearance from bright shiny silver to dull grey. Inspection with LOM indicated that this transformation had occurred through out the
entire film after 15 min. For Ag 800 nm and 2500 nm PVD thin films, annealed at 15 min, grains larger than 1 \( \mu m \) are seen in figure 17(a) and 17(b). The topography is different between the two films. On the 800 nm Ag films in figure 16(a), hot rolling marks, from the manufacturer of the stainless steel substrates, can be seen as line formations on the Ag film. This effect is however not seen on the 2500 nm Ag films. Instead Ag grains have risen on top of the surface as hills with voids underneath as shown in figure 17(b). The height of these hills is about 2 \( \mu m \), as determined by optical profilometer measurements. This is not seen on the 800 nm Ag films, figure 17(b). The average surface roughness, \( R_a \), of the 2500 nm Ag film was 233 nm, determined by optical profilometer. Figures 18(a) and 18(b) show the surfaces of electrodeposited films, for 15 and 200 min annealing, respectively. The grains tend to become more smooth and rise up on the surface when annealing for longer times. The grain boundaries that start to evolve in the 15 min annealed film show close resemblance to the fade formations seen in the unannealed film, figure 12(b).

5.1.4 Bond interfaces and bond fracture

Bond design \textit{INK-Cr}, inkjet films, was successful in creating a joint between the bottom \textit{In} substrate and the top \textit{Ag} substrate. However, the bond area was only partial, roughly estimated to be 30%. This can be seen as a black surface in figure 19(b), showing the bottom \textit{In} substrate of a bonded sample broken apart. Much this black area was located on the sample borders and in the structured edges in the middle. This corresponds to some extent to the thicker \textit{Ag} bonder defects seen on the inkjet \textit{Ag} samples in figure 13(a).
Figure 15: (a) Inkjet Ag method C, annealing at 450°C. Large grains of several μm are formed and voids end up in more Ag grains. (b) Inkjet Ag method D, Annealing at 450°C but with less heating process steps. Large grains of μm-size are formed and voids expose the substrate. Images captured with E-SEM (SE, 10 kV).

Figure 16: Evaporated Ag film, 800 nm annealed for 15 min at 400°C, side view. Line formations are seen going vertically over the image. (b) Evaporated Ag film, 2500 nm annealed for 15 min at 400°C, side view. Images captured with SEM Merlin (HE-SE2, 15 kV).
Figure 17: (a) Ag thin film, 800 nm annealed for 15 min at 400°C, close up. (b) Ag thin film, 2500 nm annealed for 15 min at 400°C, close up. Hill formation with void underneath. Images captured with SEM Merlin (HE-SE2, 15 kV).

Figure 18: (a) Electroplated 3 µm, annealed at 400°C for (a) 15 min and (b) 200 min. Grains rise up and become smooth as the annealing time increases. Images captured with SEM Leo (InLens, 10 kV).
The bond fracture was primarily between the \textit{Cr} adhesion layer and the top stainless steel substrate. This was confirmed with EDS analysis, detecting \textit{Cr} on the black area, marked as (2.), in both figure 19(a) and 19(b). The interface between (1.) and (2.) in figure 19(b) shows the complex bonding situation between \textit{In} and \textit{Ag}. In the figure, some of parts are connected and others have gaps or void formations. The cross section of bond design \textit{INK-Cr}, figure 20(a), was captured about 1 mm from the edge of the sample. At this location, the bond layer seems largely uniform with some minor void formation. The bond layer is about 11 \(\mu\)m thick.

For \textit{PVD-Thick}, bonding in scattered regions had occurred to a degree where fracture had happened between the bond film and the bottom \textit{In} substrate, as shown by figure 21(b), where a large circular area is seen exposing the substrate. More frequent, smaller areas, are seen throughout the sample, and have a size and shape in close resemblance to the hill like structures seen in the annealed 2500 nm \textit{Ag} films, as seen in figure 17(b). The more general fracture interface, that dominate the surface as seen in both figure 21(a) and 21(b), is rough with some thin void formations seen next to the fully bonded regions. It is not confirmed that this main surface is bonded between the two substrates. The cross section of bond design \textit{PVD-Thick}, figure 20(b), is captured about 6 mm from the edge of the sample. In the 7 \(\mu\)m thick bond layer a lot of voids were noticed.

Joints were also successfully created with design \textit{EL-Thick}. Fractures was observed at both substrate interfaces as seen by figure 22(b). Figure 22(a) shows a more complex fracture area where large, grey regions, look unbonded and darker areas show fracture between the bond layer and the bottom \textit{In} film. Along some of the edges of these regions, the film seem to hang over the grey areas. This indicates gaps and voids between the \textit{In} and \textit{Ag} films and is better seen in figure 23(a). Fracture areas also create a border around the actuator cavity, as seen in figure 23(b).

### 5.2 Tensile strength test

Table 4 describes the ultimate tensile strength of TLP joints by different bond designs and different bonding conditions. Bond design \textit{El-Thick} had the highest ultimate tensile strength, with the tensile test epoxy glue joint failing. Bond design \textit{INK-Cr} and \textit{INK-CrNi} yielded the lowest ultimate tensile strength. Bond designs \textit{PVD-Thin}, \textit{PVD-2Diff} and \textit{EL-InLow} were not evaluated by tensile strength tests. Design \textit{PVD-Thin} was too weak for preparing test samples, design \textit{PVD-2Diff} did not bond and design \textit{EL-InLow} was not tested for tensile strength.
Figure 19: Fractured sample of INK-Cr. Picture (a) shows the bottom In substrate with markers. The grey area (1.) is unbonded In and the black area (2.) is bonded Ag, fractured between the Cr adhesion layer and substrate. The brown area (3.) is partially bonded In fractured between In and Ag. The fracture interface (b) shows bonded interfaces and voids between surface (1.) and (2.). Image captured with SEM merlin (HE-SE2, 10 kV), sideways in direction with pointer marked View in (a).

Figure 20: (a) Cross section of bond design INK-Cr, about 2 mm from sample edge. (b) Cross section of bond design PVD-Thick, about 6 mm from sample edge. Voids are seen in the middle. Images captured with SEM Leo, (a) (SE2, 10 kV) and (b) (InLens, 5 kV).
Figure 21: Fractured sample of bond design *PVD-Thick*. (a) Side view of top Ag substrate. (b) Top view of corresponding area on bottom In substrate. Marker (1.) shows areas where the fracture interface is between the bond film and the bottom substrate. The main fracture area is in the In/Ag interface. Some void formations are seen (2.) in level with this fracture interface. Images captured with SEM Merlin (HE-SE2, 15 kV).

Figure 22: Fractured sample of bond design *EL-Thick*. (a) shows the top Ag substrate. Fracture area between bond layer and bottom In substrate is seen as a dark area (1.). This layer has at some places an overhang (4.) with hole-like structures underneath. The grey area does not look bonded. (b) shows the bottom In layer at a different location. Here, fracture have occurred between the bond layer and the top Ag substrate (2.). It also shows a region (3.) where scattered bonding and fracture is between the bottom In substrate and the bond layer. Images captured with SEM Leo (InLens, 10 kV).
Figure 23: Fractured sample of bond design *EL-Thick* showing the top *Ag* substrate. (a) Fracture area between bond layer and bottom *In* substrate with visible void formation underneath. (b) shows the actuator cavity, with unreacted *Ag* at the bottom. It also shows the bond area that have been in contact with the bottom *In* substrate. A border of fracture between the bond layer and the bottom *In* substrate is seen along the cavity. Images captured with SEM Leo (InLens, 10 kV).

Table 4: Ultimate tensile strengths for TLP joints. Sample conditions, marked by (*), are, if not otherwise stated, *Ag* grain growth annealing at 400°C for 15 min, vacuum oven at 180°C for 60 min, pressure disk fixture, 2 days post-bond annealing.

<table>
<thead>
<tr>
<th>Bond design</th>
<th>Conditions</th>
<th>Force (N)</th>
<th>UTS (MPa)</th>
<th>Failure by</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL-Thick</td>
<td>6 d post bond annealing</td>
<td>946.5</td>
<td>2.53</td>
<td>epoxy</td>
</tr>
<tr>
<td>EL-Thick</td>
<td>*</td>
<td>763.9</td>
<td>2.04</td>
<td>epoxy</td>
</tr>
<tr>
<td>EL-Thick</td>
<td>No <em>Ag</em> grain annealing</td>
<td>304.7</td>
<td>0.81</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>6 d post bond annealing</td>
<td>643.8</td>
<td>1.72</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>Clamp fixture</td>
<td>799.9</td>
<td>2.13</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>Clamp fixture</td>
<td>742.7</td>
<td>1.98</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>*</td>
<td>600.0</td>
<td>1.60</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>*</td>
<td>519.8</td>
<td>1.39</td>
<td>TLP</td>
</tr>
<tr>
<td>PVD-Thick</td>
<td>*</td>
<td>370.6</td>
<td>0.99</td>
<td>TLP</td>
</tr>
<tr>
<td>INK-CrNi</td>
<td>Solder oven, Ink method C</td>
<td>332.0</td>
<td>0.89</td>
<td>epoxy</td>
</tr>
<tr>
<td>INK-CrNi</td>
<td>Ink method C</td>
<td>473.8</td>
<td>1.26</td>
<td>TLP</td>
</tr>
<tr>
<td>INK-Cr</td>
<td>Solder oven, Ink method C</td>
<td>214.5</td>
<td>0.57</td>
<td>epoxy</td>
</tr>
<tr>
<td>INK-Cr</td>
<td>Ink method C</td>
<td>190.3</td>
<td>0.51</td>
<td>epoxy</td>
</tr>
</tbody>
</table>
5.3 Pressure test

The maximum pressure for samples E-6D, E-2D and E-NG were 30, 24 and 19 bar respectively, figure 24. The pressure load at the rim of the cavities was 1487, 1203 and 909 N/m, respectively.

5.4 Mannitol filling and encapsulation

The filling procedure worked as intended, with the weight rod pressing down liquid mannitol into the cavity inlet hole. After filling and fixture removal, solid mannitol was found in both the vertical outlet channel of the fixture and on top of the cavity outlet hole. X-ray images, figure 25(a) and 25(b), of the actuator cavities indicates that the filling is uniform, and that no large bubbles or defects are present. The membranes deflected inwards.

Tests done to encapsulate mannitol by bonding the back side stencil with a TLP joint resulted in the back side stencil being bonded and the membrane still deflecting inwards after bonding. Trials to heat the sample to 180°C resulted in a flattening of membrane
surface followed by returning to an inwards deflection when cooled, as determined by visual inspection. This indicates that the TLP bonding and mannitol expansion did not break the encapsulating structure.

5.5 Actuator

The actuator deflection measurements are seen in figure 26 and show a deflection of 20 to 25 µm at 180°C as compared to the reference measurements. It can also be visually seen that the membrane deflects inwards in room temperature, and is flat at 180°C.
6 Discussion

6.1 TLP joints

The TLP joints have a theoretical mechanical ultimate strength close to that of Ag, 170 MPa, but bond strengths determined by tensile strength tests were only between 0.51 and 2.53 MPa. To explain this, several factors that compromise full bonding has to be regarded.

6.1.1 Topography and surface roughness

Inkjet bond designs INK-Cr and INK-CrNi had a contact area of only 30%, and the uneven topography of the inkjet Ag film, with thicker regions along borders, can be related to less area being bonded. The bond strengths of bond design INK-Cr and INK-CrNi is low, at 0.51-0.57 MPa and 0.89-1.26 MPa, respectively. The cross section, figure 20(a), captured 1 mm from the substrate border, showed a bond layer thickness of 11 µm, about twice the thickness of the deposited films. This could be due to the thicker inkjet border.

For bond design PVD-thin, a 300 nm In meltalbe layer has to fill out a joint area where the hot rolling marks of the substrates is still visible, figure 16(a). As the stainless steel...
has a peak to valley height of 1.6 \( \mu \text{m} \), gap formations could be likely. Joints created with bond design \textit{PVD-thin} were weak and broke during sample preparation.

On bond design \textit{PVD-Thick}, the 2 \( \mu \text{m} \) hill formations, figure 17(b), are thicker than the 1 \( \mu \text{m} \) solder layer. This could be an explanation for the voids seen in the cross section, figure 20(b).

The annealed electrodeposited Ag films for bond design \textit{EL-Thick} did not have any ridge or hill formations, when inspected in SEM, and the surface roughness was composed of the rising effect of Ag grains, as seen by figure 18(a). No measurements were done with optical profilometer, but the surface is believed to be the flattest of all Ag substrates. Therefore, with a meltable In layer of 1000 nm, it could be the bond design with the least void formation in the bond layer. Bond design \textit{EL-Thick} has resulted in a slightly higher tensile strength than \textit{PVD-Thick}, though still having the same In thickness. Comparable samples, with a 6 days post bonding annealing, had a bond strength of 1.73 MPa for bond design \textit{PVD-Thick} and 2.53 MPa for \textit{EL-Thick}.

### 6.1.2 Bonding pressure and distribution

Another important factor for the bond area is the magnitude and distribution of contact pressure at bonding. The two different types of fixtures, clamp and pressure disk spring fixture, yielded different pressure distribution profiles. The well defined disk spring pressure of 0.4 MPa pressuring down on the cylinder and distribution plate is enough to create bonding in the centre of the substrates underneath the cylinder. Along the edges of the substrates, large areas are not bonded. This should be related to the pressure distribution plate deflecting. For the clamp fixture, pressure distribution is better and bonding occurs over a much larger area of the substrate, sometimes covering the entire substrate. This can be related to the clamp delivering pressure over a 10 mm radius onto a 10 mm thick fixture block. However, this fixture yields irregular results as the clamp is difficult to align which frequently causes pressure to be disturbed to one half of the bonding substrates. Comparable tensile strength tests of \textit{PVD-Thick} samples bonded with clamp fixtures are higher, at 2.13 and 1.98 MPa, and samples bonded with pressure disk spring fixtures are lower, at 1.60 and 1.39 MPa.

### 6.1.3 Fractures

Fractures in the In/Ag material, or bond layer, are difficult to evaluate. As there is no clear change in materials between the fracture interface, fracture surfaces look similar. For example, on figure 21(a) and 21(b), one sees the corresponding top and bottom substrate surfaces of a fractured \textit{PVD-Thick} sample. The surface, around the circular geometry, are
in the \( \text{In}/\text{Ag} \) interface. The surface topography on both sides seem to overlap and fit onto each other, suggesting that the area is bonded. However, one can not confirm if this bond layer is uniform throughout the thickness of the joint or if a void or gap interface is present, following parallel to the fracture surfaces. If such interface is present, it would affect the joint strength significantly.

The most apparent fractures have been seen at the adhesion layer interfaces. On bond design \( \text{INK-Cr} \), figure 19(b), the main fracture is between the \( \text{Cr} \) adhesion layer and the stainless steel, on the top substrate. On bond design \( \text{PVD-Thick} \), figure 21(b), fracture is seen between the joint materials and the bottom substrate. On bond design \( \text{EL-Thick} \), fractures occur between the joint materials and substrate, at both the top and bottom substrates. For both \( \text{PVD-Thick} \) and \( \text{EL-Thick} \), it is not confirmed if these fractures are between the \( \text{Ag/In} \) alloy and the adhesion layers or between the adhesion layers and stainless steel.

\[ \text{6.1.4 Leak resistance} \]

The pressure tests show that the TLP joint can sustain pressure to a 30 bar threshold before leakage occurs. It also suggests that annealing for grain growth of the Ag diffusion layer has a positive effect on bond strength and leakage resistance as the non annealed sample E-NG scored the lowest, 18 bars. This is further indicated by the tensile strength tests were a sample of bond designs \( \text{EL-Thick} \), that had grain growth annealing, held without breaking at 2.53 MPa and a sample without annealing but of otherwise the same conditions fractured at 0.81 MPa.

\[ \text{6.1.5 Bond layer} \]

In order to yield the high temperature stable solid solution of \( \text{In} \) in \( \text{Ag} \), the composition of \( \text{In} \) must be less than 21% (wt.). The theoretical calculations of thicknesses for this content in the final joints are in one dimension and based on a complete diffusion between layers at the interface. In reality, the defects seen in joints might affect the diffusion and formation of solid solution of \( \text{In} \) in \( \text{Ag} \). The joint material has not been analysed to confirm the solid solution in the bond layers. Longer post bond annealing times were however done, and showed a slight increase in bond strength for a longer annealing. The ultimate tensile strength of 6 day annealing was 2.53 MPa and 1.72 MPa for \( \text{EL-Thick} \) and \( \text{PVD-Thick} \), respectively. For 2 days annealing of comparable samples, the strengths were 2.04 MPa and 1.60 MPa, respectively.

Not much work has been focused on evaluating the bonding temperature profiles and bonding environment. Samples were bonded primarily with the vacuum oven, with only a
few samples bonded in the solder oven. Of the few samples made, there was no difference seen in bonding under vacuum or air. Tensile strength tests of comparable samples gave higher results with solder oven for bond design INK-Cr but lower results for INK-CrNi. Due to the fast diffusion of In into Ag, it was speculated that the solder oven’s rapid heating of the In solder layer would shortened the time for solid state diffusion of In into Ag before melting and bonding. It thereby would provide more In-rich melt available to flow in the bond interface. This was mainly a concern for bond design PVD-2Diff, with an extra Ag diffusion layer on the same substrate as the In solder layer, as shown in figure 5(b). However, the diffusion of In into the Ag diffusion layer had already happen during the evaporation to an extent where the In solder layer could not melt, thus making bond design PVD-2Diff unbondable.

6.1.6 Bond design recommendations

The studied TLP joints are not optimised and problems that need to be solved include voids, a small bonding area and adhesion problems to the stainless steel. The problems were well demonstrated on the tensile strength tests, as the joints strengths were below the expected properties of Ag. However, these joints are sufficient for the mannitol actuator. To improve bond strength, three topics should result in better bonds:

- Increase the thickness of the In solder layer or lower the surface roughness on the Ag diffusion layer. A thicker In solder layer will demand a thicker Ag diffusion layer and will therefore inflict with the creation of thin joints. With a lower degree of surface roughness, the same total joint thicknesses used in this work can be kept or be even thinner.
- Develop a better bonding fixture that can distribute pressure evenly over the substrates in repeatable manner.
- Improve the adhesion layer.

Both bond design EL-Thick and PVD-Thick are interesting routes for continued development of the joint, to yield stronger tensile strengths. An increase in total bond layer thickness, hence a thicker meltable layer, should be a straightforward approach into reaching higher bond strengths. Also, if Ag film deposited by evaporation is further explored, it would be of great value to find a method that does not create the 2 µm hill formations, figure 17(b). Modifications of the adhesion layers could include reducing thicknesses and changing the adhesion material. Also, a more extensive activation process of the stainless steel can be beneficial, utilising a longer etch times and a higher concentration of O₂. Another approach is to pursue adhesion through metal bonds, using plasma etching and evaporation in one step without breaking vacuum. Inkjet is not a recommended method of depositing the Ag film due to its topographical issues. Results from bond design PVD-2Diff
indicated that using Ag diffusion layers on both substrates is troublesome at these thin joint thicknesses, and is not recommended. Electroplating showed to be the best alternative to create the Ag layers. The joint of bond design EL-\textit{Thick} demonstrates that \textit{In} – \textit{Ag} TLP bonding can be done on stainless steel while in the same time being 4.35 µm thin. If joint thickness is increased slightly, it is believed that a stronger joint can be produced.

6.2 Actuator

A micro actuator was successfully fabricated and showed a confirmed deflection of the membrane at temperatures up to 180°C.

The deflection appears to be somewhat linear with temperature. This is not consistent with the sudden phase change transformation expected at 167.8°C. Instead it suggests a gradual expansion and melting of the material. In a theoretical sense, the measured 25 µm deflection implies that the membrane has yielded as the deflection is higher than the maximum limit of 14 µm. It further suggests that mannitol has a volumetric expansion of roughly 22%. In reality, it is more likely that the high deflection is associated with errors in the measurement method. The actuator structure might expand or bend in a way that the reference measurements can not compensate for. Also, the laser displacement meter had difficulties measuring over the membrane and the laser point was moved from the centre point of the membrane. When the laser point was directed at the centre point of the membrane, local irregular movements of the membrane resulted in that the laser was diverted away. Therefore, the laser point was moved away from the membrane centre where the measurements were reproducible.

7 Conclusion

\textit{In} – \textit{Ag} TLP bonding have been demonstrated for stainless steel high temperature actuators and microfluidic systems. A 4.35 µm thick joint had an ultimate tensile strength of 2.53 MPa and could sustain pressures up to 30 bars. Joining stainless steel stencils with \textit{In} – \textit{Ag} TLP bonding, filling of liquid mannitol under vacuum followed by encapsulation demonstrates a way of fabricating high temperature micro actuators.

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8 Appendix

8.1 Membrane calculation

The stress is highest at the edge of the membrane where radial stresses dominate over tangential stresses. The maximum stress over the membrane is described by

$$\sigma_r = \frac{3}{4} \frac{Pa^2}{h^2},$$

where P is the pressure over the membrane, a is the total radius and h is the membrane thickness [29]. The pressure can be calculated according to

$$P = \frac{16}{3(1 - \mu^2)} \frac{Eh^3}{a^4} y + \frac{7 - \mu}{3(1 - \mu)} \frac{Eh}{a^4} y^3,$$

where E is the young’s modulus, y is the membrane deflection and \(\mu\) is the poisson ratio [29]. For a 10 \(\mu\)m thick stainless steel grade 301 membrane with a radius of 1 mm, a yield strength of 275 MPa, young’s modulus of 193 GPa and a poisson ratio of 0.3, the maximum deflection that the membrane can withstand without exceeding the yield strength is 14 \(\mu\)m.

The volume of a spherical cap is

$$V = \frac{\pi y}{6} (3a^2 + y^2),$$

where a is the maximum cap radius and y is the height of the cap. Using this as a model for the membrane, a 10\% change of the 0.149 \(\mu\)L cavity volume equals 0.0149 \(\mu\)L which with a set to 1 mm equals a cap height 9 \(\mu\)m. This cap height correspond to the deflection of the membrane as the mannitol in the cavity transforms.
8.2 Diffusion

To evaluate diffusion times for grain boundary diffusion of In in Ag, the temperature dependent diffusion coefficient is first calculated for 25°C and 180°C according to

\[ D = D_0 \exp \left( \frac{-Q_d}{k_bT} \right) , \]

where \( D_0 \) is the temperature independent diffusion coefficient for grain boundary diffusion of In into Ag is 2.4 e-12 m²s⁻¹ and \( Q_d \), the activation energy is 0.42 eV. \( k_b \) is the gas constant, 8.1617 e⁻⁵ eV K⁻¹, and T is temperature in kelvin. The solution to fick’s second law for constant surface composition is

\[ \frac{C_x - C_0}{C_s - C_0} = 1 - erf \left( \frac{x}{2\sqrtDt} \right) , \]

where \( C_x \) is the solute concentration at length x, \( C_0 \) is the solute concentration in the material before diffusion, \( C_s \) is the surface solute concentration and t is time. With \( C_0 \) set to 0 and \( C_s \) set to 1, \( C_x \) is calculated for two cases with either \( D \) calculated for 25°C or 180°C. The diffusion time, t, is increased with 24 h for each calculation.

References


