



# Interplay of annealing temperature and Ga-Zn-O template thickness in the crystallographic properties of in-Ga-Zn-O thin films

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## ABSTRACT

We report on the synthesis and characterization of spinel In-Ga-Zn-O (IGZO) thin films, having application as channel of thin-film transistors (TFTs). To obtain the spinel IGZO phase, the deposition of the IGZO was carried out on a spinel Ga-Zn-O (GZO) layer, followed by annealing in forming gas (i.e., a gas mixture of 10% H<sub>2</sub> and 90% N<sub>2</sub>). We investigated the structural and crystallographic properties of the IGZO. To do this, we employed X-ray Diffraction and Transmission Electron Microscopy, in particular Precession Electron Diffraction. During this study, we observed the segregation of In and In<sub>2</sub>O<sub>3</sub> phases in the IGZO. Therefore, we were interested in understanding: (i) the location of the segregated phases, (ii) the crystal orientation of IGZO, GZO, In and In<sub>2</sub>O<sub>3</sub> phases, (iii) the impact of GZO thickness, and (iv) the temperature effect during the forming gas annealing. We found that In and In<sub>2</sub>O<sub>3</sub> phases form nanoparticles at the surface of the IGZO. At high annealing temperature (above 420 °C), small In and In<sub>2</sub>O<sub>3</sub> grains form also in the IGZO matrix. We explain that this is due to the reduction effect which the H in the forming gas annealing induces on the In-O species present in the IGZO crystal. Other crystallographic characteristics, such as the texture of the IGZO and the grain sizes, are related to the properties of the GZO template. In summary, this work evidenced the phase segregation in the IGZO and its crystallographic properties, both paramount for the performances of the IGZO TFTs.

## 1. Introduction

In-Ga-Zn-O (IGZO) compounds are promising materials for applications as the channel layer in thin film transistors (TFTs), due to their low off-current [1] and high field-effect mobility [2]. They can be synthesized through various physical and chemical methods including sputtering [3], pulsed laser deposition [4] and atomic layer deposition [5] combined with post-synthesis annealing treatments. The crystallographic properties of IGZO are a key factor determining the final performances of the electronic devices. Numerous IGZO crystalline configurations can be formed, by changing the deposition conditions and curing treatments [3]. Amorphous IGZO is easy to deposit at low temperatures and has a reasonable electron mobility (i.e., 10–20 cm<sup>2</sup>/(V.s)) compared to the crystalline phases (80 cm<sup>2</sup>/(V.s)) [6]. However, in the perspective of the fabrication of electronic devices, amorphous IGZO TFTs suffer from electrical instability [7]. Crystalline IGZO mostly exists in the rhombohedral and hexagonal phases, two

polytypes having space group  $R\bar{3}m$  (166) and  $P6_3/mmc$  (194), which have showed higher mobility than amorphous IGZO [8–11]. By physical vapor deposition, it is possible to grow also an intermediate crystalline phase, in which the crystal periodicity is maintained only along the c-axis, while the structure becomes disordered in the direction of the a and b-axis. This phase is called CAAC (c-axis aligned crystalline) IGZO and is less prone to oxygen vacancies formation [12]. More sophisticated configurations have been employed in TFTs: for instance, a double layer design, consisting of amorphous and CAAC-IGZO, has shown good device stability [13].

The family of IGZO compounds was recently further enriched with a new spinel poly-type, having space group  $Fd\bar{3}m$  (227) and cubic unit cell with lattice parameter of 8.676 Å [3]. By using intermediate temperature for the deposition of the IGZO film (in between the temperature used to grow amorphous and CAAC IGZO), the spinel phase is obtained, which remains stable in the spinel crystal configuration after annealing at 700 °C under O<sub>2</sub> atmosphere. As such, the spinel phase is still not

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pure, since amorphous or a “poly-CAAC” phase are also formed during the initial growth at the bottom of the film. Those phases crystallize into the hexagonal phase at temperatures above 650 °C. The presence of the amorphous or poly-CAAC bottom layer can be avoided if a spinel Ga-Zn-O (GZO) layer is deposited preliminary to the growth of the IGZO film [3,14]. After annealing at 700 °C under O<sub>2</sub> atmosphere, crystalline GZO is formed in the spinel phase (Fd3̄m (227) space group and lattice parameter of 8.36 Å). In this way, it can act as a seed for the formation of a pure spinel IGZO phase. This method allows the deposition of pure spinel IGZO at temperatures between 25 °C–250 °C. Other factors impacting the crystallographic properties of the IGZO layer are its stoichiometry [15], process conditions and the thickness of the GZO layer [3]. In general, spinel IGZO films are expected to be more robust against oxygen vacancy formation, a process that is induced by reaction with hydrogen at temperatures above 300 °C.

The aim of this paper is to further explore the crystallographic configurations in spinel IGZO films and the changes upon hydrogen annealing. To address this issue, we mainly employed electron microscopy related techniques in conjunction with X-ray diffraction (XRD). After preliminary scanning electron microscopy (SEM) observations, we conducted conventional transmission electron microscopy (TEM) imaging in both parallel beam condition (bright-field TEM or BF-TEM) and scanning TEM modes (annular-bright-field and high-angle-annular-dark-field STEM i.e., ABF-STEM and HAADF-STEM). To gain deeper insight into the crystallographic phases present in the IGZO, we utilized the precession electron diffraction (PED) technique [16]. By means of PED, a map of electron diffraction patterns can be generated point by point in STEM mode. While standard electron diffraction is significantly affected by multiple/dynamic scattering, which complicates the interpretation of diffracted intensities, PED provides better sensitivity for analyzing crystal structures. In PED, the electron beam is rocked at a fixed angle relative to the optic axis above the sample, forming a hollow cone, and then it is de-rocked below the sample. The final diffraction pattern contains a higher number of reflections compared to the case of an unprecessed beam with intensities unaffected by dynamic scattering [16]. We applied PED to the study of IGZO thin films (about 20 nm thick) having spinel structure and grown on GZO layers of different thickness (in the range of 2–10 nm). In a previous work [17], we already demonstrated the ability to accurately distinguish materials with similar electron diffraction patterns, such as IGZO and GZO, using PED. We also showed that good spatial resolution can be achieved to properly resolve narrow GZO layers, as thin as 2 nm, from the above IGZO [17]. In the present paper, we want to explore more in detail the occurrence of crystal phase separation in IGZO induced by thermal annealing. The properties of the crystallographic phases are investigated carefully, with particular attention to their growth directions and texture i.e., if a preferential crystallographic direction exists in such poly-crystalline compounds. These studies are important for controlling the crystallographic properties of IGZO, which are essential for achieving high-performance devices.

## 2. Methods

To produce the GZO/IGZO system, we initially deposited GZO on thermally oxidized 12-in (100) Si wafers. GZO was obtained via combinatorial sputtering, using Ga<sub>2</sub>O<sub>3</sub> and ZnO as a target. To form spinel GZO, annealing was performed at 700 °C for 1 hour in O<sub>2</sub> atmosphere. This corresponds to the highest possible temperature to induce GZO crystallization avoiding Zn out-diffusion. Afterwards, IGZO films with InGaZnO<sub>4</sub> stoichiometry were deposited by reactive sputtering in an Ar/O<sub>2</sub> gas environment, using a polycrystalline InGaZnO<sub>4</sub> target (In/Ga/Zn = 1:1:1, JX Nippon). This process was performed in an Applied Materials Impulse chamber, installed on an Applied Materials Endura platform with vacuum load-locks. We should remark that the initial amorphous GZO film was grown with Ga:Zn = 2:1, this composition corresponds to the stoichiometric ratio of the upper spinel IGZO,

contributing to the IGZO spinel phase stability. Hydrogen annealing treatments were performed in an A412 ASM furnace in forming gas, i.e., a mixture of 10% H<sub>2</sub> and 90% N<sub>2</sub>. Samples with different thickness of GZO template were subject to forming gas annealing (FGA) at 350 °C. Those samples were characterized by out-of-plane XRD on a Jordan Valley JYX tool with a Cu K-α source. To determine the film texture, the incident beam and detector were fixed at the characteristic diffraction angle 2Θ<sub>c</sub>, while the incident angle Ω was varied by tilting the wafer (Θ-Ω XRD). Next, a 24 nm thick spinel IGZO with the thinnest possible GZO template of 3 nm was analyzed with TEM techniques and compared to a sample with a 10 nm thick GZO template. It is worth saying that, *a posteriori*, we found that a phase segregation effect occurs in the IGZO and can be related to the increasing annealing temperature. For this reason, we wanted to study in detail a third sample, with 24 nm IGZO deposited on 3 nm thin GZO, subject to a first annealing treatment at 700 °C for 1 hour in O<sub>2</sub>, in order to avoid presence of spurious amorphous phase (as mentioned in the introduction); this latter was further annealed at 420 °C for 1 hour in forming gas to exaggerate the impact of H<sub>2</sub> annealing.

To summarize, the samples subject of particular attention in this paper are reported in Table 1.

Dual-beam Focused Ion beam (FIB)/SEM by Thermofisher instruments (i.e., Helios460 and Helios 5 FX) were used to perform preliminary SEM imaging of the samples surface with 5 kV electron beam, using a Through Lens Detector (TLD). These tools were also employed for TEM sample preparation of cross-section specimens. TEM inspections were performed using a double corrected Titan<sup>3</sup> G2 60–300 TEM operating at 200 kV. PED was performed using the NanoMEGAS platform combining the TopSpin framework and the Digistar hardware to control the rocking of the TEM beam. A 4DSTEM data set is acquired by scanning the precessed beam over the region of interest and acquiring a diffraction pattern for each scanning position. Beam convergence was set at 0.56 mrad and the precession angle was 0.4 degree. Condenser apertures of 50 or 20 μm, high spot sizes (9 and 10) and high camera length (285 mm) were used to better resolve the diffractions of IGZO and GZO. For the PED maps, we used step sizes of 3 or 1 nm, in correspondence to large-view or high-magnified regions, respectively. Data treatment was then achieved via the software suite for Phase and orientation mapping (ASTAR). This latter allowed indexing of the diffraction patterns and provides the most complete overview of the crystallographic properties of the samples.

## 3. Results

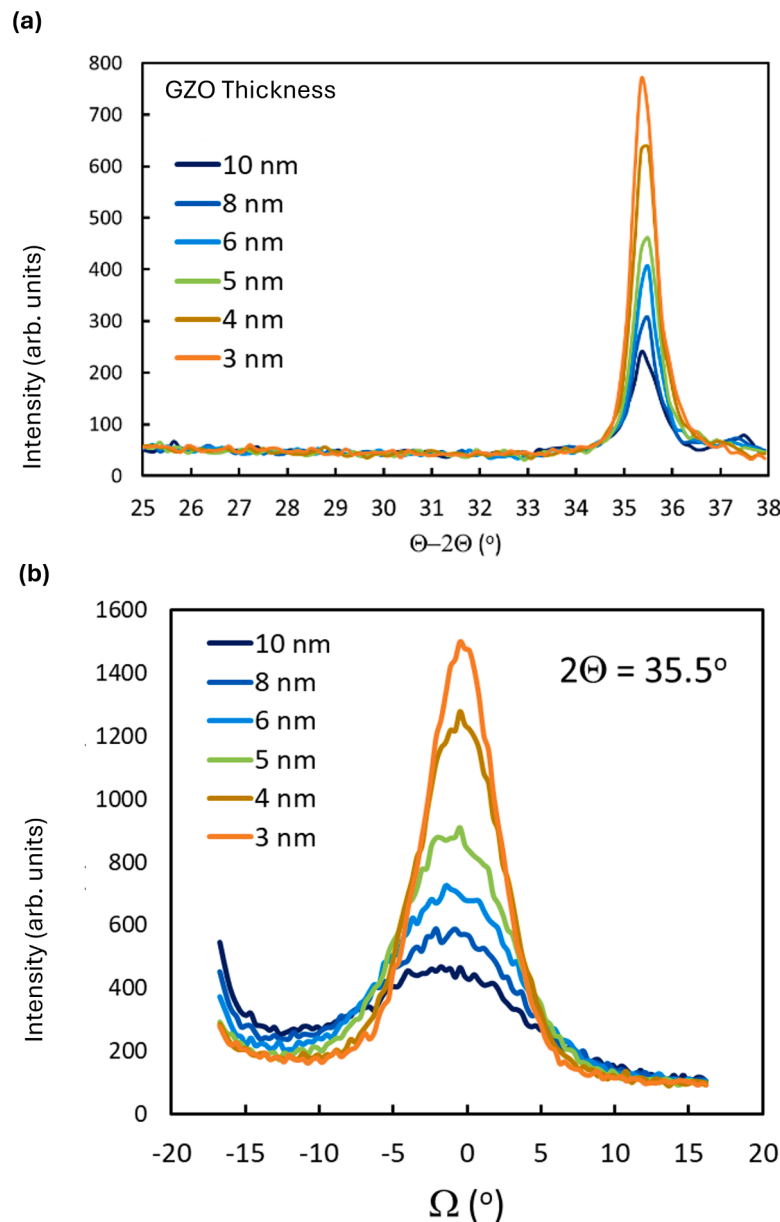
Fig. 1(a) displays an overview of the XRD curves for GZO/IGZO samples having different thickness of the GZO, while keeping constant the 24 nm nominal thickness for the upper IGZO. All the spectra show a clear diffraction peak at 2Θ = 35.5°, which corresponds to the (222) crystallographic plane of the spinel IGZO. No additional peaks in the range of 30° – 34° are observed (providing evidence for the absence of other phases like hexagonal IGZO), and any amorphous bump either. The (222) diffraction peak becomes more intense for samples having thinner GZO seed layer. This increase in intensity is attributed to an improved texture, as the Θ-Ω XRD (reported in Fig. 1(b)) confirms: more grains are having the (222) planes laying parallel to the surface.

When these films are subjected to the 350 °C FGA, other peaks

**Table 1**

Overview of the samples subject to deeper investigations via TEM techniques.

| SAMPLE | IGZO thickness | GZO thickness | Annealing treatment                                 |
|--------|----------------|---------------|-----------------------------------------------------|
| D02    | 24 nm          | 10 nm         | 1 h at 350 °C FGA                                   |
| D07    | 24 nm          | 3 nm          | 1 h at 350 °C FGA                                   |
| D17    | 24 nm          | 3 nm          | 1 h at 700 °C in O <sub>2</sub> + 1 h at 420 °C FGA |



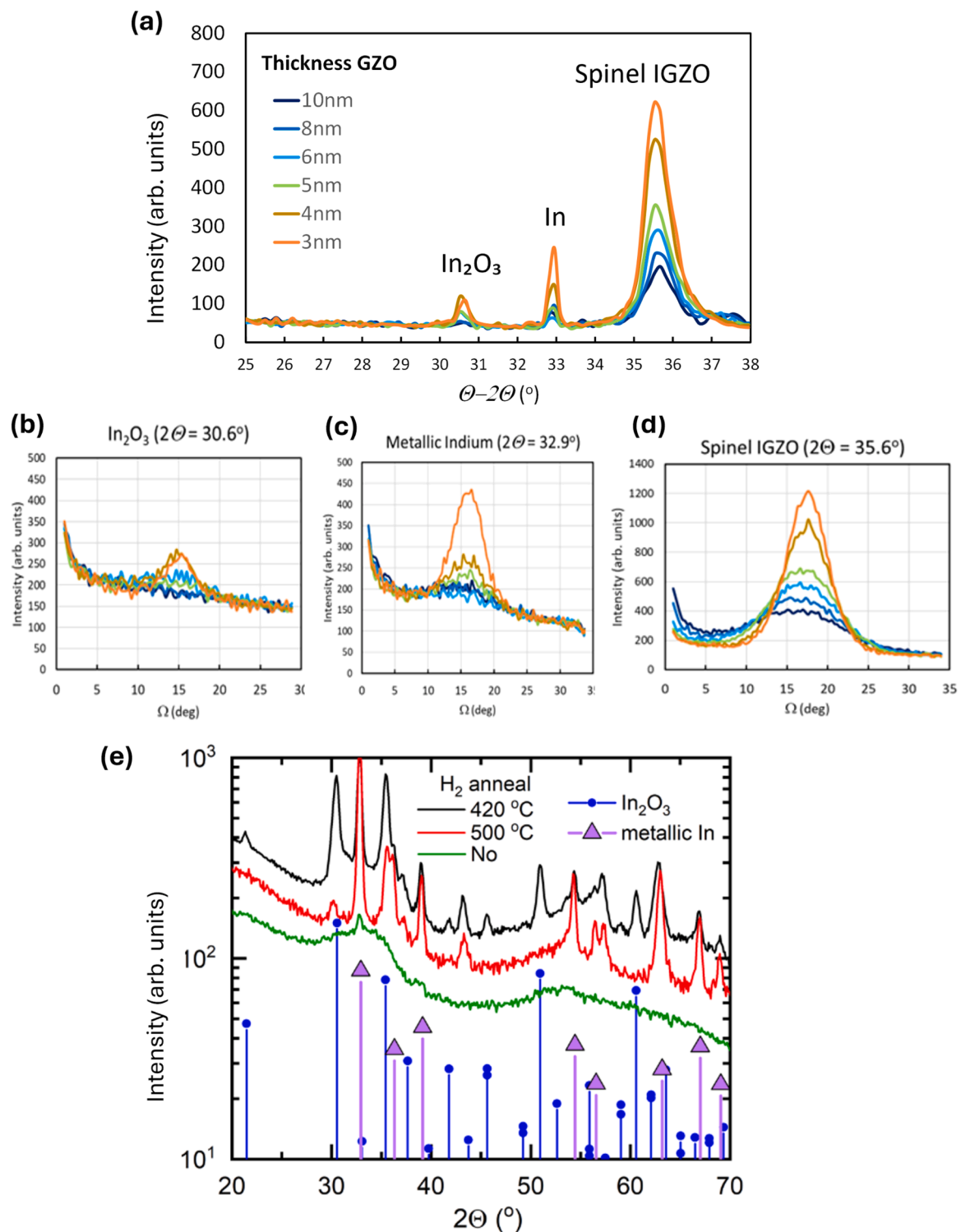
**Fig. 1.** (a) XRD curves of IGZO films having decreasing thickness of GZO seed layer, showing increased diffraction from (222) planes. (b)  $\theta$ - $\Omega$  XRD with  $2\theta$  fixed at  $35.5^\circ$ , showing a sharper distribution of sample tilt ( $\Omega$ ) for (222) diffraction for thinner GZO. This indicates more grains laying with the (222) planes parallel to the surface.

emerge, indicating phase separation (see Fig. 2(a)). The peak at  $2\theta = 30.6^\circ$  can be assigned to the (111) diffraction of  $\text{In}_2\text{O}_3$  bixbyite (i.e., a cubic phase with space-group  $\text{Ia}\bar{3}$  (206) and lattice parameters  $a=b=c = 10.18 \text{ \AA}$ ). Due to the limited thickness and preferential orientation of the spinel phase, observation of other diffraction peaks of the  $\text{In}_2\text{O}_3$  is difficult. However, using grazing incident (GI)-XRD to increase the path length of the incident beam, the full spectrum of  $\text{In}_2\text{O}_3$  was observed in amorphous IGZO after FGA at  $420^\circ\text{C}$  (see Fig. 2(e)). A second diffraction peak observed in Fig. 2(a) appears at  $2\theta = 32.9^\circ$  and can be assigned to the strongest diffraction of (101) planes of metallic In (i.e., a body-centered tetragonal phase, with space group  $\text{I4}/\text{mmm}$  and lattice parameters  $a=b = 3.26 \text{ \AA}$  and  $c = 4.99 \text{ \AA}$ ). Remarkably, a similar texture improvement of both  $\text{In}_2\text{O}_3$  and metallic In is observed by decreasing GZO thickness (see Fig. 2(b-d)). The signature of metallic In also appears in GI-XRD of Fig. 2(e). The metallic In peaks become relatively sharp and narrow after  $500^\circ\text{C}$  FGA, indicating a large agglomeration of metallic In, while the  $\text{In}_2\text{O}_3$  diffraction peaks disappear.

The ultimate evidence for the presence of metallic In after  $350^\circ\text{C}$  FGA is the in-situ XRD measurement in Fig. 3. In this measurement, the diffraction peak at  $2\theta = 32.9^\circ$  disappears around  $150^\circ\text{C}$ , close to the melting temperature of In ( $156^\circ\text{C}$ ).

To understand the structural properties underlying the XRD results, we performed thorough examinations of selected samples via TEM, as resumed in Table 1. The XRD curves of these selected samples are reported in Fig. 4. At closer look, the (222) diffraction peak of the IGZO shifts to higher  $2\theta$  with thinner GZO and a different annealing treatment, indicating a decrease in lattice constant, possibly caused by the loss of In from the spinel structure.

Firstly, we performed preliminary SEM and TEM investigations. SEM inspections of the samples surface revealed the presence of nanoparticles at the top of the IGZO, as shown in Fig. 5. The typical size of these particles differs for samples with different thickness of the GZO seed, looking larger (almost 400 nm) for the sample D02 (having thicker GZO layer), while in the sample D17 the particles look smaller (around 200

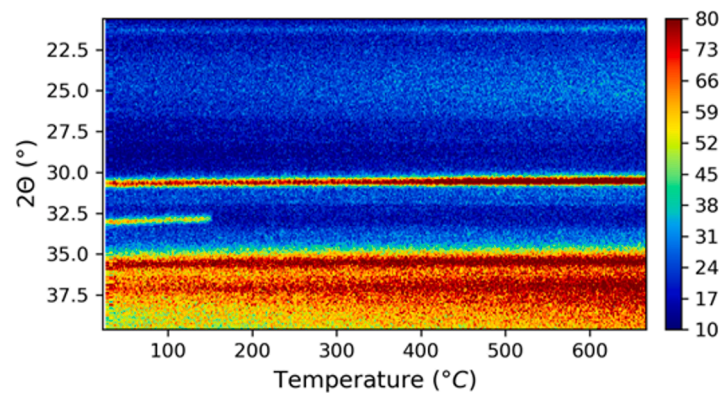


**Fig. 2.** (a) XRD pattern of similar films as in Fig. 1, but after FGA at 350 °C for 1 hour. (b-d)  $\Theta$ - $\Omega$  XRD with  $2\Theta$  fixed, respectively, (b) at the diffraction peak of  $\text{In}_2\text{O}_3$  ( $30.6^\circ$ ) and (c) metallic In ( $32.9^\circ$ ), showing similar crystallographic alignments as the (222)-planes of spinel IGZO ( $35.6^\circ$ ) (d). (e) GI-XRD pattern of amorphous IGZO films, as deposited and after  $\text{H}_2$  annealing at 420 °C and 500 °C, to obtain the diffraction from  $\text{In}_2\text{O}_3$  and In. The theoretical diffraction peaks for  $\text{In}_2\text{O}_3$  and In are given by the blue and purple lines, respectively.

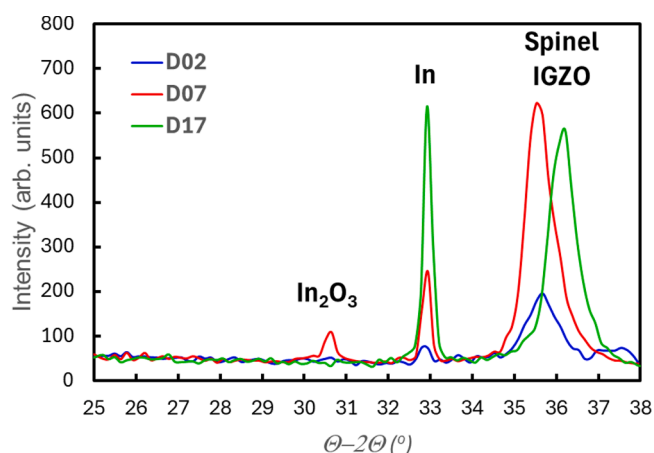
nm) than in the other samples.

Additional inspections were carried out via BF-TEM on the samples in cross-section, as depicted in Fig. 6. These preliminary analyses show the poly-crystalline nature of the three samples. The thicknesses of the different layers are in good agreement with the nominal thickness expected for the different samples.

Fig. 7 shows the HAADF-STEM images of the D02, D07 and D17 samples. It is well-known that the contrast in HAADF-STEM images is linked to compositional variations, as the image intensity depends on the atomic number  $Z$  of the constituent elements. For samples D02 and D07 (Fig. 7(a,b)), the contrast appears homogeneous across the IGZO film. On the other hand, in sample D17, as shown in Fig. 7(c), a grain



**Fig. 3.** In-situ XRD. Record of the  $\text{In}_2\text{O}_3$ , In and spinel IGZO diffraction intensity as function of temperature. Note that the In diffraction peak at  $32.9^\circ$  disappears at  $150^\circ\text{C}$ , close to the melting temperature of In.



**Fig. 4.** XRD curves of IGZO samples D02, D07 and D17.

with higher intensity than the surrounding IGZO film can be observed. This suggests that the composition of the IGZO film is uniform in samples D02 and D07, while some phase segregation occurs inside the IGZO layer for sample D17.

In order to clarify these observations, we performed STEM-EDX analyses. The results are illustrated in Fig. 8, which highlights one of the grains present in the matrix of the IGZO film. As we can see in the inset of Fig. 8(a), the grain is few nanometers in size. The EDX spectrum (Fig. 8(a)) acquired in this grain (Region 1, red color, indicated in Fig. 8(b)) shows a higher In concentration than in the surrounding matrix (Region 2, light blue color). Also, the In-map is more intense in correspondence of this grain, as it is visible in Fig. 8(b). This clearly reveals that In or  $\text{In}_2\text{O}_3$  can be present in some grains in the bulk of the IGZO. However, the diffraction peak at  $32.9^\circ$  in the XRD measurement of D17 is quite sharp, indicating that larger In grains should be present in the sample. For this reason, we explored the composition of the particles found at the surface of the samples.

To this aim, we performed additional EDX maps, as illustrated in Fig. 9. We can see that in sample D17 (Fig. 9(c)), the particle is composed of pure In and surrounded by an oxide thin layer. A small grain in the IGZO layer is also present in the vicinity of this particle, showing In composition. A similar In particle can be observed for sample D07 (Fig. 9(b)). In sample D02 (Fig. 9(a)), the particle contains a double phase of pure In and  $\text{In}_2\text{O}_3$ .

To fully investigate the phenomenon of phase separation from a crystallographic viewpoint, we conducted PED mapping of the samples and studied both the phase and the orientation maps, as reported in Figs. 10–15. IGZO and GZO have a 4% difference in lattice parameters,

which can be resolved via PED. In fact, we demonstrated that the GZO layer can be clearly resolved also in the case of GZO as thin as 2–3 nm, as shown in the phase maps for D02 and D07, displayed in Fig. 10. These maps were acquired in a region far from the particles and display the GZO/IGZO films.

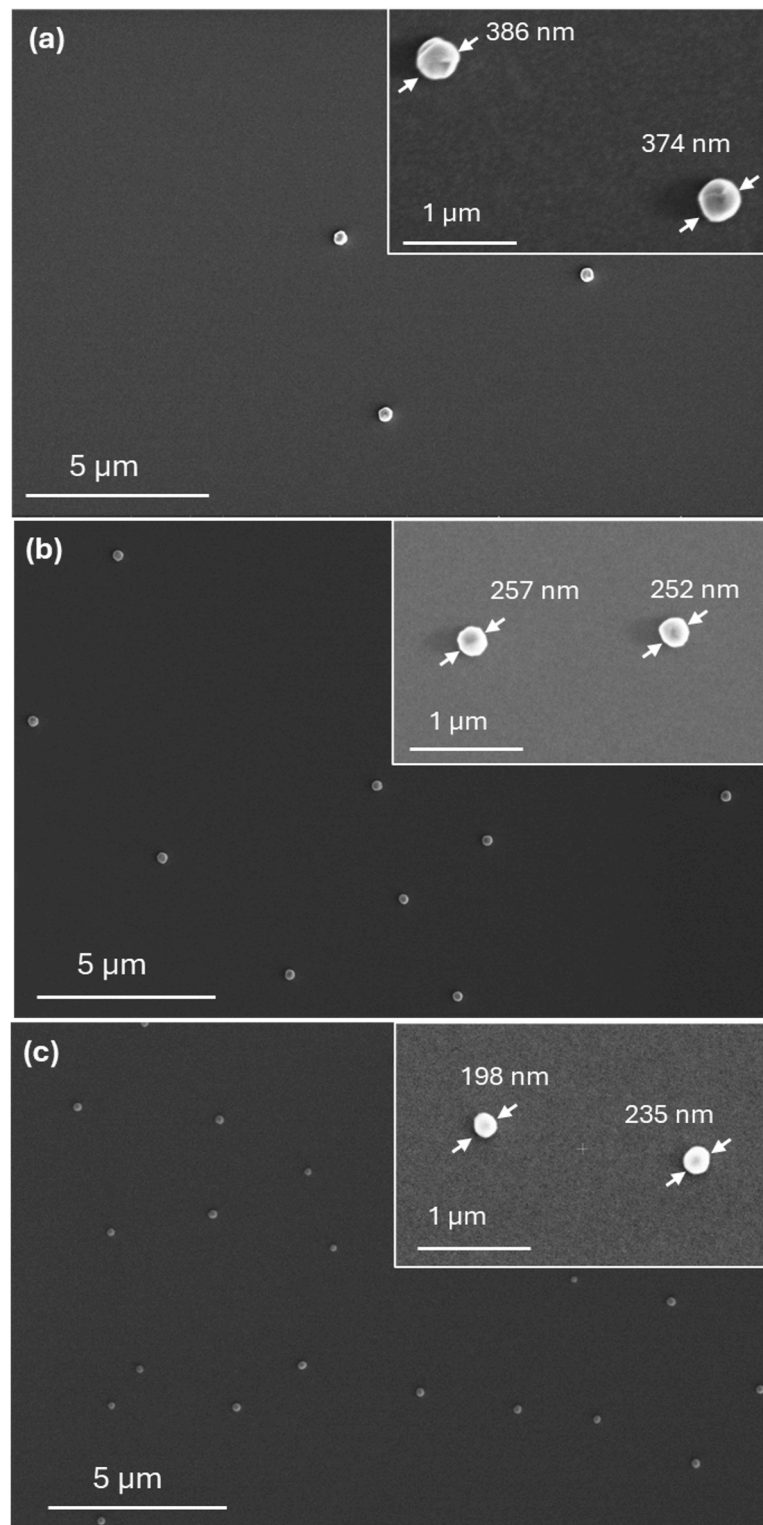
Furthermore, to get more insights about the crystallographic properties of our samples, we also analysed the orientations of the crystal grains for the IGZO, GZO, In and  $\text{In}_2\text{O}_3$  phases. To correctly interpret the orientation maps, we have to refer to the “color legend of the inverse pole figures” for the selected phases. Inverse pole figures are essentially related to the crystal systems and their Laue class. For example, since spinel IGZO, GZO and Si are all cubic phases with m-3 m Laue class, they have the same pole figure. For such phases, the color code to interpret the crystal grain orientation is illustrated in Fig. 11.

Firstly, we considered the orientation maps for samples D02 and D07, shown in Fig. 12 and acquired in the same regions displayed in Fig. 10. We can see that the grain size is larger in sample D02 (about 40–50 nm) than in sample D07 (about 10–20 nm). Moreover, we can observe that the IGZO grains grow above the underlying GZO grains and have the same orientation. Thus, we can infer from PED data that the grain size distribution is determined by the GZO film-thickness and it is not related to the annealing temperature. Then, from the comparison between Figs. 12(b) and 12(e), we can remark that along the y-direction (corresponding to the growth direction in our maps) sample D07 shows a uniform blue color, which is not the case for sample D02. Looking at the inverse pole figure reported in Fig. 11, the blue color for the GZO/IGZO phases refers to the  $\langle 111 \rangle$ -orientation, suggesting that these films present [111] texture along the growth direction. On the other hand, sample D02 presents a lower degree of texture along the growth direction.

Figs. 13 (b–e) illustrate the PED data acquired in the vicinity of the particle found in sample D02, as shown in the ABF-STEM image of Fig. 13(a). As concluded from EDX (see Fig. 9(a)), here we expect to find both In and  $\text{In}_2\text{O}_3$  phases. The color legend to interpret the orientation of these additional phases are reported in Fig. 13.

In this way, it is possible to highlight which is the growth direction of the In and  $\text{In}_2\text{O}_3$  phases. We can remark in Fig. 13(d) that the  $\text{In}_2\text{O}_3$  grows preferentially along the [111] direction (blue color in the color legend of the inverse pole figure of  $\text{In}_2\text{O}_3$ ). The In phase has a “lime” color (as evidenced by the star in the corresponding color legend), indicating that this phase grows with intermediate direction between  $\langle 001 \rangle$  and  $\langle 100 \rangle$ . If we calculate the corresponding direction for such a tetragonal phase, we can conclude that the In planes parallel to the interface are close to the (101). This confirms the texture along the growth direction identified in the XRD measurements (see comments about Fig. 2).

The PED maps corresponding to sample D07 are reported in Figs. 14 (b–e), relatively to the region depicted in Fig. 14(a). In this region, the



**Fig. 5.** SEM images of (a) sample D02, (b) sample D07, (c) sample D17. The different sizes of the particles on the surface are highlighted in the SEM at higher magnification shown in the insets.

particle shows the crystallographic characteristics of the  $\text{In}_2\text{O}_3$  phase. Also here, in the orientation map along y (Fig. 14(d)), the GZO, IGZO and  $\text{In}_2\text{O}_3$  phases exhibit [111]-texture along the growth direction. Similar comments can be applied to the crystallographic properties of sample D17, as inferred from Fig. 15. Here the particle has inner In phase surrounded by  $\text{In}_2\text{O}_3$  shell (some  $\text{In}_2\text{O}_3$  present at the center of the particle can be due to the residue of the  $\text{In}_2\text{O}_3$  shell in the TEM sample

cut across the particle). Again, in the orientation map along y (Fig. 15 (d)) the GZO, IGZO and  $\text{In}_2\text{O}_3$  phases exhibit [111]-texture along the growth direction, while the In phase grows preferentially with the (101) planes parallel with the interface.

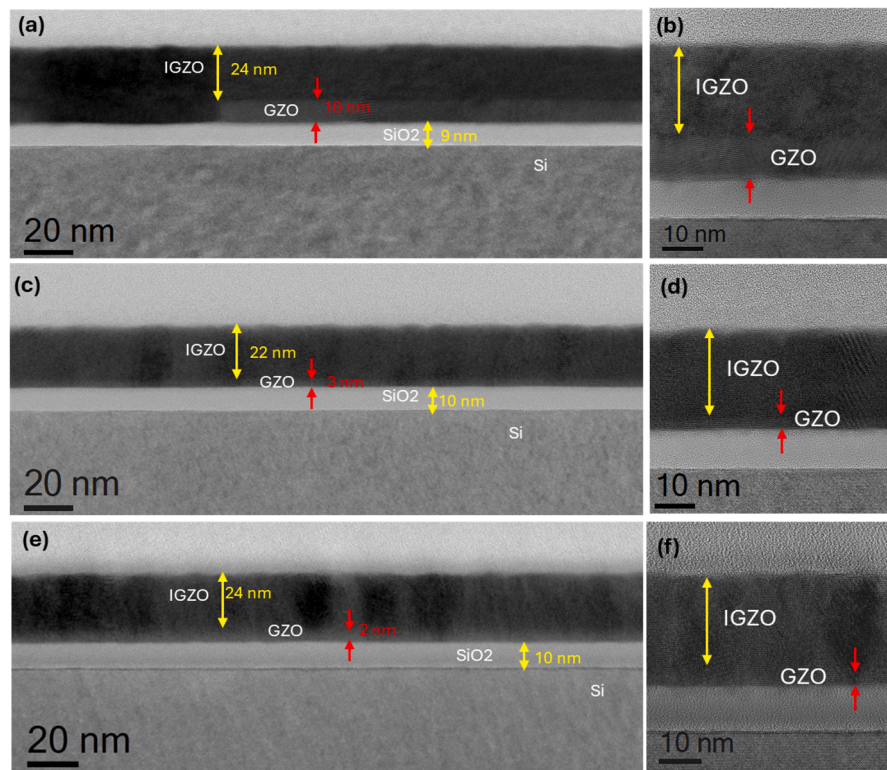


Fig. 6. BF-TEM images at low and high magnification, showing the cross section of sample D02 (a-b), D07 (c-d) and D17 (e-f).

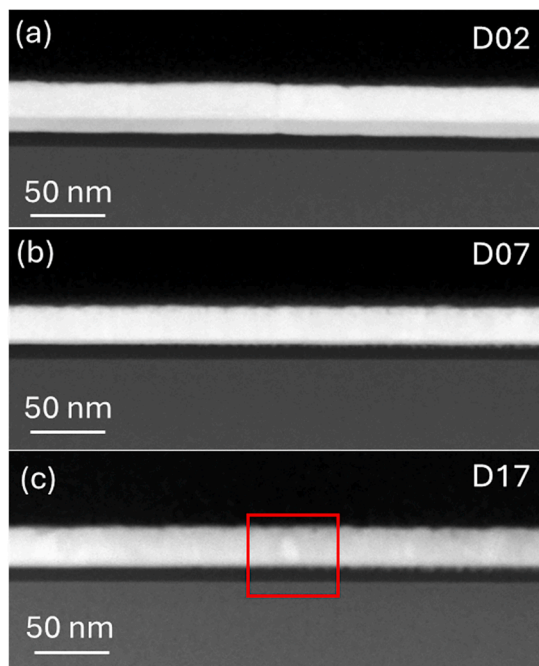
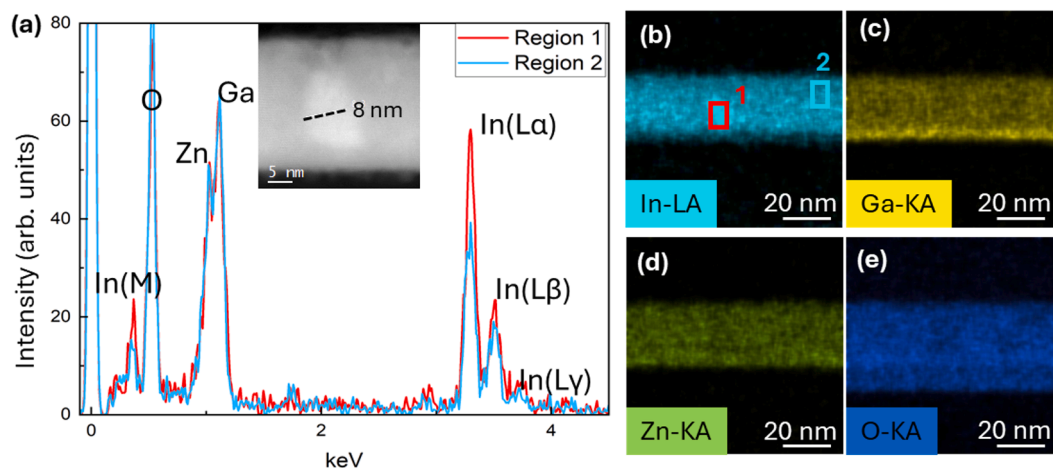


Fig. 7. HAADF-STEM images of sample D02 (a) and D07 (b) show uniform contrast of the IGZO film, while for sample D17 (c) we can see a grain with different contrast present in the IGZO film.

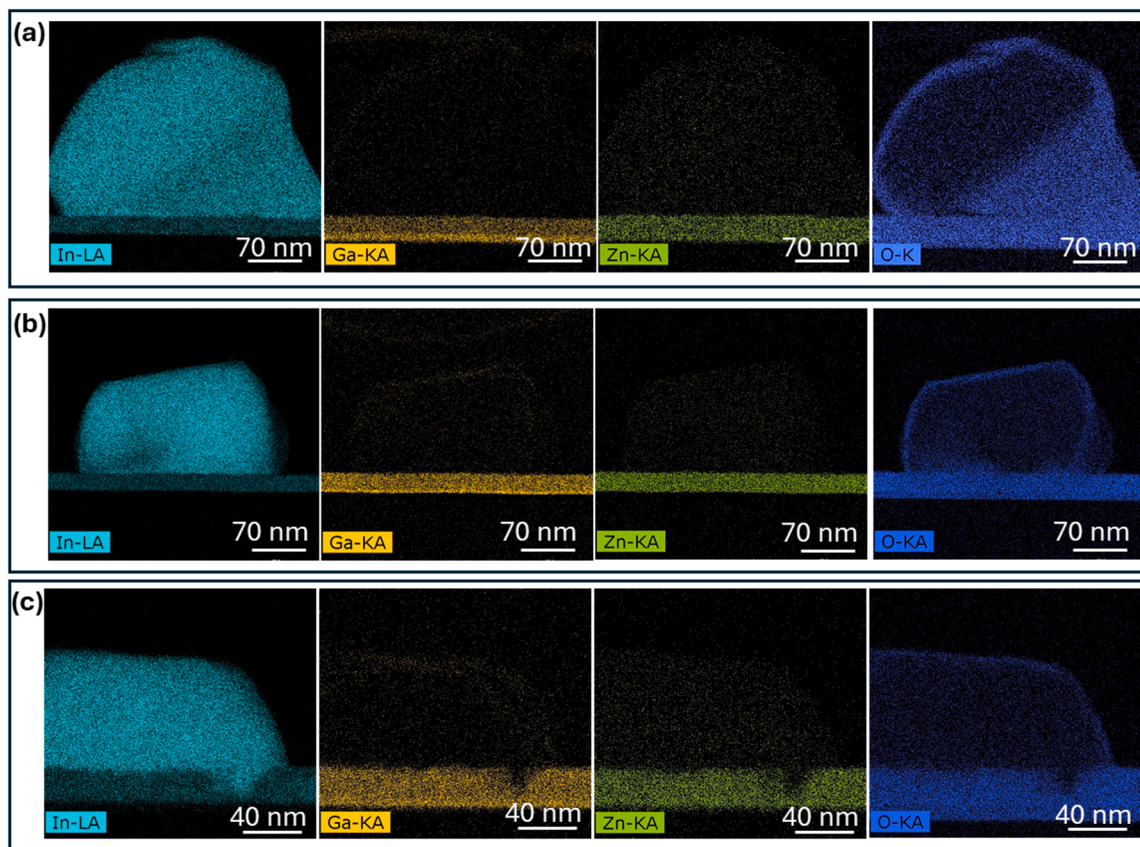
#### 4. Discussion

All the results shown in the previous section clearly demonstrate the formation of an In and  $\text{In}_2\text{O}_3$  phase for IGZO thin films subject to forming gas annealing. We demonstrated that the onset of this phenomenon occurs at 350 °C and becomes more significant at higher

temperatures. In all the samples, this phase separation phenomenon manifests itself inducing the segregation of metallic In/ $\text{In}_2\text{O}_3$  in particles at the surface of the films. The presence of In/ $\text{In}_2\text{O}_3$  grains inside the IGZO matrix was only observed when IGZO grown on thin GZO was subject to higher thermal budget. Higher thermal budget also encourages the formation of the In phase to the detriment of the  $\text{In}_2\text{O}_3$  phase (see in particular the XRD in Fig. 2(e), where the  $\text{In}_2\text{O}_3$  peaks tend to disappear for the sample annealed at 500 °C). This indicates that the  $\text{In}_2\text{O}_3$  phase is a transitional phase towards the segregation of the metallic In phase. While the temperature is the main parameter affecting the phase separation in the IGZO, the forming gas atmosphere in which the annealing is performed seems to be the key element to explain this phenomenon. As a matter of fact, recent works [3] reported in-situ XRD annealing of spinel IGZO under a He-atmosphere, showing that the spinel phase remains intact up to 900 °C. Phase separation of In has been already observed in ternary compounds, such as ITO ( $\text{In}_2\text{O}_3\text{:Sn}$ ) [18–21]. In such materials, this phenomenon is driven by  $\text{H}_2$  or  $\text{SiH}_4$  plasma at temperatures above  $T = 200$  °C and leads to the formation of metallic In and Sn droplets. The underlying mechanism is based on the reduction of ITO by hydrogen radicals. Indeed, H radical being a strong reducing species, it has the effect to weaken the bonding of ITO and liberates oxygen, thus changing the stoichiometry of the compound. In our experiments, the thermal treatment was performed in forming gas, which contains 10% of Hydrogen. IGZO is a similar semiconductor material as ITO, so it is highly likely that the reduction mechanism is the same for both. In spinel IGZO, the In and the Ga atoms are located in octahedral sites, while in ITO the octahedral sites are occupied by In and Sn. In both compounds, these cations are surrounded by six O anions which are liberated during the reduction process. In ITO, the reduction process can be easily described, as the decreasing of O leads to an abundance of In atoms, which are likely to segregate, while the small amount of Sn dopant can be found to segregate depending on the conditions. Here, only the reduction and segregation of In is observed, while the Ga is found to be stable. This can be explained by a combination of thermodynamic and electrochemical properties of the In-O bond. The



**Fig. 8.** (a) EDX spectra acquired in two different regions, as represented in the In-map reported in (b). The maps of the other elements are depicted in (c-e). The HAADF-STEM highlighting region 1 is reported in the inset of (a).



**Fig. 9.** In, Ga, Zn and O elemental STEM-EDX maps for samples D02 (a), D07 (b) and D17 (c).

reduction potential of In-O is lower than Ga-O [22], making the In species more susceptible than Ga to reduction by forming gas annealing. Moreover, GZO and  $\text{In}_2\text{O}_3$  are thermodynamically more stable than spinel IGZO. Therefore, the tendency is that  $\text{In}_2\text{O}_3$  diffuses out of IGZO, leaving GZO behind, thus preventing the segregation of Ga and Zn. This can be seen by a shift of lattice constant of the (222) peak to higher angle (reduction of the lattice constant), as shown in Fig. 4.  $\text{In}_2\text{O}_3$  is then subjected to further reduction into In by FGA, in a similar matter as happening in ITO.

While the phase segregation is explained by invoking the effect of FGA, the crystallographic properties of the IGZO seem to be related to

the presence of the GZO seed layer. In fact, the PED maps evidenced a crystallographic continuity of the IGZO and GZO grains. We speculate that preferential IGZO nucleation mechanism is primarily promoted by the structural similarity with the underlying spinel GZO, since spinel IGZO grains can form inside thick IGZO films when no template is used [3]. The columnar growth of the upper IGZO grains further endorses this templating effect of the GZO seed, regardless of the GZO thickness. On the other hand, the PED maps indicate that the size of the IGZO grains is closely related to the grain size of the underlying GZO. It is hence possible that during the deposition of GZO having different thickness, larger grains are less likely to be formed in the GZO having thickness of 3

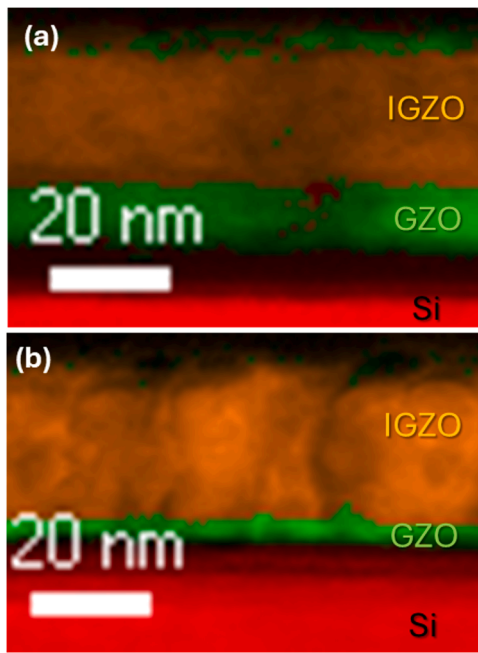


Fig. 10. Phase maps for samples D02 (a) and D07 (b).

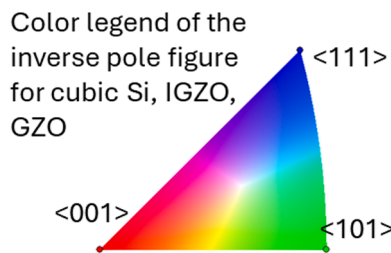


Fig. 11. Color legend to interpret the crystal grain orientation for IGZO, GZO and Si, which belong to the same cubic crystal system and have same Laue class.

nm, thus inducing the formation of IGZO grains with smaller lateral extension in samples D07-D17 than in D02 (see not only Fig. 12, but also Fig. 15 for sample D17).

As a consequence of the templating effect, the degree of texture present in the IGZO can be also related to the texture already present in the GZO. We observed that the degree of texture increases for IGZO films grown on thinner GZO. For GZO, the (111)-surface exhibits the lowest surface energy. In thin layers, the surface to bulk ratio is the highest and therefore crystallization is dominantly taking place with a [111]-texture

along the growth direction for both IGZO and GZO, when the IGZO is grown on thinner GZO. Based on our results, also  $\text{In}_2\text{O}_3$  and In phase exhibit texture along the growth direction: the  $\text{In}_2\text{O}_3$  phase grows with its (111)-planes parallel to the interface, while the In phase has its (101)-planes parallel to the interface. This aspect is demonstrated by both PED and XRD  $\Theta-2\Theta$ , where the intensity of the peaks is not related to the density of the crystallographic phases, but only to their orientation. As said in the previous paragraph, the amount of the In and  $\text{In}_2\text{O}_3$  phases is regulated by the temperature, with  $\text{In}_2\text{O}_3$  disappearing at higher temperatures. So, while the GZO thickness mainly plays a role in determining the texture and the grain size of the IGZO, the annealing temperature also affects the overall crystallographic properties of the IGZO samples since it has an impact on the characteristics of the segregated In and  $\text{In}_2\text{O}_3$  phases.

## 5. Conclusions

In conclusion, we studied the crystallographic properties of IGZO films grown on GZO as template layer and subject to different thermal annealing treatments. We highlighted that phase separation of In and  $\text{In}_2\text{O}_3$  can occur after annealing treatment of IGZO in forming gas. In this study, we could determine (i) the location of the In and  $\text{In}_2\text{O}_3$  phases, (ii) the crystal orientation of IGZO, GZO, In and  $\text{In}_2\text{O}_3$  grains, (iii) the difference between IGZO films grown on GZO having different thickness, (iv) the effect of the temperature during the forming gas annealing. In and  $\text{In}_2\text{O}_3$  phases are mainly present in the form of nanoparticles at the top surface of the IGZO. In addition, higher annealing temperature leads to the formation of small In/ $\text{In}_2\text{O}_3$  grains within the IGZO film. This happened because the forming gas environment where the annealing is performed leads to the reduction of the In-O species present in the IGZO compound, inducing the phase segregation. Moreover, IGZO grown on thicker GZO presents low texture, larger lateral grain extension and a wider distribution of crystallographic orientations, while IGZO grown on thinner GZO presents improved texture and smaller grains. In general, the crystallographic properties of the IGZO alone, including the texture and grain size, are related to the properties of the GZO templates, while the annealing temperature has an impact on the characteristics of the segregated In and  $\text{In}_2\text{O}_3$  phases.

We highlighted that the interplay between GZO thickness and annealing treatment is crucial in determining the overall crystallographic properties of the spinel IGZO film and the occurrence of phase separation phenomena during hydrogen treatments. Forming gas annealing is a well-known step often used at the end of the device processing to electrically passivate surfaces of semiconducting channels. Moreover, several process steps in the device manufacturing flow have also hydrogen involved in their chemistry. So, for future technological developments it is important to understand the phenomena occurring during FGA and relate the microstructural changes with the conductance

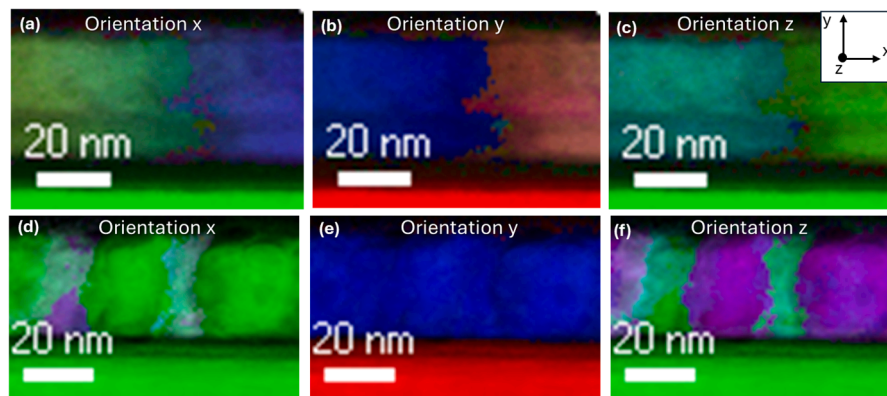
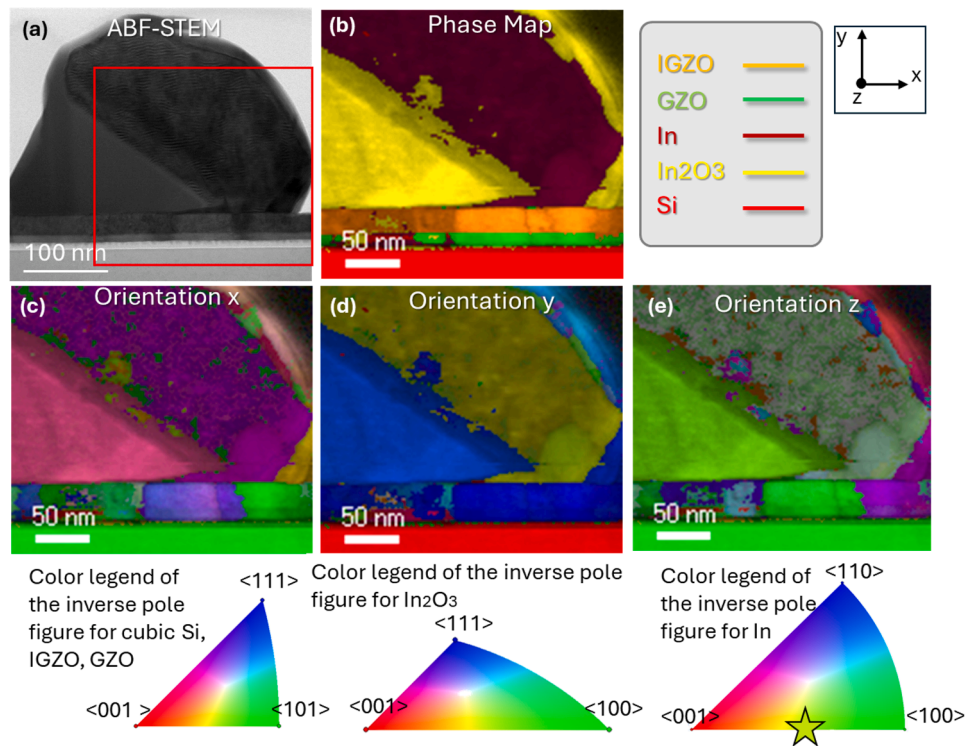
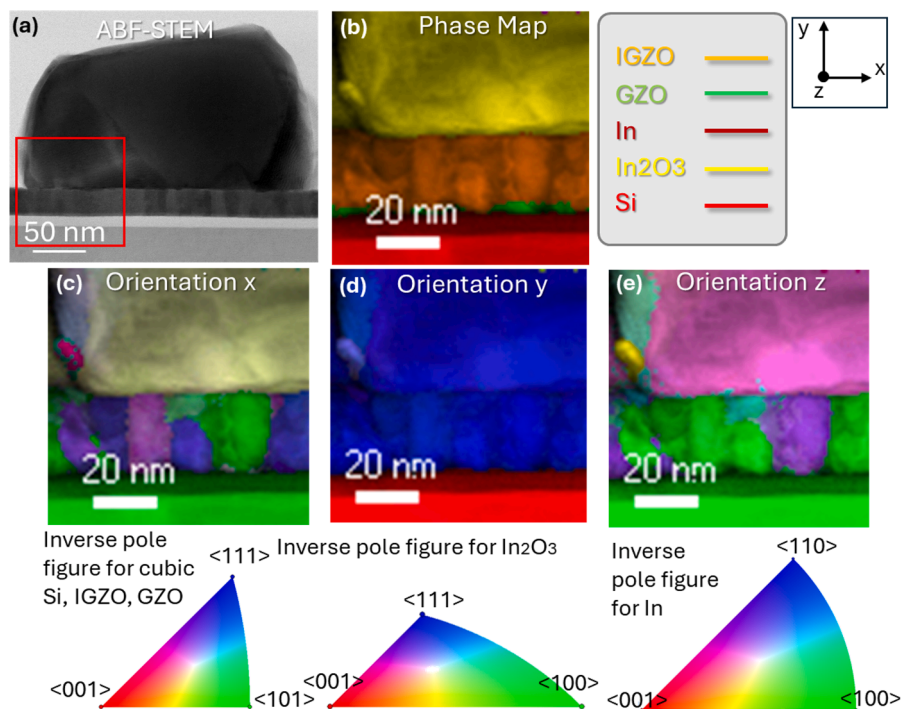


Fig. 12. (a-c) Orientation maps for sample D02 and (d-f) D07.



**Fig. 13.** (a) ABF-STEM image, (b) phase map and (c-e) orientation maps for sample D02. The color legends of the inverse pole figures to interpret the orientation of the IGZO, GZO, Si, In and In<sub>2</sub>O<sub>3</sub> phases are also reported.

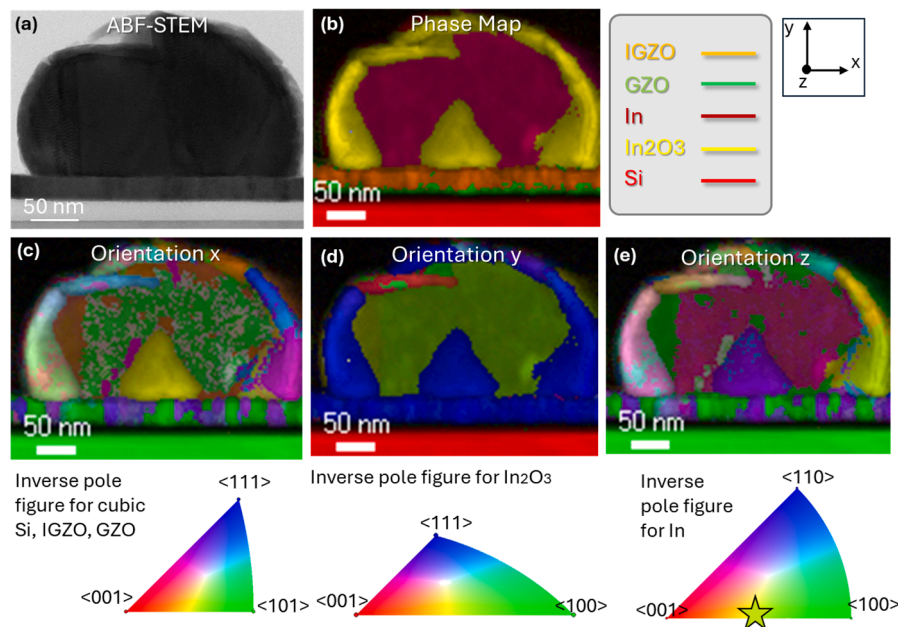


**Fig. 14.** (a) ABF-STEM image, (b) phase map and (c-e) orientation maps for sample D07. The color legends of the inverse pole figures to interpret the orientation of the IGZO, GZO, Si, In and In<sub>2</sub>O<sub>3</sub> phases are also reported.

of IGZO channels. In general, this work shed light on the crystallographic properties which affect the final performances of the IGZO TFTs.

#### CRediT authorship contribution statement

**Marta Agati:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Harold Dekkers:** Writing – review & editing, Methodology, Investigation,



**Fig. 15.** (a) ABF-STEM image, (b) phase map and (c-e) orientation maps for sample D17. The color legends of the inverse pole figures to interpret the orientation of the IGZO, GZO, Si, In and  $\text{In}_2\text{O}_3$  phases are also reported.

Funding acquisition, Data curation, Conceptualization. **Pradyumna K. Parida:** Validation, Investigation. **Olivier Richard:** Writing – review & editing, Validation, Formal analysis. **Eva Grieten:** Writing – review & editing, Validation, Resources, Project administration. **Athanassios S. Galanis:** Validation, Methodology. **Paola Favia:** Writing – review & editing, Validation, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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