Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/authorsrights

Author's personal copy

Thin Solid Films 553 (2014) 118–122

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Influence of In and Ga additives onto SnO_2 inkjet-printed semiconductor

A. Vilà [a,*], A. Gomez [a], L. Portilla [a], J.R. Morante [a,b]

[a] Electronics Department–M2E–IN2UB, Universitat de Barcelona, Martí i Franqués 1, E-08028 Barcelona, Spain
[b] Institut per a la Recerca en Energia de Catalunya, Jardins de les Dones de Negre 1, E-08930 Sant Adrià de Besós, Spain

ARTICLE INFO

Available online 28 December 2013

Keywords:
Inkjet
SnO_2
Additives
In
Ga
TFT
Thin-film transistor

ABSTRACT

Tin oxide is a multifunctional semiconductor that offers excellent capabilities in a variety of applications such as solar cells, catalysis and chemical sensors. In this work, tin-based semiconductors have been obtained by means of solution synthesis and inkjet, and compared to similar materials with In and Ga as additives. The effect of different thermal treatments after deposition is also studied. n-Type behavior with saturation mobility >2 cm^2/Vs has been observed, and suitability as a semiconductor for thin-film transistors (TFTs) demonstrated with on/off ratios of more than 8 decades. Both In and In–Ga additives are shown to provide superior environmental stability, as well as significant change from depletion to enhancement operation modes in TFTs.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Thin-film transistors (TFTs) based on a class of materials known as transparent amorphous oxide semiconductors have recently received much attention [1]. A combination of several technologically important features (high electron mobility, high transparency and low temperature process availability) has made these materials attractive for the active layer of TFTs for various applications such as flat-panel displays and e-papers [2]. However, the results point to its critical drawback: bias stability [3]. Under various stability tests (positive gate bias stress and negative illumination bias stress), a wide shift in threshold voltage has been reported, which is detrimental for commercial applications. To address this issue, as well as to optimize electrical performances, several compositions have been explored, but definitive results have not been demonstrated.

Most transparent metal oxide semiconductors are n-type conducting, but enabling different operation modes for the TFTs would open the possibilities for a complete transparent logic [4]. Among those, SnO_2 exhibits a direct band gap of 3.6 eV, high exciton binding energy (130 meV) and high carrier mobility (around 250 cm^2/Vs) [5], which makes it a promising host material for next-generation optoelectronic devices and extensively used for transparent electrodes [6]. Even solution synthesized transparent p-type conducting thin films have been previously reported by doping SnO_2 with In or In–Ga [7–9].

To process these solution-synthesized semiconductors into TFTs, jet printing is a very promising technology because it requires no physical mask, reduces manufacturing costs and time, and enables roll-to-roll processing. Moreover, digital control of ejection and good layer-to-layer registration are provided by photoquality developments. These characteristics are of particular interest in the large area electronics industry when the deposition of a material is required only at specific positions [10].

This work presents a simple and low-cost process to fabricate SnO_2-based TFTs via inkjet-printing. By adapting the fabrication of the reported thin films to the inkjet-printing technique and depositing the films on Si/SiO_2 substrates, n-type TFTs with different operation modes have been obtained.

2. Experimental

Three basic ink solutions were obtained by dissolving metallic chlorides in 2-methoxyethanol. When necessary, some acetic acid was added as a stabilizer to avoid precipitation. By mixing appropriate quantities on these basic inks, final solutions at concentrations of 0.35 M (slightly yellowish color), 0.35/0.07 M (clear yellowish) and 0.35/0.047/0.041 M (dark yellowish) for SnO_2 (TO), In:SnO_2 (TIO) and In–Ga:SnO_2 (TIGO) respectively were obtained. A Sn:In_2O_3 (ITO) ink with the standard ratio 90:10 wt.% for In_2O_3:SnO_2 was also synthesized by the same procedure for comparison. Further stirring at 50 °C for 24 h and aging at room temperature at least for 24 h allowed to rule out any sort of precipitation. Finally the solutions were inserted into respective inkjet cartridges by filtering them through a 0.2 μm polytetrafluoroethylene membrane filter.

Conventional microscope glass slides and heavily boron doped p+ silicon wafers with a 100.0 nm layer of silicon oxide and 50 nm aluminum or gold contacts spaced by 50 μm were used for optical, structural and electrical examinations, respectively. Prior to deposition, the substrates were ultrasonically cleaned in acetone for 30 min, rinsed with de-ionized water, dried with N_2 blowing and finally heated up to 500 °C in air for 30 min to further remove organic residue. A Dimatix 2800 inkjet material printer with piezoelectric cartridges that have a

* Corresponding author.
E-mail address: avila@el.ub.edu (A. Vilà).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.12.044

Author's personal copy

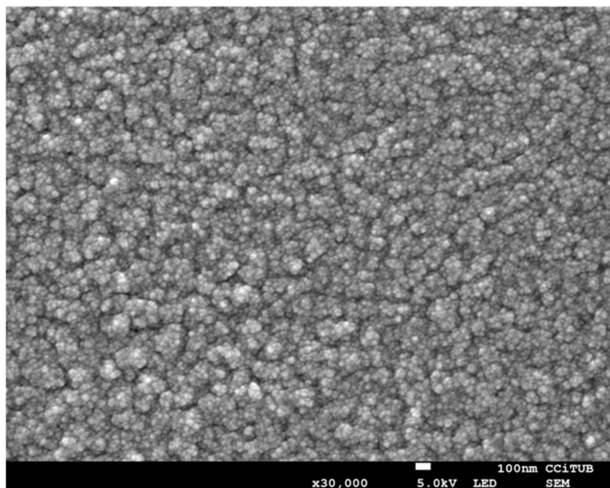


Fig. 1. FE-SEM image of a film obtained after depositing TIGO solution onto a Si wafer and annealing at 500 °C.

1 pL nominal drop volume was used to deposit films and fabricate TFTs. After deposition the films were annealed in air on a hot plate at temperatures up to 500 °C for 2 h.

UV–visible spectroscopy of the deposited films was measured using a Specord 205 from Analytik Jena, scanning electron microscopy (SEM) images were recorded with a FE-SEM Jeol JSM-840 microscope, and X-ray diffraction (XRD) patterns were obtained by means of a PANalytical X'PertPRO MPD Alpha1 powder diffractometer in Bragg–Brentano θ/2θ geometry using the Cu Kα_1 radiation. Electrical characterization was performed using an HP4140b semiconductor parameter analyzer, in a Faraday cage under dark conditions at room temperature.

3. Results and discussion

For a preliminary characterization of the materials, the ink was deposited onto different substrates and annealed at different temperatures between 300 and 500 °C. The morphology of the obtained films was observed by SEM, showing good uniformity with granular appearance up to 30 nm in diameter (Fig. 1). On the other hand, structural characterization by XRD demonstrated the dominance of the SnO_2 cassiterite phase even in the samples with In and Ga (Fig. 2, where Al and Si peaks from the substrate appear at positions of around 38 and 69° and must not be taken into account for the layer characterization). As a first approximation to the grain dimension, direct application of the Scherrer formula to the most significant peaks indicated the presence of grains around 2.3 nm large. This small crystal dimension, together with the good morphological uniformity, provides quite flat layers suitable for subsequent deposits on them for more complex structures.

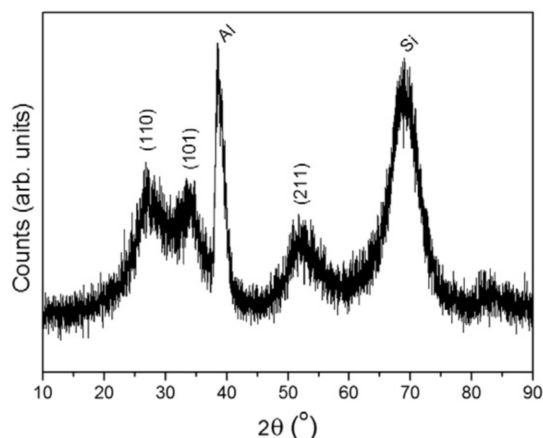


Fig. 2. XRD spectrum of the TIGO layer annealed at 500 °C, showing the main peaks of the cassiterite structure (PDF #21-1250) together with Al and Si peaks due to the substrate.

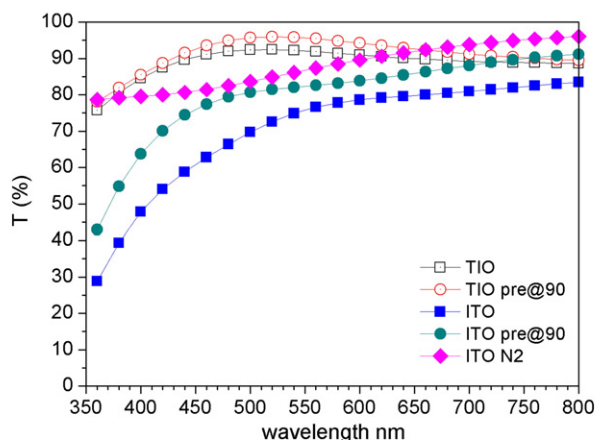


Fig. 3. Optical transmittance of the TIO and ITO layers of 250 nm thick, inkjet-printed on glass substrates with a drop spacing of 50 μm and annealed at 500 °C, without or with pre-annealing at 90 °C (marked with pre@90 °C), and an ITO film annealed at 500 °C in inert N_2 atmosphere.

As an important performance of SnO_2-based semiconductors, transparency of the films deposited by inkjet was measured. UV–visible spectrometry showed a transmittance in the visible range over 85% for all films ~250 nm thick and annealed at 500 °C (Fig. 3). A slightly darker ITO layer annealed under N_2 ambient demonstrates some influence of the annealing atmosphere, as originating less stoichiometric oxides. This result agrees with a different resistivity measured using the Van der Paw method, that gives a 2 orders of magnitude difference (from 0.008 to 0.3 Ω·cm respectively) when annealed under N_2 or air atmospheres.

Top-gate staggered TFTs have been obtained by inkjet-printing the semiconductor over gold electrodes onto Si wafers (Fig. 4), and electrically characterized. As a major issue in these solution-synthesized devices, the repeatability of the electrical characteristics between TFTs is evaluated by characterizing an array of ten of such devices for each annealing temperature. The threshold voltage (V_T) and saturation mobility (μ_{sat}) were derived from a linear fitting of the plot of the square root of I_D versus V_G. Measurements were conducted one day after

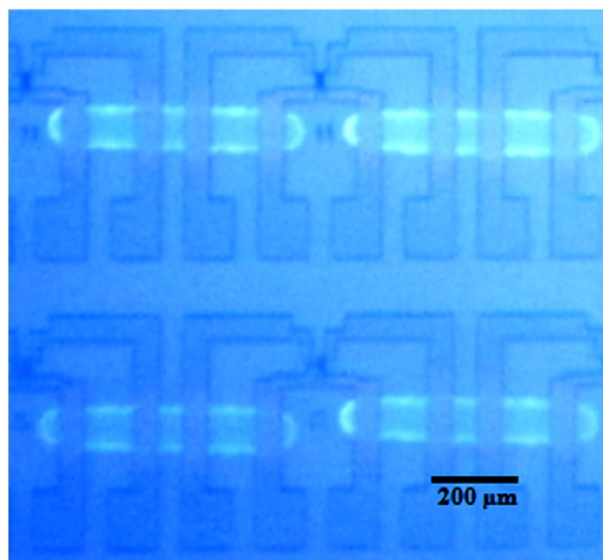


Fig. 4. Optical microscopy image of the inkjet-printed TFTs onto Si/SiO_2 substrate with gold electrodes.

Author's personal copy

Table 1
Basic statistics of SnO_2 TFTs annealed at 300 °C, 400 °C and 500 °C with V_{DS} = 1 V.

Properties	300 °C			400 °C			500 °C		
	Mean	Median	Std. dev.	Mean	Median	Std. dev.	Mean	Median	Std. dev.
Threshold voltage (V)	−30.28	−30.25	2.50	−20.95	−18.98	10.23	−23.50	−25.41	6.57
On–off current ratio (decades)	6.76	6.76	0.50	6.74	6.57	0.58	5.73	5.85	0.63
Subthreshold slope (V/decade)	4.10	3.95	0.78	4.25	4.28	1.19	4.39	4.30	1.10
Mobility (cm^2/Vs)	0.0469	0.0476	0.0033	0.0562	0.0628	0.0137	0.0280	0.0323	0.0122

annealing at V_{DS} = 1 V. The array annealed at 300 °C gives the most consistent device parameters, with a V_T standard deviation of 2.50 V. A reduction in consistency is observed in the array annealed at 400 °C, showing a V_T standard deviation of 10.23 V. However, this large deviation is mainly due to one specific sample, and discarding this sample as defective gives a standard deviation of 5.21 V. All arrays show a slow subthreshold slope with a median of ~4 V/decade and standard deviation of ~1 V/decade. Consistent on–off current ratios of $>10^6$ are present in arrays annealed at 300 °C and 400 °C. Table 1 summarizes the obtained statistical parameters from the characterized TO TFT arrays.

To appreciate the full potential of the devices, output and transfer characteristics were measured in saturation mode with V_{DS} = 20 V. TO devices annealed at 300 °C and 400 °C (Fig. 5) showed promising properties such as mobilities >1 cm^2/Vs and on–off current ratios $>10^8$ which are comparable to those of amorphous silicon TFTs [11]. Annealing at 500 °C resulted prejudicial in the device performance by reducing the mobilities to ~0.5 cm^2/Vs as well as the on–off current ratio to $>10^7$. However, TFTs showed poor stability over time when stored in a transparent container enclosed in air at room temperature. In Fig. 6, a >30 V shift in the threshold voltage of the devices can be

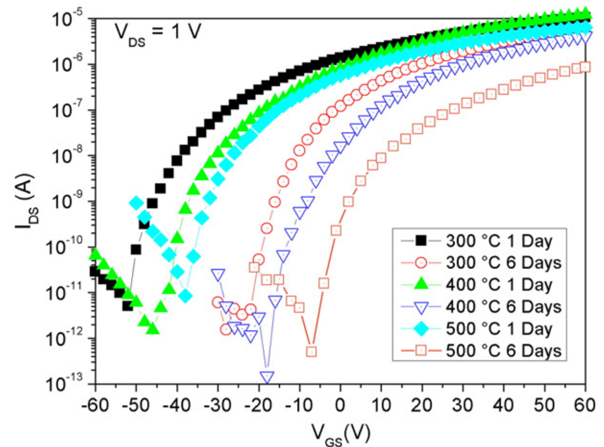
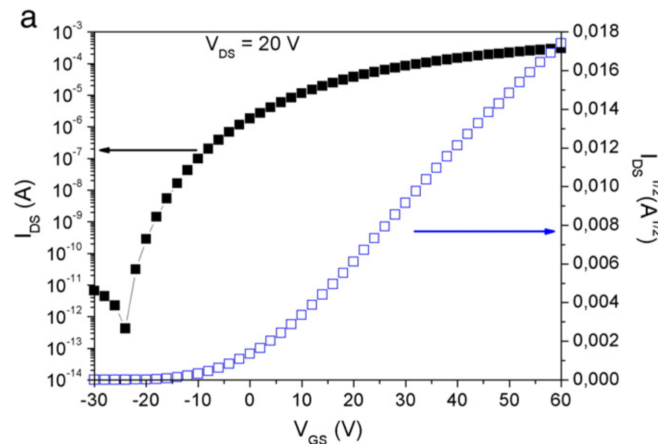


Fig. 6. Stability over time of the SnO_2 TFTs. Clear shifts in the threshold voltages can be observed just 6 days after fabrication.



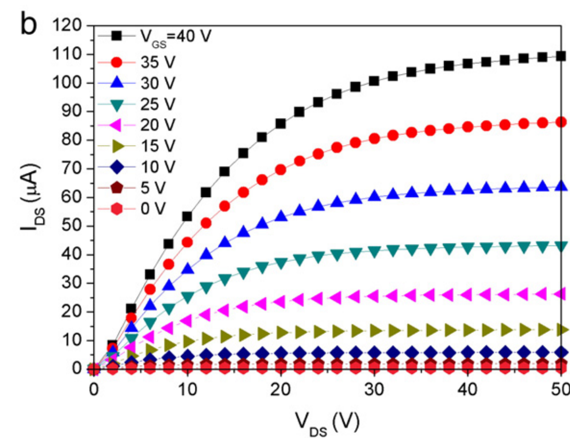
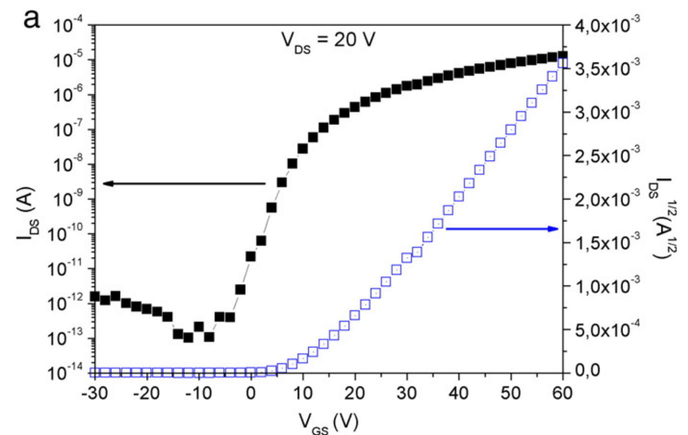


Fig. 5. Transfer and output characteristics of SnO_2 TFTs annealed at 400 °C.



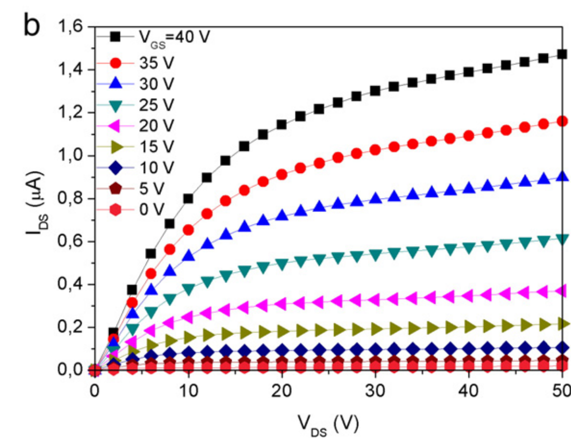


Fig. 7. Transfer and output characteristics of In:SnO_2 TFTs annealed at 400 °C.

Author's personal copy

Table 2
Basic statistics of In:SnO_2 TFTs annealed at 400 °C and 500 °C, measured one day after processing at V_{DS} = 20 V.

Properties	400 °C			500 °C		
	Mean	Median	Std. dev.	Mean	Median	Std. dev.
Threshold voltage (V)	18.84	15.47	7.80	−2.17	−2.28	4.73
On–off current ratio (decades)	7.76	7.90	0.27	7.09	6.97	0.47
Subthreshold slope (V/decade)	3.97	3.76	1.30	4.02	4.02	0.40
Mobility (cm^2/Vs)	0.20	0.18	0.05	0.16	0.17	0.05

observed after six days. Moreover the TFTs annealed at 500 °C change from working in depletion to enhancement mode. This instability in the V_T represents a major difficulty for the implementation of the technique in practical applications, as well as for the electrical characterization of the devices, independently of the consistency of other parameters. It is known that SnO_2 interacts with humidity [12], while the positive shift on the V_T could be attributed to oxygen adsorption [13].

Similarly, an array of ten TIO TFTs was fabricated, annealed at different temperatures and characterized (Fig. 7). The arrays annealed up to 300 °C showed no measurable electrical functionality, and the statistical characteristics of the devices annealed at 400 and 500 °C are shown in Table 2. Reaching a median mobility of only ~0.18 cm^2/Vs, it is shown that indium doping reduced the saturation mobility of the TFTs. Likewise in SnO_2, annealing the films at 500 °C was prejudicial to the performance of TFTs. However, it yielded devices operating in enhancement mode with V_T ranging from −2 to +18 V as well as maintaining an on–off current ratio of ~10^7. The stability study was performed 32 days after processing (Fig. 8), and shows that the V_T of TFTs annealed at 400 °C remained stable while a shift of ~30 V towards the TFTs annealed at 400 °C is present in the TFTs annealed at 500 °C. This could be due to the film being in an unstable state when annealed at 500 °C and overtime reaching a stable state, like the films annealed at 400 °C.

The In–Ga:SnO_2 arrays were similarly conducted with V_{DS} = 20 V. As in the previous case, the array showed no conduction after 300 °C annealing, and deviations of the devices annealed at 400 °C and 500 °C are summarized in Table 3. These devices operated in enhancement mode, reaching a median mobility of 1 cm^2/Vs, with a median on–off current ratio of 10^8. After observation, annealing at 500 °C is prejudicial just as in the previous cases. Fig. 9 shows the transfer and output graphs of specific devices. As referred to stability over time, less variation is observed in Fig. 10 on the V_T of the TIGO devices when compared to the previous channel materials. This stability over forty days can prove valuable for the fabrication of environmentally stable TFTs.

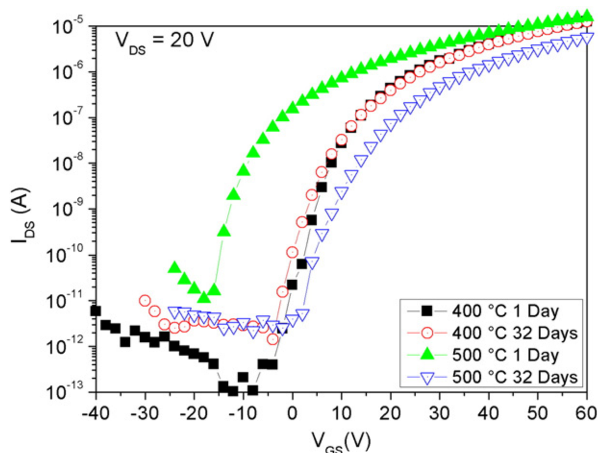


Fig. 8. Stability over time of In:SnO_2 TFTs. A clear shift in the threshold voltage can be observed on the TFT annealed at 500 °C.

According to these results, inkjet-printing of tin oxide with indium seems to produce an instable phase that is difficult to make into devices with controlled characteristics. Although In is thought to allow for high mobility that is driven by the overlap of its large and spherical 5s orbitals that enhance the cation band conduction, instability could be related to high-density oxygen vacancies, which generate high carrier density. Thus, the improvement obtained after incorporating gallium ions can be due to the less carrier generation via oxygen vacancy formation, because Ga ions form stronger chemical bonds with O than In and Sn. This observation supports the multicomponent concept, in an effort to engineer the desired properties by mainly tailoring the cationic species incorporated in the final structures. Therefore, tin oxide with both In and Ga constitutes a promising candidate for having active layers useful to contribute to the so-called post-silicon electronic era, by playing an important role in transparent electronics.

4. Conclusions

Demonstration of the inkjet technique for the fabrication of SnO_2-based TFTs was evaluated. Transistors with similar performances to those of amorphous silicon TFTs were fabricated and characterized.

SnO_2 depletion mode n-type TFTs, with >1 cm^2/Vs saturation mobilities and 10^8 on–off current ratios, were fabricated by annealing the deposited films at 300 °C. The properties of the TFTs were further improved to saturation mobilities >2 cm^2/Vs by annealing at 400 °C. However, annealing the films at 500 °C was prejudicial to the TFT performance.

By doping SnO_2 with In or In–Ga, n-type enhancement mode TFTs were fabricated. Indium-doped TFTs showed saturation mobilities of ~0.20 cm^2/Vs, while In–Ga-doped TFTs had mobilities of ~1 cm^2/Vs. In both cases, annealing the films at 500 °C deteriorated the TFT performance. TFTs annealed at 300 °C showed no measurable electrical properties.

In–Ga co-doping of SnO_2 was observed to have desirable properties such as >1 cm^2/Vs saturation mobilities, operation in enhancement mode as well as superior environmental stability compared to that of undoped SnO_2. In all cases it is observed that a 400 °C anneal is the optimal temperature.

Table 3
Basic statistics of In–Ga:SnO_2 TFTs annealed at 400 °C and 500 °C, measured one day after processing at V_{DS} = 20 V.

Properties	400 °C			500 °C		
	Mean	Median	Std. dev.	Mean	Median	Std. dev.
Threshold voltage (V)	12.73	13.93	2.83	19.36	20.43	3.87
On–off current ratio (decades)	8.64	8.64	0.88	8.38	8.19	0.32
Subthreshold slope (V/decade)	4.19	4.43	1.43	4.01	4.14	0.40
Mobility (cm^2/Vs)	0.95	1.01	0.14	0.85	0.51	0.26

Author's personal copy

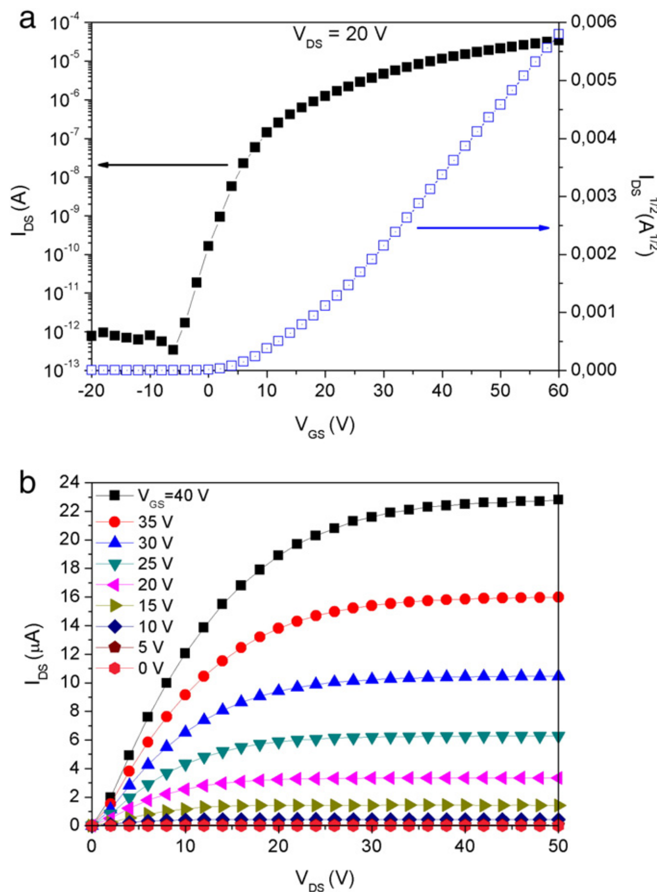


Fig. 9. Transfer and output characteristics of In–Ga:SnO_2 TFTs annealed at 400 °C.

Therefore, tin oxide with both In and Ga constitutes a promising candidate for having active layers useful to contribute to the transparent electronics era.

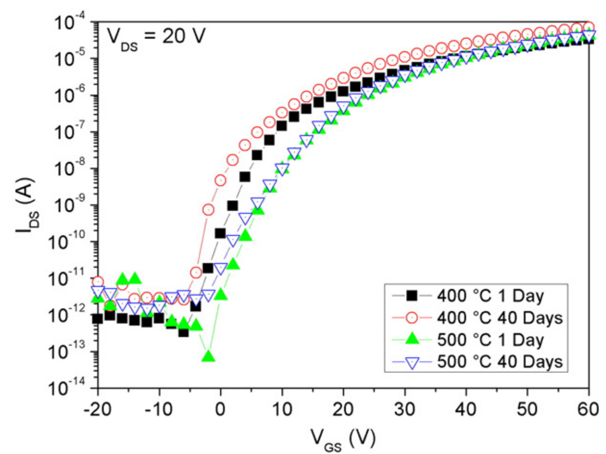


Fig. 10. Stability over time of In–Ga:SnO_2 TFTs. In this case the V_T is visibly more stable.

References

[1] H. Hosono, J. Non-Cryst. Solids 352 (2006) 851.
[2] T. Kamiya, H. Hosono, NPG Asia Mater. 2 (2010) 15.
[3] M. Fakhri, P. Görrn, T. Weimann, P. Hinze, T. Riedl, Appl. Phys. Lett. 99 (2011) 123503.
[4] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, Nature 389 (1997) 939.
[5] M. Batzill, U. Diebold, Prog. Surf. Sci. 79 (2005) 47.
[6] A.K. Singh, A. Janotti, M. Scheffer, C.G. van de Walle, Phys. Rev. Lett. 101 (2008) 055502.
[7] Z. Ji, Z. He, Y. Song, K. Liu, Z. Ye, J. Cryst. Growth 259 (2003) 282.
[8] Q. Mao, Z. Ji, L. Zhao, Phys. Status Solidi B 247 (2010) 299.
[9] D. Juan, J. Zhen-Guo, Acta Phys. Sin. 56 (2007) 2388.
[10] R.A. Street, W.S. Wong, S.E. Ready, M.L. Chabinyc, A.C. Arias, S. Limb, A. Salleo, R. Lujan, Mater. Today 9 (4) (2006) 32.
[11] S. Seo, C.G. Choi, Y.H. Hwang, B. Bae, J. Phys. D. Appl. Phys. 42 (2009) 5.
[12] F. Hernandez-Ramirez, S. Barth, A. Tarancon, O. Casals, E. Pellicer, J. Rodriguez, A. Romano-Rodriguez, J.R. Morante, S. Mathur, Nanotechnology 18 (2007) 424016.
[13] P.K. Nayak, J.V. Pinto, G. Gonçalves, R. Martins, E. Fortunato, J. Disp. Technol. 7 (2011) 640.