Biomimetics of optical micro- and nanostructures

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Abstract

The field of research of this thesis is Bionics or Biomimetics. The fraction of the nature examined is the Flora. The plant of interest is the spotted evergreen, which is a shade plant. It was suspected that the surface of the leaves has a special nano- or microstructure to trap and absorb the light better. This question was answered with the help of Atomic Force Microscopy (AFM). Due to these pictures a special chesslike pattern can be suspected.

To reproduce the structure the material Coltene President light body® was used to take imprints of the leaves. Then a material to which the structures can be transferred was searched. Twenty-two materials were tested, only two of them were suitable for further research: beeswax and crashglass.

There was the hope that the structure of shade plant leaves could be adapted to decrease the reflectivity of the coverglass for solar cells. This was tested with two solar cells under a halogen lamp. The two different materials have been tested, on the one hand with special structure, on the other hand with an even surface to have a reference. Although the results are not convincing on account of many errors, which can appear, they are promising and expandable.
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1 Introduction

Nature is full of ideas and concepts, which only wait to get discovered and copied by us to make our lives even more comfortable. Even though it seems that most of the things are obvious, because they are visible with the naked eye, there is so much hidden in the details. The nature is a wonderful playground for scientists, who are open for everything and like to discover. For these scientists bionics or biomimetics is the answer to their search.

Bionics is the operation of discovering the nature, investigating the nature and imitating the nature in technical objects. It is the ability to learn from the nature and bring these concepts into action. This was tried to be implemented in this work as well.

The leaves of shade plants should be imitated by photovoltaic cells, not by the chemical view, but by the surface structure. It was suspected that shade plants feature a special surface, optimized for their life in the shadow with little light. This was proofed circuitous with photovoltaic cells. If these provide greater performance due to the nano- and microstructured coating, there really exists a surface adjusted to its surroundings.

Naturally it could not be expected that in the process of this thesis everything would go as expected, but it was not predictable that there would be so many challenges to face. Aside from smaller problems, which were solved quickly and the frustration every scientist has to face, when absolutely nothing works or the results turn out completely different than expected, there were more serious problems, which delayed the progress of this thesis.

The first problem, which needed to be solved, was that the Atomic Force Microscope (AFM) was broken after taking the first pictures. It was not foreseeable how long it would take to repair the AFM, so it was inevitable to modify the topic of this thesis. That is the reason why the photovoltaic cells were used as a proof for the special structure.

The next problem was the disappearance of Aglaomema costatum in the botanical gardens of Vienna. The tropical gallery was prepared for the winter semester and the plant
was therefore removed for some time. After long research some specimen were found in the Federal Gardens of Vienna. It was possible to take the imprints there.

The most tricky challenge which had to be solved, was the construction of a thin beeswax layer containing the structure. This is described more detailed later.
2 Shade Plants

Nature is trying to use every little spot of the earth if not manipulated or restricted. Hence there exist many plants, which are growing under a dense canopy of leaves, needles and branches, where the light intensity near the ground is naturally lower. Nevertheless, there subsists a group of plants, which is optimized for these circumstances: the shade plants.

There are various ways for shade plants to receive the light they need. According to Schnepf the Acanthacee Fittonia verschaffeltii evolves spherical hair, which serve as converging lenses to collect the light. Furthermore, the epidermis papillae of for example the tropical Calathea zebrina or the European Oxalis acetosella resemble as well collecting lenses. Moreover, only a small part of the species Lithops, well known as living stones, grows above-ground, so a special tactic to receive light is required. Nature solves this problem brilliantly by creating tissue similar to glass fibers. The light enters the upper part of the plants through transparent window-like cells and the tissue below leads the light to the chloroplasts. [Schnepf, 2006] [Schulte et al., 2009]

Figure 1: The differences between a sun and a shade leaf of a beech, image adopted out of [Jansen et al., 1998, 51]
As can be seen in figure 1 adopted out of [Jansen et al., 1998, 51] the leaves growing in shade are much bigger than the ones growing in bright sun. This is a result of the fact that they receive less sunlight and must therefore provide extensive leaves. A connection between the difference in the thickness of shade and sun leaves and the $CO_2$ diffusion is suspected. [Jansen et al., 1998, 49 ff] [Terashima et al., 2001]

On closer examination of the shadow plants in the tropical gallery of the botanical garden of Vienna it can be observed that there are more or less two different characterisations of these special plants. There exist plants, which grow high with big leaves, like for example *Calathea zebrina*, and on the contrary, there exist plants, which grow low with rather small leaves, like for example *Geogenanthus poeppigii*. In exchange the second typ grows reminding of a carpet, so it covers nearly all of the ground.

2.1 *Aglaonema costatum*

![Image](image.png)

Figure 2: Two cions of *Aglaonema costatum* of the Federal Gardens Vienna

The *Aglaonema costatum* belongs to the family of Aracea, the tribe of Aglaonemateae and the genus Aglaonema. Nicholas Edward Brown was the first one to describe the plant and imported it in 1892 to Great Britain. The plant originates from the island Langkawi next to the northwest coast of Malaysia and is now domiciled in China, Laos, peninsular Malaysia, Mexico, Singapore, Southeast Asia, India and the United States in tropical areas. [Hor, 2017] [Zip, 2017] [Flo, 2017]
The Greek and Latin name *Aglaonema costatum* originates from the words: aglos (bright), nema (thread) and costatus (ribbed). The first term is similar to the German name Kolbenfaden and the second term refers to the white stripe covering the midvein of the leaf. Common names for the plant are Chinese Evergreen, Malaysian Evergreen and Spotted Evergreen. [Flo, 2017] [Zip, 2017]

The creeping shrub reaches a height about 12 to 40 cm. The leaves are ovate and about the size of the palm of a hand. The form reminding of a heart with obtuse edges ends in a short petiole/trunk. The foliar venation is pinnately compound and the mid-vein is covered by a broad white stripe. [Flo, 2017] [Zip, 2017] [Society, 2003, 89]

*Aglaonema costatum* is rather interesting for this thesis, due to its characterization as a shade plant and the white dots it only develops if exposed to the sun. [Flo, 2017] [Hor, 2017] [Zim, 2017]

### 2.2 Results: Surface of *Aglaonema costatum*

The surface of the leaves of *Aglaonema costatum* was copied, described in chapter 3. In order to avoid faults in the surface, the negative imprint of the leaves was directly analyzed with the atomic force microscope. Two different types of probes were investigated:

- imprints taken from leaves, where a high density of dots was given to increase the probability of analyzing the surface of a dot
- imprints of leaves without dots

It was suspected that the surface of the dots could be different to the rest of the leaves, because they only appear if exposed to the sun, as mentioned above.

It was suspected that there could be a special structure on the surface, because the dots are internal. It is not possible to remove them with wiping or scratching. The leaf is smooth at every place, there cannot be felt any borders between the dot and the area around it. This was confirmed by looking at the edges of the dots with the ProScope HR™ (Bodelin Technologies, Lake Oswego, OR 97035, USA). At Figure 3 can be clearly observed that there is a smooth transition.
Figure 3: The transition of a dot on a leaf of *Aglaoema costatum* into the area around is fluent. Picture taken with ProScope HR™.

Naturally there are plenty of different potential explanations for the formation of the dots. It could be that the chlorophyll gets destroyed by the sun light. Possibly because the plant owns collecting lenses like described in the work of Eberhard Schnepf, and they burn the chlorophyll. The purpose of the converging lenses would be to focus the spare light and the chlorophyll could possibly be more sensitive. These two arrangements would be ideal for the given lighting conditions, but then could be deadly for exceeding solar radiation. This would be comparable to a permanent sunburn. [Schnepf, 2006]

The most probably purpose of the white leaf marks is to reflect the superfluous, not digestible light. It is evident that white areas are more reflective than darker areas. Therefore the function of the white dots could be to reduce the size of the efficient foliar surface to prevent the leaves and cells from damage. However, this is jeopardized by the fact that this result could be achieved easily either by curling the edges of the leaf or by reducing the number of leaves growing from the same trunk.

As mentioned in chapter Shade Plants, there exist several plants with two types of leaves. The shade leaves are often larger and thinner, while the sun leaves appear to be smaller but thicker. It was supposed that *Aglaoema costatum* could have similar characteristics. On closer inspection, the only noticeable observation was that the leaves without dots seem darker green. All leaves appear to have the same thickness. The thickness does not vary within the leaf, which means that the leaf is not thinner at areas with dots. [Jansen et al., 1998, 49 ff]
The Figures 4 and 5 show the structure of the negative molds of a leaf of *Aglonema costatum*. The pictures were taken with an Atomic Force Microscope (AFM) in the mode AC Air Topography. On the one hand the surface of a dot of a heavily pointed leaf is pictured in Figure 4, on the other hand the surface of a leaf without dots is visible in Figure 5.

Due to this technique of taking an imprint of the leaf surface and investigating these molds, no plant was harmed by tearing off some of there leaves. Furthermore it was not necessary to transport the AFM.

At the picture of the surface of the dot there can be recesses observed with a distance between of approximately 4 to 13 $\mu$m and a diameter of approximately 8 to 21 $\mu$m. The depth of the valleys is around 60 nm, which are shown in the figure as hills, because the AFM scans and illustrates the negative mold. It seems that the recesses are arranged in a periodical chess pattern. On closer inspection of the valleys nothing particular interesting could be observed. The smaller voids are of no regularity or special standardized shape.
In contrast, the AFM picture of the leaf without dots shows absolutely no conspicuousness concerning the structure. The surface seems completely smooth, although it seems that the surface is waved. Given that the scale of depth is different colored in Figure 5, the small valleys visible could be of similar depth like the ones of the dot. Nevertheless, the surface seems smoother since there cannot be seen any additional nanostructures. The upper third is hardly usable, due to random noise. The dots visible could exist because of dirt or air inclusions, because they are not regular.

These results are rather surprising. At first thought, it would be much more reasonable that the structures are interchanged. The leaf in the shadow would have a special structure to trap the light or expand the surface and the leaf exposed to more light would reflect the light, due to its smoothness.

However, there are a lot of reasons why it is not like this. First of all it could be that the smaller structure in Figure 4 is a result of dust, chalk deposit or air inclusions. In this case, the leaf would have the same structure everywhere. The only problem could be that the chess pattern valleys exists due to the same reason. However, this is very unlikely, because they are too regularly and exist in two different molds. Another reason for the small spots could be that the chess pattern structure gets destroyed slowly, if the plant is exposed to excessive light. This would decrease the efficiency of the leaf and could be a explanation for the development of the white dots.

Considering the first reason and expecting the valleys to exist, it should be of no importance if the solar cell gets covered by the structure of a leaf with dots or without dots. Due to the fact that in the most times the leaves with dots are bigger and more even, the imprints were taken all of the same leaf covered by dots for the stamp.
3 Molding technique

The technique of transferring the structure of *Aglonema costatum* was copied from previous works. President light body® (polyvinylsiloxane (addition-type), ISO 4823, Coltène Whaledent AG, 9450 Altstätten, Switzerland) was used for the negative imprint of the plant’s surface. Hereunto the two components (base and catalyst) were mixed on a glass plate with a spatula as described on the instruction sheet and then spread on the surface of the leaves. Before this process the upper side of the leaves were freed of dirt and dust to receive an imprint as perfect as possible. Later in the process of this work, it was shown that using an injection increases the accordance of original and copy. [Schulte et al., 2009]

The stamp (85×120 cm) used for the coatings of the solar cells was made by adhering ten imprints of a leave of *Aglonema costatum* and an imprint of a CD together with Soudal Fix All Crystal® and a thin elastic plastic. Each imprint had the dimensions 2×4 cm and they were arranged to fit the polycrystalline solar module perfectly. The CD imprint was given in one corner of the stamp to have the instant test, if the nanostructures have been transferred.

One of the main purposes of this work was finding an alternative to the cancerogenous epoxy resin, which was used before to form a positive imprint of the surface. Therefore a wide span of materials was tested, listed in Table 1.

To rate the quality of the materials for positive molds and to see immediately if nano- and microstructures were transferred, a negative imprint with President Light Body® of a compact disc was used. The advantage of the CD is that you can see at once, if the imprints have worked. If you can see the rainbow colors, which the nanostructures are responsible for, on both imprints you can be sure that the structure has been transferred.

Given that the index of refraction plays a prominent role in the nanotechnology and is very difficult to identify, it was assumed that the materials own a refractive index similar to the refractive index of the commonly used epoxy resin.
Table 1: Materials tested for positive molds

<table>
<thead>
<tr>
<th>material</th>
<th>functional efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspic</td>
<td>contour can be seen, but surface is completely smooth</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>is working at the edges of the imprint, but wax is breaking easily</td>
</tr>
<tr>
<td>salt paste</td>
<td>paste is too coarse-grained, only outline can be seen</td>
</tr>
<tr>
<td>caramel</td>
<td>rainbow colors can be seen at areas without air inclusions</td>
</tr>
<tr>
<td>beeswax</td>
<td>nearly perfect copy, is flexible and gets nearly transparent if thin</td>
</tr>
<tr>
<td>almond paste</td>
<td>thin oil film forms between negative form and marzipan</td>
</tr>
<tr>
<td>chocolate</td>
<td>many air inclusions, surface uneven and stochastic</td>
</tr>
<tr>
<td>DontoMed</td>
<td>is not getting hard, stays sticky and soft</td>
</tr>
<tr>
<td>sugarglass</td>
<td>only contours, surface even</td>
</tr>
<tr>
<td>spattling compound</td>
<td>is not working</td>
</tr>
<tr>
<td>warmwax</td>
<td>sticky, imprint disappears completely after short time</td>
</tr>
<tr>
<td>sugar icing</td>
<td>is not getting hard</td>
</tr>
<tr>
<td>modeling clay</td>
<td>only a small rainbow colored dot can be seen</td>
</tr>
<tr>
<td>wall filler</td>
<td>coarse-grained and clotted</td>
</tr>
<tr>
<td>icing</td>
<td>is not working</td>
</tr>
<tr>
<td>Fix All</td>
<td>destroys negative mold, does not work</td>
</tr>
<tr>
<td>carnauba wax</td>
<td>getting hard quickly, rainbow colors can be seen at the edges</td>
</tr>
<tr>
<td>plaster</td>
<td>is not working</td>
</tr>
<tr>
<td>acrylic color</td>
<td>is not drying under the negative mold</td>
</tr>
<tr>
<td>acrylic structure gel</td>
<td>is only working at one edge</td>
</tr>
<tr>
<td>nail polish</td>
<td>nail polish adheres to mold, destroys nanostructure</td>
</tr>
<tr>
<td>crashglass</td>
<td>tiny air bubbles trapped, rainbow colors can be seen</td>
</tr>
</tbody>
</table>

The aspic was made by cooking some water with Dr. Oetker, Tortengelee klar®. Then the negative mold was laid on top and the arrangement was cooled. When the aspic was solidified the mold was removed and only the outline remained. The area of the imprint was completely smooth and it was not possible to see any reflections similar to a CD.

To make an imprint in paraffin wax, a tealight was lighted until all wax was molten. Then the candlewick was removed and the wax poured into a flat bowl. When the edges were solidified the negative mold was laid in the middle of the paraffin wax. The imprint and the rainbow reflections can be seen at the edges. However, the paraffin wax breaks easily and fissures rather quick.

By kneading salt, water and flour a material can be created known as salt paste or play dough. In this paste the negative mold was pressed and left at an open window over night until it was hard. The outline was visible, but under the mold some salt...
crystals were formed, which prevented the salt paste to adopt the nanostructures.

After some failures we succeeded to cook caramel with sugar. After the caramel cooled down a little bit an imprint was made. The caramel hardens uneven and incloses air so it is not suitable as material for the copy.

In contrast, the beeswax made a nearly perfect copy of the surface of the CD. The bleached beeswax available in pharmacies was molten in a water quench at approximately 60°C and then poured on a flat plate. The negative mold was laid upon as soon as the edges of the wax solidified. The negative mold was easy to peel of and the beeswax stays elastic and does not fissure compared to the paraffin wax. The rainbow colors are clearly visible. If thin the beeswax gets nearly transparent, which would be optimal for surface coatings of solar cell cover glasses, windows and similar objects.

Another edible material tested was almond paste (SPAR Feine Marzipan Rohmasse®). A small piece was cut off, stiwed with powder sugar and then flattened. The negative mold was pressed into the mass and peeled of when the almond paste was hard. Since a thin oil layer formed between the paste and the negative mold, the structure could impossible be transferred to the marzipan. The negative mold has to be rinsed to remove the oil film.

The S Budget Back & Kochschokolade® was molten in a water quench and the imprint was made. Instead of a copy, the surface of the chocolate was uneven and stochastic with a lot of holes and air inclusions. The chocolate beyond the borders of the imprint is completely smooth.

Another attempt was the DontoMed Haftcreme®, which purpose originally lays in fastening dentures on the gingiva. The red and soft creme stays even after long time like this and by peeling of the imprint it changed its form completely, because it is adhesive and followed the mold as long as possible.

Sugarglass can be easily fabricated at home by mixing and cooking sugar, water and agave nectar. When the mass reached a temperature of 150°C it was spread thin on a flat surface. The sugarglass gets hard rather quickly, while the one side was still poured out the other one was already hard. The negative mold was set on the soft mass and
stayed there for an hour. When it was detached, there only stayed the contour, the imprint itself was completely smooth.

One typical material of the construction industry is the spattling compound (Knauf Füllspachtel innen®). When compound with water, one receives a semi-fluid mass in which it is possible to make an imprint. However, the imprint was imperfect and had a lot of small holes.

An idea arisen from lateral thinking is using warmwax (Balea Warmwachs Roll-on®), which purpose normally is to dispose of unwanted hair. The wax was heated in a water quench and applied on an fleece-band in two different ways. On the one side the roll-on cap of the warmwax was used, on the other side the bottle was opened and a small amount of the wax was spilled. The molds were crimped inside and the arrangements were cooled. The cold wax was still sticky but hard, when the mold was peeled of, the contour was visible, but the surface was completely flat and smooth. As soon as the wax got a little bit warmer, the contours disappeared as well.

The simplest form of sugar icing can be made by mixing powder sugar with water. The negative mold then is put in and left there for a night. Although the surface seems to be hard, the area covered by the mold is not getting hard and sticks onto it.

A new development in the reparation and reconstruction field for amateurs is the Pattex Power Knete®. It can be formed and should adapt to roughness. However it requires a lot of pressure to make an imprint and so the nanostructures could hardly be transferred.

Another amateur reparation material is the wand filler (molto S.O.S. Easy Wandfüller®). This material is unuseable for the purpose of molding, due to its coarse-grained and clotted character.

A similar edible material to the almond paste is the Renshaw ready to roll icing®. Even though there exists no oil film between the mold and the material, the imprint could not be seen.

The optical optimal material would be the Soudal Fix All Crystal®, if it would work. The adhesive sealing material is transparent, easy to spread on and elastic.
tempt of making an imprint the negative mold was destroyed in the act of peeling it off. The rainbow colors are not visible.

Given that it worked well with beeswax, another natural wax was tried. The carnauba wax (Primabene Carnaubawachs®) was molten in a water quench at approximately 80°C and the imprint was made. The wax solidified in few seconds and got really hard but light. The rainbow colours are only visible at the edges. There are no holes due to air inclusions, which could have been an explanation. Although the working surface was flat, the wax is curved and it cracked while it solidified. Potentially the wax tightens while setting and destroys the nanostructure.

The typical material for molding would be the plaster (Knauf Bau- und Elektrikergips®). However the imprint was not visible.

For the acrylic color a small portion of green acrylic color was compound and then the negative mold pressed on. After a day and a night the mold was removed. Even though the color around the mold was dried, under the mold the color was still wet and would remain in this state as long as the mold stays there.

Another painter utensil tested was the SOLO GOYA Acrylic Structure Gel Gloss®. In a small amount of the gel the negative mold was pressed and left there for the night. When the impression was exposed it was visible that it only worked at one edge. The gel would be optimal because it gets transparent if dry but stays elastic.

The purpose of lacquers is to coat objects and to fit them like a second skin. Nail polish (essence the gel nail polish®) has the same purpose, with the advantages that it is nontoxic, easy to use and quick-setting. However, it adheres to mold, so it cannot copy the mold and it destroys the nanostructure. Afterwards the rainbow colors on the negative mold diminish.

For the purpose of fabricating an imprint in crashglass professional help was consulted. Crashglass granulate is molten directly and poured onto a foil restricted by four silicone soaked wooden planks. The transparent mass is reheated with a flame and the stamp doped into the mass. After 15 minutes the crashglass is hard and the stamp can be removed. The colors of the CD can be seen, but there are some small holes, caused
by air trapped between the stamp and the crashglass. In order to avoid these bubbles another technique was tried. The stamp is laid between the wooden planks and the molten crashglass is poured directly on the stamp. Another 15 minutes later the crashglass solidified and the stamp was removed carefully. The copy of the leaves was nearly perfect with only a small crack and some small bubbles trapped.

The main challenge therefore consists of fabricating a thin layer of beeswax. It must be rather transparent, thus thin and the number of air bubbles embedded should be as low as possible. Despite the unevenness of the structure of the leaves, the copy should exhibit a relatively smooth base.

Many concepts were implemented and most of them failed. The technique used in the end was a result of long testing and an accident. Great efforts were taken to develop a technique to transfer the nanostructures of the leaf to a thin layer of beeswax.

At the beginning some beeswax drops were melted in a tupperware box with the dimensions 14x9 cm in a water quench. Due to the fact that the wax does not spread constantly, but concentrates at the edges, the base of the box turned out to be domed. Furthermore the wax sticks on the plastic and it is nearly impossible to peel it off.

Two different "Fixativspritzen" were constructed, with two different diameters of the tubes. They are used to apply paint evenly via air, which lifts the paint due to the depression in the pipe and sprays the droplets on the screen. Instead of the paint liquid beeswax was used and should have been sprayed on an aluminum box lined with a foil. However, the beeswax was too viscous, heavy and got instantly hard as soon as it infiltrated the pipe.

The next experiment which failed owing to the rapid solidification of the beeswax was an Aerosol. Some drops of beeswax were molten in the bottle in a water quench, then the cap was screwed on the bottle and it was tried to spray onto the aluminum box mentioned before. The pipe was plugged approximately at the half with the solidified beeswax, so it was not able to reach the spray head.

The bottle with the roll-on cap of the warmwax was reused. The remains were washed
out and some drops of beeswax were molten inside in a water quench. However, the viscous character frustrates all efforts once again and blocked the roll of the cap.

The try of coating the stamp directly with molten beeswax failed, because it solidifies too quickly. Therefore the layer is too thick, uneven and not transparent.

A technique which seemed promising, was melting beeswax on the aluminum box heated by two tealights. The stamp was pressed in the wax and the tealights were extinguished. In the solidified wax it was visible that some places never touched the wax and others pushed the wax aside due to the pressure.

The accident named before was the breakthrough. While warming beeswax in an aerosol, the aerosol exploded and some drops of the beeswax end up in the boiling water. The water and the wax was left there to cool down, and the beeswax formed a thin film on the water surface. It was homogeneous and thin, therefore nearly transparent. This serendipity was studied and optimized.

In order to produce a thin layer of beeswax, water is heated at maximum heat. As soon as small bubbles start rising the heat is changed to minimum and the open topped vessel containing some beeswax drops is placed in the hot water. When the wax is molten the heat is turned off and the last remaining bubbles get removed. A rectangle made of straws, to ensure that the rectangle stays on the water surface, is dropped in and the liquid beeswax poured in the form. With the help of a wooden stick the wax is spread constantly in the rectangle, to get a thin layer of beeswax in the form of a rectangle. The setup is then left to cool down, as soon as wax is solidifying at the top of the stick. The wax in the floating rectangle is nearly transparent, thin and constant. The best result of this technique was used for the measurements in chapter 4.2. It can be seen in figure 7.

On account of the success, this technique was also tried for constructing a beeswax layer with leaf structure. A float for the stamp was created by using straws with greater diameter. The procedure described in the paragraph before was conducted with the only difference that the floating stamp was added after the wax coated the water, so there is no hole in the coating. As soon as the wax solidified it was clearly visible that a lot of air was trapped between the stamp and the wax. The wax layer was perforated
and the beeswax is thicker at the repaired holes. So it is not possible to correct the voids.

The technique used for the beeswax layer with leaf structure used in the end should be described here. A rectangle with thick beeswax layer produced with the successfully proved technique described before was placed on the stamp. The setup was heated in the oven by top heat at approximately 60-75°C. The beeswax molted directly on the stamp and formed a thin film and possible bubbles were removed. At the moment the wax has molten completely parchment paper was laid on top. The setup was then left to cool down. The wax was peeled off with the parchment paper. The copy of the leaves is not perfect but the best done with the available resources. It was used for the measurements.
4 Photovoltaics

The world is searching for environmentally sustainable alternatives to common energy resources like oil, coals, gas and nuclear power. Next to hydroelectric power, wind energy, geothermal power, biomass and solar heat there is one option, which this thesis will discuss: photovoltaics.

Photovoltaics is based on semiconductor technology and the internal photoelectric effect. In the simplest case a solar cell is a semiconductor with pn junction. The most utilized material is silicon. Not all photons can be used. Some have too low energy, which can not lift electrons in a higher state, other got too high energy, and only heat the cell. For further explanations concerning the operating modes of photovoltaics see the technical literature. [Mertens, 2015, 92ff] [Wesselak and Voswinckel, 2012]

The efficiency $\eta_{eff}$ of the cell can be calculated with

$$\eta_{eff} = \frac{P_{pn}}{P_{solar}}.$$  \hspace{1cm} (1)

Where $P_{pn}$ is the emitted performance of the solar cell and $P_{solar}$ is the irradiated performance.

4.1 Different surfaces of photovoltaic cells

Normally the silicon wafers exhibit irregular, non-periodic and stochastic surfaces. Given that silicon is rather reflective, it cannot easily utilize all the light available. Therefore, efforts are being made to increase the efficiency of silicon based cells by optimizing the surface amongst others. [Phillips et al., 2011]

In the recent years many different special surface structures for silicon solar cells were tested to decrease reflectivity and increase the absorption. Due to the fact that not all work in this field of activity can be described and listed, some should be mentioned in this thesis and even less described. There exist different shapes at the nanoscale, such as holes, domes, hemispheres, (inverted)cones, triangles and (inverted)pyramids. Naturally this list is only fragmentary and can touch this area of research merely superficially. [Gao et al., 2013]
Thanks to the technique of light trapping it is possible to use thinner layers of silicon, which decreases the costs for silicon, which is difficult to fabricate.

4.1.1 PERL cell

The abbreviation PERL cell stands for passivated emitter, rear locally-diffused cell. The structure of inverted pyramids on silicon wafers is known for its low recombination loss character due to its passivation properties and a layer of SiO$_2$. [Zhao et al., 1995]

The excellent light trapping properties of the special structure used for the PERL cell was discovered already in 1987. The implementation in the technique of photovoltaic cells was not carried out until 1995. With further improvements in 1996 it permits an efficiency of 23.5% and it is expected to be possible to push the efficiency up to 25%. [Campbell and Green, 1987] [Zhao et al., 1995] [Zhao et al., 1996]

Due to the enormous technical effort, this concept is not practical for the daily use. Nevertheless, there exists a commercial cell with similar surface. [Mertens, 2015, 199f]

4.1.2 honeycomb structure

Similar to the PERL cell is the development of solar cells with nanobowls shaped like honeycombs. The hexagonal recess decreases the reflection and serves the light trapping. Thanks to this special surface the efficiency of multicrystalline solar cell raised from 18.6% to 19.8%. The reflection was reduced to 2%. It was also used for monocrystalline solar cells, where it raised the efficiency of 24.0% to 24.4%. There are two possibilities to realize this special structure. [Zhao et al., 1998] [Zhao et al., 1999] [Kang et al., 2011] [Gao et al., 2013]

The newer possibility is covering the crystalline silicon solar cell in a thin silver layer, then forming identical drops with the help of a rapid thermal annealing. In this step the wafer is heated by quartz-halogen lamps to high temperatures (around 1000°C) for short times (circa 1 s). The drops in the size of a few nanometers drill the nanobowls into the silicon by metal-assisted chemical etching. To get the honeycomb form, the surface is oxidized to form a thin oxide layer, which is then eliminated by HF wet etching,
where a buffered hydrofluoric acid solution comes into operation. The nanobowls are not uniformly distributed and vary in diameter and depth with this technique. [Gao et al., 2013] [Rabus et al., 2006]

The technique originally developed by Martin A. Green shows a more regular structure of honeycomb bowls. At first a thin masking silicon dioxide layer is generated on the wafer of the multicrystalline silicon solar cell, which amounted about 30% of the commercial photovoltaic product in the year 1999 and about 58% in 2004, whilst monocrystalline silicon solar cells were about 36% and only 4% thin film amorphous silicon solar cells. Through this layer hexagonal holes are drilled with photolithography. In the last step these holes receive hemispherical wells by using an acid solution composed by hydrogen fluoride and azotic acid. [Zhao et al., 1998] [Zhao et al., 1999] [Phillips et al., 2011]

An additional feature of 2011 includes a rough surface on the base of the honeycomb called nano-honeycomb structure. This again increases the absorption and decreases the reflection. To cut the long talk short this structure improves the light trapping. [Kang et al., 2011]

4.1.3 moth-eye structure

The newest development in the surface optimizing of silicon cells is the inclusion of moth-eye structures. Some nocturnal moths need to see their surroundings in the dark night, so they cannot afford to dissipate any lights. Therefore they have a special surface on their eyes to absorb the light and for the purpose of camouflage. The nipples of the moth eye were imitated to decrease the reflectivity of the silicon. While commercial multicrystalline silicon solar cells show hemispherical reflectance in a range of 20 to 30%, the optimized solar cells have a reflectance near zero. Again there are different approaches to reach this aim. [Phillips et al., 2011] [Kuo et al., 2016] [Wilson and Hutley, 1982]

A simple technique to obtain the moth eye surface directly on the multicrystalline silicon wafer will be described here shortly. The wafer gets coated with silica microspheres in a tank filled with de-ionized water. In a short recovery the microspheres form a monolayer colloidal crystal with periodically arranged nipples reminding of the structure of
moth-eyes. This technique is rather simple, because it is self-assembling and does not require complex methods to form a homogeneous structure. [Phillips et al., 2011] [Kuo et al., 2016]

The work of Jung Woo Leem and team is the one most related one to this thesis. The structure of the moth-eyes is not directly applied on the silicon wafer, but is covering the glass, to reduce the reflectivity of the coverglass and yield a hydrophobic effect. The technique is similar to the technique used in this work. The structure is transferred in 2 steps. First an imprint of a master silicon mold is taken with Polydimethylsiloxan. This negative mold then serves as a stamp to structure the thin layer of Norland Optical Adhesive 63. This is the coating of the coverglass. The conical structure demonstrably reduced the reflectivity and the wettability of the coverglass. [Leem et al., 2015] [Kuo et al., 2016]

A similar technique to the one before is used to cover the silicon cell: the soft roller nanoimprint technique. The flexible master mold gets pressed into the UV sensitive resist spin-coated on the wafer constantly by a roller. The biomimetic moth-eye inspired nanostructures get transferred by plasma or ion etching. The master mold gets taken from a nickel master structured with the help of two-beam laser interference photolithography to receive the moth-eye pattern. [Chen et al., 2009]

![Figure 6: left: Monocrystalline solar cell; right: Polycrystalline solar module](image)

### 4.2 Results of the coated solar cells

In this work, two different photovoltaic cells were used. On the one hand a monocrystalline silicon solar cell by "Conrad electronic" with the dimensions 96×66 mm and on
the other hand a polycrystalline silicon solar panel by "Conrad" in the size 82 × 120 mm. The solar cell has a nominal voltage of 0.5 V whereas the solar panel has a nominal voltage of 6 V. The nominal current of the monocrystalline silicon cell is 800 mA and 150 mA at the polycrystalline silicon cell. The sun was imitated by a halogen lamp of 1500 W.

The measurements were performed on the 21st of September 2017. Six test series took place, all with a distance of 0.6 m and an angle of zero degree. The averaged values can be extracted from table 2. The values for the output power P were evaluated with the well known formula

\[ P = U \cdot I. \]  

Table 2: Average current I, voltage U and output power P of the solar cells coated with different materials with different structures

<table>
<thead>
<tr>
<th>Mono</th>
<th>beeswax</th>
<th>leaf beeswax</th>
<th>plastic</th>
<th>crashglass</th>
</tr>
</thead>
<tbody>
<tr>
<td>I [mA]</td>
<td>132, 50 ± 8, 77</td>
<td>130, 00 ± 9, 71</td>
<td>138, 17 ± 5, 7</td>
<td>138, 17 ± 4, 22</td>
</tr>
<tr>
<td>U [V]</td>
<td>0, 5335 ± 0, 1046</td>
<td>0, 5748 ± 0, 0044</td>
<td>0, 5752 ± 0, 0174</td>
<td>0, 5788 ± 0, 0107</td>
</tr>
<tr>
<td>P [W]</td>
<td>0, 0707 ± 0, 0146</td>
<td>0, 0747 ± 0, 0056</td>
<td>0, 0795 ± 0, 0041</td>
<td>0, 0799 ± 0, 0029</td>
</tr>
<tr>
<td>Poly</td>
<td>beeswax</td>
<td>leaf beeswax</td>
<td>plastic</td>
<td>crashglass</td>
</tr>
<tr>
<td>I [mA]</td>
<td>60, 17 ± 13, 17</td>
<td>54, 67 ± 11, 25</td>
<td>76, 5 ± 5, 56</td>
<td>64, 5 ± 9, 98</td>
</tr>
<tr>
<td>U [V]</td>
<td>6, 8417 ± 0, 1027</td>
<td>6, 5350 ± 0, 5655</td>
<td>6, 9050 ± 0, 0354</td>
<td>6, 8917 ± 0, 0203</td>
</tr>
<tr>
<td>P [W]</td>
<td>0, 4116 ± 0, 0903</td>
<td>0, 3572 ± 0, 0798</td>
<td>0, 5282 ± 0, 0385</td>
<td>0, 4445 ± 0, 0688</td>
</tr>
</tbody>
</table>

The headwords in tables 2, 3 and 4 of the materials and the used solar cells are the short version of the descriptions. "Mono" stands for monocrystalline silicon cell and "Poly" for polycrystalline silicon solar panel. The term "leaf beeswax" should refer to the beeswax layer with the structure of the leaf of *Aglaozema costatum*, whereas the single word "beeswax" describes the thin smooth beeswax layer used as reference. The situation is similar with the word "plastic" which is used as a description for the reference plastic and the "crashglass", which includes the special leaf structure stamped in the crashglass.

The values can only be compared poorly, because the beeswax with the leaf structure is less homogeneous than the reference beeswax and the crashglass is thinner than the reference plastic. In addition the crashglass contains many small air inclusions, which also adulterates the results. There are other problems, which hinder the measurements.
In the course of time the solar cells get dirty, because remains of the beeswax and the crashglass stay behind. In order to prevent distortions by melting beeswax and heated solar cells and to avoid destructions on the crashglass and the beeswax a short exposure time of approximately thirty seconds was selected. Another problem valid only for the polycrystalline solar module due to its dimensions is the corner of the stamp used to fabricate the structure on the beeswax and the crashglass. As mentioned before one corner of the stamp is an imprint of a CD for the purpose of inspection which reflects the light and causes therefore a small mistake. Since the contacts are on the back side of the solar cells, it was not always possible to keep a constant distance to the halogen lamp, so fluctuations in the distance exist.

Nevertheless the results are promising, developable and expandable. The most reasonable comparison is to contrast the output power of the materials possessing the special structure with the output power of the reference materials.

The results of the monocristalline silicon cell seems to confirm the assumption that some shadow plants feature a special surface structure at the nano- and microscale. The output power of the material with leaf structure is in each case in excess of the material without leaf structure. On closer examination of the values before averaged, one can observe that there is one voltage value in the results of the monocristalline solar cell coated with the beeswax board without leaf structure. The value of 0,3 V is completely out of range and distort the result. In order to compare the two different beeswax, the first test series should be ignored. The new averaged values of the output power are $0.0791 \pm 0.0011$ W for the reference beeswax and $0.0772 \pm 0.0016$ W for the beeswax imitating leaves. This is a more reasonable result, due to the different thickness of the beeswax layers and the higher transparency of the reference beeswax. Still the results are nearly identical, which could be a proof for the special structure of the leaves of *Aglaoema costatum*. A proof with higher probability are the results of the monocristalline solar cell concerning the plastics. Although the crashglass was much thicker than the reference plastic, the monocristalline solar cell showed a higher output power under the crashglass as coverglass, than under the even plastic. It was also directly visible at the process of measuring that the reflectivity of the plastic is higher whereas the crashglass seems more matte.

The results of the polycrystalline solar module confirms the results of the monocrys-
talline silicon cell. The output power of the crashglas resides within the range of the error of the value of the plastic. Considering the difference in the thickness and keeping the reflectivity of the CD copy in mind, along with the small bubbles trapped, it is supposable that the plant has a special surface. The results of the polycrystalline silicon cell resemble the ones of the monocystalline solar cell concerning the comparison of the beeswax layers: The beeswax copying the leaf comes off badly compared to the reference beeswax, maybe because of the reasons described above.

Naturally, it is possible that the reasons are void and the results reflects the reality. This would be a proof that *Aglonema costatum* does not feature a special surface, which favors the light absorption or the light trapping. In this case, the nature has something else for the plant in store, such could be some of the tricks described in chapter 2.

The efficiency is not of importance for this work, since the structure should serve as instrument to decrease the reflectivity of the coverglass, which should protect the silicon of pollution and damage. The contrast of the effect of the structure and the output without structure is of greater importance and provided in this thesis.
5 Conclusion

Although a lot of challenges had to be faced, the work was relatively successful. It was possible to picture the surface of *Aglonema costatum*, find two materials, which can display nanostructures and prove that *Aglonema costatum* features a special surface to improve light absorption.

*Aglonema costatum* seems to have a chess pattern of round valleys with a diameter of 8 to 21 µm, a depth of around 60 nm and an interspace of 4 to 13 µm. In the area of a dot on the leaf, there can be observed tiny voids, which are of no regularity in period or shape. These could result from dust, chalk or air inclusions or could be caused by light irradiation. This could be a special mechanism of the plant, to prevent the leaves of destruction caused by the light. The white dots reflect the light.

The well tested technique of using the molding material Coltene President light body® was improved by simply using an injection to apply the material on the required surface.

After testing twenty-two different materials, only two of them can be used as molding material. At least the Coltene President light body® can resist high temperatures, so it possible to use these materials in their liquid heated form. Beeswax is environmentally sustainable, stays elastic and is simple to use for the purposes of investigation of structures. On contrary it is really complicated to produce a thin layer containing a special structure. A special technique has been developed to cope with this challenge. However, this technique is not technically matured and there are doubtless better but more complex methods. On the other side, the crashglass is fragile, but after all, it is its main purpose to be easily breakable. The crashglass is transparent, so usable for the coverglass of solar cells and could be utilized for investigation as well. At some of the other materials, the imprint only worked at the edges of the imprint, this could be a sign of not optimal usage. For example, while the carnauba wax seems to contract in the process of solidification, the edges still get pressed in the wax and the nanostructures therefore get transferred.

The results of the measuring of the solar cells are promising, even though not significant. The structure could provide higher output power, when using crashglass. It
seems that the structure of the leaves of *Aglonema costatum* absorbs the light better.

Recapitulatory some shade plants feature special light trapping and absorbing structure. This was proven at the lead of *Aglonema costatum*, which features chess pattern arranged valleys. This structure can be used to increase the performance of photovoltaic cells. As alternative for the carcinogenic epoxy resin, beeswax or crashglass can be used.
6 Acknowledgments

First of all, I want to thank Associate Prof. Dipl.-Ing. Dr.techn. Ille C. Gebeshuber, who came up with this wonderful idea for a bachelor thesis. Naturally I want to thank my family, which was always by my side, I know I have not been so easy to handle the last months. All my gratitude goes to Simon Mörtelbauer, who showed me the art of using the AFM, Jan Hofmann, who engaged with the completely new idea of making an imprint in crashglass and succeeded, Anton Sieder, who helped with words and deeds to find a shadow plant in the Botanical Gardens of Vienna, Manfred Edlinger, who was so helpful in the Federal Gardens of Vienna and let me take my imprints of the scions of "my plant", when she was nowhere else traceable, Teresa Jiménez Puente, who supported me and assisted in the first month of this work and my best friend, Sophie Tschullik, who corrected this thesis. I also thank the Botanical Gardens of Vienna and the Federal Gardens of Vienna, who allowed me to make the imprints of *Aglaonema costatum*. 
7 Additional tables

Table 3 shows the results measured. Table 4 show the results calculated with the formula 2.

Table 3: Measured current and voltage of coated mono- and polycrystalline solarcells

<table>
<thead>
<tr>
<th>Mono</th>
<th>beeswax</th>
<th>leaf beeswax</th>
<th>plastic</th>
<th>crashglass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I [mA]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mono beeswax</td>
<td>113</td>
<td>109</td>
<td>126</td>
<td>134</td>
</tr>
<tr>
<td>U [V]</td>
<td>0,3</td>
<td>0,571</td>
<td>0,577</td>
<td>0,572</td>
</tr>
<tr>
<td>Mono leaf beeswax</td>
<td>138</td>
<td>137</td>
<td>142</td>
<td>143</td>
</tr>
<tr>
<td>I [mA]</td>
<td>0,592</td>
<td>0,576</td>
<td>0,59</td>
<td>0,593</td>
</tr>
<tr>
<td>U [V]</td>
<td>136</td>
<td>137</td>
<td>143</td>
<td>141</td>
</tr>
<tr>
<td>Mono plastic</td>
<td>0,575</td>
<td>0,582</td>
<td>0,585</td>
<td>0,581</td>
</tr>
<tr>
<td>I [mA]</td>
<td>137</td>
<td>135</td>
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</tr>
<tr>
<td>U [V]</td>
<td>0,573</td>
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<td>Mono crashglass</td>
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<td>131</td>
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<td>140</td>
</tr>
<tr>
<td>I [mA]</td>
<td>0,583</td>
<td>0,571</td>
<td>0,575</td>
<td>0,579</td>
</tr>
<tr>
<td>U [V]</td>
<td>135</td>
<td>131</td>
<td>139</td>
<td>131</td>
</tr>
<tr>
<td>Poly beeswax</td>
<td>34</td>
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<td>85</td>
<td>73</td>
</tr>
<tr>
<td>I [mA]</td>
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<td>6,54</td>
<td>6,88</td>
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</tr>
<tr>
<td>U [V]</td>
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<td>60</td>
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<tr>
<td>Poly leaf beeswax</td>
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<td>I [mA]</td>
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<td>62</td>
<td>74</td>
<td>70</td>
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<tr>
<td>U [V]</td>
<td>6,88</td>
<td>5,3</td>
<td>6,94</td>
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<tr>
<td>Poly plastic</td>
<td>63</td>
<td>55</td>
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<td>58</td>
</tr>
<tr>
<td>I [mA]</td>
<td>6,78</td>
<td>6,81</td>
<td>6,94</td>
<td>6,87</td>
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<tr>
<td>U [V]</td>
<td>61</td>
<td>61</td>
<td>83</td>
<td>65</td>
</tr>
<tr>
<td>Poly crashglass</td>
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</tr>
<tr>
<td>I [mA]</td>
<td>57</td>
<td>60</td>
<td>72</td>
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<tr>
<td>U [V]</td>
<td>6,93</td>
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<td>6,84</td>
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### Table 4: Results of the output power

<table>
<thead>
<tr>
<th></th>
<th>beeswax</th>
<th>leaf beeswax</th>
<th>plastic</th>
<th>crashglass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.0339</td>
<td>0.0622</td>
<td>0.0727</td>
<td>0.0766</td>
</tr>
<tr>
<td>2.</td>
<td>0.0817</td>
<td>0.0789</td>
<td>0.0838</td>
<td>0.0848</td>
</tr>
<tr>
<td>3.</td>
<td>0.0782</td>
<td>0.0797</td>
<td>0.0837</td>
<td>0.0819</td>
</tr>
<tr>
<td>4.</td>
<td>0.0799</td>
<td>0.0772</td>
<td>0.0826</td>
<td>0.0823</td>
</tr>
<tr>
<td>5.</td>
<td>0.0783</td>
<td>0.0748</td>
<td>0.0794</td>
<td>0.0811</td>
</tr>
<tr>
<td>6.</td>
<td>0.0776</td>
<td>0.0756</td>
<td>0.0748</td>
<td>0.0734</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Poly</th>
<th>beeswax</th>
<th>leaf beeswax</th>
<th>plastic</th>
<th>crashglass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.2258</td>
<td>0.1962</td>
<td>0.5848</td>
<td>0.5037</td>
</tr>
<tr>
<td>2.</td>
<td>0.519</td>
<td>0.4086</td>
<td>0.519</td>
<td>0.5145</td>
</tr>
<tr>
<td>3.</td>
<td>0.4885</td>
<td>0.3286</td>
<td>0.5136</td>
<td>0.4844</td>
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<tr>
<td>4.</td>
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<td>0.3746</td>
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<td>0.3985</td>
</tr>
<tr>
<td>5.</td>
<td>0.4209</td>
<td>0.4239</td>
<td>0.5735</td>
<td>0.4485</td>
</tr>
<tr>
<td>6.</td>
<td>0.3950</td>
<td>0.408</td>
<td>0.4925</td>
<td>0.3174</td>
</tr>
</tbody>
</table>

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