7 Appendix

7.1 Appendix A: Theoretical basis of material constants “n” and “k” calculation [71]

In chapter 3.3 a theoretical computer simulation of our cell is done, in order to learn about the distribution of light within the cell layers and be able to optimize this. For the computer simulation one needs to input data for each separate layer. This data includes the refraction index “**n**” and extinction coefficient “**k**” of each substance. These parameters can not be measured directly, so they have to be calculated from other measured data. With the program “Optik”, written by Kristian Peter, this is possible. From measured reflection “**R**” and transmission “**T**” of each separate layer, **n** and **k** can be calculated.

In the following section the principle of calculating **n** and **k** from **R** and **T** is described.

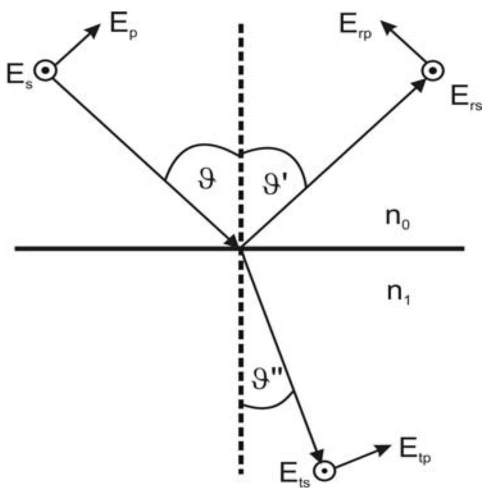

Figure 65. Reflection and transmittance of a plane wave at an interface; indices: s-perpendicular, p-parallel, r-reflected, t-transmitted

The reflection and transmittance of a plane wave $\vec{E}$ at an interface of two mediums (Figure 65) is characterized by Fresnel-law:

$$r_{\perp} = \frac{n_0 \cos\vartheta - n_1 \cos\vartheta"}{n_0 \cos\vartheta + n_1 \cos\vartheta"} \qquad r_{\parallel} = \frac{n_1 \cos\vartheta - n_0 \cos\vartheta"}{n_1 \cos\vartheta + n_0 \cos\vartheta"} \tag{1}$$

$$t_{\perp} = \frac{2n_0 \cos\vartheta}{n_0 \cos\vartheta + n_1 \cos\vartheta"} \qquad t_{\parallel} = \frac{2n_0 \cos\vartheta}{n_1 \cos\vartheta + n_0 \cos\vartheta"} \tag{2}$$

$r_{\parallel}, t_{\parallel}$: Reflection- and transmittance coefficient describing the component of the E-vector parallel to plane of incidence;

$r_{\perp}, t_{\perp}$: Reflection- and transmittance coefficient describing the component of the E-vector perpendicular to plane of incidence;

Regarding transmittance the refracted wave continues without phase skipping.

Concerning the reflected wave, two cases have to be considered:

1. $n_0 < n_1$:There is a phase shift of π in the perpendicular component. If $\vartheta + \vartheta" > \frac{\pi}{2}$ then the parallel component has also a phase shift of π.

2. $n_0 > n_1$:The perpendicular component has no phase-shift, but the parallel component has a shift of π in case $\vartheta + \vartheta" > \frac{\pi}{2}$.

Concerning absorbing materials, the refractive index $\bar{n}$ becomes complex:

$$\bar{n} = n + ik \tag{3}$$

and the absorbing coefficient α is defined as $\alpha = \frac{4\pi k}{\lambda}$, where **k** is the so called extinction coefficient.

In the case of perpendicular incidence of light the Frensel formulas can be simplified to:

$$r = r_{\perp} = \frac{\bar{n}_0 - \bar{n}_1}{\bar{n}_0 + \bar{n}_1} \tag{4}$$

$$t = t_{\perp} = \frac{2\overline{n_0}}{\overline{n_0} + \overline{n_1}} \tag{5}$$

For reflection: $R = |r|^2 = \dfrac{(n_0 - n_1)^2 + (k_0 - k_1)^2}{(n_0 + n_1)^2 + (k_0 + k_1)^2}$

(6)

The transmittance can be calculated by using the equation: $T = 1 - R$

(6a)

In order to analyze the transmittance and reflection of a thin film on a thick coplanar substrate we have to divide the problem into two sections. First reflection and transmittance of a thin coplanar film will be considered and finally reflection and transmittance of a thick coplanar layer will be examined.

Reflection and transmittance of a thin coplanar film

A thin coplanar film with thickness d and refractive index $\overline{n}_1$, which is located between two mediums with $\overline{n}_0$ and $\overline{n}_2$ is examined. A multiple reflection on the upper- and lower-side of the film occurs (Figure 66).

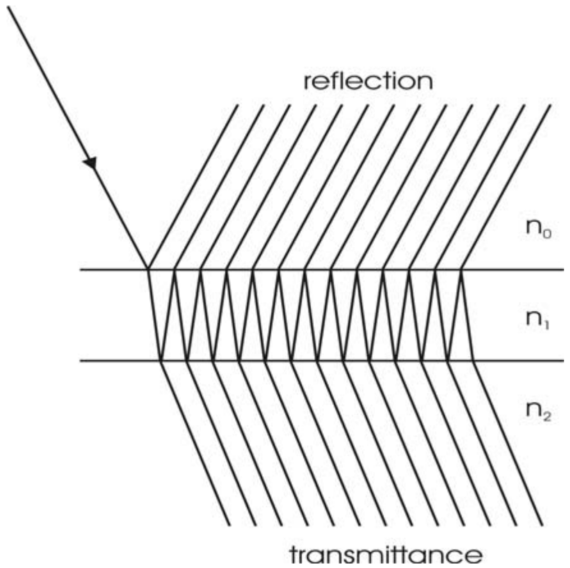

Figure 66. Thin coplanar film and its interaction with light

The amplitude decreases by the factor $\exp\left(-\frac{2\pi kd}{\lambda}\right)$ when the layer is penetrated once. Moreover a phase shift of $\Delta\varphi = \frac{2\pi nd}{\lambda}$ occurs. These effects will be taken into account by multiplying the plane wave with $e^{i\delta}$. For δ we have the formula:

$$\delta = \frac{2\pi d(n+ik)}{\lambda} \tag{7}$$

The following formulas will include the indices “i” and “j”. The index “i” means that light comes from the medium i and the index “j” denotes the medium where the light is reflected respectively where it penetrates. The reflection- and transmittance-coefficients are r_{ij} and t_{ij} correspondingly.

For the calculation of the complete transmittance coefficient after infinite reflection in the layer one get the equation:

$$t = \left[t_{01} e^{i\delta} \sum_{j=0}^{\infty} \left(r_{12} r_{10} e^{2i\delta} \right)^j \right] \cdot t_{12} \tag{8}$$

Explanation of equation (8):

$t_{01}e^{i\delta}$	• The light penetrates in the medium 1 and is weakened because of covering a distance of one layer thickness. It reaches the interface 1-2.
$\sum_{j=0}^{\infty}\left(r_{12}r_{10}e^{2i\delta}\right)^j$	• The light will be reflected into the layer infinite number of times. Every time the amplitude decreases by the factor $e^{2i\delta}$ because the light has to go twice through the layer thickness d until it will be back at the interface 1-2. The components of the light which have already been reflected more often are weaker. For this reason there is the exponent “j” in the sum.
t_{12}	• Every time the light goes with the „probability“ t_{12} through the interface 1-2.

Accordingly there is an equation for the reflection coefficient:

$$r = r_{01} + \left[t_{01} r_{12} e^{2i\delta} \sum_{j=0}^{\infty} \left(r_{12} r_{10} e^{2i\delta} \right)^j \right] \cdot t_{10} \qquad \textbf{(9)}$$

Explanation of equation (9):

r_{01}	• The part of light which is reflected immediately at the interface 0-1.
$t_{01} r_{12} e^{2i\delta}$	• The part which is transmitted at the interface 0-1 and reflected at the interface 1-2. The light has covered a distance of 2d when it reaches the interface 0-1 again. The amplitude has decreased by $e^{2i\delta}$.
$\sum_{j=0}^{\infty} \left(r_{12} r_{10} e^{2i\delta} \right)^j$	• The light will be reflected into the layer infinite times. Every time the amplitude decreases by the factor $e^{2i\delta}$ because the light has to go twice through the layer thickness d. The components of the light which have already been reflected more often are weaker. For this reason there is the exponent j in the sum.
t_{10}	• Every time the light goes with the „probability“ t_{12} through the interface 1-0

In order to simplify the equations (8) and (9) it is used $r_{01} = -r_{10}$, $t_{10} = 1 - r_{10}$ and the equations (4) and (5). Furthermore the equations (8) and (9) include geometric series which can be written as $\sum_{k=0}^{\infty} q^k = \frac{1}{1-q}$ if 0<q<1.

Consequently the following formulas arise from these transformations:

$$r = \frac{r_{01} e^{-i\delta} + r_{12} e^{i\delta}}{e^{-i\delta} + r_{01} r_{12} e^{i\delta}} \quad \textbf{(10)} \qquad t = \frac{t_{01} t_{12}}{e^{-i\delta} - r_{10} r_{12} e^{i\delta}} \quad \textbf{(11)}$$

Using the formulas (4) and (5) (that are valid for the reflection and transmittance on an interface) for $r_{01}, r_{12}, t_{01}, t_{12}$ we obtain the complete reflection and transmittance coefficient of a thin coplanar layer.

$$r = \frac{(\overline{n}_0 - \overline{n}_1)(\overline{n}_1 + \overline{n}_2)e^{-i\delta} + (\overline{n}_1 - \overline{n}_2)(\overline{n}_0 + \overline{n}_1)e^{i\delta}}{(\overline{n}_0 + \overline{n}_1)(\overline{n}_1 + \overline{n}_2)e^{-i\delta} + (\overline{n}_0 - \overline{n}_1)(\overline{n}_1 - \overline{n}_2)e^{i\delta}} \quad \mathbf{(12)}$$

$$t = \frac{4\overline{n}_0\overline{n}_1}{(\overline{n}_0 + \overline{n}_1)(\overline{n}_1 + \overline{n}_2)e^{-i\delta} + (\overline{n}_0 - \overline{n}_1)(\overline{n}_1 - \overline{n}_2)e^{i\delta}} \quad \mathbf{(13)}$$

The reflection and transmittance will be calculated with:

$$R = |r|^2 \ \mathbf{(14)} \text{ and } T = \left|\frac{\overline{n}_2}{\overline{n}_0}\right| \cdot |t|^2 \ \mathbf{(15)}.$$

Reflection and transmittance of a thick coplanar layer

While treating this problem it is assumed that the thick layer has no interference effects and that phase shifting has not to be considered. For this reason the formulas include similar sums like the equations (8) and (9) but here calculations can be started immediately by using the intensities and not the coefficients:

$$R = R_{01} + \frac{T_{01}^2 R_{12} e^{-2\alpha d}}{1 - R_{12} R_{10} e^{-2\alpha d}} \ \mathbf{(16)} \qquad T = \frac{T_{01} T_{12} e^{-\alpha d}}{1 - R_{12} R_{10} e^{-2\alpha d}} \ (17)$$

The parts R_{ij} and T_{ij} are the reflection and transmittance of an interface which can be calculated with the equations (6) and (6a).

Reflection and transmittance of a thin film which is located on a thick coplanar substrate

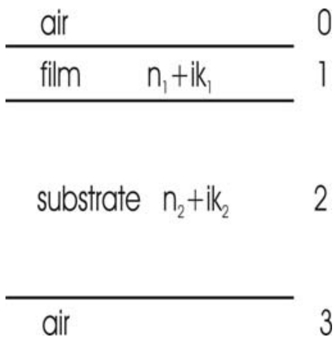

Figure 67. Thin film on a thick coplanar substrate.

Setup is similar to a real-life measurement configuration

It is assumed that a thin film shows interference but the thick substrate does not.

The task has to be solved in two steps:

1. The reflection and transmittance of the thin film between two mediums will be calculated like it was already described. The results will be denoted: R_{02}, R_{20}, T_{02} and T_{20}. Moreover it is valid: $T_{02} = T_{20}$.

2. Finally the whole system will be calculated like a thick coplanar layer. The thin film will be regarded as an interface 0-2.

For the reflectivity we obtain:

$$R = R_{02} + \frac{T_{02}^2 R_{23} e^{-2\alpha_2 d_2}}{1 - R_{23} R_{20} e^{-2\alpha_2 d_2}} \qquad \textbf{(18)}$$

For the transmittance:

$$T = \frac{T_{02} T_{23} e^{-\alpha_2 d_2}}{1 - R_{23} R_{20} e^{-2\alpha_2 d_2}} \qquad \textbf{(19)}$$

The values R_{23} and T_{23} can be calculated with: $R_{23} = \frac{(n_2 - 1)^2 + k_2^2}{(n_2 + 1)^2 + k_2^2}$ (compare equation 6 using $n_3 = 1$ and $k_3 = 0$ for air) and $T_{23} = 1 - R_{23}$.

For evaluating the values of R_{02}, T_{02} and R_{20} the formulas for the case of a thin absorbing coplanar layer between two mediums are used (equations 12 and 13 in connection with the equations 14 and 15).

Solving the equations

If the thickness of the layers is known the refractive index **n** and the extinction coefficient **k** can be determined from the measurement of reflectivity R and transmittance T. The equations (18) and (19) cannot be solved by analytical methods. For this reason the two-dimensional Newton-Raphson algorithm is used as an approximation.

In principle this method works in the same way like the Newton algorithm. How does the Newton-algorithm work? It is applied a tangent on the graph in the point (x_0,f(x_0)). You get a point of intersection with the x-axis, which is the value x_1. In the point (x_1,f(x_1)) is applied a tangent again. The procedure will be iterated until the null of the function f(x) has been found with the wanted accuracy (Figure 68).

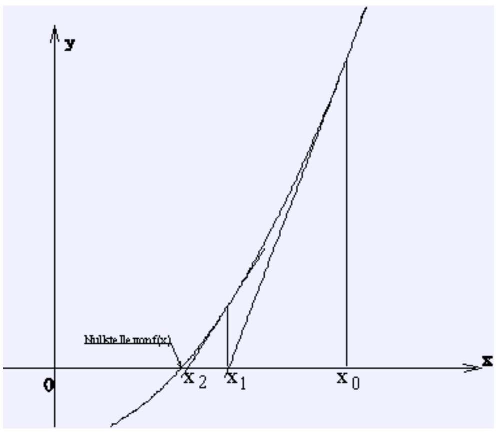

Figure 68. The Newton algorithm

In our case the reflection and transmittance depend from two parameters, n and k. That is why the algorithm has to be accomplished in a two dimensional way (Newton-Raphson algorithm).

The following system of equations has to be solved:

$$R_{ex} - R(n,k) = 0$$
$$T_{ex} - R(n,k) = 0$$

R_{ex} and T_{ex} are the experimental found values. Before beginning the approximation we have to set start values $R(n_0, k_0) = R_0$ and $T(n_0, k_0) = T_0$.

Then a Taylor expansion of R(n, k) at R_0 is done (linearization):

$$R = R_{ex} = R_0 + \left(\frac{\partial R}{\partial n}\right)_0 (n - n_0) + \left(\frac{\partial R}{\partial k}\right)_0 (k - k_0)$$
$$T = T_{ex} = T_0 + \left(\frac{\partial T}{\partial n}\right)_0 (n - n_0) + \left(\frac{\partial T}{\partial k}\right)_0 (k - k_0)$$

The following equation is obtained for the first approximation values n_1 and k_1:

$$\begin{pmatrix} n_1 \\ k_1 \end{pmatrix} = \begin{pmatrix} n_0 \\ k_0 \end{pmatrix} - M^{-1} \begin{pmatrix} R_{ex} - R_0 \\ T_{ex} - T_0 \end{pmatrix}$$

M is the Jakobi matrix:

$$M = \begin{pmatrix} \dfrac{\partial R}{\partial n_0} & \dfrac{\partial R}{\partial k_0} \\ \dfrac{\partial T}{\partial n_0} & \dfrac{\partial T}{\partial k_0} \end{pmatrix}$$

This procedure will be iterated until the values n_n and k_n deviate from n_{n-1} and k_{n-1} in the wanted limits.

The Newton-Raphson algorithm is not applicable when several solutions are possible. For that reason we used a program called "Optik", written by Kristian Peter. It uses a special calculation routine. The **n** and **k** plane is scanned in a chosen interval. For every pair of **n** and **k** the Newton-Raphson-algorithm is made. If the wanted interval for **n** and **k** is exceeded or the iteration not finished after ten steps, the procedure is interrupted and the next values for **n** and **k** are taken.

7.2 Appendix B: Cell up-scaling – sample holder, mask, encapsulation

In order to be able to perform space resolved I/V measurements on organic solar cells, they needed to be up-scaled to a size of approximately 1 cm^2 and reshaped to a rectangular form. This was made possible by designing and using during UHV material evaporation a new sample holder with a modified mask.

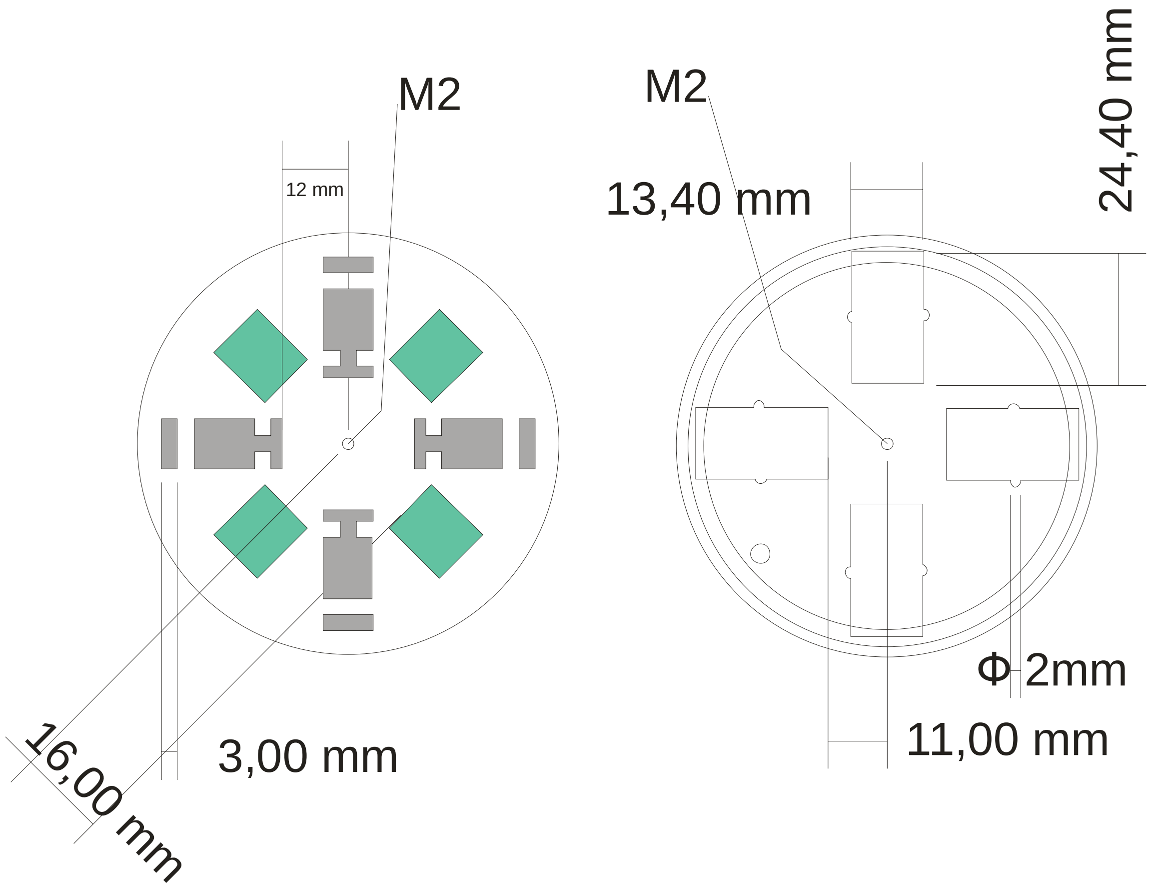

Figure 69. Mask for up-scaled solar cells (left) and sample holder (right). On the mask, the green areas are the openings through which the organics is shaped in the rectangular form of the cell. The grey areas are the openings giving shape to the aluminum contacts and defining the actual cell. The mask is being switched to 45° before contacts are being evaporated

The mask (Figure 69, left) was cut out of 1 mm thick stainless steel sheet with a laser. It was then fitted in the sample holder ring under the sample stabilizer (right on the same figure). Mask and holder were fixed together only by the holder ring, thus a free rotation of the mask at 45° was possible, for switching between organic and metal contact openings.

The up-scaled solar cells were evaporated on ITO glass substrates with size 13x24 mm. The substrates were structured with a laser cut 5 mm from the short edge, to isolate the front from the back contact (Figure 70).

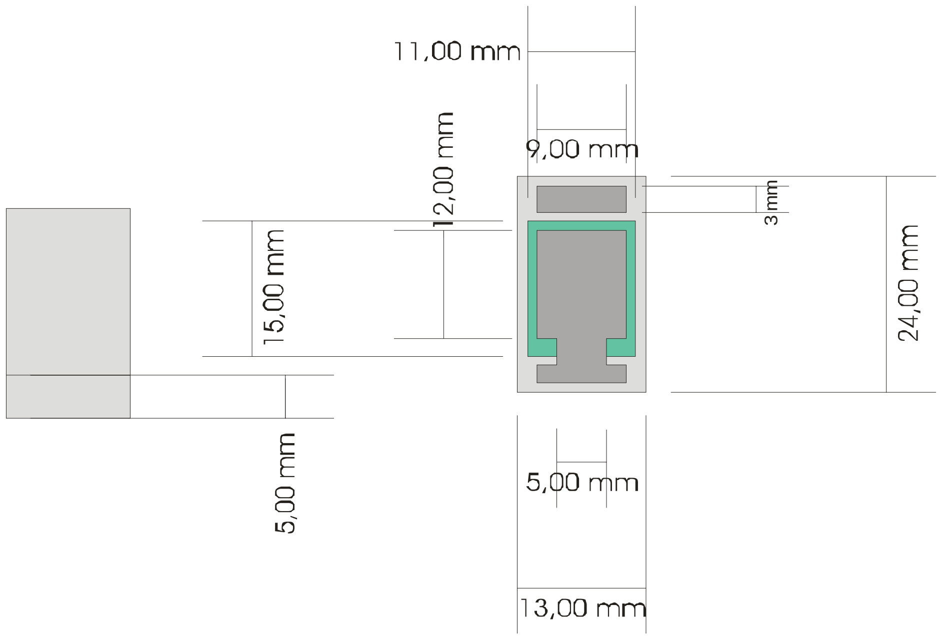

Figure 70. Scheme of a structured ITO glass for solar cell substrate (left). The ITO layer is interrupted 5 mm from the edge, done by a laser cut. Thus the front contact is separated from the back electrode, eliminating a shortcut. A scheme of the ready solar cell (right) shows how organics and contacts are situated.

The schematic view can be compared with solar cells photos on Figure 71.

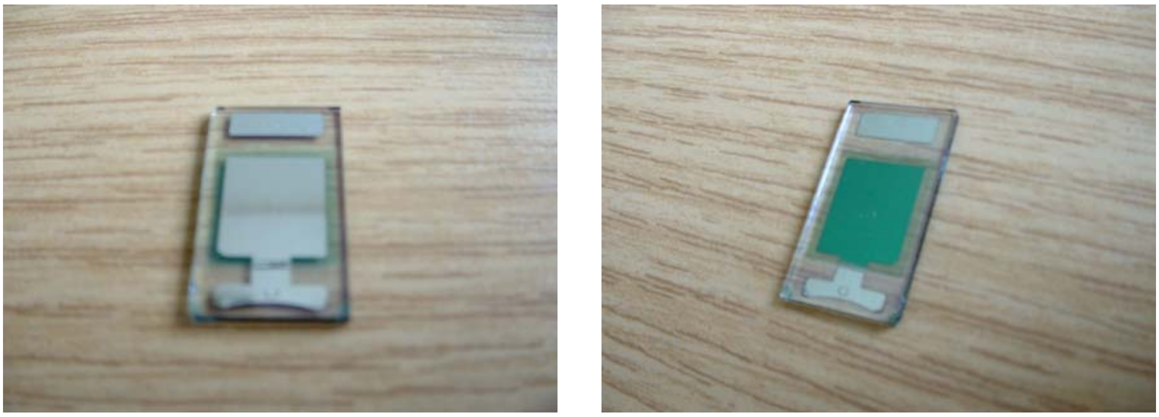

Figure 71. Photographs of the up-scaled solar cells, seen from the metal contact side (left) and through the glass (right). The green-blue coloring is the organic layer part of the cell

The up-scaled solar cells, of course degrade as their smaller predecessors. That is why a corresponding encapsulation had to be designed (Figure 72).

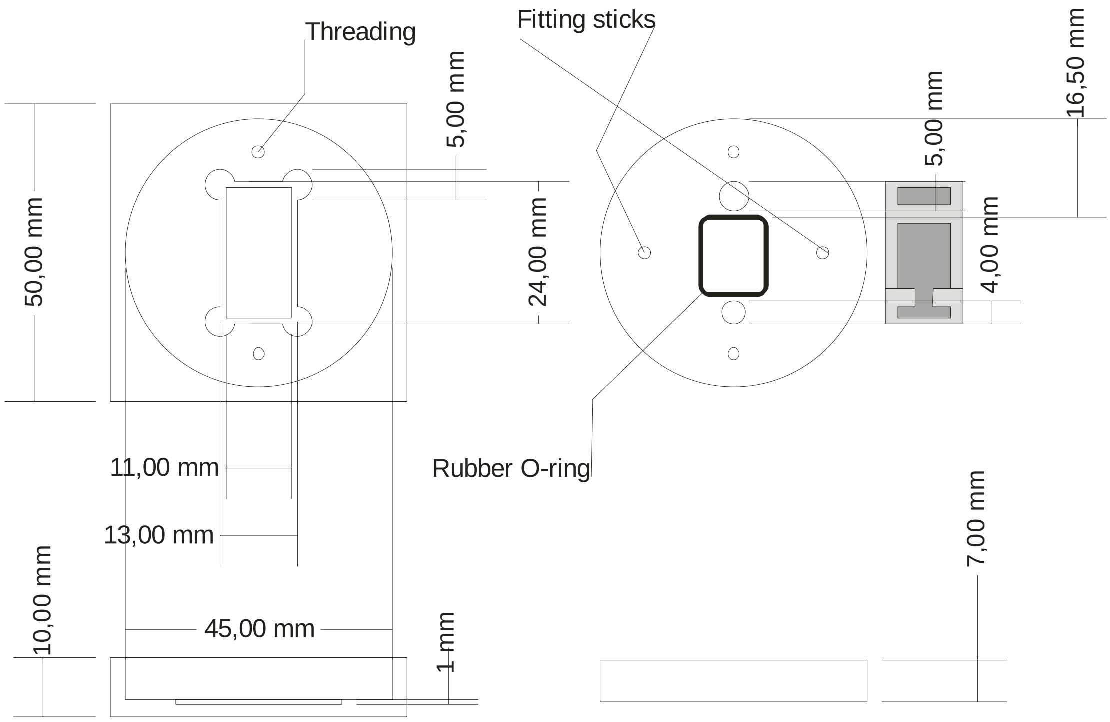

Figure 72. Up-scaled solar cell encapsulation box (left) and lid (right). The lid is fitted with an o-ring, which upon closure presses on the substrate, keeping the cell isolated from atmosphere

The encapsulation serves as an environment insulator, which keeps the solar cell under inert atmosphere. This allows longer measurements or characterizations with slowed cell degradation.