**Electronic supplementary information**

**Sample preparation**

The substrate $SiO_2$ (100 nm)/Si(n++) was purchased from ATMEL, France. The substrate was cleaned by ultrasonication in acetone to remove a polymer protection layer and, subsequently, in acetone, and propane-diol for 10 min each to obtain a clean and residue free surface. The substrate was dried and UV ozone treated for 5 min which significantly improves the wetting of the precursor formulation to the substrate. The IGZO precursor solution was prepared by dissolving organo-metallic zinc oximates[i,ii], indium oximates[iii], and gallium oximates in 2-methoxyethanol. The chemical composition ratio of IGZO precursor solution was In:Ga:Zn = 3:0.4:2 at a single layer concentration of 30 mg of precursor in a total of 1.0 g of solvent. This solution was spin coated onto the Si substrate at 2000 rpm for 30 s. The sample was subsequently placed onto a hot plate in air at different temperatures for 10 min in order to decompose the precursor and form the metal-oxide layer in a porous microstructure. It was then quench cooled to room temperature on a metal block for 30 s. Two additional layers were then coated by the same method.

**Microscopy**

The study was conducted on a FEI Tecnai Osiris operated at 200 kV and the EDX analysis was done with the Bruker Esprit software. The thickness of the IGZO films annealed at 300, 380 and 450°C was measured from SEM cross-section images (Fig. S1). As the oxide layer at 300°C is insulative, a conductive resin has been added.

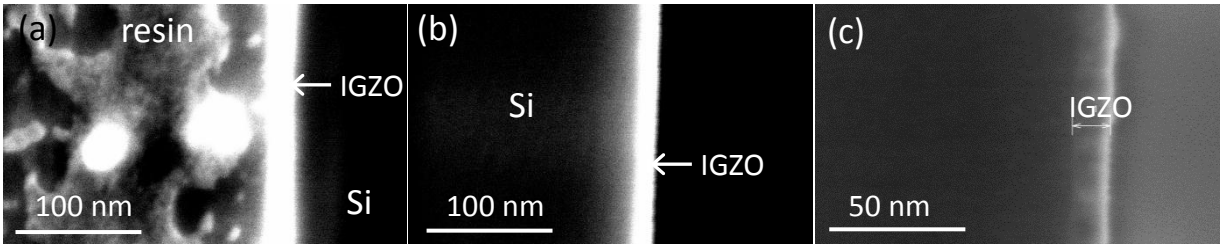


**Fig. S1** Cross-section SEM images of IGZO film annealed at 300°C (a), 380°C (b), and 450°C (c).

Figure S2 shows plane-view SEM image of the IGZO film annealed at 200°C. At the start of the SEM observation, the surface is homogeneous, then inhomogeneities appear under the electron beam.

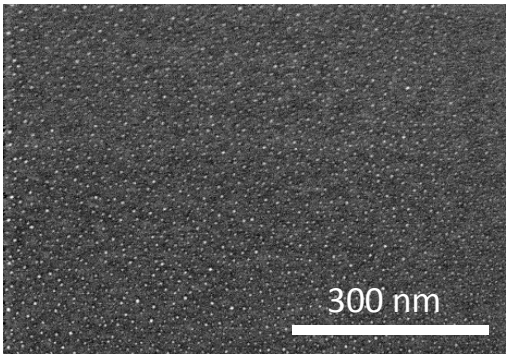


**Fig. S2** Plane-view SEM image of the IGZO film annealed at 200°C.

At 300°C and above, the SEM pictures were digitized. The software ImageJ was used to estimate the pore size.

**Anomalous grazing incidence small-angle X-ray scattering measurements**

AGISAXS experiments were performed at beamline BM02[iv] at the European Synchrotron Radiation Facility in Grenoble, France. In order to minimize scattering background, the whole setup from the optics down to the camera was under vacuum. The selected energies in the vicinity of the K-edge of

Zn were 9620, 9639, 9649, 9654 eV and those in the vicinity of the K-edge of Ga were 10314, 10354, 10362 eV. At each energy, several frames (typically 10) were recorded in order to unambiguously isolate the anomalous scattering in the highly porous multi-oxide films of a few nanometres thick. The focus on the sample was 0.1 mm (V) × 0.24 mm (H) (full width at half-maximum), i.e. the footprint of the beam at a grazing angle of 0.3° was approximately one third the size of the sample length (70 mm). Hence, the normalization of intensity was precise and the relative intensities can be compared. The sample to detector distance was 610 mm. The GISAXS was collected on a 16-bit charge-coupled-device camera (Princeton Instruments) and were corrected for dark counts, flat field, and camera distortion. We use the differential method which takes advantage of the mean intensity near a given edge to calculate the differential intensity[v]. The distance $D$ between the pores or the clusters was determined through the position of the GISAXS intensity maximum $q_m$ by $D=2\pi/q_m$. Figure S3 shows a GISAXS image of the IGZO film annealed at 200°C. A wide specular beam points out a surface roughness. Figure S3 also shows AGISAXS data in the vicinity of the K-edge of Zn (resp. Ga) for the IGZO film annealed at 200°C. Wide specular beams point out a lateral modulation in the Zn (resp. Ga) composition.

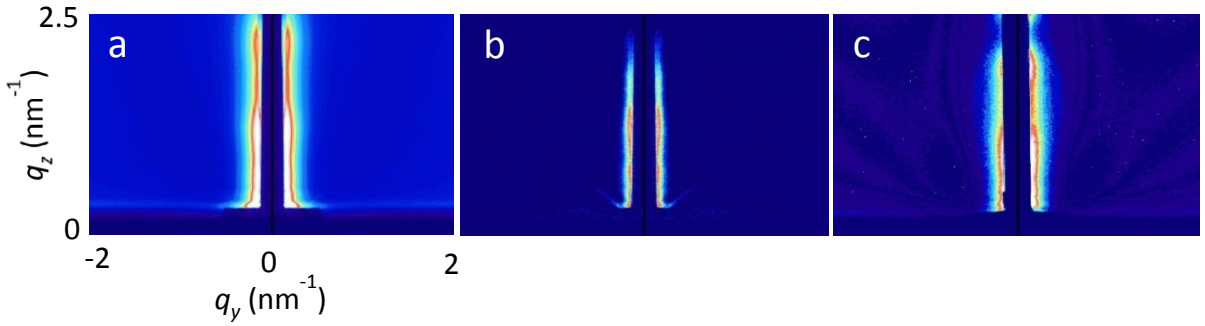


**Fig. S3** X-ray scattering data of the IGZO film annealed at 200°C. GISAXS data (a), AGISAXS data in the vicinity of the K-edge of Zn (b), and AGISAXS data in the vicinity of the K-edge of Ga (c).

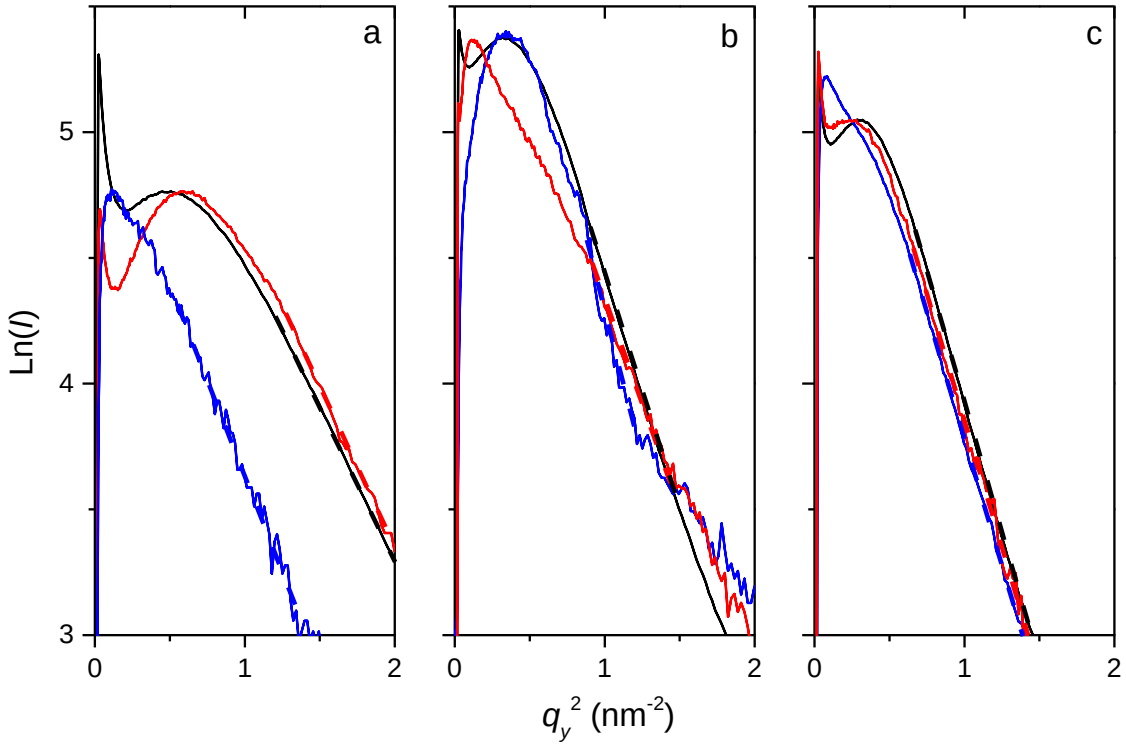


**Fig. S4** Ln($I$) as a function of $q_y^2$ for the linescans of the fourth row in Fig. 3 for IGZO films annealed at 300°C (a), 380°C (b), and 450°C (c). The dash line corresponds to the linear fit.

The sizes of pores and clusters were estimated from the radius of gyration, obtained from the slope of the Guinier plot (Fig. S4). The curve Ln($I$) as a function of $q_y^2$ is linearly fitted at small $q_y$ values. The radius of gyration $R_g$ is linked to the slope $s$ by $R_g = \sqrt{-3s}$ and the corresponding diameter $D$ is equal to $2R_g\sqrt{5/3}$ assuming spherical scatterers.

**GISAXS simulations with an oblate spheroid pore shape**

To prove the oblate spheroid pore shape, a simulation of GISAXS patterns using the software FitGISAXS[vi] was carried out to model the thermal annealing evolution of the pore morphology (Fig. S5). Full two-dimensional scattering patterns were calculated based on all relevant information about geometry and arrangement of pores. The calculation of the interference function was based on a lattice with a short-range order. The distorted-wave Born approximation was used to calculate the form factor. The shape of the pores was modelized by a spheroid shape with a $H/d_p$ ratio of 0.7, where $H$ is the height of the pores.

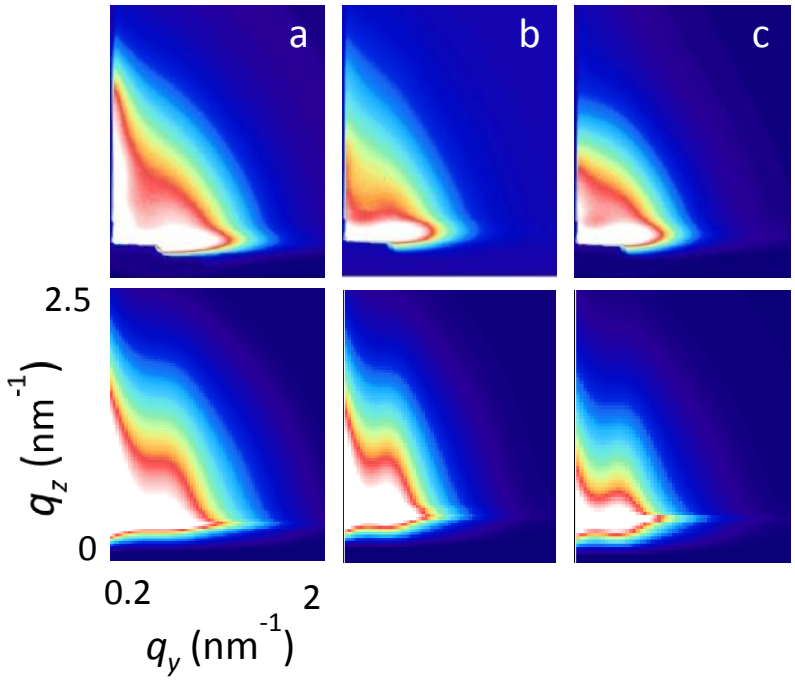


**Fig. S5** GISAXS data (first row) and simulated GISAXS patterns (second row) of the IGZO film annealed at 300°C (a), 380°C (b), and 450°C (c).

The agreement between data and simulation is good considering the idealized model. The main features such as peak position, global shape and relative intensity are well reproduced.

**Diffusion coefficient as a function of temperature**

The diffusion coefficient $D_c$ as a function of temperature $T$ is described by the Arrhenius relation,

$D_c = D_0 e^{-E_a/RT}$

where $E_a$ is the activation energy, $D_0$ is the pre-exponential coefficient and $R$ is the gas constant. The Ga diffusion data from Table 2 are fully compatible with an Arrhenius law (Fig. S6). Linear fit of the data yields an activation energy of $(4.3\pm1)\times10^4$ Jmol$^{-1}$ and a pre-exponential coefficient $D_0$ of $6.7\times10^{-16}$ m$^2$s$^{-1}$.

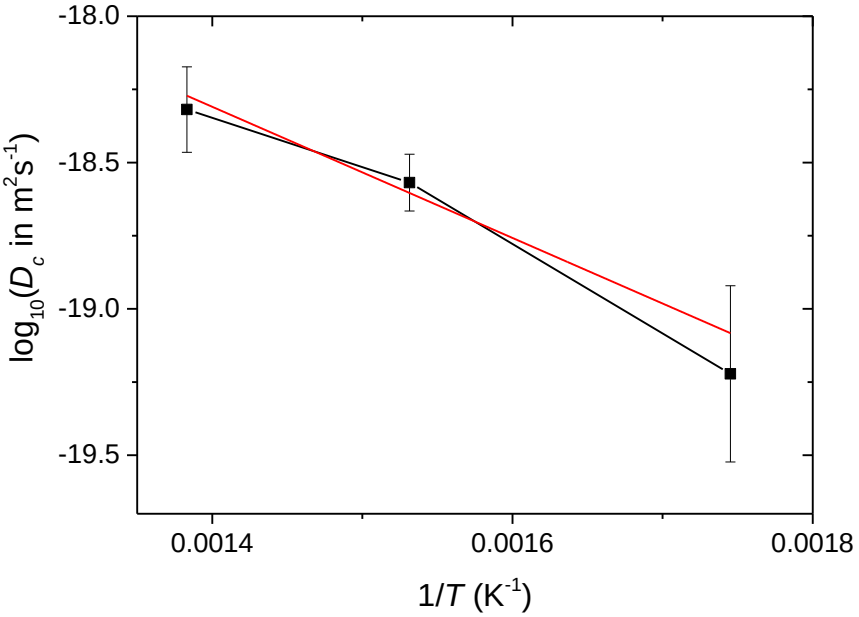


**Fig. S6** Arrhenius diagram of Ga diffusion coefficient. The black curve corresponds to the estimated diffusion constants from the AGISAXS data. The red line corresponds to the linear fit.

**Volume fraction of each inorganic component**

The volume fraction of the Zn (resp. Ga) nanoclusters can be estimated from AGISAXS. For Zn, the scattering data at 380°C yield the in-plane and out-of-plane distances between clusters. A three dimensional cell can be defined with a cluster at each apex. In a 20 nm thick film, there are three layers of Zn clusters. For spherical clusters, the volume fraction of the Zn clusters is :

$$f_v = \left(4 \times \frac{1}{4} + 4 \times \frac{1}{8}\right) \times \frac{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3}{D_{//}^2 \times D_{\perp}}$$

Using the values of Table 1, the volume fraction $f_v$ of the Zn clusters is 0.12 at 380°C. Moreover, the $q_y$ linescans at $q_z$= 0.5 nm$^{-1}$ (Fig. S7) can be integrated in order to estimate the volume fraction of clusters at the different temperatures. As the integrated intensity for Zn at 300°C is approximately 0.8 that at 380°C, the volume fraction of the Zn clusters is 0.09 at 300°C.

The GISAXS intensity is given by:

$$I(q,E) = |\Delta\rho_{Zn}(E)|^2 I^{Zn}(q) + |\Delta\rho_{Ga}(E)|^2 I^{Ga}(q) + I^{pores}(q) \quad (1)$$

where $|\Delta\rho(E)|^2$ is the electron density contrast and is equal to:

$$|\Delta\rho(E)|^2 = \left|\rho(E) - \rho_{reference}\right|^2 \quad (2)$$

where $\rho = f/V$ with $V$ the atomic volume and $f$ the scattering factor of a given element. The scattering factor is equal to :

$$f(E) = Z + f'(E) + if''(E) \quad (3)$$

where $Z$ is the atomic number of the element and $f'(E)$, $f''(E)$ are the dispersion terms.

For example, the signal of the Zn clusters is given by:

$$I^{Zn}(q) = \frac{I(q,E) - \langle I(q)\rangle}{|\Delta\rho(E)|^2 - \langle|\Delta\rho|^2\rangle} \quad (4)$$

where $\langle|\Delta\rho|^2\rangle$ is the contrast averaged over the selected energy range.

At 300 and 380°C, in the direction parallel to the surface, the Zn clusters are bordered by $Ga_2O_3$ denoted as the reference in equation (2) and the electronic contrast is given in Table S1. At 450°C, the

ratio of the integrated intensity for Zn between 450 and 380°C is 4.3. This large ratio indicates that the electronic contrast around the Zn clusters is much larger than at lower temperatures (300 and 380°C). As a matter of fact, the GISAXS results indicate that some Zn clusters may be partially in contact with pores in the direction parallel to the surface (cf. Fig. 4c). In addition, one can estimate the volume fraction of the Ga clusters by comparing the integrated intensity of Zn and Ga and by taking into account the different electron contrasts. For Ga, the electron density contrast is taken between the pores and the clusters. The integrated intensity of the $q_y$ linescans at $q_z$= 0.5 nm$^{-1}$ for Ga is approximately constant as a function of temperature and is equal to 2.6 times that for Zn at 380°C.

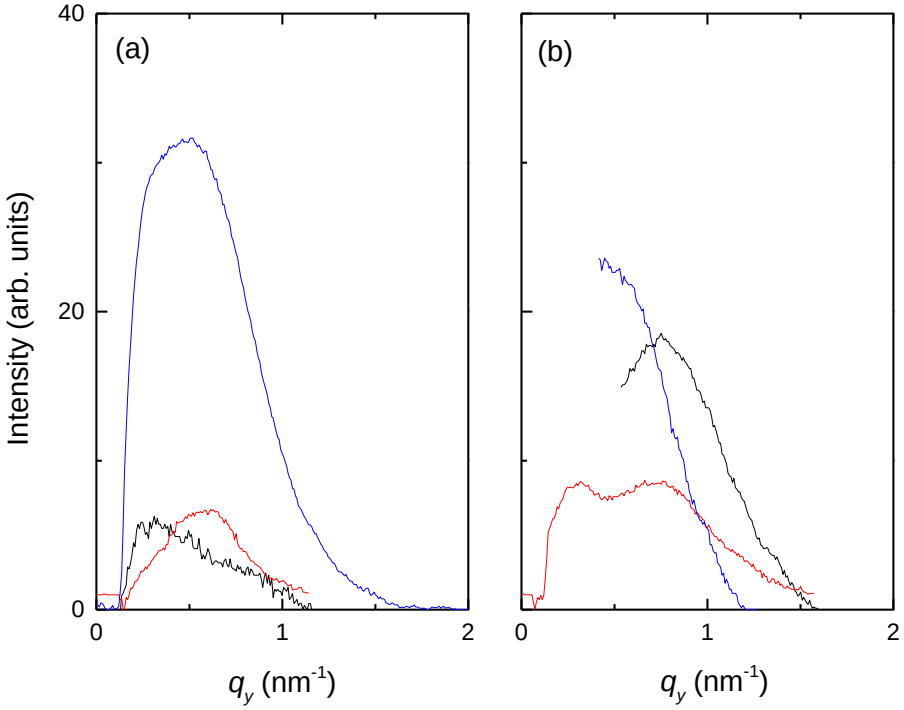


**Fig. S7** GISAXS $q_y$ linescans at $q_z$=0.5 nm$^{-1}$ from the Zn-rich nanoclusters (a) and from the Ga-rich nanoclusters (b) for films annealed at 300°C (black line), 380°C (red line), and 450°C (blue line).

| Energy (eV) | $f'_{Zn}(E)$ (electrons) | $\rho_{ZnO}$ (cm$^{-3}$) | $\lvert\Delta\rho(E)\rvert^2$ (cm$^{-6}$) |
|---|---|---|---|
| 9620 | -5.1698 | 2.2620 | 0.192 |
| 9639 | -5.8735 | 2.2135 | 0.237 |
| 9649 | -6.6092 | 2.1628 | 0.289 |
| 9654 | -7.3131 | 2.1143 | 0.343 |

**Table S1**. Term $f'_{Zn}$, electron density of ZnO and contrast with respect to $Ga_2O_3$ at the probed energies.

| Energy (eV) | $f'_{Ga}(E)$ (electrons) | $\rho_{Ga2O3}$ (cm$^{-3}$) | $\lvert\Delta\rho(E)\rvert^2$ (cm$^{-6}$) |
|---|---|---|---|
| 10314 | -4.8918 | 2.3932 | 5.727 |
| 10354 | -6.3392 | 2.3023 | 5.301 |
| 10362 | -7.2634 | 2.2443 | 5.037 |

**Table S2**. Term $f'_{Ga}$, electron density of $Ga_2O_3$ and contrast with respect to the pores at the probed energies.

For Zn, $|\Delta\rho(E)|^2 - \langle|\Delta\rho|^2\rangle$=0.073 at $E$=9620 eV with respect to $Ga_2O_3$ and for Ga, $|\Delta\rho(E)|^2 - \langle|\Delta\rho|^2\rangle$=0.372 at $E$=10314 eV. Taking into account the difference in electron density contrast, the volume fraction of the Ga clusters is estimated to be approximately 0.05 whatever the temperature.

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