

Preparation of ZnO and Ga₂O₃ nanostructures by atomic layer deposition

PD 116579- Final report

Aim of the project

The project was aimed at the research of two crucially important wide bandgap semiconductor materials: ZnO and Ga₂O₃. Both these materials as well as their alloys are expected to be important transparent conductive oxides, with ZnO being transparent in the visible range, absorbing UV light, and Ga₂O₃ only absorbing deep UV. The other difference was that ZnO is a material with a well-developed and known atomic layer deposition (ALD) process method, while the ALD of Ga₂O₃ was yet to be explored. Therefore, the project proposed to develop the method and application of Ga doped ZnO films, the basic deposition and post-deposition parameters for the preparation of Ga₂O₃ films, the development of the preparation method for Zn doped Ga₂O₃ layers, and the fabrication of nanostructures of both materials with a combination of ALD and hydrothermal growth. It was expected that these materials will find many practical applications, and the project proposed to explore some of these as well.

Results

Ga doped ZnO films

In this work I doped ZnO films with gallium, aiming at increasing the conductivity of the ZnO TCO while maintaining the excellent crystallinity of the layers. I characterised the prepared layers with different experimental methods, then, after finding the optimal parameters for this purpose, prepared transparent conductive layers for LEDs, which were also tested by an industrial LED manufacturer.

The deposition parameters for ZnO were established earlier, therefore only the ALD window for Ga doping had to be found with the ALD windows of the two material depositions slightly different. ZnO can only be grown epitaxially at temperatures exceeding 300°C, while the deposition of Ga₂O₃ at this temperature is already CVD-like with an uneven and rough growth. On the other hand, ZnO can be deposited at a temperature as low as room temperature, the used Ga precursor (hexakis(dimethylamino)gallium) needed to be heated to 130°C to achieve a sufficient vapour pressure, therefore the deposition temperature had to be above this to avoid the condensation of the precursor. The ALD window of Ga doping therefore proved to be between 130 and 300°C, with the possibility to grow epitaxial GZO films at 300°C on lattice matched substrates (GaN or sapphire). The Ga doped films were uniform, homogeneous and smooth (RMS roughness under 1nm). According to depth profiling measurements, the distribution of the Ga dopant was homogeneous along the depth of the layers. These results show the applicability of hexakis(dimethylamino)gallium compared to other Ga precursors: It makes the deposition of very low resistivity GZO films possible at the lowest achievable deposition temperatures.

Fig. 1. shows the electrical parameters of the doped films prepared at different temperatures. These results show that the added gallium atoms are in fact incorporated into the ZnO matrix, and act as dopants reducing the resistivity of the films. However, the actual doping concentration in the films deposited at 200 and 250°C is lower than the nominal value. From the series deposited at 300°C it is clear that the optimal Ga content is at 3%, which also applies to the films prepared at 200 and 250°C, but in these cases the optimum appeared at higher nominal doping levels (5-10%). Up to this doping concentration the resistivity of the layer decreases monotonously. Further increasing the Ga content, the resistivity rapidly increases again.

To further examine this effect, the carrier concentration and the mobility of the GZO films were also measured with Hall measurement. The carrier concentration of the films increases with the doping up to 3%, then starts to decrease again as the gallium content reaches the solid solubility at around 3%. Above this level Ga dopant atoms tend to occupy interstitial states, or oxygen sites, which results in acceptor levels in ZnO, and form gallium-oxide precipitates at the grain boundaries. The mobility of the films, on the other hand, decreases with the doping, as the introduction of gallium atoms increases the scattering on ionized impurities and may decrease the grain size resulting in an increased grain boundary scattering. Comparing GZO to another widespread dopant in ZnO, aluminium, it is important to note that gallium doping yields lower resistivities with far superior crystallinity.

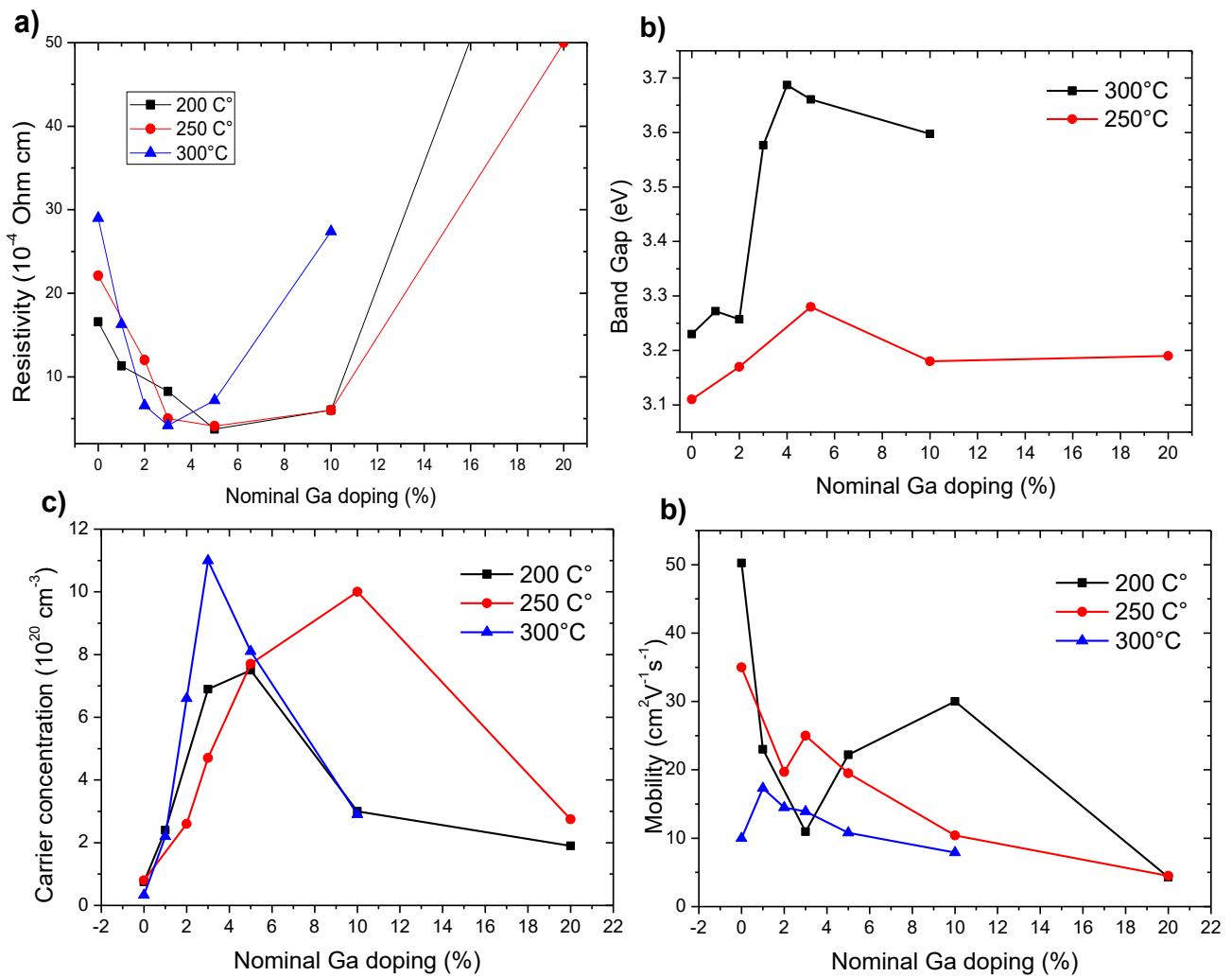


Fig. 1. Results of the Hall measurements on GZO/sapphire thin films doped with various Ga concentrations: free carrier concentration (a), free electron mobility (b), resistivity (c) and band gap (d) of the GZO films grown at different temperatures and no annealing applied

The thickness, and sheet resistance maps of the doped films on a 4" wafer were determined with spectroscopic ellipsometry and Eddy current mapping, and these are shown in fig. 2. It can be seen, that these properties are highly uniform at this scale, which proves this advantage of the ALD method.

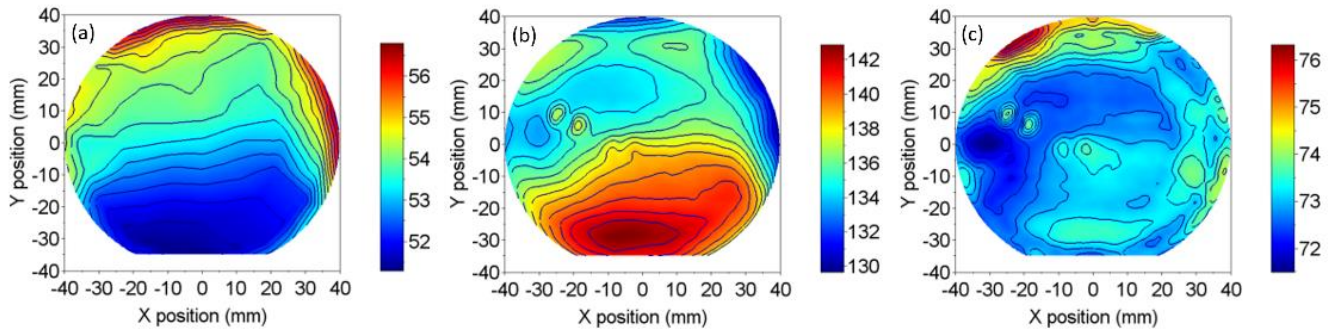


Fig. 2. Thickness in nm (a), sheet resistance in Ω/\square (b) and the calculated resistivity map in $10^{-5}\Omega\text{cm}$ (c) recorded on a limited wafer area in a diameter of 80mm.

The intrinsic ZnO films deposited at 300°C on GaN were epitaxial, but the Ga doping deteriorated this, resulting in high quality oriented films. All the films prepared at under 300°C were oriented polycrystalline. To further improve the crystallinity, and thus the mobility of the films, different annealing procedures were introduced. Already a 500°C annealing procedure improved the crystallinity of the films and thus the electron mobility, but at the same time decreased the carrier concentration due to an in-diffusion of oxygen. The heat treatments also changed the properties of the interface of the GZO film and the underlying GaN substrate due to an in-diffusion of Zn atoms into the interfacial region of the p-GaN material, later proving advantageous in LED applications.

From the different annealing experiments between 500 and 800°C with durations ranging between 5 and 15 minutes, we found that a 5 minute long annealing at 700°C proved to be an optimal compromise to result in the best conductivity, crystallinity and interface quality.

These results were used to prepare TCO layers on the LED structures of Epistar LED manufacturers. Tests by the Transmission Line Method (TLM) on ALD GZO deposited on commercial InGaN/GaN blue LED wafers covered by highly doped p-GaN layer were performed. As LED applications require low resistivity, high crystallinity and excellent interface properties at the same time, the preparation method had to be further optimised. Thus, we introduced an “interrupted growth” method, which consists of an 5 minute long annealing at 700°C after a “buffer-layer” of ca. 15 nm thickness was prepared. The deposition of the missing thickness followed after that by a second ALD step. This resulted in a thin buffer film with high mobility and low interface resistivity while the rest of the GZO film maintained its excellent crystallinity and high carrier concentration. These cases are plotted with blue lines in Fig 4a and b. The demonstrated method is thus a compromise for ensuring an electrically high quality GZO/p-GaN interface ($1.33 \times 10^{-2} \Omega\text{cm}^2$) with a limited degradation of the electrical conductivity of the bulk GZO ($5.2 \times 10^{-4} \Omega\text{cm}$).

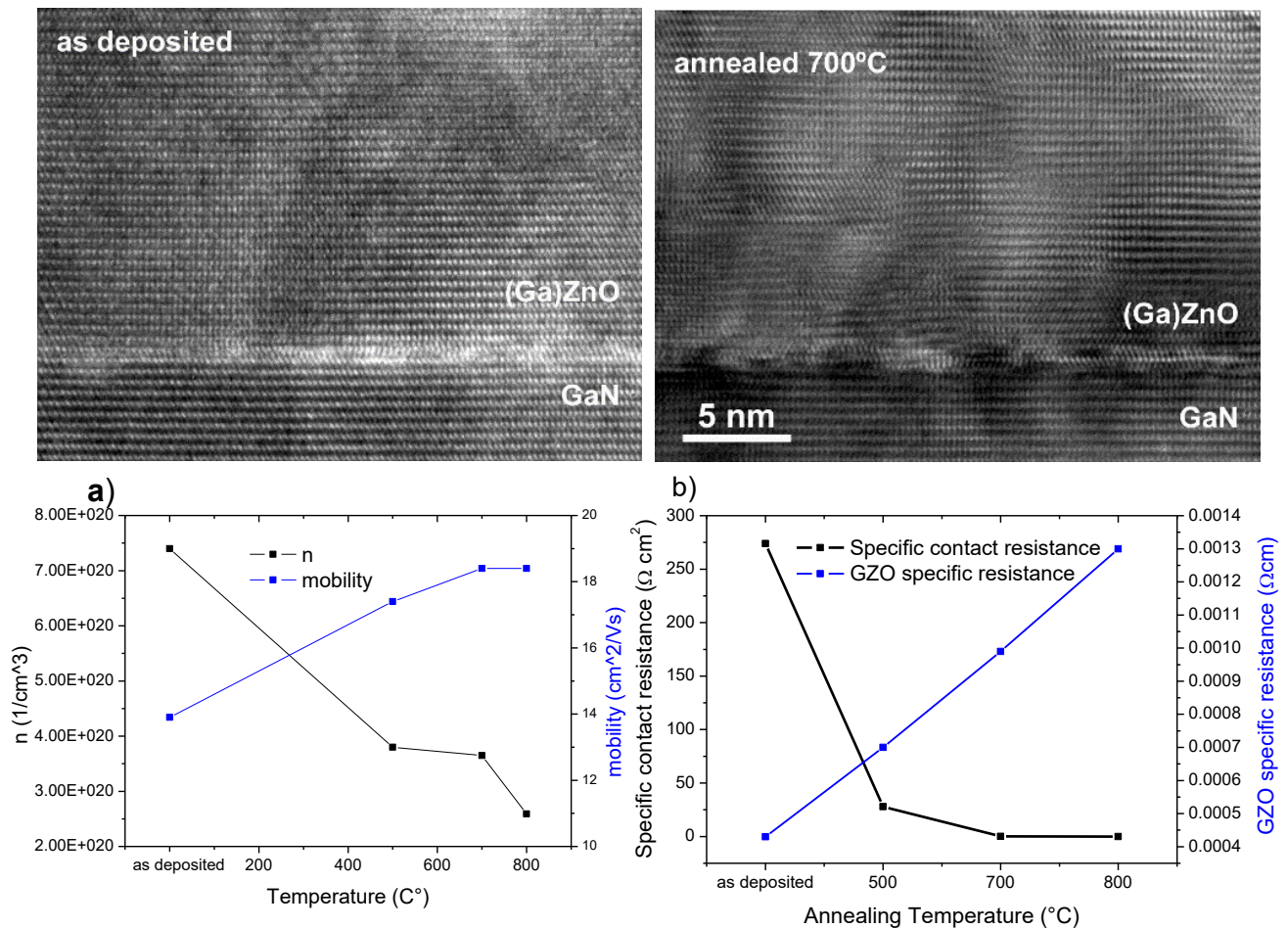


Fig. 3. Result of the annealing on GZO layers: HRTEM images of the ALD GZO layer before (top left) and after (top right) annealing at 700°C. The mobility and the carrier concentration vs. annealing temperature (bottom left), and the resistivity and contact resistance vs. annealing temperature in 3% doped GZO films deposited at 300°C (bottom right.)

The optimized buffer annealing process was also tested for LEDs. The current-voltage characteristics as well as the output electroluminescence intensity curves for the as-prepared and buffer-annealed thin (ca. 45 nm) GZO layers are compared in Fig 4.c. The two-step deposition scheme resulted in slightly improved threshold voltage compared to the as deposited one (2.8 vs 2.9 V, at $I=20$ mA). At higher currents (20-100 mA) the improvement in differential resistance is more pronounced. More importantly, the two-step annealing treatment led to a 40-times enhancement in electroluminescence intensity at a driving current of 20. As the LED layout used for these tests was originally optimized to the electrical properties and thickness of ITO, by an optimized GZO thickness and a dedicated chip layout even a more efficient current spreading and light extraction could be obtained.

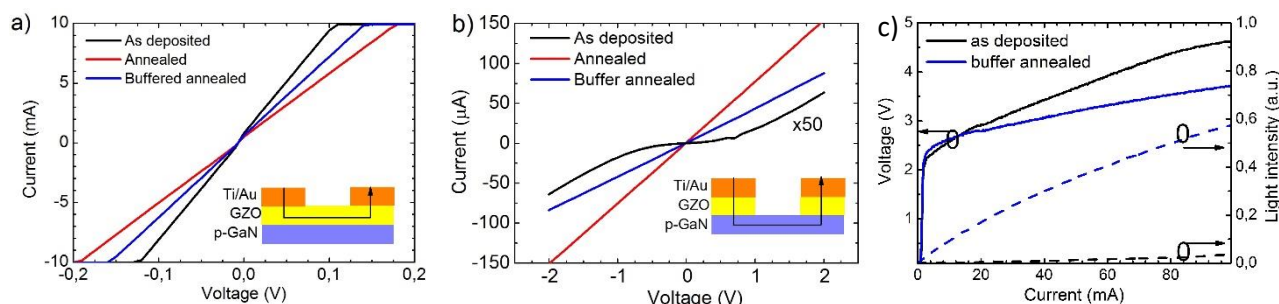


Fig. 4. Typical current-voltage curves taken between TLM contacts with a separation of $20\ \mu\text{m}$ for as deposited (black line), annealed (red line), and buffer annealed (blue line) samples before (a) and after (b) GZO etching. Note that the characteristics in (a) are dominated by the resistance of GZO, while in (b) by the orders of magnitude higher contact resistance of the interface between GZO and p-GaN is the limiting factor. c: Voltage (left vertical axis) and output electroluminescence intensity (right vertical axis) as a function of driving current recorded on the LEDs for the thin (ca. $45\ \text{nm}$) non-annealed (black) and 2-step deposited annealed GZO TCO (blue), respectively.

Preparation of nanostructures with a combination of ALD and hydrothermal method

This work focused on the development of hierarchical nanostructures with high specific surfaces and tuneable material properties. The different architectures were built with a combination of atomic layer deposition and aqueous solution growth: As in the latter case the growth of ZnO only takes place on ZnO seed layers, the properties of the formed structures can be controlled with the quality of the ALD seed. The combination of ALD for fabricating seed layers and hydrothermal growth for realising nanostructures appears very promising, as both these methods are ideal for 3D nanostructuring, whereas most deposition methods can only be applied for planar surfaces, and do not have the required step coverage for 3D structures. The combination of ALD and hydrothermal growth for the purpose of nanostructures does not require high temperatures or consist very complicated technology steps, but the parameters of hydrothermal growth (composition, pH, temperature and growth duration) have to be controlled very precisely. Then, with the different seed layers provided by ALD, a wide variety of nanostructures could be grown. As the hydrothermally grown structures follow the crystallinity of the seed layers, ordered, or aligned structures can be grown on monocrystalline c-axis oriented ZnO films. This was realized in my work by the epitaxial growth of ZnO seed layers at 300°C on GaN substrates (in which case the lattice mismatch is merely 1,8%. Sapphire substrates with a mismatch of 18% did not prove lattice matched adequately.). After a photolithographic step for the definition of the positions of the columns, the growth of aligned monocrystalline nano-columns became possible (Fig. 5.a).

ALD ZnO presents an island-like growth on Si surfaces in the first few cycles of growth. The nucleated islands may be used as seed layers for hydrothermal growth. As in the case of ZnO hydrothermal growth the nanowires only grow from ZnO covered surfaces, not from the Si substrate, the nano-island deposition may be used as a way to control nanorod growth. This method presents a simple alternative to nanowire growth by lithography, as controlling the number, size, and density of the nucleated islands is possible just by influencing the nucleation of the ALD film through the number of connections sites, that is, OH groups on the surface by plasma treatments and piranha etching and a subsequent immersing of the samples in water to fill the surface sites with OH groups. On the other hand, longer initial pulses in the deposition process also result in increased number of nucleation sites. With the combination of these surface treatments,

the grown structures can be controlled through the distribution of the ALD islands, while the orientation of the structures can be influenced with the crystallinity of the islands (through the deposition temperature). As in the case of atomic layer deposition the growth takes place on arbitrarily high aspect ratio structures, any structured surface can be covered by nanowires grown by this method. (Fig. 5.d)

By combining the above two procedures hierarchical structures can be grown, as shown in fig. 5.b. In this case, the oriented ZnO columns grown on epitaxial ZnO were covered with a few atomic layers of Ga_2O_3 , then a new, polycrystalline ZnO seed layer, and a second hydrothermal growth was conducted. The resulting cactus-like structures have very high aspect ratios and can be used as effective high specific surface electrodes.

All the prepared ZnO structures can be used as templates for the preparation of more complex structures, as ZnO can be etched very easily with acids. Nanotubes were fabricated using ZnO nanorod arrays as templates, covered with atomic layer deposited TiO_2 . After the removal of the ZnO template, free-standing, well aligned nanotubes were gained.

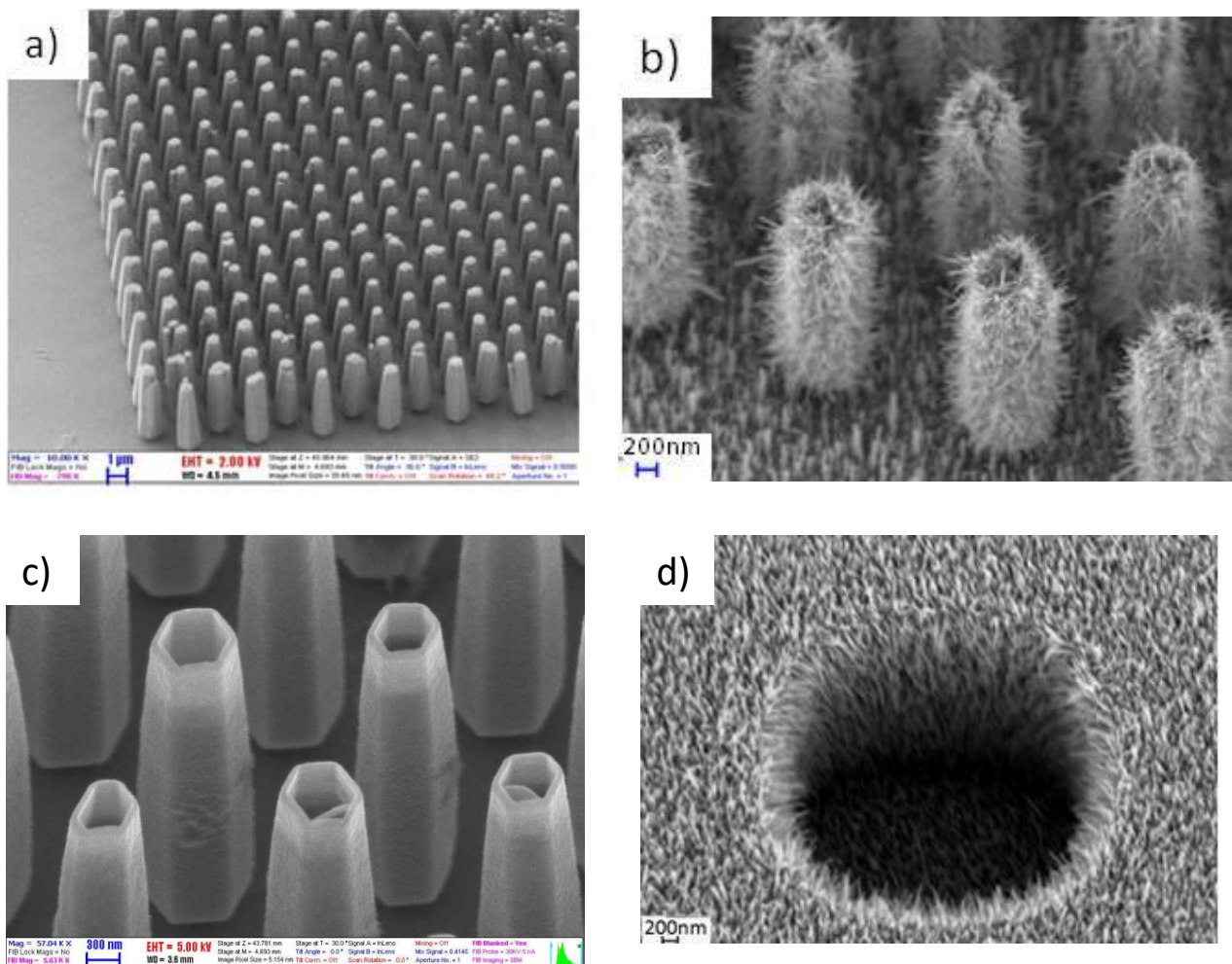


Fig. 5. ZnO micro-rods (a), micro-cacti (b), TiO_2 micro tubes (c) and a surface covered with nanowires (d)

The combination of atomic layer deposition and hydrothermal growth is ideal for the fabrication of a number of nanostructures, as both can be applied as 3D methods to ensure uniform coverages on structured surfaces, whereas most methods can only be used on planar surfaces. Another advantage of the methods is the low temperature deposition, which can easily be integrated in large scale electronic production as well.

Another application of the developed methods was the additive modification of butterfly wings, which have a nanoscale 3D structure resulting in their photonic crystal properties. By depositing 40 nm ALD oxides uniformly within the structure, the reflected light spectrum of the wings could be modified in a controlled manner. Such a precise control of the spectral shifts promised a number of practical applications. The possibility of a low temperature deposition was once again pivotal in this case: the degradation of the fine butterfly wings could be avoided with a 100°C deposition temperature.

These high aspect ratio structures may be useful in a number of applications, such as catalysis and photovoltaics. The nanopillars may effectively increase the light extraction of LEDs. The “pillar like” structures realised with this method are especially useful in gas sensors as they can react more effectively with gases than “hole-like” structures.

Atomic layer deposition and characterisation of Zn-doped Ga₂O₃ films

This work focused on the atomic layer deposition of Ga₂O₃ prepared with Ga₂(NMe₂)₆, addressing some of the most pressing issues limiting the use of Ga₂O₃: The improvement of the crystallinity was attempted with a number of annealing procedures and the in-situ Zn doping of gallium-oxide was also performed by intermitting diethylzinc pulses amongst the Ga-oxide precursor pulses. The effects of the doping on the electrical properties was analysed, and the issue of the Ohmic contact fabrication was addressed. These questions are so crucial, as Ga₂O₃ appears to be a rather promising material for deep UV photodetectors, but a number of problems hindering its use need still to be solved. DUV photodetectors absorb the 200-280 nm range of light, which regime is missing from sunlight, as this UVC radiation is absorbed by diatomic oxygen in the atmosphere. Therefore detectors with a cutoff below 280 nm can be used as solar blind detectors and find applications in flame-detection, space communication, detection of ozone holes and UV leakage measurements. For this purpose, wide bandgap semiconductors with bandgaps above 4.4 eV are required. UV semiconductor photodetectors can work in three different modes: Photoconductive detectors measure between Ohmic contacts on an n-type semiconductor material, Schottky barrier photodiodes measure between a Schottky and an Ohmic contact on the n-type material. P-n junction photodiodes require both Ohmic contacts on the n-type semiconductor and a p-n junction. As there is no reliable p-type doping in Ga₂O₃, the other two detector types would be favoured in Ga₂O₃ based DUV detectors. As both structures require Ohmic contacts, the lack of reliable Ohmic contact material and procedure on Ga₂O₃ hinders the development of such devices. My experiments started with the determination of the ALD window of the Ga₂O₃, with a stable growth between 130 and 270°C. The as-deposited films were all amorphous, but homogeneous and uniform on a 4” scale.

To determine the electrical parameters of the layers, spectroscopic ellipsometric measurements were conducted. As it is shown in fig. 2, the dielectric constants are between 3.2 and 3.5, that is, all the films are insulating, and this property was not significantly influenced by the deposition temperature. The bandgaps of all deposited layers were within the regime predicted by the literature: between 4 eV and 4.8 eV. The layers deposited at 130°C had the widest bandgaps, 4.8 eV, which is optimal for the realization of good quality DUV detectors.

To induce a crystallisation in the ALD Ga_2O_3 films, different annealing procedures were conducted. 5 minute long annealing was performed in a rapid thermal annealing equipment, in nitrogen or oxygen atmosphere at 500°C, 700°C and 900°C. This approach induced no crystallisation at 500 or 700°C, but some crystallites formed at a 900°C annealing temperature. The films submitted to a 3 hour long heat treatment have a completely transformed structure exhibiting 100-200 nm angular, crystallite-like grains. The TEM images show that the films annealed in nitrogen had some cavities in them, and the layers became slightly porous, with a weak adhesion to the substrate, while the ones in oxygen kept their density. According to the electron diffraction measurements, β - Ga_2O_3 crystallites were found in both types of layers.

In the layer annealed in oxygen for 3 hours, crystalline β - Ga_2O_3 phase was clearly visible in the XRD pattern, therefore, these films have sufficiently large crystallites and an appropriate overall crystalline quality to be considered as crystalline β - Ga_2O_3 layers, and this crystallisation procedure can be chosen to obtain crystalline gallium-oxide films. The films are textured and oriented mainly in the (-204) direction.

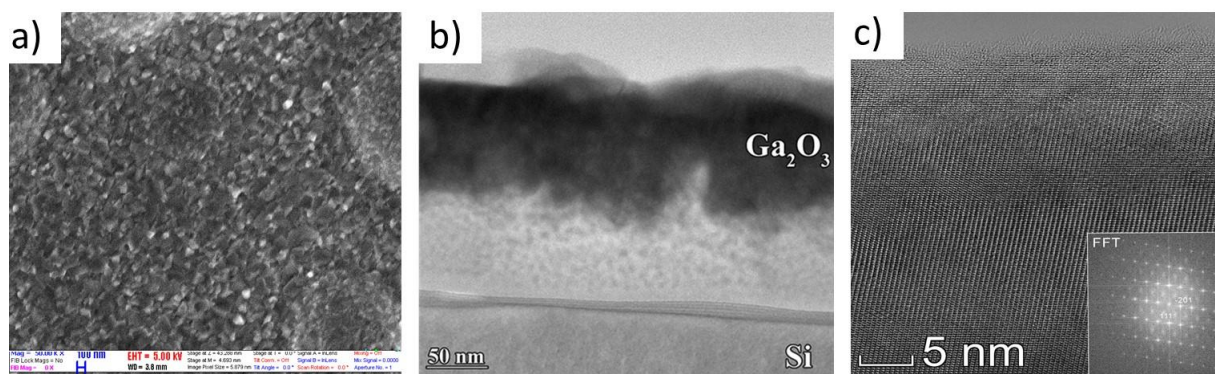


fig.6. SEM (a), (Bright field) TEM (b) and HRTEM (c) image of the Ga_2O_3 film annealed in oxygen at 900°C for 3 hours

The electrical properties of the annealed, crystalline β - Ga_2O_3 films were also measured. As fig. 7.b shows, the annealing reduced the dielectric constants of the layers significantly. The dielectric constants of the films appears to be independent of the original deposition conditions and after the annealing, all the dielectric constants were between 2 and 2.1.

The Zn-doping of the films was carried out through adding DEZ pulses amongst the $\text{Ga}_2(\text{NMe}_2)_6$ and water pulses. 2, 5 and 10% doping was achieved by changing every 50th, 20th and 10th DEZ pulse to $\text{Ga}_2(\text{NMe}_2)_6$. Fig. 9. shows the 10% doped Ga_2O_3 layer deposited at 270°C. It is clear that the Zn doped Ga_2O_3 films were homogeneous, smooth and amorphous just like the undoped gallium-oxide layers.

The results of Zn doping is still under debate in the literature. According to calculations, Zn may be incorporated into the Ga_2O_3 matrix as a p-type dopant, however, Zn ions can only yield deep acceptor levels. On the other hand, the Zn incorporation into the gallium-oxide matrix increases the density of oxygen vacancies. The intrinsic dopants in gallium-oxide can be Ga and O vacancies, with the former acting as a p-type and the latter as an n-type dopant. Zn doping promotes the formation of V_O as its formation energy decreases when a Zn atom replaces a Ga atom in the lattice. On the other hand, the contribution of V_O to the n-type conductivity is also debated.

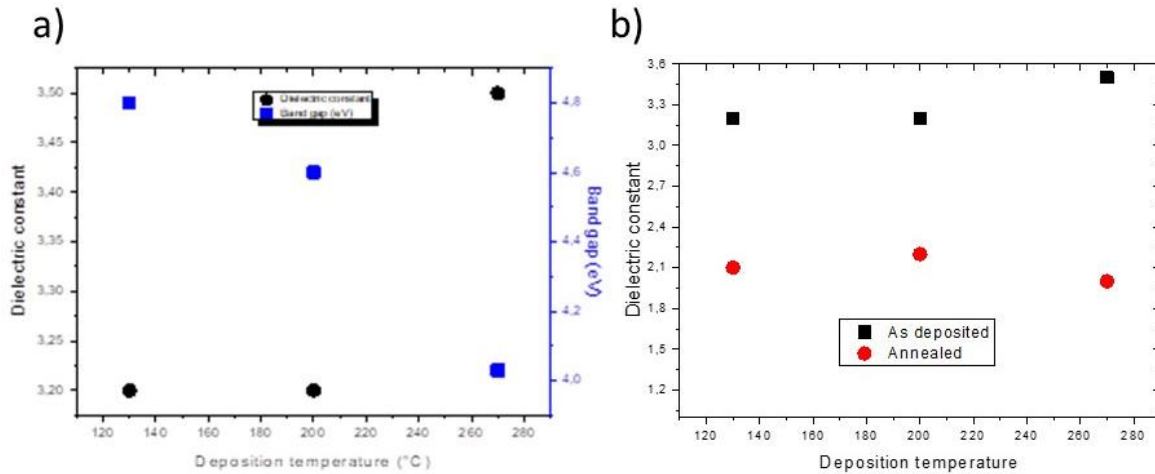


Fig. 7. Dielectric constant and bandgap of the ALD Ga_2O_3 films deposited at different temperatures (a). Dielectric constants of the as deposited and annealed (in oxygen) films as determined by spectroscopic ellipsometry (b).

The breakdown voltages of the intrinsic films could not be measured as the contacts fabricated on them proved to be Schottky type (both the Cr-Au contacts and the In contacts). The fabrication of Ohmic contacts on gallium-oxide films is a major difficulty presently, and has proved to be a problem in my experiments as well. However, in the case of all Zn doped Ga_2O_3 samples, both types of metallic contacts were Ohmic and their breakdown voltages could be measured. All of these were between 0,1 and 0,7 MV/cm, which is an order of magnitude below that of intrinsic Ga_2O_3 reported in the literature. This means that on one hand, the Zn doping resulted in an effective dopant in Ga_2O_3 reducing its resistivity, on the other hand, Zn doping may prove to be an effective method to achieve Ohmic contacts on Ga_2O_3 easily. Both of these features are considered to be huge advantages in DUV sensor applications.

The band gaps and dielectric constants of the films were measured with spectroscopic ellipsometry. It can be seen in Fig. 8. that the Zn doping decreased the dielectric constants of the films. This agrees with the results of the electrical characterisations, and rather points to an n-type doping of the films. On the other hand, the band gaps of all the doped films were around 4.8 eV, which means that the Zn doping stabilized the highest bandgap value of the intrinsic films, which can be explained with the Burstein-Moss effect. As the bandgaps of the Zn doped films are in the optimal regime, while the dielectric constants are reduced, resulting in a better conductivity, and the fabrication of Ohmic contacts becomes possible, the films properties can be optimised with Zn doping for the purpose of DUV photodetectors.

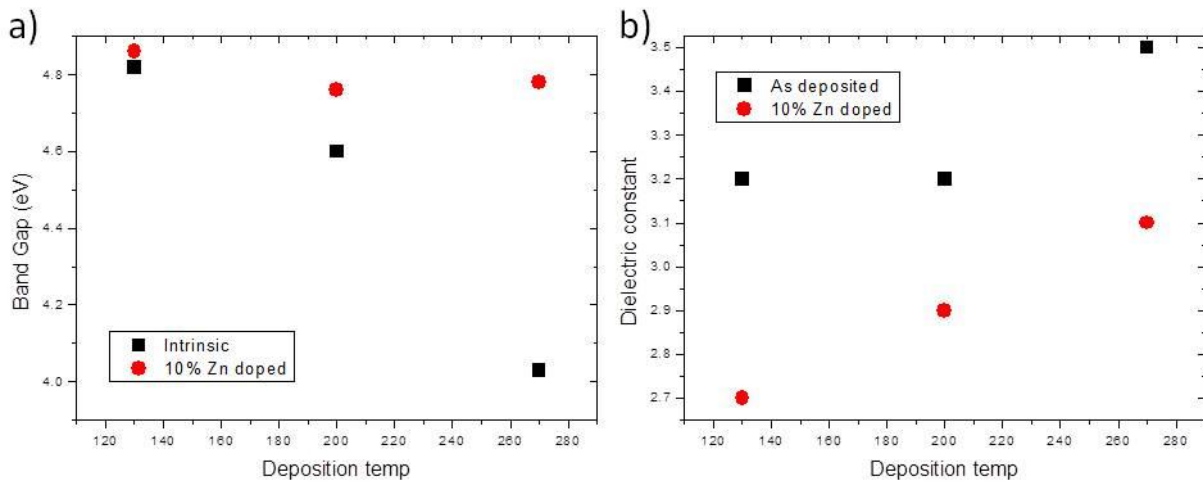


Fig 8. The electrical properties of the Zn doped Ga₂O₃ layers: Band gap vs. deposition temperature (a) and dielectric constant vs. deposition temperature

The effectivity of Ga₂O₃ films for DUV photodetector applications can be further improved by nanostructuring. Therefore the hydrothermal growth of Ga₂O₃ was performed from a water based solution of GaCl₃ and urea. In my experiments, different concentrations of the growth solution as well as growth temperatures between 100°C and 180°C were attempted. Different substrates were also used: sapphire, silicon, and ALD Ga₂O₃ seed layers. All these parameters influenced the growth slightly: at temperatures below 120°C, the growth was not dense. At and above 180°C the growth resulted in almost continual films, not real nanostructures. Between these extremes, the grown films were all very similar, quite independent of the substrate, although the structure grown on crystalline Ga₂O₃ contained slightly larger whiskers. The conclusion is, that preparing nanostructured Ga₂O₃ films with this relatively novel method is fairly straightforward and may be versatile for some applications, but an adequate control of the resulting structure properties still needs to be achieved.

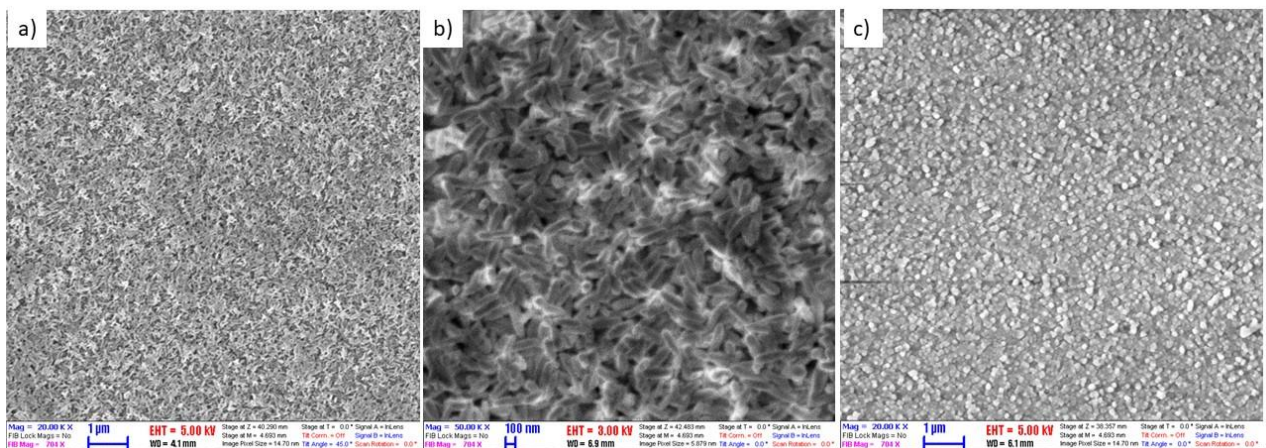


Fig.9. Hydrothermally deposited Ga₂O₃ nanostructures: hydrothermal growth at 140°C on an amorphous Ga₂O₃ seed layer (a), hydrothermal growth at 140°C on a crystalline seed layer (b), hydrothermal growth on an amorphous layer at 180°C (c)

Mg doped ZnO films

The motivation of this study was to improve the control of the bandgap and the electronic properties of ZnO. It was previously shown that Ga doping can increase the conductivity, but for the application of UV transparent TCO for UV LEDs (which has recently become more and more important), the increased conductivity must be achieved while increasing the bandgap of the ZnO material as well. The most promising dopant for this purpose is Mg, which can increase and enlarge the band gap and the absorption coefficient of the ZnO material making an effective band-gap engineering and heterostructure device design possible. MgO layers have also been applied as buffer layers for ZnO layer growth to improve the crystalline quality.

Our aim in this work was to describe the structure and the microtexture as well as the electronic properties of the MgO and Mg-doped ZnO layers grown by ALD on α -Al₂O₃ and GaN substrates, and the influence of the buffer layer orientation on the thin-film microstructure.

According to our findings, MgO starts to grow epitaxially onto the α -Al₂O₃ and GaN substrate with two main orientations and (100)-type planar defects caused by the large misfit between the substrate and the MgO. After the first ca. 50 nm random orientation of MgO crystals were formed with a well-developed texture on GaN.

The properties of the Mg doped ZnO films depended strongly on the substrate. In the case of sapphire substrates, the MgO separated as a cubic buffer layer, even though the Mg pulses were intermitted into the Zn and O pulses throughout the entire deposition. In the case of an α -Al₂O₃ substrate, the ZnO film over the segregated MgO buffer is epitaxial with some mosaicity forming a ZnO/MgO/c-plane α -Al₂O₃ hetero-structure showing higher mobility with lower carrier concentration. The higher mobility could be due to the superior crystallinity of the samples caused by the buffer layer. In the case of GaN substrates, at high doping concentrations (e.g. 10% Mg) the same segregation of MgO at the interface could be observed. On the other hand, at 1% Mg concentration, an even doping could be achieved without segregation.

This shows that the success of low concentration Mg doping in ZnO largely depends on the choice of substrate material, that is, a doped epitaxial film could be grown on GaN, while the same growth on sapphire resulted in a high quality intrinsic ZnO film on a MgO buffer layer.

Another interesting conclusion of this research (although slightly off topic), is that it shows the flaw in a commonly used research approach: It is common procedure to employ different substrates for the same deposition, and then use these for the different characterisation methods (e.g. transparent sapphire substrates can be used for transmission measurements, while Si substrates are easier to handle in SEM and ellipsometry, etc.). In the first approximation we may generally assume that these are essentially the same films (with some differences in crystallinity, but the same composition), which we can thus examine with the different methods. The present research shows an example, where the film growth is so fundamentally different on the different substrates that this approach had to be dismissed completely.

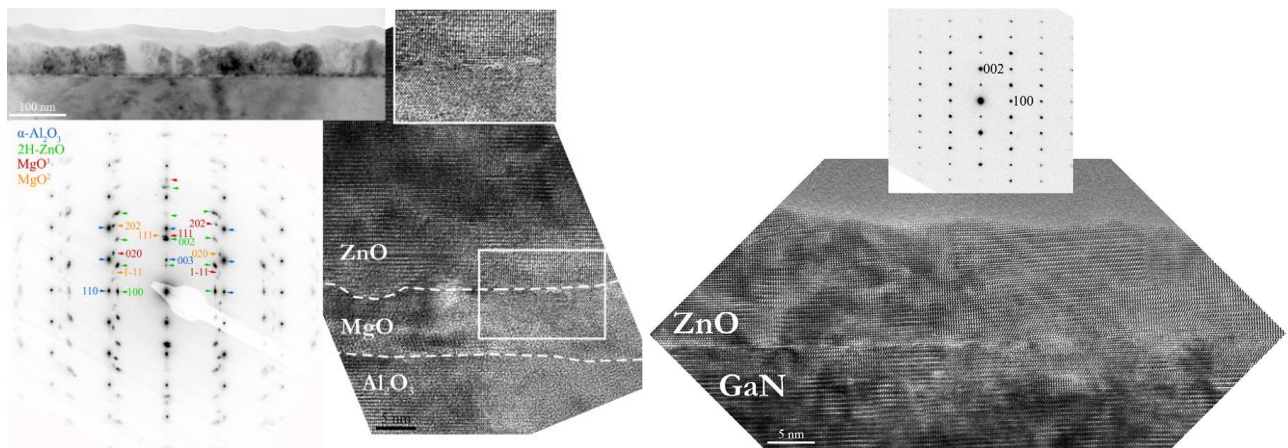


Fig. 10. Mg doped ZnO films grown on sapphire (left) and GaN (right)

Conclusions and outlook

Conclusions

At the beginning of the project, it seemed probable that the preparation and doping of ZnO will be successful. On the one hand, our team had some prior experience concerning this material, and on the other hand, according to this experience, ZnO is a very versatile material, with well controllable crystalline and electrical properties. My results proved this as well. The gallium doping was very successful and the required material properties could be reached. The crystallinity of the films could be controlled through the deposition parameters, the choice of substrate and post annealing procedures, while the electrical properties depended on the doping concentration. The atomic layer deposition of gallium oxide was a new procedure at the beginning of the project, and the used precursor was completely novel. The choice of precursor proved to be excellent, not only because uniform and smooth layers could be grown with a self-limiting and well controlled ALD process, but the growth parameters suited the specifications of our equipment perfectly. However, the versatility of Ga_2O_3 as a TCO material and the ALD deposition of the material still remain questionable. With the tuning of the deposition parameters, doping and post-annealing, a number of problems hindering the widespread use of this material could be overcome. Still, generally, it appears that the control of crystallinity of Ga_2O_3 is very cumbersome and requires heat treatments at rather high temperatures. The hydrothermal growth of this material was also successful, but especially hard to control. The grown structures are amorphous, thus their orientations and properties cannot be influenced with the seed layer. The Zn doping was effective, and resulted in improved electrical properties. As a conclusion, the control of crystallinity of the layers is cumbersome, but with the help of doping and nanostructuring this difficulty may be dodged.

Outlook

From the project, I, and our group gained important experience and knowledge, which we also shared in scientific papers. The most important for future applications are:

- The technology of ALD ZnO, and its doping with Ga is mature enough for industrial use, as it was shown by our cooperation with Epistar. Hopefully, this cooperation will continue, and there is a chance to also start a new promising cooperation with a Chinese partner to develop UV transparent TCO materials for UV LEDs. For the latter project the co-doping of ZnO with Ga and Mg might be one way, the application of gallium oxide the other.

- The technology for the preparation of a wide variety of nanostructures is very successful and promising for many applications. Currently, we are exploring their properties in water splitting and gas sensing in collaboration with other teams, therefore, this work opened new possibilities for cooperation and applications.
- There has also been considerable advance in the preparation of gallium-oxide films. The electrical properties and transmissions of the layers are well controlled, and the possibility of good quality Ohmic contacts has also been achieved. This opened the way for applications, which I will explore in the near future, especially concentrating on DUV sensors and UV transparent TCOs. Although the crystallinity of the films is far from optimal, but there are references in the literature stating that even amorphous Ga₂O₃ layers can be effective in the nanostructured form, therefore the role of hydrothermal deposition may become more important in my future work, and the disadvantages of the material may be overcome by doping and nanostructuring.
- The general knowledge gained concerning the deposition of oxide alloy films is used in our laboratory on a daily basis, and is indispensable for a number of projects, including international cooperations and industrial applications. Presently, I am trying to widen the group of oxide materials so that we will have a similarly reliable knowledge and expertise as with ZnO and Ga₂O₃. The deposition of Al₂O₃ is already such, and I am gathering growing experience in the preparation of good quality HfO₂, which would be an especially important insulating material required in our laboratory as well as by our partners. Another direction would be the preparation of vanadium oxide films, which is also a novel branch of ALD deposition, one that concerns a crucially important material for memristor and other MEMS applications, also required by a number of possible cooperations and partners of our group.

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- Zsófia Baji, Ildikó Cora, Zsolt Endre Horváth, Emil Agócs, Zoltán Szabó, Atomic layer deposition and characterisation of Zn-doped Ga₂O₃ films, submitted

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Conference presentations and posters:

- Deposition of Ga doped ZnO layers by ALD, ALD conference 2016, oral
- Preparation and characterisation of Ga₂O₃ nanostructures EMRS spring meeting 2018, poster
- Atomic layer deposition, composition and applications of Ga₂O₃ films, EMRS spring meeting 2018, oral
- Crystallisation of ALD Ga₂O₃ films
- An invited lecture (Comparison of the atomic layer deposition of ZnO and Ga₂O₃) at the Cutting edge Materials research and Nanotechnology conference was cancelled due to the pandemic