

Role of structure and composition on the performances of p-type tin oxide thin-film transistors processed at low-temperatures

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Abstract: This work reports the role of structure and composition on the determination of the performances of p-type SnO_x TFTs deposited by rf magnetron sputtering at room temperature, followed by a post-annealed step up to 200°C at different oxygen partial pressures (Opp), between 0% and 20%, but where the p-type conduction was only observed between 2.8-3.8%. The role of structure and composition were evaluated by XRD and Mössbauer spectroscopic studies. The study allows to identify the best phases/compositions and thicknesses (around 12 nm) to be used that lead to the production of TFTs with a bottom gate configuration, on glasses coated with conductive Indium Tin Oxide, followed by Aluminium Titanium Oxide dielectric layer with saturation mobility of 4.6 cm²V⁻¹s⁻¹ and on-off ratio above 7×10⁴, operating at the enhancement mode with a saturation voltage of -10 V.

Keywords: p-type TFT, p-type oxide semiconductors, SnO electrical properties; Oxide structure analysis

1. Introduction

Oxide electronics or in more generic terms transparent electronics, is emerging as an appropriate alternative to amorphous silicon (a-Si:H) and organic semiconductors, especially for thin film transistors (TFTs) and more complex electronic circuits. Oxide semiconductors are a promising class of TFT materials that have made impressive demonstration in display applications in a relatively short time, challenging silicon in the flexible electronics field. Although some initial attempts during the 60s were done for SnO₂, [1] and ZnO, [2] TFT channel layers, only forty five years later, with the work of Hosono, [3] Wager, [4] Carcia, [5] and Fortunato, [6] a significant worldwide interest appeared, especially for active matrix for organic light emitting diodes (AMOLED) technology, both in industry and academia. Oxide semiconductors have unique electronic properties like high mobility irrespective to the structure nature and excellent uniformity and homogeneity in device parameters associated to a low or room temperature deposition process allowing the use of low cost and flexible substrates such as polymer or even paper. [7]

However, there is no report on p-type oxide TFTs with performance similar to n-type, which is mainly limited by the low hole mobilities. [8] Achieving high performance p-type oxide TFTs will definitely promote a new era for electronics in rigid and flexible substrates, away from silicon. Moreover, it will shape the electronics of tomorrow by allowing the production of complementary metal oxide semiconductors (CMOS), a key device to fuel the microelectronics revolution in the so-

47 called technologies of information and communication, by allowing the use of highly compact circuits
48 with low power consumption.

49 At present, almost all reported oxide TFTs are based on n-channel devices.[1-9] The carrier
50 conduction path (valence band) in p- type oxides is mainly formed from the oxygen p asymmetric
51 orbitals, which severely limit the carrier mobility and lead to poor TFT performance. Cu_2O is a p-type
52 oxide with mobility exceeding $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.[10,11] However, TFTs prepared from Cu_2O have field-
53 effect mobilities and on-off current ratio below $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and 10^2 respectively, due to difficulty in
54 controlling the hole density in channel layer.[11-13] While conventional passive applications
55 require the maximum possible hole density for optimal conductivity, the channel layer requires a low
56 hole density in order to modulate the channel conductance by an applied electric field. Most of
57 organic TFTs reported in the literature are p-type.[14,15] Even though organic TFTs have been the
58 topic of intense research for the past few decades, the overall performance is still poor compared to
59 oxide TFTs, namely low mobilities ($< 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$),[16] poor stability and device-to-device variability.
60 Additionally, the high operating voltage is a disadvantage for portable, battery-powered device
61 applications.[15,16] Moreover, the n-type organic semiconductors have even much lower mobilities
62 (10^{-3} to $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), limiting their use in applications such as CMOS.[17]

63 In this paper, we report the fabrication of high-performance oxide TFTs using p-type SnO_x
64 channel layer deposited by rf magnetron sputtering at room temperature that is post-annealed up to
65 200°C . SnO has a specific electronic structure associated with the presence of divalent tin (Sn^{2+}), in a
66 layered crystal structure.[18,19] SnO has an indirect band structure with major contribution from Sn
67 $5s$ and O $2p$ orbitals near the valence band maximum (VBM) and Sn $5p$ orbitals towards the
68 conduction band minimum (CBM). The origin of p-type conductivity in SnO is mainly attributed to
69 the Sn vacancy and the O interstitial where tin is in Sn^{2+} oxidation state.[18,19] If there is excess
70 oxygen in the film, some cations will be transformed into Sn^{3+} to maintain electrical neutrality. This
71 process is considered as Sn^{2+} capturing a hole and forming weak bonded holes which are located
72 inside the bandgap near the top of the valence band as localized acceptor states.[20,21]

73
74 For a set of practical applications, there are a clear demand for p-type TFT able to match the
75 requirements to grow ultra-low power electronics systems, whose key components are based CMOS
76 technology [22]. Apart from that, the emerging flexible electronics, is pushing for processing devices
77 at low process temperatures, together with high mobility and high on-off ratios [7].

78 TFTs based on p-type SnO_x are expected to fulfill these requirements due to the particular nature
79 of band structure. [20,21] Contributions from Sn $5s$ states to VBM could offer appreciable hole
80 mobility in this material, without using high processes temperature [23,24]. In the present work, SnO_x
81 based TFTs are prepared by an industrial friendly rf magnetron sputtering system at room
82 temperature (RT), without any intentional substrate heating during the growth process, aiming to
83 understand the role of structure, surface finishing and composition in producing high stable TFT with
84 high electronic performances, such as field effect mobility and on-off- current ratios.

85 2. Materials and Methods

86 Prior to process the TFT devices, the material in which the channel is based was processed and fully
87 analyzed, concerning their structure, morphology, composition and electro-optical properties,
88 aiming to determine the best conditions to grow the channel layers of the TFT with a bottom gate
89 configuration

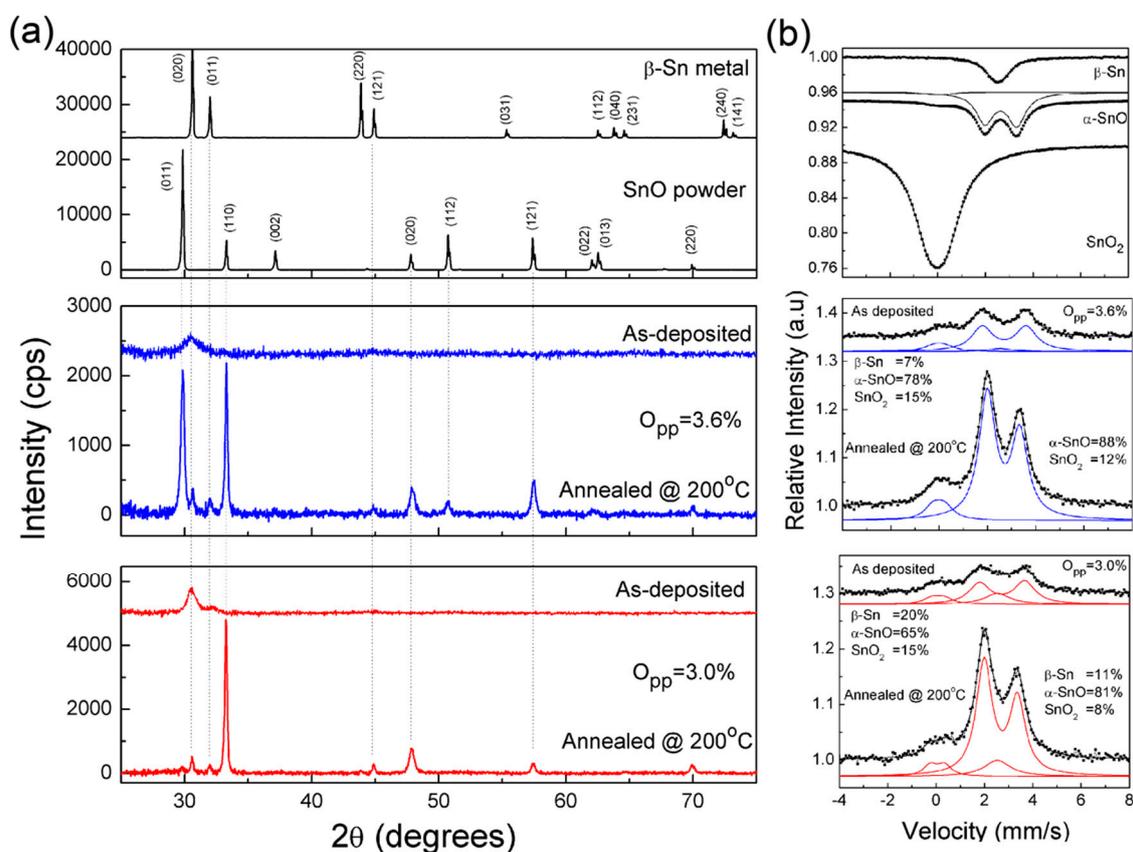
90 Films Preparation

91 SnO_x films were deposited on glass substrates using a computer controlled rf magnetron
92 sputtering system using a metallic tin target (99.999% pure). Depositions were carried out in a
93 controlled atmosphere of oxygen and argon. Sputtering power to metallic tin target was fixed at 40
94 W and substrates were rotated at a speed of 40 rpm. Experiments were performed by varying O_{pp}
95 ($O_{pp} = PO_2 / (PO_2 + PAr)$, where PO_2 and PAr are partial pressures of oxygen and argon) up to 20% in the

96 deposition chamber, keeping the total deposition pressure constant at 0.2 Pa. At this condition, the
97 deposition rate was 40 Å/min.

98 Structure and composition studies

99 X-ray diffraction analysis was performed on tin oxide thin films deposited on glass substrates,
100 using PANalytical X'Pert Pro system, as depicted in Fig.1.



101
102 **Figure 1:** (a) XRD patterns of deposited SnO_x thin films. (b) Transmission ^{119}Sn Mössbauer spectra of bulk
103 samples and CEMS spectra of as-deposited and annealed SnO_x films deposited at 3.0% and 3.6% O_{pp} .

104

105 ^{119}Sn Mössbauer spectra analysis

106 The films were analyzed by ^{119}Sn conversion-electron Mössbauer spectroscopy (CEMS) at room
107 temperature placing them inside a proportional backscatter detector RIKON-5 (Wissel) in flowing
108 5% CH_4 -95% He gas mixture (see figure 1b). Both CEMS and transmission Mössbauer spectra were
109 collected using a conventional constant acceleration spectrometer and a 5 mCi $\text{Ca}^{119\text{m}}\text{SnO}_3$ source. The
110 velocity scale was calibrated using a ^{57}Co (Rh) source and an α -Fe foil. The Sn isomer shifts (IS) are
111 given relative to BaSnO_3 reference material at 295 K and obtained by adding 0.031 mm/s to the IS
112 relative to the source. The spectra were fitted to Lorentzian lines using a non-linear least-squares
113 method. The set of estimated parameters extracted are depicted in table 1.

114

115 **Table 1.** Estimated parameters from the transmission ^{119}Sn Mössbauer spectra of bulk samples and
116 CEMS spectra of films taken at 295K.

Sample	IS [mm/s]	QS [mm/s]	Γ [mm/s]	Sn phase	I [%]
SnO_2 bulk	0.01	0.56	1.34	-	100
α -SnO bulk	2.67 -0.03	1.34 0.58	0.98 0.77	α -SnO SnO ₂	95 5

-Sn metal	2.56	-	1.03	-	100
Film	2.76	1.87	1.04	SnO	65
O _{pp} =3.0%, RT	0.11	0.52	0.84	SnO ₂	15
	2.56	-	1.3	-Sn	20
Film	2.7	1.38	0.79	SnO	81
O _{pp} =3.0%,	0.08	0.59	0.7	SnO ₂	8
200°C, 30 min	2.56	-	1.35	-Sn	11
Film	2.73	1.82	1.02	SnO	78
O _{pp} =3.6%, RT	0.11	0.53	0.81	SnO ₂	15
	2.56	-	1.3	-Sn	7
Film	2.7	1.34	0.82	SnO	88
O _{pp} =3.6%,	0.06	0.48	0.85	SnO ₂	12
200°C, 30 min					

117 IS (mm/s) isomer shift relative to metallic BaSnO₃ at 295 K; QS (mm/s) quadrupole splitting; Γ (mm/s)
 118 line-width; I relative area. Estimated errors ≤ 0.02 mm/s for IS, QS, Γ and $<2\%$ for I.

119 Electrical studies

120 It is essential to study the electrical properties of the material in order to understand the charge carrier
 121 type and transport properties. Hall Effect measurement is the most commonly used technique to
 122 identify the charge carrier and carrier mobility in the material. In contrast to n-type oxides, Hall
 123 measurement does not give reliable results for p-type oxides, primarily because of very small drift
 124 mobility of holes. Moreover, when both electrons and holes are present in a semiconductor sample,
 125 both charge carriers experience a Lorentz force in the same direction. So, both electrons and holes
 126 will pile up at the same side of the sample and consequently the measured Hall voltage depends on
 127 the relative mobilities and concentrations of holes and electrons. Hall mobility for an ambipolar
 128 semiconductor is thus given by,

$$129 \quad \mu_{Hall} = \frac{n \cdot \mu_n^2 - p \cdot \mu_p^2}{n \cdot \mu_n + p \cdot \mu_p} \quad (1)$$

130
 131 where n , p , μ_n and μ_p represent electron density, hole density, electron drift mobility and hole drift
 132 mobility respectively. This suggests a considerable reduction in Hall mobility in an ambipolar
 133 semiconductor compared to the actual drift mobilities of the charge carriers.

134 In the present analysis, RT deposited samples have shown fluctuations in the sign and magnitude of
 135 Hall coefficient. Typical carrier mobilities were of the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Because of the ambipolar
 136 nature of the RT deposited films [25], these results suggest that Hall measurement of SnO_x films
 137 highly underestimates the actual carrier mobility. After annealing up to 200°C for 30 minutes, films
 138 prepared in the O_{pp} of 2.8-3.8% have shown positive Hall coefficient consistently. There was no
 139 change in Hall coefficient sign even though the magnitudes were shown small fluctuations. This
 140 suggests a considerably large density of holes compared to the density of electrons. Figure 2 shows
 141 the resistivity variation of as prepared and annealed SnO_x films.

142

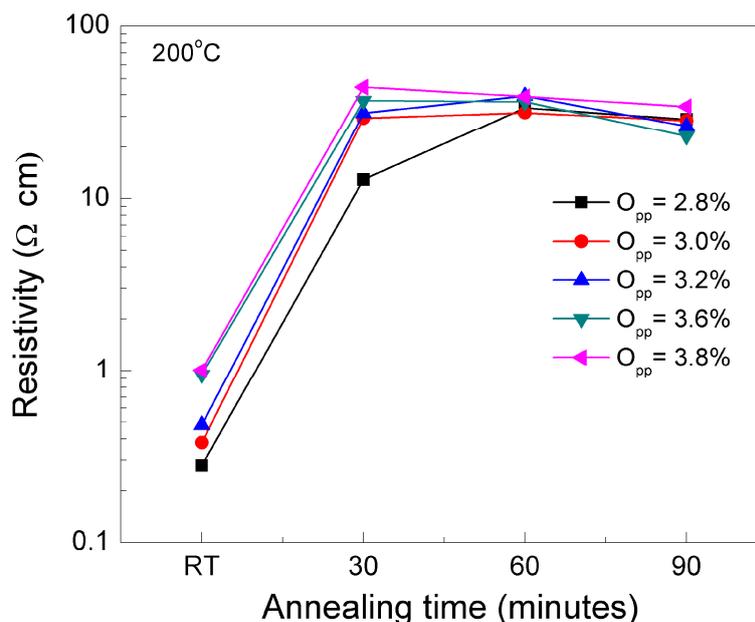


Figure 2: Variation in the resistivity of SnO_x films as a function of annealing time.

143

144

145

146 As observed in the Mossbauer spectra of RT deposited films, RT samples consist of metallic tin, SnO
 147 and SnO₂ phases. In this condition, both electrons and holes can contribute to the charge transport in
 148 the system. At 200 °C annealing in air, oxygen atoms incorporate to the films which oxidizes with
 149 metallic tin leading to SnO phase formation with reduction in electron density and increase in hole
 150 density. This may be the reason for initial increase in the resistivity of the films. In this case, the
 151 material has large density of holes compared to the density of electrons which results in positive Hall
 152 voltage with typical Hall mobility of 2 cm² V⁻¹ s⁻¹.

153 Annealing at still higher temperatures cause again a decreasing tendency in material resistivity (not
 154 shown here). This time, it is because of the phase transformation of the material from SnO (p-type) to
 155 SnO₂ (n-type). Actual carrier mobility must be much higher than the measured hall mobility value.

156

157

158 Optical studies

159 Optical transmittances of RT deposited films were very poor in the visible region, mainly because of
 160 the presence of large concentration of metallic tin in the films (Figure 4a). Annealing up to 200°C for
 161 30 minutes considerably increased the optical transmittance in the visible region. However, still the
 162 maximum transmission was around 50%. SnO has been reported as an indirect bandgap material
 163 with a direct bandgap value of around 2.5 eV and indirect band gap value around 1 eV. Whereas,
 164 SnO₂ is a direct bandgap material with bandgap value around 3.6 eV.

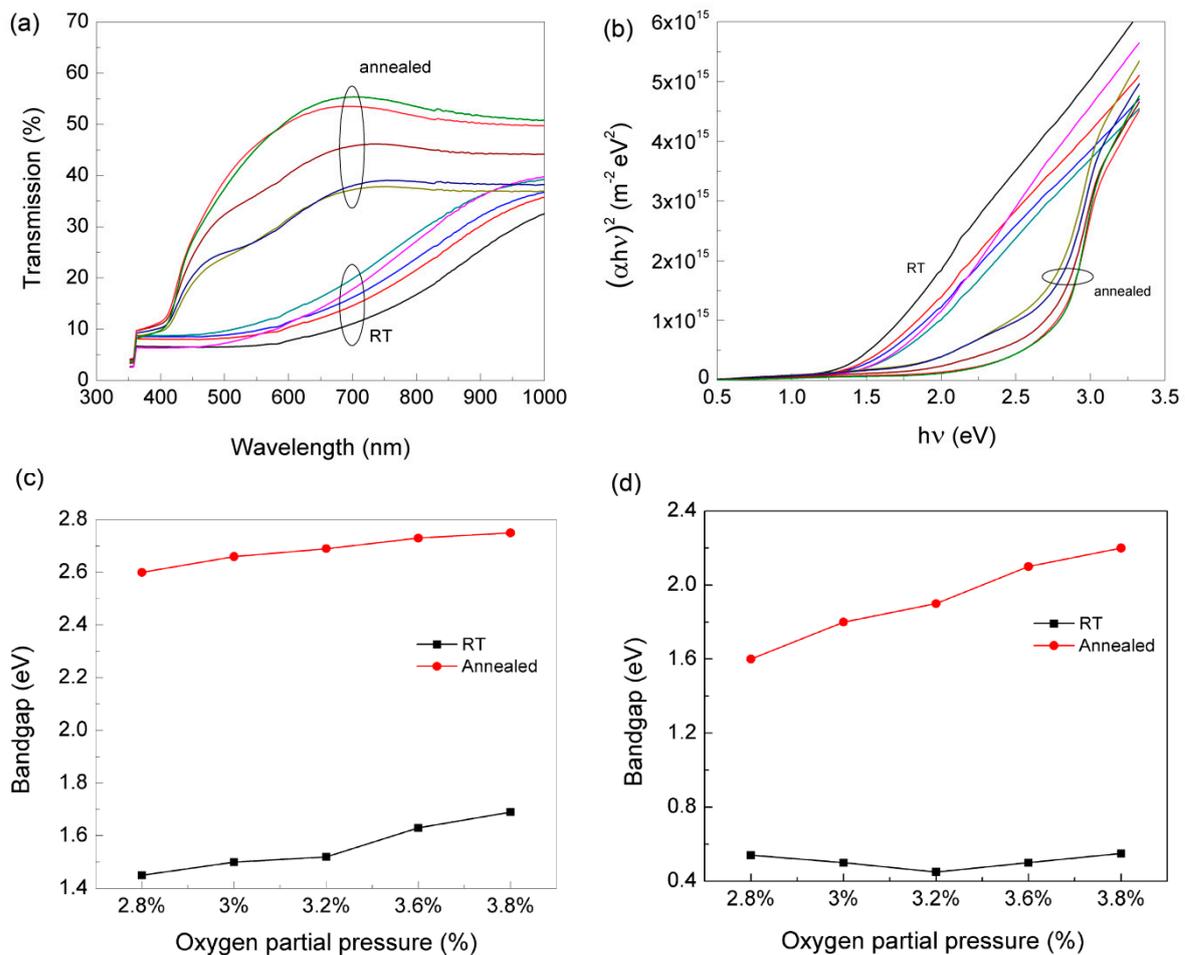
165 The optical absorption coefficient (α) of semiconductors generally follows a relationship of the form,

$$166 \quad \alpha \cdot h \cdot \nu = \text{const} \cdot (h \cdot \nu - E_g)^r \quad (2)$$

167 where $h\nu$ denotes the photon energy, E_g the optical band gap, and r a constant depending on the type
 168 of optical transition in the material. The E_g value is then obtained by linearly extrapolating the plot of

169 $(\alpha \cdot h \cdot \nu)^{1/r}$ vs $h \cdot \nu$ and finding the intersection with the abscissa. The optical data in figure 3a

170 were analyzed with $r = \frac{1}{2}$ (direct transition) and $r = 2$ (Indirect transition). Estimated direct bandgap
 171 values are in the range of 2.6 - 2.75 eV for annealed films (figure 3b and 3c). However, the presence
 172 of a narrow gap indirect band results considerable optical absorption below these estimated values.
 173 The indirect values estimated from a plot of α vs $h\nu$ results 1.6 - 2.2 eV which is around 1 - 0.55 eV
 174 below the corresponding direct bandgap values (figure 3d). These values are close to the reported
 175 bandgap values for SnO films. Small variations in these values could be understood on the basis of
 176 fractional variations of various phases (metallic tin, SnO and SnO₂) in the films.
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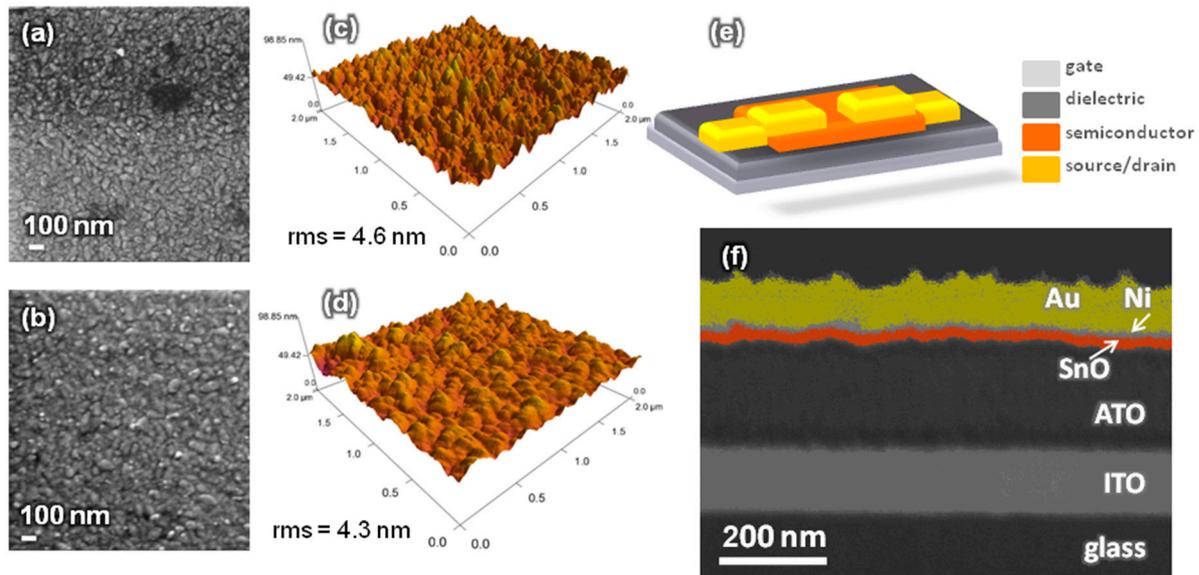
180 **Figure 3:** (a) Optical transmission of as prepared and annealed SnO_x films. (b) Plot of α vs $h\nu$ for direct bandgap
 181 estimation. (c) Estimated direct bandgap values and (d) indirect bandgap values.

182

183 **Devices architecture and structure**

184 Surface morphology of TFT channel layers was analyzed by ZEISS Auriga SEM-FIB and Asylum
 185 MFP-3D AFM, as depicted in fig.4.

186 Bottom gate TFTs were fabricated on glass substrates coated with 150 nm thick layer of sputtered
 187 ITO and a 220 nm thick layer of aluminium-titanium oxide (ATO). SnO_x channel layer
 188 (width/length=50 μm/50 μm) was deposited over this by rf magnetron sputtering. Ni/Au (9 nm/60
 189 nm) stacks deposited by electron beam evaporation were used as source and drain electrodes. After
 190 deposition, devices were annealed in air up to 200°C for 30 minutes inside a tubular furnace (see
 191 figure 4 e).



192
 193 **Figure 4.** SEM images of post-annealed TFT channel layers prepared at O_{pp} of (a) 3.0% and (b) 3.6%.
 194 Corresponding AFM images of the TFT channel layers are shown in (c) and (d). (e) Schematic illustration of SnO_x
 195 TFT structure employed for the present study. (f) Cross-sectional SEM image of the SnO_x channel TFT.

196
 197 TFT electrical characterization was performed with an Agilent 4155C semiconductor parameter
 198 analyzer and a Cascade Microtech M150 microprobe station inside a dark box at ambient atmosphere.
 199

200 Capacitance measurements

201 CV measurements have been done in TFT by short circuiting the drain and source terminals. By doing
 202 so we enhance the overall capacitance measured allowing a better discrimination on the data
 203 achieved. Under these conditions, we assume an electrical model consisting in a contact resistance R_c
 204 (equal for drain and source regions, since we have a symmetric device) in series with the combination
 205 of two parallel RC resonators as depicted in the sketch of figure 5a. One represents the semiconductor
 206 channel capacitance (C_s) that varies dynamically, depending on the extension of the
 207 accumulation/depletion layer. The other is the interface trap capacitance (C_{it}) in series with the
 208 corresponding associated interface resistance R_{it} , both depending on the interface defects given by:

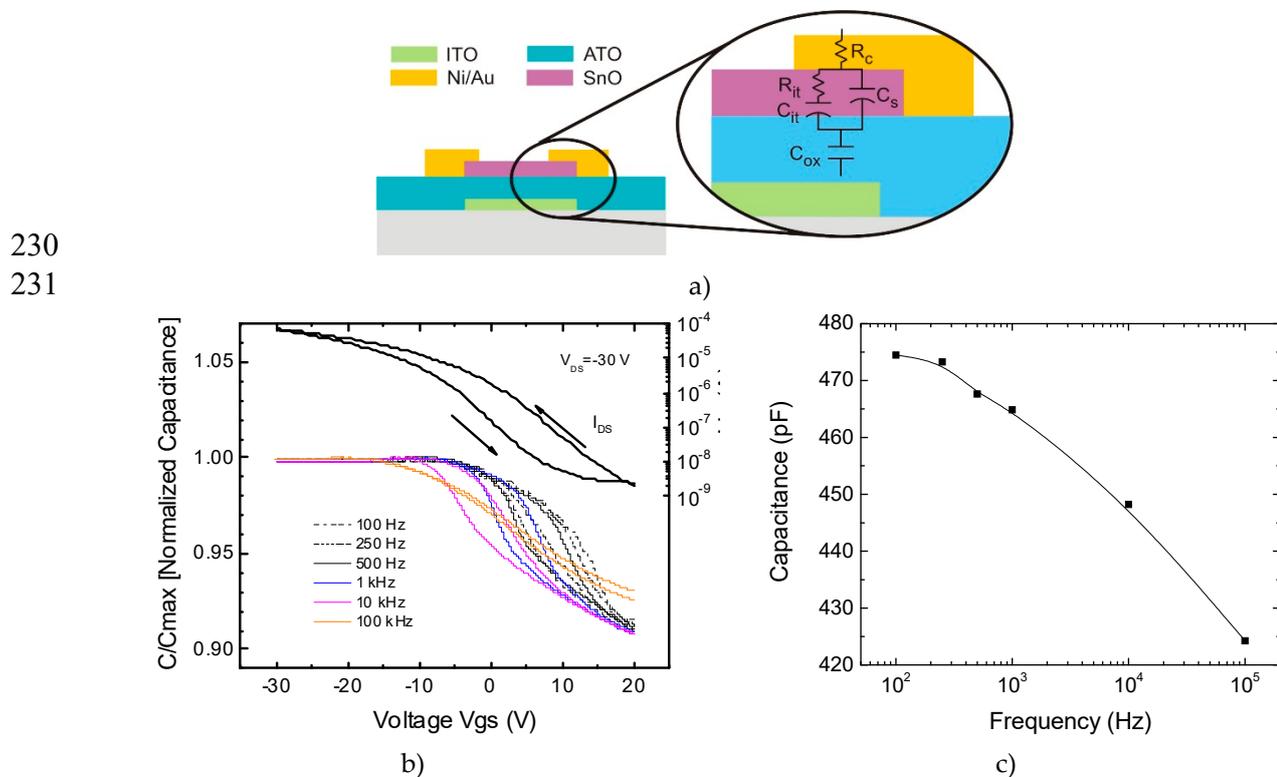
$$209 \quad C_{it} = \frac{\rho(V)}{dV/dx} = \epsilon\epsilon_0 \frac{\rho(V)}{Q} = \frac{q^2 D_{it}}{1 + \omega^2 \tau_{it}^2} \quad (2)$$

210 Where D_{it} is the interface trap density, $\tau_{it} = R_{it} \times C_{it}$ is the trap response time. Finally, we have in series
 211 the insulator geometric capacitance (C_{ox}). As the frequency tends to steady state condition, we have
 212 almost C_{it} in parallel with C_s and the resulting capacitance in series with C_{ox} . Therefore, for not perfect
 213 semiconductors (basically, the amorphous ones) by using a frequency modulation less than the

214 relaxation frequency of the semiconductor ($f_r = \frac{1}{2\pi R_B C_s} = \frac{1}{2\pi \rho_B \epsilon_S \epsilon_0}$, where R_B is the channel bulk

215 resistance), we expect that capacitance data achieved to be influenced by the number and nature of
 216 the interface defects, turning visible more and more defect states as the frequency decreases. The only
 217 limit here is the ratios between the screen length and the real thickness of the semiconductor that may

218 condition the charge penetration depth. That is, the values of the capacitance can be channel thickness
 219 conditioned for devices whose thickness is in the range of few nanometers. On the other hand, at very
 220 high frequencies, C_s dominates and $C_{it} \approx 0$, being now relevant the role of R_{it} in parallel with C_{ox} . In
 221 this case the capacitance-voltage curves can be distorted due to charging effects, leading to a decrease
 222 or even to a not well-defined flat capacitance maximum (C_{max}), as observed in the normalized CV
 223 plots of figure S3b for different frequencies and on the behaviour of C_{max} with the frequency, depicted
 224 in figure S3c. In the same picture it is also plotted the transfer characteristics of the p-type TFT under
 225 analysis (picture above whose vertical scale is on the right side of the figure). Besides the hysteresis
 226 that we associate to the role of interface defects, we notice that at a frequency of about 100 Hz the
 227 capacitance tends to reach a flat behaviour and the hysteresis voltage shift is enhanced, following a
 228 similar trend as the one of the transfer I-V TFT characteristics. We associate this behaviour to interface
 229 localized states that only respond at frequencies below f_r as expected.



232 **Figure 5.** a) Sketch of the cross section of the p-type TFT showing half of the equivalent electrical circuit based
 233 on RC resonators b) Normalized CV plot for several frequencies (below), showing also the IV transfer
 234 characteristic of the TFT (above); c) The Maximum capacitance (C_{max}) achieved as a function of the frequency
 235 used.

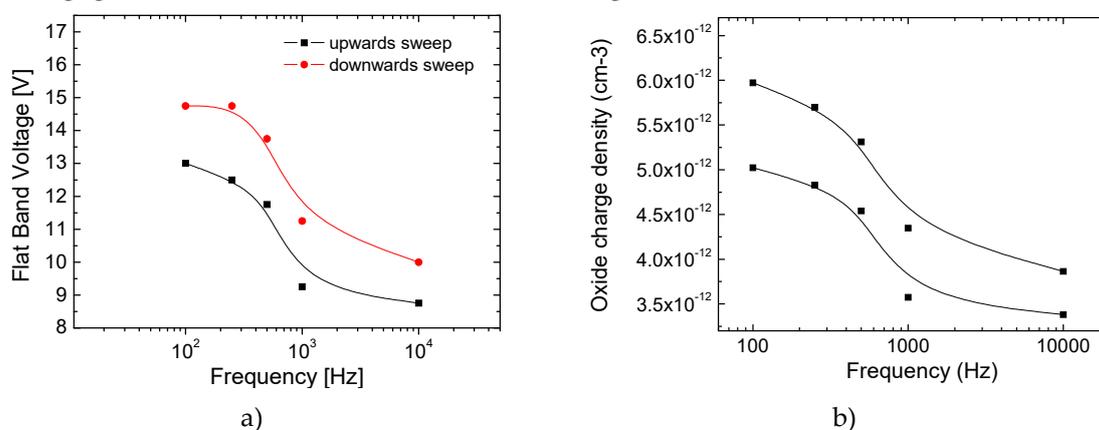
236

237 Apart from that we notice that the minimum capacitance is not fully flat. This behaviour we associate
 238 to the small thickness of the semiconductor (≤ 12 nm) that limits the maximum dimension of the
 239 depletion region we can get. As the possible maximum width of depletion region is 12 nm (the
 240 semiconductor thickness), this means that the minimum capacitance of the system won't be much
 241 lower than the total capacitance.

242

243 From the CV plots depicted in Fig. 5 we could also estimate the flat band voltage shift and the oxide
 244 charge density (proportional to defect density) as a function of the frequencies used, as depicted in

245 Fig. 6. There we indicate the two values determined for each frequency due to the hysteresis, defining
 246 so the window range of variation of such parameters. For this calculation we assumed a $N_a=10^{17}\text{cm}^{-3}$
 247 and a negligible work function difference between the gate electrode and the semiconductor.



248 **Figure 6.** a) Flat band Voltage dependence on the frequency; b) Oxide charge density as a function
 249 of the frequency.

250

251

Both plots show a similar dependence on frequency as expected, leading to an enhancement on the
 252 flat band voltage and on the oxide charge density as the frequency decreases.

253

254 3. Results and Discussion

255 The SnO_x films were prepared at different oxygen partial pressures (O_{pp}) between 0% and 20%,
 256 but the p-type conduction was observed only between 2.8-3.8%. The films deposited with O_{pp} below
 257 2.8% were metallic with poor adhesion to the substrate. Those deposited above 3.8% were highly
 258 resistive, showing n-type conduction after annealing above 200 °C. This is well understood based on
 259 tin oxide's two well-known forms: SnO (p-type conduction) and SnO_2 (n-type conduction). Since a
 260 metallic tin target was used for sputtering, very low O_{pp} was not sufficient to fully oxidize the film. It
 261 is believed that O_{pp} in the range of 2.8-3.8% are suitable to form SnO phase and for $O_{pp} \geq 3.8\%$ favours
 262 SnO_2 formation. Since TFTs were prepared for two O_{pp} , namely at 3.0% and 3.6%, most of the
 263 materials characterizations were performed using the films deposited at these conditions.

264 Figure 1 (a) shows the x-ray diffraction (XRD) pattern of the films (120 nm thickness) using Cu
 265 $K\alpha$ line. It shows that RT films have large portion of metallic tin with very small SnO phase. After
 266 annealing up to 200°C for 30 minutes in air, part of metallic tin seems to be oxidized to SnO phase.
 267 The XRD patterns obtained (in the similar conditions) from SnO powder and metallic Sn are also
 268 shown in figure 1.

269 In order to evaluate the structure, composition of the films and the ratio of SnO and SnO_2 phases
 270 present in the TFT channel layer, ^{119}Sn Mössbauer spectroscopic studies were performed for the first
 271 time in this type of work, whose results are shown in figure 1 (b). Transmission Mössbauer spectra
 272 of bulk metallic Sn, SnO and SnO_2 samples (figure 1b, table 1) were obtained in order to compare the
 273 corresponding hyperfine parameters with those of the phases detected in the films by conversion-
 274 electron ^{119}Sn Mössbauer spectroscopy (CEMS). The spectra of the bulk samples are identical to
 275 those reported in the literature for β -Sn, α -SnO and SnO_2 , respectively.[26,27] The α -SnO spectrum
 276 shows a small contamination of SnO_2 at lower Doppler velocities, which is a common contamination
 277 of α -SnO when exposed to air and is easily detectable by Mössbauer spectroscopy due to the higher
 278 recoilless fraction of Sn^{4+} in SnO_2 as compared to Sn^{2+} in α -SnO.[28,29] The typical asymmetry of the
 279 α -SnO doublet, the high velocity peak having a higher relative area than the low-velocity peak, is
 280 also observed.[27-30]

281

282 The CEMS spectra of the samples could be fitted by three contributions with typical isomer shifts
283 (IS) of Sn⁴⁺, Sn²⁺ and metallic Sn. For all spectra, the estimated IS of the absorption peak due to metallic
284 Sn (table S1) is very similar to that of β -Sn, confirming the presence of this phase in the films as
285 corroborated by XRD. The observed IS, quadrupole splitting (QS) and the line widths of Sn²⁺ in the
286 as-deposited samples are higher than the corresponding parameters for bulk α -SnO. After annealing,
287 the decrease of IS and QS lead to values, which within experimental error, are close to those of
288 crystalline α -SnO. This suggests that the Sn²⁺ oxide present in the as-deposited film is amorphous and
289 after annealing up to 200°C crystalline α -SnO is formed. This is in agreement with XRD data which
290 shows this phase in the annealed samples while in the as-deposited films only β -Sn is detected. The
291 estimated QS and line widths in the amorphous SnO are higher than in crystalline α -SnO denoting a
292 more asymmetric environment and a higher diversity of near neighbour configurations of Sn²⁺ in the
293 amorphous lattice. Furthermore, no asymmetry is observed for the Sn²⁺ oxide doublet in the as
294 deposited sample as expected for an amorphous phase. As crystalline α -SnO is formed, asymmetry
295 of the corresponding doublet becomes evident.

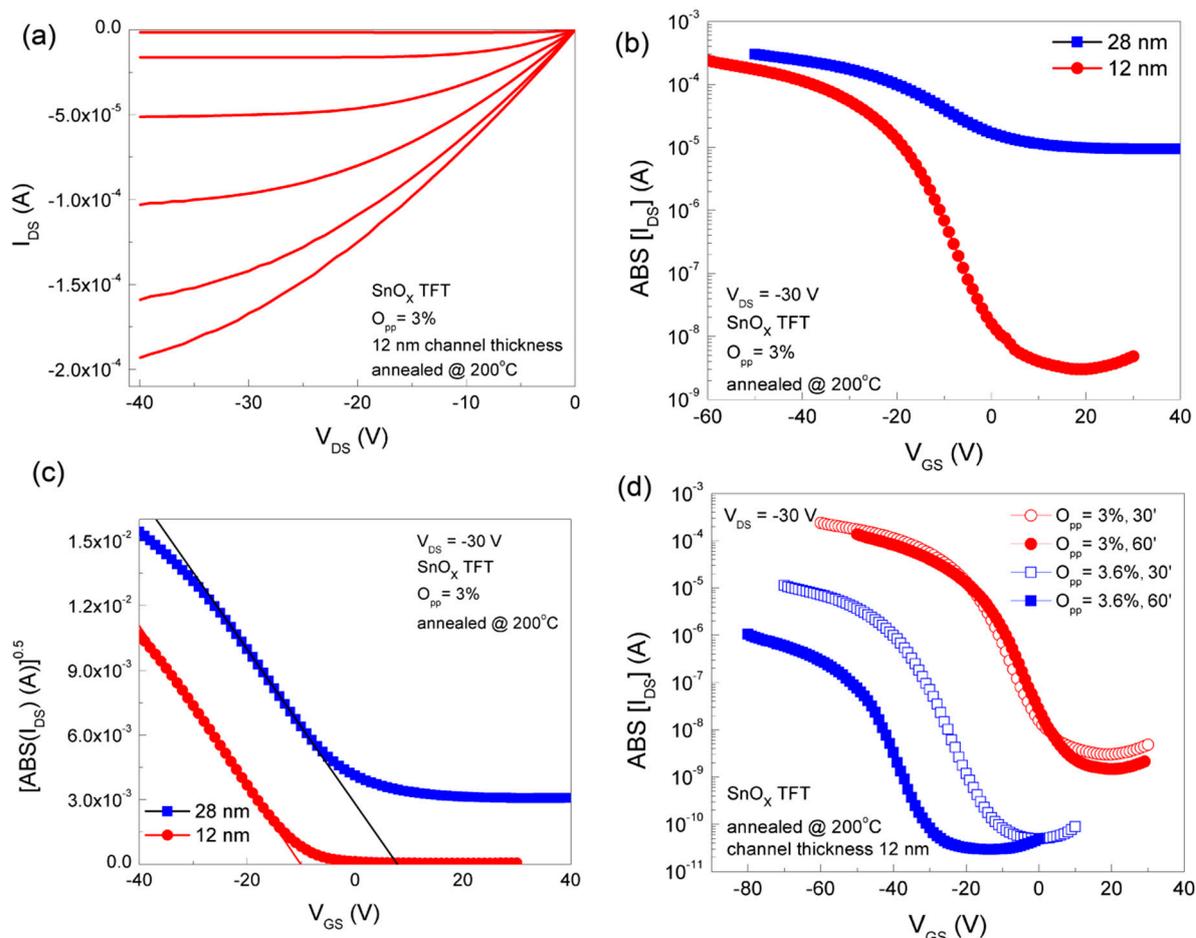
296
297 Mössbauer data, in agreement with XRD data, show that in the as-deposited films most Sn is
298 present as amorphous SnO and metallic β -Sn. Minor amounts of SnO₂, only detected by CEMS, are
299 also present. The IS and QS of this SnO₂ deduced from the spectra are slightly different from those of
300 bulk SnO₂ probably due to poor crystallinity of this oxide in the film. Even though the recoilless
301 factors of β -Sn, SnO and SnO₂ in films are not exactly known, these factors are not expected to be very
302 different for the same species in the different samples. So, the fraction of Sn atoms in each phase
303 should follow the same variation, with annealing or with O_{pp} during deposition, as the relative areas
304 of the corresponding contributions to the spectra. Not surprisingly, the fraction of Sn present as β -Sn
305 is lower in the film deposited at higher O_{pp} (3.6%), than in those deposited at 3.0%. Annealing up to
306 200°C not only crystallizes amorphous SnO to form α -SnO but also oxidizes β -Sn to α -SnO. So, it
307 suggests that the TFT channel layer is mainly composed of SnO phase with a smaller contribution
308 from metallic tin and hence we can represent the channel material composition as SnO_x with 1 < x < 2.

309
310 In order to understand the surface morphology of the channel layer, we performed scanning
311 electron microscopy (SEM) and atomic force microscopy (AFM) of the real channel layer in the TFTs
312 after annealing. The surface microstructures obtained from the films deposited at 3.0% and 3.6% O_{pp}
313 are shown in figure 2. Even though there is no difference in the shape of the grains as evidenced by
314 both techniques, the size of the grains obtained from the films deposited at O_{pp}=3.0% is slightly lower
315 than those deposited at O_{pp}=3.6%. The root mean square roughness (4.6 nm) of the films deposited
316 at O_{pp}=3.0% is slightly higher than that deposited at 3.6% (4.3 nm). Cross-sectional SEM image
317 obtained from the TFT prepared at 3.0% O_{pp} (figure 2f) shows perfect coverage of SnO_x channel layer
318 over the insulator surface with highly compact, uniform and homogeneous thin film without visible
319 defects.

320
321 Bottom gate TFTs were fabricated using aforementioned SnO_x films as channel layers (~28 nm
322 thickness) deposited at 3.0% and 3.6% O_{pp}, which were annealed in air up to 200°C for 30 minutes
323 inside a tubular furnace. Despite the high saturation mobility (4.3 cm²V⁻¹s⁻¹) the on-off ratio was very
324 poor (3×10¹) and TFTs operated in depletion mode, which may be due to a large hole density in the
325 channel layer, limiting the channel modulation.

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327 TFT performance was improved by reducing the channel thickness to ~12 nm. The output
328 characteristics (I_{DS}-V_{DS}) of such TFT (O_{pp}=3.0%) given in figure 7a shows excellent p-channel
329 behaviour. The gate voltage was varied from 0 V to -50 V in -10 V steps. Very small I_{DS} at zero gate
330 voltage indicates an almost closed channel. On increasing the gate voltage to higher negative values,
331 holes accumulated at the channel-insulator interface forms a conduction path between source and
332 drain. These TFT exhibits hard saturation at large V_{DS}, which is similar to pinch off in usual field-
333 effect transistors, revealing the high quality of the devices.

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Figure 7. (a) Output characteristics of SnO_x p-channel TFT. The gate voltage is varied from 0 V to -50 V in -10 V steps. (b) Transfer characteristics of SnO_x p-channel TFT with different channel thickness. (c) Plot of square root of drain current, at $V_{DS} = -30$ V, for evaluating saturation mobility and threshold voltage. (d) Transfer characteristics of SnO_x p-channel TFT (channel thickness 12 nm) for different annealing time.

TFT parameters (see table 2) were extracted from the transfer characteristics ($ABS(I_{DS})-V_{GS}$) of the p-channel TFTs for the different O_{pp} and annealing times used, for devices annealed at 200°C (figures 7 b and 7c). The field effect mobility (μ_{FE}), extracted from the slope of the linear region of the $I_{DS}-V_{GS}$ plot, was $3.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the TFT with 12 nm channel thickness. The saturation mobility (μ_{sat}), extracted from $[ABS(I_{DS})]^{0.5} - V_{GS}$ plot at $V_{DS} = -30$ V, was $4.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (figure 7c). With the improvement in mobility values, threshold voltage shifted from 8.1 V (28 nm thick channel) to -10 V on reducing the channel thickness to 12 nm. Negative threshold voltage indicates the enhancement mode operation of the p-channel TFTs. Moreover, the off current of the p-type TFTs decreased by several orders by reducing channel thickness which results in good switching action by increasing on-off ratio from $\sim 10^2$ to 7×10^4 . Figure 7d shows the transfer characteristics of the devices processed at different O_{pp} and for different annealing times. The data depicted show that the best device performances are achieved when using O_{pp} of about 3%, and annealing times of around 30 minutes are more than enough to process devices with excellent stable mobilities and large on-of current ratios.

357 **Table 2.** Electrical properties of SnO_x p-channel TFTs for different annealing time (channel
358 thickness 12 nm)

Annealing Conditions	Oxygen Partial Pressure [%]	Field Effect Mobility [cm ² V ⁻¹ s ⁻¹]	Saturation Mobility [cm ² V ⁻¹ s ⁻¹]	Threshold Voltage [V]	On-Off ratio
200 °C, 30 min	3.0	3.3	4.6	-10	7×10 ⁴
200 °C, 60 min	3.0	2.2	2.6	-7.2	9×10 ⁴
200 °C, 30 min	3.6	0.16	0.28	-29	2×10 ⁵
200 °C, 60 min	3.6	0.02	0.03	-38.6	3×10 ⁴

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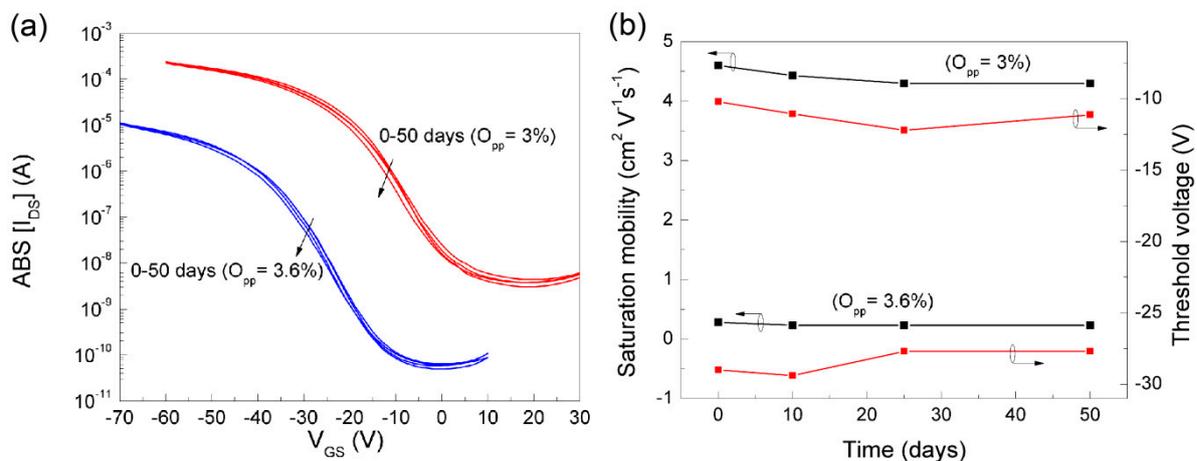
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The p- channel oxide TFTs fabricated at relatively low temperature in the present work show excellent performance, which can be made even on plastic and paper substrates, surpassing the ones known processed also at low process temperatures, compatible with low cost flexible substrates, such as paper. Moreover, the very high on current of these devices makes them ideal for AMOLED driving circuits where a TFT must supply sufficient hole current to the anode of the OLED. In addition, these SnO_x TFTs show excellent electrical stability even without any passivation layer.

Figure 8 shows the transfer curves of TFTs measured at different days after their fabrication. It is clear from the figure that, these TFTs are very stable in operation without significant variations in threshold voltage and mobility.



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372 **Figure 8.** Transfer characteristics of SnO_x p-channel TFT measured at different days after device

373 fabrication (a) and corresponding variations in saturation mobility and threshold voltage (b).

374 4. Conclusions

375 In summary, we have fabricated high performance p-channel oxide TFTs (highly reproducible)
376 on glass substrates using SnO_x channel layer, for which the proper process conditions that lead to the
377 best material phase composition were selected. The SnO phase was identified and quantified by the
378 first time by two independent techniques, XRD and Mossbauer spectroscopy, corroborating the p-
379 type oxide semiconductor behaviour obtained in the TFTs. The TFTs fabricated in this work have
380 shown typical saturation mobility of 4.6 cm²V⁻¹s⁻¹ and on-off ratio above 7×10⁴, which are the highest
381 values achieved so far from any p-channel oxide TFTs. This breakthrough will enable the production

382 of fully transparent CMOS associated with all the main advantages offered by transparent/oxide
383 electronics.
384

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387 spectra analysis J. C. Waerenborgh; validation, E. Fortunato, P. Barquinha, R. Barros, K. J. Saji; formal analysis,
388 R. Barros, P. Barquinha; investigation, R. Barros, P. Barquinha, L. Pereira; K. J. Saji; resources, E. Fortunato, R.
389 Martins; data curation, P. Barquinha, R. Barros; writing—original draft preparation, J. Saji; R. Martins; writing—
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