Printed Zinc Tin Oxide Diodes: From Combustion Synthesis to Large-Scale Manufacturing

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Abstract

Printed metal oxide devices have been widely desired in flexible electronic applications to allow direct integration on foils, reduce electronic waste and associated costs. Especially, semiconductor devices made from non-critical raw materials, such as Zn, Sn (and not, for example, In), have gained much interest. Despite considerable progress in the field, the upscale requirements from lab-to fab scale to produce these materials and devices remain a challenge. In this work, we report the importance of solution combustion synthesis (SCS) when compared with sol-gel in the production of zinc tin oxide (ZTO) thin films using a solvent (1-methoxypropanol) that has lower environmental impact than the widely used and toxic 2-methoxyethanol. To assure the compatibility with low-cost flexible substrates in high-throughput printing techniques, a low annealing temperature of 140 ºC was achieved for these thin films by combining SCS and infrared (IR) annealing in a short processing time. These conditions allowed the transition from spin-coating (lab-scale) to flexographic printing (fab-scale) at a printing speed of 10 m/min in a roll-to-roll (R2R) pilot line. The ZTO (1:1 Zn:Sn-ratio) diodes show a rectification ratio of 10^3, a low operation voltage ($\leq$ 3 V), great yield and low variability. The results provide the basis for further optimization (device size,

encapsulation) to meet the requirements of diodes in flexible electronics applications such as passive-matrix addressing, energy harvesting and rectification.

Keywords

Solution combustion synthesis; metal oxides; printed Schottky diodes; low temperature; roll-to-roll (R2R).

1. Introduction

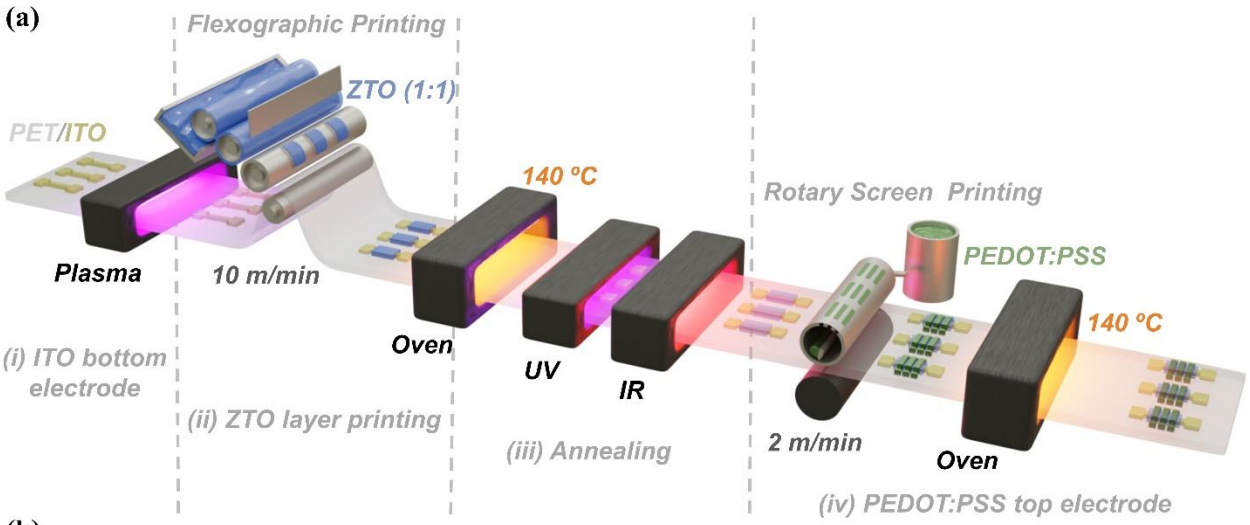
Over the last decade, printed electronics has been highlighted as one of the most promising technologies to boost the internet of things (IoT) applications (wearables, low-cost sensors, touch displays, smart packaging and security tags) that cannot be fulfilled by conventional electronics.[1–3] This new era of electronics could be realized by sustainable, additive, on-demand large-area manufacturing, where complex systems are constructed through layer-by-layer integration while, at the same time, the associated production costs are minimized through high-throughput roll-to-roll (R2R) printing.[4] In order to reach even higher performances while keeping the low cost, printed electronics can be combined with conventional, thinned silicon integrated circuits (ICs), also referred to hybrid electronics, for niche products.[5] However, to implement the visions of printed electronics, breakthroughs should be made in the design and printing of the most ubiquitous electronic components, like: transistors, capacitors, resistors, diodes, and memories.[6–10] Among them, metal oxide (MO) diodes play a crucial role for example in voltage regulation and surge protection that are required for wireless power transmission technology and in near-field communication when applied in flexible radio frequency identification (RFID) tags.[8] For this application, the diodes should have low turn-on voltage, high cut-off frequency, and low leakage current. Besides that, this field demands inexpensive and large-scale manufacturing which fits perfectly with printed techniques. However, spin-coating is the most common solution-processing technique reported in the fabrication of diodes due to its simplicity and versatility.[8,11–13] By combining this technique with adhesion lithography, high-performance ZnO diodes were achieved, reaching operation frequencies up to 100 GHz thus being able to compete with conventional electronics.[14] Nevertheless, the fabrication of these components is not readily scalable to high-throughput R2R environments and requires subtractive processes, which increase the devices' final cost and complexity. Printed MO diodes could surpass the scalability issues as no external processes

are needed to pattern these materials in a reproducible way and the amount of production waste could be significantly reduced through additive manufacturing.[15] Diverse non-contact (inkjet, aerosol jet, and EHD jet printing) and contact printing techniques (reverse-offset, flexographic, rotary screen, and gravure printing) can be used in printed electronics manufacturing. To meet the demands of high-throughput, R2R manufacturing, is desirable.[16–21] Cho et al. reported the first hybrid ZnO diodes fabricated by R2R gravure printing at a printing speed of 8 m/min and some years later implemented these in wireless sensor-signage tags for smart packaging.[22,23] However, since then only a few reports have been published, where printing techniques are used to produce MO diodes (**Table S1** in the Supporting Information). Flexographic and gravure printing can reach high throughput (up to 1000 m/min). Among these two, flexographic printing is less expensive due to the use of polymeric stamps.[18,24] Besides the printability, other important aspects to consider are the annealing temperature required to form the metal oxide semiconductors from the liquid precursor inks and the annealing duration required to achieve a sufficient quality metal oxide films. Processing temperatures are usually high (> 250 °C), which can harm flexible substrates with lower melting points and high thermal expansion.[8] Annealing times over ten minutes are unpractical to realize in R2R environment without separate off-line heating systems. To decrease the thermal budget and the annealing time to form the oxide materials, different approaches such as solution combustion synthesis (boosts the local temperature during annealing by releasing chemical energy) [25] and various post-processing methods (such as photonic annealing) have been implemented.[26,27] The photonic annealing has two main methods, pulsed (flash lamp) and continuous (ultraviolet (UV) or infrared (IR) lamp), where the power intensity, pulse duration and the number of pulses can be changed.[27–29] Tailoring these parameters allows a reduction of the processing time (deliver thermal energy within μs to ms time range) and the final temperature to form the metal oxide layers, thus being fundamental in the upscaling efforts from the lab scale to the R2R pilot

lines.[30–33] When the films are exposed to photonic annealing, this leads to the cleavage of alkoxy groups into active metals and oxygen atoms which facilitates the metal-oxygen-metal (M−O−M) network formation through radical-mediated chemical reactions.[34,35] Therefore, the thin films' densification is enhanced in a short processing time. Besides these, other aspects should be considered to allow MO semiconductor devices take the transition from the lab scale to the pilot scale R2R and even further towards systems used in the printing industry. Those include i) the use of Earth-abundant materials (Zn and Sn favoured over rareness of In); ii) inks based on solvents with lower environmental impact (i.e. greener solvents like ethanol and water) instead of commonly used toxic solvents like 2-methoxyethanol (2-ME); iii) application of low-cost flexible substrates (PET, PEN and cellulose) rather than glass or silicon; iv) processing under controlled ambient conditions (humidity, temperature and atmosphere) to allow reproducibility; and v) performing surface treatments to assure a good adhesion between layers.[24,26] Nevertheless, most of the literature reported on printed MO devices focuses on the use of printing techniques at the lab scale.

In this work, we optimized the synthesis to form ZTO in a greener solvent 1-methoxypropanol (1-MP) as compared to the currently most used solvent, 2-ME, which is highly toxic and thus limits the application of these inks at larger scale. Especially in R2R environments, where the amount of ink is considerable (> 100 ml's) and exposure of process personnel to hazardous, volatile solvents is more difficult to control than in lab-scale research environments. Low-temperature-annealed ZTO diodes were first attained by spin-coating a ZTO ink assisted by solution combustion synthesis method with IR lamp annealing. Then, ZTO layers were fabricated using flexographic printing by adjusting the viscosity of the ZTO ink and printing speed. Finally, for the first time, we performed the upscaling from the lab scale to pilot R2R scale and demonstrated fully-printed ZTO diodes with a low thermal budget (≤ 140 ºC), as depicted in **Figure 1**. The results achieved with the R2R processing were on par with the ones

processed by spin-coating, thus proving the suitability, stability and uniformity of the chosen, up-scaled procedures. This accomplishment paves a way to a new era of printed MO diodes with enormous potential for low-cost flexible applications.



(b)

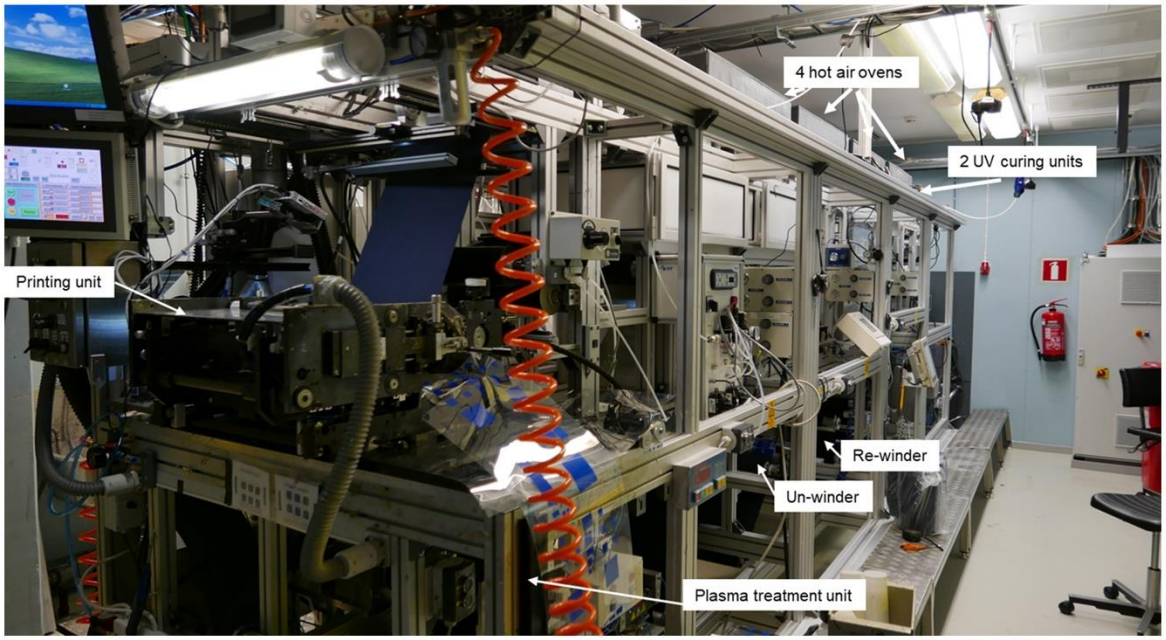


Figure 1. (a) Schematic representation of printing and annealing steps to produce the ZTO SCS diodes in the ROKO R2R-pilot line at VTT: (i) ITO bottom electrode after R2R patterning by printing an etching paste; (ii) ZTO layer printing by flexography; (iii) Annealing of the ZTO layer using in-line oven, UV and IR units; (iv) PEDOT:PSS top-electrode fabrication by rotary screen printing. (b) Picture of VTT's ROKO line located at Oulu, Finland.

2. Results and Discussion

The solvent selection of the MO precursor ink has been shown to play a crucial role in the formation of MO thin films with high quality.[36] Typically, the most common solvent is 2-ME. However, this volatile solvent has high toxicity and, thus, is not appropriate for upscaling to pilot-scale R2R environments. Greener solvents are preferable such as water and ethanol, but these suffer from smaller polymeric chain and high evaporation rate, respectively. These features lead to more defects and non-uniformity in the printed films. Another solvent with promising characteristics is 1-MP, having a low boiling point (≤ 130 ºC – compatible with low-cost flexible substrates), a larger polymeric chain like 2-ME, low evaporation rate, and most importantly lower toxicity than 2-ME, thus being suitable for large-area manufacturing. In this study, we explore the role of 1-MP to synthetize and produce ZTO thin films with solution-processing techniques ranging from spin-coating to high-throughput R2R-printing techniques.

2.1. Synthesis and design of ZTO thin films for diodes application

To achieve the optimal synthesis route to produce ZTO (1:1 Zn:Sn-ratio) thin films at low processing temperatures, two methods were considered: conventional sol-gel synthesis and solution combustion synthesis (SCS) where urea and ammonium nitrate were added as fuel and oxidizer, respectively.[25] Thermogravimetry (TG) and differential scanning calorimetry (DSC) was made on ZTO (1:1) sol-gel and SCS xerogel, as shown in **Figure 2 (a)**. The DSC analysis of the ZTO sol-gel xerogel show a broad exothermic peak at 103 ºC with a mass loss of 27 %. This conventional method requires higher temperatures, between 400 ºC and 500 ºC, to fully convert the ZTO precursors and for degradation of remaining residual mass as observed in the TG data. In comparison, the stoichiometric ZTO SCS xerogel presents two main exothermic peaks during the combustion reaction process; an intense exothermic peak at 108 ºC and a smaller broad exothermic peak at 222 ºC, resulting in a mass loss of 26 % and 38.7 %, respectively. In this case, it is possible to fully convert the ZTO precursors at approximately

250 ºC. The main differences between the two methods are related to the absence of an oxidizer (ammonium nitrate) in the tin chloride precursor and the use of urea as fuel to initiate the SCS process leading to high local temperatures at low external temperature.[25] This fuel is highly abundant, presents a high exothermicity at a low ignition temperature (as observed here at 108 ºC) and enhanced coordination ability relative to metal nitrate precursors being an ideal candidate.[37] Also, the presence of nitrates is fundamental to promote a good solubility and guarantee homogeneity. In addition, these salt precursors can be decomposed at lower processing temperatures when compared with corresponding acetate and chloride precursors.[38] The images of the solutions in **Figure S1** in the Supporting Information clearly show the effect of having a metal nitrate precursor (**Figure S1 (a)**) and the SCS method (**Figure S1 (d)**) in the 1-MP-based, upscalable solution synthesis to reach higher homogeneity and solubility once it prevents the hydrolysis of the $SnCl_2$ precursor. Also, the ZTO (1:1) SCS provide higher purity products (white foam-like powder) as depicted in the inset of **Figure 2 (a)** at low processing temperatures when compared with the sol-gel method. The ZTO SCS solution in 1-MP is stable, as it does not present any precipitation after one and half years under a controlled environment (**Figure S2** in the Supporting Information).

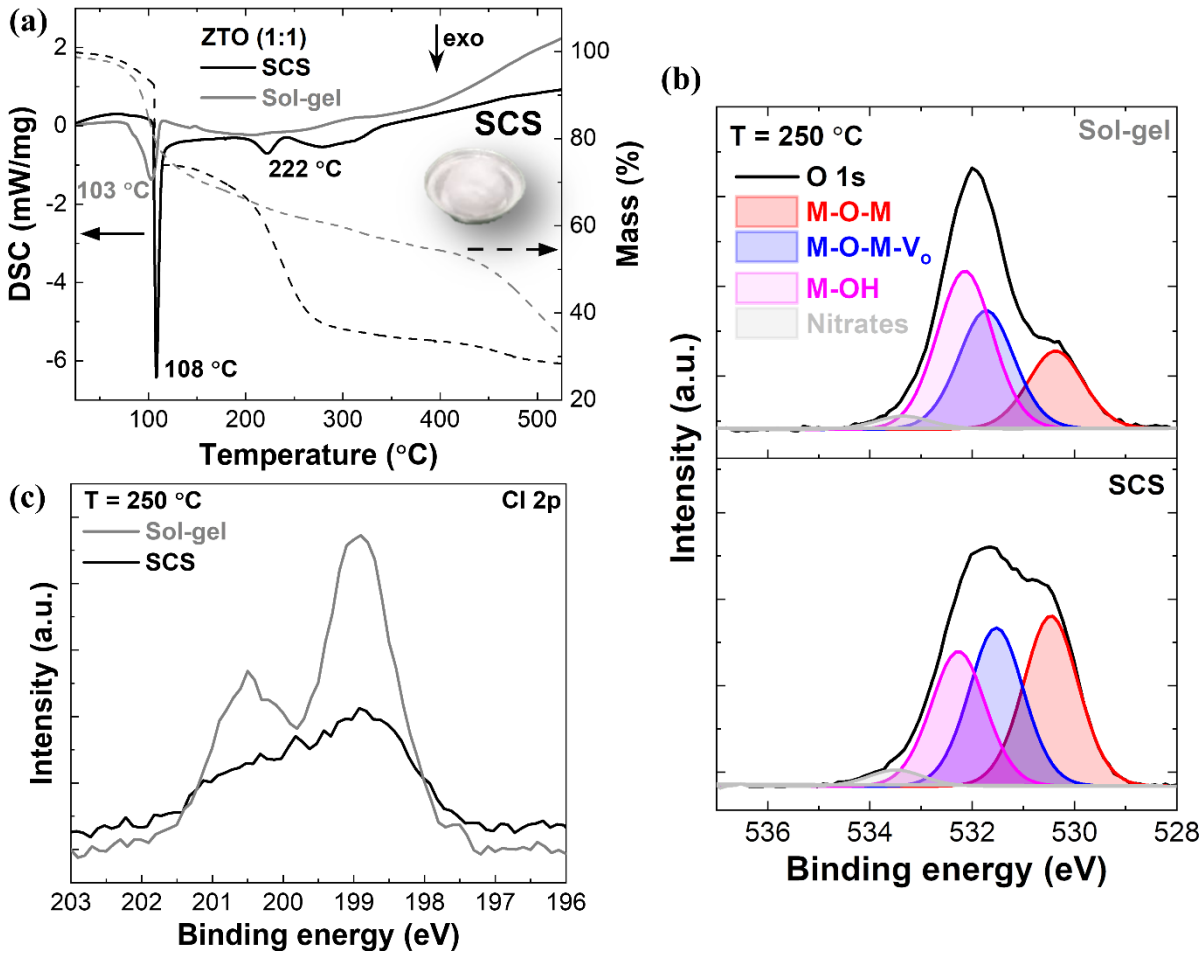


Figure 2. (a) TG-DSC analysis of ZTO (1:1) precursor sol-gel and SCS xerogel. (b) Deconvoluted XPS O 1s and (c) Cl 2p emission peaks of the ZTO thin films for different processing conditions: sol-gel and SCS.

To further study the stoichiometry and the M-O-M bonding of the ZTO thin films annealed at 250 ºC produced by the two synthesis methods, X-ray photoelectron spectroscopy (XPS) measurements were performed, as depicted in **Figure 2 (b), (c)**, and **Figure S3** in the Supporting Information. **Figure 2 (b)** shows the oxygen main peak (O 1s), which was deconvoluted into four component peaks for the two approaches (see **Table S2** in the Supporting Information). These are assigned to oxygen in an oxide lattice (M-O-M), oxygen in vicinity to oxygen vacancies (M-O-M-V_o), hydroxyl (M-OH), and nitrate groups, respectively.[39,40] When the SCS method is used, the M-O-M bonding of ZTO is enhanced in comparison with the sol-gel approach and the M-OH peak is reduced. In all conditions the

tin (Sn $3d_{5/2}$) and the zinc (Zn $2p_{3/2}$) presented peaks with a binding energy at 486.7 ± 0.1 eV and 1022.2 ± 0.1 eV, respectively (see **Figure S3** in the Supporting Information). In relation to Zn:Sn theoretical stoichiometric value (1), Zn:Sn-ratio of 1.59 and 1.26 was achieved for the sol-gel and combustion methods, respectively. The pronounced difference from the theoretical value observed for the ZTO sol-gel is due to two main reasons: the presence of tin hydroxide and unconverted tin chloride. From the appearance of the as-prepared, unfiltered solutions it can be seen that both the tin chloride (**Figure S1 (b)**) and the sol-gel ZTO (**Figure S1 (c)**) solutions are not totally transparent due to the formation of tin hydroxides. This leads to ZTO thin films with lower Sn quantity as some of it is lost in the filtration step performed prior to the deposition. **Figure 2 (c)** shows that the Cl 2p peak is more pronounced in the ZTO sol-gel when compared with the SCS being 2.3 times larger (atomic concentration percentage Cl sol-gel/SCS ratio). The residual tin chloride can be converted to tin oxide only if higher annealing temperatures are applied, which is correlated with the results attained in the TG-DSC measurements.[41]

To complement the ink and the thin-film characterizations, spin-coated ZTO diodes were produced for the different synthesis methods to determine their electrical performance. To ensure the compatibility in upscaling the fabrication process to pilot-scale R2R environments, the electrode materials need to be patternable using R2R methods. In the vertical ZTO diodes, ITO was used as the bottom (ohmic) electrode as it could be patterned using a R2R-printed ITO etching paste.[42] As the top Schottky contact, conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was selected as the initial trials performed using printed Ag contacts showed unstable switching characteristics, likely due to Ag ion migration in the oxide layer.[43] **Figure 3 (a)** depicts *I–V* characteristics of the spin-coated vertical ITO/ZTO/PEDOT:PSS-diodes with a sweep from negative to positive voltages and back with stable diode characteristics.

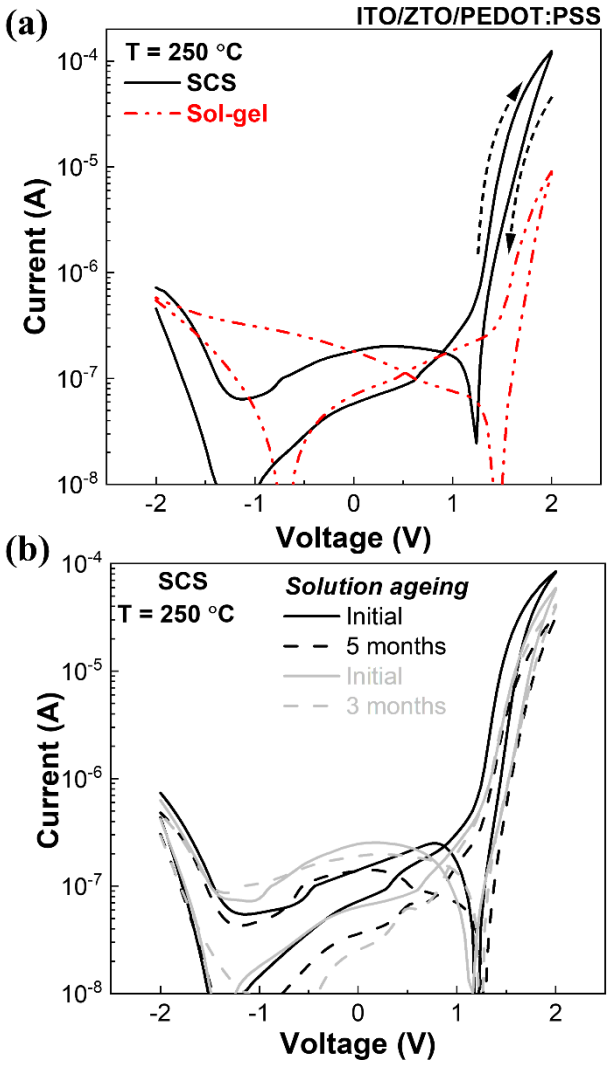


Figure 3. (a) Current-voltage characteristics shown in semi-log plot measured for a representative IZO/ZTO/PEDOT:PSS Schottky diode processed by sol-gel and SCS method. (b) Solution ageing effect on IZO/ZTO/PEDOT:PSS diodes produced using the SCS route after 3 and 5 months.

The current rectification ratio is ~10^2 and ~10^3 for the sol-gel and SCS ZTO diodes, respectively. The hysteresis and turn-on voltage are smaller for the ZTO SCS diodes than for the sol-gel diodes due to the enhanced elimination of residual groups that can act as charge traps, such as organics, metal hydroxides and tin chlorides. A total of 16 devices were measured for the sol-gel and SCS ZTO routes. The yield of working devices was 25 % and 100 % for the sol-gel and SCS, respectively. The SCS route resulted in lower variability between the working devices (**Figure S4** in the Supporting Information). These electrical results are in accordance

with the earlier results (**Figure 2**) from the ink and thin film characterization suggesting that the ZTO films obtained through the SCS route are superior to those obtained through the sol-gel route. We now focus on the ZTO diodes obtained from the SCS route. To determine the stability and use-life of the ZTO SCS ink, tests were performed by producing ZTO diodes with inks aged for 3 and 5 months, as shown in **Figure 3 (b)**. When the ZTO SCS inks are stored in fridge temperature, no significant changes in the diode performance were noticed when comparing the devices produced with aged inks with the devices produced using the fresh inks (initial), which further supports the reliability of the SCS ink.

2.2. Low temperature approach with infrared (IR) curing

To reach even lower annealing temperatures and shorter processing times which would be needed to be able to utilize the SCS ZTO inks on low-cost flexible substrates in pilot-scale R2R environments, IR annealing was incorporated to the process and compared with the typical thermal annealing done at 250 ºC for 30 min. Taking that into account, the ZTO SCS thin films were dried for 5 min on a hotplate at 140 ºC followed by an IR annealing for 7 min in air environment. This IR curing leads to the formation of high-quality ZTO thin films as it promotes the M-O-M network formation.[31,34] The ZTO SCS thin films were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to assess the solvent removal and ink conversion, as depicted in **Figure 4 (a)**. For both high temperature annealing (250 ºC) and IR curing the ZTO thin films did not afterwards present C–H and OH bonds related to organic precursors in the film which confirms the elimination of all residual organics.[34] The absorption peaks presented at 615 cm^{-1} and 582 cm^{-1} are attributed to the Sn-O and Zn-O chemical bonds, respectively.[44–46] Also, the bonding between Zn–O is in the range of 400 to 700 cm^{-1}. Both films exhibited an amorphous nature with the absence of any diffraction peaks and high transparency (≥ 85 %) (**Figure S5** and **S6** in the Supporting Information).

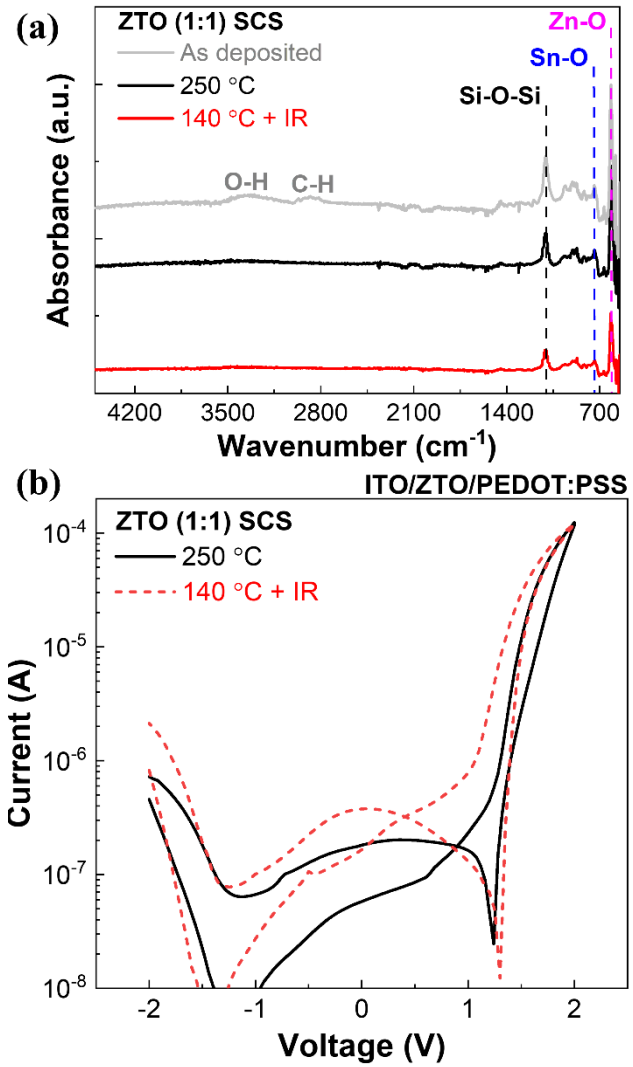


Figure 4. (a) FTIR spectra of ZTO (1:1) SCS thin films. (b) ZTO diode current-voltage characteristics for different annealing conditions with infrared (IR) curing and thermal annealing at 250 ºC.

The ZTO diodes annealed by IR presented a similar electrical performance compared to the reference devices annealed at 250 ºC, as shown in **Figure 4 (b)**. The same rectification ratio (~10^3) and turn-on voltage was achieved for both conditions, however, hysteresis is more evident in the devices annealed by IR related to charge traps. Again, these ZTO devices present a high production yield and low variability (**Figure S7** in the Supporting Information**).**

2.3. Lab-scale printing and large-scale manufacturing of the ZTO diodes

After confirming that these ZTO devices can be fabricated at low processing temperatures and that they can be produced in a short processing time using IR annealing, lab-scale printing tests

were performed before implementation in the pilot-scale R2R environment. First, ZTO thin films were printed by lab-scale flexographic printing to flexible ITO-covered polyethylene terephthalate (PET) substrates. To assure good adhesion of the ZTO layer, the substrates were exposed to 1 min O_2 plasma before printing. **Figure 5 (a)** depicts the printing of ZTO layers with different ink concentrations (0.6, 1.0 and 1.5 M) using a printing speed of 50 m/min and an anilox transfer volume of 4 ml/m^2. A visible increment of the printed semiconductor layer thickness is observed when the concentration is increased. This is directly proportional to the ink's viscosity as shown in **Figure S8** in the Supporting Information. Furthermore, the ZTO SCS ink formulation presents higher thickness when compared to the sol-gel ink formulation (SCS composition contains urea that also acts as an additive to increase the viscosity). This helps to print thicker layers that are needed for vertical diodes to avoid short-circuited devices. However, in **Figure 5 (a)** it can be observed that for the highest concentration of 1.5 M, the layer is not uniform having more defects and presenting the coffee-ring effect leading to thicker edges. Therefore, to sustain adequate thickness and a good uniformity for the ZTO diode production in the pilot-scale R2R-process, a concentration of 1.0 M was selected for the further work.

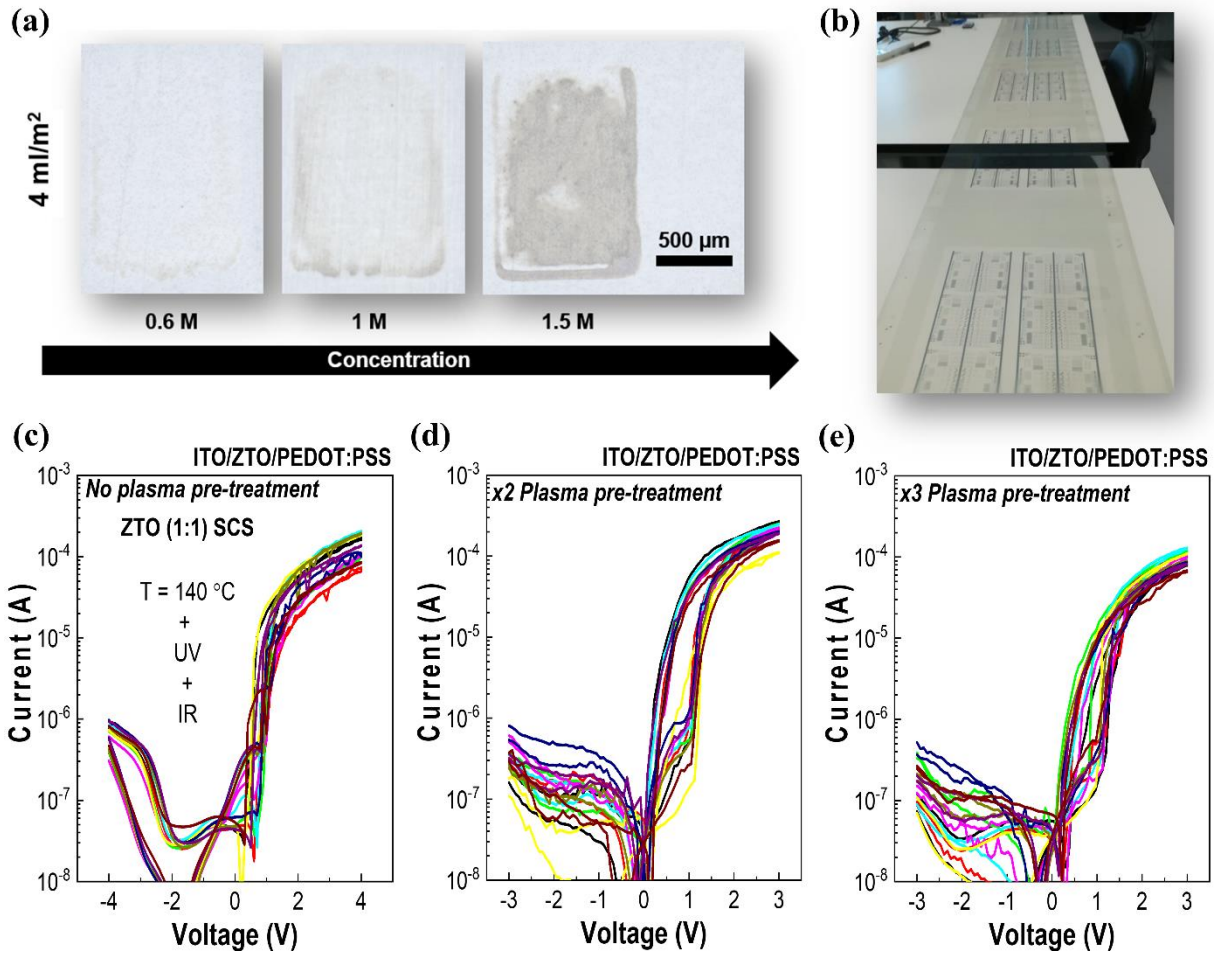


Figure 5. (a) Flexographic printing patterns of ZTO (1:1) SCS using different ink concentration for a printing speed of 50 m/min. (b) Picture of the ZTO diodes printed in the pilot-scale R2R-printing line. Current-voltage characteristics measured of ZTO diodes produced using 1.0 M SCS ink and three successive ZTO layers under different conditions using pilot-scale R2R processing: (c) no plasma pre-treatment; (d) x2 plasma pre-treatment performed before the second and third ZTO layer; and (e) plasma pre-treatment before all ZTO layers.

After the pre-trials done using the lab-scale flexography printing, the process was transferred to pilot-scale R2R-printing line (ROKO at VTT, **Figure 1 (b)** and **Figure 5 (b)**). Several optimization cycles were undertaken to optimize the printing parameters of the ZTO inks (anilox volume: 5 ml/m^2; printing speed: 10 m/min; 3 successive ZTO layers) and the curing parameters (140 °C ovens followed by two UV units and final curing using IR ovens) in the R2R pilot-line. To improve the quality of the printed ZTO layers and the overall performance of the ZTO diodes, a plasma treatment was performed to the substrate containing the R2R-patterned ITO layers as well as in between the printed ZTO to assure a good adhesion and avoid

the poor quality of the overprinted layers (**Figure S9** in the Supporting Information). **Figure 5 (c – e)** shows the electrical performance of the R2R-processed ZTO diodes printed with and without the plasma treatment before the deposition of each ZTO layer. For all conditions, at least 10 devices were measured, showing diode characteristics with a good reproducibility and low variability. Especially, the devices with 2× plasma treatment (first layer without and 2nd and 3rd layer with plasma) in **Figure 5 (c)** show ~1 V turn-on voltage, ~10^3 rectification ratio and small, consistent hysteresis loop. The comparison of these results to those obtained with spin-coated ZTO (**Figure 3(a)** and **Figure S4 (b)**) indicates that it is possible to upscale the ZTO inks from the lab-scale to pilot-scale R2R-production, while maintaining a similar level of electrical performance. To our knowledge, this is the first demonstration of such R2R MO diodes in a pilot-scale R2R environment, especially using inks consisting less-toxic solvents (1-MP instead of 2-ME). In future work, efforts in device size scaling and passivation need to assure their compatibility with various flexible electronics applications, such as a rectifier for the anti-counterfeit label combining electrochromic display and NFC reading.[47]

3. Conclusions

In summary, we reported the relevance of SCS in the formation of ZTO (1:1) thin films using a greener solvent (1-MP) and the use of low processing temperatures (140 °C). This was achieved by the combination with IR annealing in a short processing time and demonstrates upscaling from lab-scale to pilot-scale R2R environments. For the first time, fully pilot-scale R2R-processed ZTO diodes were produced with R2R-etched ITO bottom electrode and printed PEDOT:PSS top electrode. The ZTO diodes exhibit promising electrical features, such as ~10^3 rectification ratio, high yield, low variability, and low operating voltage. The achieved results take the processability of metal oxides a step closer to the production lines used in the printing industry. Such MO semiconductor devices could be of use in various large-volume flexible electronics applications and complement the new era of sustainable hybrid electronics.

4. Experimental Section

Precursor solution synthesis and characterisation:

Sol-gel ink: Zinc nitrate precursor ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, ≥ 99.0%) was dissolved in 1-methoxy-2-propanol (1-MP, $C_4H_{10}O_2$, Carl ROTH, ≥ 99.0%) to yield the zinc oxide precursor solution. For the synthesis of the Zn precursor solution, stirring at 65 ºC was performed to improve the dissolution. Afterwards, tin chloride precursor ($SnCl_2 \cdot 2H_2O$, Sigma-Aldrich, ≥ 98.0%) was dissolved in 1-MP. As soon as the tin chloride solution was clear, the two solutions (zin and tin precursors) were mixed in 1:1 Zn:Sn molar ratio and magnetically stirred (430 rpm) for at least 12 h at room temperature in air environment.

Combustion (SCS) ink: The zinc nitrate precursor and ammonium nitrate (NH_4NO_3, Carl ROTH, ≥ 98.0%) were added sequentially to 1-MP. To facilitate the precursor dissolution, the solution was stirred at 65 ºC. Afterwards, urea ($CO(NH_2)_2$, Sigma-Aldrich, ≥ 99.0%) was dissolved into the solution. To guarantee the redox stoichiometry of the combustion reaction, a molar ratio between urea and zinc nitrate of (5/3):1 was used. The oxidizing agent, ammonium nitrate, was added to act as an oxidizer for the tin chloride with a molar proportion of 2:1 between ammonium nitrate and $SnCl_2$. For the ammonium nitrate precursor, the urea molar proportion was 1:(2/3). To finalize the synthesis, the tin chloride ink was added to the solution (mixture of zinc nitrate, ammonium nitrate and urea) as described previously for the sol-gel ink to yield Zn:Sn molar ratio of 1:1. All precursor solutions were filtrated through 0.45 µm pore size hydrophilic filters (PTFE) before use.

Different solute concentrations (0.6, 1, 1.2, 1.5 M) were tested to assure good quality of the spin-coated and printed layers. The viscosity measurements of the ZTO inks were performed using a BROOKFIELD Cap 2000+ (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA) with a Cap01 spindle at 25 ºC and at 500 rpm speed.

Thermogravimetry and differential scanning calorimetry (TG-DSC) measurements (Netzsch, TG-DSC - STA 449 F3 Jupiter) were performed for the ZTO (1:1) inks (sol-gel and SCS) under air atmosphere up to 500 °C with a 10 ºC/min heating rate in an aluminium crucible. The samples were prepared by drying 10 mL of ZTO precursor solutions on a hotplate at 65 ºC with magnetic stirring at 300 rpm until a viscous gel was obtained.

ZTO film deposition and characterisation:

Prior to deposition, rigid substrates (p-type silicon wafer, glass and commercial glass with ITO with an area of 2.5×2.5 cm^2) were cleaned as described in a previous work.[34] To improve the wettability of the ZTO inks, a UV/Ozone surface activation step was performed in a PSD-UV Novascan system for 10 min at a lamp distance of 5 cm. To produce the ZTO (1:1) thin films, sol-gel and SCS precursor solutions were deposited by spin-coating with a concentration of 0.6 M for 35 s at 2000 rpm (Laurell Technologies). An immediate thermal annealing at 140 ºC for 5 min was performed to dry the samples being followed by either an infrared curing (Infrared IC heater, T-962, Reflow Oven) for 7 min or annealing at 250 ºC on a hotplate for 30 min. A second ZTO layer was deposited using the same conditions as the previous one after performing a UV/Ozone surface treatment to improve the adhesion between the layers.

Flexible substrates (polyimide and PET with ITO) were cleaned with ethanol in an ultra-sonic bath and dried with N_2. Afterwards, an O_2 plasma treatment (Diener Plasma Surface Technology) was performed for 1 min to improve wettability. To investigate the printability of the ZTO inks, flexographic printing of the ZTO layer with ink a concentration of 1.0 M was performed using RK Flexiproof 100 table-top printing machine. The printing was tested at 50 $m \cdot min^{-1}$ printing speed using anilox rolls with different transfer volumes: 3 ml/m^2 (400 lines/cm), and 4 ml/m^2 (320 lines/cm) while assuring a proper ink transfer from patterned flexo stamp to the substrate through low nip pressure (kiss pressure). After printing, all the samples

were dried at 140 °C on a hotplate in air for 10 min and investigated using an optical microscope. All the lab-scale deposition and drying tests of the ZTO inks were performed in controlled ambient conditions where the relative humidity and temperature varied between 40–44% and 23.5–24.2 ºC, respectively.

The crystal structure and the absorption peaks of the constituents of the ZTO thin films deposited on Si substrates were assessed by glancing angle X-ray diffraction (GAXRD) and attenuated total reflection Fourier Transform Infra-Red (ATR-FTIR) spectroscopy, respectively, as described in a previous work.[34] X-ray photoelectron spectroscopy was done with a Kratos Axis Supra spectrometer using monochromatic Al Kα radiation. The detail scans were recorded with a constant pass energy of 10 eV. Data analysis was conducted with CasaXPS Version 2.3.19PR1.0.

Lab-scale ZTO diode production and characterization:

Vertical ZTO Schottky diodes were prepared using the sol-gel and SCS ZTO inks on commercial glass/ITO substrates as mentioned above (ITO bottom electrode). Afterwards, poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS, Sigma-Aldrich, 5.0 wt. %, conductive screen printable ink) was deposited as the top electrode to provide Schottky contact by screen printing and annealed on a hotplate at 130 ºC for 3 min. The active area of these ZTO devices was 1000 µm x 1000 µm.

Pilot-scale R2R-processed ZTO diode fabrication and characterization:

The up-scaled ZTO diodes were processed onto ITO bottom electrodes that were patterned using R2R-printed ITO etching paste [42] on flexible PET substrates in the ROKO pilot-line at VTT facility (factory scale-up) in Oulu. Then, ZTO SCS precursor ink with 1 M concentration was printed on top of the bottom electrode lines with printing direction perpendicular to the ITO bottom electrode lines as three successive ZTO layers with overlay registration. The printing was optimized for homogeneous ZTO layers using a printing speed of 10 $m \cdot min^{-1}$ and

anilox rolls with 5 ml/m^2 transfer volume (320 lines/cm). Prior to the deposition of the ZTO thin films and between the successive ZTO layers, in-line plasma treatment (Ar/N_2, 550 W) was performed to improve the adhesion of these layers to the ITO electrode and improve the printing quality of the overlaying layers. After the printing of each ZTO layer, the PET/ITO web with the printed ZTO layer was dried with an in-line speed of 10 m/min using in-line drying oven at 140 ºC (4 ovens with total ~4 m length leading to ~24 s total drying time) and two in-line 365 nm ultraviolet (UV) drying units (160 W/cm at 55% and 80% power with total ~0.25 m length leading to ~1.5 s curing time). As mentioned earlier, this process was repeated two more times to have total 3× layer of ZTO and then, to finalize the curing of the active layer, an infrared (IR) irradiation (3× 1 kW IR lamps with 9 s treatment time with 10× cycles leading to total 90 s annealing time) was applied with a printing inline speed of 2 $m \cdot min^{-1}$. The thickness of the cured (3x) ZTO layer was approximately 60 – 80 nm when measured using a stylus profilometer (Veeco Dektak). To finalize the vertical ZTO diodes, PEDOT:PSS (AFGA Orgacon EL-P5015) top electrode was deposited by R2R rotary screen (215 meshes/inch) printing with a printing speed of 2 m/min and dried at 140 ºC (4 ovens with total drying time of ~2 min). The active area (i.e. overlap between ITO and PEDOT:PSS electrodes) of the ZTO devices was ~100 µm x ~100 µm.

The electrical characterization of the R2R-processed ZTO Schottky-diodes was performed in dark environment using a semiconductor parameter analyser (Keysight 4200SCS) and probe station (Janis ST-500).

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Printed Zinc Tin Oxide Diodes: From Combustion Synthesis to Large-Scale Manufacturing

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The supporting information contains the data related to the production and characterization of zinc tin oxide (ZTO) solutions, thin films and their applications in diodes. Table S1 shows the state-of-the-art of printed metal oxide diodes. Figure S1 depicts photographs of each initial precursor solution and their combination to form the ZTO precursor ink. Figure S2 shows ZTO (1:1) ink stability after 1.5 years in cooled conditions. Table S2 shows Zn, Sn, O, Cl emission peaks of the printed ZTO thin films. Figure S3 depicts the X-ray photoelectron spectroscopy (XPS) emission Zn $2p_{3/2}$ and Sn $3d_{5/2}$ peaks from the ZTO thin films produced by different methods. Figure S4 shows the current-voltage characteristics of the ZTO diodes made by the sol-gel and solution combustion synthesis (SCS) routes. Figure S5 and S6 depict, the XRD diffractograms and optical transmittance of the ZTO SCS thin films, respectively, under different annealing conditions. Figure S7 shows ZTO current-voltage characteristics of several devices annealed at 140 ºC combined with infrared (IR) irradiation. Figure S8 depicts the viscosity versus concentration for ZTO (1:1) precursor inks. Figure S9 shows the printing quality of the R2R-printed ZTO multilayers after various plasma treatment conditions.

Table S1. State-of-the-art properties of printed metal oxide diodes.

Year	Solvent	Active Material	Fabrication Method	Pilot Line	T_{max} (°C)	Substrate/ BE/TE	ON/OFF ratio
2012[1]	n.d.	ZnO-Polymer	Gravure	No	150	PET/ Ag/Al	2.5×10^3
2014[2]	n.d.	ZnO-Polyaniline	Gravure	No	150	PET/ Ag/Al	n.d.
2018[3]	AC/NMP	IGZO NPs	Gravure	No	150	PET/ Ag/Al	6.8×10^5
2018[4]	2-P	TiO_2	Inkjet	No	375	Glass/ FTO/Ag	10^2
This work	1-MP	ZTO	R2R-flexo	Yes	140 + IR	PET/ ITO/PEDOT:PSS	~10^3

BE: Bottom electrode; TE: Top electrode; $R_{on/off}$: Resistance on/off ratio; n.d.: not defined; T_{max}: maximum temperature; RT: Room temperature; Spin: Spin-coating; AC: acetic acid; NMP: 1-methyl-2-pyrrolidinone; a-Lith: adhesion lithography; 2-Propanol :2- ;1-MP: 1-Methoxypropanol; Flexo: Flexographic Printing; IR: Infrared; NPs: nanoparticles.

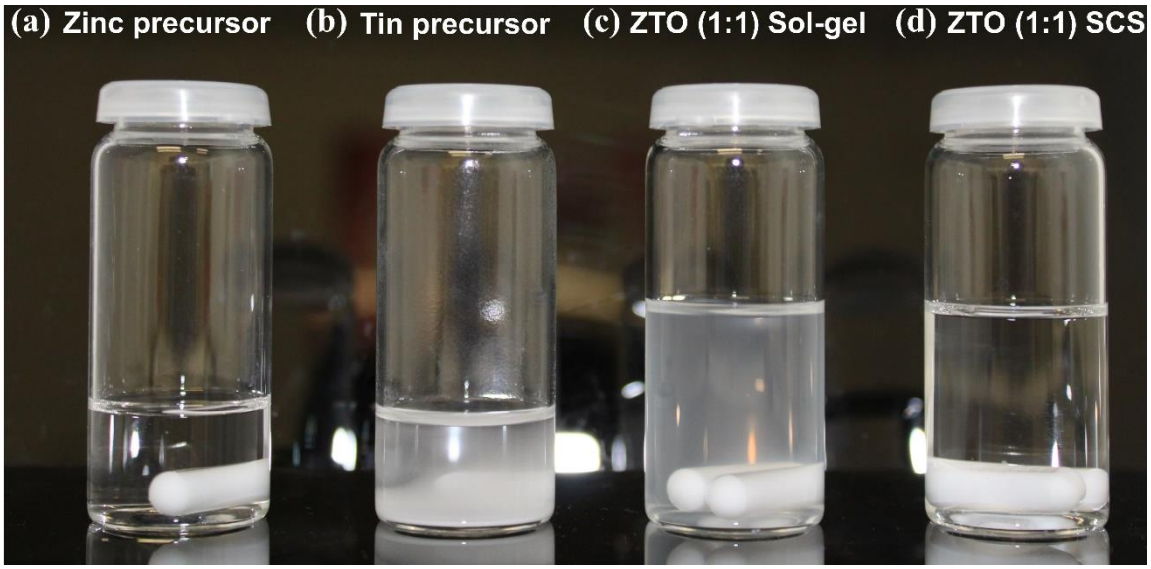

Figure S1. Photograph of the different inks mixed in 1-methoxypropanol (1-MP): (a) zinc precursor solution; (b) tin precursor solution; (c) ZTO (1:1) sol-gel precursor solution; (d) ZTO SCS precursor solution. The images are taken prior any filtering.

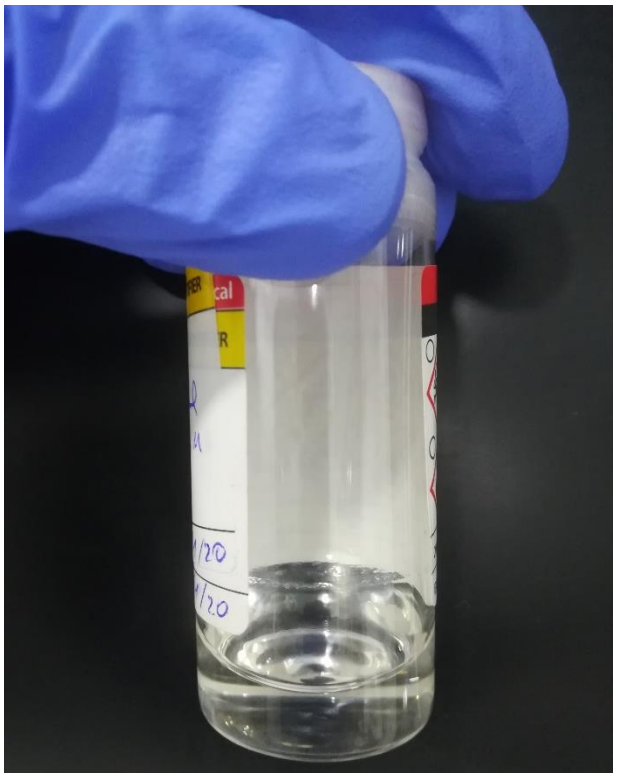

Figure S2. Photograph of ZTO (1:1) SCS precursor ink after 1 year and 6 months stored in cool conditions (5 ºC).

Table S2. Zn, Sn, O, Cl emission peaks of the printed ZTO thin films.

		Binding energy (eV)	
Peaks		**SCS**	**Sol-gel**
Zn 2p	Zn $2p_{3/2}$	1022.3	1022.2
Sn 3d	Sn $3d_{5/2}$	486.6	486.7
O 1s	M-O-M	530.4	530.4
	M-O-M-V_o	531.5	531.7
	M-OH	532.2	532.1
	Nitrates	533.5	533.3
Cl 2p	Cl $2p_{3/2}$	198.9	198.9
	Cl $2p_{1/2}$	200.5	200.5

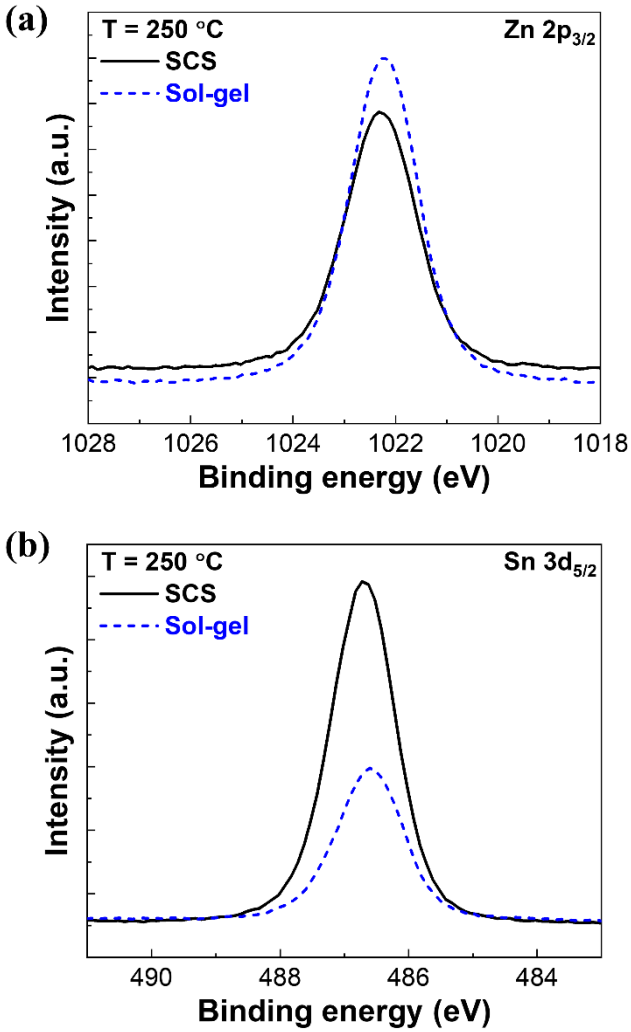

Figure S3. XPS of (a) Zn $2p_{3/2}$ and (b) Sn $3d_{5/2}$ emission peaks of the ZTO (1:1) thin films annealed at 250 ºC and produced by different methods, sol-gel and SCS.

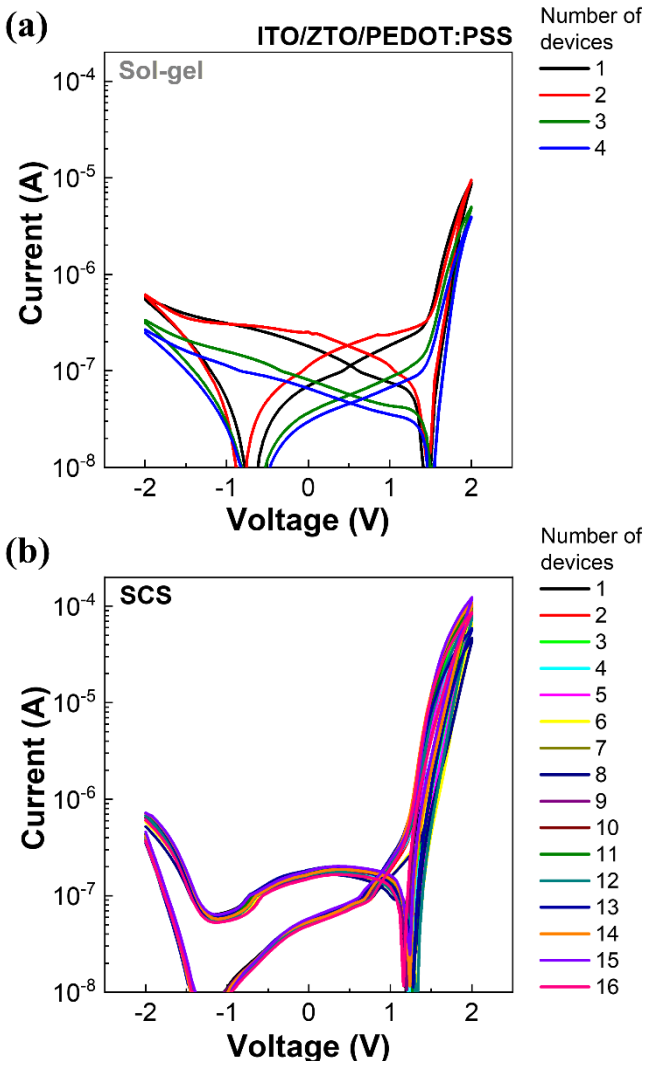

Figure S4. Current-voltage characteristics of the spin-coated ZTO diodes produced by (a) sol-gel and (b) SCS method. The 12 non-working sol-gel devices are omitted.

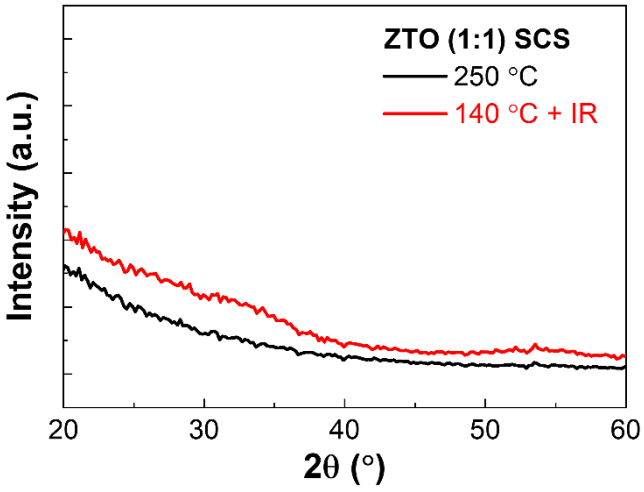

Figure S5. XRD diffractograms of ZTO (1:1) SCS thin films annealed under different conditions: thermal annealing at 250 ºC and at 140 ºC combined with infrared (IR) curing.

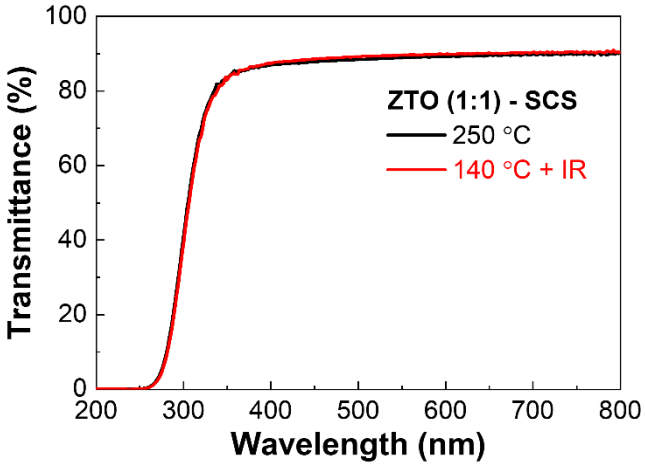

Figure S6. Optical transmittance of ZTO (1:1) SCS thin films annealed under different conditions: thermal annealing at 250 ºC and at 140 ºC combined with infrared (IR) curing.

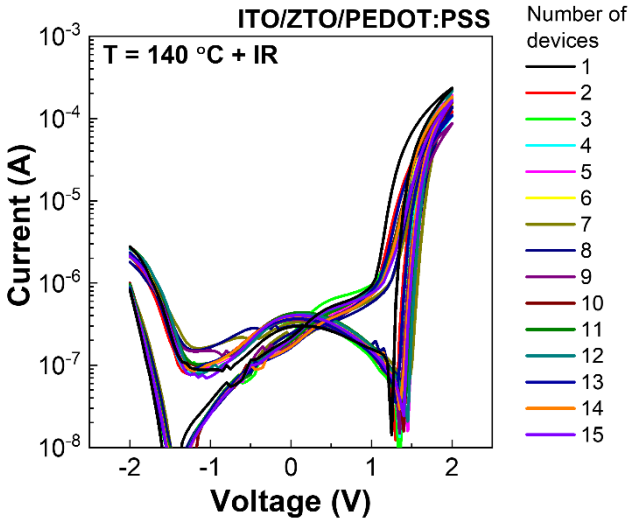

Figure S7. Current-voltage characteristics of 15 diodes produced by spin-coating the ZTO SCS ink and annealed at 140 ºC combined with infrared (IR) irradiation.

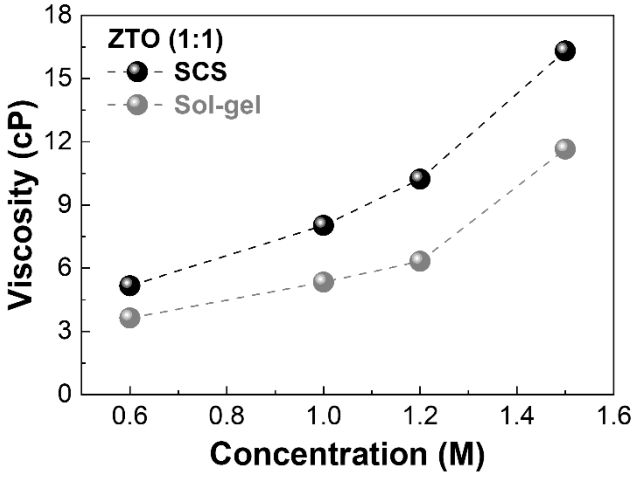

Figure S8. Variation of the viscosity with the concentration of the solution for ZTO (1:1) precursor inks made using sol-gel and SCS synthesis routes.

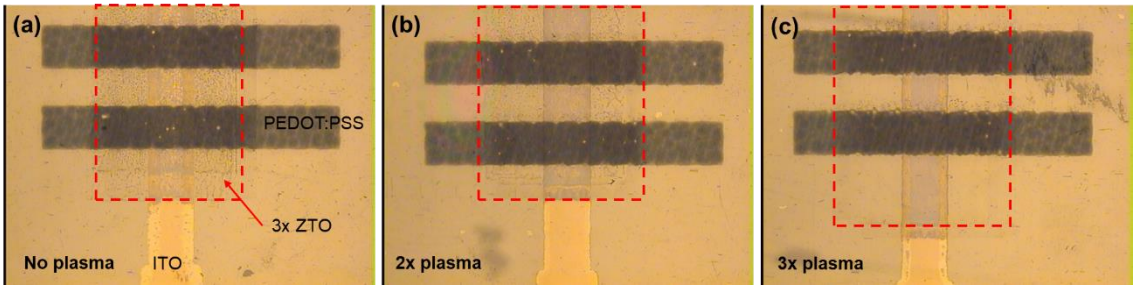

Figure S9. Optical microscope images of roll-to-roll-fabricated ZTO diodes with (a) no plasma treatment before the ZTO printing, (b) plasma treatment before the printing oft he 2nd and 3rd ZTO layer (2×) and (c) plasma treatment before the printing of each of the ZTO layers (3×). Red dashed lines highlight the location of the transparent ZTO layer. The active area (overlapping area of ITO and PEDOT:PSS) of the devices shown here was ~800 µm x ~800 µm.

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