Physico-chemical interactions at multi-material interfaces

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Physico-chemical interactions at multi-material interfaces

PROEFSCHRIFT

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1 Introduction

In the application of materials, it is clear that a single material not always can solve a problem or generate a solution that is satisfactory for all users. Of course, single materials provide interesting properties, such as electro-optically active quantum dots (1), strong (2-4) and surface active graphene (5, 6), thermal conducting carbon nano tubes (7) or bio-compatible gold nano-wires (8). In order to make use of the advantageous properties of any single material, it generally must be connected to at least one other material, which results in an interface between the two materials. Such an interface offers many new challenges to investigate, and usually a specific model system and measurement technique needs to be developed to study a particular property of this interface.

The research presented in this thesis was undertaken to clarify interfacial challenges encountered in research and development projects within Philips Group Innovation, of which Philips Research is a part. Philips Research executes projects for lifestyle, healthcare and lighting applications, as well as applications for selected external partners. This results in a wide range of challenges in interfacial science, with different types of problems to solve. In a number of cases, a material needs to be connected to a solid substrate, which results in an interaction, either chemical, physical or mechanical. These interactions between material, substrate and the application process need to be well understood in order to meet the project goals. In each of the four components of these processes mentioned: material, substrate, application and interaction, a limiting factor can be present that prevents reaching the desired result. In the five chapters of this thesis, investigations into these limiting factors in physical, mechanical and chemical field are described that have helped to reach the required results. These scientific investigations allowed to validate the solutions to overcome these limiting factors and expand the knowledge about these factors.

The research undertaken covers three specific areas. The first subject is the precisely controlled wetting and flow of a liquid over a structured substrate, the second subject is the thermal chemical reaction of a structured metal paste with a semiconductor surface, and the third subject is the mechanical interaction between adhesive with the substrate during the curing reaction. For these topics, custom made
measurement approaches and systems were developed in order to allow the study of these subjects.

1.1 Precisely controlled application of liquid material onto a structured substrate

Application of a liquid on a structured material can be done passively or actively. With passive application we mean capillary flow, only driven by surface tension and gravity, while with active application we mean technologies like spraying, printing, etc., involving external forces that are applied on the material.

Capillary flow on surfaces has been studied extensively (9-12), and the relation between fluid surface tension and surface properties was examined using optical means, also including scattering and spectroscopic techniques. However, a complete description of surface tension forces during immersion and emersion of a structured substrate has not been presented yet. This is probably due to the difficulties in obtaining data for these forces by optical means in an emersion situation.

In chapter 2 an elegant way is presented to circumvent the need for optical measurements using a modified dynamic Wilhelmy plate method, which allows the measurement of both immersion and emersion forces on a structured plate. It is shown that in addition to the predicted pinning, or flow resistance phenomena on a geometrical structure, the effects of irregularities in the tested geometries can also be characterized well using this modified Wilhelmy technique. Measurement results obtained with this method match well with theory, and in addition, evidence of meta-stable water films in emersion was obtained.

These measurements of fluid behaviour on geometrical structures form the basis for more detailed understanding of the capillary flow of fluid on structured substrates. Based on this understanding, design of structures for microfluidic products, like biosensors, pumps, connectors etc. can be executed more readily with better results.

Printing is an important way of actively applying a material onto a surface with typical resolutions of 0.1 mm for screen printing (13), and even higher resolution for flexographic (14), off-set printing and micro-contact printing (15). A large part of the application process is difficult to investigate directly, as the interesting parts of the printer touch the substrate, which renders visual observations almost impossible. In addition, printing speeds are typically upwards of 100 mm/s, which means a time
resolution of microseconds is needed in order to study phenomena with micrometer resolution. This implies that most of the research performed is executed by relating the printing quality to the process settings and material properties, and treating the process as a black box.

In chapter 3 a novel approach is presented to study the fluid flow on structured surfaces at high speed during a flexographic printing process using an UV-curable ink in combination with a lithographically defined structure of poly-acrylate on a glass substrate. This poly-acrylate structure provides both horizontal faces for the liquid to be printed onto, as well as vertical sides for the fluid to flow down on. The flow of ink onto the vertical sides is stopped within 100 milliseconds by curing the ink using UV radiation. This approach allows to ‘freeze’ the fluid on the horizontal and vertical sides of the poly-acrylate structure for off-line analysis. SEM analysis of the fluid flow length on the vertical sides of the structure presents a method to study liquid flow as a function of the print process parameters. This method allows a qualitative investigation of the influence of capillary driven flow, forced flow and other effects. Various printing process parameters and a range of ink viscosities are used. With this approach the parameter space for flexographic printing of non-decorative inks can be scanned quickly and optimal printing conditions can be obtained. This will advance the use of flexographic printing for electronic and other functional applications, especially where high resolution of the printed structure is required.

1.2 Thermal reaction of a structured metal paste with a semiconductor surface

After structured deposition of a material, a thermally activated reaction is sometimes needed in order to obtain the desired properties. In silicon wafer based solar cells, the precise control of this reaction is critical for the quality of the cell, and heating up to more than 700 °C and cooling down to room temperature within seconds is beneficial for the electrical performance of the solar cell. This is the reason for many investigations into alternative fast heating processes for solar cell applications (16-18), where silver paste is applied in a pattern on a silicon wafer. As only the deposited silver has to react with the silicon, a selective heating process for silver alone can have benefits in speed and control.
In chapter 4 the possibility to use RF inductive heating for selective local heating of a silver paste on a silicon wafer is investigated. The inductive heating technology has the potential to treat a large area, and the selectivity of the heating process is due to the electrical material differences between silicon and silver. The goal is to control and to improve the electrical contact formation between silver paste tracks on doped silicon by selective and fast heating of the silver paste tracks. It is shown that selective heating of silver tracks using RF radiation is indeed possible under these conditions and that steps forward can be made in the applicability of the induction heating process by improvements in process control. The benefits for the electrical performance of the solar cell are not so large as hoped, as the reaction time needed for contact formation does not match the induction heating process time well.

1.3 Mechanical interaction between adhesive and substrate during curing

Another way to connect two different materials is to apply an adhesive between both materials. When this adhesive subsequently cures to reach its final state, its volume decreases slightly, which is called reaction shrinkage. In most applications where adhesives are applied, this reaction shrinkage is negligible. For dentistry, this is a different matter, and the effect of shrinkage of the UV-curing adhesives has been investigated in some detail (19). Also for the fixation of optical parts for CD’s and Blu-ray players, the effect of shrinkage has been investigated (20-22), and the design of the product optimised.

For adhesives that cure at room temperature, the investigation of the effects of reaction shrinkage on the parts that are glued together is hampered by the long reaction time, which requires a stable measurement system. Still, also for these systems, the relation between adhesive properties and the final performance of the parts that are joined is important to investigate in more detail, certainly if the flatness of the part needs to be maintained in the nanometer range after adhesive bonding.

In chapter 5 the mechanical deformation of an optical part, namely a 20 × 60 mm silicon die with optical reflecting structures, due to adhesive shrinkage after mounting on a substrate is investigated. The deformations that are detrimental to the optical properties of the part are in the low nanometer range, and the curing time of the adhesives used is more than a day. Scaling conditions, a scaled setup, a finite element
model (FEM) and a measurement method are described that allow the prediction of the deformation of the silicon die due to adhesive shrinkage during curing. A measurement system was constructed that is capable to measure sub-micrometer z-displacements of the scaled setup that represents the silicon die mounted on a substrate over times of up to a week. The sub-micrometer z-displacements of the scaled setup can be related to nanometer displacements in the silicon die, and thus to the quality of its optical properties. Z-displacement measurement data of the scaled setup due to shrinkage of two adhesives were used to validate the FEM calculations.

In chapter 6 the applicability of the FEM model was investigated further for different room temperature curing adhesives by comparing their results with those from the scaled setup. Stiffness and shrinkage of the adhesive was shown to determine the mechanical response of the construction to the chemical reaction occurring during curing of the adhesive. Large discrepancies between FEM results and z-displacement measurements are indications that non-modelled interface phenomena, like adhesion failure and crack initiation occur, besides the purely mechanical response. Changes in the static mechanical properties of the adhesive by addition of particles also led to discrepancies between FEM calculations using these static properties, and dynamic z-displacement measurements during the curing process. The combination of these investigations resulted in an evidence-based advice on which adhesive should be used to meet the product specifications. The adhesive that was advised led to a better than expected optical performance of the die in its optical system.
Chapter 1

References


Chapter 2

2 Wetting forces and meniscus pinning at geometrical edges

In this chapter we show that complications in currently used optical measurements for wetting and flow resistance over edges can be circumvented by surface tension force measurements. These forces are measured by employing a modified Wilhelmy plate testing technique in which a plate with rectangular holes is immersed. The forces measured during immersion and emersion are subdivided into mass, buoyancy and surface tension related parts, where particular attention is paid to the flow resistance when the meniscus passes horizontal faces and edges of the plate. Combining this experimental method with wetting theory, we show that we can predict and measure the full force curve for meniscus shape transitions over edge geometries. Moreover, wetting effects directly linked to surface defects can be detected qualitatively. The measurement method designed is complementary to the current state of the art optical methods\textsuperscript{1}.

\textsuperscript{1} This chapter is based on W-J. A. de Wijs, J. Laven and G. de With, \textit{AIChE Journal} (15341), 2016
2.1 Introduction

Wetting of surfaces in liquids has since long been recognized as being important in many technological applications. A good example is provided by micro-fluidic devices (1). If both liquid and gas are pumped through such a device, the gas compressibility makes the pumping appearing pressure driven, even when the pump is a volume displacer. Because the Laplace pressure difference at the gas/liquid contact scales with the inverse of the channel dimension, this pressure may jeopardize the intended flow control when scaling down channel dimensions like in micro-fluidics. This has spurred many investigations of wetting at several types of surface discontinuity, transitions in roughness or chemical surface homogeneity and transitions in material and geometry (2). In this chapter we will focus on the wetting resistance at geometrical discontinuities, more specifically at edges.

The current state of the art in determining liquid spreading resistance for sharp edges can be divided into experimental and theoretical aspects. Recently some theoretical and thermodynamic studies on the subject have been reported (3-5). These studies focus on the energy balance to explain stability and instability of liquid boundaries at edges. As the theoretical framework and thermodynamic model involved are quite complex, either a 2D approach or an axisymmetric 3D approach is often used to decrease the complexity to a manageable level. In 1977, Hue and Mason described the wetting by a liquid advancing from the center of a circular horizontal surface towards and over its sharp edge using an optical setup (6). Since then, refinements in optical systems and improvements in surface production methods were reported (7-9) that allow more precise measurements than before, on different types of surfaces.

Optically measuring the liquid shape and subsequently calculating the force needed to spread over an edge is a complex procedure for non-perfect surfaces and geometries. Any imperfection in the surface or geometry translates into a change in liquid shape, and the calculation of the spreading force due to these imperfections is not trivial for a 3D configuration. The current state of the art still needs axisymmetric liquid shapes to be able to calculate spreading forces, and imperfections typically do not obey this boundary condition. This has prevented the use of optical techniques to liquid spreading resistance at an edge created with standard manufacturing technologies.
In this chapter we approach this problem by measuring the forces related to immersion and emersion directly for a vertical plate fitted with rectangular holes; We interpret these force results by theoretically analyzing the shape and position of a meniscus at vertical and horizontal faces and at plate and hole edges, from which force versus immersion depth curves can be predicted. Experimental data for different fluids and plate materials show the validity of the theoretical framework and measurement method. A great deal of attention is paid to the effect of surface imperfections on the measurement results, showing the added value of this method for characterizing surfaces with defects.

2.2 Theory

2.2.1 Wetting of the side faces of a vertical plate

Definitions
For describing the forces involved when a meniscus passes a hole in a plate as a model of a discontinuity in a microchannel, we start with establishing the shape of a meniscus and the forces involved when a liquid wets part of a side face of a vertically suspended plate. Thereafter this result is used to assess the force involved when a meniscus passes an edge at the top or bottom face of a vertical plate. Finally, that result is applied to describe the force required to let meniscus pass a hole in a plate.

The extent of wetting of a solid surface by a liquid in a gas environment is determined by the minimum in Gibbs energy of the system, which results in an equilibrium contact angle \( \theta \) across the liquid phase between the solid/liquid (SL) and liquid/gas (LG) interfaces as they emanate from the contact line. We will use the terms “wetting” and “non-wetting” surface for the cases of \( \theta < 90^\circ \) and \( \theta > 90^\circ \), respectively. The relationship between the contact angle and the interfacial energies involved is expressed by Young’s equation

\[
\gamma_{SV} = \gamma_{SL} - \gamma \cos \theta
\]  

(1)

where \( \gamma_{SV} \), \( \gamma_{SL} \) and \( \gamma \) are the Gibbs interfacial energies between solid and gas, solid and liquid and liquid and vapor, respectively (10), and where the latter quantity is addressed as surface tension. In order to satisfy the thermodynamic equilibrium requirement, the gas phase has to be saturated with vapor. A mechanical measurement
of the surface tension is often carried out at ambient conditions, so at unsaturated vapor conditions. Near a contact line, however, the evaporation flux is orders of magnitude higher than on the bulk surface due to the local curvature of the fluid (11). If the vapor above the liquid is essentially stationary, the local conditions can be close to saturation. The change in contact angle values for water and organic liquids at high wetting speeds has been reviewed by Bonn (12) and the specific deviations due to unsaturated conditions for molten metals have been reviewed by Alchagirov (13). We will restrain our discussion to wetting speeds lower than 0.1 mm/s with water and organic liquids, for which we assume saturated vapor conditions.

### 2.2.2 Meniscus shape at a side face of a partially immersed vertical plate

We will first discuss the meniscus shape of a simple, vertical plate like employed in the Wilhelmy method (14), in which a thin, rectangular plate with height $h$, width $w$, thickness $t$, volume $V$, mass $m$ and density $\rho_P$ is immersed to some extent in a liquid with density $\rho_L$, in order to determine the surface tension of a liquid. Traditionally, the measurement is based on the force needed to pull the plate out of the liquid. Our “modified Wilhelmy method” is an extension of a method that was introduced later (15) and is still widely used, according to which method the plate is first immersed to some extent and then pulled back until the lower edge of the plate comes flush with the liquid surface; at that moment the force is measured and the surface tension is derived from the value obtained. Variations of that method are measuring the force continuously (14) or moving the partly-immersed plate up and down over some distance (16); both methods yield additional information about advancing and receding angles.

All variants of the Wilhelmy method, including ours, are based on the following principle. When a plate is suspended from a balance and is immersed over some distance $d$, which is defined as the difference between the vertical positions of the base face of the plate and of the surface of the liquid far away from the plate, the downward directed force that the plate exerts on the balance is given by

$$ F = mg - \rho_L twd + 2(t+w)\gamma \cos \theta $$

(2)

where $g$ is the gravitational acceleration. The first term on the right hand side (rhs) is the force due to the mass of the plate, which is typically eliminated by tarring the balance with a non-immersed plate. The second term is the buoyancy force which originates
from the difference in hydrostatic pressure between the liquid surface and the bottom of the plate. The third term is the surface tension force, which is proportional to the length of the horizontal projection of the contact line (the boundary between the liquid/solid and the liquid/gas interfaces). The contact line is lowered at the vertical edges (“arching”), the magnitude of which was approximated by Hood (17) and numerically calculated by Scott et al. (18) for a 90° edge. A solution for a 180° edge (infinitely thin plate) seems not to be available (19) but can be expected to have even more pronounced arching. The plates employed by us, with thicknesses between 0.5 and 1.1 mm, can be expected to have an arching between those of the 90° and the 180° cases. As already explained by Laplace using pressure arguments, this arching does not lead to modifications in the force measured. An analysis of the arching effect, to some extent similar to the elegant work of Loos (20), is given in appendix 1. Hence, practically speaking, the wetting line length equals the circumference $2(t + w)$ of the cross section of the suspended plate.

The derivation of the shape of a meniscus starts from the law of Laplace which states that the local pressure difference $\Delta P$ across the interface is described by $\Delta P = \kappa \gamma$, where $\kappa$ is the local curvature. For liquid surfaces like in Figure 1, which are only curved in one direction (“cylindrical shape”), the local curvature is given by $\kappa = R^{-1}$, where $R$ is the radius of the cylinder that locally fits the interface shape, and with the understanding that the higher pressure is at the convex side of the curved interface.
Using the positional parameters $\zeta$ and $\chi$, and the local liquid surface orientation $\phi$ as defined in Figure 1, $\kappa$ is given by (21)

$$\kappa(\zeta) = \kappa^{-1}(\zeta) = \frac{d^2 \chi / d \zeta^2}{\left(1 + \left(d \chi / d \zeta \right)^2 \right)^{\frac{3}{2}}}$$

(3)

After substituting equation 3 in the Laplace equation, taking for $\Delta P$ the hydrostatic pressure difference and using $\tan \varphi = -d \chi / d \zeta$, we arrive at

$$\gamma d (\sin \varphi) = -\rho \gamma g \zeta d \zeta$$

(4)

By integrating this equation from far away from the plate to any position at the meniscus, a relationship can be obtained between the local relative liquid surface height $\zeta$ and the local liquid surface orientation $\phi$, reading

$$\sin \phi = 1 - \frac{\rho \gamma g}{2\gamma} \zeta^2$$

(5)

Note that this equation holds for any local liquid surface orientation $\phi$ between $-90^\circ$ and $+270^\circ$. Positive and negative values of the scaled height parameter $\zeta / (2\gamma / \rho \gamma g)^{\frac{1}{2}}$ correspond to $\phi < 90^\circ$ and $\phi > 90^\circ$, respectively, as shown in Figure 2. Equation 5 can
also be applied to a meniscus orientation $\phi$ at the contact line between the meniscus and any face of the plate. For this purpose it is convenient to define the orientation $\psi$ of this face, in analogy to the definition of $\phi$, as the angle between this face and the vertical direction. In this way the value of $\phi_c = \psi + \theta$ can be related to the meniscus height as

$$\sin(\psi + \theta) = 1 - \frac{\rho c g}{2\gamma} \frac{\rho^2}{\gamma_c}$$

(6)

where $\zeta_{c,\psi}$ is the meniscus height at a face with orientation $\psi$. For convenience we will use the short notation $\zeta_c = \zeta_{c,\psi=0}$. The meniscus length scaling parameter in equation 6, $(2\gamma / \rho g)^{1/2}$, is characteristic for the extension of the meniscus, both for its height and for its horizontal extension away from the contact line. As an example, at 20 °C we have $\zeta_c = 3.8$ and 2.3 mm for this length scaling parameter in the cases of water and pentane respectively, these values being identical to the meniscus heights of these liquids at a perfectly wetted vertical plate ($\theta = 0^\circ$).

**Figure 2:** Scaled local height $\zeta / (\sqrt{2\gamma / \rho g})^{1/2}$ of the meniscus with respect to the bulk liquid height, as function of the local liquid surface orientation angle $\phi$ (equation 5). The graph can also be interpreted as the height of the contact line at the side face of a vertical plate as a function of the contact angle.
2.2.3 Meniscus pinning at top and bottom of an immersed vertical plate

After having described the meniscus at the side face of a vertical plate, we will now describe the meniscus pinning at the top or the base of that plate. First the surface tension force and thereafter the buoyancy force for the process of immersing a plate will be considered, from no contact to immersing to a depth \( d \), by raising the liquid level. When the bottom face of a plate touches the liquid at \( d = 0 \) for wetting conditions (Figure 3, left), a contact line with height \( \zeta_c \) and contact angle \( \theta \) is formed immediately at any side face. The corresponding surface tension component in the vertical direction \( \gamma \cos \theta \) is, according to equation 2, directly measurable. No pinning occurs and for any \( d > 0 \), the contact line will rise along the side faces with a constant value of \( \gamma \cos \theta \) and with a buoyancy component linearly increasing with \( d \). In the non-wetting case (Figure 3, right), at \( d = 0 \) the plate touches the liquid without an instantaneous vertical force. With increasing immersion depth \( d \), the wetting line stays pinned at the base edges, causing the liquid orientation angle at the contact line \( \phi_k \) to change from 90° to \( \theta \), and the meniscus height to change from zero to \( \zeta_c \). This causes a gradual increase of the magnitudes of both the surface tension and the buoyancy components. Once \( \phi_k = \theta \) at a meniscus height of \( \zeta_c \), the contact line is unpinned and the contact line will rise over the side faces as in the wetting case. Upon further immersion, the wetting force remains constant and the buoyancy force increases linearly with immersion depth. When the immersion depth \( d \) equals the plate height \( h \), the contact line arrives at the top edges where the meniscus will pin, both for the wetting and non-wetting cases, as depicted in Figure 3.
Figure 3: Immersion of a plate into a wetting liquid (left) and a non-wetting liquid (right) by raising the liquid level. The liquid orientation at the top face edge is indicated when the maximum pinning force is measured.

When increasing \( d \) further while being pinned at a top edge, the angle \( \phi \) for the liquid orientation at the contact line changes from the value \( \theta \) to the value \( \theta + 90^\circ \), a value matching with the contact angle at the top face. At that moment the contact line is released (“unpinned”) from the top edge and moves quickly over the top face until it meets the contact line coming from the other side face. The transition of \( \phi \) from \( \theta \) to \( \theta + 90^\circ \) during pinning is gradual rather than instantaneous due to the fact that the edge is not infinitely sharp but has a small radius, which can be approximated by a cylindrical surface. Upon increasing \( d \), the contact line gradually moves tangentially over this cylindrical surface in order to obey both equation 6 and \( \phi = \theta \). This process affects both the surface tension term and the buoyancy term in the vertical force expression, equation 2. Its effect on the surface tension component is through the cosine factor for the (local) contact angle; the scaled surface tension force is plotted as a function of the scaled liquid height in Figure 4. This result for pinning at the edges of the top face is also applicable to pinning at the edges of the bottom face.
Figure 4: Scaled vertical surface tension force in immersion as function of the scaled height difference $\zeta_c / \zeta_c (\theta=0^\circ)$ between the contact line and the bulk liquid surface. Note that $\zeta_c$ depends of both $\psi$ and $\theta$.

As a summary of the different surface tension induced pinning effects, we discuss as an example Figure 5 in which the vertical surface tension force as well as liquid surface orientation for a wetting situation ($\theta = 45^\circ$) is plotted for the transition from an almost-fully to fully immersed plate, i.e., when $z_{\text{top of plate}} - z_{\text{liquid surface}} = h - d$ changes from positive to negative values. As long as the meniscus moves along the side faces from point D to E in Figure 5, the liquid surface orientation at the contact line is constant with $\phi_c = \theta$, as seen between points A and B. Upon further immersion, the contact line stays pinned while $\zeta_c / \zeta_c$ decreases to negative values. As a result, the meniscus orientation at the contact line $\phi_c$ increases from $45^\circ$ at point B to $135^\circ$ at point C, on the graph taken from Figure 2. This results in a decrease of the surface tension force, from point E to negative values, ending at point F on the graph taken from Figure 4. This is the end of the pinning situation; when the plate is immersed infinitesimally further, the wetting at any position at the top face becomes instable and the contact line will run from the edge to the center of the top plate. No liquid surface interface is present anymore, as the gas phase is completely displaced from the top face (hence no thick red line is drawn beyond point C). Also the surface tension force vanishes, as indicated by the line GH.
To clearly visualize the effects of the horizontal edges, the forces from the plate mass as well as from all buoyancy effects, as given by equation 7, are removed. As long as the meniscus moves along the side faces from point D to E in Figure 5, the liquid surface orientation at the contact line is constant with $\phi = \theta$, as seen between points A and B.

Figure 5: The vertical surface tension force (upper; in blue) and the meniscus orientation at the contact line (lower; in red) for the detachment process of a plate from the liquid surface, around the moment that the plate becomes fully submerged by immersion. The time direction is from right to left. While the meniscus passes the top face (see pictures in orange circles), the meniscus orientation at contact varies as indicated by the thick red line which is part of the dotted red curve from Figure 2. The vertical surface tension force (thick blue line) partly matches with dotted blue curve from Figure 4.
Chapter 2

Note that when the contact lines, running between F and G, meet each other, the recorded surface tension force vanishes at point G; the speed of this process may be affected by viscous and/or inertia effects. The scheme in Figure 5 is applicable to liquid detachment with any contact angle, both to pinning at the top edge in immersion and at the bottom edge in emersion. The dotted curves used to construct Figure 5 can also be used to describe the liquid attachment process (pinning at the bottom edges for immersion of a poorly wetting plate or at the top plate for emersion of a well wetting plate).

Just as the surface tension force contribution during pinning is affected by a changing liquid surface orientation at the contact line, also the buoyancy force contribution in equation 2 is affected during pinning, through the immersion depth change. This buoyancy force contribution is discussed now. As long as the meniscus is at the vertical plate faces, the buoyancy is proportional to immersed depth (the difference in hydrostatic pressure between top and bottom faces). However, during pinning at for instance the top plate, the plate gets immersed deeper than h into the fluid (the top face is below the bulk liquid level). The meniscus height is now negative with a value of \( \zeta_c \), resulting in a buoyancy related height of \( -h + \zeta_c \). A similar effect also occurs upon emersion, where the plate base is slightly above the liquid surface level but still in contact with the liquid, resulting in a buoyancy related height of the positive-valued \( \zeta_c \). In summary, for the buoyancy force we have:

\[
\begin{align*}
F_{\text{buoy}} / \rho_{\text{gwt}} &= 0 & \text{for } d < 0 & \text{no contact} \quad (a) \\
&= \zeta_c & \text{for } d < 0 & \text{with contact line at edge} \quad (b) \\
&= -d & \text{for } 0 < d < h & \text{with contact line at side face} \quad (c) \\
&= -h + \zeta_c & \text{for } d > h & \text{with contact line at edge} \quad (d) \\
&= -h & \text{for } d > h & \text{no contact} \quad (e)
\end{align*}
\]

Evidently, the surface tension and buoyancy effects are interconnected. Specifically, the transition from d to e in equation 7 corresponds to the transition FG in Figure 5. The total vertical force that the liquid exerts on the Wilhelmy plate is the sum of the surface tension and buoyancy forces detailed here.
2.2.4 The meniscus and its pinning for Wilhelmy plate with holes

Now we turn to the effect of more complex pinning structures. As a model structure, we will consider a horizontal, rectangular channel (a “hole”) in a plate, of which the orientation is along the Cartesian axes. Such a structure is indicated in Figure 6, together with how the geometrical features will be denoted. The front and back faces of the plate are simply denoted as plate faces.

![Figure 6](image)

**Figure 6:** Schematic of a Wilhelmy plate with a hole, showing the nomenclature used for the geometrical features. The front and back side faces of the plate are simply denoted as plate faces.

Figure 7 shows how the wetting process from the side face of the hole to the top face of the hole, as compared with that of the plate face. When the liquid level is at the lowest level indicated (curves 1 and 1'), the wetting and the forces involved are adequately described by the rules discussed before for a plate, with the understanding that the length of the contact line should be adjusted from \(2(w+t)\) to \(4(b+t)\) while the buoyancy force should be based on a cross-sectional area \(2bt\) rather than on \(wt\). However, once the contact line has risen to the top of a hole (curves 2 and 2'), it arrives also at the top edge of a side face of the hole, which, as we suppose, is a cylindrical surface, like we introduced before to describe the microscopic geometry of a 90° edge. In this case, the cylindrical 90° edge forces the liquid surface to locally bend more than required by the law of Laplace. The resulting local distortion of the pressure balance
across the interface makes that the contact line runs along the top face of the hole (curves 3, 4 and 5). This running ends in two ways. (i) Along the width of the hole: The contact line at some moment will meet a similar contact line running from the other hole side; the two liquid fronts merge and the top face of the hole becomes fully wetted. (ii) Along the thickness of the hole: The contact line meets the front or back edge of the top face of the hole where it can realize again the equilibrium contact angle (curve 6); further immersing is depicted by curves 7 and 7’.

Figure 7: The stages of the liquid meniscus when passing the side and top faces of a hole.

During the running of the contact line, the buoyancy component of the vertical force as probed on the plate changes abruptly, because the hydrostatic pressure at the top face of the hole, initially being atmospheric, is lowered instantaneously by $\rho g \zeta_c$ (where $\zeta_c$ is the height difference between liquid surface and the wetted top of the hole, see Figure 7). On further immersion, from curve 6 to 7, this special buoyancy force $\rho g \zeta_c$ gradually disappears: at curve 7, the top of the hole is flush with the bulk liquid surface. For the vertical surface tension force the change at the top face of the hole (between curves 2 and 6 in Figure 7) is only due to a sudden change of the length of the contact line; the orientation angle at contact is not changed (if we approximate the corners connected to curves 2 and 6 as being infinitely sharp).

The thinness of the plate makes that the arching at the front face will lower the meniscus height at the side edge of the hole by more than $\approx 40\%$ as argued in appendix 1. This very limited width of the side face of the hole will presumably also make the meniscus height at the side face of the hole stay very close to the meniscus height at its
Wetting forces and meniscus pinning at geometrical edges

edges, because this width is much less than the meniscus length scale \((2\gamma/\rho_Lg)^{1/2}\), as also discussed there.

In Figure 8, the calculated force upon immersion of the hole geometry depicted in Figure 6 into a wetting liquid is given. In order to make the graph as clear as possible, from the total vertical force we removed the contributions from the “standard” buoyancy (the buoyancy in the hypothetical case of no surface tension effects; for a plate without holes it is given by equation 7-c). Thus, the force in Figure 8 is the sum of the surface tension force and non-standard buoyancy force contributions (“special buoyancy force”). Starting at an immersion depth 0, where the liquid is flush with the bottom face, the surface tension force for the wetting length \(2(w+t)\) is recorded. At immersion depth \(b_e - \zeta_c\), the liquid is pinned to the bottom hole edge, and this pinning continues until an immersion depth \(b_e + \zeta_{90}\). Then the liquid runs over the bottom surface of the hole and the surface tension force for a wetting length \(4(b+t)\) is recorded. At an immersion depth \(t_e - \zeta_e\), the liquid wets the top edge of the hole as indicated in Figure 7, with a surface tension force of \(2\gamma (w+t)\), and a special buoyancy force \(\rho g \zeta_e [t (w-b)]\), which decreases to 0 at immersion depth \(t_e\).

**Figure 8:** The predicted standard-buoyancy-force corrected immersion force for the plate with hole geometry depicted in Figure 6, in the wetting case.
2.3 Experimental

The fluids used for measurements and their properties are given in Table 1.

Table 1: Properties of the fluids used at 20 °C.

<table>
<thead>
<tr>
<th>fluid</th>
<th>supplier, grade</th>
<th>surface tension (N m⁻¹)</th>
<th>density (kg m⁻³)</th>
<th>viscosity (mPa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>Millipore, Milli-Q deionized*</td>
<td>0.0728</td>
<td>998.2</td>
<td>1.0</td>
</tr>
<tr>
<td>decane</td>
<td>Merck, zur analyse</td>
<td>0.0238</td>
<td>730</td>
<td>0.91</td>
</tr>
<tr>
<td>DiEthylene Glycol (DEG)</td>
<td>Merck, zur synthese</td>
<td>0.0446</td>
<td>1119.7</td>
<td>36</td>
</tr>
</tbody>
</table>

The measured surface tension was constant for hours, indicating that any level of surface active species (which might diffuse to the surface) was extremely low.

Structured PMMA plates were made from a PMMA sheet of 0.5 mm thick. The pattern with holes A, B and C as depicted in Figure 9, including the circumference of the plate, was created using a CO₂ laser at low fluency. The combination of hole and full plate width below the hole is defined as a section. Geometries of the patterns were measured using a digital caliper (Mitutoyo 500-160-20, Japan) and found to vary less than 0.1 mm from plate to plate.

![Figure 9: Front view geometry of the plates used; A, B and C are holes through the plate.](image)
In order to check to what extent the local melting of the PMMA plate by laser cutting changes shapes, the topography of the edges of the holes was determined using interferometry (WykoNT1100, USA). Small local “bulges” along the cutting line were noticed. An example is shown in Figure 10 indicating a 27 μm height step over 225 μm length, resulting in an average slope of 7° and thus a similar apparent contact angle deviation.

![Graph: Topography of the edge of a lasered hole as measured with interferometry, where molten and re-solidified material results in a bulge just before the edge between position 200 to 450 μm with a maximum slope of about 12° around 260 μm. At position 550 μm, the edge is located.]

Structured glass plates were made of a glass plate of 1.1 mm thick using the same cutting equipment and procedure. Here no slope due to a bulge was present; instead small cracks and chips broken out of the edges were detected, shown in Figure 11 with a length of about 0.3 mm.
The PMMA plates were cleaned by submerging them into a 5 wt% aqueous solution of Extran MA02 and placing the beaker glass in an ultrasonic bath (Branson 5120, USA) for 5 minutes. Thereafter the samples were rinsed with water and submerged in a beaker with water placed in the same ultrasonic bath for 5 minutes. Finally, the substrates were dried in vertical orientation at room temperature. The glass plates were cleaned by manual rubbing with a 5 wt% solution of Teepol 610 liquid soap and thereafter rinsed with water. The substrates were submerged into a beaker with water placed in the ultrasonic bath (Branson 5120, USA) for 5 minutes and rinsed again with water. This process was repeated two times and thereafter the substrates were dried at 50 °C and treated with an oxygen plasma at 0.132 atm for 2 minutes at 300 Watt (Tepla, Germany).

A dynamic contact angle measuring device with thermal control unit (Dataphysics DCAT 21 and TEC 250, Germany) was used to measure the vertical force on the plate as a function of immersion depth. Measurement recording was started when a change in force larger than 0.4 mN was measured. The immersion speed for the measurements was set at 0.1 mm/s at a measurement frequency of 50 Hz, leading to a 2 μm positional resolution. The measurements with DEG were performed at 0.05 mm/s.

Except near horizontal edges, the “raw” total force measured varied linearly with immersion depth, both for full plates and for plates with holes. This linear increase was
interpreted as being solely due to the standard buoyancy; it matches with the geometrical data of the plate and was subtracted from the raw force data, leading to the total force corrected for standard buoyancy. This buoyancy correction also represents the “displaced” liquid which, in turn, leads to a rise of the bulk liquid surface in the 66 mm diameter liquid container. This means that the true immersion depth is by a factor 1.0080 (system 1) or 1.0037 (systems 2, 3 and 4) larger than the immersion as obtained from the equipment readings. It are the true immersion depth values that will be used throughout this paper. Note that a small change in bulk liquid level also occurs already before the immersion has preceded to any extent. Just when a wetting liquid starts touching the plate, the instantaneous meniscus formation lowers the bulk liquid level. Calculations show that this instantaneous lowering is never more than 76 µm, a value below any inaccuracy estimate quoted for \( \zeta \) values. The corresponding change in buoyancy force is never more than 10 \( \mu \)N, which is at or below the noise level of the equipment. Thus, this effect is not taken into account.

### 2.4 Results and discussion

Force curves as a function of immersion in or emersion from the liquids listed in Table 1 were obtained for the structured PMMA or glass plates and corrected for the standard buoyancy, as specified in section 2.2. Each of the immersion force curves will be analyzed for the “standard” wetting and pinning parameters as specified in Figure 8. Thereafter, emersion force curves will be discussed. Finally, a number of special effects observed will be discussed.

#### 2.4.1 Wetting of glass during immersion

In Figure 12, the measured immersion force curve of a glass plate in decane (“experiment type” 2 in Table 2) is shown, together with the predicted curve as based on the theory discussed. The grey areas indicate the positions of holes A, B and C. Force features at these locations are denoted by the hole label followed by a Roman number. A depth position in immersion or emersion will simply be denoted by depth, with an estimated accuracy of 0.1 mm.
Figure 12: Standard buoyancy corrected force curve for the immersion of a 1.1 mm thick structured glass plate in decane. Grey areas indicate the locations of the holes.

On immersion, the measured force on the plate changed at the moment the plate touched the liquid surface. As soon as the force was larger than 0.4 mN, force recording started and within 0.06 s wetting progressed towards the steady-state wetting at the side faces of the plate. An advancing contact angle of 15.1° (row 3, column 3 of Table 2) was derived from the average force signal of 1.18 mN over the piece of plate below hole A, with an accuracy of ±1° as determined by three times the standard deviation in measured force. In a similar way, an averaged contact angle was derived for hole A (in column 4). Analogously, this was done for holes B and C and for parts of full plate width below them (rows 4 and 5). The contact angle data for any part of full plate width below a hole show that the contact angle of the full plate has a high uniformity. For any hole in glass, the obtained contact angle is smaller than for the full width piece of glass below it, indicating better wetting. This improved wetting is due to the rough cut side faces of the hole as shown in Figure 11. In this configuration, the effect of roughness on the contact line is more accurately described by McCarthy (22) using a lowered activation energy barrier for movement of the contact line, than by increased surface contact area as described by Wenzel (23) for homogeneous areas. For hole A this effect is larger than for holes B and C, as hole A > B > C.

Pinning at the bottom edge of the hole, denoted with A-I in Figure 12, occurs at a liquid level of 5.3 mm, 2.7 mm below the bottom edge of the hole (see column 5 of
Table 2), which is of the order of $\zeta$. The discrepancy between the calculated $\zeta$ of 2.2 mm in brackets, in the same cell of the Table (using equation 6) and the measured $\zeta$ is due to chipping of glass as shown in Figure 11, which locally shifts the bottom edge of the hole downwards, so that the pinning force is noticed earlier. Pinning at the bottom edge of the hole, indicated with A-II also stops earlier than expected due to the chipping damage, as the bottom face of the hole is roughened over the full area, and as a consequence has a higher wettability. Wetting already occurs at an immersion position of 8 mm, corresponding to a local effective contact angle of 0°. As a consequence, the maximum pinning force measured is much lower than the expected value; both values are tabulated in column 6 of Table 2.

Wetting of the top edge of the hole, denoted with A-III, occurred at a liquid level of 1.8 mm below the top face of the hole at $t_e$. The zeroth order prediction of this parameter $z_c$, based on the measured contact angle, is that such wetting occurs at $z_c = 2.8$ mm below the top face. The roughness of the cut surface would even lead to somewhat larger values. However, in Appendix 1 it was explained that arching causes the contact line at the side edges and faces of the hole to have a reduction in the height difference with the liquid level of at least 40%. A 40% arching of 2.8 mm would lead to 1.7 mm, thus, the value of 1.8 mm obtained experimentally perfectly matches with the theoretical expectations, taking the mentioned uncertainties into account. Both height values are given in column 7 of Table 2. The average contact angle upon emersion are given in column 8, and the corresponding rise height $\zeta_{c, -90}$ in column 9. The effect of the narrowed side faces result in larger $\zeta_{c, -90}$ values for holes B and C.
<table>
<thead>
<tr>
<th>Experiment type</th>
<th>Immersion</th>
<th>Emersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>contact angle (°)</td>
<td>$\zeta_c$ at $b_e$ (mm)</td>
</tr>
<tr>
<td>Section</td>
<td>measured (predicted)</td>
<td>measured (predicted)</td>
</tr>
<tr>
<td>1 decane on glass</td>
<td>A</td>
<td>15.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>14.1 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.2 ± 0.7</td>
</tr>
<tr>
<td>2 water on PMMA</td>
<td>A</td>
<td>93.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>92.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>91.6 ± 0.3</td>
</tr>
<tr>
<td>3 DEG on PMMA</td>
<td>A</td>
<td>66.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>66.3 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>65.4 ± 0.3</td>
</tr>
<tr>
<td>4 decane on PMMA</td>
<td>A</td>
<td>13.8 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>14 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>13.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table 2: Contact angle data calculated from measured force; predicted and recorded $\zeta$ and pinning force for wetting and non-wetting fluids in immersion and emersion mode (n.a. = not available).
### 2.4.2 Wetting of PMMA during immersion

The main characteristics of the immersion of PMMA in water, data for experiment type 2 in Table 2 were deduced from the graph in Figure 13. As before, the hole positions are indicated in grey, and the force features are indicated by the hole label, followed by a Roman number.

![Graph showing non-wetting force as a function of immersion depth for a PMMA plate with holes into water. Grey areas indicate the positions of the holes. The dotted line indicates the prediction.](image)

Near immersion depth 0, effect A-0 is visible: Directly upon contact, a 0.3 mN positive force is observed, as if the contact angle is smaller than 90° instead of the plate contact angle of 93.4°. Then 1.8 mN pinning force at the base edge of the plate is measured, instead of the 0.2 mN pinning force based on the contact angle of 93.4°. The $\zeta$ value measured is 1.4 mm, and the $\phi$ that corresponds with this value and the measured pinning force of $-1.8$ mN is $(108 \pm 4)^\circ$. The difference between $\phi$ and $\theta$ corresponds with a maximum angle of 12° in the bulge profile as given in Figure 10. In Figure 14, the effect of this bulge on the liquid orientation at the bottom edge during immersion is schematically given by lines 1 to 7, while liquid orientation without bulge is indicated by line 1’ to 7’. Lines 1 to 3 in Figure 14 show the small positive wetting effect, due to running of the meniscus over the bulge surface until equilibrium is reached in liquid position 4, after which line 4-7 show the additional pinning effect due to other side of the bulge. Note that the distance between lines 1 and 4 is only 0.1 mm in
Chapter 2

reality, and the distance between lines 4 and 7 is 0.2 mm, leading to a total bulge size of 0.3 mm, as was measured and shown in Figure 10.

![Figure 14: Apparent contact angle $\phi_c$ increases from line 4 to 6 due to the rounded “bulge” on the edge of the PMMA plate.](image)

At immersion position 7.0 mm, effect A-I is visible: a gradual increase of measured force, followed by a small, sharp “peak” of about 0.3 mm wide, before $\zeta_c(b_e)$ is reached at an immersion depth of 8.0 mm. The sharp “peak” of 0.3 mm can be easily explained by the bulge, which first lowers and then increases $\phi_c$ over a distance of 0.3 mm. The gradual force increase before the actual bulge suggests a lower contact angle. The hypothesis is that the laser process induces oxidation of the PMMA in a zone wider than the molten bulge area, which leads to a more polar character of the PMMA. This more polar surface results in a locally lower contact angle of water, and thus an increase in the measured force. The contact angle is at most lowered by 5-10°, judged by the smaller than 0.3 mN increase in force measured. The effect for decane is not observed, as decane has no polar interactions with the surface at all, so a change in polarity has no effect. The measurement method developed allows to record these plate property changes, in contrast to optical measurements.

The end position of pinning, denoted with A-II, is at position 11.7 mm in Figure 13, which is of the order of $\zeta_c$ near the bottom edge ($b_e$) of the hole. The expected position was 12.2 mm, a deviation of 0.5 mm, of which 0.1 mm at most can be due to arching, as the $\zeta_c$ value is only ~0.2 mm. The 0.5 mm deviation of $\zeta_c$ fits well with a lowering of the contact angle of the bottom face of the hole by laser induced oxidation, so pinning does stop at $\phi_c = 173^\circ$ instead of 183°, with a corresponding $\zeta_c$ of + 0.3 mm.
Assuming this hypothesis is correct, the small, sharp, positive force peak at position 15.9 mm, indicated with A-III, is due to wetting of the top face of the hole which leads to an immediate increase in the Archimedes buoyancy force, as shown in Figure 7. The measured $z_c$ value of 0.2 mm (column 7 in Table 2) has a deviation of 0.4 mm to the predicted value. This deviation can, for $\approx 0.2$ mm, be explained by contact angle lowering to about 85°, and for $\approx 0.1$ mm by to the macroscopically rounded edge between side and top face of the hole, as indicated by the surface between line 2 and 3 in Figure 15, where the locally rounded surface pulls the meniscus to the top surface.

This effect is immediately followed by effect A-IV, due to the bulge present at the top edge of the hole, which results in extra pinning as indicated by lines 4-7 in Figure 14. The magnitude of the effect is smaller because the top edge of hole A is narrower than the base edge of the plate.

These special wetting features observed on the PMMA plate due to the bulge and oxidation also explain the larger deviations in the “standard” wetting effects and pinning data of experiment types 3 and 4, in which no additional features were observed. For experiment type 3 the large deviation in the $\zeta$ value can be explained by the fact that no force was recorded in the first 0.7 mm of immersion, as it was below 0.4
mN due to the combination of fluid, contact angle and bulge. For experiment type 4, only the pinning values are lower than predicted as the bulge locally lowers the contact angle to almost zero, just as the roughness in experiment type 1.

Two separate series of glass in water immersion tests were carried out to check that our immersion and emersion experiments were indeed carried out under the targeted quasi-static contact angle conditions. This combination was selected from the system components employed because glass can more rigorously be cleaned and because adsorption of traces of surface active species to the liquid surface is expected to be most pronounced for water. In both series, a plate was for five times sequentially moved in and out of the liquid. In the first series, cleaning procedures were employed as described in paragraph 2.3. At an immersion speed of 0.3 mm/s and below (down to 0.001 mm/s) no speed dependence in the force versus immersion depth was found; the contact angle was 59°. At 1 mm/s the contact angle had risen to 63° while the peak height of the pinning force was not significantly higher; however, the peak width increased as can be seen in Figure 16.

![Figure 16](image)  
**Figure 16:** Speed dependence of the pinning force for the immersion of a glass plate with holes in water after cleaning according to procedures in paragraph 2.3. For details, see text.

For the second series, a special cleaning procedure was followed. The glass plate and the liquid container were plasma treated prior to immersion in Millipore Q water. The plasma treatment brought the contact angle down to a quasi-static contact angle of
30° for all speeds of 1 mm/s and below. At 3 mm/s the contact had risen to 35°. From these experiments can be concluded that the tests with decane and water (experiment types 1, 2 and 4) were indeed carried out under quasi-static conditions, while, using scaling arguments based on the capillary number \( Ca = \text{speed} \times \text{viscosity} / \text{surface tension} \), the tests with DEG were near the edge of the quasi-static regime.

2.4.3 Dewetting during emersion

Dewetting effects during emersion can also be observed and quantified using the measurement method developed. The values of receding contact angle and \( \xi_{c-\infty} \) are given in column 8 and 9 of Table 2. An example is shown in Figure 17, with the force curve of experiment type 2, section A, where a receding contact angle of 49.3° was measured. The shape of the measured force curve corresponds nicely with the expected curve, the deviations are indicated with E, followed by a Roman number.

![Figure 17: Wetting force measured and calculated upon emersion of PMMA plate out of water, hole A and the plate below.](image)

Between the emersion position 16 mm \( (t_c) \) and position \( t_c-\xi_c \), the contact line moves over the side faces of the plate, thus the contact angle stays constant and only an increase in the Archimedes force is noticed. The depth \( t_c-\xi_c \) is defined by the local contact angle; for a contact angle of 49° it should be 14.1 mm, but as the local orientation of the liquid surface at contact is increased to 61°, due to the bulge surface orientation and especially its modified wetting, the actual value of \( t_c-\xi_c \) is 14.7 mm.
This discrepancy is indicated by E-I. The liquid detaches from the top face of the hole already at position 11.7 mm instead of 11 mm, indicated by E-II, which is also due to the bulge.

Often, dewetting occurred a few millimeters later. In such cases, a meta-stable film of fluid was observed, as shown in Figure 18. Such a film was typical for holes B and C, while for hole A it usually collapsed earlier. This indicates that the stability of the film of fluid is related to the width of the hole. Meta stable films, as seen with water and DEG in holes B and C, were not observed with decane.

![Figure 18: Liquid film of water attached to top face of hole A during emersion. The menisci at the small strips aside of hole A are clearly pulled up by the film in the top of hole A.](image)

Dewetting from the bottom edge of the hole during emersion, near depth position 6 mm as marked with E-III, does not occur as abruptly as predicted. The other fluids show similar dewetting curves with effects as described above.

Two series of additional tests with variation of emersion speed were conducted in order to better establish the observations on this metastable film formation. The series of tests are the same glass in water tests as described at the end of section 2.4.2. In both series the receding angle was always 0°, which corresponds to a predicted maximum for a stable film height of 5.42 mm. At such condition, the minimum plate thickness required for avoiding the two film that surfaces press against each other is 2.88 mm as can be seen in Figure 19 where the shape of the film suspended from a perfectly wetted horizontal plane is shown.
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Figure 19: Shape of film surface (height $\zeta$) and local surface orientation (angle $\phi$) as a function of the horizontal coordinate $\chi$ for a water film suspended from a perfectly wetted horizontal surface.

This requirement is clearly not fulfilled with our glass plate of 1.1 mm thickness. In Table 3 the range of film heights at rupture (i.e., the minimum and maximum values of 5 tests) are shown for a range of emersion speeds. The most typical feature is that film rupture heights at any condition show a fairly large range, of which the minimum heights under quasi-static speed conditions are close to the calculated stable height of 5.42 mm (although the plate thickness is too low).

Table 3: Ranges of the metastable film height at rupture in holes A and B (in mm), for the emersion of a glass plate out of water for regularly cleaned and for very carefully cleaned components.

<table>
<thead>
<tr>
<th>Immersion speed $\mu$m/s</th>
<th>Regularly cleaned glass in water system</th>
<th>Plasma cleaned glass in water system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hole A</td>
<td>hole B</td>
</tr>
<tr>
<td>10</td>
<td>5.0-6.2</td>
<td>5.5-6.8</td>
</tr>
<tr>
<td>30</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>100</td>
<td>5.5-6.8</td>
<td>6.4-8.5</td>
</tr>
<tr>
<td>300</td>
<td>5.3-7.3</td>
<td>6.9-8.3</td>
</tr>
<tr>
<td>1000</td>
<td>5.6-10.5</td>
<td>6.1-10</td>
</tr>
<tr>
<td>3000</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

With higher speed, the contact angle is not expected to deviate from zero; nevertheless the minimum heights increase gradually, but the range increases much more. With the regularly cleaned system the maximum range values are systematically
larger than those for the plasma-cleaned system. This suggests that the surface and/or the liquid is more pure in the latter case. The difference between both series is not pronounced at the speed at which most of the tests in this paper were conducted, giving confidence that our tests were not invalidated by surface pollution. Demonstrating whether thin and thick plates have similar minimum rupture heights because the disjoining pressure in the flat part of the film at a thin plate compensates for the local lack in Laplace pressure difference and establishing what determines the width of rupture height ranges goes beyond the scope of this chapter.

2.5 Conclusions

In this chapter, a novel method to investigate wetting and pinning phenomena on edges normal to the flow direction is described and tested. With this method accurate measurements of pinning force, pinning position and contact angle can be performed in the same measurement. A rather large advantage is that emersion pinning processes can be studied with the same method, in contrast with the optical techniques currently used.

The experimental work was complemented with a theoretical description of the pinning forces in the wetting and dewetting processes. Also the effect of arching on pinning phenomena is discussed and experimentally retrieved. In most aspects, theoretical predictions match well with experimental findings. Deviations found were due to artefacts generated in sample shaping procedures and could be explained semi-quantitatively. Most tests were conducted under quasi-static conditions; a limited number of higher speed tests indicate what can be expected at higher speeds. In particular, metastable films appeared in the emersion process, with a pronounced stochastic rupture mechanism leading to a larger spread in rupture heights at higher speeds.

A benefit of the measurement method is that it can provide extra information about the liquid wetting behavior on substrate imperfections; obtaining such information with other methods can be a great challenge. The empirically known effects of locally lower or higher contact angle on liquid flow could be visualized well. Also the effects of local surface roughness and locally increased surface polarity could be measured semi-quantitatively with the methodology used.
We conclude that this methodology can be used to further increase the knowledge on fluid behavior on macroscopic scale structured substrates, also with more complex fluids than used in this study.
References


24. M. H. Sentis, Journal of Physics 9, 384 (1890)
Appendix 1: Arching at corners

Up to now we ignored if corners between vertical faces of the plate have any effect on the vertical surface tension force. Such effect might be suggested by the fact that at corners the contact line bends downward for wetting conditions (or upward for $\theta > 90^\circ$). For concave corners like for a cuboic, Fowkes and Hood (17) summarized approximated solutions for the local lowering of the vertical position of the contact line of a wetting liquid at the corner, which they called “arching”. Scott et al. (18) evaluated this arching numerically for the 90° corner between the side faces of a rectangular cuboic aligned along the Cartesian coordinates. From their results it can be concluded that the arching reduces the absolute value of $\zeta_c$ at a side face by approximately 40% (this value changes gradually from 44% at 1° to 34% at a contact angle of 75°), both for wetting and for non-wetting cases. We will, to some extent similar to the analysis of Loos (20), investigate the effect of arching on the vertical surface tension force by examining at what happens to this force when the horizontal, ‘undisturbed’ contact lines EF and FG (dotted blue lines) at the side faces of the partly submerged cuboic in Figure 20 are deformed into curved contact lines (solid blue) due to arching at the corners. Note that a Wilhelmi plate can be seen as a thin cuboic, for which the arching will be much more than ~40%.

![Figure 20: Surface forces components for a piece ds of an arching contact line.](image)

Suppose that, due to arching, the piece dx of a contact line if arching was absent is deformed into a piece ds as shown in Figure 20. The surface tension induces a force at the side face of the cuboic, of magnitude $\gamma ds = \gamma dx / \cos \beta$ normal to the contact line, and
within the liquid surface, of which the angle it makes with the side face is equal to the contact angle $\theta$. This force is represented by vector AC which is in the plane defined by ABCH, this plane being normal to the local contact line direction, thus also normal to the side face of the cuboic. When decomposing this force into forces $AB = (\gamma \cos \theta) dx / \cos \beta$ and BC, it is clear that BC does not contain any vertical force component. The vertical component AD of the force AB is both in the surface of the cuboic and in plane ADKH. It is found on multiplying AB by $\cos \beta$, thus the vertical component of the surface tension force acting on $dx$ is $(\gamma \cos \theta) dx$, a value which is exactly the same as if arching were absent, in which case the corresponding surface would act on $dx$.

When we approximate a vertical edge, i.e., the shape of the connection between two neighboring vertical faces of the cuboic, by a series of little segments of vertical cylindrical surfaces, the contact line along such edge can be seen as the sum of infinitesimal straight-line pieces $ds$. For any of such $ds$ the same analysis as given before applies, thus again, the vertical force of such $ds$ is given by the corresponding $(\gamma \cos \theta) dx$. Thus, the total vertical surface tension force on a vertical suspended plate is given by multiplying $\gamma \cos \theta$ by the horizontal circumference the plate, for which the corresponding mathematical value $2(t+w)$ is often a good approximation.

Corner effects have in the past been suspected (24) as sources of deviation from equation 2, even after Laplace’s conclusion that such deviation is not predicted (14). The simple qualitative argument comes from looking at the weight of the liquid in the meniscus (which directly corresponds with the surface tension) around the corner: one might suspect it to be larger than that of the meniscus weight along a flat plate, because of the stretching of the meniscus around the corner. However, the arching lowers the local meniscus height at the corner, just compensating for the effect of stretching on the meniscus weight. A detailed evaluation of the meniscus volume at a corner based on its shape requires numerical analysis (18, 20) while in this appendix an alternative, straightforward route is presented, by looking at the contact line force. The contact line force, together with the pressure force at the base of the plate (buoyancy), are the only vertical forces that the liquid can transmit to the plate. As both parameters are independent of the meniscus shape, the buoyancy force is not affected by corner effects at vertical edges. In conclusion, the arching involved at vertical edges has no effect on the vertical surface tension and buoyancy forces of an immersed plate.
3 Forced ink flow in flexographic printing

In this chapter, a method is described to study the forced flow of ink down the vertical sides of a structure on a substrate in flexographic printing. The method comprises the use of UV-cureable ink which is cured directly after printing on top of a structured surface, in combination with SEM imaging of the sides of the structure on the surface. This analysis method leads to novel insights into ways to reduce line broadening in print processes. Using this method, the highly dynamic print process can be investigated and print conditions optimized for the use of flexographic printing in functional applications. It was shown that line broadening can be reduced to approximately 2 μm in this way.
Chapter 3

3.1 Introduction

Printing is a method to transfer a pattern of ink from an original template onto a substrate, creating a copy of the pattern with the properties of the ink, which in graphical printing is typically a color. Rotary printing technologies can continuously transfer an ink pattern onto a long flexible substrate. This substrate is typically a roll of foil or paper, which is rolled off before the printing station, and rolled up again after the printing station, a process called roll-to-roll printing. The roll-to-roll printing process speed and quality has been continuously developed further for graphical printing applications. This development has resulted in a very low cost per pattern deposited at increasing quality in terms of resolution and pattern deformation, at a process speed that can be as high as several meters per second.

This combination of low cost and increasing resolution makes the roll-to-roll printing process a possible alternative for lithographic application of functional patterns in various applications. For each functional application there are three prerequisites that must be met together for the application to be a success. Firstly a functional ink is needed, which must deliver the desired function and must be compatible with the printing process. Secondly a substrate is needed, which must be able to withstand the printing process and must be compatible with the processes required to deposit an additional functional layer before and after the printed layer. The third prerequisite is to have a printing process which delivers the required resolution in combination with the ink and substrate used.

The focus of our investigation is the flexographic printing process, which is schematically shown in Figure 21. In flexographic printing, ink is metered by a doctor blade into regular recesses of a rigid roll (the Anilox roll), and transferred onto a semi-flexible patterned Flexo print roll which is then pressed against the substrate by an impression cylinder, thereby transferring the pattern of ink.
It can be understood that a flexible substrate can be roll-to-roll printed, but an important advantage of flexographic printing is the semi-flexibility of the Flexo print roll, which enables printing on rigid substrates which are not perfectly flat. A further advantage of flexographic printing as compared to gravure or gravure offset printing is that the Flexo print roll is much easier to produce than a gravure roll, and thus has much lower cost. Recent advances in production of ceramic Anilox rolls with closer spaced recesses enable lower ink amounts to be used for finer details. The production of Flexo print rolls from materials which also enable higher resolution (2) have increased the potential for the use of flexographic printing in functional applications.

Within the flexographic ink process, we will investigate the process parameters that control ink flow in both the transfer of ink from Anilox to the Flexo print roll, as well as the ink transfer process from Flexo roll to the substrate. This is important as undesired flow of ink in these processes can lead to line broadening and other quality deteriorating phenomena. The flow of ink is a highly dynamic process, and we have developed a specific approach to visualize ink flow as a function of process parameters.

The approach is to use a non-structured Flexo print roll and print UV-curable ink onto a glass substrate with randomly positioned acrylic walls on top of it, as shown in Figure 22. The ink is deposited on top of the structure and can flow to either side of the structure. By immediately curing the ink after printing, the ink flow as a result of the ink

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**Figure 21:** Schematic depiction of the flexographic print process, taken from (1).
transfer process is ‘frozen’ and the ink flow can be investigated offline using SEM imaging.

Figure 22: Structures used as printing substrates; Left: A random pattern with features between 200 and 600 μm; Right: A close-up.

It can be seen that the top of the structure is smooth and slightly rounded, and the sides of the structures are rough. We expect that the influence of these substrate features on the ink flow process is minimal. Variations in ink viscosity, ink volume and print pressure were made to assess in which regime the downward flow of ink, and thus line broadening on a flat substrate, would be minimal.

From these investigations several hypotheses on the factors governing the interaction of fluid, Anilox roll, Flexo print roll and substrate interfaces were formulated. The hypotheses formulated were also argued to be valid in the situation of a structured Flexo print roll in combination with a flat substrate. The conclusion is that flexographic printing can have minimal line broadening when using the proper printing regime.

3.2 Theoretical background

First the flexographic printing process is described in more detail. Thereafter the physical effects that influence the flow of ink during the printing process are described.

3.2.1 Flexographic printing process

The first part of the flexographic print process is metering the correct amount of ink into the Anilox roll by the doctor blade, as illustrated in Figure 23. The lineature of the Anilox roll is the number of wells per cm, which in conjunction with the depth of the wells, determines the ink volume. This lineature can range from 40 lines per centimeter (l/cm) up to 1200 l/cm. The size and depth of the wells determine the volume of the
Anilox roll, given in ml/m²; typical values are between 1 and 20 ml/m². The filling process of the wells is controlled by parameters like the pressure between doctor blade and Anilox roll and the movement speed of the doctor blade relative to the Anilox roll.

**Figure 23:** Filling the Anilox wells with a precise fluid amount by metering using a Doctor blade.

It is assumed that filling of the Anilox with ink by this process proceeds without deviations due to ink flow underneath the Doctor blade or shear induced flow effects using non-Newtonian fluids. The final stage of the metering process is an Anilox roll completely and homogeneously filled with the chosen ink to the defined volume of the pattern on the Anilox roll, independent of the rheological properties of the ink.

The second part of the flexographic print process is ink transfer from the recesses in the Anilox roll to the Flexo print roll. The Anilox roll is pressed onto the Flexo print roll with adjustable force, the Anilox force. This transfer is influenced by bulk properties of the ink such as viscosity, as well as interface properties of the ink, such as surface tension and contact angle of the ink with Anilox and Flexo print roll material. The transfer process where wetting, dewetting and generation of new interfaces occur in rapid succession is depicted schematically in Figure 24.

**Figure 24:** The ink transfer process from Anilox roll to Flexo print roll and the interfaces that play a role in this process.
As can be seen, the ink splitting process that generates new ink surface between Anilox and Flexo print roll needs the surrounding air to separate the fluids. This process takes place on a microsecond time scale, which complicates experimental investigations.

This ink transfer onto the Flexo print roll is a process comparable to gravure printing, where the ink from the gravure is directly transferred to the substrate. A great deal of computational fluid dynamics work has been performed by many authors (3-10) to elucidate the mechanisms in play for this printing technology. A volume of fluid model, described by Powell (11), was used to describe the ink splitting process, and non-Newtonian properties of the ink were incorporated using the Carreau model (12). In all studies an agreement could be obtained with experimental data using a given type of ink, but the relative importance of viscosity, contact angles, groove angle and depth and transfer time varied considerably from one model to the other. This is an indication that non-modeled parameters can play a large role.

The roughness of the ink well and substrate are two of those factors that are hard to model but influence the interface area between ink and surface significantly, and thus the interfacial energy. At the same time, the roughness of these interfaces also determines the possibility of entry and exit of air between the Flexo print roll and the Anilox roll to a large extent. This entry and exit of air is an important influencing factor on the generation of new ink surface. As a consequence of the curvature of both the Anilox roll and the Flexo print roll, one side of the ink well is exposed to air earlier than the other side. This may also influence the speed and directionality of ink flow from Anilox well to Flexo print roll.

Last but not least the wetting of the ink on the Flexo print roll is a process that does significantly influence the ink distribution, and can be modeled in the same way, but is just as complicated to verify experimentally. We use a non-structured Flexo print roll in our investigations because we focus on the ink flow on the substrate. Conceptually, the ink distribution on the Flexo print roll can be seen as a collection of droplets, which size and spacing is determined by the lineature of the Anilox roll and the volume of the individual wells in the Anilox roll. The ink distribution on the Flexo print roll directly after contact with the Anilox roll is given in Figure 25. In the printing process, the droplets on the Flexo roll can spread and coalesce, depending on the surface and ink properties.
The third part of the process is transfer of the ink from the Flexo print roll to the substrate, using a print force that can be adjusted. Much research has been performed on the effect of process parameters and ink parameters on print quality on paper (13-18), while investigations on non-porous surfaces are absent. The print quality is amongst others described by dot gain, which is the area of an ink dot on the substrate divided by area of the dot defined on the Flexo print roll. The dot gain on paper was related to ink viscosity and print pressure, but the influence of the paper type (coated, non-coated) and paper porosity were found to be very significant. This is due to capillary forces, which ‘pull’ the ink from the Flexo print roll into the pores of the substrate. A schematic representation of the ink transfer process, where the black arrows indicate movement of Flexo roll surface and ink surface is given in Figure 26.

Spreading of ink (capillary and pressure assisted) and splitting of the ink surface between Flexo roll and substrate take place during the third part of the Flexo printing process. The grey arrows indicate capillary spreading in case of a porous substrate.

**Figure 25:** Droplet distribution of ink on the Flexo roll directly after contact with the Anilox roll: left: Anilox roll with 60 lines/cm, right 710 lines/cm.

**Figure 26:** Ink transfer from Flexo print roll to porous substrate. Black arrows indicate movement of Flexo roll surface and of ink surface; Grey arrows indicate capillary spreading of ink into the porous substrate.
In our investigation we exclude the capillary flow of ink into the substrate by using non-porous materials, but capillary effects on the flow between substrate and Flexo print roll still occur. As the ink from the Anilox wells is initially deposited in separate droplets on the Flexo print roll, sideways flow over the substrate structure due to the capillary formed between Flexo print roll and structure is possible, as shown in Figure 27.

![Figure 27: Capillary flow of ink between Flexo print roll and top of the structure on the substrate.](image)

It can be seen that the distance between the centers of the droplets is dependent on the lineature of the Anilox, and the size of the droplets is dependent on the Anilox volume when all other parameters remain the same. Even though it is clear that the situation depicted above is not in a steady state, an approximation of the contribution of capillary flow can be made using equation 1 for two-dimensional steady laminar parallel flow between parallel plate (19):

$$t = \frac{3\eta L^2}{h\gamma \cos \theta}$$

(1)

with time $t$ as a function of flow distance $L$, gap height $h$, viscosity $\eta$, ink surface tension $\gamma$ and contact angle $\theta$ of ink with the surface. Equation 1 can be rewritten to yield flow distance $L$ as a function of the time $t$:

$$L = \sqrt{\frac{ht\gamma \cos \theta}{3\eta}}$$

(2)

with $h$ ranging between 2 and 6 µm, $\gamma = 30$ mN/m, $\cos \theta$ close to 1, $\eta$ between 600 and 6000 mPa·s, and a time $t$ of 0.1 ms, this results in a capillary flow distance $L$ that ranges
from 0.5 µm to 4 µm. The lateral flow of ink on the top of the structure is thus largely
dependent on the print force, which generates a pressure on the ink between the Flexo
print roll surface and the substrate. An exact calculation of the print pressure obtained is
not possible because the deformation of the Flexo print roll also dissipates part of the
force, limiting the pressure on the ink.

Novel rheological measurement technologies are being developed to study this type
of flow under pressure at high shear rates (20-22), which could be used to give a direct
relation between flow of the ink and the contact pressure. However, in our case the
contact pressure due to the print force applied is not known exactly, hence this
technology is not applicable.

An important aspect to touch on qualitatively is the fact that the contact of the ink
between the rotating Flexo print roll and the substrate is asymmetrical, which means
that several physical effects that determine the ink flow can vary in space and time. The
use of a non-structured Flexo print roll in combination with a structured substrate allows
visualization of the effects of these asymmetries on ink flow, as explained in the next
section.

3.2.2 Physical effects influencing ink flow

The timing asymmetry in ink contact between Flexo roll and the substrate due to the
curvature of the Flexo print roll has several implications on the physical effects that
govern ink flow. Some relevant parameters that are asymmetric due to this difference in
timing of contact are, in arbitrary order: Capillary pressure, print pressure, interfacial
tension at the interfaces that are formed dynamically, compression of the Flexo roll,
shear dependent viscosity of the ink. The influence of the geometry of the Flexo print
roll on contact between ink with the leading and trailing edge of the acrylic walls is
schematically shown in Figure 28.
Figure 28: Leading and trailing edge of the patterned substrate relative to the Flexo print roll; Left: ink flow down leading edge; Right: Ink flow down trailing edge.

Obviously the ink on Flexo roll has contact with the leading edge before the ink contacts the trailing edge. With a print speed of 0.2 m/s and a structure width of 10 μm, the time interval between leading and trailing edge is approximately 20 μs. During this time, the interface between Flexo roll, air and substrate on the leading edge is significantly different than at the trailing edge, resulting in different interfacial tensions and capillary forces, which have an effect on the ink flow. Furthermore, the shear on the ink is different between leading edge and trailing edge, also affecting the flow of ink. The flow of ink is visualized using a UV curable ink, that is frozen in place within a second after the printing process, and is then analyzed using SEM imaging of both sides of the acrylic structure. It is assumed that the flow of ink without Flexo roll contact can be neglected due to the rheological properties of the ink. From the measured differences in downward flow length along both vertical sides, an estimation of the downward ink wetting flow speed can be made, using the estimated ink contact time difference between the two sides. A schematic representation of this downward flow of ink down both vertical sides is given in Figure 29.
Forced ink flow in flexographic printing

Figure 29: Ink flow down both sides of the structure as a function Flexo print roll position in time.

The ink layer already creates a meniscus with the leading edge at Flexo print roll position 1, and only at Flexo print roll position 3 the meniscus with the trailing edge is formed. As estimated, a contact time difference of 20 μs in forced ink flow between trailing and leading edge is present, which results in a longer downward flow length on the leading edge than on the trailing edge. The shape of the Flexo print roll that determines the timing difference is dependent on the flexibility of the roll and the print force used, as the Flexo print roll can be deformed to a limited extent. This implies that the downward flow on both vertical sides of the structure can be influenced by the printing force used, in addition to the ink viscosity and Anilox roll properties.

3.3 Experimental

A flexographic printing tester F1-100 of IGT (Amsterdam) was used to execute the print tests. A photo of the equipment is given in Figure 30, showing the positions of Anilox roll, Flexo print roll, doctor blade and substrate holder.
As can be seen this tester is not a real roll-to-roll printer, but a practical laboratory device for printing. Ink is manually deposited between the doctor blade and Anilox roll before each print. The specifications of the Anilox rolls used are given in Table 4, for more explanation see section 3.2.1.

**Table 4: Characteristics of Anilox rolls used in combination with the IGT F1-100 setup.**

<table>
<thead>
<tr>
<th>Anilox code</th>
<th>IGT number</th>
<th>Material</th>
<th>Ink volume (ml/m²)</th>
<th>Lineature (l/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>402.227</td>
<td>Chrome plated copper</td>
<td>5, 7, 9, 12</td>
<td>140-60</td>
</tr>
<tr>
<td>B</td>
<td>402-212</td>
<td>Chrome plated copper</td>
<td>16</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td>402-418</td>
<td>Ceramic</td>
<td>2.7</td>
<td>180</td>
</tr>
<tr>
<td>D</td>
<td>402-425</td>
<td>Ceramic</td>
<td>2</td>
<td>710</td>
</tr>
</tbody>
</table>

A non-structured Nylotex ACT1.7 material from Flint group (Luxembourg) was used for the Flexo print roll top surface except for the investigations into the effect of surface energy of the Flexo print roll on ink transfer from Anilox roll to Flexo print roll. For these investigations a polyimide foil of 100 µm thick was fastened onto the Flexo print roll with tape. The foil is hydrophobic, but was made hydrophilic in some cases using an oxygen plasma in a March (USA) AP1100 at an oxygen pressure of 100 Torr using 450 Watt RF power for 300 seconds. The foil was manually released and UV cured directly after transfer of ink from Anilox roll to Flexo print roll. The time which passed between transfer of ink and curing was between 0.5 and 1 minute.
Zeller & Gmelin (Germany) Flexo UV-curing ink Uvalux Y77-P400 and offset ink Uvaflex U40-P400, both 100% acrylic formulations with submicrometer dye particles, were used in different mixing ratios to investigate printing with a range of viscosities. The viscosity of the mixed inks was measured using an Anton Paar (Austria) MS300 Rheometer with cone-plate measurement system CP50-1 in controlled shear stress mode, with shear stress measured from 1 to 180 Pa. The viscosity of the different mixing ratios at maximum shear stress is given in Table 5. The fluids are Newtonian above a shear stress of 50 Pa except for fluid 5, and the tested range of viscosity covers 2 decades, from 0.5 Pa·s to 50 Pa·s.

Table 5: Viscosity of ink formulations used.

<table>
<thead>
<tr>
<th>Ink number</th>
<th>Uvalux Y77-P400</th>
<th>Uvaflex U40-P400</th>
<th>Viscosity (180 Pa shear stress)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 g</td>
<td>0 g</td>
<td>500 mPa·s</td>
</tr>
<tr>
<td>2</td>
<td>100 g</td>
<td>55 g</td>
<td>2.1 Pa·s</td>
</tr>
<tr>
<td>3</td>
<td>100 g</td>
<td>80 g</td>
<td>2.8 Pa·s</td>
</tr>
<tr>
<td>4</td>
<td>100 g</td>
<td>500 g</td>
<td>21 Pa·s</td>
</tr>
<tr>
<td>5</td>
<td>0 g</td>
<td>100 g</td>
<td>53 Pa·s</td>
</tr>
</tbody>
</table>

Flexographic printing with pure Uvaflex U40-P400 was not possible due to the high viscosity, and only inks 1 to 4 were used for the printing tests.

The printed ink was cured by transporting the substrate underneath a Fusion 300 H-bulb at 0.3 m/s, which produces an intensity of 4 watt / cm² at a distance of 2 cm.

Non-structured polyimide foil substrates of 100 µm thick were used to assess printed layer thickness and ink distribution. The ink distribution on the foil substrates was determined using a Wyckco NT1100 white light interferometer (WLI).

Irregular honeycomb like structures, as shown in Figure 22, with wall heights of 50 µm or 100 µm and wall width of 10 µm were manufactured on glass using lithographic techniques in the facilities of Philips Innovation Services. The substrates were made hydrophilic to ensure low contact angles of ink and consistent ink flow on the wall structures using an oxygen plasma in a March AP1100 at an oxygen pressure of 100 Torr using 450 Watt RF power for 300 seconds.

The glass substrate with honeycomb structures were cut to 1 × 1 cm² sample size and imaged in a Philips (Netherlands) XL40 SEM with spot 5 at 3 kV under an angle of 60º with the beam, both on leading and trailing edges of the structures.
3.4 Results and discussion

First, the transfer of ink from the Anilox roll to the Flexo print roll interface is presented, with main focus on effects of volume, viscosity and interface wetting properties. Especially the influence of wetting and flow properties are discussed, supported by ink distribution data on flat substrates directly after printing. This is the input for the subsequent description of the transfer from Flexo print roll onto the structured substrate as a function of printing force, ink viscosity, ink amount and ink distribution. In section 3.4.2 the regime of Anilox volume above 10 ml/m² on these substrates is presented, in section 3.4.3 the results in the regime of Anilox volume below 6 ml/m² are given.

3.4.1 Transfer of ink from Anilox roll to non-structured surfaces

The film thickness transferred onto the Flexo print roll using the polyimide foil as a temporary Flexo print roll surface was investigated with ink composition 1. The Anilox ink volume was varied between 2 and 16 ml/m² using Anilox A, B and D. The Anilox force between the Anilox roll and the Flexo roll was set to 10 N or 100 N, respectively, and both a hydrophilic and hydrophobic polyimide foil were used as Flexo roll surface. Time between ink transfer and UV curing of the ink on the polyimide surface was between 30 and 60 seconds, significantly more than the fraction of a second in normal printing. A typical WLI image used for extraction of layer thickness with ink composition 1 is given in Figure 31. A line scan from non-covered polyimide foil to ink covered foil was taken, where an average of the height over 0.2 mm length from unprinted (open triangle) and printed area (black triangle) was used. The distance between non covered and covered foil was minimized to <0.5 mm, to limit the effect of foil warpage on the measured height.
Forced ink flow in flexographic printing

It can be seen that the droplets of ink 1 which are deposited on the hydrophobic polyimide foil form a continuous ink layer, as the viscosity is lowest, and 30-60 seconds flow time is available. The ink thickness is obtained by subtracting the height of the foil substrate from the measured height. It can be seen that the ink thickness taken from this spot is representative for the first mm of ink deposited. Ink thicknesses as a function of Anilox volume indicating the effect of Anilox force and Flexo print roll interfacial tension effects are given in Figure 32. A spread in the values of ±0.25 μm can be assumed.

It is clearly visible in Figure 32 that within each test series the deposited layer thickness on the Flexo print roll is increasing with the Anilox volume up till a volume of 12 ml/m², where the maximum layer thickness converges to just above 4 μm. This
regime of high Anilox volume is evidently insensitive for changes in Anilox force and interfacial tension of the Flexo pint roll.

For the lower Anilox volumes tested, it can be seen that increasing the Anilox force from 10 N to 100 N leads to approximately 30% reduction of the transferred ink layer thickness. The effect of using a hydrophilic Flexo print roll is that the transferred ink layer thickness is also about 30% lower than when using a hydrophobic Flexo print roll.

A possible explanation for the lower ink transfer to the Flexo print roll with higher Anilox force is that capillary flow of ink onto the area between Anilox wells is more difficult. With low Anilox force, the Flexo roll is not deformed significantly, allowing flow of ink from at least one side of the Anilox well between Anilox surface and Flexo roll surface, as drawn schematically in the left of Figure 33. With higher applied Anilox force, the increased Flexo print roll deformation can obstruct the ink flow paths at both sides between the Anilox roll and the Flexo print roll, thus reducing the amount of ink transferred, as indicated in the right side of Figure 33.

Figure 33: Capillary wetting onto the area between the Anilox wells; Left: Low Anilox force; Right: High Anilox force.

The 30-60 seconds delay in curing the ink deposited on the Flexo print roll prevents testing of this hypothesis directly, as the flow of ink can be significant, certainly of low viscosity ink 1. The effect of Anilox force on ink distribution on the Flexo roll was therefore indirectly tested by printing on a flat substrate using ink 4. In this way the time between ink transfer and curing is reduced to <1 second, and minimal print force of 40 N between Flexo print roll and substrate was used to disturb the ink pattern on the Flexo roll as little as possible during the printing process. The high viscosity of ink 4 also reduces the unforced flow, so it is assumed that the ink distribution on the Flexo print roll as a function of Anilox force does not change significantly upon printing on a flat substrate, and is a good indication of the ink distribution on the Flexo roll. A very clear difference in ink distribution printed on the flat substrate with Anilox force at an Anilox volume of 7 ml/m² is shown in Figure 34, where blue is the height of the substrate, and yellow to red the ink height.
It can be clearly seen that at higher Anilox force, the ink is completely geometrically arranged, a copy of the Anilox well pattern. At low Anilox force, the ink is distributed also in between the Anilox well pattern. This supports the hypothesis that capillary flow between Anilox surface and Flexo roll surface can take place at low Anilox force, and is more difficult at higher Anilox forces. The same test has also been executed with high Anilox volumes, and here the ink distribution also changes as a function of the Anilox force, but the ink contact area does not change significantly, as is visible in Figure 35.

From the more regular pattern in the left side of Figure 35 it can be seen that the ink represents the Anilox pattern better when using higher Anilox forces, also with higher Anilox volumes. At the same time, the large amount of ink transferred allows the flow of ink between the individual droplets on the Flexo print roll during the printing process, even with highly viscous inks. In this regime, the effect of capillary flow of ink between Anilox roll and Flexo print roll is not dominant for the amount of ink transferred.
A possible explanation for the lower ink transfer onto the hydrophilic Flexo print roll surface than onto the hydrophobic Flexo print roll surface is the wetting energy of ink on the Flexo print roll surface in comparison with the Anilox surface. If the wetting energy of the ink with the Anilox surface is lower than the wetting energy of the ink with the Flexo print roll surface, less ink will be transferred to the Flexo print roll surface. An indication that this is indeed the case for hydrophilic polyimide surface was obtained by measuring the contact angle of ink with hydrophilic and hydrophobic polyimide surface under water. The water represents the hydrophilic Anilox surface in this measurement. The contact angle of ink on hydrophilic polyimide film under water was more than 90º, while it was 45º on the hydrophobic polyimide film. This difference in wetting energy evidently also obstructs flow, similarly as physical obstruction discussed before. This indirect measurement supports the influence of wetting energy of ink in the ink transfer process.

From these results on the ink transfer onto the Flexo print roll, it can be deduced that the ink distribution on the Flexo print roll with high Anilox volumes is significantly different from that with low Anilox volumes. The large initial contact area of ink between Flexo print roll and Anilox roll at high Anilox volumes can result in a dominant effect of applied force on the transfer process, and little influence of other variables on the transfer process. At lower Anilox volumes, the interfacial tension driven flow effects may be dominant in the ink transfer process. This difference observed is the reason to also present the results for these two Anilox volume regimes separately in section 3.4.2 and 3.4.3, respectively.

3.4.2 Ink distribution on structured substrates: high Anilox volume

The print behavior of inks 1 to 3 as a function of print force on a structured substrate was first investigated in the regime with a high Anilox volume of 12 ml/m², where the amount of ink transferred from the Anilox roll onto the Flexo print roll can be considered as relatively constant, as deduced in the previous section. The goal is to evaluate the effect of printing conditions on the difference in ink flow down the leading and trailing edge of the acrylic structures. After UV curing of the applied ink, the substrates were analyzed in the SEM for ink flow down the sides of the structured surfaces, at both the leading and trailing edge side.
The difference in the distance over which the ink flows down the leading and trailing edge for the different inks and print force combinations investigated are schematically indicated in Table 6. As quantitative data are difficult to extract from the SEM images, the qualitative differences in ink flow distances are indicated using colors, where green indicates lowest difference, and red indicates highest difference.

**Table 6:** Differences in ink flow along leading and trailing edges of the structure: green is least difference, red is largest difference.

| Print force (Anilox force 10 N, Anilox volume 12 ml/m²) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ink             | 40 N            | 125 N           | 300 N           | 500 N           |
| 3               |                 |                 |                 |                 |
| 2               |                 |                 |                 |                 |
| 1               |                 |                 |                 |                 |

It can be concluded that a high print force with low ink viscosity results in the least difference in ink flow length. Beside the difference in ink flow length on leading and trailing edge, the evenness of the downward ink flow on each edge is also changed with the printing parameters in the same way, so lowest viscosity and highest printing force results in best ink flow evenness per side. A representative example for large difference and unevenness is a print with ink 3 using Anilox A with 12 ml/m² with Anilox force of 10 N and print force of 125 N, as shown in Figure 36, where the leading edge is imaged and Figure 37, where the trailing edge of the same substrate is imaged.

**Figure 36:** Variation in downward ink flow along the length of the leading edge of the vertical structure, using ink 3 with Anilox A with 12 ml/m², Anilox force of 10 N, and a print force of 125 N.
The white line is drawn as a guide to the eye, indicating the ink front. It can be seen that the ink has flown down the rough vertical surface of the structured substrate in a thin layer and has smoothed out the roughness in the substrate material. The variation in the ink distribution along the length of the leading edge can be due to the fact that the ink is distributed in droplets on the Flexo print roll. The distance between two ink droplets in Anilox A at 12 ml/m² is 160 μm, and with ink 3 these droplets likely do not coalesce completely, resulting in uneven availability of ink to flow down the sides of the acrylic structures. Another observation is the greater ink flow in the corner between two straight structures, which is due to capillary forces in the edge as touched upon in chapter 2.

The difference in downward ink flow length between the leading and trailing edge is also large, as can be seen in Figure 37, where the trailing edge from the same substrate is imaged. It can be clearly seen that the ink does not flow over the trailing edge of the structured substrates over the whole length of the structure.

![Figure 37: Variation in downward ink flow along the length of the trailing edge of the vertical structure, using ink 3 with Anilox A with 12 ml/m² and a print force of 125 N.](image)

The same unevenness in the downward length of the ink front along the length of the acrylic structure is observed as in Figure 36. The much lower overall downward ink flow on the trailing edge relative to the leading edge is due to the fact that the ink contacts the leading edge earlier than the trailing edge. In this time, a significant amount of ink has already flown down the leading edge, leaving little ink to flow down the trailing edge, even in the corner. This is a confirmation that the differences in ink flow as explained in section 3.2.2. for leading and trailing edge can be large due to the asymmetry in contact between flexo roll and substrate, and are also dependent on substrate geometry, such as a corner.
It is clear that the combination of high print force and low viscosity leads to the lowest difference in ink flow between leading and trailing edge, although the absolute downward flow length is large. This can probably be explained that with high print force the Flexo print roll is deformed significantly, decreasing the wedge as indicated in Figure 28. The subtle differences in ink flow between trailing and leading edge are indicated in Figure 38, where the white circles indicate some uncoated areas, and the white rectangles indicate some flow of ink onto the glass.

It can be seen that ink flow onto the glass is only visible in the corners, and that both on trailing and leading edge some patches of the walls remain uncovered. Beside the effect of deformation of the Flexo print roll, the small difference in ink flow is probably due to the fact that ink 1 has the lowest pseudoplasticity, and thus reacts quickest on the printing forces applied.

A feature of the structure which limits downward flow over the glass structure is an edge close to the glass surface as indicated with the white squares in Figure 38. This edge is basically a pinning structure as explained in Chapter 2, presenting a barrier for the downward ink flow, and schematically shown in Figure 39.
The effect of time between printing and curing was found to be insignificant on downward ink flow. From the observed 80-100 μm downward ink flow during the contact time of approximately 0.02 ms (with print force of 500 N), it can thus be concluded that the forced ink wetting process proceeds at a speed of 4-5 m/s. The average downward flow of ink 3 at 125 N of only 15-20 μm shows a downward speed of about 1 m/s, with a variation between leading edge and trailing edge of >50%.

### 3.4.3 Ink distribution on structured substrates: low Anilox volume

The print behavior of inks 2 to 4 as a function of print force was investigated with a lower Anilox volume of 5 ml/m$^2$ and lineature of 140 l/cm. In this regime the amount of ink on the Flexo print roll is more dependent on the process conditions, and these can be changed to obtain the lowest downward flow difference between leading and trailing edge. Thereafter, the effect of Anilox rolls with a higher lineature on the unevenness of flow down the length of the edge was investigated. In all tests the Anilox force was kept at 10 N to assure maximum ink contact area on the Flexo print roll.

The downward ink flow differences between leading and trailing edge, as well as the evenness of ink flow within one edge for the different inks and print force combinations investigated are schematically indicated in Table 7. As quantitative data are difficult to extract from the SEM images, the qualitative differences in ink flow distances are indicated using colors, where green is smallest difference and red is largest difference.

<table>
<thead>
<tr>
<th>Inks</th>
<th>Print force (Anilox force 10 N, Anilox volume 5 ml/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 N</td>
</tr>
<tr>
<td>4</td>
<td>![Green]</td>
</tr>
<tr>
<td>3</td>
<td>![Yellow]</td>
</tr>
<tr>
<td>2</td>
<td>![Red]</td>
</tr>
</tbody>
</table>

It can be seen that in the low Anilox ink volume regime the exact opposite is observed as with high Anilox ink volume. The combination of high viscosity and low print force give the least difference in ink flow lengths between leading and trailing...
edge. A hypothesis for the low difference in downward flow between leading and trailing edge can be that the lower ink height reduces the asymmetry in contact between Flexo roll and substrate, and that increased viscosity increases this effect. Some remaining unevenness was observed along the length of the structures, as can be seen in Figure 40. The periodicity of the unevenness corresponds well with the distance between Anilox wells of 60 µm, resulting in similar droplet distances on the Flexo print roll.

![Figure 40: Downward flow of ink 4 printed with Anilox roll A, 140 lines/cm, 5 ml/m², 40 N printing force; Left: Trailing edge; Right: Leading edge.](image)

The downward flow of ink is reduced in this case both because less ink is available to flow, and the viscosity of the ink resists the flow more. Decrease of the applied print force is the third factor that results in the low downward ink flow obtained. As can be seen by the ink front flow line in Figure 40, the unevenness in ink flow occurs with a period of approximately 60 µm, which corresponds to the lineature of the Anilox roll used. Increasing the Anilox lineature should decrease these remaining fluid flow inhomogeneities. Indeed, when increasing the lineature of the Anilox roll from 140 lines/cm to 710 lines/cm, the unevenness decreased significantly, as shown in Figure 41.
Figure 41: Downward flow of ink 4 printed with Anilox roll D, 710 lines/cm, 2 ml/m², 40 N printing force.

It can be seen that the ink front is mainly on the top of the acrylic structure, and a hint of 15 μm periodicity can be observed along the sides of the structure, again corresponding to the Alinox lineature. The maximum downward flow length has decreased to less than 2 μm due to the decreased Anilox volume. The same estimation of force flow speed as performed in section 3.4.2 leads to a forced flow speed of 2 μm in 0.02 ms, or 100 mm/s, which indicates that also this slowed down forced flow process is very dynamic and difficult to investigate using other approaches.

The lineature of the Anilox roll determined the unevenness, and not the Anilox volume, as was checked using Anilox roll C, with comparable volume (2.7 ml/m²) but a lineature of only 180 lines/cm. A periodicity of downward flow unevenness of about 50-60 μm was seen, comparable to that shown in Figure 40. This dominant effect of the droplet pitch on flow inhomogeneity can be due to the fact that the ink droplets are much smaller, which lowers the total surface of the droplets touching the structure, as can be seen in Figure 42. Only the droplets touching the structure (light grey) can flow and coalesce under influence of the print force, the rest remains on the Flexo print roll (dark grey).
Forced ink flow in flexographic printing

The lower contacting droplet surface area lowers the amount of liquid that is available to flow down the sides of the structure on the substrate. At the same time a larger part of the droplet area directly touches the top of the substrate interface, reducing the variation in interfacial tension balance, and the distance between droplets is lower. This may promote capillary sideways flow and droplet coalescence before downward flow over the vertical sides. Before downward flow is possible, the fluidic resistance of the edges of the structures needs to be overcome, and evidently this resistance approximately balances the print force applied in the print conditions used, prohibiting forced downward ink flow. Further quantitative investigation into the fluidic resistance of the edges on the substrate is not possible in this system unfortunately. Using low viscosity fluids and low flow speeds this fluidic resistance can be quantitatively determined, as was explained in chapter 2.

These results indicate that forced flow in flexographic printing can be reduced to less than 2 µm using an Anilox lineature of > 700 l/cm, a viscosity of ink of 20 Pa·s and a printing force of 40 N. With porous substrates, the forced flow results mainly in lateral spreading, leading to line broadening. The hypothesis is that line broadening can thus be reduced to less than 2 µm.

The complete reversal of the process, using a structured Flexo print roll and a non-porous substrate results in a similar ink transfer process, and line broadening limited to ± 2 µm should thus be possible using these print parameters. This should enable printing of 20 µm wide lines with a line width variation of 10%. This resolution is significantly higher than typically needed for graphical applications, and also better than screen print resolutions. These process conditions for minimum line broadening offer the possibility of a significant step forwards in the use of flexographic printing in functional...
applications, where high print speed and relatively low cost can be combined with high resolution.

3.5 Conclusions

For a typical flexographic printing process the print quality was investigated as a function of the ink amount, ink distribution, ink viscosity, Anilox force and print force. The extent of ink flow on the printed substrate was made visible by stopping the ink flow soon after application, UV-curing the ink. The combination with structured substrates allows investigation of the highly dynamic forced wetting processes that occur during roll-to-roll printing techniques. Even estimations of forced wetting speeds occurring in the printing process can be made.

The features that influence the flow of ink can be identified and qualitatively investigated using this methodology. The logical effects of print pressure, ink viscosity and deformation of the Flexo print roll on ink flow stability were confirmed. The importance of the Anilox pressure, interfacial energy of the Flexo print roll and lineature of the Anilox roll on the print quality was also proven.

Process conditions were found that allows printing of structures with a width variation of only 2 µm using flexographic printing. This enables the use of this technology for functional applications. At this low level of width variation the technology compares favorably with inkjet technology on resolution, and with gravure printing on cost.
Forced ink flow in flexographic printing

References


4 Reduction of contact resistance by selective RF heating of silver on silicon

In this chapter, fast and selective inductive heating of pre-sintered silver lines on silicon as present in solar cells using 27 MHz radio-frequency inductive fields is shown. IR measurements of silicon substrates show that above 450 °C the heating rate of the samples increases sharply, indicating that both the silver and the silicon are heated. By moving the substrate with respect to the RF antenna and modulation of the RF field, silicon wafers were heated reproducibly above 450 °C with heating rates in excess of 200 °C/s. Furthermore, selective heating of lines of pre-sintered silver paste was shown below the 450 °C threshold on silicon substrates. The orientation of the silver tracks relative to the RF antenna appeared to be crucial for homogeneity of heating. Contact resistance between silver and silicon using Transmission Line Measurements (TLM) show a clear decrease of contact formation between the silver lines and the silicon substrate. To lower the contact resistance sufficiently for industrial feasibility, a high temperature difference between the Si substrate and the Ag tracks is required. The present RF heating process does not match the time scale needed for contact formation between silver and silicon sufficiently, but the significantly improved process control achieved shows promise for applications requiring fast heating and cooling rates.

1 This chapter is based on W-J. A. de Wijs, S. Ljevar, M.J. van de Sande and G. de With, Journal of Micromechanics and Microengineering 26, 065003 (2016)
4.1 Introduction

The efficiency of silicon solar cells, in combination with their manufacturing cost, determines their payback time. The efficiency is amongst others determined by the contact resistance between the electrically conductive ‘grid’ at the front side of the solar cell. The conductive grid is typically made of screen printed silver paste, which is sintered at high temperatures during a short time in a belt furnace. Investigations into Rapid Thermal Processing (RTP) is a description of faster heating and cooling technologies. In research to increase the performance of crystalline silicon solar cells, RTP was shown to achieve this by mainly reducing the electrical resistance in the contact area between silver and doped silicon \( (1, 2) \). The currently accepted view is that a higher heating rate increases the area in which silver diffusion into the doped silicon emitter layer occurs, which lowers the contact resistance. Depth of the silver diffusion is lowered when the time at peak temperature is shortened, hereby reducing the risk of shunting the doped silicon layer, and allowing the use of shallower doped silicon emitters with higher sheet resistance and lower recombination losses \( (3) \).

Work of Rohatgi \( (3-6) \) on string ribbon Si cells has also shown the contribution of increased hydrogen passivation with high cooling rates, also leading to higher efficiency of the solar cells. This indicates the importance of RTP as a process for improving solar cell efficiency.

The RTP processes that have been investigated are batch processes, not suitable for high throughput manufacturing. A possibility for RTP is induction heating, where a strong electromagnetic (EM) field is emitted by an antenna, which induces electrical (eddy) currents in magnetic and/or conductive materials to counteract this field. The resistive losses that occur in these materials result in heating of the material. Most induction heating processes are performed with a relatively low frequency \( (<100 \text{ kHz}) \), which can be used to effectively heat thick layers of metal. Radio Frequency (RF, \( >10 \text{ MHz} \)) inductive heating can be used to heat thin layers of materials present in solar cells, as pioneered by Pelleg \( (7) \) on sputtered Ta layers on silicon. Pelleg reported that TaSi formation occurs, but that in the stationary experimental setup used, the control of the process is limited by what he calls ‘heat explosions’.

The hypothesis in our research is that the structured silver tracks provide a better basis for a controlled process, as the heating is concentrated in these tracks, while the
Reduction of electrical resistance by selective RF heating

Silicon base material acts as a heat sink. An extra measure of process control is provided by moving the substrate with respect to the RF antenna, thereby controlling the time that the substrate is exposed to the RF field. Furthermore, substrate movement implies a development route that is compatible with currently used belt furnaces in solar cell manufacturing industry. In addition, process improvement by modulation of the RF field coupled to the position of the substrate is shown in this chapter. All these measures increase the reproducibly achievable heating and cooling rate of screen printed silver paste on silicon, and thus have the potential to lower the contact resistance between silver and silicon.

Conventional electrical temperature measurements are not possible because the RF field also disturbs the electrical readings from an NTC-resistor. Temperature measurements using an infrared camera, also known as thermography, were optimized for use on thin silicon substrates. One of the steps was, to determine the correct emission coefficient ε to use at higher temperatures than already reported (8). This is important because thin silicon layers are largely transparent for IR radiation, and only emit a small portion that can be used for measurements. Also for determining the contact resistance, specific TLM samples were made and treated with RF to quantify the electrical effects of the heating process. Electrical Transmission Line Model (TLM) measurements on solar cell samples with different emitter resistances and pre-sinter conditions are used to verify the suitability of the obtained heating and cooling rates for decreasing the contact resistance on solar cells. Different types of TLM measurements as applied in solar cell characterization (9, 10) are used and discussed.

4.2 Theoretical background

The theoretical description of contact formation between metal and silicon has been well described for homogeneous contacts (11). This model is well applicable for vapor phase deposited pure metal films on pre-etched silicon surfaces with exactly controlled doping concentrations. Under these conditions we have lateral current flow, and the contact resistance $R_c$ can be related to the contact resistivity $\rho_c$ using the transfer length $L_T$:

$$R_c = (L_y / Z)R_c \coth(L / L_y), \quad \text{and} \quad L_y = \sqrt{\rho_c / R_c}$$

(1)
in which $R_s$ is the sheet resistance of the emitter layer in the silicon, $L$ the width of the contact, and $Z$ the length of the contact (Figure 43). In our experiments we measure the contact resistance between silver and doped silicon using the Transmission Line Model (TLM) methodology (Figure 43), where the contact resistance and emitter sheet resistance are determined by varying the distance $D$ between the contacts.

![Diagram of Transmission Line Model (TLM) results and measurement setup](image)

**Figure 43**: Representation of Transmission Line Model (TLM) results and the measurement setup used to determine the contact resistance and sheet resistance of the emitter by varying the distance $D$ between adjacent contact bars.

However, the sintered silver paste metallization, emitter doping concentration and firing processing conditions used in solar cell manufacturing result in non-homogeneous contacts. The contact resistance can therefore not be linked directly to the contact resistivity, and thus only $R_c$ measured by the TLM methodology is reported.

The generally accepted model for inhomogeneous contact formation between silver paste and a doped silicon emitter layer (13) is shown in Figure 44, where the possible current paths are depicted in order of importance for current transport: 1) Direct connection between silver crystallite and the emitter; 2) Tunnel current via a very thin isolating glass layer, and 3) Multi-tunnel current via the insulating glass and small Ag and Pb precipitates. For completeness, also a fourth, isolating path is shown, where the glass layer is too thick and does not contain precipitates.
Figure 44: Schematic diagram of the existing contact formation model for screen printed solar cell contacts, with three possibilities for electrical contact (1-3), and one isolating case (4).

The surface of a solar cell is typically textured for maximum surface area and minimal light reflection, so besides the electrode inhomogeneity, also the influence of roughness on the contact resistance must be taken into account, for instance, using the model first reported by Komvopoulos (14), that was later on further refined and applied to electrical contacting in MEMS devices (15-17). However, the influence of the distribution of the area fractions of the four different contact possibilities mentioned in Figure 44 is more determining than the roughness. Also the amount of glass in the paste and the type and extent of pre-treatment of the silver particle in the paste has been shown to significantly affect the microstructure after firing (18). We limit ourselves here to a short discussion of the effect of firing processing conditions.

The firing processing conditions are used to modify the microstructure of the contact by extremely rapid heating and cooling, using the hypothesis that the fraction of type 1, 2 and 3 contacts is increased relative to the type 4 non-conducting contacts. The formation of silver crystallites, type 1 contacts, has been shown to initiate from surface defects (13). The hypothesis is that our RF RTP process tuned for silver paste on silicon helps to initiate crystallite formation, while preventing shunting of the emitter. It has been shown that extreme RTP by laser processing can help in forming only NiSi, while preserving the surface smoothness of the emitter layer in the case of pure nickel metallization on silicon (19). Tunneling contact, via contact types 2 and 3, proceeds via precipitates in the glass phase. The thermal treatment of silver nano-precipitates in glass by pulsed laser heating has been reported to result in a redistribution into many more,
but smaller precipitates in the glass (20, leading to more type 3 contacts and less type 4 contacts.

For larger area application of ultra-fast heating and cooling, we have chosen to investigate RF induction heating in more detail as a potential low cost option that can be integrated in existing furnaces. The 27 MHz band has been cleared from safety suspicions for use in high power applications and, as will be described in the next section, this frequency is well suited for silver tracks of 0.1 mm wide. The ten times lower frequencies more commonly used for induction welding are less suited as the incoupling of the radiation in the 0.1 mm wide track is less optimal. The even lower frequencies used for home induction cooking applications are completely unsuitable for the 0.1 mm wide silver tracks.

In induction heating, an eddy current $I$ induced by the RF field results in resistive losses $R$ in the material to be heated. The power $P$ developed in the material is

$$P = I^2R$$

(1)

In order to increase the temperature sufficiently, the RF field needs to be strong enough, and to have strong interaction with the material to be heated. This interaction is heavily dependent on material properties.

Knowledge about the interaction of 27 MHz RF fields with materials is rather limited, which was one of the incentives to perform the experimental work reported here. Some authors (21-23) have made attempts to model the RF field strength and interaction with metals, where the problem had to be defined by very strict boundary condition assumptions in order to solve it numerically. None of the authors have addressed 27 MHz fields in combination with very thin metal structures. Qualitatively, the field strength near the surface depends on both the current through the antenna, the geometry of the antenna and the distance between antenna and substrate. As a rule of thumb, the smaller the area enclosed by the antenna and the smaller the distance to the substrate, the higher the field strength. The homogeneity of the field strength is hard to predict, as shape and electrical characteristics of both antenna and substrate have an influence on this parameter. In one earlier 27 MHz study, the substrate was completely enclosed by an antenna, which results in large differences in field strength between the edge and the centre of the substrate (24).

An elongated antenna can span the full substrate width and due to the limited distance between the two legs of the antenna, at the same time generate a strong and
homogeneous field over the whole width of the substrate. Moving the silicon substrate relative to the antenna allows exposing the whole length of the substrate to the same field strength. In our experiments we use patterned metal structures, and alignment of these patterns parallel to the width of the antenna results in inhomogeneous heating. One side of the pattern is already heated with reduced resistance while the other side still has a higher resistance, but the eddy current is forced through the complete pattern, resulting in most resistive losses at the coolest spots. If the pattern is perpendicular to the antenna, there is no larger conductive ring then the pieces just underneath the antenna, resulting in a lot of smaller eddy current rings with more homogeneous heating as a result, as indicated in Figure 45.

![Diagram showing eddy currents with conductive patterns. Left: Parallel alignment of structure and antenna, leading to a large eddy current ring; Right: Perpendicular alignment of structure and antenna, leading to many small eddy current rings.](image)

Figure 45: Eddy currents with conductive patterns. Left: Parallel alignment of structure and antenna, leading to a large eddy current ring; Right: Perpendicular alignment of structure and antenna, leading to many small eddy current rings.

Many small eddy current rings (Figure 45b) lead to a more homogeneous heating, while the larger current rings (Figure 45a) leads to more localized heating. Especially sharp corners that are aligned with the antenna corners (Figure 45a) give rise to problems, as the RF field density is highest in these areas, which leads to even more localized heating at these corners.

The interaction of an electromagnetic field with carbon steel in induction heating has been modelled under very strict boundary conditions (20), which are not applicable to our investigations. We will use the expression for the typical depth of penetration of the EM field into a material as a basis. The penetration depth is defined as the depth at which the intensity of the field has fallen by a factor 1/e. The conductivity \( \rho \), the relative magnetic permeability of the metal \( \mu_r \) and the frequency of the electromagnetic field \( f \) determine the penetration depth \( \delta (m) \), as is given by
The numerical values used to obtain the penetration depth for silver and silicon in 27 MHz RF field are $\rho = 16 \times 10^{-9} \, \Omega \cdot m$ for Ag, $2.5 \times 10^9 \, \Omega \cdot m$ for doped silicon, $f = 27 \times 10^6$ Hz and $\mu_r = 1$. The resulting penetration depth for Ag is about 12 $\mu$m, for silicon about 150 mm. As a rule of thumb the dimensions of the material to be heated should be at least about three times the penetration depth in the direction perpendicular to the magnetic field, as the intensity of the field has fallen by 90%, to ensure effective heating. Hence, 0.12 mm wide silver tracks should be heated efficiently, while the 0.3 mm thin silicon substrate would not be heated.

Electrical conductivity and magnetic permeability of the materials can change an order of magnitude with increasing temperature, often in a non-linear way. Both for pure silver and silicon, the conductivity and its overall temperature coefficient in linear approximation are known while the magnetic permeability remains approximately constant. In our experiments however, we use a glass containing silver paste and doped silicon with a thin emitter layer, for which the conductivity as a function of temperature is less predictable. As the material parameters will change during the process, estimating the effect on temperature homogeneity during the process is problematic.

4.3 Experimental

4.3.1 RF heating setup

The setup constructed for the controlled RF heating experiments is schematically shown in Figure 46. The position of the substrate carrier below the RF antenna is controlled via a programmable power source which also controls the RF power generated, so that the various positions receive designated RF power. The output of the RF generator is tuned with a variable capacitor and monitored with a capacitively coupled voltage gauge to allow reproduction of RF intensity between experiments. The distance between the RF antenna and the substrate carrier was set at 1 mm, unless stated otherwise. Between the RF antenna and the linear axis, pre-heating oven and IR camera, a first cage of Faraday was constructed using wire mesh, and the cables between the components were shielded additionally using aluminum foil. The whole setup was placed in a second cage of Faraday, to prevent interference with the rest of the building.
Reduction of electrical resistance by selective RF heating

Figure 46: Schematic representation of the setup constructed for controlled RF heating of silicon wafers.

The 27 MHz 1.6 kW RF generator (HIMMEL HG3303, Germany) was modified with a custom-made water cooled antenna using hollow 4 mm diameter copper tube with a 6×160 mm enclosed area and a 200 pF variable capacitor in series (see Figure 46). The electrical connection from the antenna to the generator was made in the middle of one long side, to realize a symmetrical potential drop along the long sides of the antenna. A high voltage gauge was placed parallel to the RF antenna to be able to reproduce the settings between experiments.

The silicon wafers were put on a ceramic carrier with a thermocouple inside, attached to a linear axis, programmed to run at a constant speed (Yamaha, Japan). Unless stated otherwise, the substrate speed was 300 mm/s. The door of a conventional radiation oven (Heraeus, Germany) was opened and a ceramic plate, having an opening just large enough for the substrate carrier to move through, replaced this door. The full size wafers were pre-heated to 500 °C, while the TLM pieces were pre-heated to 150 °C. An optical sensor in combination with a metal ‘comb’ with 16 teeth provides a position trigger to the programmable power source PM2813 (Philips, the Netherlands), used to modulate the RF power output during the substrate motion. The resulting experimental setup, with the IR camera and wire mesh cage of Faraday removed, is shown in Figure 47.
Figure 47: Photo of the experimental setup used.

In inlay 1 the high voltage gauge can be seen which was used to check and reproduce the RF settings. In inlay 2 the variable capacitor to tune the antenna is visible, which in turn determines the power transferred to the substrate. In inlay 3 the TLM sized substrate, the thermocouple to measure pre-heating temperature and the RF antenna are shown.

4.3.2 Temperature measurements

An IR camera (AGEMA type 900SW, USA) with glass filter was used, which detects radiation with a wavelength between 4.76 – 5.6 µm. Thick (0.7 mm) and thin (0.3 mm) silicon wafers were partially coated with Pyromark 2500 lacquer. This lacquer is thermally stable up to 1300 °C and, at temperatures over 250 °C, has $\varepsilon = 0.96$ (24), which we used for the calculations. The partially coated silicon wafers were put on a ceramic carrier and pre-heated in the oven to $T = 800$ °C, as measured with the thermocouple present in the substrate table. The table was transported out of the oven with 600 mm/s to limit cooling during transport into the field of view of the IR cameras.
From the temperature measured during cooldown in the Pyromark coated areas, the emission coefficient of the silicon was determined using

\[ \frac{E}{\varepsilon_{\text{Pyromark}}} = (T_1^4 - T_2^4) = \frac{E}{\varepsilon_{\text{silicon}}} \]  

Here \( E \) is the emitted radiation from the target, assumed to be a blackbody and division by the emission coefficient of the Pyromark coating, \( \varepsilon_{\text{Pyromark}} = 0.96 \), yields the temperature via the internal calibration curve of the camera from which the unknown \( \varepsilon_{\text{silicon}} \) of the silicon wafer is determined. The calculated value for \( \varepsilon \) per frame was rounded off to 0.01, corresponding to the accuracy of the temperature measurements of about 10 °C. The temperature was measured during cooling down in the Pyromark coated areas. The effective emission coefficient of the silicon substrates outside the Pyromark coated areas was calculated from these temperature data. Further measurements were performed with a faster camera (Thermo-Sensorik, Germany) with the same glass filter but much higher frame rate at reduced field of view, which is especially suitable when the substrate is moving fast while being heated. The field of view of this camera is located less than 100 mm from the oven exit, just after the RF coil, so that the start temperature of the wafer can be assumed to be identical to the temperature of the oven. Care was taken to keep the camera orientation identical during all measurements in order to keep variations in emitted radiation as constant as possible.

### 4.3.3 Substrates used

Samples for TLM measurements were obtained from GP solar (Germany), custom made on their standard equipment and processes. The starting material used was 125x125 mm 300 μm thick 1.5 Ω m boron doped p-type mono-crystalline Si wafers to eliminate variations induced by base material differences as much as possible. Three different n-type emitters with 60, 90 and 130 Ω/sq sheet resistance were created on this material by thermal diffusion of phosphorus. Standard etching, SiNx layer deposition and printing of standard silver at the front side and aluminum paste on the back side followed. Pre-sintering was done to ensure good conductivity of the silver structures, and this was done in a production belt furnace to enable comparison with, and quantification of improvements relative to, the standard IR firing process. This is also the reason why the aluminium paste at the backside of the wafer needs to be present, as the sintering process is tuned with aluminium paste present. The four pre-sintering peak temperature
settings for each of the three emitter types are given in Table 8 (including a reference pre-sinter setting of 845 °C).

Table 8: Coding and characteristics of the 12 types of samples investigated.

<table>
<thead>
<tr>
<th>Emitter resistance</th>
<th>60 Ω/sq</th>
<th>90 Ω/sq</th>
<th>130 Ω/sq</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>Ref 60</td>
</tr>
<tr>
<td>D</td>
<td>E</td>
<td>F</td>
<td>Ref 90</td>
</tr>
<tr>
<td>G</td>
<td>H</td>
<td>I</td>
<td>Ref 130</td>
</tr>
<tr>
<td>Peak temperature setpoint (°C)</td>
<td>750</td>
<td>780</td>
<td>810</td>
</tr>
</tbody>
</table>

The produced wafers were laser cut into TLM sized pieces and each piece was labeled with wafer number, emitter resistance, peak firing temperature and original position in the wafer according to Figure 48. After pre-firing, the aluminum paste was completely removed by mechanical grinding because the 27 MHz RF energy also couples into the sintered aluminum layer (penetration depth about 17 μm). Only the front side metallization shown in Figure 48 is present on the TLM samples. The so-called bus bars are silver paste lines of 4 mm wide, where all the current is collected from the whole surface, to be transported from solar cell to solar cell through strips of metal.

Figure 48: Wafers for TLM samples: Silver metallization pattern, laser cutting pattern, sample numbering and motion direction under the RF antenna.
Figure 48 also shows that the samples are taken from locations on the wafer between the three bus bars since these have to be excluded from the TLM samples. The orientation during RF processing is also indicated, which assures correct alignment of silver patterns and the antenna to obtain heating as homogenous as possible.

4.3.4 Electrical measurements

TLM measurements of all samples before RF firing were performed using a 4 point resistance measurement on one point on the $I/V$ curve (GP 4-test pro, GP Solar, Germany). This means that it can only be used for fully Ohmic contacts. On individual TLM pieces, a full $I/V$ curve was measured with a four-point resistance measurement setup with golden probes (Agilent 4155B with Agilent Easy expert software, USA).

4.4 Results and discussion

In this section first the temperature measurements will be described, followed by the resistance experiments on heating of full size wafers. Finally the results of electrical measurements on TLM samples will be described.

The temperature was measured on the Pyromark coated section on the silicon wafer using an emission coefficient $\varepsilon = 0.96$ for each recorded frame during cooling down from 700 °C to 340 °C. The recorded temperature was used to calculate the effective emission coefficient of Si using equation 3. The data is presented in Figure 49. As can be seen, the measurement variation on the emission coefficient is ± 0.02 units, which is due to accuracy of about 10 °C for the temperature.

![Figure 49: Effective emission coefficient $\varepsilon$ of a 0.7 mm thick Silicon wafer as a function of temperature.](image)
The $\varepsilon$ of the measured silicon wafers is higher than the value of 0.7 for heavily doped silicon as reported by Timans (26) over the relevant temperature range. The values for lightly doped silicon are strongly temperature dependent, starting from 0.1 at 200 °C and rising to 0.7 above 600 °C as measured by Sato (27). The higher $\varepsilon$ measured in our experiments may be due to the heavily doped emitter layer and the SiNx anti-reflection coating on the wafers used in our investigation. The calculated $\varepsilon$ was rounded off to 0.01 units, according to the accuracy of the temperature measurements on bare silicon of about 10 °C.

We conclude that the absolute temperature of the silicon wafers can be measured with an uncertainty of 3-6% due to the variations in perceived emission coefficient over the whole temperature range covered, hence the temperature rise during the RF treatment can be measured with the same accuracy.

### 4.4.1 Temperature increase with RF fields

In order to determine the rate of temperature increase on solar cells in an RF field, first a stationary test was performed. Doped silicon substrates (thickness 0.30 mm) with silver lines of 0.12 mm wide were placed on a pre-heated ceramic carrier under the stationary 27 MHz antenna at a distance of 1 mm. The gauge for the RF voltage was tuned to 10 kV and turned on for 1 second, and the resulting rise in temperature was recorded using thermal imaging as described above. As shown by the parts of the light grey line labelled with dots in Figure 50, the silicon substrate does heat up at a rate of $\approx 550 \, ^\circ C/s$ until the temperature of the silicon rises above 450 °C. As soon as this threshold is passed, the heating rate increases with a factor of five to $\approx 2450 \, ^\circ C/s$ until local melting of silicon and breakage of the wafer is observed. This causes the discontinuity in the heating curve after 0.6 second. A second test was performed with 2 mm distance between antenna and wafer, shown by the dark grey line labelled with dashes in Figure 50. Although the absolute heating rate is lower, the about five-fold increase in heating rate above 450 °C, as compared to below 450 °C is maintained. Also here the heating process is discontinuous above 0.9 seconds. The difference in start and end time observed is due to manually switching of the RF field. The effect of the conductivity change in the silver lines is largely linear, and thus cannot account for this jump in heating rate.
Reduction of electrical resistance by selective RF heating

Figure 50: Temperature rise of silicon with 0.12 mm wide silver structures, using 27 MHz RF field; light grey line: 1 mm distance between RF coil and silicon substrate, dark grey line: 2 mm distance between RF coil and substrate.

The five-fold increase in heating rate above 450 °C is due to a reduction of the electrical resistance of silicon by several orders of magnitude, which results in an increased effective RF incoupling in the 0.30 mm thick silicon. Because the penetration depth of the 27 MHz field decreases to about 0.1 mm, the increased incoupling leads to an increase of the heating rate. This effect was theoretically described by Pelleg (28), and by using equation 2, the resistance of the doped silicon samples used here can be estimated to be lower than $\approx 2 \times 10^{-6} \Omega \cdot m$ at 450 °C to account for this measured effect.

It must be stressed that in these tests, the temperature increase of the silicon is measured. Temperature measurements on the silver fingers of 0.12 mm wide are not possible because the resolution of the IR camera is limited to 0.2 mm per pixel with the available objectives. It can be assumed that the heating of the Si up 400 °C is due to heat conduction from the silver structures, which must have a (much) higher temperature than 400 °C, as the thermal mass of the silver is less than 0.1% relative to silicon.

4.4.2 Full wafer heating with RF field modulation

Experiments on heating were performed at different RF field modulation settings. Some of the results of these experiments are plotted side by side in Figure 51, shifted 150 image frames for easy comparison. The left curve is the reference with RF field off, the
middle curve line is with constant RF field (input voltage 3.5 V), and the right curve is modulated with decreasing input voltage from 7 V at image 450 to 3.5 V at image 550. As a guide to the eye, the temperature difference between start and end of the heating of the 156 mm long wafer is indicated with a black line.

Figure 51: Wafer temperature measured with a frequency of 200 Hz while the wafer is transported underneath the RF antenna. Blue line: RF off; Red line: RF power constant; Green line: RF power modulated with input voltage between 7 and 3.5 V.

Without RF field, it can be seen in the blue line that the temperature of the wafer start is 500 °C, but at the end it is 550 °C, due to the fact that the start of the wafer is cooled more by ambient air than the end, which remains in the oven longer. Secondly, the 4 mm wide bus bar locations are evident by the seemingly lower temperature measured, which is due to the lower \( \varepsilon \) of the silver paste. With constant RF field strength, both start and end of the wafer are heated about 50 °C, as shown in the red line, and the effect of the ambient air cooling is constant, as is evident by the same slope of the black line above the red and blue line. Around the bus bar locations, the temperature increase is much lower due to higher conductivity than the silver lines, and consequently lower heating power. When the RF field is modulated by the programmable power source, the start of the wafer is heated about 100 °C, while the end of the wafer is heated about 50 °C as depicted by the green line in Figure 51, counteracting the cooling by ambient air and increasing the heating homogeneity. The
lowered heating effect at the bus bars is not affected by this RF field modulation. In order to allow homogeneous RF heating of a solar cell, a metal structure that is evenly distributed over the front side of the wafer is needed.

With a process time of 0.5 s for a full length wafer, the heating rate appears to be 100-200 °C/s, much less than in the stationary case. However, taking the 15 mm width of the RF antenna into account, implying that each part of the silicon wafer is exposed to the RF field only 10% of the process time, the observed heating rate is in line with that measured in the stationary experiment.

The reproducibility of the experiments is addressed next. Two experiments have been done in duplicate and are plotted in the Figure 52 for easy comparison. As can be seen, the black and green lines for experiment 1, and the blue and red lines for experiment 2, shifted 350 images, are within 10 °C in all parts of the temperature curves. The curves for each duplicate experiment are slightly shifted in time for ease of comparison.

![Figure 52: Reproducibility of temperature measurement during exposure to RF field in two different experiments, shifted 350 images.](image)

The two curves starting at image number 100 in Figure 52 are almost identical, just as the two curves starting at image number 350. This shows that both the pre-heating process and the RF process as well as the IR camera temperature measurement is
reproducible from experiment to experiment, and that the differences observed by tuning the RF power are significant.

The maximum temperature increase obtained is about 100 °C within 0.5 s. Further increase of RF field intensity was impossible due to electrical breakdown. Lowering the linear speed of the sample table in order to increase RF exposure time does limit electrical breakdown. However, cooling of the wafer proved to be a significant effect in the current test setup, lowering the maximum achievable temperature during RF exposure. If the RF process were to be integrated in a belt oven to limit cooling, electrical breakdown could be prevented, while the maximum achievable temperature could be increased.

4.4.3 Electrical resistance on TLM samples

To relate the fast heating process as discussed above to a functional improvement in contact resistance, the behavior of TLM samples was evaluated. The contact resistance after pre-sintering but before RF heating were determined, and the average values of the results per group, based on single $I/V$ point measurement are given in Figure 53. This provides a representative overview of the differences in starting values.

![Figure 53: Average contact resistances per sample group before RF treatment; for labels of the sample groups, see Table 8.](image)

In Figure 53 a reduction of contact resistance with firing temperature can be seen per emitter. In each case, the lowest resistance is reached for the reference (maximum) setting. The contact resistance $R_c$ for the reference samples of 90 $\Omega$/sq and 130 $\Omega$/sq emitter, respectively, are about 8 and 70 times higher than for the standard 60 $\Omega$/sq emitter at the reference settings. Improvements in heating and cooling rates could thus
potentially lead to a significant improvement in contact resistance, where a longer residence time in the RF field by varying the sample speed could be advantageous.

As only the temperature underneath the silver lines is important, selective incoupling of the RF field into the silver is desired, and therefore the temperature of the silicon needs to remain below 450 °C. The TLM samples were pre-heated to 150 °C, and at maximum RF field strength, the sample translation speed was reduced to obtain the longest possible residence time in the RF field. The minimum velocity possible (keeping the silicon temperature under 450 °C) was dependent on the doping level of the emitter layer. The lowest velocity possible for group A-C was 3.3 mm/s, for group D-I it was 2.2 mm/s, and hence 50% more residence time in the RF field was possible. Contact resistances based on single I/V point measurement with the GP 4-test Pro for samples from group G-I are given in Figure 54, but do not show a consistent lowering of the contact resistance.

![Figure 54: Contact resistance for samples of different groups (see Table 8) measured before RF heating (light grey bars) and after RF heating (dark grey bars).](image)

The only significant decrease was observed in the Ref 130 group. Therefore, the effect of RF heating on contact resistance is much lower than expected based on the temperature increase that can be realized by RF heating. One hypothesis is that the diffusion process of silver is too slow for the RF heating rate, so more time at high temperature is needed than can be realized with the current RF heating setup. Another hypothesis is that the temperature difference between the silver and the silicon causes the process needed for contact formation to stop when it reaches the relatively cool silicon. Additives to the silver paste that increase silver diffusion speed or improve the
contact formation process with silicon might provide a means to better match the RF heating profile and the contact formation process.

When measuring a full \(I/V\) curve of selected samples from the different groups, non-linear curves were obtained from samples of groups A, B, D, E, G and H, indicating non-ohmic contact. As an example, full \(I/V\) curves of a representative TLM sample from group A, measured before (upper curve) and after (lower curve) RF heating are shown in Figure 55. The improvement in linear behaviour is clearly visible.

**Figure 55**: Full \(I/V\) curves, measured between the line 1 and subsequent lines, of a representative TLM sample (see Figure 48) from group A showing non-linear behavior before RF heating (top) and linear behavior after RF heating (bottom).

From these \(I/V\) curves, the resistances between the lines were calculated in three different ways: from the full curve, from a single point at 0.015 V and from a single point at 0.03 V. Before RF heating, the difference from linear behavior is so large that
the contact resistance determined in the three ways indicated varied between 31 and 51 Ohm. After RF heating, with full linear behavior, the contact resistance varied only 10%, from 33 to 37 Ohm. This is a clear indication that the values for the groups A, B, D, E, G and H given in Figure 53 have only indicative value.

The change from non-ohmic to ohmic contact shows that the contact formation between silver and silicon was improved in the RF heating process, as compared to the contact formed during the pre-sinter process with setpoint of 750 °C. However, the contact resistance value reached in this way is still higher than the reference. We conclude that significant tuning of the silver metallization paste to the RF process is required before industrial application of the technology can be considered. In addition, the print pattern of the metallization on both front and back side of the solar cell should be optimized to allow simultaneous sintering of both silver paste at the front side, as well as aluminum paste at the backside metallization. Interdigitated back cell contacted solar cells which have been reported in literature (29) could be compatible with RF heating. A solar cell design with homogeneous silver coverage and patterned aluminum rear contacting like the ASPIRE concept of ECN (30, 31) would be an ideal concept for further development of the RF heating technology.

4.5 Conclusions

In this chapter, the influence of 27 MHz RF heating on electrical contact formation between silver and silicon was investigated, as a reduction of contact resistance due to faster heating and cooling rates directly leads to more efficient solar cells. We have shown that very fast and selective heating of 0.12 mm wide pre-sintered silver paste lines on silicon is possible, and that the measures taken to improve process control lead to a reproducible RF heating process.

However, the contact formation between the silver paste and the silicon is not well matched to the extremely short timescale of the 27 MHz RF heating process, due to the properties of the materials used. The non-homogeneous geometries of the silver pattern also have a direct impact on the suitability of the RF heating process developed for this application, however, the strongly improved process control of the 27 MHz RF heating process provides a good basis for other applications that require an extremely fast heating profile with a more suitable material property combination.
References

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5 Predicting nanometer scale displacements by scaled systems

In this chapter a method is presented for the determination of minute mechanical displacements of the top surface of an optical part during the room temperature curing phase of the adhesive used to adhere that part onto a mechanical support. These displacements are typically a few nanometers over a few days. The method comprises the scaling of a piece of the optical part using scaling conditions that assure that the scaled displacements are representative for the actual part. For the upscaled part, displacements are sufficiently large for a reliable measurement using a specially developed dedicated displacement measurement system. A finite element model (FEM) of both the displacement measurement system and the optical part was constructed to verify the scaling rules. In this way nanometer size displacements can be predicted well.
Chapter 5

5.1 Introduction

Adhesives are widely used in bonding optical parts to mechanical supports, where the benefits of easy assembly and positional stability are very much appreciated. Deformations of such a part due to the shrinkage of the adhesive during its cross linking are typically not disturbing the performance of the optical part. In our situation however, the optical demands on the top surface of the optical surface are so strict that a quantitative analysis of deformation due to shrinkage of the adhesive is needed at an unprecedented accuracy level.

The surface under examination is the top surface of a silicon part of 20 × 40 mm, 0.7 mm thick, which needs to be flattened and mounted securely. The top surface needs to be extremely flat, angular deviations of 5 μrad already reduce the optical performance. Investigations on wafer stage designs by Une et al. (1-7) describe the development and use of a pin structure to flatten silicon wafers and describe the factors influencing the performance of this design. In this configuration, any pre-existing curvature of the part is removed by the vacuum force that pulls the part onto the pins. Positioning the pins sufficiently close together (at a distance of 1 mm) prevents the vacuum force from excessively pulling the optical part down between the pins and results in a well defined flat starting situation. However, vacuum is not suited for longer term mounting; hence there is a need for an adhesive technology that is able to maintain this flat starting position.

To hold the silicon part, in our approach the bottom of the part is fastened onto the holder using room temperature curing adhesive that initially fills the space between the pins. The use of room temperature curing allows circumventing the deformation of the optical top surface due to thermo-mechanical stresses as a result of difference in coefficients of thermal expansion when the temperature is increased or decreased. Only the deformations due to shrinkage of the adhesive upon cross linking play a role and remain to be quantified and minimized. The maximum allowable vertical displacement of the optical surface between the support pins that are spaced 1 mm apart is 2.5 nm in order to meet the flatness specification of 5 μrad.

The fact that adhesives shrink during the curing phase is well known. The fundamental reason for shrinkage of an adhesive is that two separate reactive groups occupy a larger volume than the reaction product of these groups in a single molecule.
A simple explanation is given by the fact that the distance between atoms of different molecules is two times the van der Waals radius, typically between 3 and 5 Ångstrom (8), while the bond length between atoms in a molecule is typically between 1 and 2 Ångstrom (9). For acrylic adhesives the reaction is between the double bonds of the acrylic group, forming a polyacrylic structure after curing. Epoxy-based adhesives are mixtures of epoxy containing resins and amine containing hardeners, forming polyamino-alcohol structures after curing. Dependent on the reactivity of the amine and epoxy groups, the adhesive can be formulated as a ‘one-pot’ system, which is activated by raising the temperature, or a ‘two-pot’ system, which requires mixing and starts reacting at room temperature. The latter system, further described as 2K-epoxies, will be used in our investigation as it is has the lowest intrinsic reaction shrinkage of all room temperature curing adhesives. The drawback is that these adhesives have curing times of up to 200 hours, which means the deformations of the optical part also needs to be measured on this timescale.

A cross-section of the optical part after curing of the adhesive is presented in Figure 56, where the deformation due to shrinkage of the adhesive is exaggerated. Also indicated is the area of two pins with a bending section that resembles the smallest representative section, in which the deformation can be analyzed, either as an angular deformation $\Delta \theta$ or as a mechanical displacement $\Delta z$ of the surface between the pins.

![Figure 56: Cross section of the optical part on support 'pins', with angular deformed top surface due to shrinkage of the adhesive, leading to vertical displacement $\Delta z$ between the 'pins'.](image)

Current state of the art in measuring mechanical displacement due to shrinkage of adhesive does not meet the very demanding specifications of nanometer range accuracy...
over days of measurement time. Accuracy levels of micrometer level were described by e.g. Watts (10-12) using optical interference technologies. However, the measurement systems used are only suited to measure over time intervals of minutes onto hours. Mechanical drift of the used displacement measurement system necessitates frequent calibration to assure accuracy. A further increase of accuracy of these optical systems to the nanometer scale is not feasible, as the process to cure the adhesive interferes with the measurement. For adhesive curing times between one and three days, the effect of shrinkage of an adhesive layer was measured by optically quantifying the amount of bending of a thin substrate with a layer of epoxy on top (13). The bending effects measured due to shrinkage were typically in the sub-millimeter displacement range, and environmental circumstances were not controlled over this interval, reducing the achievable accuracy. Temperature control is thus one of the first requirements when measuring accurately. Theoretical work (14) described a thermally cured epoxy system as a visco-elastic material allowing to model the relaxation of residual stresses and dimensional changes. However, experimental validation of the model is not possible, because the time scale of the effect is more than 10 days, for which no suitable measurement system is present.

State of the art in deformation measurement techniques is laser deflectometry as described by Krey (15), which can reach µrad resolution. This method, however, has practical drawbacks that will be discussed in the experimental section, one of which is the maximum part height of 50 mm. Hence we will focus on measurement techniques to determine positional displacement instead of angular deformation.

This nanometer displacement measurement problem thus needs to be solved by increasing the scale of the problem, where the logical approach is to increase the size of one ‘bending unit cell’, as shown in Figure 56. This ‘bending unit cell’ is basically a bending beam fixed onto supports, where the scaling factor is chosen to result in a sub-micrometer mechanical displacement $\Delta z$ of the surface of the middle of the beam. The scaling conditions used will be verified by finite element modeling (FEM) of the ‘bending unit cell’ to confirm that the adhesive in the scaled unit cell behaves in a similar but scaled way as in the original size unit. To achieve the needed measurement accuracy, a capacitive proximity sensor with suitable resolution was selected. A mechanical construction around this sensor was designed to assure stability of the
displacement measurement system over multiple days. This will be presented in the experimental section.

The combined result of these efforts, given in the next sections, shows that the scaling theory, the measurement approach and the measurement system are suitable to study the effects of shrinkage of adhesive on deformations of a bending beam over a time frame of multiple days. Translation of the bending beam results into predictions for the mechanical behavior of the optical part on the holder pins using the FEM model will be discussed. Further investigations on the possibility to modify the shrinkage behavior by the use of other adhesives will be presented in chapter 6.

5.2 Theoretical background

First an analytical description of a plate on cylindrical support pins is given in section 5.2.1, and then a scaling translation to a 10× and 50× bending unit cell is described in section 5.2.2. These descriptions are based on analytical equations, and the boundary conditions that apply give insight in the applicable bending beam theories. Also the scaling conditions will be explained using analytical descriptions in section 5.2.3, as these can be verified to be correct. The theory used to describe the load on the beam during shrinkage of the adhesive is described in section 5.2.4, and completes the theoretical background used in our approach. This allows a reliable prediction of z-displacement on the nanometer scale with a FEM model of the bending beam.

5.2.1 Analytical description of the optical part on support pins

The vertical displacement of the bottom surface position \( t \) of a plate between circular pins, as a result of a homogeneously applied force (pressure) on the plate surface between the pins, can be derived from the bipotential equation as described in section C5 in (16).

\[
\frac{d^4t}{dx^4} + 2 \frac{d^4t}{dx^2dy^2} + \frac{d^4t}{dy^4} = \frac{Q(x,y)}{N}
\]  

(1)

where \( d \) is the mechanical displacement of the bottom of the plate in \( x \) and \( y \) direction, \( Q \) is the load on the plate, and \( N \) is the bending stiffness of the plate. With rotational symmetry of the load around one pin, this equation transforms into the Eulers differential equation.
\[
\frac{d^4 t}{dr^4} + 2 \frac{d^3 t}{dr^3} - \frac{1}{r^2} \frac{d^2 t}{dr^2} + \frac{1}{r^3} \frac{dr}{Q(r)} = \frac{N}{N}
\]  

(2)

For the situation of a plate on a rectangular array of pins as depicted in Figure 57, the $z$-displacements $\Delta t$ of the bottom surface of the plate at positions A and B is derived in (17) and given by

\[
\Delta t_A = 0.092 \frac{Qa^4}{N}, \Delta t_B = 0.069 \frac{Qa^4}{N}
\]

(3)

Figure 57: Plate supported by circular support pins with radius $r$, where $z$-displacements at position A and B can be calculated.

Even though the displacement at position A is larger than at position B, the maximum angular deformation, which defines the optical quality of the plate, is defined by the bending line through position B and the two adjacent pins. This is because of the assumptions of homogeneous force distribution under the plate and homogeneous stress distribution in the plate, with maximum bending stress between position B and two adjacent pins. As the smallest distance between pins dictates the maximum deformation angle, this distance must be used for the bending beam unit cell.

The boundary conditions that need to be satisfied in order for equations 1 and 2 to be valid are that the plate thickness is small compared to the lateral dimensions, and the vertical displacement is also small. These boundary conditions are met in our case. However, a further boundary condition for the applicability of equation 3 is that the plate thickness $t$ may be $2r$ at most. In our case the plate thickness is slightly larger than
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4r, which means that equation 3 cannot be used to predict the displacement of the bottom of our plate.

These considerations lead to the conclusion that Finite Element Modeling (FEM) is needed to calculate \( z \)-displacement of top and bottom of the deforming optical part. The rotational symmetry of the plate-on-pins deformation, where the maximum angle is found in the line through B and two adjacent pins, allows simplification of the measurement approach to a rectangular shaped beam on square supports. This argument leads to a ‘bending unit cell’ that is representative for the plate-on-pins optical part.

In the next paragraph the analytical equations for the bending beam are used to illustrate the importance of beam support fixation boundary conditions, transverse shear deformations and load homogeneity.

### 5.2.2 Analytical description of the bending beam unit cell

Analytical formulas that describe bending beams, describe the \( z \)-displacement of only the bottom surface of the beam. The classical Bernoulli-Euler beam theory \((18)\) describes deformation without any transverse shear deformation contribution, and is applicable to thin beams, with thickness less than 10% of their length. The general equation for displacement of the bottom surface is given by

\[
\Delta z = C \frac{Ql^3}{EI}
\]

where \( l \) is the length of the beam between the supports, \( E \) is the \( E \)-modulus of the beam material and \( I \) is the area moment of inertia of the beam cross section. For a beam, \( I = 1/12 \times w \times l \), where \( w \) is the width of the beam. The constant \( C \) is dependent on the exact manner of supporting the beam and distributing the load \( Q \), exact values of this factor for different load distributions and support cases can be found in section C4 of \((16)\). The cases for simply supported beams \((C = 5/384)\) and for beams fixed laterally and vertically at both support ends \((C = 1/384)\) with homogeneously distributed load are schematically indicated in Figure 58.

![Figure 58: Left: Simply supported beam; Right: Beam fixed at both support ends.](image)
In our case we need to consider the original optical plate when deciding what type of support should be used. The restrained lateral motion at each support pin dictates use of a beam with fixed support at both ends.

If shear effects in thick beams are included, the analytical functions that describe the $z$-displacement of the bottom surface of the beam can only be solved exactly for simply supported beams and cantilever beams. These analytical solutions have the generalized form

$$
\Delta t = \Delta t_{\text{classical}} \left[ 1 + w_s (1+\nu) \left( \frac{d}{l} \right)^2 \right]
$$

where $w_s$ is the proportionality constant due to transverse shear deformation effect, $\nu$ is Poisson’s ratio, $d$ is the beam thickness and $l$ is the beam length. The calculation of the proportionality constant for beams fixed at both ends with different models, as summarized in (19), shows that the contribution of transverse shear deformation for beams with fixed support at both ends is significantly larger than for simply supported beams (9.6 vs. 1.9 for $w_s$). It is directly evident that the shear component in the $z$-displacement of the bottom surface of the beam increases rapidly with increasing beam thickness $d$. This is graphically represented in Figure 59, with $z$-displacement presented as a fraction of the beam thickness for 1 bar pressure on a 1 mm long beam of different thicknesses, fixed at both support ends, thus calculated using equation 5, with $w_s$ is 9.6 and $\nu$ is 0.3.

![Figure 59: Scaled bottom z-displacement $\Delta t$ with and without transverse shear deformation for different beam thicknesses with beam length $l$ is 1 mm.](image)

It can be seen that the effect of shear deformation is negligible for a beam with a thickness of less than 10% of its length. In our case we have to consider the shear
deformation for the top and bottom surface, as the thickness of our beam is 70% of the length, which is not possible with the analytical functions available. Fortunately the dependence of the proportionality constant $w_s$ on the load distribution is negligible for beams with fixed support at both ends (79). This means that the non-homogeneous distribution of force due to the shrinking adhesive is not affecting the $z$-displacement due to transverse shear of the bending beam unit cell significantly.

These considerations lead to the conclusion that we can avoid the complexity of taking any inhomogeneous force distribution on the beam into account when we discuss the scaling conditions for the bending beam unit cell in the next paragraph. It does also point to the importance of assuring fixed supports at both ends, which is easily assumed but more difficult to realize in practice.

### 5.2.3 Scaling conditions for the bending beam unit cell

The dominant scaling condition that applies is that the stresses due to shrinkage of the adhesive on the scaled part remain identical to the stresses on the original size part. The second scaling condition is that the mechanical strain and the adhesive strain also remain constant. The third scaling condition is that the aspect ratio of the adhesive remains constant, to avoid differences in lateral contraction of the adhesive. If these scaling conditions are met, only the $z$-displacement of the beam is increased, but not the angular deformation.

Equations that describe the stress that strains the beam will be derived for our bending beam unit cell, leading to the geometric scaling conditions used for the bending beam measurement systems. As described in the previous paragraphs, the situation that is described analytically is the mechanical displacement $\Delta t$ of the bottom surface of a thin bending beam, as indicated in Figure 60.

![Figure 60: Vertical displacement $\Delta t$ of the bottom surface of the bending beam between two supports due to shrinkage of the adhesive.](image)

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The total displacement $\Delta t$ of the bottom surface of such a beam in terms of strain can be written as:

$$\Delta t = \left(\varepsilon_{\text{shrink}} + \varepsilon_{\text{mech}}\right)t = \varepsilon_{\text{total}}t$$

(6)

in which $t$ is the thickness of the adhesive layer, $\varepsilon_{\text{total}}$ is the total strain of the adhesive, built up by a mechanical strain $\varepsilon_{\text{mech}}$ and an adhesive free shrinkage strain $\varepsilon_{\text{free}}$. The total displacement $\Delta t$ of the bottom surface of the beam due to a load $Q$ can be described as:

$$\Delta t = -\frac{Ql^3}{3CEI} = -\frac{Q}{K_{\text{beam}}}, \text{ with } K_{\text{beam}} = C\frac{El^3}{t^3} = C\frac{Ebd^3}{l^3}$$

(7)

in which $C$ is a factor dependent on the way the beam is fixed at both ends, $E$ is the Young’s modulus of the beam material, $K_{\text{beam}}$ is the bending stiffness of the beam, $d$ the thickness of the beam, $b$ the width of the beam and $l$ the length of the beam between the supports. Combining equation 6 and 7, the total strain becomes:

$$\varepsilon_{\text{total}} = \frac{\Delta t}{t} = -\frac{Q}{K_{\text{beam}}t} = -\frac{\sigma_{\text{beam}}lb}{K_{\text{beam}}t}, \text{ with } Q = \sigma_{\text{beam}}lb$$

(8)

where the load originates from the stress $\sigma$ exerted onto the beam by the adhesive. Combination of equation 4 and 5 leads to the expression of the stress that bends the beam:

$$\sigma_{\text{beam}} = -\varepsilon_{\text{total}}\frac{K_{\text{beam}}t}{lb} = -\left(\varepsilon_{\text{free}} + \varepsilon_{\text{mech}}\right)C\frac{Ed^3l}{t^4}$$

(9)

When both stress and strain have to remain identical and when the factor $C$ is assumed to be equal for non-scaled and scaled system, it follows logically from equation 9 that $\frac{Ed^3l}{t^4}$ needs to be identical in scaled and non-scaled systems. To assure an identical adhesive load on the system, the ratio between $t$ and $l$ also needs to remain identical when the system is scaled.

These scaling conditions translate into the values for $E$, $d$, $t$ and $l$ given in Table 9 for the different scaled systems. For completeness also the holder height is given, as the
holder on with the beam is fixed at both needs to be stiff enough to resist deformation by both the adhesive and the bending beam.

Table 9: Values for E, d, t and l for the actual and scaled systems.

<table>
<thead>
<tr>
<th>System</th>
<th>E</th>
<th>d</th>
<th>t</th>
<th>l</th>
<th>Holder height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x bending beam</td>
<td>100 GPa</td>
<td>0.73 mm</td>
<td>0.01 mm</td>
<td>1 mm</td>
<td>10 mm</td>
</tr>
<tr>
<td>10x bending beam</td>
<td>215 GPa</td>
<td>5.7 mm</td>
<td>0.1 mm</td>
<td>10 mm</td>
<td>20 mm</td>
</tr>
<tr>
<td>50x bending beam</td>
<td>215 GPa</td>
<td>28.3 mm</td>
<td>0.5 mm</td>
<td>50 mm</td>
<td>100 mm</td>
</tr>
</tbody>
</table>

5.2.4 Load on the beam by adhesive strain

In the previous paragraph the scaling conditions were established for the mechanical system, leading to equation 9 that describes the stress that bends the beam. The stress in the adhesive layer and the beam are equal in magnitude after shrinkage as there is equilibrium, giving

\[ \sigma_{\text{adhesive}} = -\sigma_{\text{beam}} \quad (10) \]

The stress that strain the adhesive after shrinkage can be expressed as

\[ \sigma_{\text{adhesive}} = \varepsilon_{\text{mech}} E_{\text{adhesive}} \quad (11) \]

Substituting (9) and (10) in (11) to find \( \varepsilon_{\text{mech}} \) gives

\[ \varepsilon_{\text{mech}} = -\frac{\varepsilon_{\text{free}}}{E_{\text{adhesive}}} \left( \frac{K_{\text{beam}} t}{lb} \right) + 1 \quad (12) \]

which shows that the mechanical strain is dependent on the independently measurable adhesive properties shrinkage and stiffness, and the factor \( C \) (as component of \( K_{\text{beam}} \)) that depends on the beam fixing at both ends. The uncertainty in the beam fixing at both supports thus also translates into uncertainty in the adhesive strain after shrinkage. It will be clear that all model descriptions of the beam deflection do not take into account the finite stiffness of the systems that clamp the beam. That is why the scaling
experiments are complemented with calculations based on a finite element model (FEM) where issues like finite stiffness are taken into account.

5.3 Experimental

The system for the direct measurement of angular deformation due to shrinkage of the adhesive is described first. Secondly, the design of the measurement system around a commercially available mechanical displacement sensor is described. Thirdly, the measures taken to control the environmental conditions and the adhesives used to validate the measurement system are described. Finally, the FEM calculation method is detailed.

5.3.1 Deflectometer measurement system

The direct relative measurement of shape deformations with μrad resolution is possible using laser deflectometry as described by Krey (15). Laser deflectometry is an optical measurement technique in which the angle of deflected laser light from a reflecting surface is measured. From a large number of spatially separated reflected angles the shape of the object is calculated. The combination of the high angular coherence of the laser beam and a careful design of the mechanical mounting of laser and sensor to detect reflected light results in the reported μrad resolution. A significant benefit of the fact that the shape of the reflecting surface is measured is that variations in distance and angle due to mechanical drift of the measurement setup do not influence the measurement significantly. However, there are also a number of drawbacks that limit the use of this technique only as a reference for the mechanical displacement measurement system designed.

The first practical problem regarding this measurement technique is that it takes 10-15 minutes to carry out a measurement of a single 10 mm line on the top surface of the part with a measurement spot of 100 um diameter. A second problem is that calculation of the surface shape takes hours. A third problem is the fact that the available measurement setup can only accommodate a sample with a maximum height of 50 mm, limiting the scaling factor. This limited scaling results in relatively small number of measurement points (300) from which the shape is reconstructed, limiting the confidence in the accuracy of this calculated shape.
A 3D picture of the 10× scaled bending beam setup for deflectometer measurements is given in Figure 61. Clamping blocks are used to fix both ends of the bending beam onto the holder. The beam is in this case a dog-bone geometry to allow room enough for firm fixation to the supports at both ends, the bending part is rectangular. The support in the holder surface and the groove with with $l$ in the holder surface that defines the adhesive thickness and width are also indicated.

![Figure 61: 3D drawing of the 10× scaled bending beam setup with clamping blocks to hold the bending beam.](image)

The bottom of the clamping block is structured to assure localized transfer of the force without influencing the stiffness of the bending beam. It can be seen that the 18×15 mm clamping blocks are larger than the 10 mm width and length of the bending beam to accommodate the M6 screw holes in the centre of the clamping blocks. It was decided not to use smaller bolts than M6 because the clamping force must be high to reach a completely fixed beam at both ends. To prevent deformation of the clamping blocks, they have been made from the same height as the holder, assuring their mechanical stiffness. After clamping of the beam onto the holder, the construction was left to rest for 1 hour to avoid disturbances due to mechanical hysteresis (20). Then adhesive was capillary applied in the groove between beam and holder. The deflectometer tests were executed in a room with temperature of 23 °C ± 1°C. The temperature of the setup was not measured.
5.3.2 Capacitive z-displacement measurement system

To circumvent the practical limitations of deflectometry, a capacitive proximity sensor to measure mechanical displacements was chosen. The principle of operation is to measure the electrical capacitance of the air gap between two parts. Careful design of electrodes and amplifier electronics result in proximity sensors that are very accurate over a relatively long range. Further benefits of this type of sensor are the stability over longer periods of time, the high measurement sampling rate and the robust mechanical form factor. A practical requirement here is that the sensor needs to be located within 5 µm of the top surface of the bending beam, and the mounting structure of the sensor should not influence the bending of the beam. For this reason a double leaf spring construction was used, highlighted with black circles in Figure 62. This enables the decoupling of any horizontal motion of the bending beam from the mounting structure of the capacitive sensor. At the same time, this mechanical construction is used as a clamping block to fasten the beam onto the support.

Figure 62: 50x scaled bending beam setup with shrinking adhesive and integrated capacitive sensor system, decoupled with leaf springs.

A capacitive C7C sensor with DMT22 amplifier (Lion precision, USA) was used, set at maximum amplification, leading to a range of ± 5 µm with an accuracy of 0.5% of the measurement range, as assured by factory calibration (21). A sampling rate of once per 20 seconds was chosen, limited by the datalogger used (Agilent, USA). The high measurement sampling rate relative to the displacement speed means that averaging is possible to increase this accuracy. The data were sent to a PC using RS232 and
processed in Microsoft Excel and Matlab. A 3D drawing of the 50× bending beam with mechanical construction for the capacitive sensor is given in Figure 63, where the groove in the holder defines the adhesive geometry under the bending beam.

![3D drawing of 50× scaled bending beam with integrated mechanical displacement measurement sensor.](image)

The groove in the holder is used to apply the adhesive in the gap under the assembled bending beam by capillary flow. Fastening of the sensor in the mechanical construction was done using an interface ring which is compressed slightly by an M2 screw. This method avoids direct mechanical contact between screw and sensor which might influence measurement stability, and assures stable fixation without stress on the sensor. The clamping of the 50× setup was at each end of the beam realized with two sets of two M6 bolts at a mutual distance of half the beam width, in order to assure fixing of both beam ends onto the supports surface in the holder. After clamping of the beam onto the holder, the setup was left to rest for one hour to reduce influences of mechanical hysteresis. Thereafter, the adhesive was introduced between holder and beam by capillary flow.

The temperature was measured using bi-metal temperature sensors, one fixed on the measurement setup using adhesive aluminum foil, the other one fastened onto the capacitive sensor wiring with adhesive aluminum foil. The reflecting foil is used to minimize the influence of radiation on the measured temperature. The whole capacitive setup itself was covered with a box to limit air flow around it and to keep the temperature as constant as possible. The environmental temperature was conditioned to ± 1 °C. The dependence of the setup on temperature will be shown in the results section.
The measurement setup was placed on a granite table of 500 kg, isolated from vibrations of the building by rubber mounts.

5.3.3 Adhesives used

Two commercial adhesives were used, Epotek 301-2fl and Delo Duopox 6823. For Epotek 301-2fl, the A and B components were weighed in a 100:35 ratio, as prescribed by the manufacturer (Epoxy Technology, Inc, USA), and mixed intimately for 90 seconds at 3600 rpm in a Speed mixer type DAC FV150.1 PV-K. An amount of 3 ml adhesive was pipetted on one side of the gap defined by the bending beam and the base plate. It was visually confirmed that the adhesive flowed to the other side of the bending beam over the full width of the capillary. The curing time specified by the supplier is at least 3 days at 23 °C. In our experiments with the deflectometer we measured for a total time of 90 hours, to have ample curing time. In the experiments with the capacitive displacement sensor the curing process was followed for 124 hours. The E-modulus and free shrinkage of the adhesive were determined to be 2.5 GPa and 0.78%, respectively. These values were used in the FEM calculations, while for Poisson’s ratio values of 0.3 and 0.4 were taken.

For Delo Duopox 6823, the A and B components were weighed in a 5:2 ratio by weight, as prescribed by the manufacturer (DELO industrial adhesives, Germany), and mixed and applied in the same manner as described above. As the curing time prescribed by the manufacturer is only 48 hours, 60 hours was taken as measurement time for both the displacement and the deflectometer setup. The E-modulus and free shrinkage of the adhesive were determined to be 120 MPa and 1.73%, respectively. These values were used in the FEM calculations, while for Poisson’s ratio values of 0.3 and 0.4 were taken.

5.3.4 FEM model description

The FEM requires a realistic value for Poisson’s ratio as input to also take shear and lateral contraction into account. Poisson’s ratio used for hard materials in the calculations is 0.3, for the adhesive both 0.3 and 0.4 are used in the absence of measurement data.

As both the beam and the support deform under stress of shrinkage of the adhesive, resulting in a displacement in z-direction, relative displacements between defined points
need to be used. A few representative locations in the bending beam geometry are used to compare the vertical displacements of the interfaces in the differently scaled systems, as schematically indicated with black ovals in Figure 64. The numbers 1, 2 and 3 indicate the $x$-position in the centre, edge of pin and middle of pin respectively, the letters a, b and c indicate $z$-positions of these interfaces in the system; top beam surface, bottom beam surface and top holder surface respectively. The typical deformations of the surfaces are indicated with the dashed lines, the mechanical displacement $\Delta z$ in the centre of the top surface of the beam is also indicated. In white the screws fastening the beam onto the holder are schematically shown, their exact locations are specified in section 5.3.1 and 5.3.2. The movement restrictions applied are depicted by the small arrows.

![Figure 64](image.png)

**Figure 64:** Bending beam with shrinkage of the adhesive indicated, with representative locations for the FEM calculations in black circles, as well as the movement restrictions in $x$ and $z$-direction.

Half of the bending beam system as shown in Figure 64 was modeled in LISA 7.7 with Quad 4 elements in a 2D static model. The bottom of the beam holder was constrained in $z$-motion, and an $x$-movement constraint was placed in the middle of the beam.

The $\Delta z$ value of the beam centre position 1a to the pin edge position 2a is defined as $z$-displacement value from centre to pin edge, the $\Delta z$ between position 1a and 3a is defined as $z$-displacement from beam centre to centre of the pin. Position 1 has $x$ value 0, position 2 has $x$-value - 5 mm and position 3 has $x$-value - 5.5 mm for the 10× scaled
situation. For the 50× scaled situation, the x for 1, 2 and 3 are 0, - 25 mm and - 27.5 mm respectively.

The free shrinkage value of the adhesive was incorporated in the FEM model as a coefficient of thermal expansion. Lowering the temperature of the adhesive with 1 °C then results in a stress-free strain due to shrinkage of the adhesive $\Delta t$. The density of the element mesh was increased until the change in calculated $z$-displacement at the representative locations with mesh densification was less than 1%. The highest mesh density was used in the adhesive and holder pin area, where the elements have a typical size of 2 by 20 micrometer (10× model) or 10 by 100 micrometer (50× model), and gradually increased in size further away from the adhesive. The mesh size distribution is schematically shown in Figure 65. In the 50× model also the mechanical mounting system of the integrated $z$-displacement measurement sensor was modeled.

Figure 65: Mesh sizes (right) used in different parts of the FEM models (left) for the 50× and 10× scaled bending beam setup.

The 1× bending beam model was designed without decreasing the number of elements to preserve the accuracy of the model. This resulted in typical element sizes in $z$-direction of 1 to 5 micrometer in the centre of the model. Finally an extra $x$-movement restriction was applied in the centre of the beam support in the 1× bending beam model to simulate the situation in the optical part, where motion on the support is restricted.

5.4 Results

Our goal is to predict the $z$-displacement of the top of the optical part at the nm scale, which requires a validated FEM calculation. Validating whether the FEM calculations
capture the essential aspects of the physical system has to be performed by comparing the FEM results with the scaled physical system with cured adhesives. The scaling is necessary to be able to measure the z-displacement with the required accuracy. The validity of the scaling factor is also investigated by comparing the FEM with the physical reality.

The effect on the scaling conditions of the non-ideal fixing of the beam on the supports used in the FEM is investigated in 5.4.1. Secondly the stability of the capacitive z-displacement measurement system is investigated in 5.4.2. Thirdly the z-displacement measurements when curing Epotek 301-2fl and Delo 6823 in the 50× scaled geometry is measured in 5.4.3, in which also the end result is compared with the FEM results. Finally, predictions for the z-displacement of the optical part are presented in 5.4.4.

5.4.1 Validity of scaling rule for Δz-displacements

The measured $E$-modulus and shrinkage of each of the adhesives Epotek 301-2fl and Delo 6823 were put into the model, and two values of Poisson’s ratio were used: 0.3 and 0.4. Differences in displacement values $\Delta z$ of the beam top surface (a) between beam centre position 1, support edge position 2 and support centre position 3 were taken for each adhesive and Poisson ratio, and shown in Table 10. The average ratio of values when comparing the 10× and 50× setups was determined to be $5.0 \pm 5\%$ for both adhesives and both Poisson’s ratios, as summarized in Table 10.

Table 10: FEM calculated $\Delta z$-displacement values in nm of beam centre relative to edge (2-1) and centre of pin (3-1) in the 10× and 50× scaled system for both adhesives and both Poisson’s ratios, with the average ratio shown in the last column.

<table>
<thead>
<tr>
<th>Measurement position</th>
<th>Poisson’s ratio 0.3</th>
<th>Poisson’s ratio 0.4</th>
<th>Average scaling factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delo Diupox 6823</td>
<td>Epotek 301-2fl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10x 50x 10x 50x</td>
<td>10x 50x 10x 50x</td>
<td></td>
</tr>
<tr>
<td>3a-1a</td>
<td>127 638 301 1520</td>
<td>147 735 330 1665</td>
<td>5.0</td>
</tr>
<tr>
<td>2a-1a</td>
<td>110 571 259 1350</td>
<td>127 659 284 1478</td>
<td>5.2</td>
</tr>
<tr>
<td>3b-1b</td>
<td>216 1114 506 2649</td>
<td>249 1284 554 2900</td>
<td>5.2</td>
</tr>
<tr>
<td>2b-1b</td>
<td>201 1038 459 2398</td>
<td>232 1196 502 2621</td>
<td>5.2</td>
</tr>
<tr>
<td>3c-1c</td>
<td>-146 -699 -343 -1638</td>
<td>-169 -806 -374 -1789</td>
<td>4.8</td>
</tr>
<tr>
<td>2c-1c</td>
<td>-139 -651 -314 -1459</td>
<td>-160 -751 -342 -1587</td>
<td>4.7</td>
</tr>
</tbody>
</table>
This shows that the beam top surface (a) follows the scaling rule almost exactly. The slight (± 5%) deviations in scaling factor for the bottom beam surface (b) and holder top surface (c) are due to the non-ideal fixing of the beam at both supports.

5.4.2 Stability of the capacitive measurement system

To confirm the stability of the setup against external factors, the response of the system without adhesive was measured. The capacitive displacement signal and the temperature of the setup were recorded over a 21 hour time period, where the displacement measured at $t = 0$ was set to 0, as shown in Figure 66.

![Figure 66: Measured displacement $\Delta z$ with the 50× setup without adhesive: 80 nm drift over 21 hours time period.](image)

The displacement data show a profile which appears to be somewhat correlated with the temperature of the setup. The most constant average displacement over time was obtained when a linear drift of 50 nm over 21 hours was subtracted, meaning 2.5 nm per hour. The resulting displacement data was plotted with scaled temperature data in Figure 67. The dashed line indicates the time averaged displacement value.

![Figure 67: Variation in measured displacement $\Delta z$ when 2.5 nm linear drift per hour is subtracted, the dotted line is the average displacement.](image)

It can be seen that only a weak correlation exists between setup temperature and variation of the measured distance $\Delta z$, too weak to be statistically relevant but too clear...
to discard completely. These measurement data show that the variation on the displacement measurements is well within ±50 nm. This indicates that the measurement setup is stable enough for meaningful measurements of mechanical displacement due to shrinkage of the adhesive on the sub-micrometer scale.

5.4.3 Z-displacement and deflection measurements and comparison with the FEM predictions

For the 50× scaled setup, the mechanical displacement $\Delta z$ between capacitive sensor and bending beam due to curing of Epotek 301-2f1 was measured over a period of 126 hours. The setup temperature and air temperature were also recorded during this time. The results are given in Figure 68.

![Mechanical displacement during curing using Epotek 301-2f1](image1)

![Temperature of measurement system and air](image2)

Figure 68: Top: Measured displacement $\Delta z$ at the centre of the beam with the 50× scaled setup in combination with Epotek 301-2f1. Bottom: Measured temperature of air (green line) and setup (blue line).

The final $\Delta z$ measured after 126 hours due to adhesive shrinkage is 880 ± 50 nm. It can be seen that temperature of the setup does not fluctuate more than 0.3 °C during the whole measurement period, with a clear day and night rhythm. Z-displacement data can be continuously recorded during the curing process, data analysis is straightforward and
the simple sensor and electronics allow measurement of multiple 50× scaled systems in parallel.

The angular deformations of the top surface were measured in the 10× scaled deflectometer setup due to the shrinkage of the adhesive Epotek 301-2fl. Deflections were determined after 10, 30, 50, 70 and 90 hours of curing. The angular data measured were transformed into a shape of the surface, and subtracting the data obtained after 90 hours curing time from the data obtained after 10 hours results in a deformation due to shrinkage as shown in Figure 69. From this deformation curve the maximum displacement in the centre of the beam is taken as the displacement value Δz.

Deformation measured using deflectometry due to shrinkage of Epotek 301-2fl

![Deformation measured using deflectometry due to shrinkage of Epotek 301-2fl](image)

**Figure 69:** Measured shape deformation with the 10× scaled setup in combination with Epotek 301-2fl.

The maximum angular deformation is located close to the edges of the beam. In order to obtain some form of measurement accuracy, the squared residual values from a quadratic fit on the deformation curve in Figure 69 were calculated to be 4.8 nm. This is of course not a standard deviation of the measurement, but it provides an indication that the true value of the measured displacement is likely to be 185 ± 15 nm.

In Table 11, a comparison is made between relative z-displacement values Δz between position 1a and 2a (see Figure 64) as obtained experimentally and by FEM analysis. This is shown both for the 10× and 50× scaled cases, for both adhesives investigated assuming Poisson’s ratio of 0.3.
Predicting nanometer scale displacements by scaled systems

Table 11: Displacement $\Delta z$ data of 10× and 50× measurement setups and FEM calculations, position 2a-1a.

<table>
<thead>
<tr>
<th></th>
<th>Epotek 301-2fl, Poisson’s ratio 0.3</th>
<th>Delo Duopox 6823, Poisson’s ratio 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10× FEM result</td>
<td>259 nm</td>
<td>110 nm</td>
</tr>
<tr>
<td>10× measured</td>
<td>185 ± 15 nm</td>
<td>75 ± 15 nm</td>
</tr>
<tr>
<td>Difference</td>
<td>28%</td>
<td>32%</td>
</tr>
<tr>
<td>50× FEM result</td>
<td>1350 nm</td>
<td>570 nm</td>
</tr>
<tr>
<td>50× measured</td>
<td>880 ± 50 nm</td>
<td>225 ± 50 nm</td>
</tr>
<tr>
<td>Difference</td>
<td>35%</td>
<td>60%</td>
</tr>
</tbody>
</table>

It can be seen that the measured values for the $z$-displacement for the 10× setup differ ~30% from the calculated values. For the 50× setup the difference with the FEM calculation is ~35% for Epotek 301-2fl. The larger difference observed between FEM and 50× scaled measurement system with Delo Duopox 6823 is probably due to the fact that the $z$-displacement value measured is only 5 times the inaccuracy of the measurement system.

The measurements are leading in describing the actual situation so the FEM calculations are validated with an offset of 35%.

5.4.4 Prediction of the displacements in the real optical system from FEM calculations

It was shown in the previous paragraphs that the scaling rules used for the bending beam measurement setups are correct and the measurement setups used are accurate enough to validate the FEM model. The real optical part and holder combination differs in two ways from the bending beam setups. Firstly, the optical part is made of a different material than the holder. Secondly, the real optical part has no possibility to have a different $x$-displacement of top- and bottom of the plate around the support pin, in contrast with the bending beam setup, where shear is possible.

Calculations to illustrate the effect of these differences on $z$-displacements were performed with adhesive Epotek 301-2fl, using a Poisson’s ration of 0.3. Different materials and cases are considered. The results for these case are presented in Table 12.
Table 12: FEM calculations predicting the displacement values for different geometries and materials. Adhesive: Epotek 301-2fl, Poisson’s ratio used: 0.3.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Difference in displacement Δz</th>
<th>Case: N219 Steel beam and holder</th>
<th>Case: Si beam/plate and SiC holder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Beam, 50×</td>
<td>Beam, 10×</td>
</tr>
<tr>
<td>2a-1a</td>
<td>1350 nm</td>
<td>259 nm</td>
<td>25.8 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.6 nm</td>
<td>17.2 nm</td>
</tr>
<tr>
<td>2b-1b</td>
<td>2398 nm</td>
<td>459 nm</td>
<td>45.8 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.1 nm</td>
<td>43.2 nm</td>
</tr>
<tr>
<td>2c-1c</td>
<td>-1459 nm</td>
<td>-314 nm</td>
<td>-29.2 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-13.5 nm</td>
<td>-9.8 nm</td>
</tr>
</tbody>
</table>

It can be seen in column 4 and 5 of Table 12 that the effect of a change in materials combination on z-displacement of a bending beam is limited for the optical surface (a), and more significant for beam bottom surface (b) and holder surface (c). The change in relative displacement of surface (b) and (c) is of course due to the fact that the softer Si beam ($E = 100$ GPa) deforms much more than the harder SiC holder and supports ($E = 400$ GPa) when exposed to the shrinkage of the adhesive.

The significantly lower predicted displacement in the actual plate-on-pins situation, 17.2 nm instead of 27.6 nm, shows the effect of the applied restriction of the $x$-movement of the sides of the modeled part, as explained in section 5.3.4.

When applying the 35% offset determined in 5.4.3, a 12 nm z-displacement between the pins relative to the pin edge position is predicted for Epotek 310-2fl. This translates into a predicted maximum angular deformation of 18 μrad, when the deformation is assumed to have a sinusoidal shape.

5.5 Discussion

The quality of the prediction of the z-displacement of the top of the optical part due to shrinkage of the adhesive is dependent on several factors, and the discussion on these factors is divided into three parts: Firstly, the difference in boundary conditions between the scaled physical systems and the FEM model will be discussed, secondly the effect of the measurement techniques used, and finally some hypotheses on other possible influences will be shared.
5.5.1 Influence of boundary conditions on prediction certainty

In the FEM model, the mechanical coupling between the beam and the square supports on the holder is absolute, which allows only deformations due to shear, no lateral displacement is possible. The resulting deformations of the setup are shown in Figure 70, where $\Delta x$- and $\Delta z$- displacements are exaggerated by the LISA software. As can be seen, the holder surface is much less deformed than the bending beam. The clamp that holds both the beam and the capacitive sensor is itself not deformed by the adhesive, only the leaf springs are deformed. This leaf spring deformation results in a $z$-displacement of the sensor of 0.15 μm relative to position 3 (centre of pin), which is equal to the $z$-displacement of position 2 relative to position 3.

![Figure 70: Exaggerated deformation of the left half of the FEM-simulated 50x scaled capacitive measurement system after curing of Epotek 301-2f.](image-url)
In the real 50× scaled system, the beam is fixed on the square supports due to a vertical force imposed by the M6 bolts, and lateral movement of the beam over the holder surface can be possible over a sub-μm distance, as the lateral motion is not physically restricted other than by friction between the beam and holder. Modeling of this contribution is not possible in LISA. A consequence of (slight) lateral motion of the beam can be that the pressure on the holder support is reduced, leading to lower deformation of the support, and thus a lower z-displacement of the beam itself, as is measured indeed.

A second difference in boundary conditions between the reality and the FEM is that in reality, the adhesive can contract laterally in the y-direction at the sides of the beam, which is not modeled in the 2D model. In the first 40 hours of adhesive shrinkage, no z-displacement of the beam is observed in the real case, which may be an indication that at this stage shrinkage is mainly translated in lateral flow of adhesive. Also this aspect leads to a lower measured than calculated z-displacement.

### 5.5.2 Influence of measurement inaccuracies on prediction certainty

All the inputs for the FEM calculations have their uncertainties, which lead to uncertainty in the prediction. Inaccuracies in determining the free shrinkage of the adhesive linearly translate into an inaccuracy in the mechanical strain, according to equation 11. The same equation shows that inaccuracies in $E$-modulus of the adhesive have a much lower impact on the mechanical strain.

The mechanical tolerances used in the design of the parts of the 10× and 50× scaled setups were sufficiently small to ignore the effect of geometric uncertainties. Especially the z-dimension of the groove that defined the adhesive dimensions was specified to be within ±2% tolerance, and the flatness of the holder supports was specified to be 5 μm, to maximize friction and prevent lateral motion of the beam on the holder.

The positional detection accuracy of the capacitive sensor used is ±25 nm, and the total stability of the measurement system including all environmental factors is ±50 nm. Some correlation with temperature variations may be supposed. A factor which was not controlled is the relative humidity of the surroundings, and this may also have an influence on the measurement, as the insulation value of air changes with humidity and this can affect the measured capacitance. However, the difference in dielectric constant
of air at room temperature between 0 and 100% relative humidity is only $2 \times 10^{-4}$ (22) and thus can be neglected.

The $z$-displacement of the measurement construction towards the 50× scaled bending beam as visible in Figure 70 is equal to the $z$-displacement of position 2a, so the displacement of position 2a relative to 1a is unaffected by this measurement construction displacement.

5.5.3 Other factors than may influence prediction certainty

The epoxy-amine curing reaction is affected by moisture, but given the aspect ratio of the adhesive layer this effect is probably negligible. Another possibility with moisture is that it can diffuse into the adhesive layer, increasing the volume of the adhesive which in our case will reduce the measured $z$-displacement. The diffusion lengths are large, but the displacement values measured are so low, and the measurement times so long that this might still be a factor to consider.

Factors not included in the FEM calculations, such as local delamination at the surfaces of the adhesive and the formation of micro-cracks in the adhesive may also contribute to the difference between FEM calculations and measurements. These factors lead to stress release and lower deformation of the bending beam, thus a lower measured $z$-displacement value.

Differences in the allowed curing time can also cause differences in the measurements of $z$-displacements: For the curing of Epotek 301-2fl in the 10× scaled deflectometer setup, 90 hours was used, and in the 50× scaled capacitive setup 120 hours was used. The different room temperature of the deflectometer setup (23 °C instead of 21 °C) does result in a slightly faster reaction rate. With an activation energy for the reaction between 50 and 100 kJ/mol/K (23, 24), the adhesive in the 10× scaled setup reacts 9-18% faster per °C. This means that the 90 hours reaction time at 23 °C is equivalent to between 107 and 125 hours at 21 °C as used in the 50× scaled capacitive setup.

5.6 Conclusions and final remarks

For fastening a high-tech optical part securely in a horizontal and flat position, a room temperature curing adhesive can be used that will shrink upon crosslinking. This crosslinking will gradually induce nanometer sized displacements and μrad level deflections
in the optical part, compromising its performance. In this chapter, a method was proposed and successfully applied to assess such minute displacements that cannot be measured directly.

The method comprises the prediction of nanometer displacements using a finite elements simulation model (FEM), of which the quality of the results should be validated by comparing them with displacement measurements on real ‘physical’ systems. Such displacement measurements can, with the required accuracy over the time scale of the cross linking reaction (90-120 hours), only be performed on scaled up systems.

Scaling up the optical part requires extraction of a ‘bending unit cell’ from the optical part. The boundary conditions for fixing the resulting bending beam geometry on the holder supports are of crucial importance in determining the FEM.

The scaling methodology presented enlarges the physical dimensions and displacements while keeping the strains and stresses equivalent to those in the unscaled object. By comparison with FEM results the correctness of the scaling methodology was confirmed.

Scaling factors of 10× and 50× were found to be suitable for the measurement technologies used. Successful design of a capacitive displacement system with an accuracy and long term stability of ± 50 nm led to generation of reliable displacement results.

The FEM calculations typically led to ~30% higher values of displacement predicted than found in the physical systems. Possible causes for this discrepancy were discussed.

It was shown that the adhesive properties, like free shrinkage and $E$-modulus, have a large impact on measured and predicted $z$-displacement. The constrained shrinkage of less than 0.2% as measured in this chapter is in some case confused with free shrinkage (0.78% for Epotek 301-2fl and 1.73% for Duopox 6823). If the conditions of measuring shrinkage are not clearly communicated, the myth of ‘non-shrinking’ adhesives can be created.

Using this methodology and measurement systems, the most accurate prediction of $z$-displacement of the top surface of the original optical part are obtained by FEM analysis after correction for the abovementioned 30% discrepancy. Typically predicted
z-displacement values are 12 nm for an optical part resting on pins spaced at a distance of 1 mm.

The measurement system designed to measure the z-displacement of a 50× scaled systems was shown to have a resolution of ± 25 nm and measurement stability of ± 50 nm over a measurement time of 22 hours, and is well suited to measure the z-displacement.
References


6 Reduction of displacement by reduced shrinkage and stiffness of adhesive

In this chapter, the possibilities are explored to minimize the minute displacements of the top surface of an optical part, as induced by the room temperature curing of the adhesive used to adhere that part onto a mechanical support. The scaled bending beam unit cell of the optical part and the FEM model described in the previous chapter were used to relate the displacement of the beam to the thermo-physical properties of the adhesive. The thermo-physical properties of a range of adhesives with low intrinsic shrinkage or low adhesive stiffness were measured and combined with displacement measurements. The results show a clear link between thermo-physical properties of the adhesive and displacement, and indicate that the desired 2.5 nm level of displacement of the top surface of the optical part can be reached. One of the adhesives tested contained filler particles, and the influences of filler particles on thermos-physical properties and shrinkage are discussed.
6.1 Introduction

In the previous chapter, the problem of measuring minute displacements of an optical part as a result of shrinkage of the adhesive used to mount this part on pins, was presented. The measurement problem of the nanometer sized displacement was solved by first scaling the problem to sub-micrometer displacements of a bending beam. Subsequently a dedicated integrated capacitive measurement system was designed to measure the displacement of this bending beam. The correctness of the scaling conditions used was verified both experimentally and by FEM calculations. This means that the dedicated integrated capacitive measurement solution can also be used for further investigations of potentially suitable adhesives. We will use this scaled measurement system to investigate the possibilities to minimize the displacements of the optical part due to shrinkage of the adhesive used in mounting the part. The allowed vertical displacement is 2.5 nm in the centre of the optical part, which translates to 200 nm in the scaled measurement setup, as explained in the previous chapter. The focus of the investigation reported in this chapter is to investigate the possibilities to sufficiently lower the displacement due to shrinkage by testing a range of adhesives, in order to meet the specification. A second issue to address is the overestimation of the displacement values calculated with the FEM model and the actual displacement measurements performed on the scaled optical part using the capacitive measurement system, as reported in chapter 5. The possible sources of this overestimation will be discussed.

Reduction of the shrinkage of an adhesive by decreasing the cross-link density was reported (1), but the adhesive strength and the glass transition temperature $T_g$ were lowered at the same time. When the $T_g$ is lowered to below room temperature, the adhesive behaves as a rubber, which does not lead to a stable geometry of the optical part under varying circumstances. A second drawback of this method to reduce shrinkage is that it leads to increased creep for lower $T_g$ adhesives, as reported in literature (2-4). Creep is deformation of adhesive under strain, reducing mechanical stability as well, which is unfavorable for stable mounting of the optical part. The third issue when using an adhesive with a low $T_g$ is that the stiffness of the adhesive varies considerably around the $T_g$, increasing the temperature sensitivity of the parts assembled using the adhesive.
A second option to reduce adhesive shrinkage is to use a high volume fraction of filler particles, as reported by Sadeghinia (5) in epoxy molding compounds. This approach was shown to reduce free shrinkage up to 50%, depending on the volume fraction used, and appears to be a promising route. However, as discussed in chapter 5, we are not interested in free shrinkage, but strained shrinkage, for which the situation could be quite different.

The combined results of these efforts will show that the FEM model is suitable to predict displacement due to shrinkage for a large variety of adhesives. Larger deviations between FEM prediction and measurement are obtained with the adhesive that contains filler particles, and the possible sources for the deviations will be discussed. Sufficient reduction of displacement is achieved in the range of tested adhesives to meet the requirements for mounting the optical part using a non-filled room temperature curing adhesive.

**6.2 Theoretical background**

First the parameters of the adhesive that influence stress and strain in the bending beam setup will be described. Subsequently, the load situation of the bending beam in our investigations will be described relative to the situations in measurement of creep and stress relaxation. Some aspects of adhesion as a function of stress in the adhesive will be described next. Finally, the different effects of adding particles into the adhesive will be described.

**6.2.1 Parameters of the adhesive influencing stress and strain in the bending beam**

As described in the previous chapter, the mechanical stress and strain need to be considered at the bottom surface of the bending beam, where the displacement in the adhesive is $\Delta t$, as indicated in Figure 60. The 50× scaled bending beam setup has length $l$ and width $w$ of 50 mm, a thickness $d$ of 28.3 mm and a nominal adhesive thickness $t$ of 0.5 mm.
The total change in thickness $\Delta t$ of the adhesive can be written as:

$$\Delta t = (\varepsilon_{\text{free}} + \varepsilon_{\text{mech}}) t = \varepsilon_{\text{total}} t$$  \hspace{1cm} (1)$$

in which $t$ is the thickness of the adhesive layer, $\varepsilon_{\text{total}}$ is the total strain of the adhesive, built up by mechanical strain $\varepsilon_{\text{mech}}$ and vertical adhesive shrinkage under stress free conditions $\varepsilon_{\text{free}}$. The bending of the beam due to a load $Q$ can be described as:

$$\Delta t = \frac{-Q l^3}{CEI} = \frac{-Q}{K_{\text{beam}}}$$, with $K_{\text{beam}} = C \frac{EI}{l^3} = C \frac{Ebd^3}{l^3}$ \hspace{1cm} (2)$$

in which $C$ is a constant dependent on the method of clamping of the beam, $E$ is the Young’s modulus of the beam material, $d$ the thickness of the beam, $b$ the width of the beam and $l$ the length of the beam between the supports. The distribution of the load $Q$ over the width of the beam is not dominant for the resulting beam displacement for the thick beam used in our setup, as described in chapter 5.2.2. The total strain can thus be expressed as:

$$\varepsilon_{\text{total}} = \frac{\Delta t}{t} = \frac{-Q}{K_{\text{beam}} t} = \frac{-\sigma_{\text{beam}} lb}{K_{\text{beam}} t}$$, with $Q = \sigma_{\text{beam}} lb$ \hspace{1cm} (3)$$

Using equation 1, 2 and equation 3 with $l = b$, the stress that bends the beam can be expressed as:
Reduction of displacement by reduced shrinkage and stiffness of adhesive

\[ \sigma_{\text{beam}} = -\varepsilon_{\text{total}} \frac{K_{\text{beam}} l}{lb} = -(\varepsilon_{\text{free}} + \varepsilon_{\text{mech}}) \frac{C Ed^3 l}{l^4} \]  

(4)

The stress that strains the adhesive layer after shrinkage can be expressed using the stiffness of the adhesive:

\[ \sigma_{\text{adhesive}} = \varepsilon_{\text{mech}} \cdot E_{\text{adhesive}} \]  

(5)

When taking the effects of bulk compression into account (6), equation 5 translates to:

\[ \sigma_{\text{adhesive}} = \varepsilon_{\text{mech}} \cdot \frac{1 - \nu}{(1 + \nu)(1 - 2\nu)} E_{\text{adhesive}} = \varepsilon_{\text{mech}} \cdot E'_{\text{adhesive}} \]  

(6)

in which \( \nu \) is the Poisson’s ratio of the adhesive and \( E'_{\text{adhesive}} \) is the effective modulus for this case. Because there is equilibrium, these two stresses are equal in magnitude, giving

\[ \sigma_{\text{adhesive}} = -\sigma_{\text{beam}} \]  

(7)

Substituting (4) and (5) in (7) gives:

\[ \varepsilon_{\text{mech}} = -\frac{\varepsilon_{\text{free}}}{\frac{K_{\text{beam}} (l^2)}{l \cdot b} + 1} \]  

(8)

This result shows that when the mechanical properties of the beam remain constant, the mechanical strain depends only on the adhesive shrinkage strain \( \varepsilon_{\text{free}} \) and the effective adhesive stiffness \( E'_{\text{adhesive}} \). The product of these properties is defined as adhesive stress. The minimum value of this adhesive stress is defined by the vacuum pressure used to initially hold the optical part at a level of 0.05 MPa, which is related to geometry stability requirements. The maximum adhesive stress allowed in order to keep the displacement of the top surface of the optical part below 2.5 nm will be calculated with FEM and presented in section 6.4.1. The adhesive tested has a thickness of 0.5 mm and a width of 50 mm, so we expect that the horizontal shrinkage is negligible.

As the exact Poisson’s ratio that leads to \( E'_{\text{adhesive}} \) was not determined in the experimental investigations, it is assumed that they are comparable and constant for all adhesives, so we can use the measured value \( E_{\text{adhesive}} \). In the FEM model as described in
the previous chapter, the $E$-modulus and free shrinkage of the adhesive are varied to investigate the effect of these parameters on the displacement $\Delta z$. In the FEM, values for Poisson’s ratio used were 0.3 and 0.4 respectively to take horizontal shrinkage into account and estimate the effect of the decision to only measure $E_{\text{adhesive}}$. The $z$-displacement between positions 1a and 2a in Figure 71 will be used in the rest of the chapter to indicate the $z$-displacement of the beam. As the scaling rules were validated in the previous chapter, FEM calculations will be made using the $1\times$ beam model. The specification to meet is a $z$-displacement of less than 2.5 nm between the positions 1a and 2a in Figure 71, to result in a maximum allowed angular deformation of 5 µrad of the optical part. Due to the fact that the FEM calculations result in a $\sim35\%$ larger displacement value than the measured displacement value, the calculated displacement must be lower than 4 nm to correspond with an actual displacement within specifications for the optical part. In the experimental $50\times$ bending beam setup, this translates into a maximum displacement of 200 nm between positions 1a and 2a.

### 6.2.2 Creep and stress relaxation measurements in relation to our measurement method.

As described in the introduction, lowering the adhesive stiffness or the $T_g$ also lowers the adhesive stability over time as an undesired side effect. Two measures for this effect have been defined when considering adhesive stability over time. The first is creep, which is the displacement of an adhesive over time at constant strain. The second is stress relaxation, which is the lowering of adhesive strain over time at constant stress. The two load cases and their corresponding indicative test curves measured are given in Figure 72.
Reduction of displacement by reduced shrinkage and stiffness of adhesive

Figure 72: Load cases and corresponding test curves for the stability of adhesives: Left: Creep load case, measuring displacement over time at constant stress; Right: Stress relaxation load case, measuring stress decrease over time at constant displacement.

The creep behavior of a given adhesive is dependent on its visco-elastic properties, and is influenced by time, temperature and applied stress. Furthermore, the adhesive chemistry and formulation influence the creep behavior over time. The commercial relevance of predicting the stability of an adhesive joint has spurred on many investigations in determining the creep behavior of adhesives using accelerated tests. Some examples of investigations on structural adhesive joints are given in (4, 7, 8). Some examples of investigations on stability of adhesive joints for electronic components, both measurements and modeling, are reported in (9, 10). Modeling efforts are important as the creep effects continue over very long periods of time, making real time measurements cumbersome.

Stress relaxation of an adhesive over time is dependent on the same material factors as in creep. Recently, theoretical investigations were conducted into stress relaxation of thin epoxy layers on silicon by Chen (11), who related creep with stress relaxation in already formed layers, where the stress was due to a mismatch in the coefficient of thermal expansion (CTE). The model was only compared to other models and not experimentally verified.

An important difference between the measurement techniques used in previous work and the present investigation is that the load on the adhesive below the bending beam is different. The stress and strain that influence the adhesive during buildup of the network are not constant, but change continuously. This is schematically indicated in Figure 73.
As the load condition shown in Figure 73 is completely different from those specified for creep and stress relaxation measurements, we cannot use creep and stress relaxation as terms in the explanation of displacement values after complete curing. However, effects similar to those in creep and stress relaxation are not absent, and may play a role in the 35% difference between FEM calculated displacement and measurement results.

If any flow of adhesive from the sides to compensate for volume reduction is possible during the first hours of curing, the horizontal component of the shrinkage of the adhesive is not negligible during this time. The FEM is a 2D model where the adhesive is constrained on all sides, where in practice the adhesive between beam and holder is only contained on four of the six sides. This might be a way to explain the observed 35% difference between FEM calculated displacement and measurement results.

6.2.3 Adhesion as a factor in adhesive strength under stress

Adhesion of an adhesive to an interface cannot be measured independent of the cohesive strength of the adhesive. The generally accepted way of getting an indication of the contributions of adhesive and cohesive joint strength of an adhesive to an interface is by testing different bond geometries, as described and modeled in literature (12, 13). Some often used test geometries are schematically drawn in Figure 74.
Reduction of displacement by reduced shrinkage and stiffness of adhesive

**Figure 74:** Joint geometries used for strength testing; Left: Lap joint, Middle: Butt joint; Right: Thick adherent shear.

It can immediately be seen that the load cases are completely different, and the corresponding adhesive stress at failure is also different from geometry to geometry. In the thick adherent shear test the strain is more on the bulk of the adhesive, and in the lap joint geometry the strain is more at the interfaces, purely because of geometrical arguments.

The difference of the measurement methods and the difference in load cases complicate the comparison of adhesive strength values between investigations. Furthermore, the determination of cohesive and adhesive strength of the adhesive is analyzed in a simple way: If the adhesive detaches from the interface at the failure stress, the adhesive strength is said to have been limiting. If the adhesive does not detach from the interface upon failure, the cohesive strength is said to be limiting. In the former case, the adhesion strength is lower than the failure stress, and in the latter case the adhesion strength is higher than the failure stress.

Comparisons of adhesives under similar experimental conditions have indicated that large differences in adhesion strength exist between adhesives. Typical values for pressure that can be applied on epoxy adhesives in lap shear strength where adhesive failure is not limiting are between 50 and 150 bar. Interface modification has been reported in several publications (14, 15) to increase the adhesion strength of adhesives. Results of such modifications cannot be directly generalized due to the differences in experimental conditions. In our tests, we do not modify the interfaces used and assume that predominantly adhesion strength with the interfaces is tested during shrinkage because of the low adhesive thickness used.

### 6.2.4 Effects of filler particles on thermo-physical properties of adhesives

When filler particles are introduced in an unfilled adhesive, the first effect to be expected is a decrease of shrinkage $\varepsilon_{\text{free, composite}}$ of the adhesive due to a lower volume fraction of reactive polymer as given by:
where $\phi$ is the volume fraction of filler material. For most filler materials, $\epsilon_{\text{filler}}$ is negligible, so a significant reduction of shrinkage can be realized for high volume fractions of filler. The second effect is an increase in stiffness of the composite because of the higher $E$-modulus of the particles relative to the polymer. The $E$-modulus of the filler particles can be orders of magnitude higher than that of the adhesive, dependent on the filler material. In recent investigations, large differences in measured $E$-modulus upon addition of filler particles were reported, ranging from 30% increase at $\phi$ is 12% (16) to 700% increase at $\phi$ is 30% (17). This large difference is an indication that measurements must be performed to determine the $E$-modulus of a given filled epoxy system. The balance of the parameters $E$ and $\epsilon$ must be considered to determine if the addition of filler particles leads to a reduction of displacement due to shrinkage of the adhesive.

Besides these obvious effects, the adhesive system changes from homogeneous to heterogeneous, and extra interactions also have to be considered, such as adsorption of adhesive polymer on the sub $\mu$m filler particles and interaction between such particles. The interactions between particles are well known, and the effect of polymers in between particles is investigated in colloidal chemistry (18). The effects of the interactions between polymers and filler particles on the mechanical properties of adhesives in its shrinkage during curing are not well known. Many studies on composite materials have focused on fracture dynamics over time (19, 20), and strength of composites under sliding load (21, 22), but not on displacement during the curing stage. Recently some work has been published on the interactions between filler interfaces and the polymer matrix (23, 24), which is a starting point towards more fundamental understanding on what happens on an even smaller length scale. Our measurement approach can help to assist the research in this area, but more extensive investigations are needed for better understanding of the effect of these molecular interactions on the mechanical interaction of the adhesive during its shrinkage.

### 6.3 Experimental

The measurement technique to determine free shrinkage of the adhesive during curing is described first. Then the measurement technique to determine the $E$-modulus of the
used adhesives after curing is described. The capacitive displacement measurement system and the FEM model used are briefly described, the extensive description can be found in chapter 5. Finally the adhesives used are listed, including the preparation methods used.

6.3.1 Free shrinkage of the adhesives

Free shrinkage measurements were performed on a thermal mechanical analyzer (TMA) 841E (Mettler Toledo, USA), which is a temperature controlled displacement measurement setup with nanometer resolution. Samples were prepared by placing a round droplet of 0.15-0.3 mm wide on a sand blasted glass plate and covered with a 0.1 mm thick silicon plate, forming a confined droplet of known thickness, as shown schematically in Figure 75. A force of 0.02 N was applied to ensure good mechanical contact between the displacement transducer and the Si plate.

![TMA sample geometry used for displacement measurements due to shrinkage of the adhesive.](image)

The geometry of the TMA sample, especially the thin Si cover plate, ensures ‘free’ shrinkage of the adhesive as much as possible, in contrast with the constrained shrinkage in the optical part. The temperature was held constant at 25 °C in a flow of nitrogen, so the relative humidity can also be said to be constant and low. An example of a representative TMA measurement for one of the adhesives, DELO Duopox 6823, is given in Figure 76. The analysis of the shrinkage step was performed in STAR® software (Mettler Toledo, USA).
Figure 76: TMA measurement of DELO Duopox 6823, the vertical position of the glass rod on top of the Si plate is recorded as a function of time.

It can be seen that the displacement is only 2.16 μm, or 1.73% of the original adhesive thickness. The displacement of 0.25 μm in the first 1000 minutes of the curing process can be an artifact, indicating that a 10% uncertainty in the measurement can occur, despite the high resolution of the instrument.

6.3.2 $E$-modulus and $T_g$ of the adhesives

Young’s modulus $E$ and glass transition temperature $T_g$ were determined using dynamic mechanical thermal analysis (DMTA), which is a rheological technique that strains the sample and records the force needed to achieve this strain. DMTA samples of the adhesive were cast in a Teflon geometry of $10 \times 4 \times 1$ mm and cured at room temperature for the time prescribed by the supplier (16-168 hours). The cured samples were ground to assure equal thickness over the whole length and the exact dimensions were determined using a Mitutoyo digital caliper. The samples were measured with an RDA II (Rheometrics, USA), using a 2 °C/min temperature ramp from -50 °C to +200 °C with a frequency of 1 Hz and 0.03% strain, and an initial static force of 0.1 N. The temperature ramp also allows the determination of $T_g$ in the same measurement. As an example, representative DMTA curves for DELO Duopox 6823 are given in Figure 77, as measured after two different curing times, the one specified by the supplier and approximately three times longer.
Reduction of displacement by reduced shrinkage and stiffness of adhesive

It can be seen that a longer curing time than prescribed by the supplier has a significant influence on both the measured $T_g$, which increases from 30.2 °C to 39.6 °C, and the $E$ modulus, which increases from 120 MPa to 1.2 GPa when determined at 22 °C. This again shows that variations in the preparation of the samples have to be excluded as much as possible. It also shows the importance to use adhesives with a $T_g$ that is as high as possible.

6.3.3 System and method to determine and calculate displacement

As discussed in chapter 5, a bending beam was demonstrated to be representative for the bending of the optical part. A 50x scaled up design of that bending beam was equipped with a capacitive measurement system for evaluation of the induced bending, as discussed in chapter 5. The combination of scaled bending beam and capacitive measurement system is schematically shown in Figure 78. The FEM model of the bending beam, as described in chapter 5 was used to predict the displacement of the middle of the top surface of the beam for the various adhesives.
6.3.4 Materials and preparation

A wide variety of room temperature curing 2K-epoxies is available from different suppliers, and a selection was made to get a variety of adhesives with different stiffnesses and shrinkages. Nine adhesives selected for low free shrinkage or low E-modulus, as based on indications of the suppliers, are given in Table 13.

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>Masterbond</th>
<th>Emerson &amp; Cuming (Stycast)</th>
<th>Huntsman (Rencast)</th>
<th>Delo</th>
<th>Epo-Tek</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP30LV</td>
<td>W19 / LV24</td>
<td>CW2418/HY5160</td>
<td>Duopox 6823</td>
<td>301-2</td>
<td></td>
</tr>
<tr>
<td>1265</td>
<td></td>
<td>CW219/HY5160</td>
<td></td>
<td>301-2fl</td>
<td></td>
</tr>
</tbody>
</table>

Components A and B of the two component adhesives were weighed on a PM400 balance (Mettler Toledo, USA) in the ratio prescribed in the technical data sheet of the supplier with a total weight of about 7 gram. Mixing was performed in a Speed mixer type DAC FV150.1 PV-K (FlackTek Inc, USA) at 3600 rpm for 90 seconds.
6.4 Results

Firstly, the $z$-displacement is given of the middle of the top surface of the 1× bending beam, predicted by FEM calculations as a function of the thermo-physical adhesive properties $E$-modulus and shrinkage $\varepsilon$. Secondly, the measured $E$-modulus, $T_g$ and shrinkage $\varepsilon$ of the selected adhesives are reported and a subset of adhesives was chosen for displacement measurements on the 50× scaled setup, which can be simply compared to the 1× calculations because the scaling rules were validated in chapter 5. Thirdly, the displacement results of the selected adhesives are presented and compared with FEM predictions, and the discrepancies between these results discussed. Finally, displacement results are given for filled adhesives, and the limit of the applicability of the FEM model for these adhesives is discussed.

6.4.1 Displacement dependency on thermo-physical properties of adhesives: FEM results

The beam displacement during strained adhesive shrinkage as a function of different values for the thermo-physical properties stiffness and shrinkage has been calculated using the 1× bending beam FEM model, as described in the previous chapter. This gives an indication of the dependency of beam displacement on effective $E$-modulus and adhesive free shrinkage. A graphical representation of the resulting $z$-displacement of the middle of the top surface of the beam between the pins is given in Figure 79. The limit of 4 nm displacement to meet the angular deformation specification of 5 μrad is indicated with the dashed line.
Different combinations of $\varepsilon_{\text{free}}$ and $E$ lead to a $z$-displacement equal to the maximum allowed value of 4 nm in the FEM model of the 1x bending beam, which corresponds with 2.5 nm $z$-displacement and 5 μrad deformation of the optical part. A low $E$-modulus combined with a relatively large shrinkage $\varepsilon_{\text{free}}$ as well as a low shrinkage $\varepsilon_{\text{free}}$ combined with a higher $E$-modulus can lead to that maximum allowed displacement of 4 nm, as is shown in a different way in Figure 80.

Figure 79: Displacement due to shrinkage of the adhesive for different levels of stiffness $E$ and free shrinkage $\varepsilon_{\text{free}}$.

Figure 80: $E$-modulus of adhesive combined with adhesive free shrinkage, related to displacement of a bending beam as calculated with the FEM model.
The maximum allowed stress in the adhesive \((E\text{-modulus} \times \text{free shrinkage})\) decreases non-linearly with increasing shrinkage of the adhesive from more than 1 MPa for an \(\varepsilon_{\text{free}}\) of 0.25%, to less than 0.5 MPa for an \(\varepsilon_{\text{free}}\) of 2.5%.

When an adhesive with an \(E\)-modulus of more than 1 GPa is selected, an \(\varepsilon_{\text{free}}\) below 0.2% is needed, and these low free shrinkage levels are not attainable in commercially available adhesives. When an adhesive stress of less than 0.05 MPa is present in the final state, the optical part is not sufficiently held in place.

### 6.4.2 Thermo-physical properties of selected 2K-epoxies

For the epoxies listed in Table 13, thermo-physical properties were measured and listed in Table 14. The \(E\)-modulus is given in column 4, the \(T_g\) given in column 5, and the free shrinkage is given in column 6. In the last column, the calculated adhesive stress \((E\text{-modulus} \times \text{free shrinkage})\) is given, as this indicates what the predicted strained shrinkage level is from the 1× bending beam FEM model, as explained in section 6.4.1.

**Table 14: Thermo-mechanical properties of the selected 2K-Epoxy adhesives.**

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Adhesive</th>
<th>Curing time (hrs) @ 23 °C</th>
<th>(E)-modulus MPa @ 22 °C</th>
<th>(T_g) (°C)</th>
<th>(\varepsilon_{\text{free}}) (%)</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Master bond</td>
<td>EP30LV</td>
<td>24 – 36</td>
<td>400 (^a)</td>
<td></td>
<td>2.31</td>
<td>86</td>
</tr>
<tr>
<td>Emerson &amp; Cuming</td>
<td>Stycast W19 / Stycast LV24</td>
<td>16</td>
<td>970-2000 (^b)</td>
<td>34.44 (^b)</td>
<td>1.53</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Stycast 1265</td>
<td>250</td>
<td>0.65</td>
<td>-2.4</td>
<td>0.4</td>
<td>0.0025</td>
</tr>
<tr>
<td>Huntsman</td>
<td>Rencast CW219 / Ren HY5160</td>
<td>168</td>
<td>4380</td>
<td>54.8</td>
<td>1.85-1.9</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Rencast CW219 / Ren HY5160</td>
<td>168</td>
<td>2700</td>
<td>55.6</td>
<td>0.43-0.71</td>
<td>17</td>
</tr>
<tr>
<td>Delo</td>
<td>Duopox 6823</td>
<td>48</td>
<td>120-1270 (^b)</td>
<td>30.2-39.6 (^b)</td>
<td>1.73</td>
<td>2</td>
</tr>
<tr>
<td>Epotek</td>
<td>301-2</td>
<td>100</td>
<td>3200</td>
<td>59.6</td>
<td>0.96</td>
<td>31</td>
</tr>
<tr>
<td>Epotek</td>
<td>301-2fl</td>
<td>100</td>
<td>2500</td>
<td>&gt;45</td>
<td>0.78</td>
<td>20</td>
</tr>
<tr>
<td>Epotek</td>
<td>77-167-1</td>
<td>100</td>
<td>90</td>
<td>25.5</td>
<td>2.11</td>
<td>1.12</td>
</tr>
</tbody>
</table>

\(^a\) Data given by supplier.

\(^b\) First value is taken after the specified curing time while the second value is taken after 168 hours curing, as post curing effects were suspected.'
The only product of which the A component contains filler particles is Ren
cast CW 2418, all the other adhesives are non-filled adhesives. The difference between Ren
cast CW2418 and Ren
cast CW 219 is that only the first contains filler particles, which leads to a significant increase in E-modulus. Stycast 1265 has a $T_g$ below 0 °C, radically different from the other adhesives. The relation between stiffness and $T_g$ for this series of non-filled adhesives (excluding Stycast 1265) is clearly linear, as seen in Figure 81.

![Figure 81: Young’s moduli at 22 °C for the different adhesives listed in Table 14 as a function of $T_g$.](image)

Figure 81: Young’s moduli at 22 °C for the different adhesives listed in Table 14 as a function of $T_g$.

The linear relation between stiffness and glass transition temperature is probably due to the fact that the chemistry of all tested adhesives is similar. The adhesives with low E-modulus all have a $T_g$ close to room temperature, which means that its physical properties are sensitive to fluctuations in temperature. To maintain mechanical stability of the optical part, the temperature of the part needs to be kept constant when adhesives with a low $T_g$ are used.

The filler particles in Ren
cast CW2418 are 80 µm in diameter, which prevents its use in the final system, and the same product without filler particles, Ren
cast CW219, mixed with the B-component Ren
cast HY5160 is very similar in final properties to Epotek 301-2f1 but much more viscous. Hence it was decided not to test the Ren
cast products on displacement in the 50x scaled bending beam setup.

Stycast 1265, the product with the lowest shrinkage measured also has a low E-
modulus which predicts that the deformation will be very low. Unfortunately, the stress level is lower than the minimum of 0.05 MPa needed to maintain the initial condition of the optical part. Initially, the optical part is pulled flat onto the pins of the substrate using 0.5 bar vacuum, corresponding to 0.05 MPa adhesive stress. This adhesive also has a very low $T_b$, indicating that the temperature stability of the bonded construction...
will be low. Furthermore the curing time of 10 days is very impractical. Still it is tested with respect to displacement in order to verify the predicted low $z$-displacement.

The other adhesives with a low $E$-modulus are Epotek 77-167-1 and Delo Duopox 6823, of which the latter is preferred as it is a commercial product, whereas Epotek 77-167-1 is a research sample. Still this sample was used in deformation measurements as it would fit the requirements very well, even though also with this adhesive the low $T_g$ is a risk for mechanical stability.

6.4.3 Displacement of bending beam by non-filled adhesives: FEM and measurements

The 50× scaled bending beam with integrated capacitive displacement measurement setup, as described in the previous chapter, was used to determine the $z$-displacement of the top surface due to shrinkage of the adhesive.

The measurement uncertainty in the displacement measurements was determined to be ±50 nm as based on beam displacement measurements without adhesive during 24 hours, as reported in chapter 5. For the longer measurement times, as used for a few of the adhesives, the measurement uncertainty was based on displacement measurement data using the low $E$, low $T_g$ adhesive Stycast 1265. Figure 82 shows the displacement for this adhesive during the measurement time of 250 hours, where the average displacement is indicated with the dashed line.

![Figure 82: Displacement of the middle of the top surface of the bending beam due to the shrinkage of Stycast 1265.](image)
It can be seen that the displacement of 50 nm in the first 3 hours is followed by a fluctuating deformation without a clear pattern other than that due to day and night thermal fluctuations of the test setup. These random results indicate that the deformation due to shrinkage is much lower than the measurement system stability, as predicted. It can be seen that some correlation with temperature fluctuations during day and night cycles exist in addition to the larger system variation. This effect of temperature on deformation might be due to the effect that the adhesive $E$-modulus increases with lower temperatures and decreases with higher temperatures, although this effect results in variations of 20 nm at most.

The variation of ± 75 nm from the mean measured displacement of -125 nm can be taken as the measurement system stability over these 10 days. This uncertainty is larger than the value of ± 50 nm obtained in the previous chapter for a time period of 1 day but not unexpected given the much longer measurement period.

The displacement measurement data for all selected adhesives and their uncertainties are plotted in Figure 83 together with the calculation results from the FEM model. These data are plotted as a function of the calculated adhesive stress ($E$-modulus $\times$ free shrinkage), as this value is predictive for the FEM displacement calculations. The grey dashed line indicates the 200 nm displacement value below which mounting of the optical part is according to specifications.

![Displacement measured](image1)

**Figure 83:** Displacement of the centre of the beam due to shrinkage of the seven adhesives tested values are plotted as a function of the adhesive stress ($E$-modulus $\times$ free shrinkage).
It can be clearly seen that three of the tested adhesives can be used for mounting the optical part with displacement within specifications, as judged from the measured displacements. Delo Duopox 6823 is the most suitable candidate as it has the highest $T_g$ and is commercially available. Next to the displacement values, also the stresses in the adhesive layer are calculated in the FEM model. The values typically seen are between 10-30 MPa, which place high demands on the adhesion, as explained in section 6.2.3.

Epotek 77-167-1, Masterbond EP30LV and Stycast W19, indicated with the circles, show FEM displacement results that differ very much from measurement results. This indicates the possibility of partial delamination or adhesive failure under the stress that occurs under the bending beam. The Epotek 77-167-1 is an experimental adhesive, where adhesion failure can be expected. In the technical data sheet of Masterbond EP30LV excellent adhesion is claimed, but in small print it is mentioned that chemical etching and sanding should be performed on non-porous metal surfaces as used in the test setup. Stycast W19 is marketed as a low viscosity, isolating impregnant for electronic boards, and not specifically as an adhesive. Also here adhesion failure could be a reason for the much lower value for displacement.

The other four tested adhesives give fair comparability of experimental bending and FEM results, when using the 35% difference discussed earlier.

6.5 Discussion

Some items in the relation between thermo-physical properties of adhesives and displacement due to shrinkage are still under discussion. Firstly, the accuracy of determination of thermo-physical properties is discussed for adhesives without and with filler particles. Secondly, the determination of adhesion strength is discussed in more detail. Thirdly, the possibility to reduce adhesive shrinkage with particles is discussed. Finally, an outlook is given on methods to improve the prediction of displacement and to come to an adhesive that has high $T_g$, high stiffness and low shrinkage.

6.5.1 Issues in determining thermo-physical properties

A prerequisite for accurate predictions is an accurate model with appropriate inputs, such as accurate measurements of free shrinkage. The TMA measurement setup as used has its limits, as even the thin silicon cover plate used has a certain stiffness which means that the shrinkage is not completely ‘free’. However, this configuration was
identical for all adhesives in this study, and the temperature control and high displacement resolution of the setup means that it is still the best available measurement method.

The second input for the model is a correct stiffness of cured adhesive. For high $T_g$ adhesives the DMTA measurement shows that the $E$-modulus is stable at room temperature and can be used safely. The DMTA measurements on adhesives with low $T_g$, however, show that the $E$-modulus is strongly temperature dependent. A reliable $E$-modulus measurement is also relevant when filled adhesives are considered, as the interface between filler particles and adhesive matrix can be separated under strain. The DMTA system has its limits in the maximum strain it can put on a sample, in the scaled measurement system 0.1-0.2% strain is applied for more than 24 hours, while the DMTA system applied only 0.03% strain on the sample for 1 hour. This can lead to a higher measured $E$-modulus than in the reality of the scaled measurement system, as it is possible that the bond between filler particles and organic matrix is maintained under the lower applied strain in the measurement setup than in reality. Destructive optical fracture analysis by Wang (27) has been used to determine the interface strength between particles and different epoxy matrices. In these investigations it was shown that non-functionalized filler particles could be separated from the polymer matrix under strain, while particles functionalized with epoxy- or amine reactive groups were not separated from the polymer matrix.

6.5.2 Adhesion strength determination

The hypothesis of partial adhesive failure under the stress of the bending beam in the case of Stycast W19, Epo-Tek 77-167-1 and Masterbond EP30LV needs some discussion. The lap shear method is used most widely in determining the adhesion of adhesives, but the outcome of the test is very much dependent on the experimental conditions. This test is also a combination of cohesive and adhesive failure, which prevents pinpointing the exact adhesive failure mechanism. Again, determination of adhesive strength is mixed with effects from bulk adhesive properties. The 50x scaled bending beam measurement method combined with the FEM simulation used in our investigations might be a good starting point for a separate determination of adhesive strength and adhesion strength. The bending beam test species can be designed using geometry variations in the FEM model to result in a certain adhesive stress. The
displacement measurement error measured during curing can then be an indication if adhesive failure occurs at this stress level.

6.5.3 Outlook

The current FEM calculations use a single end point value for the adhesive stiffness, while in reality the adhesive stiffness increases as the curing process progresses. In our 2D model this would not have a significant effect, but in a 3D model such a time-dependent stiffness would allow horizontal flow of adhesive during the first stage of curing, yielding a more accurate prediction. Mathematical methods that could be used to incorporate such a time dependent stiffness are reported in literature (28, 29).

It was shown that reduction of shrinkage induced displacement of a beam by lowering adhesive stiffness can only be done to some extent, as the stability of the construction prescribes a certain minimum adhesive stress. The ideal adhesive would have a chemical reaction that does not decrease the bond length between the reactive groups. This is only possible if the volume of the reactive groups in the non reacted separate molecules is smaller than in the reacted polymerized molecules. This can be achieved by using so-called strained molecules as a source for reactive groups, as reported in literature for strained monomers capable of kationic radical (co)polymerization (30, 31). The fundamental cause of shrinkage would then be addressed, potentially leading to a stiff and non-shrinking adhesive with a high $T_g$.

6.6 Conclusions

The best option to minimize displacement of an adhesively bonded part due to shrinkage of the adhesive is to lower the $E$-modulus of the adhesive below 200 MPa, as free shrinkage values of adhesives cannot be lowered below 0.2%

Using adhesives with $E$-modulus below 200 MPa but above 1-10 MPa (dependent on the adhesive free shrinkage), the extreme flatness specifications for adhering an optical part to a holder can be reached.

The stresses in the adhesive due to its cure shrinkage can reach values of 10-30 MPa in our system as calculated in the FEM model, mainly due to the stiffness of the beam used, which can result in adhesive failure for adhesives that have sub-optimal adhesion to the materials used.
When a large difference between measured and predicted displacement is seen, it may be a clue for effects like adhesive failure.

Prediction of nanometer size displacements due to shrinkage of an adhesive is well possible for a wide range of adhesives with very different properties.

The methods used for determining thermo-mechanical properties in this investigations have been thoroughly developed for accuracy and reliability, but still leave room for improvements needed in order to be able to only use FEM modelling based on these data and not to verify anymore with (scaled) measurements.
Reduction of displacement by reduced shrinkage and stiffness of adhesive

References

Chapter 6

Summary

Often, when a new interface between two materials is being created, an exciting research subject is opened. The physics and chemistry governing the interaction between the materials at such an interface is most of the time already partly known from previous theoretical and experimental efforts. When the physico-chemical interactions at a specific interface have a large effect on product performance or product reliability, a deeper level of understanding about these interactions is required. Specific model systems have to be realized that keep most parameters constant, and allow detailed study of the quality determining interactions only.

In this thesis, three of these physico-chemical interactions were investigated. Firstly, wetting of liquid onto a structured surface was studied in two seemingly different model systems, where mainly the velocity of the liquid and the pressure that was applied onto the liquid differed significantly, while the viscosity range investigated was complementary. Secondly, the electrical effect of a thermally induced chemical reaction between a silver paste and doped silicon surface was analysed. RF radiation was used to allow extremely fast selective heating and cooling of the silver, and the change in electrical resistance between the silver and the silicon as a result of diffusion and reaction was monitored. Thirdly, the effect of the shrinkage of an adhesive material during the chemical curing reaction on a mechanical beam structure was investigated, while the scale of the deformations of the structure were in the order of 1µm.

For the study of wetting effects on a structured substrate using a velocity of the liquid of less than 1 mm/s, the well-known Wilhelmy plate method was extended by using a structured model substrate. The wetting resistance over the structured model substrate used could be described well theoretically, and the measurements showed very good agreement with the theory, also upon receding of the liquid, which was previously impossible to measure using other approaches. Furthermore, it was shown that under conditions that are relevant for microfluidic devices with micro-capillaries, the surface structure has a significant influence on the forces occurring during flow over this structure.

In the case of applying printing pressure on UV curable ink with a range of viscosities during less than a millisecond, the same principles for capillary flow and fluid resistance over surface structures still apply, only the relative influence of the
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different contributions changes. Using a model system with vertical structures onto which a UV curable ink could flow during the printing process and be solidified using UV radiation afterwards, the forced flow process has been visualized. Measurements of the flow length under different process conditions using SEM microscopy showed that the influence of these process parameters on ink flow could be determined well in this way. It was found that the ink flow was significantly different at either side of a wall over which the printing roll moved, indicating the asymmetry of the printing process. It was shown that at both extremes of the process window of printing pressure, liquid viscosity and applied volume of fluid per surface, the flow of fluid was symmetric at both sides of the structure. Also for this combination of process time and motion speed, alternative analysis techniques prevented the investigation of this process in this level of detail, while the value of homogeneous fluid deposition using this printing technique and others is significant, especially at the high resolution of 10 µm investigated.

Similar challenges in investigating a highly dynamic process of heating a silver paste using RF radiation within 1 second to more than 700 °C and back to room temperature again were met in chapter four. Direct temperature measurement of the thin lines of silver paste was impossible, and only the conductive heating of the surrounding silicon substrate could be measured using thermography. Significant technological steps in process control of heating using RF radiation were made, where the energy could be tuned as a function of position of the substrate. Using this approach, the effects of different heating process conditions on the electrical resistance between the silver and silicon could be measured. It became clear that the diffusion of silver and the reaction kinetics between silver and silicon were not favorable enough for significantly improved electrical contact formation at the silver-silicon interface at these process conditions.

The third physico-chemical interaction investigated was the mechanical effect of shrinkage of an adhesive on an optical structured during curing, where the maximum allowed deformation of the optical structure was in the low nanometer range. In order to have the possibility to reach these deformation values, two component room temperature adhesives with low intrinsic shrinkage were selected, which need more than two days to reach full strength. Existing measurement systems with the required accuracy have difficulties with stability over such a long period, which led to the development of a scaled system with an integrated capacitive measurement system. The
validity of the scaling was confirmed using two different scaling factors, two different measurement systems and two adhesives, and also with Finite Element Modeling, using independent measurements as input. Different adhesives were subsequently tested on shrinkage in the capacitive test setup as well as using FEM to predict the shrinkage. It was shown that stiffness of the adhesive in combination with ‘free’ shrinkage was a very good predictive set of parameters for mechanical deformation of a defined structure. In addition, it was shown that deviations from the FEM prediction for the tested adhesives were most likely due to adhesive failures on the interface. The combination of scaling, test setup, FEM and adhesive testing led to a choice for an adhesive that helped to fulfill the flatness requirements of the optical part.

Concluding remarks

As summarized in the preceding section, the three types of multi-material interfaces described in this thesis have a largely different focus. However, in all cases the transport of matter at an interface under influence of external stimuli is investigated, and the effect that the interface has on this transport or vice versa. The combination of material transport, interface and external stimuli was chosen in order to investigate and solve a limiting factor in Philips’ projects.

The common factor in all projects is that the number of variables that is present in the real product necessitated the development of a model system with a reduced number of variables in all cases. The model systems and accompanying measurement strategies can be re-used in other applications where the same gap in knowledge is present with a different set of materials that make up the interface, and even a different external stimulus that drives material transport.

When one limiting factor is removed, the rest of the project typically runs relatively smoothly, explaining the large variety in subjects covered in this thesis.
Summary and concluding remarks
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Dankwoord

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