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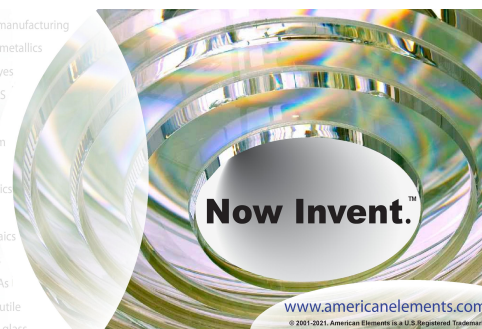
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ABSTRACT

The amorphous *n*-type multi-cation and multi-anion compound zinc magnesium oxynitride was fabricated by reactive long-throw magnetron co-sputtering from a metallic zinc and a metallic magnesium target. We achieved magnesium cation compositions in the thin films between 1 at. % and 7.5 at. % by varying the magnesium target power (variable-power approach) and compared this approach to a continuous composition spread. Both approaches lead to a reduction in Zn²⁺, an addition of Mg²⁺ cations, and a correlated increase in the oxygen content. Both these methods have the same effect on the optoelectrical properties: The increased magnesium content leads to a systematic decrease in the free charge carrier concentration regime from 10¹⁹ cm⁻³ to 10¹⁵ cm⁻³, a decrease in Hall mobility from 54 cm² V⁻¹ s⁻¹ to 9 cm² V⁻¹ s⁻¹, and a spectral shift of the absorption edge from 1.3 eV to 1.7 eV. The amorphous phase of zinc magnesium oxynitride is maintained until MgO crystallites form at a magnesium content ≥ 3 at. %. The electrical properties of the zinc magnesium oxynitride thin films show excellent long-term stability for at least 12 months.

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I. INTRODUCTION

Research on amorphous oxide semiconductor (AOS) materials developed rapidly over the last few decades driven by the search for advances in thin-film transistors (TFTs) for display technologies (e.g., 3D high-resolution) and for performance optimization of sensing networks on flexible substrates (e.g., radio-frequency identification chips) that can be incorporated into *smart clothing*. AOS materials, such as amorphous indium gallium zinc oxide (a-IGZO), and the indium-free alternatives, amorphous zinc tin oxide (a-ZTO) and amorphous zinc oxynitride (a-ZnON), combine various advantages compared to polycrystalline semiconductors: they can be fabricated by magnetron sputtering enabling cost-effective deposition at low temperatures on large areas,¹ a low surface roughness and high uniformity, mechanical flexibility for the deposition on bendable plastic substrates,^{2,3} and at the same time high electron mobilities

$\mu > 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ suitable for fast-switching TFT applications close to the thermodynamic limit.^{4–7} It is well known that AOS properties can be easily tuned by varying cationic or anionic disorder.^{8–10} These disorder dependencies have been extensively studied to optimize device performance of the well established multi-cation compounds a-IGZO¹¹ and a-ZTO.^{12–15} However, a-ZnON, as the most promising amorphous multi-anion compound with outstanding charge carrier mobilities up to $\mu_{\text{Hall}} \approx 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{16,17} has only been studied in depth regarding anion variation^{18,19} but very rarely in terms of cation variation. There are reports on amorphous and polycrystalline zinc tin oxynitride^{20–22} and zinc gallium oxynitride TFTs.²³ Amorphous ZnON has been proven to be a suitable material for metal-insulator-semiconductor field-effect transistors (MISFETs),^{24–26,29} and quite recently, metal-semiconductor field-effect transistors (MESFETs)²⁷ have been reported. However, the free charge carrier concentrations of a-ZnON are not easily tunable below $n < 10^{18} \text{ cm}^{-3}$ limiting pn-diode and Schottky-diode

performance. Even though there are reports on a-ZnON with $n < 10^{18} \text{ cm}^{-3}$, there are scarcely published results on pn-diodes with n-type ZnON. A further known disadvantage of the a-ZnON thin films is the poor air-stability that causes a degradation of TFT performance.²⁸

The aim of this work is to investigate the free charge carrier tunability of a-ZnON by the addition of magnesium cations while maintaining the amorphous phase of the material and a high electron mobility. Moreover, the effect of magnesium incorporation on the absorption behavior of the non-transparent material a-ZnON with an absorption edge of $E = 1.3 \text{ eV}$ is analyzed. By incorporation of magnesium cations, we expect an absorption edge shift to higher energies comparable to the alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$.²⁹

We realize the magnesium cation incorporation by reactive radio-frequency magnetron co-sputtering from a metallic zinc and a metallic magnesium target in nitrogen and oxygen atmosphere. The composition of the fabricated zinc magnesium oxynitride (termed chemically non-exactly ZnMgON) is altered by magnesium target power variation for single samples (variable-power approach, VPA) and by fabricating a continuous composition spread (CCS) gradient. The effects of changes in chemical composition on the electrical and optical properties are studied using Hall effect measurements and spectroscopic ellipsometry, respectively. Furthermore, we investigate the crystallization effects that occur with the increase in magnesium cation concentrations using X-ray diffraction (XRD) and study the bonding preferences of magnesium cations using X-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL METHODS

The ZnMgON thin films were co-sputtered from a metallic zinc (99.99% purity) and a metallic magnesium target (99.99% purity) using a radio-frequency magnetron sputtering system from *Mantis Deposition* with a target-to-substrate distance of 25 cm. The targets were pre-sputtered for 10 min in argon atmosphere to remove surface contamination. In addition, N_2 and O_2 gases were introduced at a gas inlet close to the zinc target for reactive sputtering. In total, a sputter pressure of $p = (1.35 \pm 0.05) \times 10^{-3} \text{ mbar}$ was achieved with flow rates of 15 sccm Ar, 20 sccm N_2 , and 1 sccm O_2 . The a-ZnON reference sample was deposited from the single zinc target at $p = (3.30 \pm 0.05) \times 10^{-3} \text{ mbar}$ with flow rates of 10 sccm Ar, 100 sccm N_2 , and 1 sccm O_2 . The magnesium concentration in the sputtered films was varied in two different ways: in a first approach, the power at the zinc target was kept constant, $P(\text{Zn}) = 50 \text{ W}$, and the power at the magnesium target was varied, $P(\text{Mg}) = 20 \text{ W} - 50 \text{ W}$ (VPA). In this case, the thin films were deposited on $10 \times 10 \text{ mm}^2$ CORNING Eagle XG glass substrates with substrate holder rotation to obtain a homogeneous chemical composition. In a second approach, the power at both targets is kept constant at $P(\text{Zn}, \text{Mg}) = 50 \text{ W}$, and without substrate rotation, a continuous composition spread (CCS)^{30,31} is realized on a $50 \times 50 \text{ mm}^2$ CORNING Eagle XG substrate. The film thickness was determined using spectroscopic ellipsometry and ranges between 80 nm and 150 nm.

To determine the cation ratio of zinc and magnesium and the anion ratio of nitrogen and oxygen, energy dispersive X-ray spectroscopy (EDX) was conducted. An acceleration voltage, small

enough to not penetrate the substrate, of 4 kV was used. The K_α line at 1.253 keV for magnesium and the L_α line at 1.012 keV for zinc were analyzed. The distinction between the K_α line at 0.392 keV for nitrogen and the K_α line at 0.525 keV for oxygen is difficult due to the bremsstrahlung background. Thus, our EDX measurements only give relative changes and ratios and no reliable absolute elemental compositions. For the CCS sample, an EDX line scan along the concentration gradient was performed.

The electrical properties of the thin films were obtained by Hall effect measurements in van-der-Pauw geometry with four ohmic gold contacts at the corners of the sample. The measurements were conducted at room temperature using a Hall effect setup with a magnetic field of 0.43 T. The $50 \times 50 \text{ mm}^2$ substrate was cut into $5 \times 5 \text{ mm}^2$ pieces along the gradient for evaluation. The variation of the magnesium cation ratio $\text{Mg}/(\text{Mg} + \text{Zn})$ on such samples is typically 0.3 at. %, and the variation of the oxygen anion ratio $\text{O}/(\text{O} + \text{N})$ is 1.1 at. %.

The dielectric function (DF) $\epsilon = \epsilon_1 + i\epsilon_2$, in the spectral range of 0.7 eV–8.0 eV, was determined from the spectroscopic ellipsometry³² measurements using commercial ellipsometers (RC2 and VUV-VASE, J.A. Woollam Co.). We employ a substrate-film-roughness layer model in a transfer-matrix algorithm for modeling. The substrate DF is obtained from a reference measurement and the surface roughness is modeled in the effective-medium approximation³³ (50% film, 50% void). The line shape of the thin film DF is given by $\epsilon = \sum_{j=1}^3 \epsilon_j^{\text{TL}} + \epsilon^{\text{G}}$, where ϵ_j^{TL} are the standard Tauc–Lorentz oscillators^{34,35} with common³⁶ Tauc gap parameter E_{Tauc} . DF contributions from higher photon energies are taken into account by a Gaussian oscillator ϵ^{G} .³⁷ The absorption coefficient was calculated from the DF.

The structural properties of the thin films were evaluated using X-ray diffraction (XRD) 2θ – ω wide-angle scans to investigate the amorphous or possibly crystalline phases of ZnMgON . A PANalytical X'pert PRO MRD diffractometer with Cu K_α radiation was used. To increase the signal-to-noise ratio, the measurement time per step was set to 300 s/2.5°. The CCS sample is measured in a 1D scanning line mode for 25 s/2.5°.

Depth-resolved X-ray photoelectron spectroscopy (XPS) measurements were performed at a JEOL JPS-9030 setup, using the radiation of a monochromatic Al x-ray source, to investigate the composition and bonding environment. Argon at a pressure of $3 \times 10^{-4} \text{ mbar}$ and with an acceleration energy of 300 eV was used for depth profiling via sputtering to analyze the thin film properties as a function of distance from the sample surface and to avoid the influence of surface contamination.

III. EXPERIMENTAL RESULTS

A. Chemical composition

Measurements of the chemical composition using EDX show that the magnesium cation ratio $\text{Mg}/(\text{Mg} + \text{Zn})$ can be varied by the VPA and by the CCS approach. In the first case, varying the power at the magnesium target between 20 W and 50 W while keeping the power at the zinc target constant $P(\text{Zn}) = 50 \text{ W}$ leads to relative magnesium cation concentrations between 1 at. % and 7.5 at. %, as illustrated in Fig. 1(a). In the second case, concentrations of $\text{Mg}/(\text{Mg} + \text{Zn}) = 3 \text{ at. \%}$ to 5.5 at. % along the diagonal of the

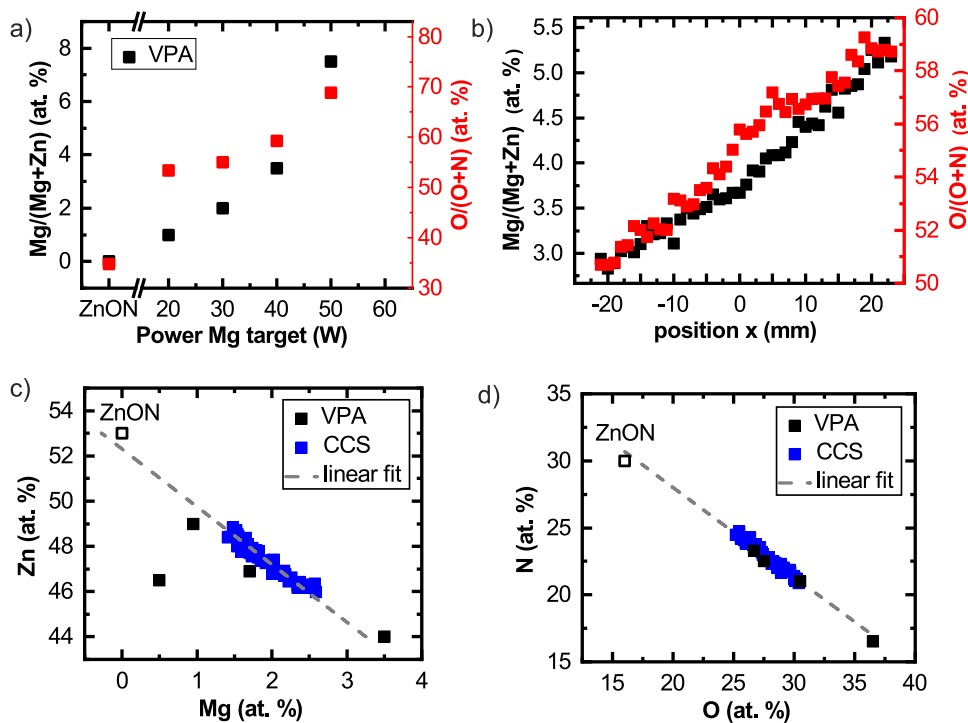


FIG. 1. Chemical composition determined with energy-dispersive X-ray spectroscopy (EDX): The magnesium cation concentration $\text{Mg}/(\text{Mg} + \text{Zn})$ and the oxygen anion concentration $\text{O}/(\text{O} + \text{N})$ for (a) the variable-power approach with constant $P(\text{Zn target}) = 50 \text{ W}$ and (b) the continuous composition spread. The ratios between (c) the magnesium and zinc cation content and (d) the oxygen and nitrogen anion content are compared for both approaches.

substrate are obtained, as shown in Fig. 1(b). The total magnesium concentration increases with the decrease in zinc concentration, as shown in Fig. 1(c). Whereas the reference a-ZnON thin film has a zinc content of 53 at. %, the zinc content of ZnMgON decreases down to 44 at. %. This implies a substitution of Zn^{2+} with Mg^{2+} cations, which is expected due to the similar ionic radii of Mg^{2+} and Zn^{2+} cations of $0.74 \text{ \AA}$ and $0.72 \text{ \AA}$,³⁸ respectively. Under the specific growth conditions, we found from the slope in Fig. 1(c) that ten zinc atoms are replaced by four magnesium atoms. Simultaneously to the cation substitution, the nitrogen content decreases from 30 at. % down to 17 at. % by increasing oxygen content, and a nitrogen-to-oxygen ratio of 7:10 is observed under the chosen growth parameters [Fig. 1(d)]. This implies that higher magnesium contents are always accompanied by higher oxygen contents. The oxygen anion ratio correlates positively with the magnesium cation ratio: It increases from $\text{O}/(\text{O} + \text{N}) = 35 \text{ at. \%}$ for a-ZnON up to 67 at. % for the VPA and up to 59 at. % for the CCS approach, as seen in Figs. 1(a) and 1(b). In summary, we can derive the following molecular formula from the zinc, oxygen, and nitrogen content in dependence on the magnesium content by linear fitting (cf. Eqs. S1–S4 in the [supplementary material](#): $\text{Mg}_x\text{Zn}_{52-2.5x}\text{O}_{19+4.8x}\text{N}_{29-3.2x}$ with x in atomic percent).

B. Electrical properties

The electrical properties of two sample series with Mg target power variation deposited 6 months apart, which are measured at room temperature, are presented in Fig. 2. The higher charge carrier concentrations in the series reproduced later can be attributed to an altered target condition due to the erosion track formation,

leading to slightly different deposition conditions despite using nominally identical sputter parameters. Taking this into account, we found similar electrical properties for the VPA and the CCS approaches. The electrical properties of the ZnMgON thin films are strongly related to the chemical composition. An exact differentiation between the cationic $\text{Mg}/(\text{Mg} + \text{Zn})$ and anionic influence $\text{O}/(\text{O} + \text{N})$ is not possible because of the positively correlated magnesium and oxygen content. With the increase in magnesium cation concentration up to 7.5 at. %, the free charge carrier concentration n_{Hall} is significantly reduced from 10^{19} cm^{-3} for

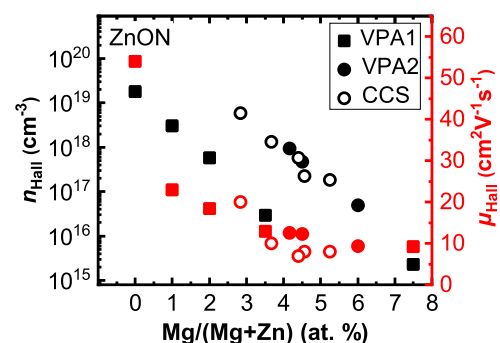


FIG. 2. Electrical properties of a-ZnON and ZnMgON thin films at room temperature: free electron charge carrier concentration n_{Hall} and Hall mobility μ_{Hall} decrease with the increase in magnesium content. Due to target variations between sample series VPA1 and VPA2, run 6 months apart, we observe an offset in charge carrier concentration n_{Hall} . The results of the CCS are in good agreement with the magnesium power variation for single samples.

a-ZnON to 10^{15} cm^{-3} . This reduction can be explained by the correlated increase in oxygen. The doping in a-ZnON is assigned to nitrogen related defects³⁹ and more specific to undercoordinated cations where missing nitrogen anions leave vacancy-like defects as shallow donors similar to Zn_3N_2 .^{40,41} An increase in oxygen anion concentration decreases the amount of undercoordinated cations and the amount of donors.

The electron Hall mobility μ_{Hall} decreases by decreasing charge carrier concentration from $54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a-ZnON to $9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ZnMgON. Likewise, the reduction in mobility can be attributed to the changes in the anion ratio with correlated Mg incorporation: a higher oxygen content and lower nitrogen content leads to lower mobilities as already observed for a-ZnON.³⁹ A further important effect causing lower electron mobilities is the formation of the crystalline phases MgO and ZnO as shown in Sec. III D that enhances grain boundary scattering. It is notable that for $\text{Mg}/(\text{Mg} + \text{Zn}) \geq 4 \text{ at. \%}$, a *saturation effect* occurs: there is no further decrease in mobility even though the magnesium concentration increases.

The electrical properties of the ZnMgON thin films are highly stable over time. The thin films were stored in a desiccator ensuring a constant, low-humidity air atmosphere, and even for storage times longer than 12 months, no significant changes in the electrical properties were observed, as presented in Fig. S1 in the [supplementary material](#). This is remarkable since a-ZnON is known for its poor air stability.²⁸

C. Optical properties

The dielectric function and the calculated absorption coefficients of two single VPA samples ZnMgON with $\text{Mg}/(\text{Mg} + \text{Zn}) = 3.5 \text{ at. \%}$ and $7.5 \text{ at. \%}$ were compared to a-ZnON, as shown in Figs. 3(a) and 3(b). The model parameters, the mean-square errors (MSE), and the thickness values are tabulated in the [supplementary material](#) (Table S1). The optical absorption of ZnMgON in the visible spectrum is reduced in the range of 1.1 eV – 2.7 eV . The absorption edge, defined here as the energy at which $\alpha = 10^4 \text{ cm}^{-1}$, shifts from 1.3 eV to 1.7 eV and accordingly the obtained Tauc gap parameter increases with the magnesium concentration: for the VPA from 0.96 eV to 1.45 eV for $\text{Mg}/(\text{Mg} + \text{Zn}) = 7.5 \text{ at. \%}$ and for the CCS from $E_{\text{Tauc}} = 1.25 \text{ eV}$ – 1.4 eV for $\text{Mg}/(\text{Mg} + \text{Zn}) = 3 \text{ at. \%}$ to $5.5 \text{ at. \%}$. In general, it is visible in the DF ϵ_2 that a-ZnON and a-ZnMgON show a typical amorphous characteristic compared to the sharp band edges in the DF of crystalline ZnO⁴² and MgO shown in Fig. 3(a) for comparison. The optical absorption edge of a-ZnON is reduced compared to ZnO with $E \leq 3.36 \text{ eV}$. This is due to the occupation of N 2p orbitals that shift the valence band edge upwards.²² For the reduction in absorption of a-ZnMgON compared to a-ZnON, two effects are responsible: First, for a-ZnON the conduction band minimum consists mainly of Zn 4s orbitals similar to Zn_3N_2 .^{40,41} Cation addition leads to additional Mg s-orbitals overlapping with the Zn s-orbitals creating an upward shift of the conduction band minimum. Second, less N 2p orbitals close to the valence band edge are occupied

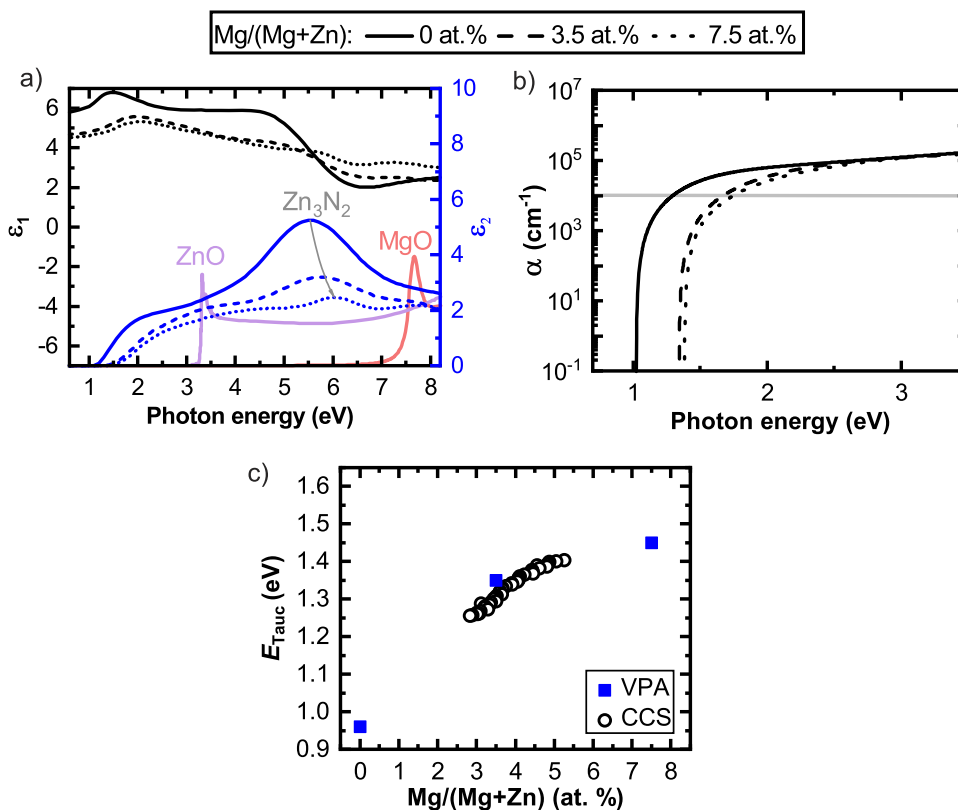


FIG. 3. (a) Dielectric function (DF) $\epsilon = \epsilon_1 + i\epsilon_2$ of amorphous ZnON and ZnMgON fabricated by VPA compared to the DF of the binary crystalline compounds ZnO⁴² and MgO in the spectral range of 0.7 eV – 8.0 eV . The peak at $\epsilon_2 \approx 6 \text{ eV}$ may be attributed to the binary Zn_3N_2 compound. (b) Absorption coefficient of a-ZnON and ZnMgON thin films fabricated by VPA obtained from the imaginary part of the dielectric function ϵ_2 (inset). (c) The Tauc gap parameters E_{Tauc} determined from the coupled Tauc-Lorentz model. The VPA samples are quantitatively comparable to the CCS.

leading to less absorbance due to the decreasing nitrogen content in a-ZnMgON compared to a-ZnON.

An additional absorption feature is observed in the DF ε_2 at approximately 5.5 eV–6 eV, as indicated in Fig. 3(b). It shifts to higher energies for the increase in Mg/(Mg + Zn) content and the absorption decreases with the decrease in nitrogen content in the thin films. The peak is not visible in the DF of crystalline ZnO⁴² and MgO and, therefore, may be attributed to the binary Zn₃N₂ compound with reference to Jiang *et al.*,⁴³ who performed spectroscopic ellipsometry on Zn₃N₂ thin films presenting a maximum in the extinction coefficient at ≈ 6 eV. Furthermore, DFT calculations on bulk Zn₃N₂⁴⁴ reveal a maximum at ≈ 6 eV in the calculated density of states function.

The broad peak structure in ε_2 at $E = 7.67$ eV observed for ZnMgON with the increase in magnesium content can be assigned to the occurrence of crystalline MgO phases as a comparison to the DF of monocrystalline MgO.⁴²

The results of the CCS sample are in good agreement with the VPA samples [Fig. 3(c)]. As already observed for the electrical properties, a *saturation effect* is visible. The absorption edge shift does not increase linearly with the magnesium content and shows a saturation at 3.5 at. % and the Tauc gap increases slightly further with a saturation between 3.5 at. % and 7.5 at. %.

D. Structural properties

The diffraction patterns of single sample ZnMgON thin films grown with magnesium concentrations between 1 at. % and 7.5 at. % are shown in Fig. 4(a). In addition, the results of the CCS with Mg/(Mg + Zn) = 3 at. % to 5.5 at. % are presented in Figs. 4(b)

and 4(c). The diffraction peaks of the binary compounds zinc oxide in crystalline wurtzite phases (100), (002), and (101) and magnesium oxide in crystalline cubic phases (111), (200), and (220) are indicated. The peak at $2\theta = 44.6^\circ$ is a measurement artifact of the sample holder. The ZnMgON thin films are x-ray amorphous up to 3.5 at. % magnesium content. With the increase in magnesium content, the x-ray diffractograms show a broad peak at $2\theta \approx 37^\circ$ that corresponds to the MgO (111) peak at $2\theta = 36.9^\circ$.⁴⁵ The vertical expansion of the MgO crystallites can be approximated to 5 nm using the Scherrer equation,

$$L_z \approx \frac{\lambda}{\Delta(2\theta) \cos(\theta)}, \quad (1)$$

with $\lambda = 1.54$ (Cu K α radiation) and the FWHM $\Delta(2\theta)$ at the peak position 2θ . For magnesium concentrations ≥ 7.5 at. %, the character of the crystallites changes: The MgO (111) peak vanishes and an asymmetric peak emerges at $2\theta \approx 33.7^\circ$ with a broad shoulder at $2\theta \approx 35^\circ$. This feature can be assigned to the (002) peak at $2\theta = 34.42^\circ$, indicating a formation of *c*-oriented ZnO crystallites with the lattice constant $c \approx 5.31(3)$ Å slightly higher than the reference value $c = 5.204(2)$ Å.⁴⁶ This can be related to the corresponding oxygen increase as expressed in the molecular formula in Sec. III A and illustrated in Fig. 1(b). The broad shoulder of the peak at $2\theta \approx 35^\circ$ might be attributed to the formation of the Mg_xZn_{1-x}O wurtzite phase with a broad distribution of the out of plane lattice constant $c \approx 5.12(3)$ Å, smaller compared to ZnO. However, according to Ohtomo *et al.*,^{29,47} such a lattice shift of 0.19 Å is not expected for Mg_xZn_{1-x}O with $x < 0.5$, which is an argument against Mg_xZn_{1-x}O formation.

In addition to the MgO crystallites observed in XRD, depth-dependent XPS analysis indicates the formation of Mg–O bonds.

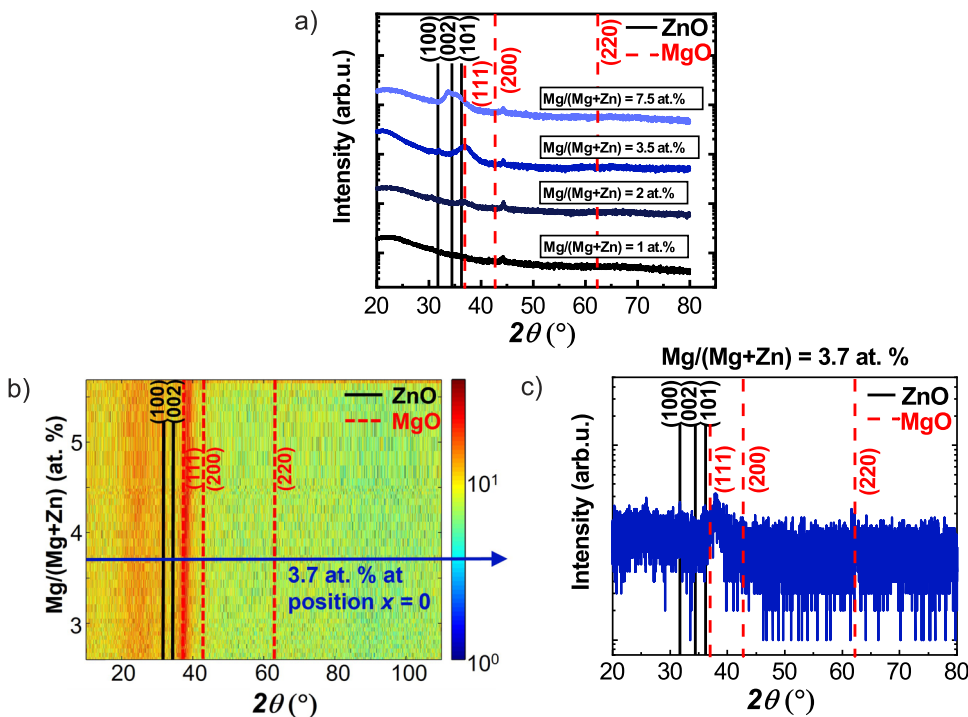


FIG. 4. XRD 2θ - ω -scans of ZnMgON as a function of the magnesium content. As a reference, the theoretically expected peaks of wurtzite ZnO (100), (002), and (101) and cubic MgO (111), (200), and (220) are indicated. (a) Diffractograms of individual samples grown using different powers at the Mg sputter target. (b) X-ray diffractogram of the CCS with MgO (111) phase for Mg/(Mg + Zn) = 3 to 5.5 at. %. (c) X-ray diffractogram selected from position $x = 0$ with Mg/(Mg + Zn) = 3.7 at. %.

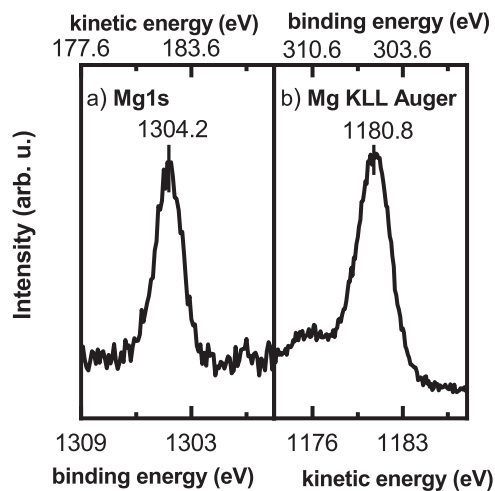


FIG. 5. XPS-spectra of ZnMgON thin films with $\text{Mg}/(\text{Mg} + \text{Zn}) = 5.5$ at. % fabricated by VPA: (a) Mg1s core level and (b) Mg KLL Auger peak positions yield an Auger parameter of 998.4 eV, indicating the formation of Mg-O bonds.

The thin films with $\text{Mg}/(\text{Mg} + \text{Zn}) = 5.5$ at. % fabricated by VPA show a Mg1s binding energy of 1304.2 eV [Fig. 5(a)] and a kinetic energy of the Mg KLL Auger peak of 1180.8 eV [Fig. 5(b)], yielding an Auger parameter of 998.4 eV, a clear indication for the formation of Mg-O bonds.⁴⁸ Overall, the measured nitrogen concentration of 6 ± 1 at. % is too low compared with the published results for a-ZnON.¹⁶ This might be an effect of the overall denitrification of the films due to argon sputtering during XPS depth profiling as observed by Futsuhara *et al.*⁴⁹ This makes the detection of Mg-N bonds very unlikely, and the observed peaks in XPS can be unambiguously assigned to the Mg-O bond.

IV. DISCUSSION

We propose the following structural model to explain our findings: a-ZnON is a multiple phase system with an amorphous ZnON phase and nanocrystalline wurtzite ZnO and cubic Zn_3N_2 as already proposed by Lee *et al.*²² When magnesium is added, two processes are considered: first, the Mg cations are incorporated in the amorphous ZnON matrix as a substitute for Zn cations and amorphous ZnMgON forms. The XRD data for small magnesium concentrations and the SE data, strongly indicating subband gap states below the band edge of ZnO with $E \leq 3.36$ eV,⁵⁰ support this hypothesis. The reduction in zinc with the increase in magnesium content gives evidence for a cationic substitution [Fig. 1(c)]. Second, an additional crystalline cubic MgO phase forms for $\text{Mg}/(\text{Mg} + \text{Zn}) \geq 3$ at. %. The MgO oscillations in the DF at $E = 7.67$ eV, the emerging MgO (111) reflex in the XRD, and the Mg-O bonding observed in XPS are strong indications for this crystallization. We assume that these two processes happen simultaneously. However, the formation of the amorphous ZnMgON phase decreases with the increase in the magnesium content in favor of the formation of MgO crystals. The increasing amount of Mg-O bonds with the increase in magnesium content as observed in XPS (Fig. 5) and the correlated magnesium

and oxygen increase [Fig. 1(d)] strengthen this hypothesis. In addition to the MgO crystallites, more ZnO crystallites form with the increase in magnesium and correlated oxygen content.

This structural model can explain the observed changes in the electrical and optical properties of a-ZnMgON compared to a-ZnON for $\text{Mg}/(\text{Mg} + \text{Zn}) \geq 3$ at. %–4 at. % and gives an explanation for the saturation effect.

The effect of the cationic addition is summarized in Fig. 6. Three different material regimes are obtained: the homogeneous amorphous alloy ZnMgON, the amorphous ZnMgON matrix with MgO phase separation, and third with MgO and ZnO phase separation. The formation of ZnMgON phase leads to a shift in the absorption edge to higher energies, as already described in Sec. III C. When, instead of Mg incorporation in the amorphous ZnMgON matrix, MgO crystallites with $E_G = 7.67$ eV are formed, the position of the absorption edge of the amorphous ZnMgON does not change. This explains the observed saturation effect for the optical properties: Although the overall magnesium composition is increased, the Tauc gap E_{Tauc} remains in principle constant. Regarding the electrical properties, the charge carrier concentration is tunable with the increase in Mg content. One important factor to explain the decrease in carrier concentration and the drop in charge carrier mobility especially for $\text{Mg}/(\text{Mg} + \text{Zn}) \leq 2$ at. % is the change in anion ratio, as discussed in Sec. III B. Furthermore, the addition of magnesium cation and the related widening of the optical bandgap from 1.3 eV to 1.7 eV can lead to changes in the conduction band

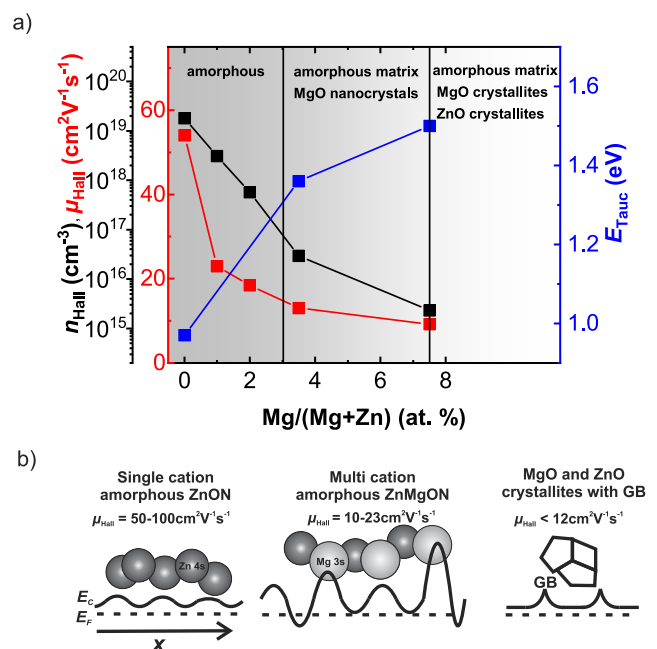


FIG. 6. (a) Tunability of charge carrier concentration of ZnMgON by the addition of magnesium cations with the decrease in the charge carrier mobility and the increase in the absorption edge. The amorphous phase is maintained up to a magnesium cation concentration of $\text{Mg}/(\text{Mg} + \text{Zn}) = 3$ at. %. (b) Assumed schematic band diagrams with related charge carrier mobilities of a-ZnON, a-ZnMgON, and a crystalline MgO or ZnO phase with grain boundary (GB) scattering.

dispersion having a strong impact on the electrical properties. Assuming that the donor level of a-ZnON stays constant with respect to the vacuum level under magnesium cation addition, then the changes in charge carrier concentration from 10^{19} cm^{-3} for a-ZnON to 10^{15} cm^{-3} can already be explained by an upward shift of the mobility edge in the range of $\approx 0.23 \text{ eV}$. The remaining 0.17 eV could then be assigned to the downward shift of the valence band caused by the less occupied N 2p orbitals. Light metal cations, such as magnesium, are prone to lower dispersion relations of the conduction band minimum, which leads, therefore, to a higher electron effective mass explaining the lower charge carrier mobilities for ZnMgON.⁵¹

As known for disordered amorphous materials, the percolation random barrier model can be considered to describe the charge carrier transport in more detail.^{52,53} The addition of magnesium cations might have an effect on the potential fluctuations of the mobility edge and therewith change the transport behavior. Here, the differences in potential landscape between the single cation a-ZnON and the multi-cation ZnMgON are especially interesting. For further verification, temperature dependent Hall-effect measurements are necessary.

For higher magnesium concentrations $\text{Mg}/(\text{Mg} + \text{Zn}) \geq 3 \text{ at. \%}$, grain boundary scattering occurs and charge carrier mobilities are limited to $\mu_{\text{Hall}} \leq 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This *saturation effect* in charge carrier mobility can be assigned to this dominance of grain boundary scattering. The assumed schematic band diagrams with the related charge carrier mobilities of the single cation a-ZnON, the multi-cation a-ZnMgON, and a crystalline MgO and ZnON phase with grain boundaries are depicted in Fig. 6(b).

V. CONCLUSION

In summary, we fabricated ZnMgON thin films in an electrically conductive regime with free electron charge carrier concentrations from 10^{18} cm^{-3} to 10^{15} cm^{-3} , showing excellent long-term stability. We demonstrated that tuning carrier concentrations of a-ZnON by the addition of magnesium cation below $n_{\text{Hall}} < 10^{18} \text{ cm}^{-3}$ are possible with magnesium cation concentrations $> 1 \text{ at. \%}$. Simultaneously, the electron mobility decreases below $\mu_{\text{Hall}} < 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the absorption edge increases up to 1.7 eV . We could not find significant differences in the optoelectrical properties between the variable-power approach and the continuous composition spread. Structural analysis suggests the formation of an amorphous ZnMgON phase including MgO and ZnO crystallites with the increase in magnesium content. The amorphous phase is maintained up to $\text{Mg}/(\text{Mg} + \text{Zn}) = 3 \text{ at. \%}$. Thus, the presented results demonstrate that the addition of magnesium cations has the potential to increase the application range of a-ZnON in devices for integrated circuits.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for long term stability measurements of ZnMgON thin films depicted in Fig. S1. Concerning the optical properties, a detailed description of the Tauc-Lorentz and Gaussian oscillators used for modeling the line shape of the dielectric function and the parameters determined are given in Eqs. S5 and S6 and in Table SI, respectively. In addition, the equations

describing the chemical composition in dependence on the magnesium content (Eqs. S1–S4) derived by linear fitting of the EDX data are provided in Figs. 1(c) and 1(d).

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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