Supporting information:

**Amorphous In-Ga-Zn-oxide semiconducting thin films with high mobility from electrochemically-generated aqueous nanocluster inks**


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**Table S1: Electrochemical parameters for different In:Ga:Zn composition**

<table>
<thead>
<tr>
<th>Chemical composition (In:Ga:Zn)</th>
<th>Electrochemical duration (min)</th>
<th>Total charge (C)</th>
<th>Charge/metal ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33:0.33:0.33</td>
<td>60</td>
<td>640</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1131</td>
<td>0.78</td>
</tr>
<tr>
<td>0.41:0.33:0.26</td>
<td>60</td>
<td>512</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1071</td>
<td>0.74</td>
</tr>
<tr>
<td>0.32:0.26:0.42</td>
<td>60</td>
<td>590</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1215</td>
<td>0.84</td>
</tr>
<tr>
<td>0.60:0.10:0.30</td>
<td>60</td>
<td>844</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1046</td>
<td>0.72</td>
</tr>
<tr>
<td>0.69:0.12:0.19</td>
<td>60</td>
<td>820</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1004</td>
<td>0.69</td>
</tr>
<tr>
<td>0.81:0.06:0.13</td>
<td>60</td>
<td>1149</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1202</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Structure and composition of surface “islands”. To determine the crystal structure of the surface islands observed in the SEM study of film derived from the simple salt precursor solution (In:Ga:Zn = 0.32:0.26:0.42) a TEM sample of the film was prepared (Figure S1). The high-resolution TEM image and Fast Fourier transform (FFT) show that the island (region 1) is polycrystalline. However, the film (region 2) remains amorphous, as evidenced by both TEM
and FFT analyses. TEM-EDX line scan indicates that the islands are In-rich compositions, which appear to be In$_2$O$_3$ crystallites.

**Fig. S1:** (a) HRTEM image and FFT analyses as well as (b) TEM-EDX line scan of the IGZO film made from salt solution with an In:Ga:Zn = 0.32:0.26:0.42.
**Film smoothness by AFM.** The electrolysis-derived films with In:Ga:Zn = 41:33:26 have a very smooth surface with a root mean square (RMS) roughness of ~ 0.24 nm while those obtained from salt solution and sol-gel precursors have an RMS roughness of ~ 1.42 nm and 2.33 nm, respectively (Figure S2). This higher degree of flatness is likely because electrochemically-generated cluster precursors contain fewer counterions and thus produce denser films with less porosity and surface structure. Dense and smooth films are important for achieving high-performance devices.

![AFM images of 550 °C air-annealed IGZO thin films prepared using (a) salt solution, (b) electrochemically-generated cluster, and (c) sol-gel precursors.](image)

**Figure S2:** AFM images of 550 °C air-annealed IGZO thin films prepared using (a) salt solution, (b) electrochemically-generated cluster, and (c) sol-gel precursors.

**Control TFTs fabricated from counter electrode compartment electrolyte.** Figure S3 shows the electrical characteristics of films made using the solution from the fritted compartment containing the counter electrode. The TFT exhibits enhancement-mode behavior with poor gate modulation and very low mobility values, supporting our hypothesis that the fritted compartment solution contains excess counterions.

![TFT transfer characteristics and μ_{AVE} for 550 °C air-annealed films made using a solution from the fritted compartment with In:Ga:Zn = 32:26:42.](image)

**Figure S3:** (a) TFT transfer characteristics and (b) μ_{AVE} for 550 °C air-annealed films made using a solution from the fritted compartment with In:Ga:Zn = 32:26:42.
Additional supporting transistor performance data. Figure S4 compares the device properties of the IGZO channel layer with In:Ga:Zn = 69:12:19 in TFTs processed from the electrochemically-generated cluster precursors with those made using a starting nitrate salt solution. All the TFT devices demonstrated a depletion-mode behavior with a $V_{ON}$ of ~ -30 V. The $\mu_{AVE}$ of electrolysis-derived films was higher than those obtained from starting salt solution films (Figure S14b), yielding an $\mu_{AVE}$ of ~ 15 cm$^2$ V$^{-1}$ s$^{-1}$ at $V_{GS} = 60$ V.

![Figure S4](image1.png)

Figure S4: (a) TFT transfer curves and (b) $\mu_{AVE}$ of In:Ga:Zn = 69:12:19 films made using starting nitrate salt and electrochemically-synthesized cluster precursors. All these films were annealed at 550 ºC in air.

Figure S5 shows the electrical characteristics of an “control” ITZO interface layer composed of In:Sn:Zn = 9:1:1. The TFT devices exhibit a $V_{ON}$ of ~ 13 V and an $\mu_{AVE}$ of ~ 6 cm$^2$ V$^{-1}$s$^{-1}$, which is much smaller than that of ITZO-IGZO TFT devices of > 30 cm$^2$ V$^{-1}$ s$^{-1}$.

![Figure S5](image2.png)

Figure S5: (a) Transfer characteristics and (b) $\mu_{AVE}$ as a function $V_{GS}$ for a TFT based on an active channel layer of annealed ITZO at 550 ºC. The thickness of the ITZO channel layer was made ~ 10 nm in order to compare the electrical properties with those of ITZO/IGZO films.
Fitting TFT transfer characteristics to the comprehensive depletion mode model (CDMM).

Figure S6 shows the depletion-mode modeling of TFT devices with an IGZO channel layer (In:Ga:Zn = 32:26:42) processed using the 1 h electrochemically-generated cluster precursor. Mobilities extracted from CDMM simulation are found to be bulk mobility $\mu_{\text{bulk}} = 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{interface}} = 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The carrier concentration ($N_D$) of $8.0 \times 10^{16} \text{ cm}^{-3}$ and $8.0 \times 10^{17} \text{ cm}^{-3}$ were extracted from left- and right-side plots, respectively.

![Figure S6](image)

**Figure S6:** Depletion-mode fitting (red) of TFT transfer characteristics (blue) for TFTs with an active channel layer of In:Ga:Zn = 32:26:42 annealed at 550 °C.

Figure S7 shows the depletion-mode modeling of TFT devices with an IGZO channel layer (In:Ga:Zn = 60:10:30) processed using the 1 h electrochemically-generated cluster precursor. Mobilities extracted from CDMM simulation are found to be $\mu_{\text{bulk}} = 4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{interface}} = 18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The $N_D$ of $4.0 \times 10^{18} \text{ cm}^{-3}$ and $9.0 \times 10^{18} \text{ cm}^{-3}$ were extracted from left- and right-side plots, respectively.

![Figure S7](image)

**Figure S7:** Depletion-mode fitting (red) of TFT transfer characteristics (blue) for TFTs with an active channel layer of In:Ga:Zn = 60:10:30 annealed at 550 °C.
Figure S8 shows the depletion-mode modeling of TFT devices with an IGZO channel layer (In:Ga:Zn = 69:12:19) processed using the 1 h electrochemically-generated cluster precursor. \( \mu_{\text{interface}} \) extracted from CDMM simulation are found to be 17 cm\(^2\) V\(^{-1}\) s\(^{-1}\). The \( N_D \) of 3.0\( \times \)10\(^{18}\) cm\(^{-3}\) and 9.0\( \times \)10\(^{18}\) cm\(^{-3}\) and \( \mu_{\text{bulk}} \) of 9 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 5 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were extracted from left- and right-side plots, respectively.

Figure S9 shows the depletion-mode modeling of devices with an ITZO/IGZO dual-channel layer. The \( \mu_{\text{interface}} \) extracted from transfer curve CDMM simulation fits of ITZO/IGZO TFTs experimental data are found to be 34 cm\(^2\) V\(^{-1}\) s\(^{-1}\). The \( N_D \) of 9.0\( \times \)10\(^{16}\) cm\(^{-3}\) and 7.0\( \times \)10\(^{16}\) cm\(^{-3}\) and \( \mu_{\text{bulk}} \) of 6 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 11 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were extracted from left- and right-side plots, respectively.

**Figure S8:** Depletion-mode fitting (red) of TFT transfer characteristics (blue) for TFTs with an active channel layer of In:Ga:Zn = 69:12:19 annealed at 550 °C.

**Figure S9:** Depletion-mode fitting (red) of TFT transfer characteristics (blue) for TFTs with a dual-active channel layer of ITZO/IGZO.