RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

PAPER

Influence of Moisture on the Electrical Properties of Solution Processed Multilayer High-k ZrO_2-Capacitors

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mareiki Kaloumenos*[a], Philipp Pacak[a], Rudolf Hoffmann[b], Dieter Spiehl[c], Klaus Hofmann[a], and Klaus Bonrad[d]

The dielectric performance of ZrO2 thin films - which were manufactured by solution deposition of a single-source precursor - strongly depends on the surrounding atmosphere. Capacitors were constructed and impedance measurements were carried out under different environments. The electrical performance under inert atmosphere in a glove box could be explained with a capacitor and a parallel resistance, whereas the behaviour in ambient air was more complex. Accordingly, further measurements were carried out in a vacuum chamber which allowed flushing with specific components of ambient air. Nitrogen and oxygen did not strongly influence the device characteristic, whereas the presence of water leads to considerable deviations. This effect could also be monitored by X-ray photon spectroscopy which indicated a change in the O1s peak attributed to surface hydroxylation. Although thicker ZrO_2 films were obtained by repeated deposition of thinner layers, the overall deposit appeared uniform and no evidence of the individual layers could be detected by Scanning Electron Microscopy. The multilayer characteristic of the film only appears by X-ray reflectometry (XRR), revealing a density of 4.4g/cm³, which is only 75% of the density of monoclinic ZrO_2 and must be attributed to porosity within the films. The corruption of the dielectric in the presence of moisture is thus an effect in the bulk and it is not restricted to the film surface.

1. Introduction

During recent years, much research has been conducted in printed inorganic electronics.[1,2,3] One of the major advantages targeted by the research in this field is the possibility of a low-cost process compared to the conventional silicon technology[4,5], not least because the processing should take place under ambient conditions and not under vacuum.[6]
Whereas materials deposited via CVD and PVD show a good quality, these processes generally require vacuum. In the conventional microelectronic technology, these vacuum processes are one of the main cost factors[7]. Additionally, they limit the size of the substrates, which should be coated. Moreover, with this processes a structuring is only possible with supplementary process steps including photolithography and etching.
Printing of functional materials is suggested as an attractive low-cost alternative, give that films can be directly structured during the deposition. It is also suitable for large-scale applications and it can take place under ambient conditions. [7] However, for a process under ambient conditions the materials also need to be suitable for such conditions.
Consequently, an identification of potential influencing factors through the environment is quite important to avoid negative influences or to develop solutions to overcome them.
One candidate for inorganic dielectrics applicable for printed field effect transistors and capacitors known from literature is ZrO_2.[8,9] Whereas semiconductors like indium zinc oxide (IZO) or indium gallium zinc oxide (IGZO) have already been studied quite well[1,10], further investigations on printed inorganic dielectrics are necessary[11,12]. Not only semiconductors but also gate dielectrics have a major impact on the performance of transistors.[13,9] Besides a high permittivity, a low leakage current density and especially no or only low degradation behaviour is required for gate dielectrics. Moreover, in contrast to semiconductors, a flawless dielectric is imperative for functional devices. Defects like holes or particles will prevent any dielectric to work properly. In addition, dielectrics are used for capacitors in many circuits - e.g. in active matrix liquid crystal displays[14] - where a low leakage current and / or only low degradation behaviour is also quite important. The degradation of dielectrics is one of the major influencing factors for the reliability of devices.[15]
In a capacitor or as gate dielectric in a thin film transistor (TFT) with top gate structure, the dielectric ZrO_2 is in direct contact with the environment, which may lead to a degradation of the device performance.[16] Even with other TFT topologies like

[a] Department of Electrical Engineering and Information Technology, Integrated Electronic Systems Lab, Technische Universität Darmstadt, Merckstr. 25, 64283 Darmstadt, Germany.
[b] Department of Chemistry, Eduard-Zintl-Institute, Inorganic Chemistry, Technische Universität Darmstadt, Alarich-Weiss-Str. 12, 64287 Darmstadt, Germany.
[c] Department of Mechanical Engineering, Institute of Printing Science and Technology, Technische Universität Darmstadt, Magdalenenstr. 2, D-64289 Darmstadt, Germany.
[d] Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany.

bottom gate, where the dielectric in the final device is covered by the semiconductor, the environment may influence the device performance through the direct contact during the process. However, this does not necessarily have to implicate a non-functional device, given that the factors causing degradation might be suppressed after the process, e.g. by encapsulation. Nonetheless, in order to apply an effective encapsulation, it is mandatory to know against which influencing effect and to understand its mechanism. From this, it could be derived whether an encapsulation is reasonable and how the device should be prepared for encapsulation to avoid including the disadvantageous influence.

From literature, it is known that ZrO_2 could be used as a humidity sensor[17] as well as oxygen sensor[18]. Therefore, the environment must have an influence on the material. According to literature, the hygroscopic nature of high-k metal oxides like ZrO_2 might cause problems in TFTs[16], while moisture is omnipresent and always difficult to avoid[19].

In this paper, impedance measurements have been used to analyse the influence of the environment on solution processed ZrO_2 capacitors. Capacitors have been used rather than transistors to investigate the effects caused through the dielectric without the influence of the semiconductor. It could be demonstrated that a degradation of the performance of the dielectric in air is caused by humidity. XPS and XRR have been used to further understand the influencing factors. The insights obtained in this paper through the passive electrical component capacitor can allow conclusions on influencing factors through the application of ZrO_2 as gate oxide in the active electrical component transistor.

Although the basically effects are known, for the research in printable inorganic dielectrics hardly any attention has been devoted to this topic up to date.

2. Experimental

The earlier published ZrO_2-Precursor[20] has been dissolved in 2-Methoxyethanol to form a solution with 10wt%. A sandwich structure was used for the capacitors with structured ITO as lower electrode and sputtered Au as top electrode, as shown in principle in Fig. 1.

The capacitance is formed by the cross-hatched area where the electrodes overlap. At the beginning of the process the solution was spin-coated for 30s at 1500rpm on the structured ITO-glass substrates. This was repeated to form multiple layers on the substrate. After each layer, the substrates were calcined on a hot plate for 1min at 350°C and for additional 5 minutes after the last layer. At this temperature, an amorphous ZrO_2 layer is formed.[10]

According to Schneider et al.[20], a temperature reduction down to 275°C could be possible for the calcination although this is not within the scope of the current study. Lower process temperatures may cause a worse film quality, which could impair the device performance[21].

The number of layers and the precursor concentration has been varied to further analyse observed device degradations.

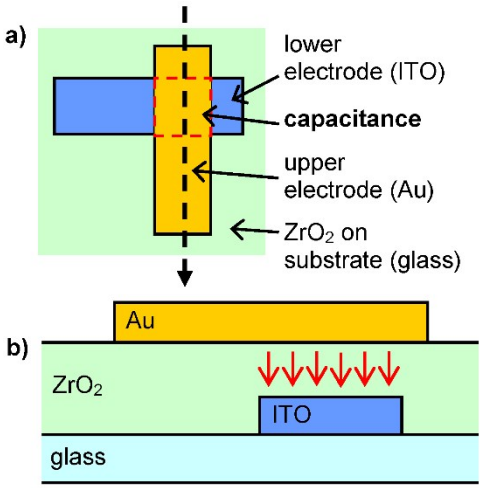


Fig. 1 Section of a substrate that shows the sandwich structure used for the capacitors (not true to scale) - a) top view and b) cross section along the dashed line in a). Seve capacitors are placed on each substrate and the substrate is much larger than the capacitors to avoid influences of the edge of the spin coated film.

In a final step, the 40nm Au top electrode was sputtered. On some devices, additional layers were applied on top. These additional layers of ZrO_2 were used to form an encapsulatio Furthermore, the precursor concentration was varied (5wt% and 15wt%) for some devices to change the thickness of the single layers inside the multilayer film. The size of the fabricated capacitors is 250µm x 250µm. As the layer thickness does not exceed 0.1% of the edge length of the capacitor, the fringing effect of the field can be neglected.[22]

Impedance measurements were performed using a ModuLab system by applying an AC voltage in the range of 1MHz down to 10mHz at an amplitude of 500mV. The ambient conditio have been varied to analyse influencing factors. An overview of the ambient conditions used can be found in Table 1. Every impedance measurement described in this paper is referenced to Table 1, where the relevant ambient conditions for the individual experiments are listed.

Tab 1. Overview about the ambient conditions used for the experiments. The room temperature for all experiments was approx. 25°C.

condition	ambient	measurement
a)	argon glove box	- after annealing for 10min at 130° (O2 <0.5ppm, H2O <0.5ppm)
b)	environmental conditions	- in air (relative humidity ~25%)
c)	vacuum chamber	- in vacuum (approx. 10^{-6}mbar) - with N_2 induced (up to 0.3mbar) - with O_2 induced (up to 1mbar) - with H_2O induced (up to 1mbar)
d)	flow box with dry air	- with a relative humidity from ~25% down to <3%

The flow box used (Table 1, condition c)) is a cabinet of 60x40x40cm with the ability to flush with dry air. The relative humidity inside this box was measured with a DKRF400 humidity sensor from Driesen + Kern GmbH. A constant low relative humidity is achieved by constant flushing. The front door could be opened to place devices and measurement tips inside or increase the humidity rapidly to the level of the surrounding atmosphere.

Beside this, the vacuum chamber (Table 1, condition d)) used for the experiments is part of a high vacuum system and has been modified for investigations like the one described. It offers the possibility to flush with selected gases and raise their partial pressure. A special appliance to measure electrical devices inside of this chamber under different conditions was used to connect the devices with the impedance measurement tool. An annealing step inside this chamber is also possible.

SEM was used to analyse the bulk morphology of the film and it was carried out in a ZEISS Leo 1530. XRR and XPS measurements were performed to measure the film density and the elemental composition, respectively. The XPS measurements were carried out in an ESCALab 250 from Thermo VG Scientific using monochromated Al Kα radiation (1486.6eV) in constant analyser energy mode with a pass energy of 50eV. The XRR take place on a Rigaku SmartLab diffraction system utilising Cu Kα radiation from a rotating anode. As incident optics, an X-ray mirror was used for beam parallelisation. On the secondary (received) side, a long soller slit with an acceptance angle of 0.112° has been installed prior to the scintillation counter.

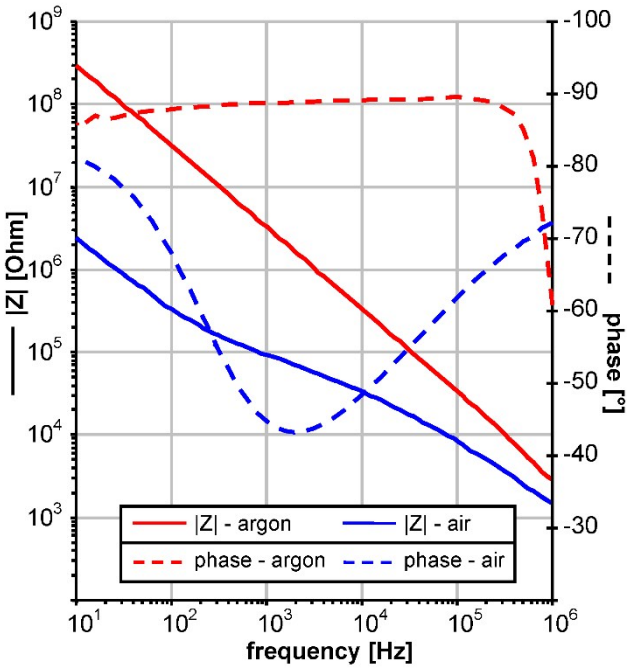


Fig. 2 a) Impedance (absolute value |Z| and phase θ) of a device measured in air (Table 1, condition b)) and after annealing the device for 10min at 130°C in argon (Table 1, condition a)). A major difference between the impedance dependent from the ambient conditions could be observed.

3. Results & Discussion

3.1 Analysis of environmental influences on ZrO_2-capacitors

For impedance measurements, the devices were transferred into a glove box with argon. An additional annealing step for 10min at 130°C was used (Table 1, condition a)). The resulting impedance shows a constant behaviour that can be fitted with a capacitor and a parallel resistance. This simple model can be explained with the geometrical capacitance of the dielectric and its bulk resistance in parallel.[23]

Fig. 2 shows the behaviour of the same device measured under argon ((Table 1, condition a)) and under environmental conditions (Table 1, condition b)), reflecting significant differences between both measurements. The model of a capacitance with a parallel resistance is no longer sufficient to explain the measured data under environmental conditions. To fit this data, additional elements would have to be added to the equivalent circuit. Nonetheless, an adequate physical model cannot be achieved without knowing the influencing factors.

For an impedance model with more than two elements several equivalent circuits will often fit to the same measured data as explained by Macdonald et al.[23]. Further investigations on the device behaviour are necessary to achieve a physical-based model.[24]

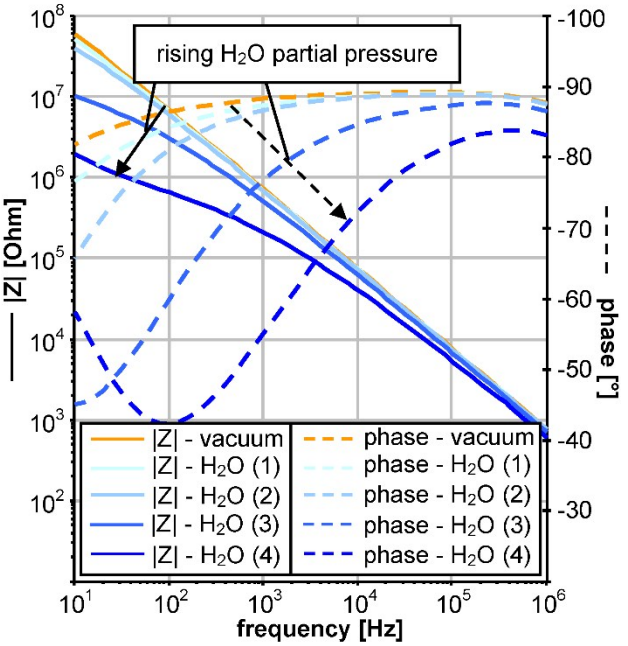


Fig. 3 Impedance (absolute value |Z| and phase θ) of a device measured after 1 day in vacuum and under the influence of H_2O in vacuum with rising H_2O partial pressure (Table 1, condition c)). A major change in the impedance behaviour could be observed immediately. Measurements (1), (2), (3) and (4) are continuous measurements while the H_2O partial pressure was rising from 0,15mbar (1) to 1mbar (4). By keeping the H_2O partial pressure constant, and saturation of the change was observed for (1) and (4) for each within 10 minutes at the level shown in the diagramm. Same occures for every other H_2O partial pressure. This change observed here is comparable with the impedance behaviour measured in air (Table 1, condition b)).

Additional impedance measurements have been carried out in a vacuum chamber (Table 1, condition c)). After several hours a performance comparable to that known after annealing in argon (Table 1, condition a)) was achieved.

By inflowing gases, the influence of N_2, O_2 and H_2O has been analysed. No significant influence of N_2 or O_2 on the impedance performance could be detected (Fig. S1). Exclusively adding H_2O shows significant influence (Fig. 3).

The humidity partial pressure in the vacuum chamber was raised in four steps from 0,15mbar to 1mbar. Within 10 min for each humidity partial pressure a saturation behaviour was observed, shown in Fig. 3 with the data (1)-(4). After the impedance had saturated, a further change was achieved through a higher humidity partial pressure.

The effect caused by H_2O in vacuum is identical to the effect observed under ambient conditions and both are reversible.

The influence of H_2O has been additionally approved in a flow box with dry air (Table 1, condition d)). During continuous impedance measurements, the relative humidity was reduced from 25% down to <3% within 30min. Subsequently, the conditions were kept constant for additional 20min. These measurements demonstrate the influence of the (Fig. 4).

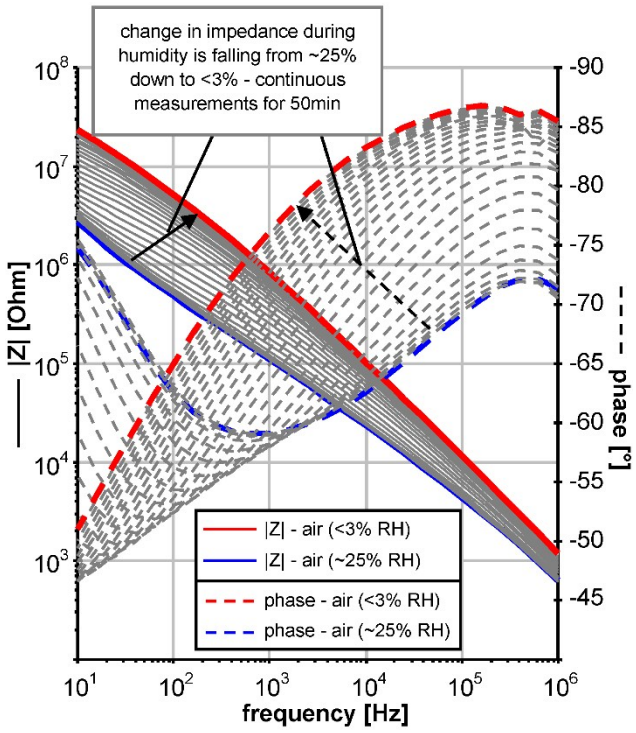


Fig. 4 Impedance (absolute value |Z| and phase θ) of a device measured continuously in a flow box in air during the relative humidity is falling from ~25% down to <3% (Table 1, condition d)). A change in the impedance towards the behaviour observed in argon (Table 1, condition a)) could be observed. Every second measurement is shown in gray between maximum and minimum humidity to depict the transition. The scattering of the phase in the high frequency regime can be neglected, it is caused by the measuring instrument.

After a certain time, the change caused through the absence of moisture starts to saturate. When the humidity is increased from <3% up to ~25%, the reaction of the system to the presence of moisture is faster and it only takes a few minutes to achieve a saturated state (Fig. 5). This behaviour can be explained by the hygroscopic nature of ZrO_2 reported in literature.[25] An annealing step like applied in argon can be used to accelerate the regeneration of the device in vacuum or dry air.

While the relative humidity was technically limited to ~25%, it can be assumed from the observed data that a higher humidity level will just cause a further change of the impedance like shown under vacuum. The change of the impedance according to the relative humidity may become independent of the surrounding relative humidity at a certain point, when the absorbability of the ZrO2 layer is reached.

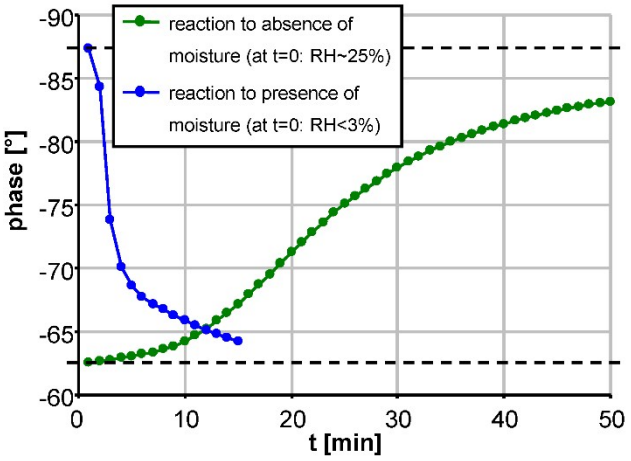


Fig. 5 Saturation behaviour of the devices performance depending on the presence or absence of moisture measured in a flow box (Table 1, condition d)). To visualize the effect the phase measured at 10kHz was extracted from continuous measurements during falling or rising humidity. Both cases started with a device in an almost saturated state. It is obvious, that the reaction to the presence of moisture is much faster than the reaction to the absence of moisture.

3.2. Morphology and influence of interfaces inside the film

The morphology of two devices with a similar overall thickness yet a different number of layers was analysed by SEM and XRR. Impedance measurements were used to examine whether the influence of humidity is associated with interfaces inside the film. No significant differences were found in the electrical performance between devices with a variable number of interfaces inside the film in argon (Table 1, condition a)). The same is true for devices measured under environmental conditions (Table 1, condition b)) (Fig. S2). No interfaces within the film can be revealed by SEM (Fig. 6). Accordingly, the two devices cannot be distinguished by these measurements. In contrast, XRR data (Fig. S3) indicates a distinct multilayer film characteristic with extractable single layer thicknesses of the uppermost layer. Multiplied with the number of layers, these single layer thicknesses are in good agreement with the observed total film thickness by SEM of approximately 200nm. Given that XRR is a quite sensitive method to determine interfaces[26,27], it becomes clear that the interfaces inside of

the film in SEM are simply not recognisable and have no huge influence on the overall device bulk morphology.

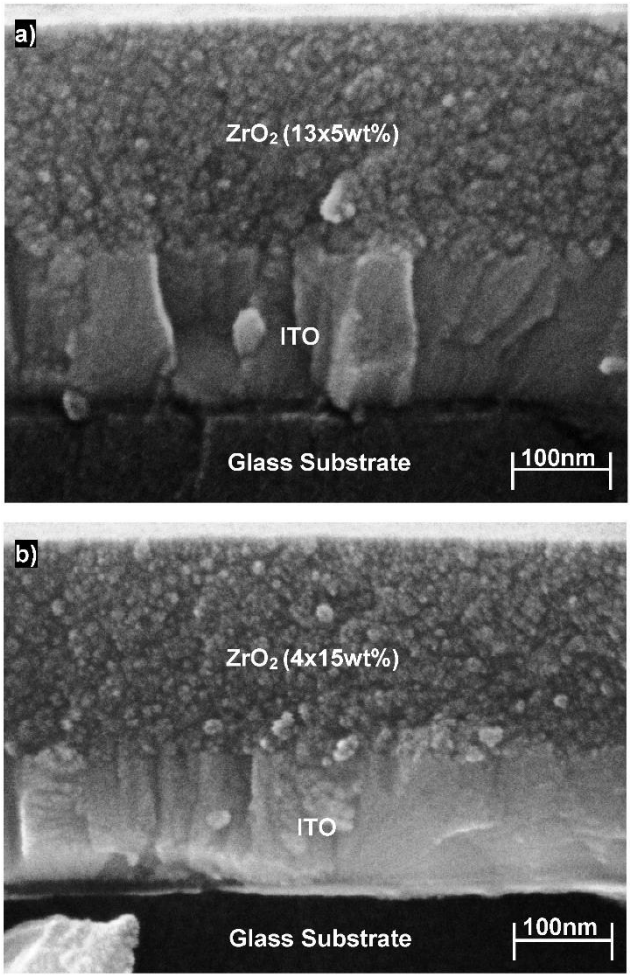


Fig. 6 SEM at the cross sections produced by breaking a) a device with 13 layers (5wt-% precursor concentration) and b) with 4 layers (15wt% precursor concentration). The top electrodes are missing. No visible difference in the bulk morphology of both films recognizable in these images.

By fitting the XRR data, it is apparent that the device with the low number of layers can only be explained with a model of low layer number, and vice versa (Fig. S3). For these devices, it is not possible to determine the exact number of layers by fitting, although the correlation between XRR measurement data and low or high number of layers in the fit is distinct.

However, although measurable interfaces exist inside the film, one can summarise that they have no influence on the electrical behaviour. There is no correlation between the boundary layers inside of the multilayer film and the influence of humidity, thus proving that the influence of the moisture affects either the surface or the bulk.

The extracted density from the XRR data is the same for both devices (4.4g/cm³), at approximately 75% of the density of monoclinic ZrO_2 (ρ_{mono}=5.89g/cm³)[28]. According to the theoretical calculations in literature[28,29], the density for a robust amorphous ZrO_2 lies in the range between 4.86g/cm³ and 5.32g/cm³. As the extracted density from XRR is lower, it can be concluded that the bulk material for these devices will probably contain defects like small pores.[28]

The reason for this porosity might be found in the decomposition process of the precursor, in which many gaseous components occur. By escaping from the film in the thermal process, these may leave pores inside of the amorphous ZrO_2.[30]

The XRR also exhibits that the surface of the films is relatively smooth as already published by Schneider et al.[20] with a roughness of approximately 6Å.

Measurements with sputtered ZrO_2 have been performed to exclude that the observed effect is caused through the electrodes or substrate used. No significant influence of humidity could be observed, thus prompting the assumption that the influence of H_2O is connected to the morphological properties of the solution processed dielectric.

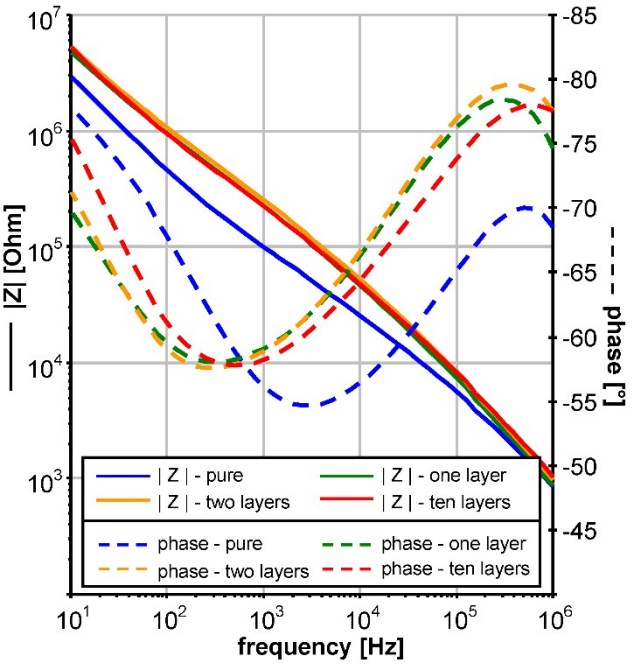


Fig. 7 Impedance (absolute value |Z| and phase θ) of four devices with different number of layers on top of the physical device measured in air (Table 1, condition b)): no encapsulation (pure), one layer, two layers and 10 layers. A difference in the impedance can be observed between measurement data achieved with encapsulation or no encapsulation, but there is no significant influence of the number of encapsulation layers observable.

3.3 Analysis of the influence of moisture through additional layers of ZrO_2 on top of the devices

As shown in Section 3.2, moisture affects either the surface or the bulk of the devices. We used additional layers of ZrO_2 on top of the capacitors as encapsulation, as described in Section 2, to further investigate the degradation caused by H_2O. The results of the impedance measurements demonstrate that one additional ZrO_2 layer placed on top of the device causes a change in the behaviour measured in air (Table 1, condition b)) (Fig. 7).

While this effect is comparable to the change caused through the absence of moisture in principle, the encapsulation layer only causes a small change. Accordingly, a state comparable to the one achieved e.g. in argon (Table 1, condition a)) cannot be observed under ambient conditions, as would be expected for a functional encapsulation against moisture. Further additional ZrO_2 layers on top of the device do not show any further improvement (Fig. 7). Even with an encapsulation layer of ZrO_2 twice as thick as the device itself, the effect caused through moisture remains present.

Annealed for 10 min at 130°C in argon (Table 1, condition a)) the devices with the encapsulation demonstrate an even better behaviour than observed by a device without encapsulation (Fig. S4). However, if measured under environmental conditions (Table 1, condition b)) again afterwards, the performance of all devices with and without encapsulation is comparable to the initial state. This suggests that the effect caused through moisture is not mainly a surface effect but rather a bulk effect, because the humidity also influences a device under a thick layer ZrO_2.

From literature it is known that moisture is attracted to ZrO_2. It tends to form surface hydroxyl groups on which moisture is able to form multiple layers.[19,31] The authors assume that the change in the electrical performance caused through the first ZrO_2 encapsulation layer of the device is related to the loss of the direct contact of the moisture multilayer on top of the ZrO_2 and the device. Nonetheless, with the bulk material being porous (Section 3.2), the presence of hydroxyl groups and moisture inside the bulk cannot be excluded.

However, with the devices being affected by moisture under a thick ZrO2-encapsulation, we are able to demonstrate, that even thick ZrO2-films can be completely interfused.

The reason for the slightly better performance of the encapsulated devices in argon can also be justified by the missing direct contact between the device and the surrounding atmosphere. According to Raghu et al.[19] the multiple moisture layers already form below the saturation pressure of moisture. Accordingly, the small amount of residual moisture in the argon glove box used for this experiment might be sufficient to influence the performance of a device without additional ZrO_2 layers as encapsulation.

3.4. XPS of ZrO_2

XPS has been performed to analyse the ZrO_2-layers produced. The overview spectra (Fig. S5) matches the expected spectra for ZrO_2 known from literature[32]. According to Häming et al.[33], the small amount of carbon found in the spectra is caused by contaminations on the sample surface. With the precursor containing nitrogen, its lack in the spectrum demonstrates it being completely decomposed.[33]

XPS measurements before and after an annealing step inside the XPS-vacuum-chamber were carried out to observe changes in the spectrum: first took place immediately after the inward transfer into the XPS chamber, followed by the second measurement after the sample was stored for 1h at approximately 130°C inside vacuum. This temperature step was chosen, due to the rapid change in the impedance caused through 10min at 130°C under argon. However, based upon the knowledge that the vacuum in the XPS chamber already influences the humidity in the film before the first measurement, a longer time was used. A control impedance measurement in argon after 1h at 130°C demonstrated a small further improvement in the device performance, comparable to that observed before. Accordingly, the effect seems to be the same.

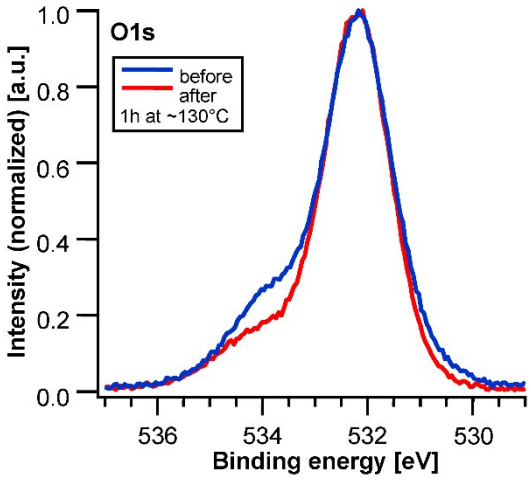


Fig. 8 O1s Peak from ZrO_2 sample directly measured per XPS after inward transfer and after tempering for 1h at ca. 130°C in vacuum.

The comparison of the individual peaks of the spectrum before and after the annealing step in vacuum shows that the peaks attributed to zirconium experienced no change due to the heat treatment. In the O1s-peak (Fig. 8), the only significant change in the spectra can be found: the shoulder of the peak becomes smaller after annealing.

Hydroxyl groups can be found on oxide surfaces caused through humidity. The part of the O1s peak that decreases, is indicative for hydroxyl groups (OH-)[34,35,36]. Accordingly, it is not only the moisture but also the originated hydroxyl groups that result in the degraded impedance behaviour detected in air, as already assumed in Section 3.3.

Given that XPS measurements can only be performed in a vacuum, the influence of moisture as it exists at normal atmosphere cannot be detected by this measurement technique. Nevertheless, the change in the XPS spectra is significant. These observations match the results achieved via device variations and impedance spectroscopy.

The differentiation between bulk and surface hydroxyl groups is not possible by XPS because it is a surface method[37]. However, the conclusion that the impedance degradation effect is caused through humidity the bulk can be deduced from the porosity of the material (Section 3.2) and has been proved by the impedance measurement results on the encapsulated devices described in Section 3.3.

A similar behaviour in XPS can be found in literature for titanium with a surface finished under air or water conditions,

whereby the height of the shoulder of the O1s-peak is also connected to the amount of hydroxyl groups.[38] Since titanium is in the same subgroup of the periodic table as zirconium, it exhibits the same electron configuration on the outermost shell, thus suggesting a similar behaviour.[39]

4. Conclusions

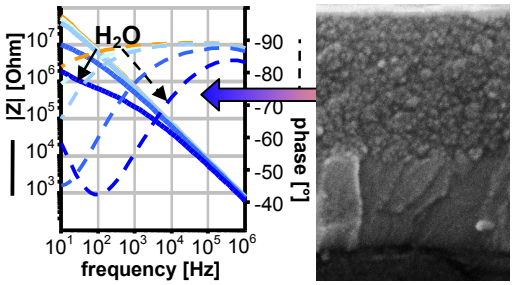
In this paper, we have demonstrated a significant influence of moisture on the performance of solution processed ZrO_2-capacitors. By contrast, N_2 and O_2 do not influence the device performance. In addition, we were able to show that the influence on the devices is neither an effect caused through the interfaces inside a device nor exclusively through a moisture layer on top of the device, but rather a bulk effect of the device: the moisture penetrates even thick encapsulation layers of the solution processed ZrO_2. XPS measurements prove a change in the amount of hydroxyl groups. XRR observed a reduced density of the multilayer films, which indicates defects or small pores inside the film. Summarising, this shows that the change in the impedance through humidity is caused by hydroxyl groups and water inside the porous film. Regarding a possible use as gate oxide in a TFT, this significant influence caused through moisture must be taken into account. Moreover, the effect described in this contribution will also significantly affect the performance of a transistor under environmental conditions.

Acknowledgements

This work is financial supported by Merck KGaA. The authors wish to acknowledge Stefan Koehl from the Merck KGaA for the SEM investigations and discussions, Dr. Joachim Brötz from the institute Strukturforschung at TU Darmstadt for the XRR measurements and discussions and Ruben Precht from the institute Surface Science at TU Darmstadt for the XPS measurements and discussions.

Notes and references

1 J. Y. Kwon, J. K. Jeong, Semicond. *Sci. Technol.* 2015, 30, 024002.
2 S. J. Kim, S. Yoon, H. J. Kim, *Jpn. J. Appl. Phys.* 2014, 53, 02BA02.
3 T. T. Baby, S. K. Garlapati, S. Dehm, M. Häming, R. Kruk, H. Hahn, S. Dasgupta, ACS Nano 2015, 9, 3075.
4 C. Avis, Y. G. Kim, J. Jang, *J. Mater. Chem. C* 2012, 22, 17415.
5 R. H. Reuss, B. R. Chalamala, in *Solution Processed Inorganic Materials*, ed. D. B. Mitzi, John Wiley & Sons Inc., New Jersey, 1, 2009, Introduction to solution-deposited inorganic electronics, 1.
6 H.-Y. Tseng, V. Subramanian, *Organic Electronics* 2011, 12, 249.
7 E. Fortunato, P. Barquinha, R. Martins, Adv. Mater. 2012, 24, 2945.
8 F.K. Shan, A. Liu, G.X. Liu, Y. Meng, E. M. Fortunato, R. Martins, *J. Disp. Technol.* 2015, 6, 541.
9 J. F. Wager, D. A. Keszler, R.E. Presley, *Transparent Electronics*, Springer Science+Business Media LLC, New York 2008.
10 J. H. Park, Y. B. Yoo, K. H. Lee, W. S. Jang, J. Y. Oh, S. S. Chae, H. K. Baik, *ACS Appl. Mater. Interfaces* 2013, 5, 410.
11 W. Xu, H. Wang, F. Xie, J. Chen, H. Cao, J.-B. Xi, *ACS Appl. Mater. Interfaces* 2015, 7, 5803.
12 J. W. Hennek, Y. Xia, K. Everaerts, M. C. Hersam, A. Facchetti, T. J. Marks, *ACS Appl. Mater. Interfaces* 2012, 4, 1614.
13 W. Yang, K. Song, Y. Jung, S. Jeong, J. Moon, *J. Mater. Chem. C* 2013, 1, 4275.
14 W. den Boer, *Active Matrix Liquid Crystal Display*, Elsevier Inc., Oxford, 2005.
15 S. Lombardo, J. H. Stathis, B. P. Linder, K. L. Pey, F. Palumbo, C. H. Tung, *J. Appl. Phys.* 2005, 98, 121301.
16 S. Jeon, H. Hwang, *J. Appl. Phys.* 2003, 93, 6393.
17 I. B. Vinnik, I. V. Uvarova, V. S. Zenkov, *Powder Metall. Met. Ceram.* 1998, 37, 632.
18 A. D. Brailsford, M. Yussouff, E.M. Logothetis, *Sens. Actuator B-Chem.* 1997, 44, 321.
19 R. Raghu, C. Yim, F. Shadman, Susceptibility of SiO2, *AIChE J.* 2004, 50, 1881.
20 J. J. Schneider, R. C. Hofmann, A. Issanin, S. Dilfer, *Mater. Sci. Eng., B* 2011, 176, 965.
21 S. R. Thomas, P. Pattanasattayavong, T. D. Anthopoulos, Chem. Soc. Rev. 2013, 42, 6910.
22 A. Hastings, *The Art of Analog Layout*, Pearson Prentice Hall, New Jersey, 2006.
23 J. R. Macdonald, W. B. Johnson, in: *Impedance Spectroscopy*, ed. E. Barsoukov, J. R. Macdonald, John Wiley & Sons Inc., New Jersey, 2, 2005, Fundamentals of impedance spectroscopy,1.
24 V. Petrovsky, T. Petrovsky, S. Kamlapurkar, F. Dogan, *J. Am. Ceram. Soc.* 2008, 91, 1817.
25 Y. Zhao, *Materials* 2012, 5, 1413.
26 S. Kohli, C. D. Rithner, P. K. Dorhout, A. M. Dummer, C. S. Menoni, *Rev. Sci. Instrum.* 2005, 76, 023906.
27 K. Stoev, K. Sakurai, *The Rigaku Journal* 1997, 14, 22.
28 X. Zhao, D. Ceresoli, D. Vanderbilt, *Phys. Rev. B* 2005, 71, 085107.
29 D. Ceresoli, D. Vanderbilt, *Phys. Rev. B* 2006, 74, 125108.
30 D. E. Walker, M. Major, M. B. Yazdi, A. Klyszcz, M. Häming, K. Bonrad, C. Melzer, W. Donner, H. von Seggern, *ACS Appl. Mater. Interfaces* 2012, 4, 6835.
31 N. Rana, R. Raghu, E. Shero, F. Shadman, *Appl. Surf. Sci.* 2003, 205, 160.
32 B. V. Crist, *Handbooks of Monochromatic XPS Spectra Volume 2 – Commercially Pure Binary Oxides*, XPS International LLC, California, 2005.
33 M. Häming, A. Issanin, D. Walker, H. von Seggern, W. Jägermann, K. Bonrad, *J. Phys. Chem. C* 2014, 118, 12826.
34 T. Hanawa, *J. Periodontal Implant Sci.* 2001, 41, 263.
35 J.-C. Dupin, D. Gonbeau, P. Vinatier, A. Levasseur, *Phys. Chem. Chem. Phys.* 2000, 2, 1319.
36 J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Inc., Minnesota, 1995.
37 C.J. Powell, A. Jablonski, *Nucl. Instrum. Methods Phys. Res. A* 2009, 601, 54.
38 T. Onoki, in *Biomaterials Science and Engineering*, ed. R. Pignatello, InTech, Rijeka, 1, 2011, Porous apatite coating on various titanium metallic materials via low temperature processing, 67.
39 D. K. Jha, *Atomic and Nuclear Structure*, Discovery Publishing House, New Delhi, 2004.



Significant influence of moisture on performance of solution processed ZrO_2-capacitors was found to be connected to low material density.