

# Support effect of Fe-Cu-Co thin film catalyst on CO oxidation

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The effect of inert and active substrates on the catalytic activity and stability of non-crystal Fe-Cu-Co thin film catalyst deposited on stainless steel grid mesh (SSGM) and copper grid mesh (CUGM) by pulsed-spray evaporation chemical vapor deposition (PSE-CVD) technique, was investigated for CO oxidation [1].

The Fe-Cu-Co thin film catalyst was thoroughly characterized in terms of structure, morphology, chemical composition, ionic state and optical properties. The obtained results showed that the performance and stability depended on the nature of the interphase between the metal substrate and the deposited thin film ternary oxides. The physicochemical properties disclosed the formation of needle-like shaped morphology with amorphous structure of ternary oxides, which provided abundant sites for oxygen evolution. This structural microcopy was probably due to the incorporation of copper oxides (ball-like morphology) and cobalt oxide (cubic-shape morphology), and agglomeration of corresponding iron oxide (plate-shape morphology), resulted in small distinct particles [2, 3].

Moreover, metallic species ( $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) and oxygenated species were confirmed to co-exist at the surface and offered effectual synergetic effects on oxidation reaction. The open porosity of nano-grains, abundance of surface metallic and oxygen species, thermal and electrical conductivities, high reducibility at low temperature due to low optical bandgap energies played together a crucial role in the catalytic oxidation reaction. The amalgamation of three transition metals with varying oxidation states caused a structural change and an interruption of the band structure, which was responsible for the shift of the  $E_g$  of the Fe-Cu-Co thin film catalyst to lower value. As commonly known, low  $E_g$  facilitates the electronic transition that resulted in high electron mobility and high electron mobility leads to high catalytic performance [4, 5].

The ternary oxides exhibited excellent performance towards the total oxidation of CO with a high gas hourly space velocity of  $75,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ . The catalytic tests indicated that the inert and active substrates played key roles in the catalytic activity and durability of the ternary oxides. The light-off curves shifted towards lower temperature, when ternary oxides thin film deposited on CUGM and used in the reaction, as displayed in Fig. 1. The catalyst stability of Fe-Cu-Co thin film catalyst grown on SSGM and CUGM were examined by carrying out the oxidation reaction for 25 hours at ~75% fuel conversion, respectively (Fig. 2). The Fe-Cu-Co thin film catalyst grown on SSGM showed better stability as compared to Co-supported Pt/ $\text{Al}_2\text{O}_3$  catalyst that showed 20% loss in 20 h [6].

Therefore, the doping strategy of active substrate is used to adapt highly active transition-metal ternary oxides at low temperature, which could further be a very promising way to significantly increase the activity of ternary based thin film catalyst for catalytic applications. This work provides a new approach for the development of efficient ternary oxides thin film catalyst over active substrates by PSE-CVD technique owing to the properties of high efficiency, ecology and energy saving.

[1] G.F. Pan, S.B. Fan, J. Liang, Y.X. Liu, Z.Y. Tian, RSC Adv. 5 (2015) 42477–42481.

[2] N. Bahlawane, E.F. Rivera, K. Kohse-Höinghaus, A. Brechling, U. Kleineberg, Appl. Catal., B 2004, 53, (4), 245-255.

[3] Z.Y. Tian, H.J. Herrenbrück, P.M. Kouotou, H. Vieker, A. Beyer, A. Gölzhäuser, K. Kohse-Höinghaus, Surf. Coat. Technol. 2013, 230, 33-38

[4] E. Lee, A. Benayad, T. Shin, H. Lee, D.S. Ko, T.S. Kim, K.S. Son, M. Ryu, S. Jeon, G.S. Park, Scientific reports 2014, 4, 4948

[5] Y.H. Lin, H. Faber, J. G. Labram, E. Stratakis, L. Sygellou, E. Kymakis, N. A. Hastas, R. Li, K. Zhao, Adv. Sci. 2015, 2, (7), 1500058

[6] N.E. Nuñez, H. P. Bideberripe, M. Mizrahi, J. M. Ramallo-López, M. L. Casella, G. J. Siri, Int. J. Hydrogen Energy 2016, 41, (42), 19005-19013

# Defect engineering of atomic layer deposited TiO<sub>2</sub> for photocatalytic applications

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Photoelectrochemical (PEC) water splitting is one of the potential methods of storing solar energy into chemical form as hydrogen. A major issue with the method and a challenge of renewable energy production is the development of efficient, chemically stable and cost-effective semiconductor photoelectrodes. Crystalline TiO<sub>2</sub> as such is extremely stable and capable of unassisted photocatalytic water splitting but the efficiency is limited by the bandgap (3.0–3.2 eV) to harvest photons only in the UV range. Recently, otherwise unstable semiconductor materials that can harvest the full solar spectrum has been successfully stabilized by amorphous titanium dioxide (am.-TiO<sub>2</sub>) coatings grown by atomic layer deposition (ALD) [1]. However, the stability of am.-TiO<sub>2</sub> without additional co-catalyst has remained unresolved [2].

In our recent studies, we have reported means to thermally modify the defect structure of ALD grown am.-TiO<sub>2</sub> thin film under oxidative [3] and reductive [4] conditions. TiO<sub>2</sub> films were grown on silicon and fused quartz substrates by ALD at 200 °C using tetrakis(dimethylamido)titanium (TDMAT) and deionized water as precursors. The influence of heat treatment on the structure and properties of TiO<sub>2</sub> was analyzed by X-ray photoelectron spectroscopy (XPS), Ultraviolet photoelectron spectroscopy (UPS), X-ray diffraction (XRD), UV–Vis spectroscopy, current–voltage and PEC analysis.

Based on the results, the as-deposited am.-TiO<sub>2</sub> is chemically unstable and visually black exhibiting both enhanced absorbance in the visible range and exceptionally high conductivity due to the trapped charge carriers (Ti<sup>3+</sup>). Heat treatment in air at 200 °C induces oxidation of Ti<sup>3+</sup>, decrease in absorbance and conductivity but has only a minor effect on the stability. However, a reasonable stability is obtained after oxidation at 300 °C, simultaneously with the crystallization of TiO<sub>2</sub> into rutile. Furthermore, oxidation at 500 °C results in stable rutile TiO<sub>2</sub> that produces the highest photocurrent for water oxidation. In contrast, reductive heat treatment in ultra-high vacuum (UHV) at 500 °C retains the amorphous phase for TiO<sub>2</sub> but enhances the stability due to the formation of O<sup>-</sup> species via electron transfer from O to Ti. The schematic illustrations of the effect of oxidative and reductive heat treatments on the defect structure of ALD TiO<sub>2</sub> are shown in Figures 1 and 2.

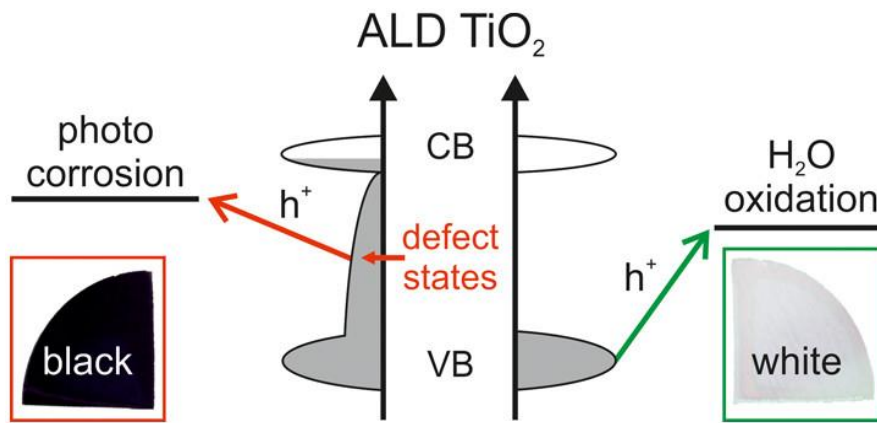
As a conclusion, ALD TiO<sub>2</sub> has proven its diversity. Conductive as-deposited black TiO<sub>2</sub> is photoelectrochemically unstable but it can be transformed into stable phases of photocatalytically active rutile or electrically “leaky” amorphous black TiO<sub>2</sub> by heat treatment in oxidative or reductive conditions, respectively.

[1] S. Hu, M.R. Shaner, J.A. Beardslee, M. Lichterman, B.S. Brunshwig, N.S. Lewis, *Science* 344 (2014) 1005–1009

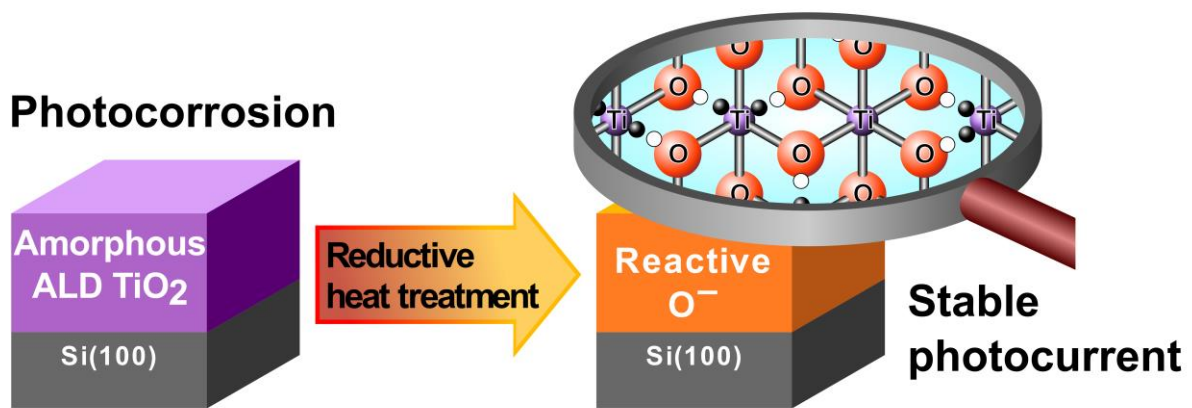
[2] K. Sivula, *ChemCatChem* 6 (2014) 2796–2797

[3] H. Ali-Löytty, M. Hannula, J. Saari, L. Palmolahti, B.D. Bhuskute, R. Ulkuniemi, T. Nyysönen, K. Lahtonen, M. Valden, *ACS Appl. Mater. Interfaces* (2019) In press

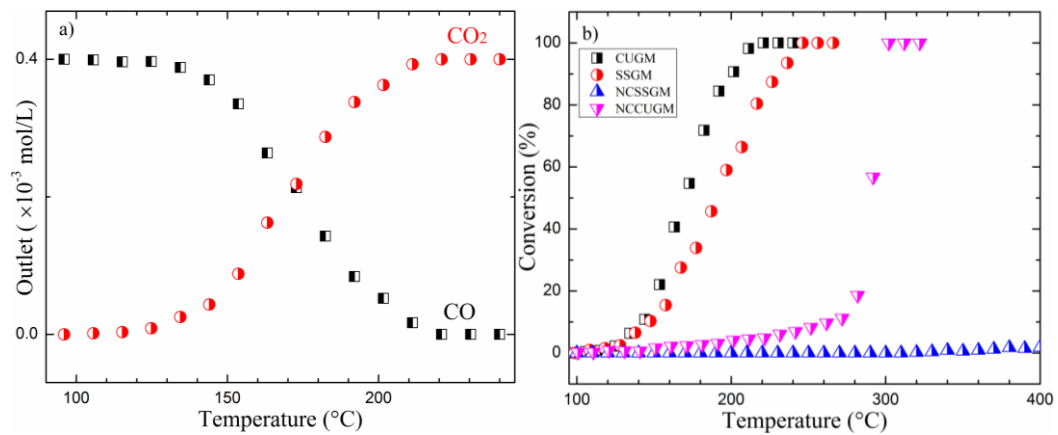
[4] M. Hannula, H. Ali-Löytty, K. Lahtonen, E. Sarlin, J. Saari, M. Valden, *Chemistry of Materials* 30 (2018) 1199–1208



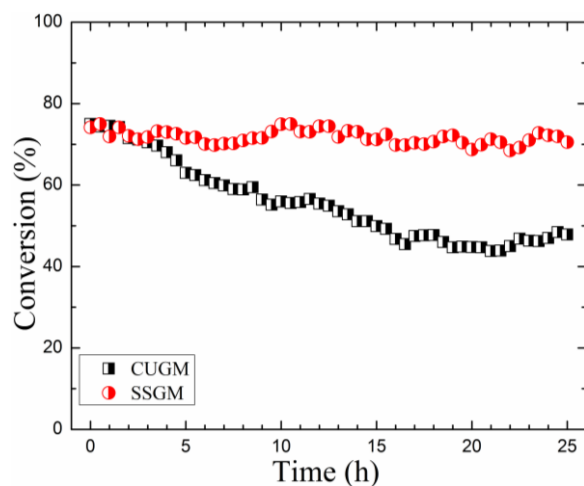
**Figure 1.** The as-deposited am.-TiO<sub>2</sub> is chemically unstable and visually black. Heat treatment in air at 500 °C results in stable rutile TiO<sub>2</sub> that produces the highest photocurrent for water oxidation.



**Figure 2.** The reductive heat treatment in ultra-high vacuum (UHV) at 500 °C retains the amorphous phase for TiO<sub>2</sub> but enhances the stability due to the formation of O<sup>-</sup> species via electron transfer from O to Ti.



**Figure 1.** Light-off curves of CO conversion (a) and (b) comparison of the catalytic performance for oxidation of CO.



**Figure 2.** Durability test of Fe-Cu-Co thin film catalyst deposited on different substrates.

# ALD deposition of $\text{Eu}^{3+}$ doped yttrium oxide thin films on various substrates for quantum technologies

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Rare-earth doped materials create a growing interest for applications in quantum technologies [1]. Indeed, since the coherent manipulation of quantum states is strongly affected by the fluctuations caused by the environment, the use of rare-earth ions allows to partially reduce this issue due to their sub-layer 4f valence electrons being screened by outer layers. This has enabled the observation of the longest coherence time in a solid for  $\text{Eu}^{3+}$  ions in  $\text{Y}_2\text{SiO}_5$  bulk crystals at cryogenic temperatures (up to 6 hours) [2].

Other simple binary systems such as  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  can be produced in a variety of forms such as small single-crystals, transparent ceramics, films and nanoparticles, and have also very promising quantum properties [3][4]. Thin films appear as an alternative approach, allowing advantages such as easier integration with other hybrid quantum systems and the ability to be processed in a more efficient way. However the fabrication of high crystalline quality “quantum grade” rare-earth oxide films still needs to be demonstrated. In this work, we have searched to evaluate the optical properties and the potential of thin  $\text{Y}_2\text{O}_3$  films elaborated by Atomic Layer Deposition (ALD) for quantum technologies applications. This technique has been chosen for its great conformality, its precise control of doping and thicknesses and high flexibility for deposition on various substrates.

The first depositions have been realized on Si(100) substrates, and then, later, various substrates have been used for the depositions of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin films: fused silica, sapphire with different orientations,  $\text{Y}_2\text{O}_3$  transparent ceramic, and  $\text{Y}_2\text{O}_3$  thin films on Si(100) elaborated by Chemical Vapor Deposition (CVD) (**Figure 1**). The aim of this study is to analyze the effect of substrate on the crystalline quality and the optical properties of ALD thin films. The results are promising and better than the depositions on Si(100) (**Figure 2**).

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin films with thicknesses between 9 and 400 nm have been analyzed by X-ray diffraction (XRD), scanning electronic microscopy (SEM), and photoluminescence (PL). A study of the deposition parameters has been realized to determine the best synthesis conditions for obtaining high quality thin films in terms of structural and optical properties. The use of specific annealing steps after deposition, at temperatures between 600°C and 1200°C have allowed strongly improving the films.

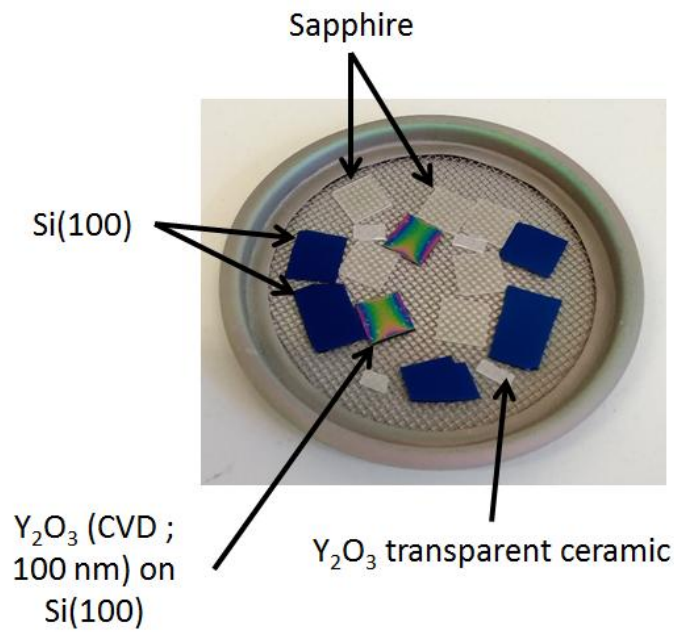
The study of optical properties revealed the existence of a mixture of cubic and monoclinic phases. The annealing step allows not only reducing the presence of the unwanted monoclinic phase, but also increasing the luminescence intensity and narrowing the emission peaks, which is a proof of the improvement of crystalline environment around the emitting ions in the films. The next step is the implementation of the coherence properties experiment of rare-earth ions contained in the thin films.

[1] P. Goldner et al., Chapter 267 in Handbook on the physics and chemistry of rare earths Vol 46, Eds J.C.G. Bunzli and V.K. Pecharsky (2015).

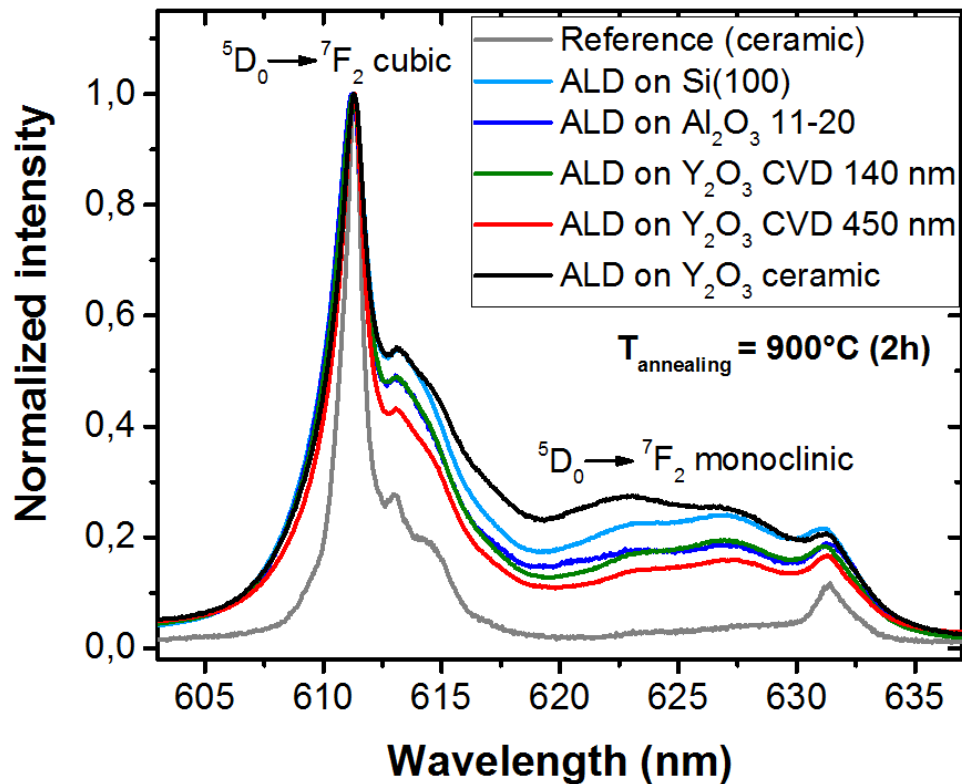
[2] M. Zhong, M. P. Hedges, R. L. Ahlefeldt, J. G. Bartholomew, S. E. Beavan, S. M. Wittig, J. J. Longdell, M. J. Sellars, Nature 517 no.7533 ( 2015) 177–180.

[3] N. Kunkel, A. Ferrier, C. W. Thiel, M. O. Ramírez, L. E. Bausá, R. L. Cone, A. Ikesue, P. Goldner. APL Materials 3 no. 9 (2015) 96103.

[4] J. G. Bartholomew, K. de Oliveira Lima, A. Ferrier, P. Goldner, Nano. Lett., vol. 17 no. 2 (2017) 778-787.



**Figure 1.** ALD deposition of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> thin films on various substrates: Si(100), sapphire with different orientations, Y<sub>2</sub>O<sub>3</sub> transparent ceramic, and Y<sub>2</sub>O<sub>3</sub> thin films on Si(100) elaborated by Chemical Vapor Deposition (CVD).



**Figure 2.** Room-temperature photoluminescence spectra of 100nm-thick Y<sub>2</sub>O<sub>3</sub> thin films doped with 5% Eu<sup>3+</sup> on various substrates after an annealing step at 900°C, showing the main Eu<sup>3+</sup> emission lines in a cubic or monoclinic environment. A ceramic with the same composition is used as a reference.

# ZnO thin films grown by plasma-enhanced atomic layer deposition: material properties in and outside the ALD window

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ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices (e.g., gas, bio, and UV sensors, piezoelectric nanogenerators and actuators). Being able to tailor these material properties to meet specific technological requirements is crucial for enhancing the device efficiency or sensitivity.

In a previous study [1], the effect of plasma power on plasma-enhanced atomic layer deposited (PE-ALD) ZnO had been investigated at room temperature. By tuning the power, properties such as the bandgap and crystallite size had been tailored. However, the power had shown little influence on the growth behavior and texture of the films.

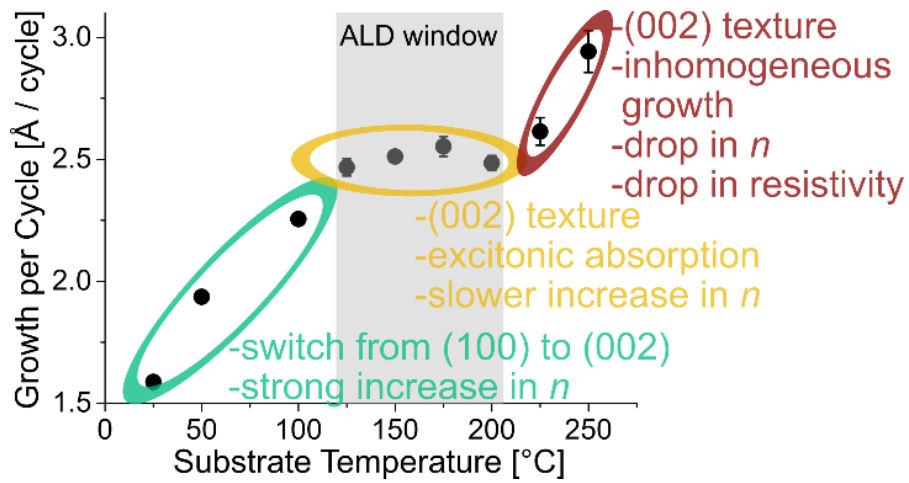
In this study, we investigated the effect of substrate temperature in the range 25 °C – 250 °C on the ZnO material properties. The films were grown by direct PE-ALD adapting diethylzinc and O<sub>2</sub>-plasma as reactants. The growth per cycle (GPC, obtained by spectroscopic ellipsometry) ranged from 1.6 to 2.9 Å/cycle and showed a constant behavior in the range 125 °C – 200 °C, the so called ALD window (Figure 1).

Several material properties showed a temperature dependence closely related to the temperature dependence of the GPC. The texture of the films investigated by X-ray diffraction (XRD) showed a switch from (100) to (002) up to the onset of the ALD window and remained (002) when the temperature was further increased (Figure 2). The GPC in the ALD window was around 2.5 Å/cycle which is close to the interplanar spacing along the [002] orientation (2.60 Å), pointing out a clear correlation between these parameters. For high temperatures outside the window, the GPC increased to values larger than the interplanar spacing whereas XRD suggested a (002) texture. The growth in this region could therefore be identified as a chemical vapor deposition (CVD)-like growth happening in a non-self-limiting manner.

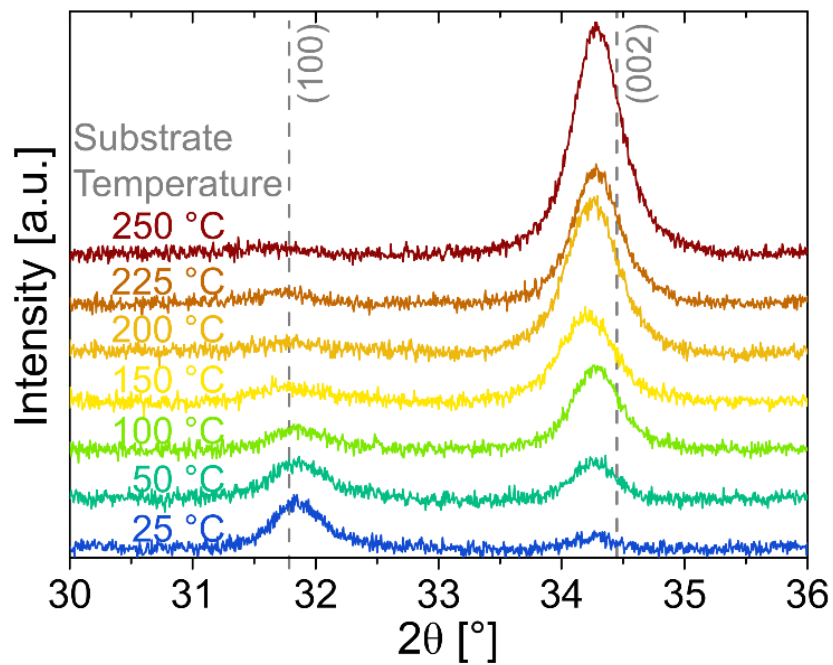
The refractive index (at 633 nm) measured by spectroscopic ellipsometry (SE) showed an increase from 1.90 to 1.96 with increasing temperature and a rapid drop to 1.86 at 250 °C. UV-Vis spectroscopy showed that all samples were highly transparent (~ 90 % transmission) over most of the visible range. Samples prepared at temperatures within the ALD window and slightly above (100 – 225 °C) exhibited a peak which could be attributed to excitonic absorption. These excitonic features point out the high optical quality of the films prepared in this temperature region. The absorption edge was found to red shift with increasing substrate temperature with a fairly constant region around the ALD window. The resistivity of the samples was very high ( $> 4 * 10^4 \Omega cm$ ) for samples below and within the ALD window and dropped above the ALD window to 10  $\Omega cm$  at 250 °C suggesting an increased amount of defects at high temperatures.

In a nutshell, the results of this work show how the growth and material properties of ZnO films deposited by PE-ALD are affected by the substrate temperature. Crystalline, optical, and electrical properties show trends that are closely related to the temperature dependence of the GPC. Investigating these correlations, fundamental insights into ALD basics such as the role of the ALD window can be gained. Furthermore, the possibility to tailor ZnO properties with temperature for application in functional devices is presented.

[1] Pilz et al. "Tuning of material properties of ZnO thin films grown by plasma-enhanced atomic layer deposition at room temperature." *J. Vac. Sci. Technol. A* 36.1 (2018): 01A109



**Figure 1.** Growth per cycle as a function of substrate temperature and description of the material properties of the films prepared at different temperatures.



**Figure 2.** Specular XRD spectra of ZnO films prepared at different substrate temperatures.