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# Structure and electrical properties of Ga<sub>2</sub>O<sub>3</sub> thin films grown by atomic layer deposition on Ru and TiN electrodes

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The composition, structure, and electrical properties of Ga<sub>2</sub>O<sub>3</sub> thin films, grown by atomic layer deposition (ALD) from GaI<sub>3</sub> and O<sub>3</sub> precursors, were characterized. The films were deposited on Si substrates and on Ru and TiN bottom electrodes at temperatures of 200–500 °C. Growth of κ- and ε-Ga<sub>2</sub>O<sub>3</sub> was observed on Ru and TiN at substrate temperatures ≥ 325 °C, while temperatures ≥ 425 °C were needed to deposit crystalline Ga<sub>2</sub>O<sub>3</sub> on bare Si. The formation of both ε-Ga<sub>2</sub>O<sub>3</sub> and predominant κ-Ga<sub>2</sub>O<sub>3</sub> phases in crystalline films was confirmed by high-resolution transmission electron microscopy studies. Films deposited at 375–450 °C exhibited low leakage current densities (down to 10<sup>-9</sup> A cm<sup>-2</sup> at an electric field strength of 0.1 MV cm<sup>-1</sup>), breakdown fields up to 6.5 MV cm<sup>-1</sup>, and permittivity values up to 22 at 10 kHz. These results demonstrate that Ga<sub>2</sub>O<sub>3</sub> deposited in this ALD process is suitable for implementation as high permittivity dielectrics in advanced electronic devices. Furthermore, the findings highlight the importance of deposition temperature and substrate choice in optimizing the dielectric properties of Ga<sub>2</sub>O<sub>3</sub> films deposited for these applications.

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## 1. Introduction

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) is a wide-bandgap semiconductor with promising potential in many important applications.<sup>1–5</sup> For example, the possibility of using Ga<sub>2</sub>O<sub>3</sub> as a wide-bandgap material in radiation detectors,<sup>6,7</sup> chemical sensors,<sup>8,9</sup> and high-power electronic devices<sup>3,10,11</sup> has been demonstrated. In addition, since the conductivity of Ga<sub>2</sub>O<sub>3</sub> can be varied in a wide range, thin films of this material have been employed as dielectrics in resistive switching metal–insulator–metal structures<sup>12</sup> as well as transparent conducting electrodes for optoelectronic devices.<sup>13</sup>

Ga<sub>2</sub>O<sub>3</sub> has been obtained in α, β, γ, δ, ε, κ, and amorphous phases, exhibiting markedly different properties. For instance, one can find densities of 4.98–5.18 g cm<sup>-3</sup> for cubic (space group *Ia3̄*) δ-Ga<sub>2</sub>O<sub>3</sub><sup>1</sup> and 6.48 g cm<sup>-3</sup> for rhombohedral (*R3̄c*) α-Ga<sub>2</sub>O<sub>3</sub><sup>1</sup> in the literature. Similarly, the relative permittivity (*k*)

is phase dependent, with values reported to be 9.2–11.9 for amorphous Ga<sub>2</sub>O<sub>3</sub>,<sup>14,15</sup> 9.3–12.4 for monoclinic (*C2/m*) β-Ga<sub>2</sub>O<sub>3</sub>,<sup>16–19</sup> and 15–32 for the orthorhombic (*Pna2<sub>1</sub>*) phase of Ga<sub>2</sub>O<sub>3</sub>.<sup>20,21</sup> Notably, in different publications, the orthorhombic phase of Ga<sub>2</sub>O<sub>3</sub>, which has been shown to exhibit the highest *k* values and therefore is of particular importance for some electronic applications, is referred to as κ-Ga<sub>2</sub>O<sub>3</sub><sup>21–23</sup> and also as ε-Ga<sub>2</sub>O<sub>3</sub>.<sup>20</sup> This is likely because, in thin films, a structure consisting of 120° rotational nanoscale domains of orthorhombic κ-Ga<sub>2</sub>O<sub>3</sub> results in an X-ray diffraction (XRD) pattern very similar to that of hexagonal ε-Ga<sub>2</sub>O<sub>3</sub> (space group *P6<sub>3</sub>mc*), making it difficult to distinguish these two phases.<sup>22–25</sup>

Owing to the strong dependence of material properties on its phase composition, selecting and stabilizing the most suitable phase for each application are important tasks. In thin films, the phase composition depends on the fabrication method, process parameters, and substrates used for deposition. For instance, previous publications have described the deposition of α-Ga<sub>2</sub>O<sub>3</sub> on differently orientated sapphire<sup>1,26</sup> and α-Cr<sub>2</sub>O<sub>3</sub>,<sup>25,27</sup> monoclinic (*C2/m*) β-Ga<sub>2</sub>O<sub>3</sub> on sapphire,<sup>1</sup> silicon,<sup>28</sup> MgO,<sup>7</sup> GaN,<sup>29</sup> TiN,<sup>30</sup> Pt,<sup>19</sup> and Ru,<sup>31</sup> hexagonal (*P6<sub>3</sub>mc*) ε-Ga<sub>2</sub>O<sub>3</sub> and/or orthorhombic (*Pna2<sub>1</sub>*) κ-Ga<sub>2</sub>O<sub>3</sub> on c-cut sapphire,<sup>23,24</sup> silicon,<sup>25</sup> yttria-stabilized zirconia,<sup>32</sup> MgO,<sup>32</sup> GaN,<sup>33,34</sup> SiC,<sup>34</sup> AlN,<sup>33,35</sup> MgAl<sub>2</sub>O<sub>4</sub>,<sup>35</sup> SrTiO<sub>3</sub>,<sup>36</sup> indium-tin oxide,<sup>20</sup> and Pt;<sup>21</sup> cubic (*Fd3̄m*) γ-Ga<sub>2</sub>O<sub>3</sub> on MgAl<sub>2</sub>O<sub>4</sub>,<sup>26,35</sup> MgO,<sup>35</sup> and GaN;<sup>35</sup> δ-Ga<sub>2</sub>O<sub>3</sub> on β-Fe<sub>2</sub>O<sub>3</sub>.<sup>37</sup> Earlier studies also demonstrated that the choice of deposition

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temperature,<sup>26,34,35</sup> deposition method,<sup>21,28</sup> precursors, and precursor dosing<sup>35</sup> is of comparable importance in the stabilization of selected crystalline phases during the thin-film growth.

Besides several other material properties, the concentration of residual impurities, which in turn affects the charge carrier concentration and transport in semiconductors and dielectrics, may also depend on the phase composition. For example, the concentration of residual impurities has been lower in the rutile-phase TiO<sub>2</sub> grown by atomic layer deposition (ALD) on RuO<sub>2</sub> electrodes than in the anatase films obtained on the Si(100) surface in the same ALD process at the same temperature.<sup>38</sup> Lower concentrations of impurities were also obtained in orthorhombic Hf<sub>x</sub>Ti<sub>1-x</sub>O<sub>y</sub> grown on Ru seed layers compared with amorphous Hf<sub>x</sub>Ti<sub>1-x</sub>O<sub>y</sub> deposited on Pt and Si(100) at the same process parameters.<sup>39</sup> Studies on ALD of Ga<sub>2</sub>O<sub>3</sub> from GaI<sub>3</sub> and O<sub>3</sub>, yielding amorphous and  $\kappa(\epsilon)$  modifications of Ga<sub>2</sub>O<sub>3</sub> on silicon and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> on  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> seed layers,<sup>25</sup> gave a similar result. The  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> seed layers, supporting the formation of a high-density  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> phase, simultaneously resulted in lower concentrations of impurities in the Ga<sub>2</sub>O<sub>3</sub> films.<sup>25</sup>

In previous studies, Ga<sub>2</sub>O<sub>3</sub> films grown on the surfaces of dielectrics or semiconductors have mainly been characterized. Only a limited number of publications have described the growth of Ga<sub>2</sub>O<sub>3</sub> on highly conductive electrode materials.<sup>19–21,30,31</sup> However, in many electronic applications, the deposition of wide-gap semiconductors and dielectrics on materials with high (metallic) conductivity is required. Motivated by this need, the present study investigates the ALD of Ga<sub>2</sub>O<sub>3</sub> on TiN- and Ru-coated substrates and examines how these electrode materials influence the properties of Ga<sub>2</sub>O<sub>3</sub> films. The main task was to evaluate how well our novel GaI<sub>3</sub>- and O<sub>3</sub>-based ALD process<sup>25,27</sup> is suited for the deposition of Ga<sub>2</sub>O<sub>3</sub> on these electrode materials.

Although oxidation of the bottom electrode during O<sub>3</sub>-based ALD was anticipated, TiN was selected due to its widespread use in semiconductor devices. Ru, which forms conductive oxides, was included as an alternative electrode material to mitigate the oxidation-related decrease in the bottom electrode conductivity.

The results presented in this report demonstrate that crystalline Ga<sub>2</sub>O<sub>3</sub> can be obtained on both TiN and Ru at significantly lower temperatures than on uncoated silicon substrates. This enabled us to investigate the influence of substrates on crystal growth and to better understand the effect of crystallization on the growth per cycle (GPC) and other characteristics of thin films deposited in this ALD process. Most importantly, this study provides new insights into how the phase composition influences the electrical properties of Ga<sub>2</sub>O<sub>3</sub>, which is crucial for its implementation in devices such as field effect transistors and different types of memories based on metal–dielectric–semiconductor and metal–dielectric–metal structures.

## 2. Experimental details

The Ga<sub>2</sub>O<sub>3</sub> films were deposited on bare Si(100) and on Ru- and TiN-coated Si(100) substrates using a flow type ALD reactor

described previously.<sup>40</sup> The Ru and TiN coatings were deposited by magnetron sputtering and pulsed chemical vapor deposition techniques, respectively. For the deposition of Ga<sub>2</sub>O<sub>3</sub> films, ALD cycles including a GaI<sub>3</sub> vapor pulse, purge, ozone pulse, and another purge, each with a duration of 2 s, were used. Sufficient vapor pressure of GaI<sub>3</sub> was obtained by heating GaI<sub>3</sub> powder (99%, Strem Chemicals, Inc) at 130 °C. Ozone was generated from O<sub>2</sub> (99.999%, AS Linde Gas). The Ga<sub>2</sub>O<sub>3</sub> films were deposited applying 700 ALD cycles at  $T_G$  of 200–500 °C and 250 cycles at 325–500 °C. Other details of the ALD process are described in our previous publication.<sup>25</sup>

The elemental compositions and mass thicknesses of films were measured with an X-ray fluorescence (XRF) spectrometer ZSX-400 (Rigaku). The phase composition was characterized by grazing incidence X-ray diffraction (GIXRD) using an X-ray diffractometer Smartlab (Rigaku) working at a tube power of 8.1 kW (CuK $\alpha$  radiation). The X-ray diffraction database PDF-2 of the International Centre of Diffraction Data (version 2020) was used for qualitative phase analysis. The thickness, density, and surface roughness were calculated from the X-ray reflectometry (XRR) results recorded with the same X-ray diffractometer. Additionally, the thickness values were measured using a GES-5E (Sopra-Semilab) spectroscopic ellipsometer (SE).

High-angle annular dark-field (HAADF) STEM imaging, and EDX analysis were performed using a double-corrected FEI Titan3 S/TEM, operated at 300 kV, equipped with a Super-X EDX detector. TEM imaging and selective area electron diffraction (SAED) were performed on a FEI Tecnai G2 TEM operated at 200 kV. FFT patterns of TEM images were indexed using program CrystBox.<sup>41</sup>

The top electrodes needed for the electrical characterization of Ga<sub>2</sub>O<sub>3</sub> were fabricated by electron beam evaporation of Pt through a shadow mask. The sizes of circular top electrodes were determined by diameters of the mask openings (50, 250, and 500  $\mu$ m), while the thicknesses of the electrodes were around 50 nm. Electrical characteristics were measured using a light-proof and electrically shielded Cascade Microtech MPS150 probe station, Keithley 2636A source-meter and Agilent E4980A LCR analyzer. Capacitance was measured at frequencies ranging from 5 kHz to 2 MHz.

## 3. Results and discussion

### 3.1. Composition and structure

According to the results of XRF studies, the O/Ga atomic ratio was  $1.5 \pm 0.1$  in the samples with films grown applying 700 ALD cycles on bare Si substrates at 200–500 °C, on TiN bottom electrodes at 275–450 °C, and on Ru bottom electrodes at 275 °C (Fig. S1). With the decrease of  $T_G$  down to 200 °C and its increase up to 500 °C, the O/Ga ratio gradually rose reaching  $1.7 \pm 0.1$  in the samples where these films were grown on Ru and TiN at 200 °C, and on TiN at 500 °C. In the case of films grown with 700 cycles on Ru and with 250 cycles on TiN, the mean O/Ga ratio increased from  $1.6 \pm 0.1$  to  $2.1 \pm 0.1$  with the  $T_G$  increase from 325 to 500 °C. An even steeper increase in



the O/Ga ratio (from 1.6 to 2.5) was observed for films grown with 250 cycles on Ru as  $T_G$  increased from 325 to 500 °C (Fig. S1). As the characteristic X-ray emission recorded in our XRF studies was emitted from the material layer that was much thicker than the  $\text{Ga}_2\text{O}_3/\text{Ru}$  and  $\text{Ga}_2\text{O}_3/\text{TiN}$  stacks, the O/Ga ratio determined from the XRF data also depended on the amount of oxygen absorbed by the Ru and TiN layers. Therefore, the increase in O/Ga ratio with increasing  $T_G$  and decreasing film thickness was evidently caused by the oxidation of Ru and TiN surfaces at higher  $T_G$  as confirmed by the TEM and STEM data presented in Fig. 1 for  $\text{Ga}_2\text{O}_3$  deposited at 450 °C on Ru (Fig. 1a and b) and TiN (Fig. 1c and d).

The STEM-EDX line scans across the  $\text{Ga}_2\text{O}_3/\text{Ru}$  and  $\text{Ga}_2\text{O}_3/\text{TiN}/\text{Si}$  interfaces revealed that a  $\text{RuO}_x$  layer with a thickness of around 4 nm was formed on Ru in the former structure (Fig. 1b) while  $\text{TiO}_x\text{N}_y$  was formed as a result of TiN oxidation throughout the bottom electrode in the latter case (Fig. 1d). The O peak at the interface between  $\text{TiO}_x\text{N}_y$  and the Si substrate in Fig. 1d probably comes from the native  $\text{SiO}_2$  layer.

The XRF data demonstrate that the concentration of residual iodine impurities, which remained in the  $\text{Ga}_2\text{O}_3$  films because of incomplete removal of Ga precursor ligands in the ALD process, decreased to  $10^{-2}$  at% with the increase of  $T_G$  to 375–500 °C (Fig. 2). At  $T_G$  of 275–400 °C, the iodine concentrations were slightly lower in the films deposited on Ru and TiN

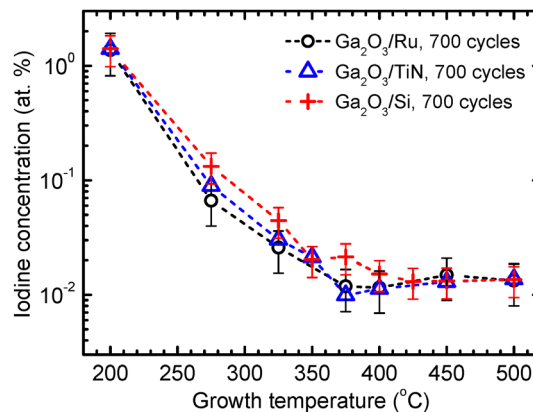


Fig. 2 Iodine concentration as a function of  $T_G$  in  $\text{Ga}_2\text{O}_3$  films deposited on Ru, TiN, and bare silicon using 700 ALD cycles.

than in the films deposited on bare Si at the same temperatures. However, the difference did not exceed the experimental uncertainty (Fig. 2).

GIXRD studies revealed the presence of crystalline  $\text{Ga}_2\text{O}_3$  in the films grown on Ru and TiN with 250 ALD cycles at  $T_G \geq 350$  °C and with 700 cycles at  $T_G \geq 325$  °C (Fig. 3). All films deposited on Ru and TiN at lower  $T_G$  values (Fig. 3), similar to the films deposited on bare Si substrates at  $T_G < 425$  °C,<sup>25,27</sup>

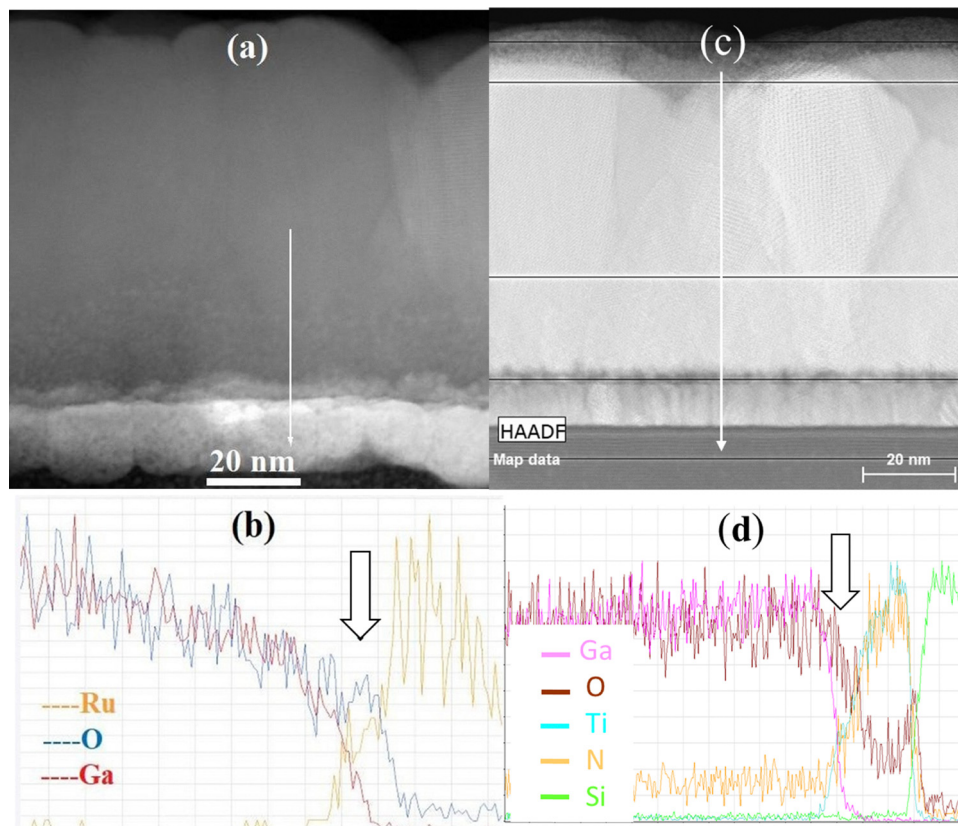


Fig. 1 (a) and (c) HRTEM images and (b) and (d) elemental composition profiles determined by STEM-EDX for  $\text{Ga}_2\text{O}_3$  films deposited on (a) and (b) Ru and (c) and (d) TiN-coated silicon substrates at 450 °C. The arrows indicate (a) and (c) the ranges and directions of STEM-EDX scans, and (b) and (d) the interface between  $\text{Ga}_2\text{O}_3$  and the bottom electrode.



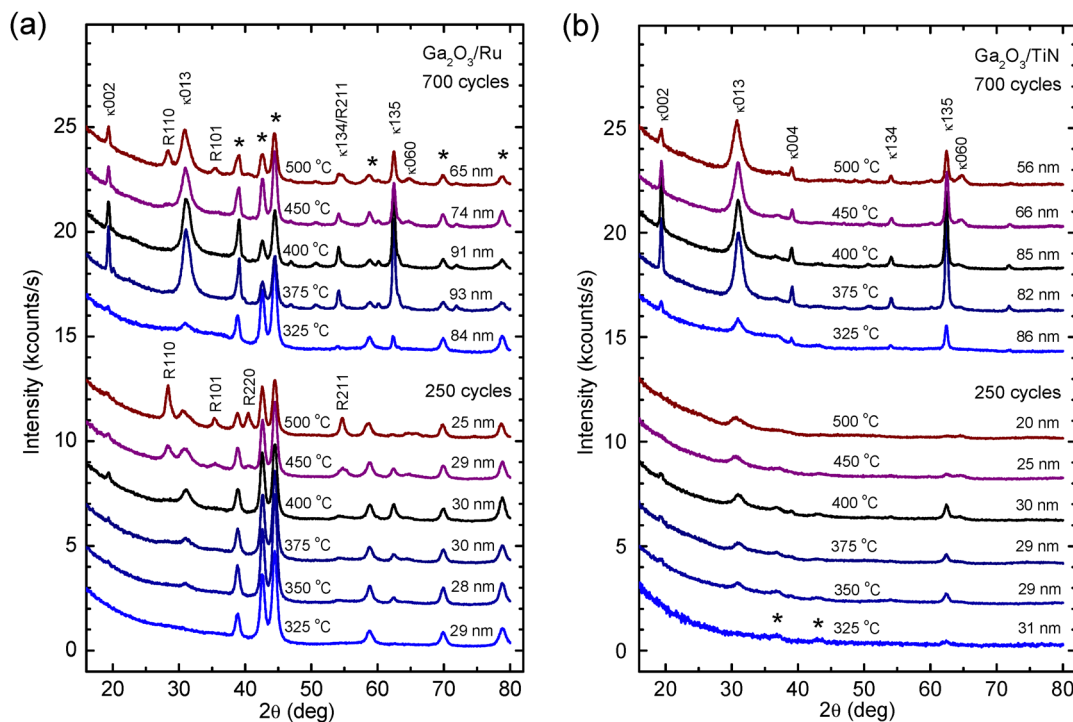


Fig. 3 Grazing incidence X-ray diffractograms of  $\text{Ga}_2\text{O}_3$  films deposited on (a) Ru and (b) TiN-at different temperatures using 250 and 700 ALD cycles. The growth temperatures and thicknesses of films are shown at corresponding diffractograms. Miller indices of  $\kappa$ - $\text{Ga}_2\text{O}_3$  ( $\kappa$ ) and rutile-phase  $\text{RuO}_2$  (R) are shown at respective reflections. The reflections marked with asterisk (\*) originate from (a) Ru and (b) TiN.

were amorphous. Comparison of diffractograms depicted in Fig. 3 with XRD databases indicated that  $\kappa$ - $\text{Ga}_2\text{O}_3$  was formed in the crystalline films. This conclusion is based on reflections peaking at  $19.4^\circ$ ,  $31.0^\circ$ ,  $54.1^\circ$ , and  $62.4^\circ$  (Fig. 3a and b). These reflections belong to  $\kappa$ - $\text{Ga}_2\text{O}_3$  and can be indexed as 002, 013, 134, and 135, respectively. In addition, a reflection at  $39.1^\circ$  in the diffractograms of films grown on TiN (Fig. 3b) was identified as the 004 reflection of  $\kappa$ - $\text{Ga}_2\text{O}_3$ . However, it is possible that the  $\epsilon$ - $\text{Ga}_2\text{O}_3$  phase was also present in the films because the reflections peaking at  $19.4^\circ$ ,  $54.1^\circ$ , and  $62.4^\circ$  may also be attributed to this phase.

In the diffraction patterns of samples with  $\text{Ga}_2\text{O}_3$  films grown on Ru at  $T_G \geq 375^\circ\text{C}$ , reflections attributable to the rutile phase of  $\text{RuO}_2$  can also be seen at  $28.3^\circ$ ,  $35.3^\circ$ ,  $40.4^\circ$ , and  $54.6^\circ$  (Fig. 3a). The intensities of these reflections increase with increasing  $T_G$  and decreasing film thickness. Therefore, the GIXRD results confirm the STEM-EDX data (Fig. 1b) indicating that a  $\text{RuO}_2$  interface layer was formed on Ru during the initial stage of  $\text{Ga}_2\text{O}_3$  deposition at higher  $T_G$ . Although the oxidation of TiN was also evident from the STEM results (Fig. 1d), no reflections of crystalline  $\text{TiO}_2$  phases appeared in the GIXRD patterns of samples with  $\text{Ga}_2\text{O}_3$  films grown on TiN at temperatures up to  $500^\circ\text{C}$  (Fig. 3b). However, crystalline  $\text{TiO}_2$  (anatase) was observed in the samples containing  $\text{Ga}_2\text{O}_3$  deposited at  $550^\circ\text{C}$  (Fig. S2).

With the increase of  $T_G$  to  $450$ – $500^\circ\text{C}$ , a reflection at  $64.6^\circ$ – $64.8^\circ$  and a reflection tail at  $31.5^\circ$ – $32.0^\circ$  appeared in the GIXRD patterns (Fig. 3a and b). A possible reason for these changes

could be the formation of  $\beta$ - $\text{Ga}_2\text{O}_3$  in addition to  $\kappa/\epsilon$ - $\text{Ga}_2\text{O}_3$  in the films deposited at higher  $T_G$ . As shown in Fig. S2, a significant number of  $\beta$ - $\text{Ga}_2\text{O}_3$  reflections can be indexed in the diffractogram of a  $\text{Ga}_2\text{O}_3$  film deposited on TiN at  $550^\circ\text{C}$ . Therefore, in a  $T_G$  range of  $450$ – $500^\circ\text{C}$ , a transition from the growth of  $\kappa/\epsilon$ - $\text{Ga}_2\text{O}_3$  to that of  $\beta$ - $\text{Ga}_2\text{O}_3$  started.

The data displayed in Fig. 3 also show that with increasing number of ALD cycles, the intensities of  $\text{Ga}_2\text{O}_3$  GIXRD reflections increase faster than the film thicknesses do. Therefore, the crystallinity of the films improved during the deposition process either due to the crystallization of the amorphous material initially synthesized in the ALD reactions or because of increasing lateral sizes of crystallites with increasing film thickness. As can be seen in TEM images (Fig. 1) the latter reason seems to be more probable because the crystalline films contain pyramidal or conical grains with lateral sizes increasing with the distance from the film/substrate interface (Fig. 1c). Fig. 1c further shows that the material density in these grains is higher than that between the grains. Therefore, the grains evidently contain crystalline material as confirmed by the results of HRTEM studies presented in Fig. 4 and 5. Correspondingly, the increase in the lateral sizes of these grains with the increasing distance from the substrate surface means that the relative amount of crystalline material is higher at the top region of a film and in thicker films.

More information about the presence and location of different phases in crystalline  $\text{Ga}_2\text{O}_3$  was obtained from HRTEM studies of a film deposited at  $450^\circ\text{C}$  using 700 ALD cycles.



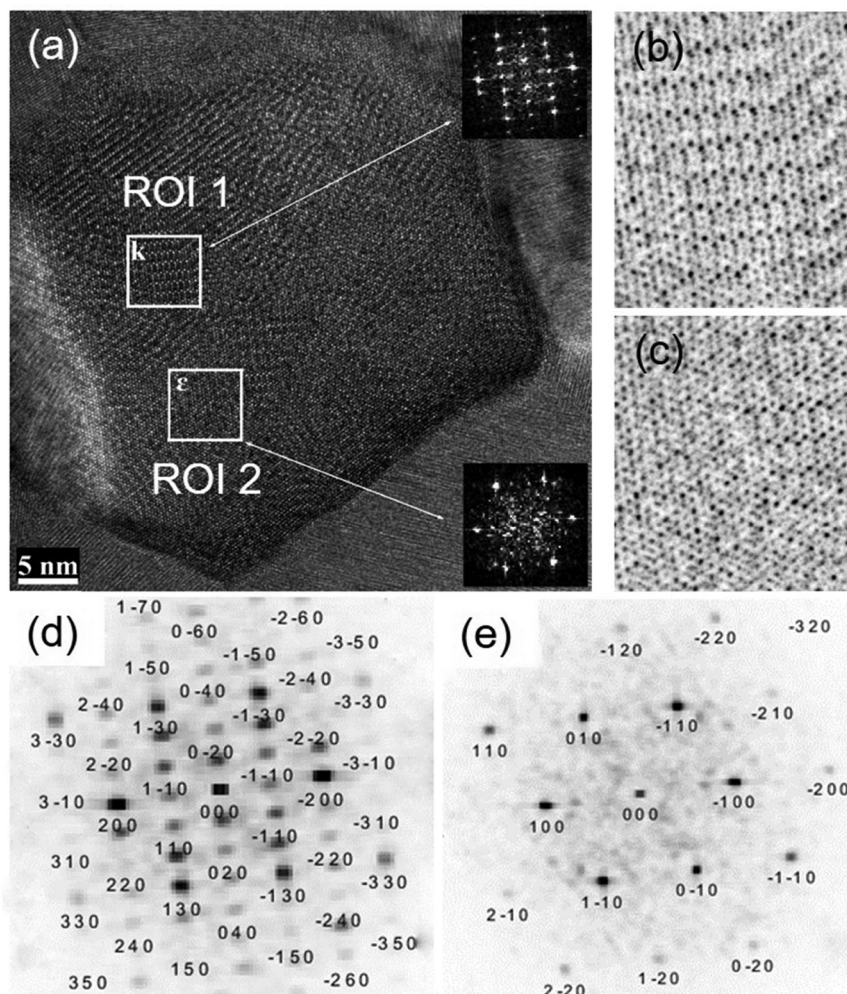


Fig. 4 (a) Top-view TEM image of a  $\text{Ga}_2\text{O}_3$  grain showing ranges of interest ROI 1 and ROI 2 with different structures (denoted with  $\kappa$  and  $\epsilon$ , respectively). (b) and (c) Enlarged high-resolution images of (b) ROI 1 and (c) ROI 2, and (d) and (e) FFT patterns of (d) ROI 1, indexed assuming lattice symmetry of  $\kappa$ - $\text{Ga}_2\text{O}_3$ , and (e) ROI 2, indexed assuming lattice symmetry of  $\epsilon$ - $\text{Ga}_2\text{O}_3$ .

The  $\kappa$ - $\text{Ga}_2\text{O}_3$  phase that was identified in the films by XRD is orthorhombic with cell parameters of  $a = 5.0566 \text{ \AA}$ ,  $b = 8.6867 \text{ \AA}$ , and  $c = 9.3035 \text{ \AA}$ , while  $\epsilon$ - $\text{Ga}_2\text{O}_3$  has a hexagonal structure with lattice parameters  $a = 2.99 \text{ \AA}$  and  $c = 9.3 \text{ \AA}$ . In both crystal structures, the O atoms are arranged in a 4H (ABAC) close-packed stacking arrangement. The difference between the two structures is that in  $\kappa$ - $\text{Ga}_2\text{O}_3$ , Ga atoms occupy tetrahedral ( $\text{Ga}_\text{I}$ ) and octahedral ( $\text{Ga}_\text{II}$ ,  $\text{Ga}_\text{III}$ ,  $\text{Ga}_\text{IV}$ ) sites, while in  $\epsilon$ - $\text{Ga}_2\text{O}_3$ , Ga atoms occupy octahedral and tetrahedral sites in a disordered manner. Previous work reported that  $\kappa$ - $\text{Ga}_2\text{O}_3$  and  $\epsilon$ - $\text{Ga}_2\text{O}_3$  have crystal relationships  $[0001]_\epsilon/[001]_\kappa$ ,  $[1010]_\epsilon/[100]_\kappa$  and  $[11-20]_\epsilon/[010]_\kappa$ .<sup>23</sup> Because the films have a strong fiber texture along the  $c$  axis, we can distinguish  $\kappa$ - $\text{Ga}_2\text{O}_3$  from  $\epsilon$ - $\text{Ga}_2\text{O}_3$  in the  $\text{Ga}_2\text{O}_3$  film with TEM in top-view along the  $c$  axis (Fig. 4) and in the cross-section from the  $[1-100]_\epsilon$  or  $[100]_\kappa$  direction, but not from  $[11-20]_\epsilon/[010]_\kappa$ , as the HRTEM patterns are the same along the latter direction.

Fig. 4a shows a plan-view image of a  $\text{Ga}_2\text{O}_3$  grain that consists of several nano-domains. High-resolution images and corresponding FFT patterns are presented in Fig. 4b–e.

Most of the domains are  $\kappa$ - $\text{Ga}_2\text{O}_3$ , as indicated by the high-resolution image (Fig. 4b) and corresponding FFT pattern (Fig. 4d). However, it was also possible to find a domain with a hexagonal structure (Fig. 4a and c), which was indexed as  $\epsilon$ - $\text{Ga}_2\text{O}_3$  (Fig. 4e). In this domain, which has a diameter of around 5 nm, no  $120^\circ$  twin of  $\kappa$ - $\text{Ga}_2\text{O}_3$ , described by Cora *et al.*,<sup>23</sup> was found. This result was confirmed by the convergent beam electron diffraction patterns (CBED) shown in Fig. S3a.

It is worth noting that the reflections observable in Fig. 4e can also be indexed as those of  $\kappa$ - $\text{Ga}_2\text{O}_3$  (Fig. S4). In this case, the standard deviation of fitting ( $\Delta d = 0.0010 \text{ nm}$ ) is even smaller than that for  $\epsilon$ - $\text{Ga}_2\text{O}_3$  ( $\Delta d = 0.0012 \text{ nm}$ ). However, the absence of 110, 020, and 120 reflections of  $\kappa$ - $\text{Ga}_2\text{O}_3$  in the FFT pattern (Fig. S4) indicates that the domain contains  $\epsilon$ - $\text{Ga}_2\text{O}_3$  rather than  $\kappa$ - $\text{Ga}_2\text{O}_3$ .

The cross-sectional image in Fig. 5 shows a  $\text{Ga}_2\text{O}_3$  grain, that mainly consists of  $\kappa$ - $\text{Ga}_2\text{O}_3$  but also contains a domain of  $\epsilon$ - $\text{Ga}_2\text{O}_3$  co-growing with  $\kappa$ - $\text{Ga}_2\text{O}_3$  in the top region of the grain. The enlarged high-resolution images, corresponding FFT patterns, and SAED patterns of both phases are shown in



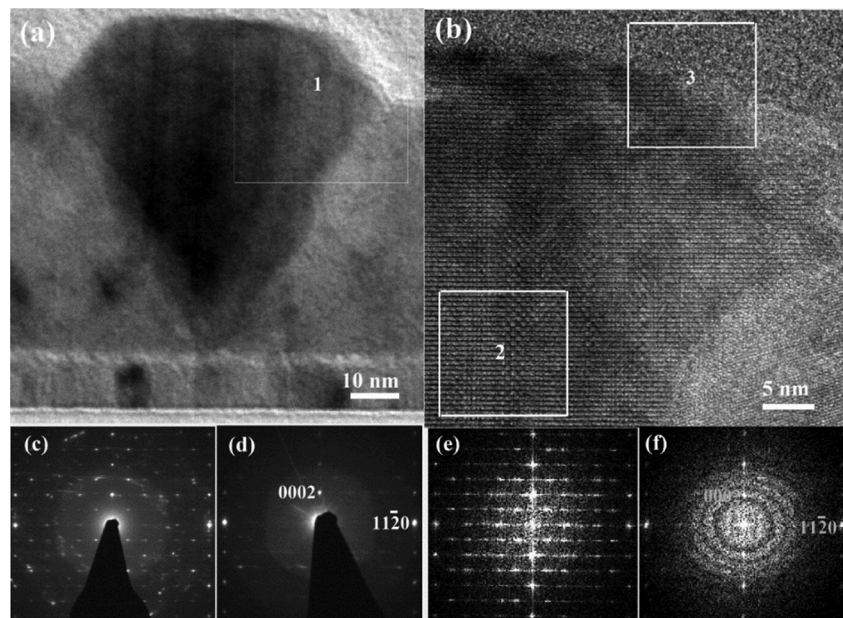


Fig. 5 Cross-sectional HRTEM of (a) one Ga<sub>2</sub>O<sub>3</sub> grain and (b) an enlarged image of region 1 in panel (a) showing κ-Ga<sub>2</sub>O<sub>3</sub> in box 2 and ε-Ga<sub>2</sub>O<sub>3</sub> in box 3. (c) and (d) Electron diffraction patterns (SAED) and (e) and (f) FFT patterns of (c) and (e) κ-Ga<sub>2</sub>O<sub>3</sub> from box 2 and (d) and (f) ε-Ga<sub>2</sub>O<sub>3</sub> from box 3.

Fig. S5 and S6. These results confirm the growth of ε-Ga<sub>2</sub>O<sub>3</sub> in addition to the predominant κ-Ga<sub>2</sub>O<sub>3</sub>. Furthermore, in the HRTEM studies, some Ga<sub>2</sub>O<sub>3</sub> grains with space distance around 0.59 nm (Fig. 6), corresponding to the (200) plane of the β-Ga<sub>2</sub>O<sub>3</sub> structure, were found. Therefore, the reflection peaking at 64.60°–64.80° in the GIXRD diffractograms of films deposited at  $T_G > 450$  °C (Fig. 3) can be attributed to β-Ga<sub>2</sub>O<sub>3</sub>.

In the previous studies, κ-Ga<sub>2</sub>O<sub>3</sub> was observed in films grown on bare silicon substrates at  $T_G \geq 425$  °C.<sup>25,27</sup> Thus, the  $T_G$  values leading to the formation of κ-Ga<sub>2</sub>O<sub>3</sub> and ε-Ga<sub>2</sub>O<sub>3</sub> on Ru and TiN (Fig. 3) were about 100 °C lower than those

required for crystallization of Ga<sub>2</sub>O<sub>3</sub> on silicon. A reason for the lower crystallization temperatures on Ru and TiN could be a local epitaxial growth similar to that of TiO<sub>2</sub> on RuO<sub>2</sub>.<sup>42</sup> However, no significant epitaxial relationship between Ga<sub>2</sub>O<sub>3</sub> and Ru (RuO<sub>2</sub>) or Ga<sub>2</sub>O<sub>3</sub> and TiN (TiO<sub>2</sub>) was found by TEM. Hence, there should be other reasons leading to more preferential crystallization of Ga<sub>2</sub>O<sub>3</sub> on Ru and TiN than on silicon. For instance, rougher surfaces of Ru and TiN compared with the surface of bare silicon (Fig. 1) and the higher reactivity of GaI<sub>3</sub> towards Ru and TiN, leading to more efficient release of iodine ligands (Fig. 2), might contribute to the nucleation of Ga<sub>2</sub>O<sub>3</sub>. This conclusion is in line with the results of previous studies showing that an increase in surface roughness promoted more efficient nucleation of Ga<sub>2</sub>O<sub>3</sub> on Ru.<sup>31</sup>

In contrast to the results of the present study, thin films of β-Ga<sub>2</sub>O<sub>3</sub> were deposited by radio frequency magnetron sputtering on TiN with preferential (111) orientation<sup>30</sup> and on epitaxial Ru (0001).<sup>31</sup> Differences in seed-layer orientation and growth mechanisms were likely the main factors responsible for these dissimilarities.

### 3.2. Density, surface roughness, and growth rate

Results of XRR studies demonstrate that together with a  $T_G$  increase from 200 to 325 °C, the densities of films deposited on Ru and TiN bottom electrodes gradually increased (Fig. 7a). This increase in density was similar to that previously observed in the same  $T_G$  range for amorphous Ga<sub>2</sub>O<sub>3</sub> films grown on bare Si substrates,<sup>25,27</sup> and was likely due to the increase in material purity related to the decrease of iodine content from 1.4 to 0.03 at% (Fig. 2). A more significant increase in the density of films deposited on Ru and TiN was observed with the increase of  $T_G$  from 325 to 375 °C that caused the transition from

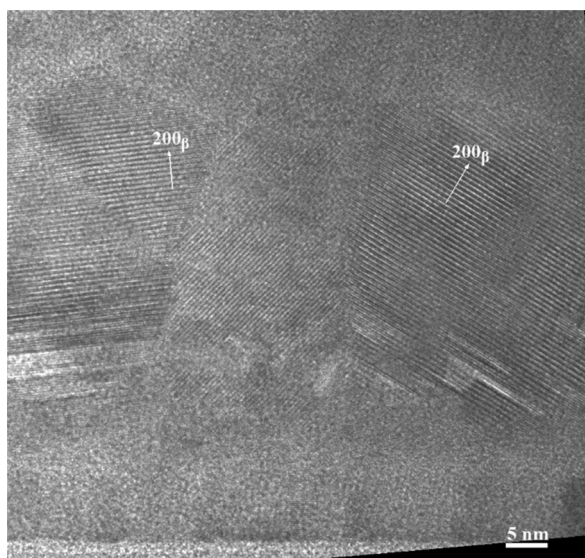


Fig. 6 HRTEM image showing the 0.59 nm lattice fringe, which was assigned to the (200) lattice planes of β-Ga<sub>2</sub>O<sub>3</sub>.



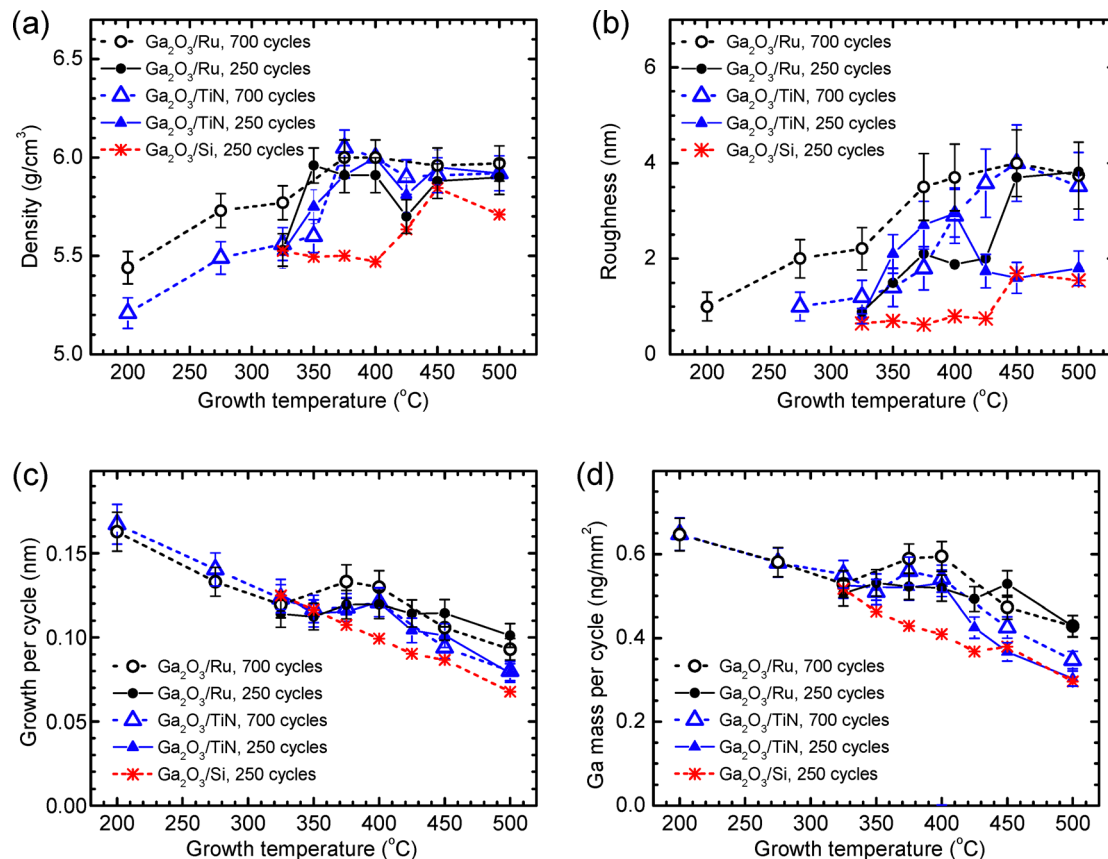


Fig. 7 (a) Density, (b) surface roughness, (c) thickness growth per cycle, and (d) Ga mass growth per cycle as a function of  $T_G$  for films grown with 250 ALD cycles on Ru, TiN, and Si, and with 700 ALD cycles on Ru and TiN.

amorphous to crystalline material growth (Fig. 3). As a result, the density increased to 5.96–6.05  $\text{g}/\text{cm}^3$ , *i.e.*, close to the bulk density of single crystal  $\kappa$ -Ga<sub>2</sub>O<sub>3</sub> (6.11  $\text{g}/\text{cm}^3$ ). Similar densities have been reported in XRD databases for  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> (6.196  $\text{g}/\text{cm}^3$ , PDF-2 file 01-082-3196) and in previous publications by Playford *et al.*<sup>22</sup> for  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> (6.0622  $\text{g}/\text{cm}^3$ ) and Cora *et al.*<sup>23</sup> for  $\kappa$ -Ga<sub>2</sub>O<sub>3</sub> (6.108  $\text{g}/\text{cm}^3$ ). In the case of films deposited on bare Si substrates, a density increase, attributable to the crystallization of the film material,<sup>25,27</sup> was observed with the increase of  $T_G$  from 400 to 450  $^{\circ}\text{C}$  (Fig. 7a). This result is in good agreement with the data of earlier studies.<sup>25,27</sup>

It is worth noting that in the  $T_G$  range of 325–450  $^{\circ}\text{C}$ , where the most significant changes in the density were observed (Fig. 7a), the influence of iodine impurities on the density could not be significant because of very low iodine concentrations ranging from 0.01 to 0.03 at% (Fig. 2). However, the low iodine concentration was a plausible reason why the crystal growth leading to the increase in the material density became possible.

The crystal growth also led to a significant increase in the surface roughness of films grown on Ru and TiN as well as on bare Si (Fig. 7b). As a result, the XRR roughness that was 0.6–1.0 nm in the case of amorphous films increased up to 3.7–4.0 nm when  $T_G$  increased to 450  $^{\circ}\text{C}$  (Fig. 7b). For comparison, the XRR roughness values of bare Si, Ru, and TiN surfaces

were <0.5,  $0.6 \pm 0.1$ , and  $1.0 \pm 0.2$  nm, respectively. Thus, the substrate roughness had a considerable direct effect only on the roughness of amorphous films. However, according to recent data of Baunthiyal *et al.*,<sup>31</sup> the surface roughness of Ru can enhance the nucleation of Ga<sub>2</sub>O<sub>3</sub>. This effect might also be a reason for rougher surfaces of amorphous films grown on Ru at 275  $^{\circ}\text{C}$  compared with those of similar films grown on TiN (Fig. 7b).

Considerable differences in the surface roughness of crystalline films grown on different substrates are at least partially related to the differences in the film thicknesses. Indeed, a comparison of results presented in Fig. 7b and c shows that the differences in the surface roughness are in correlation with differences in GPC. However, there is also a positive feedback between surface roughness and growth rate because higher surface roughness results in a higher specific surface area<sup>43,44</sup> and, correspondingly, higher amounts of precursors adsorbed during an ALD cycle.<sup>25,27,44</sup> This effect is one of the reasons for the increase in GPC (Fig. 7c) and Ga mass growth per cycle (Fig. 7d) with the increase in  $T_G$  leading to the crystal growth (Fig. 3).

An additional effect that can influence the growth rate is the difference in the reactivities of amorphous and crystalline materials towards the precursors, as discussed in previous publications.<sup>25,27,43,44</sup> Higher reactivity leads to more efficient



removal of precursor ligands in surface reactions and, correspondingly, an increase in the amount of film material adsorbed in an ALD cycle. The latter causes a proportional increase in the mass growth per cycle. Unfortunately, the separate determination of the contributions from surface roughness and reactivity to GPC is a complex task requiring measurement of specific surface area throughout the whole deposition process.<sup>44</sup> As this kind of very specific studies were not performed in this work, corresponding quantitative analysis was not possible. However, comparing the data presented in Fig. 7b and d, one can see that the changes in the Ga mass growth per cycle are in a very good correlation with corresponding changes in the surface roughness of crystalline films. Therefore, in the present case, the surface roughening seems to be the main reason for the higher growth rates of crystalline films.

### 3.3. Electrical properties

Electrical characterization of Pt/Ga<sub>2</sub>O<sub>3</sub>/Ru and Pt/Ga<sub>2</sub>O<sub>3</sub>/TiN structures demonstrated that symmetrical current–voltage (*I*–*V*) curves (Fig. 8) were typical for structures with amorphous and quasi-amorphous Ga<sub>2</sub>O<sub>3</sub> layers deposited at *T*<sub>G</sub> values up to 325 °C. Breakdown voltage amplitudes, recorded for these samples at different voltage polarities, were similar to each other (blue curves in Fig. 8a and b) while the breakdown electric field strengths (*E*<sub>b</sub>) of these Ga<sub>2</sub>O<sub>3</sub> films were 4.8–5.5 MV cm<sup>-1</sup> (Fig. 9). The deposition of Ga<sub>2</sub>O<sub>3</sub> at higher *T*<sub>G</sub> caused an increase in the current recorded at the positive top-electrode voltage polarity, leading to the asymmetry of the *I*–*V* curves (Fig. 8). This result indicates that the potential barrier between the bottom electrode and Ga<sub>2</sub>O<sub>3</sub> decreased with increasing *T*<sub>G</sub> or the contribution of trap-assisted tunneling<sup>45</sup> increased due to the formation of a defective interface region at the bottom electrode. Based on the STEM scans (Fig. 1b and d) that revealed mixing of the bottom electrode materials with Ga<sub>2</sub>O<sub>3</sub> at higher *T*<sub>G</sub>, one can conclude that the growth of interface layers with graded composition was probably the main reason for both effects. Because of these changes in *I*–*V* curves, the *E*<sub>b</sub> of the Ga<sub>2</sub>O<sub>3</sub> layers deposited at *T*<sub>G</sub> ≥ 350 °C were reliably measurable only at the negative top-electrode biases (Fig. 8b).

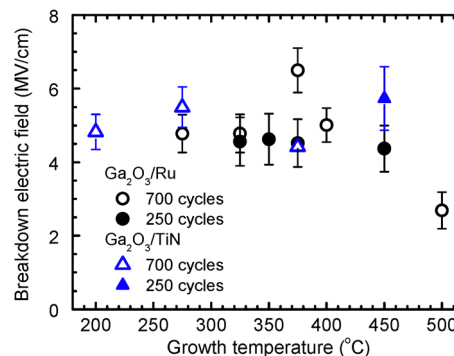


Fig. 9 Breakdown electric field strength as a function of *T*<sub>G</sub> of Ga<sub>2</sub>O<sub>3</sub> films deposited on Ru and TiN using 250 and 700 ALD cycles.

The highest *E*<sub>b</sub> of 6.5 MV cm<sup>-1</sup> (Fig. 9) was recorded for crystalline Ga<sub>2</sub>O<sub>3</sub> deposited at 375 °C. Although *E*<sub>b</sub> decreased to 2.7 MV cm<sup>-1</sup> with the *T*<sub>G</sub> increase to 500 °C (Fig. 9), all *E*<sub>b</sub> values of our films were higher than those of around 1.2 and 2.0 MV cm<sup>-1</sup>, reported for κ-Ga<sub>2</sub>O<sub>3</sub> and (β + κ)-Ga<sub>2</sub>O<sub>3</sub> films deposited on epitaxial Pt(1 1 1) bottom electrodes by metalorganic chemical vapor deposition (MOCVD), and plasma-enhanced ALD (PEALD).<sup>21</sup> Higher *E*<sub>b</sub> values, for example, 6.5–7.6 MV cm<sup>-1</sup> for amorphous Ga<sub>2</sub>O<sub>3</sub>,<sup>14,15</sup> 5.2–8.8 MV cm<sup>-1</sup> for β-Ga<sub>2</sub>O<sub>3</sub>,<sup>10,19,46,47</sup> and 11 MV cm<sup>-1</sup> for ultrathin (2.7–2.9 nm) native Ga<sub>2</sub>O<sub>3</sub> grown on liquid metals,<sup>48</sup> can also be found in the literature. As a rule, the *E*<sub>b</sub> values have been higher for Ga<sub>2</sub>O<sub>3</sub> films deposited on Si or n<sup>+</sup>-Ga<sub>2</sub>O<sub>3</sub> substrates<sup>10,46</sup> than for the films with the same crystal structure grown on highly conductive bottom electrodes.<sup>19,47</sup> Comparing the parameters of films deposited on highly conductive substrates, the *E*<sub>b</sub> values of 5.2 MV cm<sup>-1</sup> for β-Ga<sub>2</sub>O<sub>3</sub> transferred onto graphene<sup>47</sup> and 5.5 MV cm<sup>-1</sup> for β-Ga<sub>2</sub>O<sub>3</sub> deposited on Pt electrodes<sup>19</sup> can be found in the literature.

Therefore, the literature data and results depicted in Fig. 3 and 9 indicate that amorphous Ga<sub>2</sub>O<sub>3</sub> (Fig. 9), β-Ga<sub>2</sub>O<sub>3</sub>,<sup>19,47</sup> and films that contain κ-Ga<sub>2</sub>O<sub>3</sub> and ε-Ga<sub>2</sub>O<sub>3</sub> (Fig. 9), all deposited on substrates with metallic conductivity, have comparable breakdown electric field strengths. As also shown in Fig. 9, the

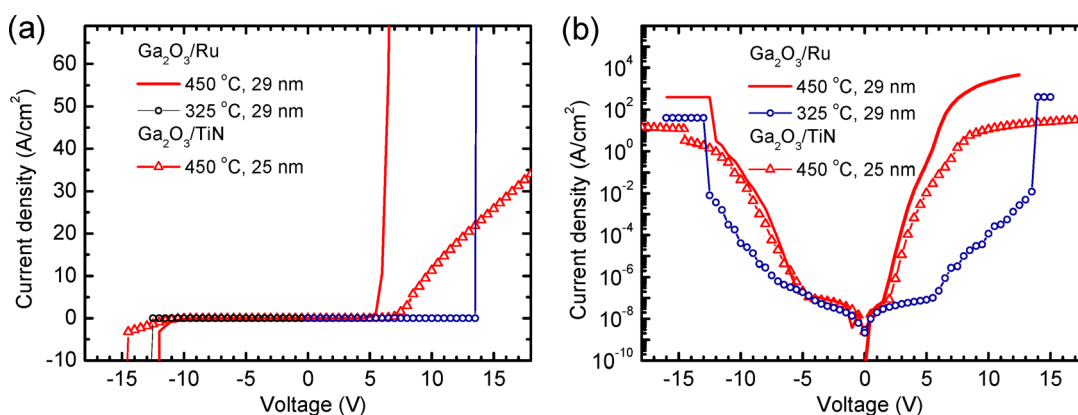


Fig. 8 Current density presented in (a) linear and (b) logarithmic scale as a function of voltage for Ga<sub>2</sub>O<sub>3</sub> films deposited on Ru at 325 and 450 °C, and on TiN at 450 °C. The films were deposited using 250 ALD cycles. The film thicknesses are specified in the figure panels.



increase of  $T_G$  from 200 to 275 °C that resulted in the most significant decrease of the iodine content in amorphous films (Fig. 2) caused only a minor increase in the breakdown electric field strength (Fig. 9).

At low voltages and, thus, low-electric field strengths, the current densities recorded for crystalline films grown with 250 cycles at 375 °C and with 700 cycles at 325–400 °C were lower than those recorded at the same electric field strength for amorphous films grown with 250 cycles at 325 °C and with 700 cycles at 275 °C (Fig. 10, 11 and Fig. S7). At higher voltages, the current densities through crystalline  $\text{Ga}_2\text{O}_3$  considerably exceeded that through amorphous  $\text{Ga}_2\text{O}_3$  (Fig. 8). A possible reason for this effect is the diffusion of the bottom electrode materials into a  $\text{Ga}_2\text{O}_3$  layer, causing an increase in the defect concentration and higher contribution of trap-assisted tunneling. Another reason for this difference is the higher surface roughness of crystalline films which increases the local electric field strength leading to higher probability of tunneling.

In the structures with thin  $\text{Ga}_2\text{O}_3$  layers deposited on Ru electrodes at  $T_G > 375$  °C, the leakage current density increased with  $T_G$  even at low voltages (Fig. 10a and 11). For example, a  $T_G$  increase from 450 to 500 °C caused an increase in the current density determined at an electric field strength of

0.1  $\text{MV cm}^{-1}$  by 3 orders of magnitude (Fig. 11a and b). Assuming that thermionic emission controlled the current transport across the metal/dielectric interface at low electric field strengths,<sup>49</sup> a reduction of effective energetic barrier causing a comparable increase in current density was estimated to be about 0.2 eV. Since no such increase in the current density was observed in the case of thicker  $\text{Ga}_2\text{O}_3$  layers (Fig. 10b and 11a, b), the effect can be related to the diffusion of Ru into  $\text{Ga}_2\text{O}_3$  leading to a growth of more defective film material during the initial stage of deposition. In the thicker films grown using 700 ALD cycles, the contribution of the defective interface layer was evidently much smaller and therefore the increase in  $T_G$  did not cause a considerable increase in the current density (Fig. 11).

In the TEM image (Fig. 1a) and STEM-EDX scans (Fig. 1b) of the cross section of film deposited at 450 °C, a defective interface layer with a graded composition can be seen at the  $\text{Ga}_2\text{O}_3/\text{Ru}$  interface. The thickness of this layer ranged from 2 to 5 nm (Fig. 1a). Considering that at 500 °C an even thicker interface layer was formed, a significant effect of this layer on the  $I$ - $V$  characteristics of a 25-nm-thick film is a predictable result. Although the influence of the interface layer on the leakage currents of 56-nm-thick films grown at 500 °C with

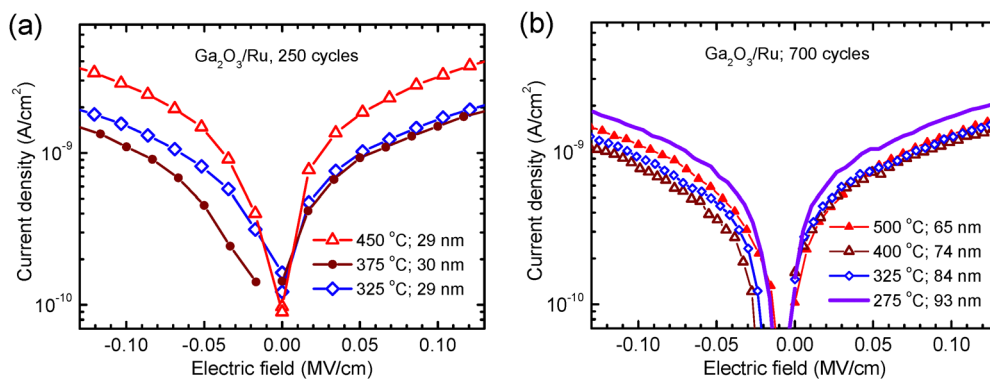


Fig. 10 Current density recorded as a function of electric field strength for  $\text{Ga}_2\text{O}_3$  films deposited on Ru at different  $T_G$  using (a) 250 and (b) 700 ALD cycles.  $T_G$  and film thicknesses are shown in the figure panels.

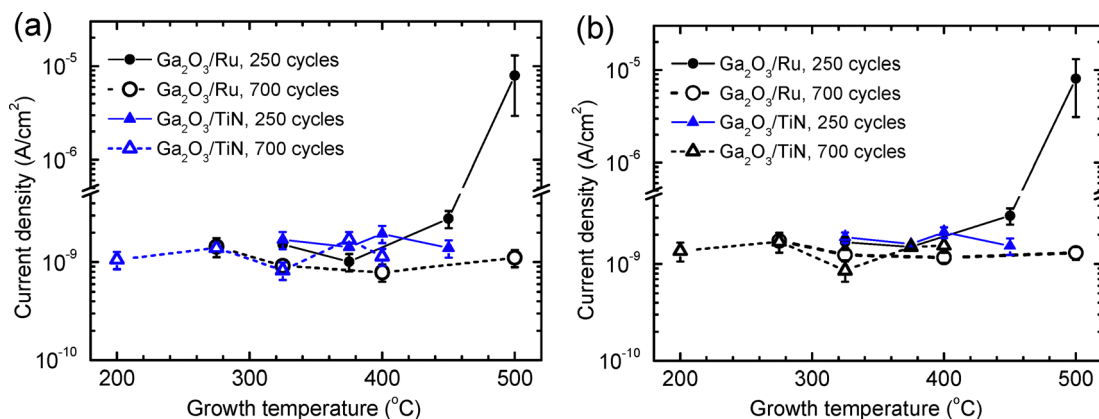


Fig. 11 Current densities measured at (a) negative and (b) positive top-electrode voltage polarities for  $\text{Ga}_2\text{O}_3$  films deposited at 200–500 °C on Ru and TiN using 250 and 700 ALD cycles. The current densities were determined at an electric field strength of 0.1  $\text{MV cm}^{-1}$ .



700 ALD cycles was expectedly weaker (Fig. 11), additional interface roughening related to the interface layer formation (Fig. 1a) evidently contributed to the reduction of the breakdown field with the increase of  $T_G$  to 500 °C (Fig. 9).

A notable result is the weak influence of  $T_G$  on the electrical characteristics of amorphous films obtained in the temperature range of 200–275 °C where the most considerable change in the concentration of residual iodine impurities occurred (Fig. 2). Thus, the role of these impurities in determining the charge carrier transport was not significant in the case of structures studied in this work.

The direct-current  $I$ - $V$ -curves (Fig. 8a) and the data of alternate-current measurements showed that the series resistance of samples with  $\text{Ga}_2\text{O}_3$  films deposited on TiN bottom electrodes at higher  $T_G$  was too high for reliable capacitance and permittivity measurements. A probable reason for this was the TiN oxidation during the ALD of  $\text{Ga}_2\text{O}_3$  at higher  $T_G$  as can be concluded from the STEM-EDX line scans shown in Fig. 1d. Therefore, the results of permittivity measurements of the films grown on TiN are shown in Fig. 12 only for a limited  $T_G$  range. There was no such problem in the case of samples with Ru bottom electrodes because the  $\text{RuO}_2$  formed on the surface of Ru (Fig. 1b) is conductive enough. Nevertheless, owing to the high leakage current densities of the  $\text{Ga}_2\text{O}_3$  films deposited on Ru at 500 °C using 250 ALD cycles, accurate capacitance measurements of these films were not possible either.

The  $k$  values of  $\text{Ga}_2\text{O}_3$ , calculated from the capacitances measured at a frequency of 10 kHz, are depicted in Fig. 12. As can be seen, markedly higher  $k$  values were obtained for crystalline  $\text{Ga}_2\text{O}_3$  films deposited at 375–500 °C than for the amorphous and quasi-amorphous films deposited at  $T_G \leq 325$  °C. The  $k$  values of 29–93 nm thick films containing  $\kappa$ - $\text{Ga}_2\text{O}_3$  and  $\epsilon$ - $\text{Ga}_2\text{O}_3$  ranged from 15 to 22 at a frequency of 10 kHz, while the highest  $k$  was recorded for a 74 nm film deposited at 450 °C (Fig. 12).

The  $k$  values of our amorphous films, ranging from 13.0 to 14.2 (Fig. 12), were somewhat higher than the  $k$  of 9.2–11.9 published for amorphous  $\text{Ga}_2\text{O}_3$  grown by ALD on Si substrates.<sup>14,15</sup>

As the latter films showed higher breakdown fields,<sup>14,15</sup> it is possible that an interface  $\text{SiO}_2$  layer that can easily be formed on the surface of Si in ALD processes<sup>50</sup> was responsible for the somewhat lower  $k$  and higher  $E_b$  of those.

The oxidation of the bottom TiN electrode also resulted in the underestimation of  $k$  in the case of our films because the formation of interfacial  $\text{TiO}_2$  layer was not considered in the calculations of  $k$ . However, as the  $k$  of  $\text{TiO}_2$ <sup>42</sup> is higher than that of  $\text{Ga}_2\text{O}_3$  (Fig. 12) and the thickness of an oxygen-rich region of  $\text{TiO}_x\text{N}_y$  formed on a TiN electrode at deposition temperatures up to 450 °C did not exceed 2 nm (Fig. 1d), the underestimation of  $k$  should not exceed 6% for 30-nm-thick  $\text{Ga}_2\text{O}_3$  layers. In the case of thicker  $\text{Ga}_2\text{O}_3$  films, this underestimation is even smaller. Therefore, the corresponding error in the determination of  $k$  is smaller than the experimental uncertainties shown in Fig. 12.

The  $k$  values determined at frequencies of 1–2 MHz for our amorphous and quasi-amorphous films deposited at 275–325 °C (Fig. 13) are comparable to those (up to 12.4) determined for single-crystal  $\beta$ - $\text{Ga}_2\text{O}_3$  at 1 MHz<sup>17</sup> and 0.2–1 THz.<sup>17,18</sup> By contrast, the  $k$  values of films that contained  $\kappa$ - $\text{Ga}_2\text{O}_3$  and  $\epsilon$ - $\text{Ga}_2\text{O}_3$  grown at  $T_G \geq 375$  °C in our experiments (Fig. 12 and 13) significantly exceeded the values reported for  $\beta$ - $\text{Ga}_2\text{O}_3$ ,<sup>17–19</sup> being well comparable to  $k$  reported for orthorhombic  $\text{Ga}_2\text{O}_3$ .<sup>20,21</sup>

Significant variation of  $k$  values, similar to that recorded for our films containing orthorhombic  $\text{Ga}_2\text{O}_3$ , has also been observed in earlier studies. For instance, Yuza *et al.*<sup>20</sup> reported  $k$  values of 15 and 32 at 10 kHz for orthorhombic films with the thicknesses 89 and 136 nm, respectively. At the same frequency, He *et al.*<sup>21</sup> obtained  $k = 18$  for a 700 nm thick MOCVD film predominantly containing  $\kappa$ - $\text{Ga}_2\text{O}_3$ , and  $k = 27$  for a 50 nm thick PEALD film containing mixed  $\kappa$ - $\text{Ga}_2\text{O}_3$  and  $\beta$ - $\text{Ga}_2\text{O}_3$  phases. The latter result, showing that  $k$  values determined for a mixture of phases is much higher than the  $k$  of any component of the mixture, is somewhat surprising and requires further study. An explanation proposed by He *et al.*<sup>21</sup> was that the MOCVD films, showing lower  $k$ , also contained considerable amounts of

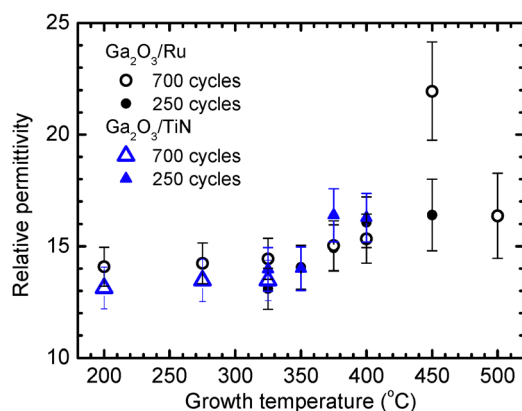


Fig. 12 Relative permittivity determined at a frequency of 10 kHz as a function of  $T_G$  for  $\text{Ga}_2\text{O}_3$  films deposited on Ru and TiN using 250 and 700 ALD cycles.

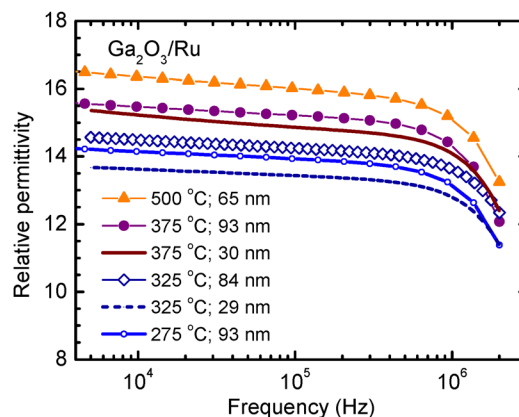


Fig. 13 Relative permittivity determined as a function of frequency for  $\text{Ga}_2\text{O}_3$  films deposited on Ru at different  $T_G$ .  $T_G$  and film thicknesses are specified in the figure panel.



$\beta$ -Ga<sub>2</sub>O<sub>3</sub>, but due to the location of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> at the film-substrate interface, its effect on the data of electrical measurements was stronger than the influence on the XRD results.

Results of XRD and TEM studies indicated that some amounts of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were also present in the films deposited in our experiments at 450 °C (Fig. 3, 6 and Fig. S2). However, the  $T_G$  increase from 450 °C to higher temperatures, causing an increase in the intensity of the XRD reflections attributable to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (Fig. 3 and Fig. S2), led to a decrease in  $k$  (Fig. 12). Therefore, the formation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> together with  $\kappa/\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> does not seem to be the main reason for obtaining high  $k$  in our studies.

The marked differences in  $k$ , measured for Ga<sub>2</sub>O<sub>3</sub> films, can also be related to dissimilar concentrations of oxygen vacancies in the films. For instance, in a recent study,  $k$  values as high as 18.1–20.8 at 10 kHz were reported for 3–7- $\mu$ m-thick aerosol-deposited  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> films.<sup>19</sup> However, annealing of these films at 800 °C under oxygen-containing ambient conditions resulted in a decrease of  $k$  to 8.8–9.3, that is, to the values that are more common for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Simultaneously the leakage current through the dielectric decreased and the breakdown field increased from 1–2 MV cm<sup>-1</sup> to 5.5 MV cm<sup>-1</sup>.<sup>19</sup> Based on these results, Lee *et al.*<sup>19</sup> concluded that high concentration of oxygen vacancies was the reason for the very high  $k$  obtained for aerosol-deposited films before annealing at high-temperature. In our experiments, in contrast, the increase of  $T_G$  from 325 to 400 °C for thinner films and from 325 to 450 °C for thicker films, leading to the increase in  $k$  (Fig. 12 and 13), did not cause corresponding decrease in breakdown electric field (Fig. 9) and an increase in leakage current (Fig. 11). Thus, the relatively high  $k$  values of our films (Fig. 12 and 13) were not due to a high concentration of oxygen vacancies.

The possible contribution of residual iodine impurities to  $k$  also seems to be insignificant because no correlation between these two parameters could be found. In particular,  $k$  did not vary considerably when the iodine concentration decreased from 1.4 to 0.03 at% with the increase of  $T_G$  from 200 to 325 °C (Fig. 2 and 12). Instead,  $k$  most significantly increased with  $T_G$  in a temperature range of 350–450 °C where iodine concentration variations did not exceed 0.02 at%. Consequently, the predominant growth of  $\kappa$ -Ga<sub>2</sub>O<sub>3</sub> together with inclusions of  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> is the main reason for the high  $k$  of films deposited at 375–450 °C in our studies.

Unfortunately, due to the structural similarities of  $\kappa$ -Ga<sub>2</sub>O<sub>3</sub> and  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub>, finding the process parameters for separate growing each of these two phases and clarifying the individual contribution of each phase to the electrical properties of Ga<sub>2</sub>O<sub>3</sub> thin films is a task that requires additional investigation. Nevertheless, the results of our study already demonstrate that the films containing these phases have promising dielectric properties for the application of those in capacitor structures and gate stacks of field effect transistors. In addition, the ALD process based on GaI<sub>3</sub> and O<sub>3</sub> as precursors is suitable for growing these films on the Ru and TiN surfaces at relatively low  $T_G$ . However, because of the detrimental effect of GaI<sub>3</sub> and O<sub>3</sub> on the substrate surfaces, especially at higher temperatures,

careful selection of process parameters is of significant importance in the implementation of this ALD process.

## 4. Conclusions

This study shows that the ALD process based on GaI<sub>3</sub> and O<sub>3</sub> as precursors allows the growth of Ga<sub>2</sub>O<sub>3</sub> films with high breakdown electric field strength and permittivity values. Crystalline Ga<sub>2</sub>O<sub>3</sub> with a predominant  $\kappa$ -Ga<sub>2</sub>O<sub>3</sub> phase was formed in the films deposited on Ru and TiN seed layers at temperatures down to 325 °C. In addition, minor amounts of  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were found in the films by TEM studies. A comparison of Ga<sub>2</sub>O<sub>3</sub> deposition on Ru and TiN with that on Si indicated that the formation of crystalline phases in the films caused a considerable increase in growth per cycle and an expected increase in the density and surface roughness. The effect of crystallization on the breakdown electric field and leakage current density was weak. At the same time, the highest breakdown field (6.5 MV cm<sup>-1</sup>) and the lowest leakage current densities (1.0–1.1 nA cm<sup>-2</sup> at a mean electric field of 0.1 MV cm<sup>-1</sup> applied to the Pt/Ga<sub>2</sub>O<sub>3</sub>/TiN structure) were recorded for crystalline Ga<sub>2</sub>O<sub>3</sub>. The relative permittivity determined at a frequency of 10 kHz reached values up to 14 in the case of amorphous films, deposited at 275 °C, and up to 22 in the case of  $\kappa/\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> films deposited on Ru at 450 °C. These results demonstrate that the GaI<sub>3</sub>-O<sub>3</sub> ALD process can be applied for deposition of high-quality Ga<sub>2</sub>O<sub>3</sub> films on both Ru and TiN bottom electrodes. It should further be noted that, at higher temperatures, this ALD process has a detrimental effect on the concerned electrodes. A marked increase in the resistance of TiN appeared because of its oxidation while, at  $T_G > 450$  °C, the degradation of Ga<sub>2</sub>O<sub>3</sub>/Ru interface properties, related to the diffusion of Ru into the Ga<sub>2</sub>O<sub>3</sub> layer, caused a decrease in the breakdown voltage and increase in the leakage current density.

## Author contributions

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

The authors declare that there are no financial or any other types of conflicts of interest to declare for this submission.

## Data availability

Data are available from the authors upon request.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5tc04544d>.



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