

## INVESTIGATIONS ON A CUSTOM-MADE SILICON-BASED MICROCHANNEL PLATE AS ACTIVE TRANSVERSE ENERGY FILTER FOR THE KATRIN EXPERIMENT

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Münster, October 2022

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## Introduction

The neutrino was first postulated in 1930 by Wolfgang Pauli to explain the energy spectrum of the  $\beta$ -decay [1]. With radioactivity being discovered in 1896 by Henri Becquerel and Ernest Rutherford separating two types of radioactive emissions, namely  $\alpha$ - and  $\beta$ -emissions, a discrepancy in their decay spectra was observed [2]. While  $\alpha$ -emissions showed discrete energy lines for the same material, the spectrum for  $\beta$ -decay was shown to be continuous in 1914 by James Chadwick. At the time, both processes were thought to be a two-body-process, with one emission particle leaving the atom respectively. This explained the discrete spectrum of  $\alpha$ -decays, however, the continuous spectrum of  $\beta$ -emissions could not be reconciled with a two-particle-decay under conservation of momentum and angular momentum. Pauli suggested the existence of a third particle, light and uncharged, that is emitted in the decay process but not yet observed [3]. One year later, this particle was named neutrino (italian: "little neutral one") by Enrico Fermi. For a long time, the mass of the neutrino was assumed to be zero, however, the observation of neutrino oscillations serves as evidence for massive neutrinos. Since then, many experiments have attempted to measure its mass. But up to this day, only upper limits on the mass could be determined.

The Karlsruhe Tritium Neutrino (KATRIN) experiment is taking measurements with a goal sensitivity of 0.2 eV with a confidence level of 90%. Currently, the background level is much higher than anticipated, with a large contribution assumed to be caused by electrons of low transverse energy, the so-called Rydberg background [4]. These background electrons arrive at the detector with the same total energy as the signal electrons, but their incidence angles are limited and less distributed. An angular selective detection mechanism could enable differentiation. As a possible solution to reduce this background, the active transverse energy filter (aTEF) concept has been proposed and has been proven to work in principle [5].

This thesis serves to investigate methods and materials for the manufacture of such a filter, based on existing microchannel plate (MCP) technology, with the goal to enable the assembly of a first prototype of an MCP-aTEF.

well as a description of the KATRIN experiment and the aTEF concept. Commercial MCPs are discussed in Chapter 3, followed by considerations and investigations on methods and materials for the manufacture of an MCP-aTEF. Chapter 4 presents a summary of this thesis and a short outlook.

## Neutrino Experiments

This chapter will briefly cover experiments leading up to the discovery of neutrinos, as well as the flavor oscillation that delivered evidence for a massive neutrino. Additionally, the KATRIN experiment, the Rydberg background and the proposed aTEF will be further described.

## 2.1 Discovery of the Neutrino

After its postulation, the neutrino was finally detected in 1956 by Clyde Cowan and Frederick Reines by inducing an inverse  $\beta$ -decay in hydrogen [6]:

$$p + \bar{\nu}_e \rightarrow n + e^+$$
 (2.1)

Two tanks of water with solved cadmium chloride,  $CdCl_2$ , served to detect the neutrinos produced in a nuclear reactor. In the event of a neutrino interacting with a proton in the water, both the created positron and neutron give options for detection. The positron reacts with an electron in its environment, annihilating into most commonly two  $\gamma$ -rays of 511 keV, perpendicular to each other as shown in the following equation:

$$e^- + e^+ \rightarrow \gamma + \gamma$$
 (2.2)

Additionally, the produced neutrons could react with the solved cadmium chloride, creating an excited state of <sup>109</sup>Cadmium, which subsequently emits a  $\gamma$ :

$$n + {}^{108} \operatorname{Cd} \to {}^{109m} \operatorname{Cd} \to {}^{109} \operatorname{Cd} + \gamma$$
(2.3)

The water tanks were surrounded by two tanks filled with a liquid scintillator, creating flashes of light in response to each  $\gamma$ , which would finally be detected by photomultiplier tubes. The detection of the annihilation radiation from the positronelectron-pair, followed by the  $\gamma$  of the neutron absorption, allowed to confirm the existence of the neutrino.

## 2.2 The Mass of the Neutrino

As the neutrino is electrically uncharged and only interacts via the weak force and gravity, interactions with matter are rare. Just like the detection of neutrinos, measurements involving neutrino interactions require large detection media and great sensitivity with low background rates.

In 1957 Bruno Pontecorvo investigated the theoretical oscillation of neutrino flavors, letting a neutrino of a specific lepton flavor periodically change its flavor along its flight path. For this oscillation to occur, the mass difference between different neutrino flavors must be non-zero. The neutrino oscillation was first observed by the Super-Kamiokande experiment in 1998 [7], confirming that neutrinos are massive particles. The experiment used a tank with 50 000 tons of ultrapure water surrounded by photomultiplier tubes to detect Cherenkov radiation following a neutrino interaction.

Cosmic rays consisting of mostly protons interact with the earth's atmosphere and create unstable particles with their decay products, including so-called atmospheric neutrinos. As neutrinos interact rarely enough, it is possible for them to pass through the earth before interacting in the detector medium. The experiment was able to show that the number of muon neutrinos detected coming from the other side of the earth was reduced compared to muon neutrinos only passing through the atmosphere above the detector location. As the predicted total number of observed neutrinos was uniform regardless of direction, the resulting conclusion was that a part of those neutrinos traveling the additional distance through the earth oscillated into flavors of neutrinos not detectable in this experiment [7].

A similar lack of neutrinos was observed in the Homestake experiment in the 1960s [8] when solar electron neutrinos were studied. Here, solar neutrinos with a maximum energy of 26.73 MeV were detected in a large tetra-chloroethylene tank using the process

$$v_e + {}^{37}\text{Cl} \to {}^{37}\text{Ar} + e^-.$$
 (2.4)

In principle, all neutrino flavors can induce this process, creating their lepton partner of the same flavor in the process. However, with  $m_{\mu} = 106$  MeV and  $m_{\tau} = 1777$  MeV, the maximum neutrino energy is not sufficient to create these particles. Therefore, only electron neutrinos were detected and a lack of  $\frac{2}{3}$  of the expected neutrinos was observed [9]. At the time, the lack in detection could not be explained. Since then, other experiments like GALLEX could confirm the results, while experiments like Sudbury Neutrino Observatory (SNO) experiment, sensitive to not only  $\nu_e$  were able to detect a higher count of neutrinos from the sun [10]. The most direct way to measure the neutrino mass is by observing the kinematics of  $\beta$ -decays. Two other methods exist, using either cosmological methods or the neutrinoless double beta ( $0\nu\beta\beta$ ) decay, however, both these methods are highly model dependent. One advantage in kinematic measurements is the independence of an underlying model.

## 2.3 The KATRIN Experiment

The KATRIN experiment is ongoing since 2019 and aims to directly measure the neutrino mass with a target sensitivity of 0.2 eV at a confidence level of 90%. A world record limit of  $m_{\gamma} < 0.8 \text{ eV}$  (90% C.L) has already been achieved with the data taken from the first year of measurements.[4]

In this section, parts of the experimental setup of the KATRIN experiment will be described, and the Rydberg background will be discussed to be able to introduce the aTEF.

#### 2.3.1 Neutrino Mass from the $\beta$ -decay of Tritium

As previously mentioned, one way of determining the absolute mass of the neutrino is by observing the energy spectra of electrons produced in  $\beta^-$ -decays, where a neutron in an atomic nucleus decays into a proton under emission of an electron and electron antineutrino:

$$n \to p + e^- + \bar{\nu}_e \tag{2.5}$$

The KATRIN experiment serves to determine the effective average neutrino mass by measuring the  $\beta^-$ -spectrum from electrons produced in the decay of tritium to <sup>3</sup>He:

$$T \rightarrow {}^{3}\text{He}^{+} + e^{-} + \bar{\nu}_{e} \tag{2.6}$$

The energy spectrum of electrons produced in this experiment has an endpoint of  $E_0 = Q - E_{\text{rec}}$ , with Q denoting the total decay energy and  $E_{\text{rec}}$  being the total recoil energy shared by the electron and antineutrino. Each point of the spectrum displays a different energy distribution on the electron and antineutrino, with electrons in the upper end of the spectrum receiving almost all kinetic energy in the decay process.

As the neutrino mass is non-vanishing, the actual end of the measured spectrum will be lowered by  $m_{\nu}$  as figure 2.1 shows [11]. The spectrum can be described by

$$\frac{\mathrm{d}N}{\mathrm{d}E} = C \cdot F(Z, E) \cdot p(E + m_{\mathrm{e}}c^2) \cdot (E_0 - E) \cdot \sqrt{(E_0 - E)^2 - m_{\mathrm{v}}} \cdot \Theta(E_0 - E - m_{\mathrm{v}}^2) \,, \, (2.7)$$

where F(Z, E) is the Fermi function, p the momentum of the electron and  $\Theta(E_0 - E - m_v)$  is the Heaviside step function.  $E_0$  is again the endpoint energy in the case of  $m_v = 0$ . C depends on the Fermi constant  $G_F$ , the Cabibbo angle  $\theta_C$ , as well as the nuclear matrix element M and is defined as [12]:

$$C = \frac{G_{\rm F}^2}{2\pi^3} \cos^2\theta_{\rm C} |M|^2 \tag{2.8}$$

By fitting a measured spectrum with equation 2.7, it is possible to determine  $m_{\nu}^2$  as a fitting parameter, with  $m_{\nu}^2$  itself being the squared effective neutrino mass consisting of an incoherent sum of the distinct mass values  $m_i$  of the different neutrino flavors, weighted by their contribution to the electron-flavor state. Using the Pontecorvo–Maki–Nakagawa–Sakata matrix elements  $U_{\rm ei}$ , the squared effective mass follows as [4]:

$$m_{\nu}^2 = \sum_i |U_{\rm ei}|^2 m_i^2 \tag{2.9}$$

Figure 2.1, as well as equation 2.7 presenting  $\frac{dN}{dE} \propto (E_0 - E)^2$  with the total number of decays towards  $E_0$  scaling with  $\frac{1}{E_0^3}$ , show a tiny count rate for the relevant energy region close to the endpoint [12]. In total, the most relevant region includes about 1 in  $10^{13}$  total counts [4]. Therefore, the signal source needs to be as intense as possible. The Tritium Laboratory Karlsruhe (TLK) provides the largest supply of tritium in Europe, making it the most optimal location with a  $10^{11}$  Bq gaseous tritium source and a daily throughput of up to 40 g of tritium.

The choice for tritium as a source has multiple reasons and benefits: It offers the second lowest  $\beta^-$ -decay endpoint energy combined with a relatively short half-life of 12.3 years that allows for a higher signal rate compared to other sources. The low atomic numbers of T and <sup>3</sup>H reduces energy losses of signal electrons scattering in the source, and the electron structure of the source material allows for easier calculations compared to more complex atoms, but the final state distribution of the T<sub>2</sub> is already much more difficult than for atomic tritium [13].



Fig. 2.1.: Integral energy spectrum for the  $\beta^-$ -decay of tritium for two different neutrino masses  $m_{\nu}$ . The endpoint region around 18 574 keV is enlarged, showing the difference of the two models and the impact of a non-vanishing neutrino mass. The extremely low relative count rate near the endpoint presents a hurdle for this neutrino mass measurement. Figure taken from [11].

### 2.3.2 Experimental Setup

The KATRIN experimental setup can be divided in several segments. In this section, these segments will be presented.

#### Source section

The experimental setup of the KATRIN experiment is depicted in figure 2.2. The source system, as previously mentioned, is capable of delivering up to  $10^{11}$  signal electrons per second with its main feature being the 10 m long windowless Gaseous Tritium Source (WGTS). The source has been kept at a temperature of 30 K for the two initial runs and is currently at a temperature of 80 K [4]. A laser-Raman spectroscopy system monitors the purity of the continuously pumped and circulated tritium. Electrons created in  $\beta^-$ -decays are magnetically guided along the beam line, either towards the spectrometer section of the setup, or towards the rear system where they are absorbed by the gold-plated rear wall and lost for the experiment.

#### **Rear System**

The rear system features an angular selective, monoenergetic UV-photoelectron source (Electron-Gun) [14], used for calibration and monitoring purposes. This allows for measurements of the column density of the gaseous tritium source, as well as for the gas composition or voltage stability in the main spectrometer, which will be described later in this chapter. Additionally, time-of-flight measurements can be taken.

#### Transport Section

The signal electrons are further guided along the experimental setup by superconducting magnets. As the WGTS is windowless to enable uninhibited electron transmission without energy losses, the gaseous tritium needs to be contained in other ways. Two differential pumping sections (DPS) actively pump out the remaining tritium and ions in front and behind the source system in the beam line setup. The transport section features two additional pumping sections, reducing the flow of tritium further: First, another differential pumping section with a bend beam line trajectory and no direct sight from the source towards down the beam line is used. The two kinks in the trajectory cause heavier, charged particles to deviate from the beam line and can be pumped away by a setup of turbo-molecular pumps, while electrons are light enough to remain on their path towards the spectrometer. This system reduces the tritium flow by five orders of magnitude [13].

The system is followed up by the CPS (Cryogenic Pumping Section) where similarly to the DPS a bent beam line is used to cause remaining tritium to collide with the inner walls of the setup. The section is cooled down to 3 K and uses an argon frost layer to efficiently capture tritium with a cryosorbtion processes. This allows for the flow of tritium to be reduced by another 7 orders of magnitude [13].

#### Spectrometer System

The pumping section is followed up by a setup of two spectrometers, being the preand the main spectrometer. Currently, however, the pre-spectrometer is not in use as it was discovered that the tandem operation of both spectrometers lead to an increase in background [4]. The main spectrometer (just as the pre-spectrometer did) applies a technique called magnetic adiabatic collimation with electrostatic filtering (MAC-E) [15]. An electron created in the WGTS has its kinetic energy distributed on a component  $E_{||}$  parallel to the guiding magnetic field and a component  $E_{\perp}$ perpendicular to it. To be able to properly filter electrons by their kinetic energy, they need to be collimated first.

To achieve adiabatic collimation, the magnetic field along the electron's path needs to be spatially reduced slowly enough to preserve the magnetic moment  $\mu$  of the electron. This allows for transformation of  $E_{\perp}$  according to

$$\mu = \frac{E_{\perp}}{B} = \text{const.}$$
 (2.10)

This means, an electron starting in a strong magnetic field  $B_{\rm src}$  (magnetic field at electron source) and adiabaticly moving into a weaker field  $B_{\rm A}$  (magnetic field at analysing plane) will see the following transformation for  $E_{\perp}$  [15]:

$$E_{\perp, A} = E_{\perp, \text{ src}} \frac{B_A}{B_{\text{src}}}$$
(2.11)



**Fig. 2.2.:** Schematic illustration of the approximately 70 m long experimental setup located at the KIT. Figure taken from [13].

As seen, the remaining  $E_{\perp, A}$  is dependent on the change of magnetic field and so is the resolution of the MAC-E filter:

$$\Delta E = E \frac{B_{\rm A}}{B_{\rm src}} \tag{2.12}$$

With the design-fields  $\frac{B_{\rm A}}{B_{\rm src}} = \frac{6 \,{\rm T}}{0.3 \,{\rm mT}}$ , KATRINS MAC-E filter reaches an energy resolution of  $\Delta E = 0.93 \,{\rm eV}$  at the approximate endpoint energy of 18.6 keV. Figure 2.3 illustrates the concept of the MAC-E spectrometer. All collimated electrons with a kinetic energy too low to overcome the applied retarding potential  $U_{\rm ret}$  are reflected before passing the analysing plane, while all electrons behind the plane are accelerated towards the spectrometer exit and to the detector system.

#### **Detector System**

The detector system houses the focal plane detector (FPD) with a detector radius of 9 cm to count all remaining electrons. The detector consists of a pixelated silicon PIN diode featuring 148 equal-area pixels. Figure 2.4 displays the backside of the wafer with visible pixel distribution. The detector is cooled to -30 °C to reduce electronic noise and leakage current to improve signal clarity. With a resolution of 1.4 keV FWHM it offers sufficient resolution to investigate the spectrum of the electrons accelerated towards the detector and allows to reject parts of the background with cuts in the energy spectrum [11]. The magnetic field in this region is about 2.5 T.



**Fig. 2.3.:** Schematic illustration of the working principle of the MAC-E filter. An Electron entering the spectrometer experiences a slowly reduced magnetic guiding field, causing a collimation of the electron's momentum and aligning it to the field lines. With  $E_{||} < qU_{\rm ret}$  electrons are able to traverse the analysing plane, otherwise they are reflected by  $U_{\rm ret}$ . Figure taken from [16].



Fig. 2.4.: The backside of the FPD silicon PIN diode is depicted, with its 148 pixels visible. Image taken from [17].

#### 2.3.3 Background

To reach the target sensitivity of 0.2 eV (90 % C.L), improvements will still need to be made. One limiting factor is the background, which is currently higher than anticipated with about 150 mcps. This value is 15 times higher than the target value [4]. While many different background sources like electrons induced by external radiation have been reduced by electrostatic reflection and the detector background being comparatively low, one primary contribution to the current background comes from low energy electrons produced in the main spectrometer, behind the analysing plane. These electrons are then accelerated unhindered towards the detector section. This so-called Rydberg background will be further discussed in the following section. Efforts to reduce this background source have already been implemented, for example by shifting the analysing plane featured in figure 2.3 further down the beam line. This shifted analysing plane (SAP) reduces the volume in which background electrons can be generated [18]. The SAP is now part of the standard operation for KATRIN, however background reduction remains a priority [4].

#### **Rydberg Background Hypothesis**

As of current understanding, the background electrons generated in the main spectrometer are caused by highly excited, so-called Rydberg atoms: During construction of the main spectrometer, the inner walls were exposed to ambient air, containing naturally occurring <sup>222</sup>Rn, which adsorbed to the surface. The decay chain of <sup>222</sup>Rn contains <sup>210</sup>Pb with a half-time of about 22 years, which has accumulated in the spectrometer walls. Further decays yield the  $\alpha$ -emitter <sup>210</sup>Po, before finally arriving at <sup>206</sup>Pb with an energy excess of 5.4 MeV [4].

The recoil of the included  $\alpha$ -decay can sputter atoms from the vessel walls, causing the highly excited Rydberg atoms inside the spectrometer volume. These free atoms, mainly oxygen and hydrogen, are able to move freely as they are still electrically neutral. However, their excited state allows them to be ionized by mere thermal radiation. Should this happen behind the SAP, these electrons with a low kinetic energy will be accelerated towards the detector section [4]. The process is illustrated in figure 2.5.

One aspect separating this Rydberg background from signal electrons originating in the source is their maximum kinetic energy perpendicular to the guiding magnetic field. Rydberg-background-induced electrons will have initial energies in the meV range, distributed isotropically. Their trajectories along the magnetic field lines will al-



**Fig. 2.5.:** Illustration of the process leading to the Rydberg background. Following the  $\alpha$ -decay of <sup>210</sup>Po, atoms are sputtered off the vessel walls. These excited, but still electrically neutral atoms can enter the flux tube before black body radiation ionizes them, yielding a low energy electron. Figure taken from [4].

ways yield very small cyclotron radii, as well as low angles of incidence at the detector. Signal electrons towards the endpoint region of the spectrum feature  $E_{\rm kin} \approx 18.6$  keV with mostly a much larger component of transverse energy orthogonal to the field lines in a strong magnetic field like at the detector. Figure 2.6 depicts the angle of incidence for signal and Rydberg background electrons [5].

## 2.4 The active Transverse Energy Filter (aTEF)

The Rydberg background could be addressed by the ability to filter electrons according to their incident angles and cyclotron radii. The idea of a transversal energy filter was first initiated by R. G. H. Robertson in 2019 [19]. First concepts focused on passively inhibiting the path of background electrons, while relying on the large angular distribution of signal electrons to circumvent the filtering mechanism, as depicted in figure 2.8. A layered grid structure blocks the direct flight path towards the detector, which blocks most background electrons with low incidence angles as well as some signal electrons. Electrons with a large angle of incidence are able to pass the filter. However, even in best configurations, 75 % of signal electrons would be lost. As the KATRIN experiment already has low count rates, such a cut would not improve the statistics, even with a 95 % reduction of Rydberg background [19].



Fig. 2.6.: Simulation of the angular distribution for  $10^5$  signal electrons and Rydberg background electrons. While signal electrons are distributed predominantly between  $10^{\circ}$  and  $50^{\circ}$ , the vast majority of background electrons are found below  $10^{\circ}$ . Figure taken from [5].

Building on the TEF idea, Prof. Dr. Weinheimer suggested the aTEF concept. Instead of passively inhibiting the narrow flight of Rydberg background electrons with minimized impact on signal electrons, the focus is shifted on how the wide flight path of signal electrons can be used for detection. A filter, or detector, made up of microstructured channels with sensitive channel walls could minimize the Rydberg background with much lower loss of signal. A Monte Carlo simulation for electron flight paths of signal and Rydberg background electrons is depicted in figure 2.7.A honeycomb structure, as displayed, using hexagonal channels with an edge length of 100  $\mu$ m and a wall thickness of 10  $\mu$ m would enable an open-area-rato (OAR) of 90 % and could allow reducing the Rydberg background down to 10 % while maintaining 81 % of the signal, considering only the geometry and neglecting other efficiency reductions [4]. Preliminary etching results using inductively coupled reactive ion etching (ICP-RIE) on silicon for a hexagonal channel structure are also depicted in figure 2.7. This etching procedure will be further discussed in the next chapter.

Two possible aTEF implementations are currently being investigated in Münster [5][20][21][22]: Firstly, a filter similar to a microchannel plate (MCP) could be placed in the beam line in front of the FPD to change the signal amplitude compared to background electrons. Secondly, a microstructured silicon PIN-diode (Si-aTEF)



(a) Monte Carlo simulation for aTEF concept

(b) Preliminary etching of silicon

**Fig. 2.7.:** A Monte Carlo simulation of signal electron and Rydberg background flight paths through a hexagonal aTEF structure is illustrated in a). In b), a scanning electron microscope (SEM) image of microstructured silicon is depicted. Both figures taken from [5].



**Fig. 2.8.:** Working principle of the first transverse energy filter concept. On the right, Rydberg electrons (blue) with limited incidence angles are blocked fully by the grid. To the left, signal electrons (red) with high incidence angles are able to pass the filter, while those with low angles are blocked aswell. Figure taken from [19].

with passivated channel floors could implement the aTEF concept directly into the detector [5][20][21][22]. For the topic of this thesis, only the implementation of an MCP-aTEF will later be discussed.



**Fig. 2.9.:** Schematic illustration depicting the working principle of an MCP-aTEF. Electrons are guided by the magnetic field towards the MCP-aTEF, where signal electrons cause secondary electron emission due to their large cyclotron radii and incidence angles. Rydberg background electrons pass the filter without any amplification, due to their low transverse energy, allowing distinction at the detector. Figure taken from [4].

## 2.5 Validation of the Principle for an MCP-aTEF

To be able to test the MCP-aTEF concept before committing further to its development, regular microchannel plates were used, as these are widely available for purchase. Figure 2.10 presents a schematic MCP setup. Between the front and back side, a bias voltage serves to accelerate the initial incident electron, as well as any secondary electrons freed in contact with the channel walls. MCPs will be further discussed in the chapter 3.

Figure 2.11 depicts the schematic test setup used to validate the MCP-aTEF concept. As the channels of commercial MCPs feature a non-zero tilt angle in respect to the surface normal plane, the MCP position needed to be corrected to counteract the tilt. Electrons originate at the angular selective electron source (Egun) [14] and are magnetically guided by the beam tubes towards the detector, consisting of two *tectra*<sup>1</sup> MCPs in chevron configuration [24]. In the middle of the setup, the electrons are guided through a *RoentDek*<sup>2</sup> MCP [25]. The magnetic field in the beam tube, guiding the electrons from the source to the filter, was varied, primarily changing the phase of the electrons' cyclotron motion. This method was used, as a 0° alignment

<sup>&</sup>lt;sup>1</sup>tectra GmbH, Reuterweg 51-53, 60323 Frankfurt/M, Germany

<sup>&</sup>lt;sup>2</sup>Roenteck- Handels GmbH, Im Vogelshaag 8, 65779 Kelkheim, Germany



**Fig. 2.10.:** Schematic illustration of an MCP. An applied bias voltage accelerates an incident electron. Upon hitting the angled channel walls, secondary electrons are created, forming an electron avalanche towards the exit of the channel. Figure taken and edited from [23].

of all setup components was too difficult.

In aTEF mode, the MCP was operated at a potential difference of 700 V, amplifying the signal of electrons hitting the MCP walls. In pTEF mode, no potential difference was applied and the MCP absorbed electrons upon wall contact. As the magnetic field at the MCP was around 14 mT, and was mostly independent of changes in the beam coil current, the electrons' cyclotron radii were in the order of 190  $\mu$ m, much larger than the MCP channel diameter of 10  $\mu$ m. However, as the electrons' transversal movement accounted for only 20 $\mu$ m during transit of the 400 $\mu$ m channels, a suitable angle of entry, caused by the phase of their cyclotron motion, allowed the electrons to pass without wall contact.

In the data displayed in figure 2.12, this is visible as a periodic drop in count rate of measurements in aTEF mode during change of the beam coil current. This observation is confirmed by the pTEF mode, where a signal is only produced when electrons can pass the filter without wall contact [5]. It was therefore possible to confirm the MCP-aTEF concept and justify further commitment and investigations.



**Fig. 2.11.:** Schematic test setup used to validate the MCP-aTEF concept. A commercial MCP at an angle is used to filter electrons guided along a magnetic field. Figure taken from [5].



**Fig. 2.12.:** Results of measurements to validate aTEF principle. Measurements in aTEF mode at a potential difference of 700 V, as well as measurements without any applied voltage in pTEF mode, are depicted. Figure taken from [5].

# 3

## Considerations for an MCP-aTEF

In this chapter, the design of commercially available MCPs will be briefly summarized to visualize the need for a new design and to highlight the required components for an MCP-aTEF. Building on this, investigations for these components will be presented.

## 3.1 Commercial MCPs

In principle, three main components are required to construct an MCP: As the foundation, a suitable substrate and assembly or preparation process is required to give the desired geometry to the chip and channels. To allow for the required potential difference between front and back side of the MCP without excessive heat build-up, a high total resistance for the device is required. At the same time, the resistance needs to be sufficiently low to allow for a sufficient supply of electrons. Thus, a conducting layer of appropriate resistance, the so-called strip-resistivity-layer (SRL), is required. The very top layer on the channel walls, the secondary electron emission layer (SEEL), needs to allow for reliable release of secondary electrons to enable suitable signal gain. Lastly, a common way of contacting the MCP is achieved by covering the front- and backside with a conducting material like NiCr [26].

As commercial MCPs need to be economically viable, efficient methods for production have been developed. The following paragraph is based on [26] and [27]. The plate itself is traditionally composed of electrically isolating lead glass (PbO<sub>x</sub>) capillaries, bundled together. Recently, different glass substrates are being used, as MCP manufacturing gets further developed [28]. To activate the MCP, the chip is annealed in a hydrogen bath, stripping the inner walls of oxygen and forming a thin lead layer. Lead makes for an acceptable secondary electron emitter in conventional use cases with a secondary electron yield (SEY)  $\delta_{Pb} < 1.5$  [29] and allows building up a conducting layer to achieve the desired total resistance. Therefore, both the functionality of the SRL and SEEL is covered efficiently in one process and layer.

MCPs typically have a total resistance between  $10^7 \Omega$  and  $10^9 \Omega$  and are operated at about 1 kV with a gain of  $10^4$  to  $10^7$  [26]. The channels themselves are tilted by around 8 ° with respect to the chip surface to prevent electrons from passing through the channel without interaction and have a diameter usually in the order of 10 µm [30][26].

## 3.2 Implementation for an MCP-aTEF

The commercially available MCPs are sufficient and reliable for many applications, with production choices being cost-driven in most cases. However, to ensure the costeffective, scalable manufacturing process, potential optimizations to the functionality of MCPs might not (yet) be implemented due to diminishing returns or concepts that are simply not economically viable at the current time, besides for custom-built models.

For the KATRIN experiment, low dark count rates are crucial, as signal electrons with kinetic energy close to the endpoint  $E_0$  are created with increasingly low probability in respect to their energy. With many radioactive isotopes, a lead-based substrate is out of question. Furthermore, the fiber-bundling process for glass MCPs generally carries undesired spatial defects with it [31]. Typical dark count rates for commercial MCPs are in the order of  $1 \frac{\text{cps}}{\text{cm}^2}$  translating to about 255 cps for the full FPD surface with a radius of 9 cm [26]. For comparison, the initially projected total background rate for the KATRIN experiment lies in the order of 10 mcps [4].

As previously discussed, common MCP channel size makes the distinction between signal and Rydberg background difficult. Additionally, the OAR should be as large as possible to minimize signal losses and therefore maximize the signal-to-backgroundratio.

Finally, the high kinetic energy of signal electrons needs to be considered, as the SEY depends on it. With an energy of 18.6 keV, plus a potential post-acceleration of additional 10 keV, many common secondary electron emitting materials fall out of question for the MCP-aTEF [4]. Common MCPs show a detection efficiency of around 0.2 for electrons with  $E_{kin} \approx 18 \text{ keV}$  [32].

These criteria demand a new design and the implementation of optimized methods to fabricate an entirely new chip. The considerations will be discussed in more detail as part of the following sections.

## 3.3 Choice of Substrate and Processing

As previously mentioned, lead glass can not be considered for an aTEF design, as the abundance of radioactive isotopes would hamper the desired background rates. Additionally, the OAR will be reduced with respect to a hexagonal channel shape. An alternative manufacturing process using micromachined silicon has been developed but does currently not see common, commercial implementation due to high costs [31]. The radiopurity of silicon [13] and the option for different channel geometries of micromachined silicon allow for optimized dark count rates and OAR. The ideal honeycomb structure has previously been mentioned in chapter 2.2.4. To create such a microstructure, inductively coupled reactive ion etching (ICP-RIE) has previously been and still is investigated for an MCP-aTEF, as well as for etched detectors [20][21]. As part of a collaboration with M. Stappers and W. Pernice, many parameters for the microstructuring process have been previously optimized. This thesis merely makes use of the process, no research or development on it has been done as part of this work.

A short summary of the ICP-RIE principle will be given, followed by the methods and results of this work.

#### **ICP-RIE Principle**

Dry etching methods like ICP-RIE allow for anisotropic etching and good reproducibility, as control over the total etching time is given. Process gases are ionized by the ICP source and accelerated towards the sample by the RF source, as depicted in figure 3.1. To achieve the desired structures, parts of the sample are covered with a protecting photoresist mask. Using SF<sub>6</sub> and O<sub>2</sub> as an example, F radicals are created by the ICP source and etch the silicon on contact with the sample. The ion bombardment removes any passivating etching products on the surface towards the RF source, that are not covered by the protective mask, while SiO<sub>x</sub>F<sub>y</sub> builds up on the side walls and largely passivates these for the etching process. Additionally, the sample can be



Fig. 3.1.: Illustration of the chamber of an ICP-RIE system. Ions are produced by the ICP source and then accelerated towards the sample by a separate radio frequency (RF) source. Figure taken from [33].

cooled to increase the wall passivation and influence the anisotropy of the etching process.

#### Methods for Microstructuing of the Si Substrate

Six chips cut from a 200 µm silicon wafer by *MicroChemicals*<sup>1</sup> were cleaned using an ultrasonic acetone bath and a plasma asher system *Diener*<sup>2</sup> *Zepto-W6* and coated with the photoresist *Su-8 3035* by *Kayaku*<sup>3</sup> using the spin coater *SPS*<sup>4</sup> *SPIN150i* and imprinted with a preliminary  $7 \times 7 \text{ mm}^2$  hexagon mask of 100 µm and a wall thickness of 20 µm in an *EVG*<sup>5</sup> 620 *NT* nano imprint lithography system, similar to the design proposed in [5]. The chips were then etched for 30 min in an *Oxford*<sup>6</sup> *PlasmaPro 100* using the previously mentioned process gases.

<sup>&</sup>lt;sup>1</sup>MicroChemicals GMBH, Nicolaus-Otto-Str. 39, D-89079 Ulm, Germany

<sup>&</sup>lt;sup>2</sup>Diener electronic GmbH + Co. KG, Nagolder Straße 61, D-72224 Ebhausen, Germany

<sup>&</sup>lt;sup>3</sup>Kayaku Advanced Materials, Inc., MA 01581 Westborough, USA

<sup>&</sup>lt;sup>4</sup>SPS-Europe B.V, Midden Engweg 41, NL-3882 TS Putten, The Netherlands

<sup>&</sup>lt;sup>5</sup>EV Group GmbH, DI Erich Thallner Str. 1, A-4782 St.Florian am Inn, Austria

<sup>&</sup>lt;sup>6</sup>Oxford Instruments plc, OX13 5QX Abingdon Oxfordshire, England

#### **Resist Removal and Isolation**

After the etching process, the chips were placed in a Dimethylsulfoxid (DMSO) bath to loosen the photoresist still remaining on the surface of the samples. After multiple hours at approximately 70 °C, most of the photoresist film could be pulled from the chips, however, some residues could not be fully removed. Additional strategies for removal are necessary for future samples. A much more aggressive piranha solution could be used, but was not tested in this work.

The MCP-aTEF silicon substrate needs to be electrically isolated, since the silicon structure itself would be too conducting, as will be shown in Chapter 3.4. For this purpose, the thermal growth of SiO<sub>2</sub> was tested using a *Nabertherm<sup>7</sup> R120/500/13*, allowing annealing at up to 1100 °C in ambient air. Referring to the wafer manufacturer [34], a layer of 0.5  $\mu$ m could be expected after annealing at this temperature in a pure oxygen atmosphere for 12 h. With a dielectric strength of 10<sup>7</sup> V/cm [35], a 0.5  $\mu$ m layer would suffice for an applied voltage of up to 500 V. For initial tests, the sample was annealed for 12 h at 1100 °C in ambient air, since pure oxygen is not featured by the available system.

Figure 3.2 depicts three samples after attempts to fully remove the photoresist and after annealing. A sample with an intact resist mask, that was neither etched, nor annealed, is also depicted. A difference in reflective properties can be seen, indicating the oxide layer after annealing. Small, burned residues from the photoresist are visible on the microstructured area of chip 3. Unevenness in the photoresist of chip 2 has caused damage to the chip during etching.

#### Investigations on the Channel Quality

In this work the microstructured chips were studied with an optical microscope, further investigations were not done, yet. Microscope images of the previous chips 1 and 2 are shown in picture 3.3. These two chips were chosen, because they show all relevant features that were visible in a less pronounced way in chips 3 to 6. Both chips show a mostly intact honeycomb structure in the foreground with some defects visible in chip 2, besides the areas with large damage, visible by eye as in figure 3.2.

<sup>&</sup>lt;sup>7</sup>Nabertherm GmbH, Bahnhofstr. 20, G-28865 Lilienthal, Germany



**Fig. 3.2.:** Depicted are three chips after attempted photoresist removal and annealing. The unnumbered chip in the bottom right corner still features the photoresist and was neither etched, nor annealed and serves for comparison. On chip 3, residue from the photoresist in the form of darkened spots can be seen on the microstructured area. Unevenness in the photoresist layer of chip 2 translated to damage during the etching process that is visible by eye. All three annealed chips feature a colorful reflective pattern, indicating the grown oxide layer that is not visible on the comparison chip.

Channels in chip 1 are mostly etched through, with some silicon remaining. For chip 2 only a small area at the edge was etched through, with figure 3.3 depicting the middle of the chip, where no channels are etched through.

Figure 3.4 displays the rearview of both chips, backside-illuminated by the microscope lamp. Here, the small area of fully etched channels of chip 2 is shown. Compared to chip 1, the edges are much rougher and wall thickness seems reduced.

Figure 3.5 shows images of chip 1 taken with the focus being moved through the channel. It is visible that remaining silicon artifacts are predominantly located in the middle of the chip, at least for the observed channel.

With figures 3.2 to 3.5 multiple factors for the success of microstructuring can be considered. First and most obvious, correct application and development of the protective photoresist layer plays a large role in effective and consistent etching, including the production of the chromium mask used in the lithography process to apply the photoresist mask. However, this is beyond the scope of this thesis. Secondly, the etching time, but also other process parameters, might still offer room for optimization. A longer etching time might reduce the remaining silicon structures in the channels as seen on chip 1, however, integrity of the walls needs to be ensured. A first test showed that hexagonal 200 µm deep structures can be fabricated, however, the channel quality is questionable at the time. It is unclear, in what scale the secondary emission and response homogeneity of a final MCP-aTEF could be affected. More work is necessary to produce chips of higher quality.



front

(a) Microscope image of chip 1 lighted from the (b) Microscope image of chip 2 lighted from the front

Fig. 3.3.: In (a) most of the silicon is removed from the channels with some artifacts remaining. In (b) no visible channels are etched through. Images taken by Kevin Gauda.



(a) Microscope image showing the backside of chip 1, backlight-illuminated



(b) Microscope image showing the backside of chip 2, backlight-illuminated

Fig. 3.4.: View from the backside of the chips. In (a) channels of chip 1 display mostly round openings with small defects visible. Chip 2 shows a more damaged channel wall with ragged edges. Images taken by Kevin Gauda.



Fig. 3.5.: Backside-illuminated Channel of chip 1 with the focus moved through the channel from left to right. Remaining silicon artifacts along the path seems more common towards the middle of the channel. Images taken by Kevin Gauda.

## 3.4 Investigations on the SRL and its Application

The previously prepared substrate is isolated by an oxide layer and a SRL of appropriate conductivity needs to be applied, allowing for the necessary potential difference without generating too much heat and causing a thermal runaway of the conductivity. Calculations for different material resistivities were performed, preliminarily considering a channel length of  $l = 200 \,\mu\text{m}$ , a hexagon side length  $k = 100 \,\mu\text{m}$  and a total wall thickness  $d = 20 \,\mu\text{m}$ , as used before in the microstructuring process. The chips' total resistance R for a given resistivity  $\rho$  can be calculated as

$$R = \rho \frac{l}{A} = \rho \frac{l}{\frac{2}{3}\sqrt{3}(k^2 - (k - s)^2)N},$$
(3.1)

where SRL thickness is denoted as s and N is the number of hexagonal channels per chip. The number of channels was calculated by dividing the chip area,

 $A_{7\text{mm,total}} = 49 \text{ mm}^2$  for a square microstructure and  $A_{9\text{cm,total}} = 255 \text{ cm}^2$  for the round FPD surface, by the space occupied by a channel and half the surrounding wall  $A_{\text{Channel}} = 31436 \,\mu\text{m}^2$ . This results in  $N_{7\text{mm}} \approx 1559$  and  $N_{9\text{cm}} \approx 810000$  respectively.

Figure 3.6 displays the results, with the resistance range of common MCPs highlighted in blue. As the aTEF merely needs to allow to differentiate signal from background electrons, a reduced gain compared to typical MCPs is acceptable. While a high gain is preferred, the FPD only needs to be able to differentiate the amplified signal from singular background electrons. Voltage requirements are likely much lower than common MCP parameters, therefore a heat runaway could already be avoided at lower total resistance. That being said, aiming for the given range makes a resistivity between  $10^2 \Omega m$  and  $10^4 \Omega m$  desirable for a first prototype.



**Fig. 3.6.:** Calculations for the total resistance of a preliminary MCP-aTEF considering 100 µm side length, 20 µm total wall thickness and a 200 µm channel length for a square chip of  $7 \times 7 \text{ mm}^2$  ( $R_{7\text{mm}}$ ) and a round chip with r = 9 cm ( $R_{9\text{cm}}$ ). Highlighted in blue is the typical resistance range for commercial MCPs.

#### Film Fabrication by Atomic Layer Deposition (ALD)

One process that allows for controlled and uniform layer deposition, especially on microstructured samples, is the atomic layer deposition, a variant of the broader chemical vapor deposition (CVD) [36]. It was developed and made known around 1980 by Tuomo Suntola in Finland [37]. Generally, a thin film is grown on a sample by sequentially exposing it to two gaseous chemicals, called precursors, that together react to the desired deposition material. Upon exposure to one precursor, a monolayer of said chemical builds up on the sample surface. After evacuation and flushing of the chamber with an inert gas, the second precursor is delivered and reacts upon contact with the first precursor layered on the sample, ideally creating a mono-atomic layer of the desired material on the surface. This cycle can be repeated as required. Figure 3.7 depicts the ALD process for Trimethylaluminium (TMA) and water. It has previously been shown that atomic layer deposition (ALD) can be used effectively in the context of MCP manufacturing [27].

Different implementations exist to allow for precursor reaction and purging of ALD systems. For this work, a *Cambridge NanoTech<sup>8</sup> Savannah 100*, located in the Münster Nanofabrication Facility ( $MNF^9$ ) was used. This device utilizes thermal ALD, in which the substrate inside the reactor chamber is heated to enable precursor reaction. In this device, a constant flow of N<sub>2</sub> accompanies the delivery of precursor pulses in a low pressure environment of around 0.05 mbar and quickly purges the chamber of remaining gasses, before the second precursor is pulsed.

#### 3.4.1 Choice of Material and Adjustment of the Resistivity

In the case of the silicon substrate, an obstacle for the SRL is presented in the required resistivity, as previously depicted in figure 3.6: Essentially, no natural materials within the required range exist [27]. Of the available materials at the MNF ALD system, titanium oxide ( $TiO_x$ ) was chosen for first measurements, as it has been studied and

<sup>&</sup>lt;sup>8</sup>Levidian Nanosystems Limited, formerly Cambridge Nanosystems, 17 Mercers Row, Cambridge, Cambridgeshire Cb5 8HY Cambridge, England

<sup>&</sup>lt;sup>9</sup>University of Münster, Münster Nanofabrication Facility, Busso-Preus-Str. 10, 48143 Münster, Germany



**Fig. 3.7.:** A simple ALD cycle for the precursors TMA and water to deposit layers of Al<sub>2</sub>O<sub>3</sub>. The reaction is self-limited and the growth is limited by the periodic exposure and purging sequence. Figure taken from [38].

applied in many fields, including the application of it via ALD [39] and resistivity values in the required range had been seen in literature [40].

#### **Methods for Initial Measurements**

To create samples with the ALD system, a *MicroChemicals* Prime Si n-type (phosphor) (100) 4 inch wafer with a thickness of  $(525 \pm 25) \mu m$  and  $5 \mu m$  of wet-annealed SiO<sub>2</sub> wafer was cut into square chips with an edge length of 2 cm, serving as the substrate to be coated. These were cleaned in an ultrasonic acetone bath before usage in the ALD system.

For ALD operation, the flow of  $N_2$  was set to 20 sccm. The precursor Ti(NMe<sub>2</sub>)<sub>4</sub> (TDMAT) by *Strem*<sup>10</sup> was used and heated to 75 °C for all depositions. The pulse time for TDMAT was chosen to be 0.1 s. For the water serving as second precursor, a pulse time of 0.015 s was used. Each pulse was followed by a waiting period of 5 s to evacuate the reactor chamber of any remaining precursors.

After sample manufacture, the samples were connected to measurement devices via thin copper fibers, glued to the sample surface with *Plano<sup>11</sup> ACHESON 1415 silver conductive varnish*, as visible in figure 3.8. The first measurement setup consisted of a

<sup>&</sup>lt;sup>10</sup>Strem Chemicals Inc., 15 rue de l'Atome, Z.I. 67800 Bischheim, France

<sup>&</sup>lt;sup>11</sup>Plano GmbH, Ernst-Befort-Strasse 12, D-35578 Wetzar, Germany



(a) Schematic setup for van-der-Pauw resistivity measurement, taken from [42]



(b) Van-der-Pauw resistivity method applied to chip in measurement box

Fig. 3.8.: Depiction of the vdP method schematically (a) and as used for the resistivity measurements with the sample and copper wires connected to it with silver varnish (b).

metal box with an isolated floor using  $Kapton^{12}$  © tape. Four electrical feed-throughs enabled switching of contacts without tearing off the silver varnish. Resistivity measurements of the TiO<sub>x</sub> layer were performed with the van-der-Pauw (vdP) method [41], as no system with equal probe distance for common 4-point-measurements was available in the laboratory. The vdP method allows elimination of the influence of sample geometry for resistivity measurements by performing a 4-point-measurement with cycling contacts, placed on symmetry axes and as close to the edge of the sample as possible [41]. Figure 3.8 depicts the schematic setup, as well as a contacted chip. The resistivity results as

$$\rho = \frac{\pi s}{\ln 2} \cdot \frac{R_{\text{AB,CD}} + R_{\text{BC,DA}}}{2} \cdot f \quad [41], \tag{3.2}$$

where f is a correction factor depending on the proportion of the two measured sheet resistances and s is the layer thickness. The sheet resistances in this instance are determined as follows, using the contact denomination of figure 3.8:

$$R_{\rm AB,CD} = \frac{U_{\rm CD}}{I_{\rm AB}} \tag{3.3}$$

While the vdP method ideally uses a cloverleaf sample structure to minimize uncertainties, the setup depicted in figure 3.8 was sufficient for the intended measurements, as for the SRL achieving the correct order of magnitude would be sufficient.

Initial tests showed that the edges of the cut  $Si-SiO_2$  chips were not isolating the silicon core. As the ALD process coats all accessible surfaces and, thus, generates a bridge between the SRL and the silicon core of the chip, a method of isolation

<sup>&</sup>lt;sup>12</sup>CMC Klebetechnik GmbH, Rudolf-Diesel-Strasse 4, 67227 Frankenthal, Germany

between silicon core and SRL was needed. After ALD, a diamond-tipped pen was used to scratch predetermining breaking lines, on which each sample was broken to isolate the deposited layer.

As an alternative, it was considered to coat the chip edges in a varnish, that could be removed after ALD. For this purpose, heating tests with the photoresist *Microposit*<sup>13</sup> *S1813 G2* were performed. The resist was burned, but seemingly the covering was still intact, after being heated to  $180 \degree C$  for 90 min, roughly simulating the environment during the ALD process. For removal, an ultrasonic bath in acetone was tested without success. For the purpose of resistivity measurements, the prior method of isolation was sufficient, so no further investigation was done. In future work, more effective removals for a varnish should be tested to avoid damaging the chip during breaking of the edges.

### 3.4.2 Influence of the Process Temperature

As the first parameter, the temperature in the ALD reactor was varied. Four chips were coated at different temperatures spanning from  $150 \degree C$  to  $250 \degree C$ . Figure 3.9 displays the results with the resistivity being at about the same level for  $150 \degree C$  and  $180 \degree C$  and then falling. As ALD deposited  $TiO_x$  is rutile up until  $180 \degree C$  according to [43], before the share of anatase in the layer rises, a possible explanation for the observed drop is that the resistivity of amorph  $TiO_x$  is higher and consequently drops as more anatase  $TiO_x$  is built up.

With a growth rate of 0.39 Å to 0.40 Å for the given temperature range [43], a 20 nm layer was aimed for by running 500 ALD cycles per sample. Thickness measurements using a *Filmetrics*<sup>14</sup> *F20* with a measurement range down to 15 nm showed a variation around 25 %. This deviation is likely due to being so close to the end of the measurement spectrum and as the *F20* uses light reflection and had measurement presets that differentiated between structures of  $TiO_x$  Anatase mixed with amorph parts might have deteriorated the results. However, the 25 % thickness variation was considered for uncertainty calculations, in which it is the biggest contributing factor. Considerations for the uncertainties can be found in the appendix.

<sup>&</sup>lt;sup>13</sup>micro resist technology GmbH, Köpenicker Str. 325, 12555 Berlin, Deutschland

<sup>&</sup>lt;sup>14</sup>Filmetrics Applikationslabor Deutschland, Hauptstr. 42, 82008 Unterhaching, Germany



**Fig. 3.9.:** Resistivity  $\rho$  depending on reactor temperature at time of deposition. At temperatures higher than 180 °C,  $\rho$  falls as temperature rises.

All the acquired resistivity values are orders of magnitude below the necessary values for the SRL, with the maximum value obtained being ( $0.18 \pm 0.05$ )  $\Omega$ m. For following measurements, a reactor temperature of 180 °C was chosen to allow the highest temperature for precursor reactions without decreased  $\rho$ .

### 3.4.3 Adjustment of the Resistivity

To achieve the necessary values, the exponentially increasing resistivity for nano films with decreasing thickness was investigated [44]. Different  $\text{TiO}_x$  samples were created using a varying amount of total ALD cycles ranging from 500 down to 50 corresponding to 20 nm and 2 nm film thickness. For a thickness down to 8 nm the previously described vdP method was applied to determine the resistivity. At this point a *Keithley*<sup>15</sup> 2450<sup>16</sup> constant current source was used, supplying its minimal 50 nA over the front panel, as no higher current could be supported at 42 V without circumventing the interlock for higher voltage.

<sup>&</sup>lt;sup>15</sup>Keithley Instruments by Tektronix Uk Ltd., The Capitol Building, 8FZ Oldbury, Bracknell, England <sup>16</sup>Thanks to the group of Prof. Dr. Schuck for kindly lending this constant current source for this thesis.



(a) Setup of two chips for the resistivity measurements of samples below 8 nm layer thickness



(b) Sample on electrical through-put flange for vacuum setup

**Fig. 3.10.:** Setup in ambient air and flange for setup in  $10^{-5}$  to  $10^{-6}$  mbar vacuum used for measurements on increasingly thinner samples.

Measurements on thinner samples were instead performed by increasing the contact sizes to allow higher current and measuring the full resistance with the *Keithley 2450* on the front panel contacts at 42 V, which was calculated back to the corresponding resistivity from the sample geometry. Figure 3.10 displays the setup for these measurements, as well as an electrical through-put flange for a  $10^{-5}$  mbar to  $10^{-6}$  mbar vacuum setup to investigate the influence of ambient air and moisture for samples of higher resistance.

Figure 3.11 presents the measurement series of  $\rho$  depending on layer thickness. Between 20 nm and 10 nm virtually no change in resistivity is observed, with a slight increase down to 6 nm. Below that,  $\rho$  rises exponentially as the thickness decreases. The previously targeted range is highlighted in blue, with a thickness of 4.5 nm and 5 nm both delivering resistivites in the mid-range and the 4 nm sample exceeding the range with  $(3.4 \pm 1.9) \cdot 10^4 \Omega m$  in vacuum and a sample resistance of  $(3 \pm 1) T\Omega$  being at the measurement limit for this setup. For the 2 nm sample, no measurements could be conducted as the resistance was too high.

No significant difference between vacuum and ambient air measurements was visible, indicating a negligible influence of moisture on the setup, with resistances being too low for the measurements to be influenced by a thin water film. A slight deviation for the 4 nm chip between vacuum and ambient air measurements might hint at a non-negligible influence, should higher resistances be investigated, if it is not an artifact of the measurement limit of this setup.



**Fig. 3.11.:** Measurements of  $\rho$  depending on layer thickness. An exponential decrease in conductivity can be observed for thickness values below 6 nm. Highlighted in blue is the resistivity range corresponding to figure 3.6.

To further investigate potential influences of humidity and pressure, additional measurements during the venting process of the vacuum chamber were taken in an attempt to visualize any potential changes, or the lack thereof. As already shown, no lasting difference was observed. For the comparatively well conducting 15 nm sample used for this test, there was, however, a brief drop in measured voltage in vdP measurement setup, as visible in figure 3.12. As air is let into the setup very slowly, it can expand rapidly inside the chamber. Following this, a possible explanation could be that the air cools down and its relative humidity increases, potentially beyond saturation and causing condensation, leading to a reduced measured voltage in the vdP setup. As pressure and temperature stabilize, the water could evaporate again and so the resistance and measured voltage would return to previous values.



**Fig. 3.12.:** Voltage measurement on 15 nm sample in vdP measurement setup during venting process of the vacuum chamber. A spike in conductivity is observed, which levels out completely shortly afterwards. The current on the opposing two contacts was  $I_{1,2} = 1 \,\mu$ A.

To exclude inconsistencies caused by defects in the first couple layers that are deposited for each sample and to confirm reproducibility, further samples for 4 and 4.5 nm thickness were created. Table 3.1 displays the results. Deviations for the 4.5 nm samples are within uncertainty ranges and the values itself are grouped very tightly, with deviations under 10%. For the 4 nm samples, deviations are slightly higher but still included in the uncertainties. Higher deviations were expected for 4 nm samples, as the total resistance was closer to the measurement limits of the setup.

These results conclude successful adjustment of the resistivity and display a consistent deposition method by use of ALD in the context of the measurement, however, additional investigations might be necessary to rule out any local differences that could cause inhomogeneity in the MCP-aTEF response.

#### **Composite Layer**

In case the exponential dependency on layer thickness for the adjusted resistivity should cause inconsistencies further down the line during coating and measurement of microstructured chips, a second approach was briefly investigated. As used in [27],

**Tab. 3.1.:** Repeated measurements for 4 nm and 4.5 nm samples in air. Displayed are the resistivity results for two samples of a 4 nm thick layer and three samples for 4.5 nm thickness. For uncertainty calculations, influences by sample thickness and the contacting dimensions have been considered. Additional influences caused by the form of the chip and the contacts have been neglected.

d (nm)	$ ho_1$ (k $\Omega$ m)	$ ho_2$ (k $\Omega$ m)	$ ho_3$ (k $\Omega$ m)
4	$17,6\pm9,0$	$15,6\pm9,2$	-
4, 5	$3,2\pm 1,4$	$3,4\pm1,1$	$3,2\pm 1,4$

composite layers consisting of an isolating and conducting material can be used to adjust the resistivity of the full layer. While ALD of metals was not possible with the available ALD system, an attempt at creating TiO<sub>x</sub>:Al<sub>2</sub>O<sub>3</sub> composites with the purpose of resistivity regulation was made, as composites of this kind have already successfully been created in literature [45]. Al<sub>2</sub>O<sub>3</sub> has a resistivity of  $\rho_{Al_2O_3} \approx 10^{16} \Omega m$  [46] and is a commonly applied ALD material.

For the deposition of  $Al_2O_3$  the *Strem* precursor Trimethylaluminium (TMA) was used in combination with water. The TMA cylinder did not need to be heated, as the vapor pressure was high enough at room temperature. As reactor temperature 180 °C was chosen again to deposit amorph layers of both composite materials and a growth rate of 1.2 Å per cycle for  $Al_2O_3$  [43].

Two samples of cycle proportions 2:8 and 8:2 were created. An Al<sub>2</sub>O<sub>3</sub> content of 20 % at 500 total cycles and a thickness of 28 nm lead to a resistivity of  $\rho_{20 \,\%\,Al_2O_3} = (5.68 \pm 2.15) \,\Omega m$  and a content of 80 % at 250 cycles and 26 nm resulted in  $\rho_{80 \,\%\,Al_2O_3} = (12 \pm 5) \,k\Omega m$ . Both of these layers are thick enough to not observe exponential effects resulting from the layer thickness itself. Therefore, a composite layer with an Al<sub>2</sub>O<sub>3</sub> content of about 80 % might be a suitable alternative, should the previous presented method of resistivity adjustment not be applicable to a microstructured chip.

Further tests for different composite proportions were intended to display the change depending on mixing proportions. However, a defect in the ALD system has resulted in it being inoperable at the time of this work. Should the composite approach be followed further, more samples are recommended to investigate the observed resistivities.



Fig. 3.13.: Depiction of the secondary electron yield curve given by equation 3.4 [48].

## 3.5 Considerations for the SEEL

Lastly, investigations on the secondary electron emission layer for a potential MCPaTEF were conducted. As the main topic of this thesis was the investigation of SRL materials and the adjustment of resistivity, any potential implementations for the SEEL have only been considered and researched in literature.

Just as for the SRL, an application via ALD is ideal to achieve a controlled, uniform deposition for the SEEL. The main obstacle is presented by the high energy of signal electrons close to the endpoint energy  $E_0$  in the KATRIN experiment, which are currently even further accelerated towards the FPD. It is not clear, if and in what form the post acceleration would be changed, should an MCP-aTEF be considered for implementation.

Secondary electron emission can be empirically described by equation 3.4, where the maximum yield  $\delta_m$  at the corresponding incidence energy  $E_m$  is used to be able to calculate the yield  $\delta$  at any given incidence energy  $E_0$  [47]. Figure 3.13 depicts the resulting yield curve.

$$\frac{\delta}{\delta_{\rm m}} = 1.28 \left(\frac{E_0}{E_{\rm m}}\right)^{-0.67} \left(1 - {\rm e}^{-1.614 \left(\frac{E_0}{E_{\rm m}}\right)^{1.67}}\right)$$
(3.4)

As can be seen, the yield drops continuously after the incidence energy surpasses  $E_{\rm m}$ . For many materials,  $E_0$  lies below 1 keV, significantly hindering emissions for energies as encountered in KATRIN. Research on ALD-applied SEEL materials for MCPs has already been conducted for MgO and Al<sub>2</sub>O<sub>3</sub> in literature [27]. Figure 3.14



Fig. 3.14.: SEY curves for Al<sub>2</sub>O<sub>3</sub> and MgO applied by ALD. Figure taken from [27].

depicts the yield curves measured for these materials. While Al<sub>2</sub>O<sub>3</sub> does not provide the necessary SEY, a 20 nm MgO layer provided  $\delta_0 = 6.9$  at  $E_0 \approx 800$  eV. Using equation 3.4, this would correspond to  $\delta_{MgO,18.6keV} > 1$  at 18.6 keV for signal electrons at KATRIN, potentially sufficient for detection. This does however neglect any post acceleration. MgO layers thicker than 20 nm were not studied in the available literature, as the high resistivity of MgO caused charge-up effects in the investigated configuration [49]. Due to the low signal rate in the KATRIN experiment, as well as the lower voltage requirements, further investigation might be justified.

Multiple materials of high SEY were found [50], with a tendency of crystalized materials offering higher SEY, as a single crystal of MgO was shown to have a maximum yield of 24.3 at an incidence energy of 1300 eV [51].

Similar to  $\text{TiO}_x$  layers investigated in this thesis, a higher ALD reactor temperature might yield MgO depositions with an increased share of crystalized MgO, potentially resulting in an improved SEY.

It has been found in literature, that ALD deposited MgO begins to form a polycristaline structure at and above a deposition temperature of 200 °C [52][53]. As the *Cambridge NanoTech Savannah 100* is capable of achiving temperatures as high as 450 °C, the SEY depending on reactor temperature could be measured.

However, before commiting to investigations on MgO, all other components for a potential MCP-aTEF should be tested together. Considering successful microstructuring and isolation, as well as deposition of an appropriate SRL, first SEEL tests could use a layer of  $Al_2O_3$  for simplicity to investigate the general functionality, given at a lower incident electron energy.

## **Conclusion and Outlook**

## 4

In this thesis, methods and requirements for the fabrication of an initial MCP-aTEF prototype were investigated and potential implementations for the required components have been presented.

As the substrate, silicon with a hexagonal honeycomb structure, microstructured using inductively coupled reactive ion etching can be implemented, with further investigations necessary to achieve reliable microstructuring processes. Subsequent annealing was used to grow an isolating  $SiO_2$  layer required to enable high voltage application, however, the growth rate and the isolation properties still need to be verified.

Atomic layer deposition was considered as an effective method to apply the stripresistivity layer and secondary electron emission layer for a microstructured substrate. To achieve the required device resistance of  $10^7 \Omega$  to  $10^9 \Omega$  to inhibit thermal runaway, while still maintaining enough current for the supply of electrons for emission, investigations on the SRL of desired resistivity have been made. Studies on the exponentially increasing resistivity of thin, ALD-applied TiO<sub>x</sub> have been performed in air and in vacuum to achieve the required resistivity of  $10^2 \Omega$ m to  $10^4 \Omega$ m, which was possible with a layer thickness of around 4.5 nm. In stable conditions, no significant difference in conductivity for measurements in air and vacuum was observed.

Additionally, first measurements for a potential alternative in the form of a  $TiO_x:Al_2O_3$  composite have been made, should the exponential dependence on layer thickness cause inhomogeneity in the response of a later MCP-aTEF prototype. More research will be necessary, should this approach be considered for the SRL.

Lastly, materials for the secondary electron emission layer were searched, as not many materials allow for reliable emission for the high energy of incidence electrons in the KATRIN experiment. ALD-applied MgO has been found to be a potential candidate, that could allow for the detection of high energy signal electrons. Further studies for its SEY would be needed.

With investigations towards the components of an MCP-aTEF, a step towards the manufacture of a prototype has been made. However, attempts to build an MCP-aTEF prototype have yet to be carried out: The individual components investigated in this thesis have not been applied to a singular sample and extensive studies will be required to test the functionality and properties of such a first prototype.

## Bibliography

- [1]W. Pauli. Pauli letter collection: Letter to Lise Meitner. 1930. URL: https://cds.cern. ch/record/83282? (cit. on p. 1).
- [2]T. Trenn. *Rutherford on the Alpha-Beta-Gamma Classification of Radioactive Rays*. The University of Chicago Press, Isis vol. 67, 1976 (cit. on p. 1).
- [3]E. Fermi. Versuch einer Theorie der  $\beta$ -Strahlen. Z. Physik 88, 1934. DOI: 10.1007/bf01351864 (cit. on p. 1).
- [4]M. Aker et al. *KATRIN: status and prospects for the neutrino mass and beyond*. J. Phys. G: Nucl. Part. Phys. 49 100501, 2022. DOI: 10.1088/1361-6471/ac834e (cit. on pp. 1, 5, 6, 8, 9, 12–14, 16, 20).
- [5]K. Gauda S. Schneidewind et al. An active transverse energy filter to differentiate low energy particles with large pitch angles in a strong magnetic field. 2022. DOI: 2203.06085 (cit. on pp. 1, 13–15, 17, 18, 22).
- [6]E. Anderson. *Reines-Cowan Experiments-Detecting the Poltergeist*. Los Alamos Science 25, 1997 (cit. on p. 3).
- [7]Y. Fukuda et al (The Super-Kamiokande Collaboration). *Evidence for oscillation of atmospheric neutrinos*. Phys. Rev. Lett. 81, 1998 (cit. on p. 4).
- [8]W. Haxton. *The Solar Neutrino Problem*. Annual Reviews of Astronomy and Astrophysics, 1955 (cit. on p. 4).
- [9]W. Hampel et al. *GALLEX solar neutrino observations: results for GALLEX IV.* Physics Letters B 447.1, 1999 (cit. on p. 4).
- [10]A. Bellerive et al. The Sudbury Neutrino Observatory. Nuclear Physics B., Vol 908, 2016. DOI: 10.1016/j.nuclphysb.2016.04.035 (cit. on p. 4).
- [11]J. Behrens. *Design and commissioning of a monoenergetic photoelectron source and active background reduction by magnetic pulse at the KATRIN experiment*. PhD Thesis. Westfälische Wilhelms-Universität Münster, 2017 (cit. on pp. 6, 7, 10).
- [12]J. Angrik et al. KATRIN design report. Forschungszentrum Jülich, FZKA Scientific Report 7090, 2005. DOI: 10.5445/IR/270060419 (cit. on p. 6).
- [13]M. Aker et al. *The Design, Construction, and Commissioning of the KATRIN Experiment*. Journal of Instrumentation, 2021. DOI: 10.1088/1748-0221/16/08/T08015 (cit. on pp. 6, 9, 10, 21).

- [14] J. Behrens et al. A pulsed, mono-energetic and angular-selective UV photo-electron source for the commissioning of the KATRIN experiment. Eur. Phys. J. C vol 77, 2017. DOI: 10.1140/epjc/s10052-017-4972-9 (cit. on pp. 8, 16).
- [15]E.W. Otten C. Weinheimer. *Neutrino mass limit from tritium beta-decay*. Rep. Prog. Phys. 71, 2019. DOI: 10.1088/0034-4885/71/8/086201 (cit. on p. 9).
- [16]L. Schimpf. Characterisation of energy loss process of 18.6 keV electrons inside the windowless tritium source of KATRIN. PhD Thesis. Karlsruher Institut für Technologie, 2021 (cit. on p. 11).
- [17]Karlsruhe Institut f
  ür Technologie. Detector. 2011. URL: https://www.katrin.kit. edu/84.php (visited on Oct. 11, 2022) (cit. on p. 11).
- [18]A. Lokhov et al. *Background reduction at the KATRIN experiment by the shifted analysing plane configuration*. Eur. Phys. J. C 82, 2022. DOI: 10.1140/epjc/s10052-022-10220-4 (cit. on p. 12).
- [19]R.G.H. Robertson. *Transverse Energy Filter*. KATRIN Collaboration internal meeting, 2019 (cit. on pp. 13, 15).
- [20]K. Gauda. Background reduction studies through angular-selective electron detection in the KATRIN experiment. Thesis in preparation. PhD Thesis. Westfälische Wilhelms-Universität Münster, to be published 2023 (cit. on pp. 14, 15, 21).
- [21]S. Schneidewind. Improvement of the neutrino mass sensitivity and background reduction of the KATRIN experiment. Thesis in preparation. PhD Thesis. Westfälische Wilhelms-Universität Münster, to be published 2023 (cit. on pp. 14, 15, 21).
- [22]L. Pöllitsch. Charakterisierung des neuen Teststands für aktive Transversalenergiefilter für das KATRIN-Experiment. Bachelor's Thesis. Westfälische Wilhelms-Universität Münster, 2022 (cit. on pp. 14, 15).
- [23]Andreas 06. Mcp-de.svg. 2008. URL: https://commons.wikimedia.org/w/index.php? curid=3369081 (visited on Oct. 11, 2022) (cit. on p. 17).
- [24]P. Oelpmann. Angular Selective electron detection using microchannel plates for a possible background reduction at the KATRIN experiment. Westfälische Wilhelms-Universität Münster, 2021 (cit. on p. 16).
- [25]T. König. Simulations and measurements of angular selective electron transmission and detection for the KATRIN experiment. Bachelor's Thesis. Westfälische Wilhelms-Universität Münster, 2021 (cit. on p. 16).
- [26]J. Wiza et al. *Microchannel Plate Detectors*. Nuclear Instruments and Methods, Vol. 162, 1979. DOI: 10.1016/0029-554X(79)90734-1 (cit. on pp. 19, 20).
- [27]A. Mane et al. *Fabrication of low cost and robust large area microchannel plates (MCPs) for photodetection and imaging applications*. Argonne National Laboratory, 2015 (cit. on pp. 19, 29, 36, 38, 39).
- [28] Photonis Technologies. Photonis TOF Brochure. 2022 (cit. on p. 19).

- [29]C. Walker et al. The Secondary Electron Emission Yield for 24 Solid Elements Excited by Primary electrons in the Range 250-5000 eV: A Theory/Experiment Comparison. Wiley Periodicals Inc., Scanning, Vol 30, 2008. DOI: 10.1002/sca.20124 (cit. on p. 19).
- [30] MCP (microchannel plate) assembly. Hamamatsu Photonics K.K., 2015 (cit. on p. 20).
- [31]C. Beetz et all. Silicon-micromachined microchannel plates. Nuclear Instruments and Methods in Physics Research A 442 (2000) 443 451, 2000. DOI: doi.org/10.1016/ S0168-9002(99)01271-1 (cit. on pp. 20, 21).
- [32]R. Blase et al. Microchannel plate detector detection efficiency to monoenergetic electrons between 3 and 28 keV. The Review of scientific instruments, 2017. DOI: doi.org/10. 1063/1.4983338 (cit. on p. 20).
- [33]V. Gili. All-dielectric nonlinear nanophotonics. PhD Thesis. Université Sorbonne Paris Cité, 2018 (cit. on p. 22).
- [34]MicroChemicals. Silicon Wafers with SiO2 or Si3N4. 2022. URL: https://www.microchemicals. com/products/wafers/wafers\_sinx\_si3n4\_sio2 (visited on Oct. 11, 2022) (cit. on p. 23).
- [35]L. Filipovic. *Topography Simulation of Novel Processing Techniques*. PhD Thesis. TU Wien, 2012 (cit. on p. 23).
- [36]M. Ritala M. Leskelä. Handbook of Thin Films Chapter 2 Atomic layer deposition. Elsevier Inc., 2002. DOI: 10.1016/B978-0-12-512908-4.X5000-0 (cit. on p. 29).
- [37]M. Oikkonen et al. *X-Ray diffraction study of microstructure ZnS thin films grown from zinc acetate by atomic layer epitaxy*. Elsevier Inc.Thin Solid Films, 124, 1985 (cit. on p. 29).
- [38]P. Martin. Handbook of Deposition Technologies for Films and Coatings (Third Edition). Elsevier Inc. ISBN: 9780815520320, 2010 (cit. on p. 30).
- [39] J. Niemelä. *Titanium dioxide thin films by atomic layer deposition: A review*. Semiconductor Science and Technology 32(9), 2017. DOI: 10.1088/1361-6641/aa78ce (cit. on p. 30).
- [40]L. Varghese et al. *Visible absorbing TiO2 thin films by physical deposition methods*. Philips technical Review, Volume 26, 2010 (cit. on p. 30).
- [41]L. van der Pauw. A Method of Measuring the Resistivity and Hall Coefficient on Mamellae of Arbitrary Shape. Philips Technical Review No. 8, 1958 (cit. on p. 31).
- [42]Unknown. Vanderpauwshape.png. 2015. URL: https://commons.wikimedia.org/ wiki/File:Vanderpauwshape.png (visited on Oct. 11, 2022) (cit. on p. 31).
- [43]Cambridge Nanotech Inc. CambridgeNanoTech Simply ALD Savannah Film Recipe (cit. on pp. 32, 37).
- [44]L. Dong et al. Thermal Conductivity, Electrical Resistivity, and Microstructure of Cu/W Multilayered Nanofilms. ACS Applied Materials and Interfaces, 2020. DOI: 10.1021/ acsami.9b21182 (cit. on p. 33).

- [45]H. Tiznado et al. *TiO2 and Al2O3 ultra thin nanolaminates growth by ALD; instrument automation and films characterization*. Universidad Nacional Autonoma de Mexico, 2012 (cit. on p. 37).
- [46]M. Groner et al. Electrical characterization of thin Al2O3 films grown by atomic layer deposition on silicon and various metal substrates. Thin Solid Films 413, 2002. DOI: 10.1016/S0040-6090(02)00438-8 (cit. on p. 37).
- [47]Y. Lin et al. *A new examination of secondary electron yield data*. Surf. Interface Anal., 2005. DOI: doi.org/10.1002/sia.2107 (cit. on p. 38).
- [48] R.O. Jenkins et al. *Electron and Ion Emission from solids*. 1965 (cit. on p. 38).
- [49]S. Jokela et al. Secondary electron yield of emissive materials for large-area micro-channel plate detectors: surface composition and film thickness dependencies. Elsevier Physics Procedia 37 (2012) 740 – 747, 2011. DOI: 10.1016/j.phpro.2012.03.718 (cit. on p. 39).
- [50]S. Tao et al. Secondary Electron Emission Materials for Transmission Dynodes in Novel Photomultipliers: A Review. MDPI, 2016. DOI: 10.3390/ma9121017 (cit. on p. 39).
- [51]N. Whetten et al. Secondary Electron Emission of Single Crystals of MgO. AIP Journal of Applied Physics, 1956. DOI: 10.1063/1.1722788 (cit. on p. 39).
- [52]M. Putkonen et al. *Enhanced growth rate in atomic layer epitaxy deposition of magnesium oxide thin films*. Journal of Materials Chemistry 8, 2000. DOI: 10.1039/B000643M (cit. on p. 39).
- [53]S. Vangelista et al. Low-temperature atomic layer deposition of MgO thin films on Si. J. Phys. D: Appl. Phys. 46 485304, 2013. DOI: 10.1088/0022-3727/46/48/485304 (cit. on p. 39).

## Colophon

This Bachelor's thesis was typeset with  $\[Matheback{E}]$  and uses the *Clean Thesis* style developed by Ricardo Langner, available at http://cleanthesis.der-ric.de/.

# A

## Appendix

#### Measurements with vdP Method

The resistivity for the vdP method was calculated with

$$\rho_{\rm vdp} = \frac{\pi s}{\ln 2} \cdot \frac{R_{\rm AB,CD} + R_{\rm BC,DA} + R_{\rm CD,AB} + R_{\rm DA,BC}}{4} \cdot f \quad , \tag{A.1}$$

where the contacts were cycled around for a full rotation to increase accuracy and

$$R_{\rm AB,CD} = \frac{U_{\rm CD}}{I_{\rm AB}} \,. \tag{A.2}$$

As mentioned in chapter 3.4.2, an uncertainty for layer thickness  $u(s)_{rel}=25$  % was assumed. This is likely an overestimate but was left as-is due to potential other, less quantifiable or disregarded uncertainties, like the distance between sample edge and contact positions. The current output by the *Keithley* constant current source was neglected, as no fluctuations were observed and the voltage measurements dominate the uncertainty for the sheet resistance in equation A.2. With the same uncertainty for voltage values u(U) of one resistivity measurement and a constant current *I*, the uncertainty for sheet resistance measurements is

$$u_{R_{\text{tot}}} = u(R_{\text{AB,CD}} + R_{\text{BC,DA}} + R_{\text{CD,AB}} + R_{\text{DA,BC}}) = \frac{\sqrt{4 \cdot u(U)^2}}{I}.$$
 (A.3)

The uncertainty for the resistivity follows as

$$u_{\rho_{\rm vdp}} = \sqrt{\left(\frac{\partial \rho_{\rm vdp}}{\partial R_{\rm tot}} u(R_{\rm tot})\right)^2 + \left(\frac{\partial \rho_{\rm vdp}}{\partial s} u(s)\right)^2} \tag{A.4}$$

$$=\sqrt{\left(\frac{\pi}{\ln 2} \cdot \frac{u(R_{\text{tot}})}{4}f\right)^2 + \left(\frac{\pi}{\ln 2} \cdot \frac{u(s)}{4}f\right)^2} \tag{A.5}$$

This method was used in figures 3.9 and 3.11 down to an assumed layer thickness of 8 nm, as described in chapter 3.4.3. For figure 3.12, only the uncertainty of the measured voltage was considered.

#### Measurements using Layer Geometry

For samples of higher resistivity than could be measured with the vdP method, it was calculated from the total sample resistance, measured as depicted in figure 3.10. The resistivity follows as

$$\rho = R \frac{A}{l} \,, \tag{A.6}$$

where *l* denotes the distance between the contacts and  $A = s \cdot b$  is the surface resulting from the sample thickness *s* and the contact width *b* and

$$u(A) = \sqrt{(l \cdot u(s))^2 + (s \cdot u(b))^2}.$$
(A.7)

The uncertainty of contacting size and distance was u(l) = u(b) = 1 mm and the layer thickness was again assumed to be  $u(s)_{rel}=25$ %. Further influences by the non-ideal chip and contact form were neglected. The uncertainty of measured resistance Rwas taken from the fluctuation range of the *Keithley 2450*. In total, the uncertainty for the resistivity  $u(\rho_{geo})$  was calculated as

$$u(\rho_{\text{geo}}) = \sqrt{\left(\frac{\partial \rho_{\text{geo}}}{\partial R}u(R)\right)^2 + \left(\frac{\partial \rho_{\text{geo}}}{\partial A}u(A)\right)^2 + \left(\frac{\partial \rho_{\text{geo}}}{\partial s}u(l)\right)^2}$$
(A.8)

$$=\sqrt{\left(\frac{A}{l}u(R)\right)^2 + \left(\frac{R}{l}u(A)\right)^2 + \left(\frac{RA}{l^2}u(l)\right)^2}.$$
(A.9)