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NanoQI

Multimodal X-ray and Hyperspectral Thin-Film Nano-material Evaluation and Quality Imaging

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Verification of performance of HSI in evaluation of ALD coatings: Detection of deviations ≥ in 1 monolayer in < 30 seconds on 15 x 15 cm2 sample area; detection of changes in residual carbon through > 2% change in electron density

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AUTHOR

Author	Organization	Contact (e-mail, phone)
Christine Boeffel	Fraunhofer IAP	Christine.boeffel@iap.fraunhofer.de

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Point of Contact	Name: Fabiano Rimediotti Partner: **Nordmeccanica AS** E-Mail: rimediotti@nordmeccanica.com

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Executive Summary

Within task 6.2 ALD deposited layers were characterized with respect to the deposition homogeneity, the thickness of deposited layers and the conversion degree of the layer formation aiming to detect remaining carbon from the precursor. HSI investigations were performed at-line close to the ALD chamber on a substrate size of 150 mm x 150mm with a scanning speed of 2.78 mm/s leading to 54s scan time for 150 mm. Thickness variation of oxide layers could be proven with an estimated statistical error of 5-10%. The application of the HSI for the characterization of active layers in OE devices is promising as could be shown for the examples of Pedot:PSS and PVK.

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1. Introduction

Subject of Task 6.2 is the demonstration of the characterization of Atomic Layer Deposition in a cooperation between FhG-IAP, FhG-IWS, NEO, and TUDO. The HSI system was implemented in the glovebox of the S2S pilot line at Fraunhofer IAP within WP5. Different series of oxide depositions (Al_2O_3, TiO_2) on silicon wafers as reference, glass and PEN substrates on sizes up to 150 mm x 150 mm were prepared to evaluate their thickness, homogeneity and morphology and to elaborate the sensitivity of the setup and compared with SoA offline systems. ALD layers of different composition were prepared on different substrates (Si-wafers as reference, glass, polymer substrates) on sizes up to 150 mm x 150 mm. The spatial homogeneity of these layers was evaluated by HSI and compared to off-line characterization by optical spectroscopy, lab-based XRR (FhG-FEP) and spectroscopic ellipsometry and synchrotron based spatially-resolved XRR (resolution few 100 µm, TUDO). This spatial information from off-line characterization is obtained by the investigation of different sample areas, which was be correlated to the HSI results. Furthermore, a “quasi in-situ” test on Al_2O_3 and TiO_2 with nominal deposition differences of 1 or 2 nm were prepared and measured to get information of the sensitivity of the HSI to thickness changes as low as 1 nm. Another test was prepared with Al_2O_3 deposition with conditions out of the optimum process conditions. Besides the thickness evaluation the samples were investigated with XPS to determine remaining carbon content and sense how sensitive HSI can image insufficient process conditions. In order to integrate the HSI into the daily work at FhG-IAP in processing of flexible electronic stacks several functional layers deposited by spincoating were investigated to which extend complex structures will be sensitive for HSI investigations such as complete OLED layer stacks including the ALD thin film encapsulation layer (together with NEO). Thus, we were able to characterize layers of PEDOT:PSS, an often used charge carrier material in organic electronic devices, as well as PVK (poly N-vinylcarbazol), a functional polymer, which is part of the active layer in OE devices.

2. Results and discussion

The HSI camera together with connecting cables and computer was delivered by NEO. The controlling and imaging software Imanto, the illumination system and the sample stage with PTFE layer was provided FhG-IWS within WP5. The setup is shown in Figure 1 after its implementation into the glovebox. Image processing is performed using the software Imanto, data processing is achieved with the software Breeze software supplied by Prediktera. Stability tests and calibration was performed during training visits of Fraunhofer FEP and NEO at Fraunhofer IAP. HSI imaging of both ALD-deposited oxide layers as well as thin layer deposition of various organic materials was performed. For data evaluation samples were prepared testing homogeneity and thickness variation as a function of the processing conditions, independent characterization was performed by ellipsometry or surface profilometry.

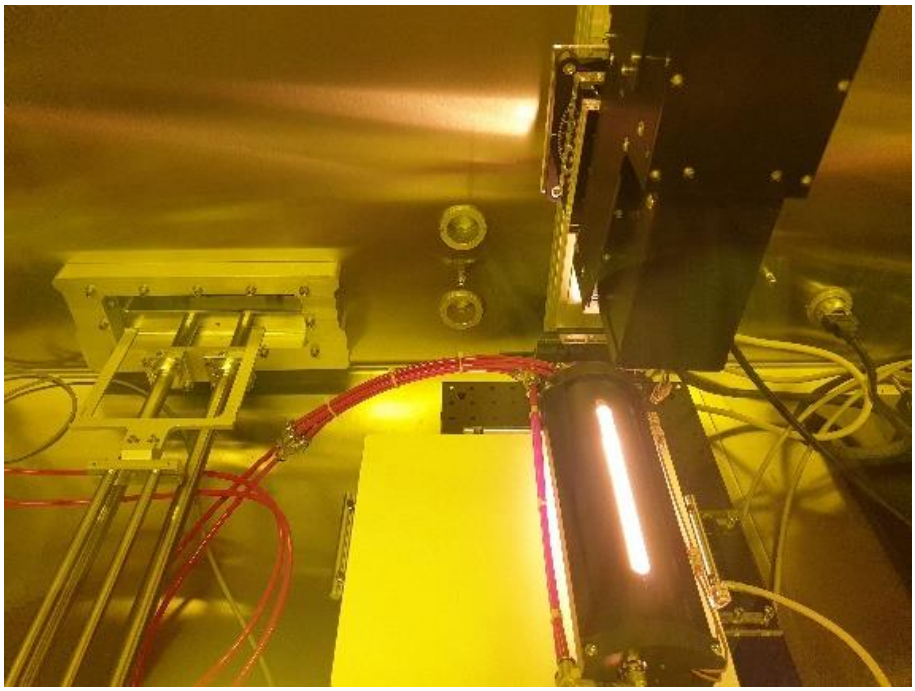


Figure 1 Setup of the HSI camera system with illuminated sample stage in the glovebox of the organic electronics pilot line close to the ALD deposition system, the sample transfer system is visible on the left hand side of the HSI-setup.

2.1. Evaluation of the homogeneity of ALD deposited oxide layers

2.1.1. Homogeneity of a 50 nm deposited Al_2O_3 layer on a 150 mm x 150 mm silicon wafer

For evaluating the homogeneity of the ALD deposition, a 50 nm Al_2O_3 layer from precursor Trimethylaluminum (TMA 98%, provided by ABCR) and oxygen/nitrogen plasma was deposited on nine silicon wafers on a total area of 150 mm x 150 mm (**Error! Reference source not found.**). HSI images were taken of each of the nine 50 mm x 50 mm samples. For the further analysis each sample was divided into nine measuring areas. For reference data thickness evaluation was independently taken by spectroscopic ellipsometry resulting in nine thickness values for each of the nine wafers. Consistently, the HSI images were also decomposed into nine sub-images so that the HSI date were available for each thickness measurement. These data were used to produce a statistical model (PLS regression) than can calculate layer thicknesses from the spectral HSI data. For this task, the software Breeze was used. A regression plot of the data obtained from ellipsometry versus the ones from statistical model is shown in Figure 3.

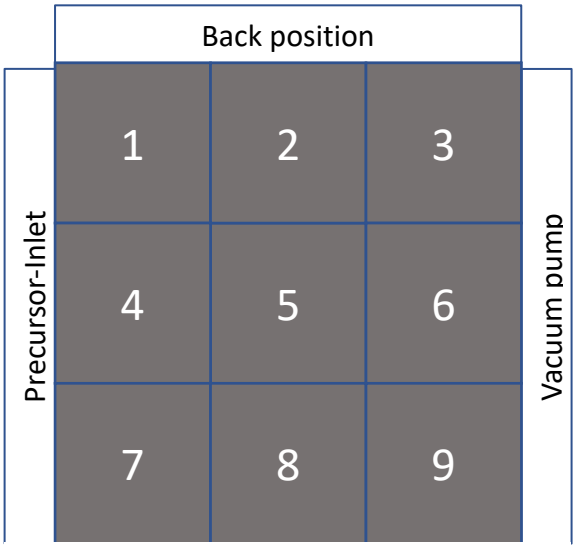


Figure 2 Sample setup for the homogeneity investigation of the Al_2O_3 ALD layers.

The process conditions were set for achieving a thickness of 50 nm. As can be seen in Figure 4 the thickness variation is a deviation from the nominal thickness of up to 10 nm over the whole area. The inhomogeneity in the ALD layer deposition is clearly visible in this 3D presentation. Whereas the plateau of the intended nominal thickness has been reached over a large area there is a considerable inhomogeneity close to the precursor inlet into the ALD chamber. Obviously, the process conditions for the plasma enhanced deposition are not optimized sufficient to reach a homogeneous deposition over the complete 150 mm x 150 mm of the sample. Additionally, there is a further drop in thickness at the edges which is due to the construction of the process chamber and the plasma head with a more centric power distribution.

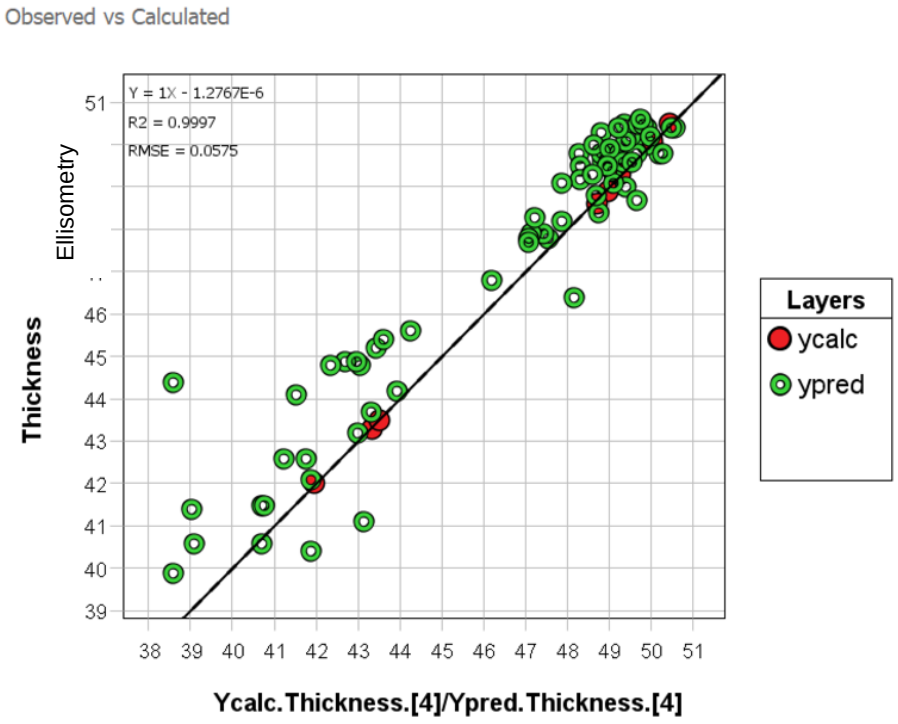


Figure 3 Regression plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI applying the PLS model for Al_2O_3. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,999) could be created.

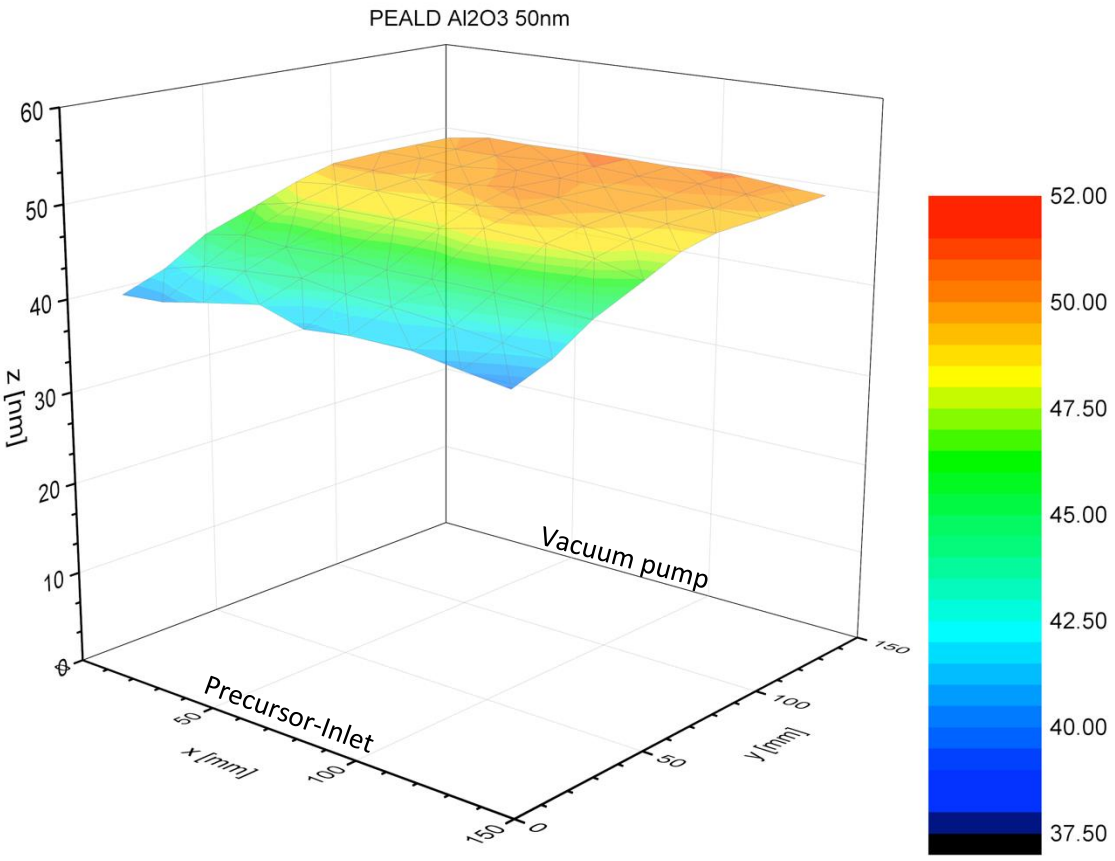


Figure 4 3D thickness plot of the 150 mm x 150 mm deposition of Al_2O_3 on silicon wafers. The thickness inhomogeneity of the deposition process can clearly be seen. A considerably lower thickness is obtained close to the precursor inlet, reaching a more homogeneous area after about 50 mm from the center of the sample.

2.1.2. Homogeneity of a 50 nm deposited TiO_2 layer on a 150 mm x 150 mm silicon wafer

In the same way 50 nm TiO_2 was deposited on nine silicon wafers using precursor Titantetrachloride (TTC 99,9% provided by Acros) and an oxygen/nitrogen plasma. The data evaluation was performed in the same way as described above for Al_2O_3. The result from the PLS regression model is shown in Figure 5. The homogeneity map is presented in Figure 6. The deviation of the obtained deposited layer thickness from the nominal aimed one is much more pronounced than for Al_2O_3. One obvious reason is a considerably lower growth per cycle than expected from the previous machine and literature data for this system. The layer thickness close to the precursor inlet is much lower than on the pump side of the reactor. Additionally, for TiO_2 a drop in thickness at the outer edges of the sample carrier is observed. This is likely due to the design of the reactor, which combines a round plasma head with a square sample holder, which can result in poorer plasma coverage at the corner of the samples. The pronounced gradient in the anterior half could be due to insufficient precursor concentration or plasma density in this region.

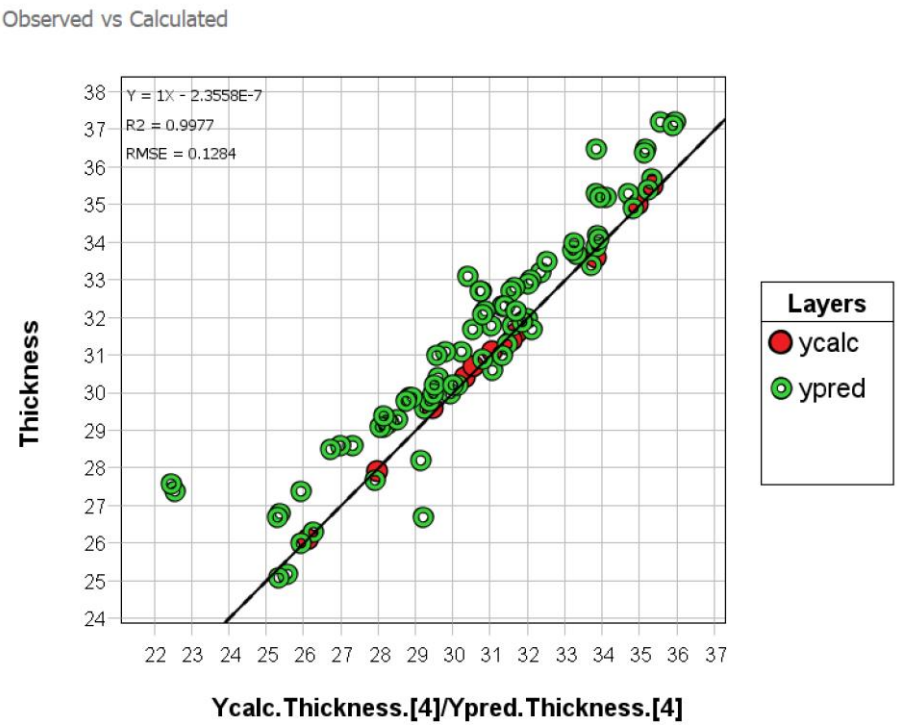


Figure 5 Regression plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI applying the PLS model for TiO_2 . Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,997) could be created.

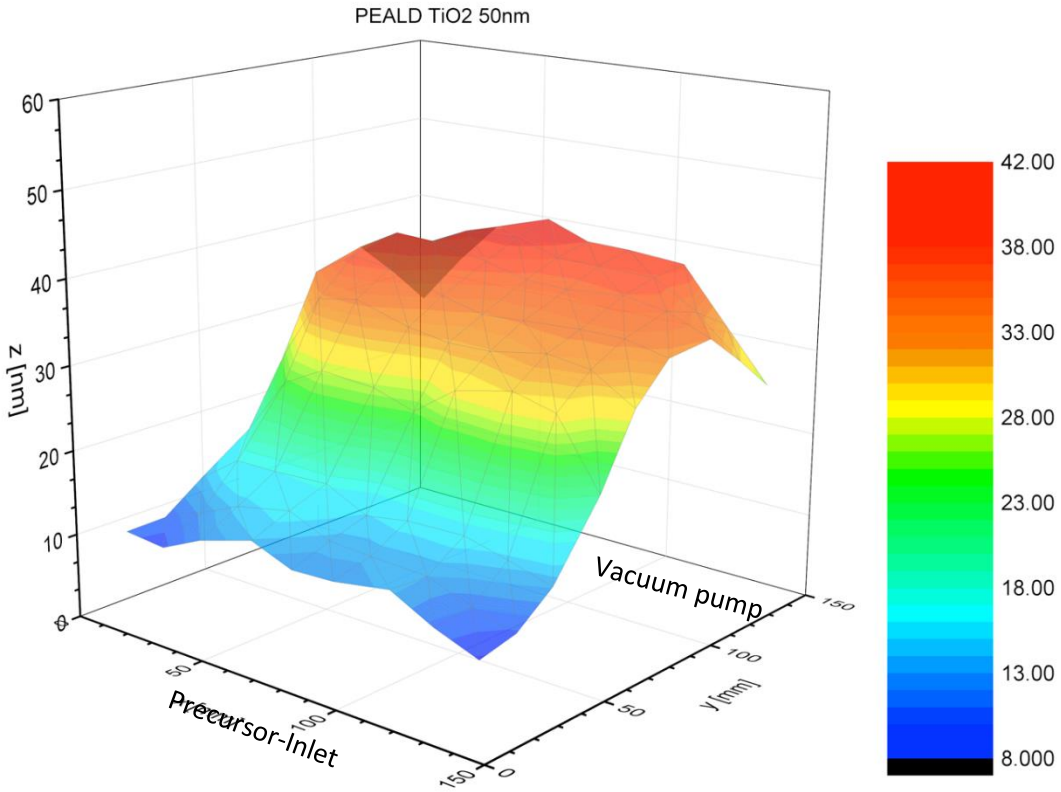


Figure 6 3D thickness plot of the 150 mm x 150 mm deposition of TiO_2 on silicon wafers. The thickness inhomogeneity of the deposition process can clearly be seen and is much more pronounced as for Al_2O_3. A considerably lower thickness is obtained close to the precursor inlet, reaching a more homogeneous area after about from the center of the sample. All four edges show an even more pronounced thickness drop probably due to the reactor design.

2.2. HSI sensitivity on thin layer deposition of oxides with nominal variation of 1 nm

One of the aims to implement HSI as at-line characterization tool for thin layer deposition was to sense thickness variations with high accuracy. It was aimed to differentiate thickness of monolayer depositions during the ALD cycling. Therefore, a sample series was prepared with nominal thickness variations of 1 – 2 nm for the ALD deposition of Al_2O_3 and TiO_2, performed on three 50 mm x 50 mm substrates of silicon, glass and PEN TeonexQ65, as shown in Figure 7. Silicon samples were used as describes above to obtain the reference thickness data from ellipsometry for the training using the PLS regression model. The homogeneity data obtained from the previous experiment were used to calculate correction factors for the depositions on glass and PEN, where independent thickness measurements could not be performed.

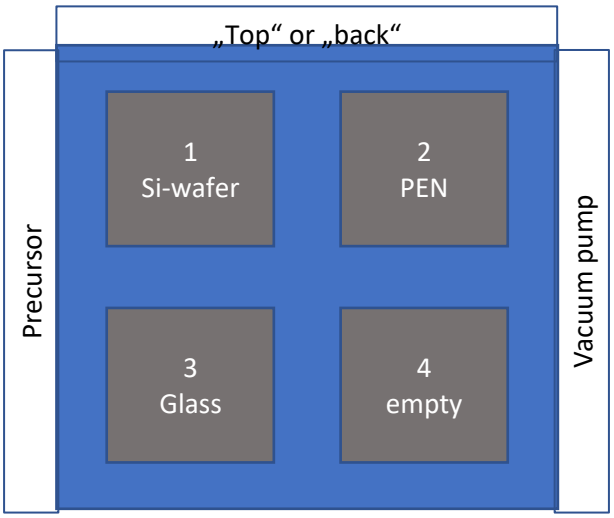
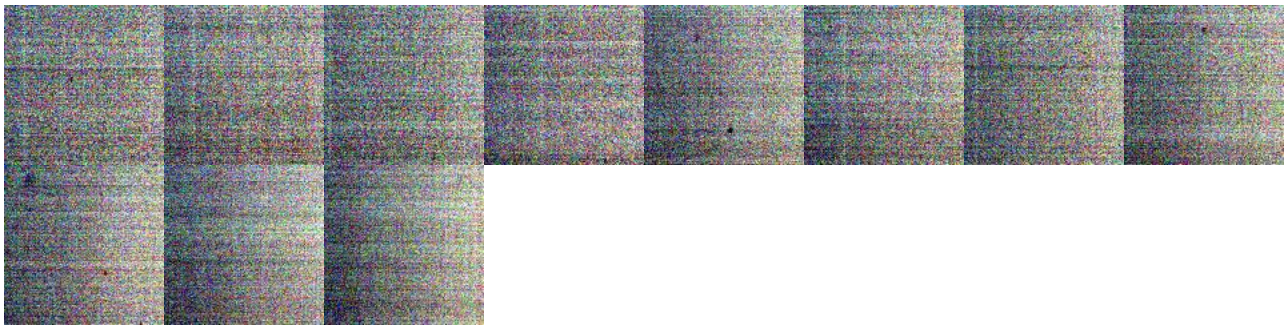


Figure 7 Sample holder for the deposition of the series with nominal thickness variation of 1 and 2 nm, respectively. The positioning of the substrates on the 150 mm x 150 mm sample stage is visualized in the sketch outside the edges where the deposition tends to be less homogeneous.

2.2.1. Deposition of Al_2O_3 on silicon, glass and PEN substrates between 30 and 40 nm nominal thickness

For the deposition of ALD layers of Al_2O_3 a nominal thickness range between 30 and 40 nm was chosen with a thickness variation of 1 nm between the samples. The layers deposited on silicon wafers were independently characterized with respect to their thickness by ellipsometry as described above. As described above for the homogeneity investigations the 50 mm x 50 mm samples were divided into nine sub-samples which were individually investigated by HSI and ellipsometry for the layers deposited on silicon. Samples deposited on glass or PEN were only investigated by HSI, as mentioned above reference thickness data were derived from the samples deposited on silicon, corrected with factors obtained from the homogeneity investigations. Figure 8 shows HSI images of the sample series for the central sample, which was used for the training of the HSI (sample no. 5, Figure 9). Below the HSI images a table is shown with thickness data predicted by the Breeze software for other areas of the same silicon wafer (position 1 was chosen for this comparison). These data are compared to the thickness obtained by ellipsometry.

The agreement between the thickness estimations of the two methods is in the range of $\pm$ 1.5 nm for this data set. Samples, the statistical error was estimated to 5-10%. For this measurement series the silicon sample was placed close to the precursor inlet, where the nominal thickness was not reached as described above for the homogeneity investigations, leading to the lower thickness range as intended to. Figure 9, Figure 10 and Figure 11 show the regression plots of the thickness from ellipsometry data versus HSI evaluation, where part of the data have been used for the PLS training (red dots) and the rest were calculated using the training data in the model (green dots).



Nominal thickness [nm]	30	31	32	33	34	35	36	37	38	39	40
Ellipsometry	24.9	26.7	28.6	29	29.8	30	29.3	29.9	32.3	33.5	34
HSI	26.26	25.48	29.92	31.03	31.98	29.46	31.32	29.03	33.83	33.84	33.23

Figure 8 HSI images of the 11 Al_2O_3 samples with nominal thicknesses between 30 and 40 nm. The 50 mm x 50 mm sample was divided in nine sub squares, the image shown is the central one of each sample. The Table below summarizes the results for the sub square no. 1 for ellipsometry and predicted HSI thickness evaluation, respectively.

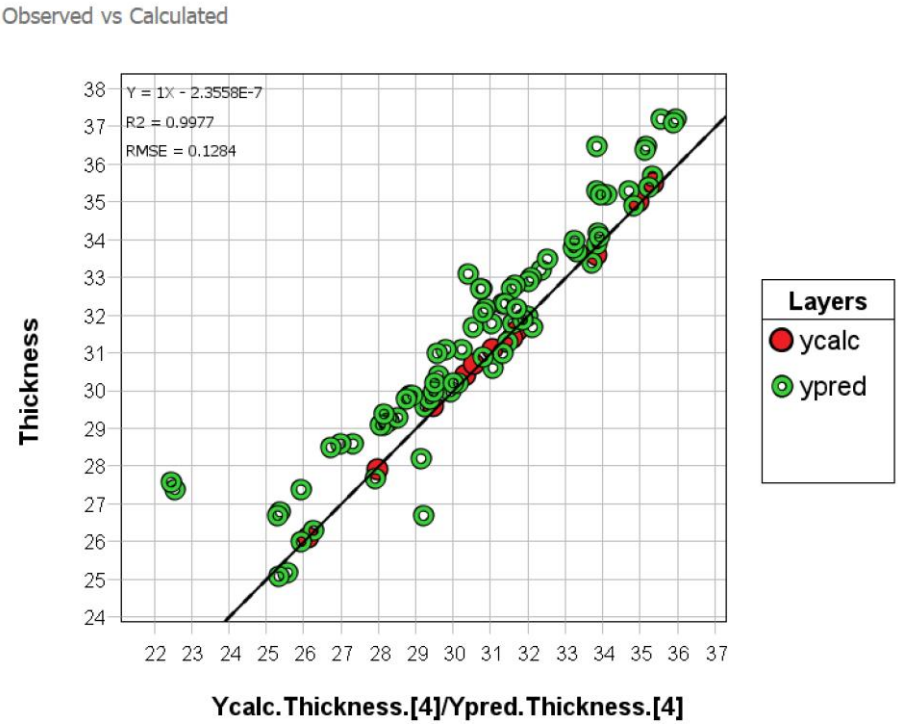


Figure 9 Regression plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the Al_2O_3 deposited on silicon with thickness variation between nominally 30 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,997) could be created.

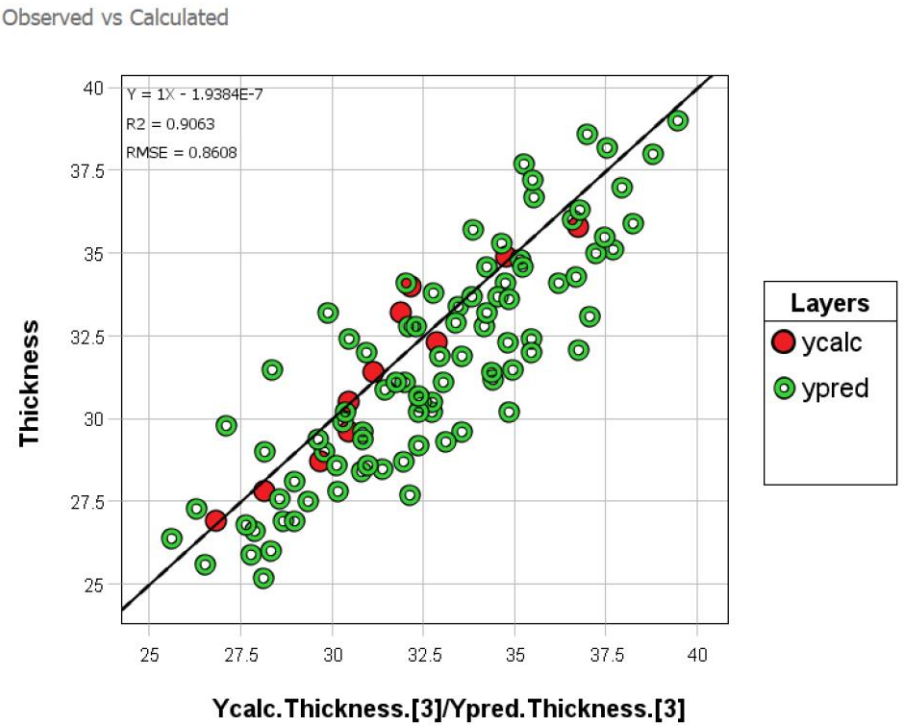


Figure 10 Plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the Al_2O_3 deposited on glass with thickness variation between nominally 30 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,906) could be created.

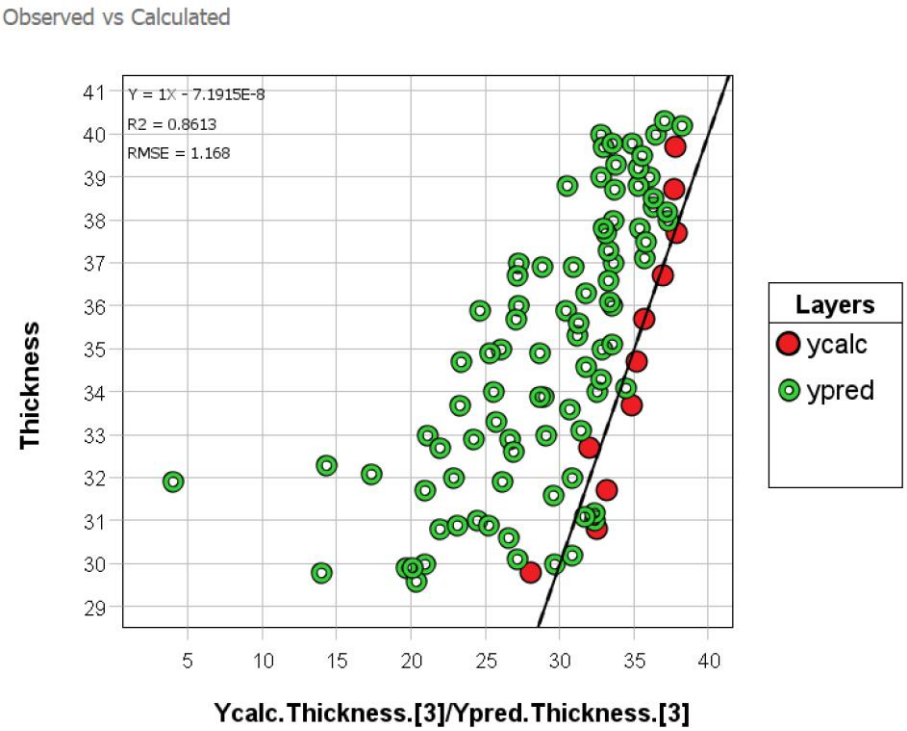
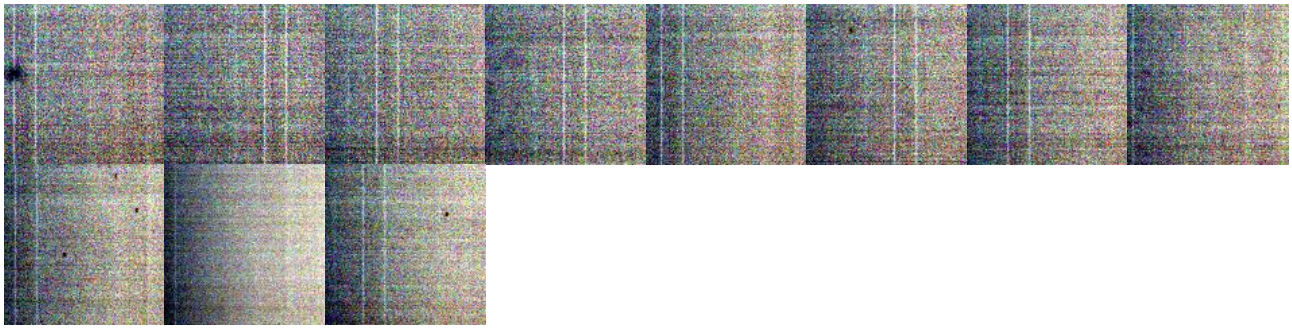


Figure 11 Plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the Al_2O_3 deposited on PEN Teonex Q65 with thickness variation between nominally 30 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,861) could be created.

2.2.2. Deposition of TiO_2 on silicon, glass and PEN substrates between 20 and 40 nm nominal thickness

The same series of experiments was performed depositing TiO_2 on silicon, glass and PEN Teonex Q65 substrates with sizes of 50 mm x 50 mm. Nominal thicknesses between 20 nm and 40 nm were chosen with steps of 2 nm due to the known overestimation of the growth rate per cycle which is more pronounced for TiO_2 than for Al_2O_3. Figure 12 shows the HSI images of each of the samples for the central square No. 5 as well as the predicted thickness data from HSI compared to those obtained by ellipsometry for square No. 1 in the table below. These data show the large deviation from the nominal thicknesses both from ellipsometry and HSI. This is due to the fact, as also pointed out above for Al_2O_3, that the placement of the silicon substrate is in the area, where we found a large deviation from the nominal thickness due to the combination of non-optimized process conditions and an overestimated growth rate per cycle. The agreement between HSI and ellipsometry is also higher than for Al_2O_3 with deviations of up to almost 6 nm. The data evaluation over the whole data set for the deposition on silicon, glass and PEN Teonex Q65 is shown in Figure 13, Figure 14 and Figure 15.



Nominal thickness [nm]	20	22	24	26	28	30	32	34	36	38	40
Ellipsometry	6.3	7.6	7.5	13	8.5	8.7	8.8	9.5	10.2	12.4	11
HSI	12.22	11.6	11.6	9.75	9.21	9.6	8.06	9.84	11.52	16.12	11.42

Figure 12 HSI images of the 11 TiO_2 samples with nominal thicknesses between 20 and 40 nm in 2 nm steps. The 50 mm x 50 mm sample was divided in nine sub squares, the image shown is the central one of each sample. The Table below summarizes the results from the thickness evaluation by ellipsometry and HSI for square number one with predicted HSI results.

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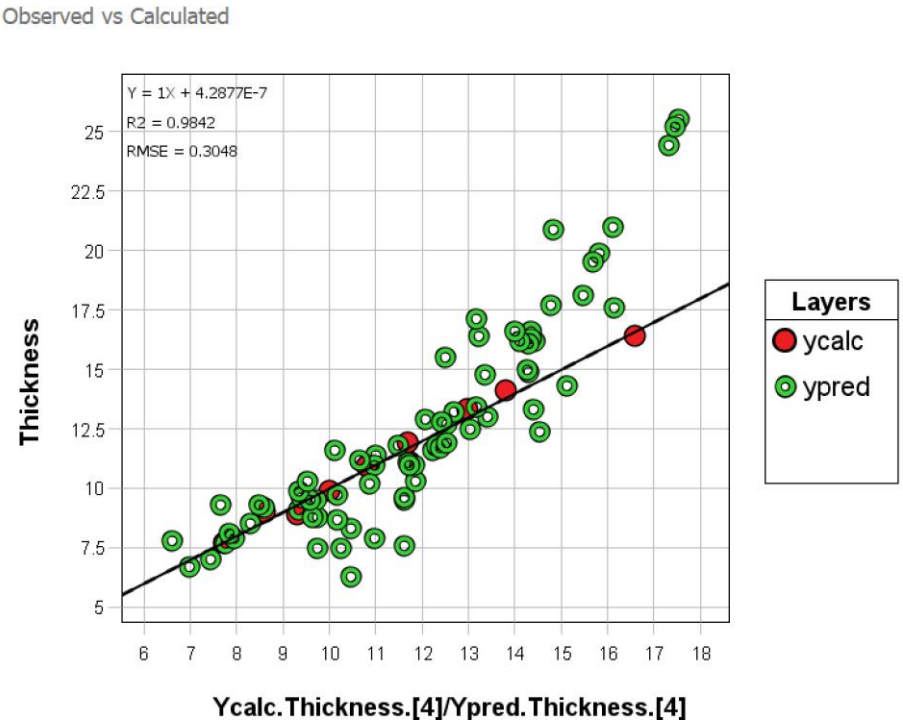


Figure 13 Plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the TiO_2 deposited on silicon with thickness variation between nominally 20 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,984) could be created.

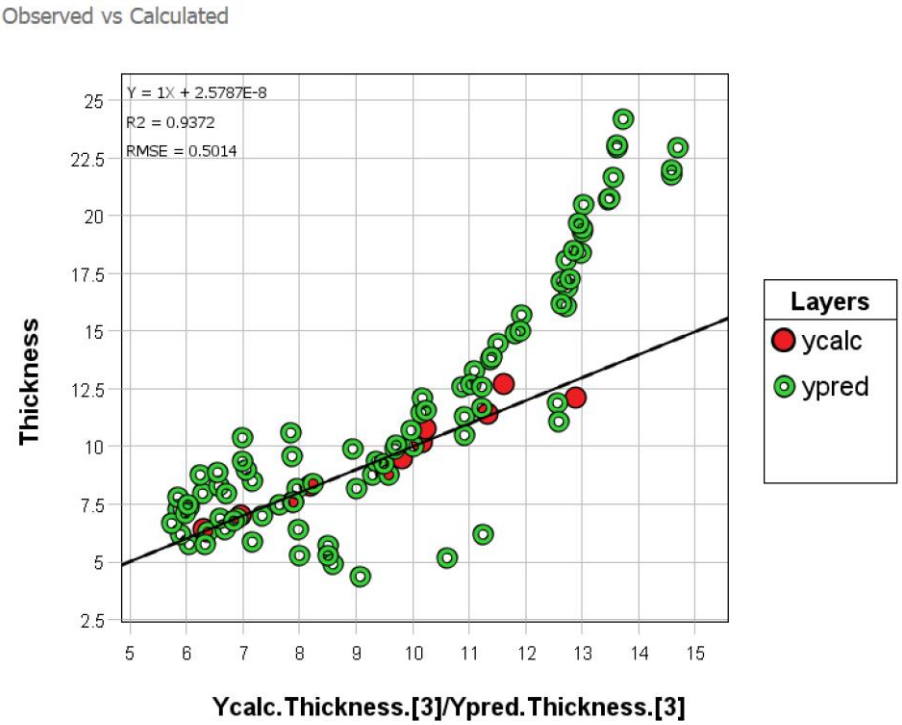


Figure 14 Regression plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the TiO_2 deposited on glass with thickness variation between nominally 20 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,937) could be created.

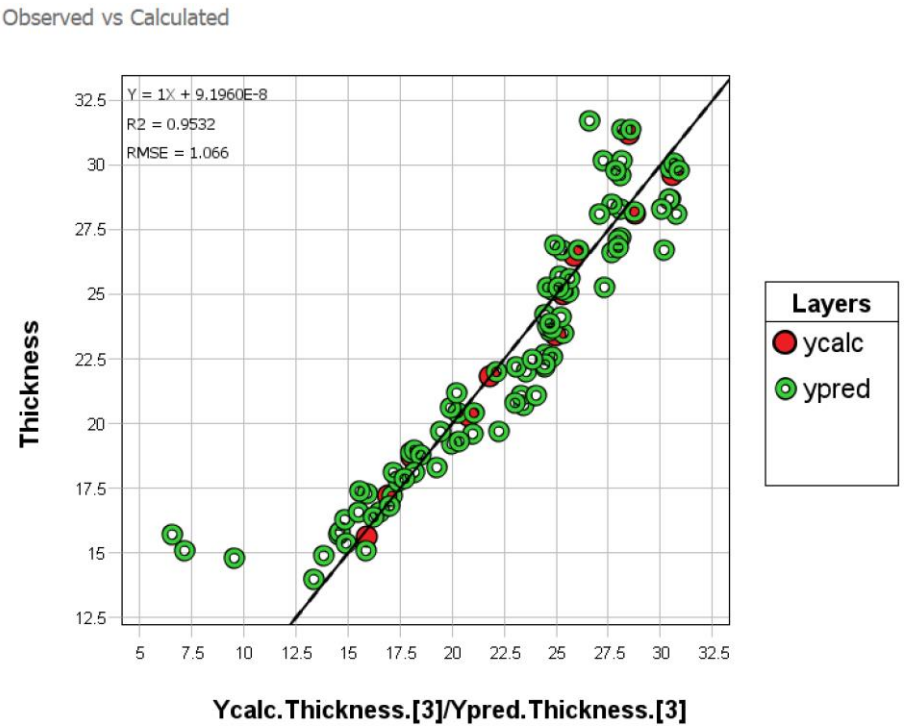


Figure 15 Regression plot of the thickness data evaluated from ellipsometry versus thickness obtained from HSI for the TiO_2 deposited on PEN Teonex Q65 with thickness variation between nominally 20 and 40 nm applying the PLS model. Red data points were taken for the training, green points are the predicted thicknesses from the model. The PLS thickness model with good accuracy (R^2 = 0,953) could be created.

2.3. Determination of remaining carbon in ALD deposited Al_2O_3 layers

HSI is also an interesting tool as quality control for the deposition of thin films. Besides the homogeneity of the deposition the quality of the layer with respect to the chemical uniformity is an interesting parameter to be followed during processing. For the ALD deposition several parameters are crucial to guarantee a perfect reaction of the deposited precursor monolayer to the final product, in the case of Al_2O_3 this is the transformation from the trimethylaluminum to the aluminum oxide. Insufficient plasma energy provided in this process might cause a non-complete conversion of the precursor to oxide leading to remaining carbon in the layers. The goal was to analyze how sensitive the HSI is to detect such insufficient deposition and remaining carbon in the layers. A series of depositions was performed with plasma energies varying between 10 J and 110 J. Each sample was measured by XPS (Kratos Axis Supra, monochromatic Al Ka x-ray, hybrid mode, pass energy 160 eV) on three different positions for the carbon content. Adsorbed carbon was removed by etching with argon ions with a kinetic energy of 5 keV for 3x 60 seconds (see Figure 17). The film thickness was determined with ellipsometry as before. The results are shown in Figure 18. The corresponding statistical model was built with the corresponding HSI data and shows good correlation for thickness and carbon content (Figure 18). Unfortunately, changing the ALD plasma energy affects both carbon content and layer thickness. Therefore, a statement about the sensitivity of the HSI measurement with respect to the carbon content alone is not possible.

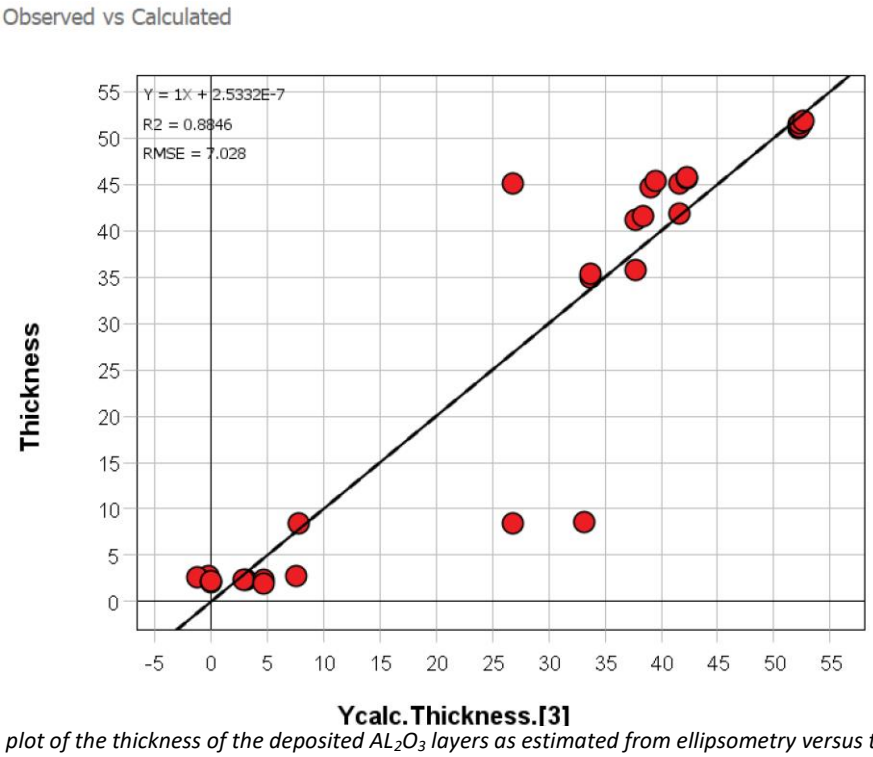


Figure 16 Regression plot of the thickness of the deposited AL_2O_3 layers as estimated from ellipsometry versus the ones obtained by HSI imaging. Almost no layer deposition could be proven for low plasma energies.

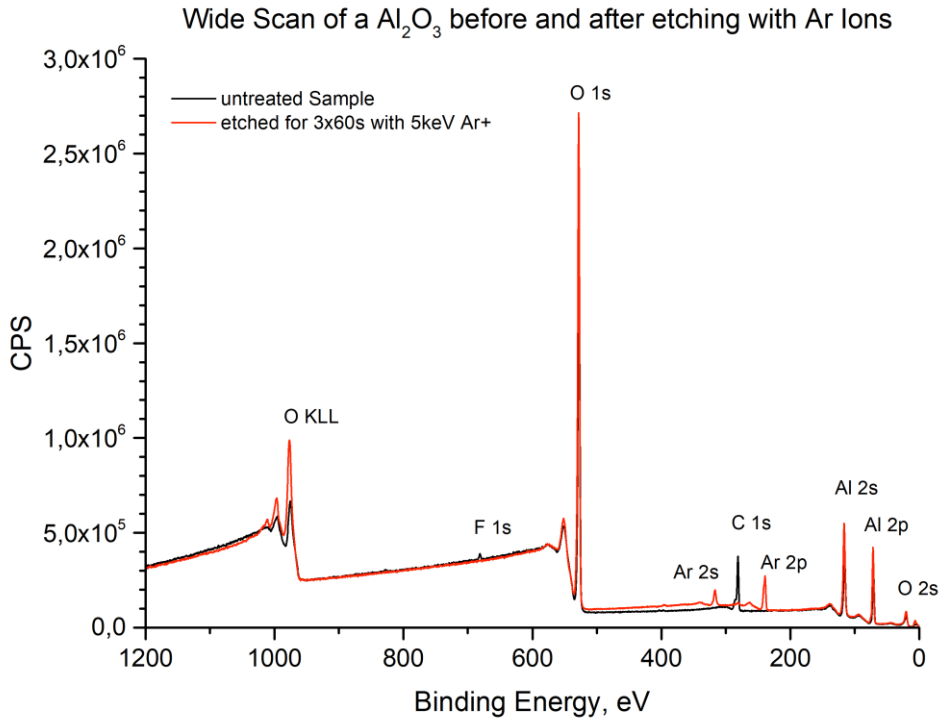


Figure 17 XPS spectrum of ALD deposited Al_2O_3 on silicon with 110 Joule plasma energy. The untreated sample shows a signal relating to adsorbed carbon (C1s), which is removed after ion etching. The remaining carbon (barely visible) is the carbon in the ALD layer.

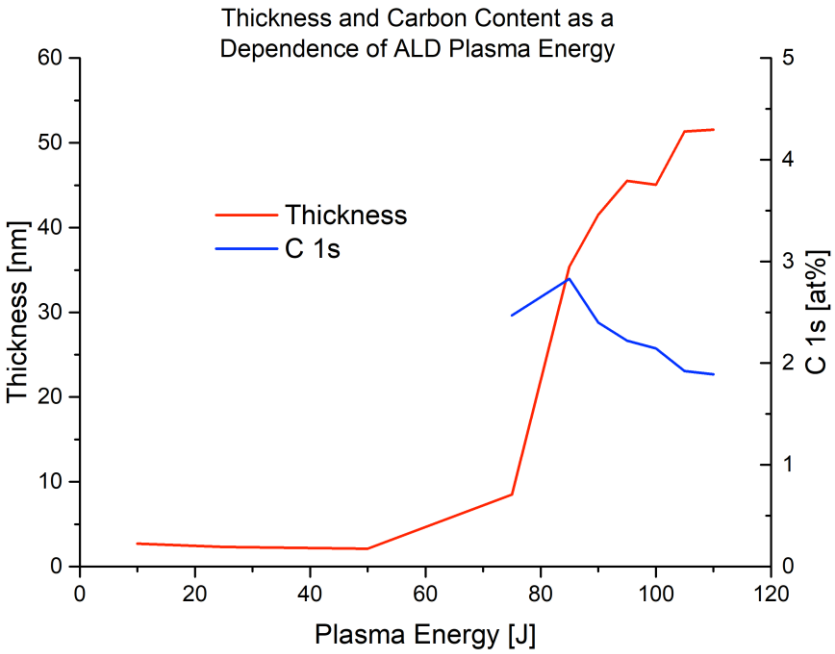


Figure 18 Dependence of the thickness of deposited Al2O3 on the plasma energy and resulting carbon content as extracted from XPS measurements.

2.4. Investigation of solution processed organic layers for OE devices

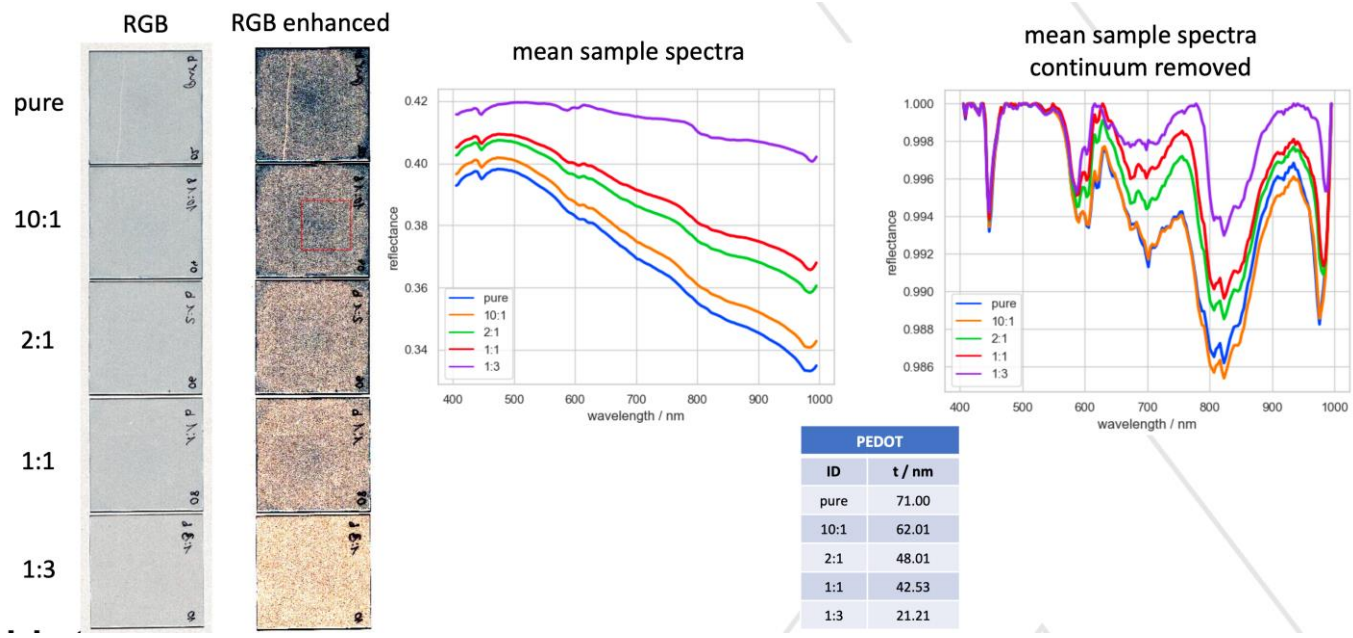
Fraunhofer IAP is engaged in the development of organic electronic devices, i.e. organic light emitting diodes (OLEDs), organic solar cells (OPV), perovskite solar cells (PKSC) and quantum dot based devices such as QD-LEDs. Common to all these systems is that they consist of a stack of different thin layers and usually the performance of processed devices depends on both the correct layer thickness and the homogeneity of the deposited layer. Another important task is the deposition of defect free layers in order to avoid dark spot generation which often leads to shorts in the device and thus their failure. Therefore, it is interesting to which content HSI can provide process control to the fabrication of organic electronic devices both with single layer inspection up to the inspection of a whole device. In order to evaluate the effectiveness of HSI for this type of process control several sets of samples for the investigation by HSI were prepared and analyzed. These were often used materials in several types of OE devices such as the charge carrier material Pedot:PSS, a semiconductive polymer used often as matrix material for different kind of device poly vinyl carbazole PVK and different light emitting materials used for OLEDs. All materials are soluble and are usually processed by either spin coating or printing processes. For the investigations within NanoQI the samples were spin coated with varying concentration and spinning speeds leading to different layer thicknesses. All samples were prepared on glass substrates. Reference thickness measurements were performed by surface profilometry after scratching the layer. Table 1 summarizes all solution processed samples under investigation.

Table 1: Summary of the different solution-processed samples prepared by spin coating for HSI evaluation. A good thickness range was obtained for Pedot:PSS and PVK, for the emitting materials the thickness was not sufficient for modelling by HSI.

PEDOT		PVK		PEDOT + PVK		Super Yellow		SPR 001		MEH-PPV	
ID	t / nm	ID	t / nm	ID	t / nm	ID	t / nm	ID	t / nm	ID	t / nm
pure	71.00	2.5%	203.56	1:3_2.5%	216.66	5g/l_1000rpm	93.26	10g/l_1000rpm	75.91	5g/l_1000rpm	40.81
10:1	62.01	2.0%	137.21	1:3_2.0%	162.37	5g/l_2000rpm	80.54	10g/l_2000rpm	59.29	5g/l_2000rpm	44.40
2:1	48.01	1.5%	75.40	1:3_1.5%	106.88	5g/l_3000rpm	71.70	10g/l_3000rpm	56.84	5g/l_3000rpm	40.92
1:1	42.53	1.0%	46.16	1:3_1.0%	70.55	2.5g/l_1000rpm	28.76	5g/l_1000rpm	30.56	2.5g/l_1000rpm	18.76
1:3	21.21	0.5%	21.85	1:3_0.5%	40.58	2.5g/l_2000rpm	26.16	5g/l_2000rpm	23.45	2.5g/l_2000rpm	19.76
						2.5g/l_3000rpm	27.00	5g/l_3000rpm	22.73	2.5g/l_3000rpm	17.64

2.4.1. Spin coated PEDOT:PSS layers

HSI images and the related spectra are shown in Figure 19. HSI data evaluation for these samples is presented in the graph of Figure 20.



PEDOT	
ID	t / nm
pure	71.00
10:1	62.01
2:1	48.01
1:1	42.53
1:3	21.21

Figure 19 HSI images of the different solution processed Pedot:PSS layers with their spectra, the variation in concentration and thickness obtained from surface profilometry are summarized in the table. (Data recording and evaluation in cooperation with NEO).

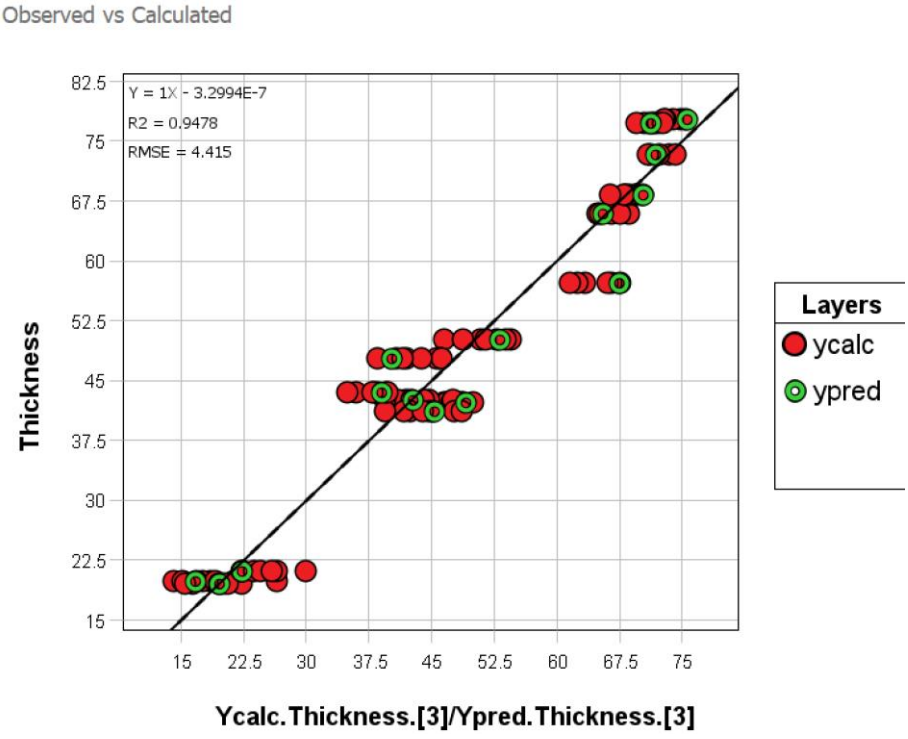
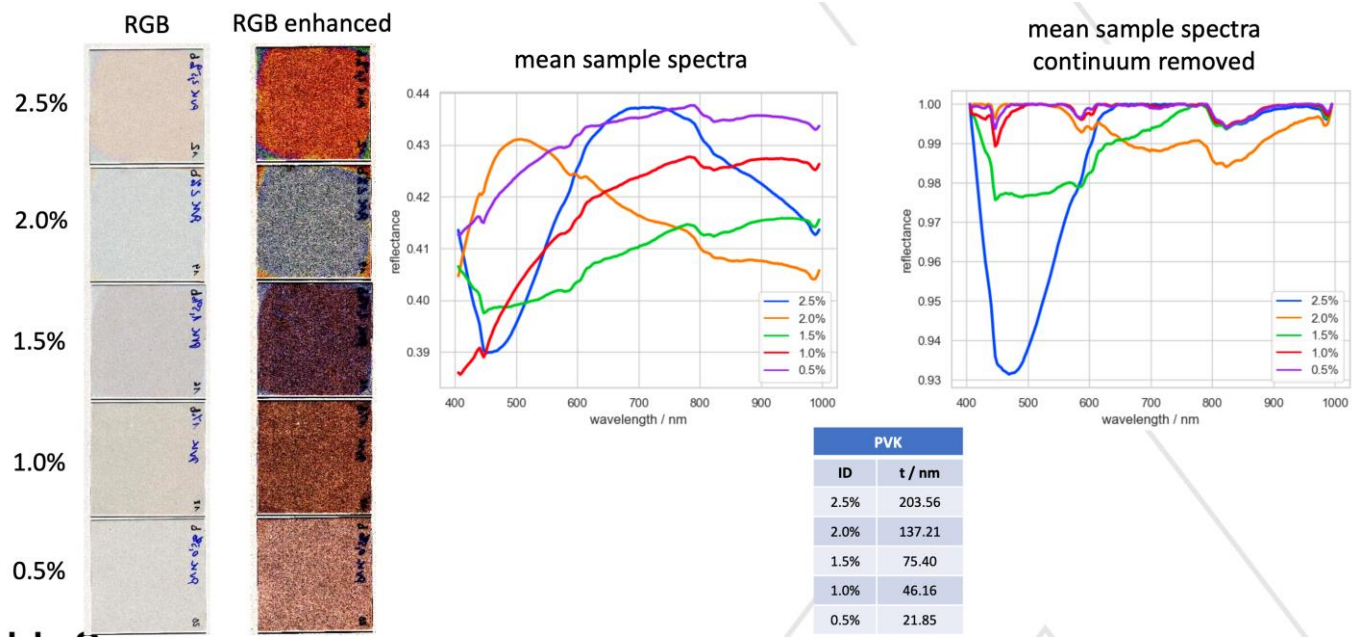


Figure 20 HSI evaluation of the thickness variation for different Pedot:PSS layer deposited by spin coating from different concentrations leading to thickness variations between 21 to 71 nm. Red dots were used for the training, green ones are predicted thicknesses. The PLS thickness model shows good accuracy with R^2 = 0,948 (created with Breeze).

2.4.2. Spin coated PVK layers

For PVK a series of samples was prepared with thicknesses between 20 and 200 nm varying processing conditions and concentration. A graph showing the thickness evaluation from HSI is shown in Figure 21. The data evaluation of the HSI measurements is presented in Figure 22.



PVK	
ID	t / nm
2.5%	203.56
2.0%	137.21
1.5%	75.40
1.0%	46.16
0.5%	21.85

Figure 21 HSI images of the different solution processed PVK layers with their spectra, the variation in concentration and thickness obtained from surface profilometry are summarized in the table. (Data recording and evaluation in cooperation with NEO).

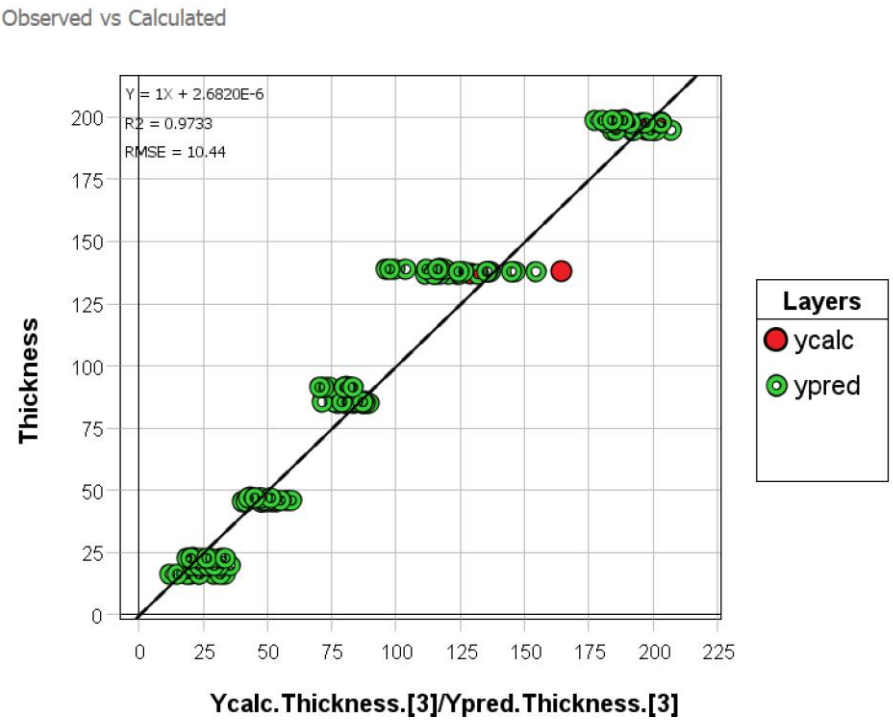


Figure 22 Plot of thicknesses measured by surface profilometry versus the ones evaluated by HSI imaging. Red dots were used for the training, green dots are predicted thicknesses. The PLS thickness model shows good accuracy with R^2 = 0,973 (Plot created with Breeze).

3. Conclusions

Within Task 6.2 the application of HSI for the evaluation of thin films could be shown. One target was the at-line investigation of ALD deposited layers of different oxides. This was achieved after the installation of the HSI measuring system close to the ALD chamber in the glovebox of the Fraunhofer pilot line for processing of organic electronic devices. It could be proven that HSI can sensitively monitor the thickness and prove the layer homogeneity over the area of 150 mm x 150 mm. For this sample size the scan speed of the HSI imaging was 2.78 mm/s, which results in a total scan time of 54s. The sensitivity of the HSI towards thickness differences was evaluated in a series of samples with nominal layer differences of 1 and 2 nm, respectively. The agreement of the HSI thickness evaluation with independent methods was within $\pm$ 2 nm. The application of the HSI for the characterization of active layers in OE devices is promising as could be shown for the examples of Pedot:PSS and PVK. As shown for the light emitting materials it is important that a sufficient number of training samples can be provided for the calibration of the method.

4. Degree of progress

Degree of fulfilment of the task activities respect of what reported in the DoA is 100%.

5. Dissemination level

This Deliverable is Public.