

# Functional oxide layers for electrical isolation and chemical passivation of steel substrates

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## Abstract

A thin zirconium oxide layer was applied via doctor blading on a steel foil substrate with the goal of get an moeglichst homogeneous and insulating layer. The layers were characterized over the current-voltage curve and the operational variables were optimized with an pso swarm optimization algorithm.

## Preface

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## Acronyms

**1F** one-fold concentrated solution. 7

**2F** two-fold concentrated solution. 7

**3F** three-fold concentrated solution. 7

**4F** four-fold concentrated solution. 7

**5F** five-fold concentrated solution. 7

**AcOH** acetic acid. 7

**BuOH** 1-buthanol. 6, 7, 13

**CIGS** copper indium gallium sulfide. 5

**DB** doctor blading. 7, 8

**FTO** fluorine doped tin oxide. 6, 10

**H<sub>2</sub>O** deionized water. 6, 7

**H<sub>2</sub>SO<sub>4</sub>** sulfuric acid. 6, 7

**Hacac** acetylacetone. 6, 7, 13

**HCl** hydrochloric acid. 6, 7

**IPO** 2-Propanol. 6, 7

**IR** infrared. 8

**ITO** indium doped tin oxide. 6, 10

**N<sub>2</sub>** nitrogen. 6

**NaOH** sodium hydroxide. 6, 7

**PV** photovoltaic. 5

**SDS** sodium dodecyl sulfate. 6, 7

**SEM** scanning electron microscopy. 8, 10

**SG** sol-gel. 5

**XRD** X-ray diffraction. 8

**Zr(PrO)<sub>4</sub>** zirconium(IV)propoxide. 6, 7, 13

**ZrO<sub>2</sub>** zirconium dioxide. 5, 7

# 1 Introduction

**describe everything what is mentioned in 4** Photovoltaic (PV) is one big hope when trying to become carbon neutral as it uses the energy provided by sun directly in contrast to renewable energy sources (e.g. wind and water) or even carbon based sources. One sort of PV are copper indium gallium sulfide (CIGS) [1] cells. In order to make a module, multiple cells are operated in series. The cells must be applied to a non-conducting surface. Glass is a good non-conducting substrate, but very rigid and brittle. An alternative is steel, which is ductile, inexpensive and highly available, but conducting. An insulating layer must therefore be applied to the steel substrate before any CIGS cells can be applied. A non-toxic material which is suitable for this application is zirconium dioxide ( $\text{ZrO}_2$ ). An economic and scalable method is doctor blading via a sol-gel (SG) process. SG processes often produce porous layers. In this work a dense, insulating and homogeneous layer is pursued. ML can help to uncover complex non-linear relations, such as the influence of the production factors on the thickness and resistance of the resulting layer. The minisation of the conductance if performed with a particle swarm optimization algorithm.

# 2 Aims and Objectives

The aim of this work is to develop a non-conducting layer on steel based on non-toxic materials like Aluminium or Zirconium via doctor blading. This layer can then be used as insulator for CIGS modules on steel sheets. Doctor blading - or tape casting - is a widely used precision coating method to apply thin films on large area surfaces[2]. This sol-gel process was chosen because of the availability to the industrial partner. In order to optimize the resulting layer the multitude of parameters was optimized with an particle swarm optimization ansatz. The conductivity (dependent variable), the number of layers and calcination time (both independent variables) should be minimized.

# 3 Theoretical Background aka How does is work?

## 3.1 Sputtering

## 3.2 SEM

<https://doi.org/10.1016/B978-0-12-816806-6.00017-0>

## 3.3 Infrared absorbance

## 3.4 X-Ray Diffraction

<https://doi.org/10.1016/B978-0-12-816806-6.00017-0>

[https://chem.libretexts.org/Courses/Franklin\\_and\\_Marshall\\_College/Introduction\\_to\\_Materials\\_Characterization\\_\\_CHM\\_412\\_Collaborative\\_Text/Diffraction\\_Techniques/X-ray\\_diffraction\\_\(XRD\)\\_basics\\_and\\_application](https://chem.libretexts.org/Courses/Franklin_and_Marshall_College/Introduction_to_Materials_Characterization__CHM_412_Collaborative_Text/Diffraction_Techniques/X-ray_diffraction_(XRD)_basics_and_application)

## 3.5 Particle Swarm Optimization

## 3.6 Machine Learning

## 3.7 Principal Component Analysis

## 4 Experimental

In this section the used chemicals and substrates, experimental procedures and any used equipment are described.

### 4.1 Substrate Preparation

Five different substrates were used throughout this work: microscope glass slides ( $2.5\text{ cm} \times 7.5\text{ cm}$ ), squared glass plates ( $2.5\text{ cm} \times 2.5\text{ cm}$ ), indium doped tin oxide (ITO) glass plates ( $2.5\text{ cm} \times 2.5\text{ cm}$ ), fluorine doped tin oxide (FTO) glass plates ( $5\text{ cm} \times 5\text{ cm}$ ) and steel foil ( $10\text{ cm} \times 10\text{ cm}$ ) provided by Sunplugged GmbH (<http://sunplugged.at/>). The glass slides and FTO were scored with a diamond scribe and broken with a running plier into pieces of dimensions  $2.5\text{ cm} \times 2.5\text{ cm}$ . The steel foil was cut with a foil cutter. All substrates were cleaned in three steps before usage:

1. 15 min in 50 mL deionized water ( $\text{H}_2\text{O}$ ) and 1 mL of Hellmanex III alkaline concentrate in a sonic bath
2. 15 min in  $\text{H}_2\text{O}$  in a sonic bath
3. 15 min in 2-Propanol (IPO) in a sonic bath

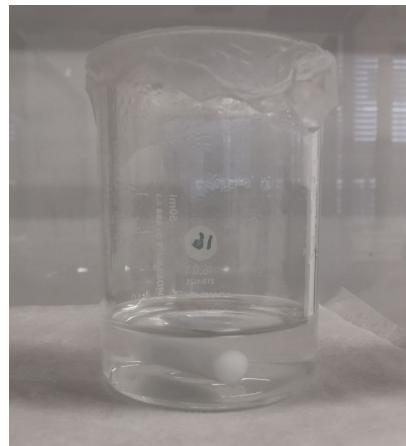
After the last cleaning step, the samples were blown dry with dry nitrogen ( $\text{N}_2$ ) gas and kept in a clean plastic container until the doctor blading step.

### 4.2 Solutions

All recipes for solutions can be divided into two categories: the first recipe - adopted from Anwar et. al. [3] - was based on zirconium(IV)propoxide ( $\text{Zr}(\text{PrO})_4$ ) in acetylacetone (Hacac) and  $\text{H}_2\text{O}$ . The second recipe - adopted from Hu et. al. [4] - was based on  $\text{Zr}(\text{PrO})_4$  in 1-buthanol (BuOH).



(a) Aquatic solution



(b) Buthanolic solution

Figure 1: Aquatic and buthanolic solution in beaker glass with magnetic stirring bars sealed with Parafilm

#### 4.2.1 Aquatic solution

$\text{Zr}(\text{PrO})_4$  was added to Hacac while stirring and in a separate vessel  $\text{H}_2\text{O}$  (including any optional additives such as sodium dodecyl sulfate (SDS), hydrochloric acid (HCl), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or sodium hydroxide (NaOH)) was added to IPO and both were stirred for one hour. The  $\text{H}_2\text{O}$ -IPO mixture was added to the other solution and stirred over night. The exact volumes can be taken from table 1.

Table 1: Compositions of different aquatic solutions

recipe	1	2	3	4	5	6	7
Zr(PrO) <sub>4</sub> [mL]	8	8	8	8	8	8	8
Hacac [mL]	8	8	8	8	8	8	8
IPO [mL]	2	2	2	2	2	2	2
H <sub>2</sub> O [mL]	2.6	2.6	2.5	2	2	2	2
SDS [mg]	-	5.9	-	-	-	-	-
HCl [mL]	-	-	-	-	0.5	-	-
H <sub>2</sub> SO <sub>4</sub> [mL]	-	-	-	-	-	0.5	-
NaOH [mL]	-	-	-	-	-	-	0.5

#### 4.2.2 Buthanolic solution

Five different concentrations of the buthanolic solutions were prepared. The one-fold concentrated solution (1F) was closest to the recipe proposed by Hu et. al. [4]. The other four solutions (two-fold concentrated solution (2F), three-fold concentrated solution (3F), four-fold concentrated solution (4F), five-fold concentrated solution (5F)) were similar with higher concentrations of Zr(PrO)<sub>4</sub> (see table 2).

Table 2

recipe	1F	2F	3F	4F	5F
BuOH [mL]	4.95	4.9	4.85	4.8	4.75
Zr(PrO) <sub>4</sub> [mL]	0.05	0.1	0.15	0.2	0.25
Hacac [mL]	0.0125	0.025	0.0375	0.05	0.0625
IPO/acetic acid (AcOH) [mL]	2	2	2	2	2

The solvent (BuOH) was put into a beaker glass (or similar, preferably with an air-tight cap) with a magnetic stirring bar and Zr(PrO)<sub>4</sub> was added while stirring. After stirring 15 min one mole equivalent chelating agent (Hacac) was added and stirred for another 15 min. Finally, the stabilisation solvent[4] (IPO or AcOH) was added to the mixture and stirred for additional 30 min. In order to make a 2F solution, the volume of Zr(PrO)<sub>4</sub> and Hacac was doubled and BuOH was decreased by the volume of Zr(PrO)<sub>4</sub>.

#### 4.3 Doctor blading

An Erichsen Coatmaster 510 with a heatable plate was used for doctor blading. The plate had round patches of porous metal where underpressure could be applied to keep substrate in place (see figure 2). After setting the heating plate temperature, the vacuum plate temperature and the doctor blading (DB) velocity, the DB blade was put into position, the sample was placed on the vacuum plate and the vacuum was switched on. 100 µL of solution were applied with a 10-1000 µL pipette and the blade moved over the sample distributing the liquid evenly. After evaporation of the solution, the vacuum was turned off, the 'blade pusher' put into initial position, the blade removed and excess solution removed with a wipe. The small metal plate was transferred to the hot heating plate and rested on there for 3-5 min. This process of applying a ZrO<sub>2</sub> layer was repeated as many times as needed.

#### 4.4 Calcination

A LabTech EH45C heating plate (HP) and a Naberterm LB410 furnace were used to calcinate the doctor bladed samples. The heating plate can hold temperature for a certain amount of time, but heated with a fixed rate of circa 10 °C/min. In order to achieve a lower overall heating rate several temperature ramps and plateaus were alternated (see table 3 and figure 3). This procedure was called HP1. The HP1 procedure was optimized for the available hardware by a colleague working on the project prior to the author.



Figure 2: (a) Temperature regulator (1) on the left, vacuum pump (2) in the background and Erichsen Coatmaster 510 (3) with heatable vacuum plate. (b) Close up of the DB blade in position. The majority of the suction areas is sealed with tape to increase the underpressure at the remaining ones.

HP1												
T [°C]	80	100	150	160	170	180	190	200	250	300	350	400
t [min]	10	10	5	5	5	5	5	10	10	10	10	60

Table 3: Time the temperature was held constant at certain temperatures on the heating plate

The NT1 heating program was used to mimic the HP1 heating procedure in the Naberterm furnace. NT2 is a simplification of NT1 and programs NT3-NT6 are the same as NT2 with altered heating rate and partly increased calcination temperature  $T_{Cal}$  (NT5). NT2-NT6 had only 2 variables (heating rate and calcination temperature) instead of 4 (three different heating rates and calcination temperature). All heating programs were held at the calcination temperature for one hour. In figure 3 the different heating curves are depicted.

Name	80-150°C [°C/min]	150-200°C [°C/min]	200°C-T <sub>Cal</sub> [°C/min]	T <sub>Cal</sub> [°C]	t <sub>Cal</sub> [min]
NT1	2		2	400	60
NT2	2	2	2	400	60
NT3	3	3	3	400	60
NT4	4	4	4	400	60
NT5	4	4	4	500	60
NT6	1	1	1	400	60

Table 4: Heating rates and calcination temperature holding times.

#### 4.5 Characterisation

All scanning electron microscopy (SEM) micrographs were taken with a Zeiss Supra 40. Infrafred (IR) **absorbance** spectra were recorded with a Bruker Vertex 70 spectrometer. X-ray diffraction (XRD) spectra were obtained with a Thermo Scientific ARL Equinox 100 X-Ray Diffractometer. All XRD spectra were taken at 5° incident angle and compared to the internal database. The current-voltage curves were measured with Agilent 4156C Precision Semiconductor Parameter Analyzer after sputtering aluminium contacts through a mask with a Leybold UNIVEX450C Sputter System. **Directional current sputtering argon as inert gas.**

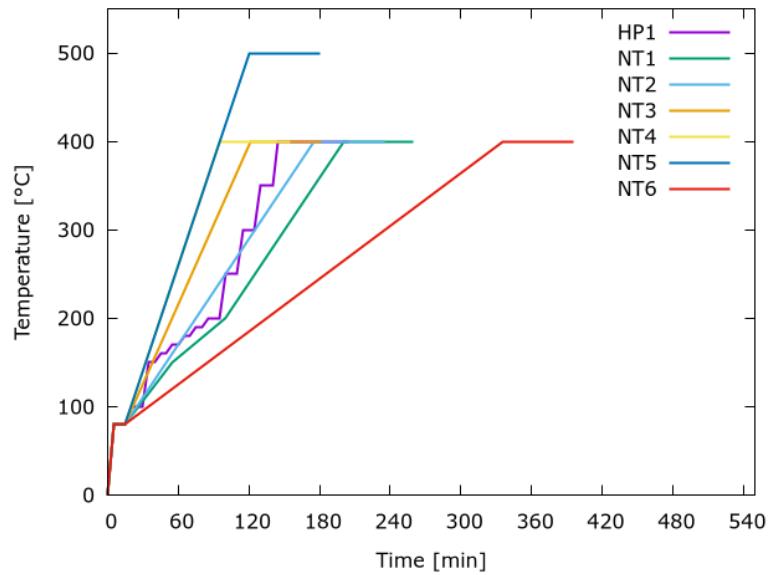


Figure 3: Different heatings curves

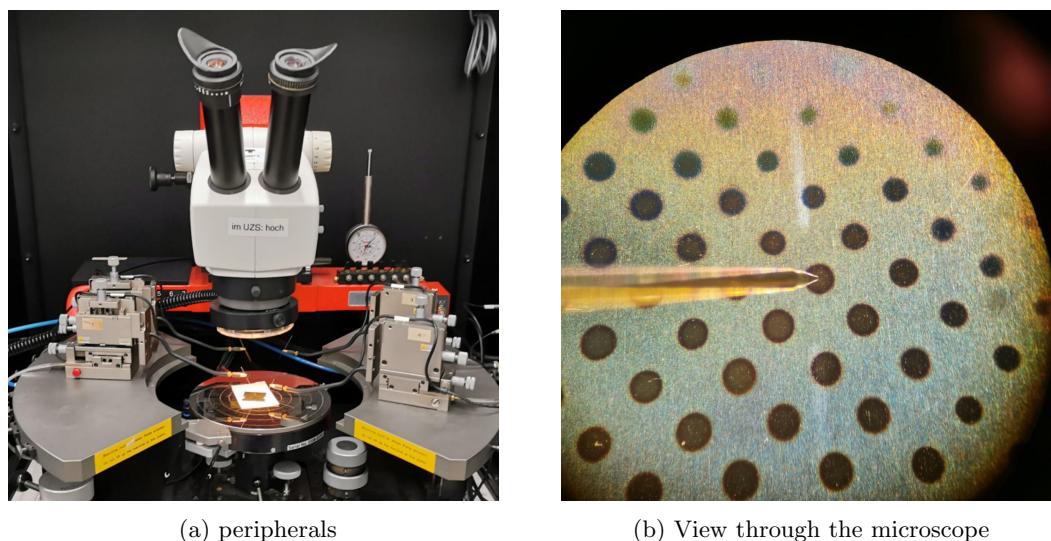


Figure 4: I-V curve abnehm aperature und sicht durch das micro scope.

## 4.6 Finding base process/Preliminary study

Initially glass plates were doctor bladed manually with aquatic solution and calcinated via HP1. Glass was used because of its availability and in order to be able to make IR transmission spectra. In order to measure the resistivity of the produced layer FTO and ITO (both conductive) were used as substrate. Conducting substrates were also needed for SEM micrographs. Different additives were included in the recipe and the resistance was checked with a multimeter. Chemicals were added to influence pH and surface tension with the goal to influence the resulting layer. As no homogeneous layers resulted from any aquatic recipe a new recipe was introduced, which gave more homogeneous films. With this new buthanolic recipe the limits of the optimization problem were explored in a preliminary study. In the preliminary study only steel was used as substrate. Latin squares were used to chose which experiments should be ausgefuehrt to get an ueberblick of the optimization room. Some additional hand picked experiments were introduced to further eingrenzen the limits of the optimization as every reduction in variables or levels meant a faster convergence.

After a fitting recipe was found, the process to produce an acceptable layer was untersucht. There were many variables which had to be taken into account. The damals current procedure produced clear and continuous films, but was plagued from unhomogenities due to drying stains. Using a heat gun the drying stain can be surcumvented (umgangen), but the results were unreproduceable. The glass unterlage was therefore exchanged with a metal plate which allowed both to hold the sample via underpressure and heat it to a certain temperature. The bounds fore the process were then explored. Especially the doctor blading velocity.

## 5 Evaluation and Computational Details

### 5.1 Evaluation of Samples

For every I-V curve (aluminium dot) the gradient  $g$  at  $V = 0$  is calculated by taking 5 points after the origin and 5 points before the origin, averaging their V and I values and calculating i

$$g = \frac{I_{n+1} - I_n}{V_{n+1} - V_n}. \quad (1)$$

As a measure of conductance a distance D from an ideal non-conducting case. The average of the negative base 10 logarithm subtracted from an ideal non-conducting gradient of  $10^{-13}$

$$D = \sum_i^N \frac{-\log_{10}(g_i) - 13}{N} \quad (2)$$

Another measure is the density of shorted species  $\rho_s$  is calculated in following way:

$$s_i = \begin{cases} 1 & \text{if } -\log(g_i) < 5 \\ 0 & \text{if } -\log(g_i) \geq 5 \end{cases} \quad (3)$$

$$\rho_s = \sum_i^N \frac{s_i}{N} \quad (4)$$

Other estimates of the conductance are the averages:

$$G_1 = \log \left( \sum_i^N \frac{g_i}{N} \right) \quad (5)$$

$$G_2 = \sum_i^N \frac{\log(g_i)}{N} \quad (6)$$

## 5.2 Sample Selection

An evolutionary approach was chosen, namely a multi-objective Particle Swarm Optimization (PSO) with a multi-response Multivariate Adaptive Regression Splines (MARS) model[5, 6, 7, 8]. "PSO is a population based heuristic inspired by the flocking behavior of birds. To simulate the behavior of a swarm, each bird (or particle) is allowed to fly towards the optimum solution." [5] Initially the input parameters (independent variables), their boundaries and number of equidistant levels for each parameter are declared (see table 5). Next, the output variables (dependant variables), their weights in the objective function (the function which should be optimized) are specified and if they should be minimized or maximized is noted.

Zr(PrO) <sub>4</sub> conc. [21 g/L]	layers	$T_{DB}$ [°C]	$v_{DB}$ [mm/s]	$T_{cal}$ [°C]	$v_{cal}$ [°C/h]
2	4	40	10	300	120
3	6	50	12	400	360
4	8	60	14	500	600
5	10	70	16		840
	12	80	18		1080
			20		

Table 5: Discrete levels of each input parameter **are concentrations correct?**

The first step is to select an initial population (ensemble of experiments), which is chosen randomly from the population space. The samples are made, measured and evaluated according to section 4 and the distance  $D$  (see eq. 2),  $\rho_s$  (see eq. 4),  $n_{layers}$  (numbers of layers) and  $v_{cal}$  (heating rate of calcination process in °C/min) are supplied to the program. The program uses this data to estimate a response for each output variable (and to choose a fraction of the initial population which is allowed to propagate). The response variables for the entire population space is calculated. The current population - each of the particles independently - moves towards the optimum solution. The population for the next time step is outputted and the experiments are again executed, measured and evaluated.

## 5.3 EMMA Propagation

## 5.4 Fitting via Machine Learning

**scarce data may lead to overfitting[9]**

Python and sci-kit learn **cite** was used to implement a linear fit model, and SVR with the kernels polynomial, rbf and sigmoid. The space of hyper parameters C, the degree (in case of polynomial), epsilon and gamma was scanned.

The independent variables are located on a partially irregular grid.

conc	layers	vDOC	TDOC	vCal	Tcal	
1	10	5	20	120	400	
1	4	0.1	20	120	500	
5	10	0.1	20	120	500	
5	4	5	20	480	400	
1	5	5	80	120	500	
1	10	1	80	480	400	
5	5	1	80	120	400	
5	10	5	80	480	500	
2	8	0.5	40	360	470	
2	6	2	40	360	430	
1	4	12	70	120	500	
1	9	18	80	240	400	
4	6	14	60	240	500	
4	6	14	60	240	500	
4	6	14	60	240	500	
2	10	20	40	120	500	6113
3	8	18	70	1080	300	2850
3	6	10	50	1080	400	5526
3	10	16	80	120	500	6554
4	6	16	80	1080	300	2947
3	12	12	80	840	500	8318
3	10	14	50	600	500	7374
5	6	10	60	1080	400	5648
5	10	20	60	360	300	3956
5	12	14	60	1080	300	2700
2	4	10	80	1080	300	6101
2	4	10	40	600	300	7201
3	4	12	60	600	300	1462
4	4	10	80	1080	300	2883
5	12	20	70	600	300	1680
2	4	10	40	120	300	1
2	4	10	40	120	500	6001
3	4	10	40	120	500	6102
5	4	10	80	1080	300	2884
5	12	20	60	120	300	360
3	4	10	40	600	400	4202
2	6	20	40	120	500	6105
5	12	14	60	600	300	1500
3	6	14	60	600	300	1486
4	4	14	80	1080	300	2923
4	8	18	80	1080	300	2971
3	8	10	50	1080	300	2530
2	12	16	40	120	400	3077
2	10	18	60	1080	300	2733
4	10	10	50	1080	300	2535

Table 6

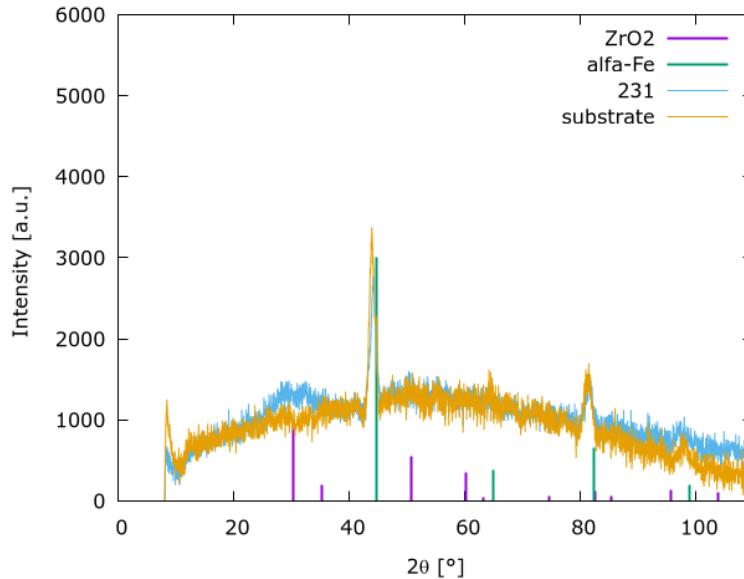


Figure 5: XRD spectra

## 6 Results and Discussion

**Following stirring times (in minutes) were tested and didn't have an influence on stability of the solution: 10-10-20, 10-10-45, 30-30-180.** The space seems to be too big for the small sample size. Look at relation of space size and sample size here and in Hu2016.

Would be easier to fit with single factor at a time variation or latin hyper cuber? Would it also be easier for PSO or ML to find fitting function? Every output var is independent of each other, so  $v_{cal}$  can act as test

plot predictions from EMMA and ML. the data has a lot of error, but because the production process takes so long nad the limited time and the chosen optimisation method, the experiments weren't weiderholt how much variance is in data?

The most time consuming part was definitively the preliminary studies. this time could have been verkürzt by testing a wide array of diverse recipes from the literature

The data is spread across the datenraum, such that it is not trivial to (1) find the variable with the most variance and (2) to fit in order to understand to impact of noise on the data. Dimension reduction bietet sich stark an bei solcher Datenlage. Welche methode funktioniert bei relativ vielen variablen, wenig datenpunkten und Noise. Am besten waere feature extraction (variable x1 hat am meisten einfluss. ginge auch wenn man bei pca den einfluss von verschiedenen

heating rate was one of the dependent variables with the intention of minimizing the variable. It can also be used as test to see how well the GA performs. It doesn't influence the fit for the other splines, but it influences the choice of samples therefore it might have slowed down the process. Overall there were too many variables involved for such a small dataset

### 6.1 XRD

## 7 Outlook

Making of the solution for the sol-gel process: For a single concentrated solution 0.05 mL of Zr(PrO)<sub>4</sub> are added while stirring to 4.95 mL of BuOH and stirred for 15 min. 0.013 mL (or one molar equivalent of Zr) of Hacac is added to the stirring solution. After another 15 min 1 mL of acetic acid is added and stirred for 30 min to stabilize the solution up to 24 h.

The concentration can be increased up to 5 times being stable for a minimum of 4 h. The sol-gel process produces am homogeneous transparent crystalline zirconia oxide layer. homogeneity can be mainly controlled via blade velocity and temperature and layers can be stacked.

It should have been also verglichen with grid search with comparable size but most time was used to find a vernuenfig base recipe and process

It is still very human Der process is - as it the case with all ML and most fitting processes - is very abhaengig von hyper parameters, In the current work population size, number of generations, and most importantly boundaries (grenzen).

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