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Precursor- route ZnO films from mixed casting solvent for high performance aqueous electrolyte- gated transistors

Talal M. Althagafi[1*], Saud A. Algarni[1], Abdullah Al Naim[2], Javed Mazher[2], Martin Grell[1]

[1] *Physics&Astronomy, University of Sheffield, Hicks Building, Hounsfield Rd, Sheffield S3 7RH, UK*
[2] *Physics department, King Faisal University, Al-Ahsa, Saudi Arabia.*

Abstract

We significantly improved the performance of precursor- route semiconducting zinc oxide (ZnO) films in electrolyte- gated thin film transistors (TFTs). We find that the organic precursor to ZnO, Zinc Acetate (ZnAc), dissolves more readily in a 1:1 mix of ethanol (EtOH) and acetone than in either pure EtOH, pure acetone, or pure isopropanol. XPS and SEM characterisation show improved morphology of ZnO films converted from mixed solvent cast ZnAc precursor compared to EtOH cast precursor. When gated with a biocompatible electrolyte, phosphate buffered saline (PBS), ZnO thin film transistors (TFTs) derived from mixed solvent cast ZnAc give 4 times larger field effect current than similar films derived from ZnAc cast from pure EtOH. Sheet resistance at $V_G = V_D = 1V$ is 30 kΩ/▢, lower than for any organic TFT, and lower than for any electrolyte- gated ZnO TFT reported to date.

Key Words: Thin film transistor, Zinc oxide, Zinc acetate, precursor, PBS, Biosensor

Introduction

Horowitz *et al.*[1] discovered that semiconducting organic films can be gated by field effect with very low threshold using deionised (DI) water as gate medium. Gating is due to the high capacitance electric double layer (EDL) that develops at the water/semiconductor interface even for DI water as 'electrolyte'. This discovery has triggered an interest in developing such thin film transistors (TFTs) into a novel type of biosensor, wherein an aqueous sample under test is an active part of the transducer. TFT devices gated by a biologically realistic aqueous electrolyte, phosphate- buffered saline (PBS) solution, were sensitised (e.g. by enzymes) either at the semiconductor/water interface [2, 3], or at the gate electrode [4]. The latter is easier and more versatile as it requires no chemical modification of the semiconductor, which can lead to loss of performance. Compared to DI water, more concentrated electrolyte gate media like PBS favourably display higher capacitance up to somewhat higher frequencies. However, organic semiconductors often suffer stability problems under concentrated electrolytes, and may become doped by penetrating ions, *i.e.* electrochemical transistor behaviour competes with field effect gating

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[a] *Author to whom correspondence should be addressed.*
Electronic mail: tmalthagafi1@sheffield.ac.uk

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[5], which makes the transducer's output difficult to interpret. This can largely be avoided when an inorganic semiconducting film is used instead. Ong *et al.* [6] had shown that the II-VI semiconductor Zinc oxide (ZnO) can be prepared by casting a soluble precursor, Zinc acetate (ZnAc, $Zn(O_2CCH_3)_2$), with subsequent thermal conversion into ZnO under atmosphere. Ong *et al.* reported n- type field effect transistors using such films, with electron mobility $\mu \sim 5\ cm^2/Vs$ and good on/off ratio. However, their conventional 'dry' dielectric gate medium with low capacitance lead to high operational voltages. Al Naim *et al.* have since shown that precursor route ZnO can also be gated with aqueous media [7]. Electrolyte- gated precursor- route ZnO transistors may show similar mobility as reported by Ong et al. for dry- gated devices at much reduced threshold due to the high EDL capacitance, thus delivering a solution-processed electrolyte gated TFTs that do not suffer from electrochemical doping. However, so far, mobility in precursor- route ZnO still falls short of the performance of ZnO when deposited by methods such as magnetron sputtering or pulsed laser deposition [8-11].

Here, we report on the preparation of precursor- route ZnO films that perform significantly better in electrolyte- gated TFTs than any previously reported precursor- route ZnO films. The key to improved performance is the use of a mixed solvent for the ZnAc precursor.

Experimental

We dissolved 0.1M ZnAc in EtOH, isopropanol, Acetone, or 1:1 EtOH/Acetone, by continuous stirring at elevated temperature for prolonged periods. TFT contact substrates with geometry factor width/length (W/L) = 1 mm/30 µm = 33.3 were prepared using a shadow mask on synthetic quartz substrates sourced from Ossila and thermal evaporation of Au contacts with an underlying Cr adhesion layer under high vacuum. ZnAc solution was casted onto contact substrates at 2000 rpm for 50s and thermally converted into ZnO under atmosphere on a hotplate at 450^o C for 12 minutes. ZnAc coating and conversion was repeated three times. Resulting ZnO films were characterised by XPS and SEM. XPS was calibrated by the graphitic carbon C 1s peak [12]. Graphitic carbon is adsorbed on the surface during exposure of the sample to ambient atmosphere, and is commonly used for ZnO XPS calibration[13]. ZnO surfaces were imaged by SEM at 15 kV. For transistor manufacture, we applied a droplet of the aqueous electrolyte 0.01M phosphate buffered

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saline (pH =7.4) (PBS, Aldrich catalogue No P4417) as a gate medium. The gate medium was electrically addressed by an L- shaped Au gate needle that was lowered to very close proximity (200 µm adjusted by a glass cover slip used as spacer) using a probe head. The ‘foot’ of the L was oriented along the width W of the transistor channel and overlapped the channel completely. Source and drain (S/D) were contacted by Tungsten (W) needles that readily pierced through the ZnO film that had formed on the evaporated Au contacts. We recorded TFT output and transfer characteristics with two Keithley source/measure units configured for TFT characterisation.

Results and discussion

Previous reports [7, 14] on water- gated ZnO transistors from ZnAc precursor used ethanol (EtOH) as the casting solvent for the precursor. However, we observe that pure EtOH is not a good solvent for ZnAc. To completely dissolve 0.1 M ZnAc in EtOH, we need to heat and stir the mixture for prolonged periods (5 hours), and on storage at ambient temperature, ZnAc precipitates within an hour. To re- dissolve, we need to repeat heating and stirring for 30 minutes before processing. We find similarly poor solubility of ZnAc in pure acetone, and 2-propanol. Ong *et al.*[6] instead used methoxyethanol to dissolve ZnAc but they do not clearly report solvent quality. However, we here observe that a 1:1 mix of EtOH and acetone is a far better solvent for ZnAc than either EtOH, 2-propanol, or acetone, alone. Heating and stirring is still required to dissolve ZnAc in mixed solvent, but only a small amount of precipitate forms even after several days of storage, which quickly re- dissolves on gentle heating.

We cast films of ZnAc dissolved in mixed EtOH:Acetone (1:1) solvent, and similar films from pure EtOH for comparison, onto contact substrates, thermally converted into ZnO. We first characterised both resulting ZnO film surfaces by X-ray photoelectron spectroscopy (XPS). Fig.1 shows the detected peaks for Zn 2p orbitals for precursor- route ZnO films cast from EtOH (top) and mixed solvent (bottom), Fig. 2 shows O 1s XPS spectra for precursor-route ZnO films cast from EtOH (top) and mixed solvent (bottom). For Zn 2p orbitals, we find the usual split into Zn $2p_{1/2}$ Zn $2p_{3/2}$ orbitals [15-19]. The (non- Gaussian) O 1s peaks in Fig. 2 have been resolved into a superposition of two overlapping Gaussians. The lower energy Gaussian has been attributed to O^{2-} ions bound into the regular wurtzite structure of ZnO

(Zn-O-Zn), the higher energy Gaussian to oxygen in metal-OH (M-OH) surface groups [15]. All XPS peak positions, and their widths (FWHM), are summarised in table 1.

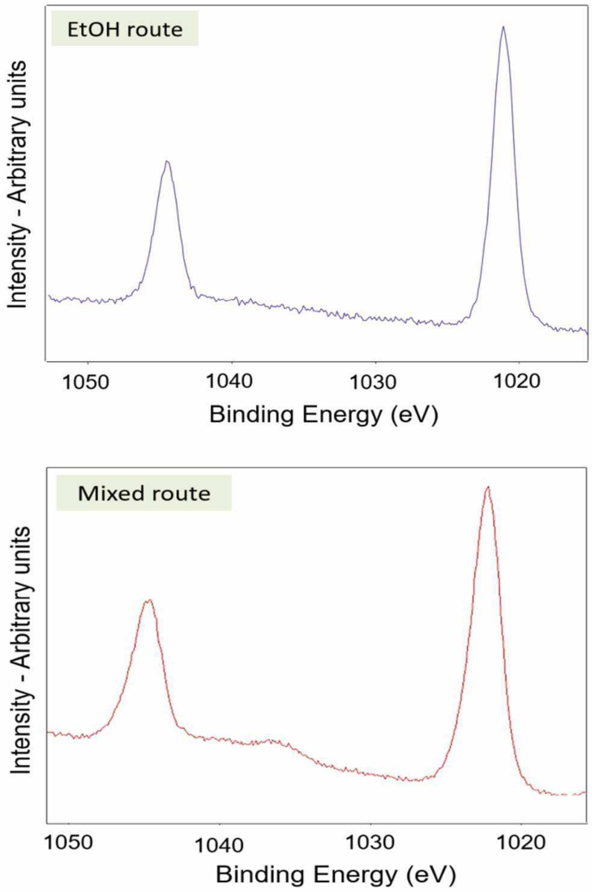

Fig. 1: XPS spectra of Zn 2p orbitals in ZnO films resulting from the thermal conversion of precursor, ZnAc, cast from different solvents. Top: ZnAc cast from EtOH, bottom: ZnAc cast from mixed solvent, EtOH:Acetone 1:1.

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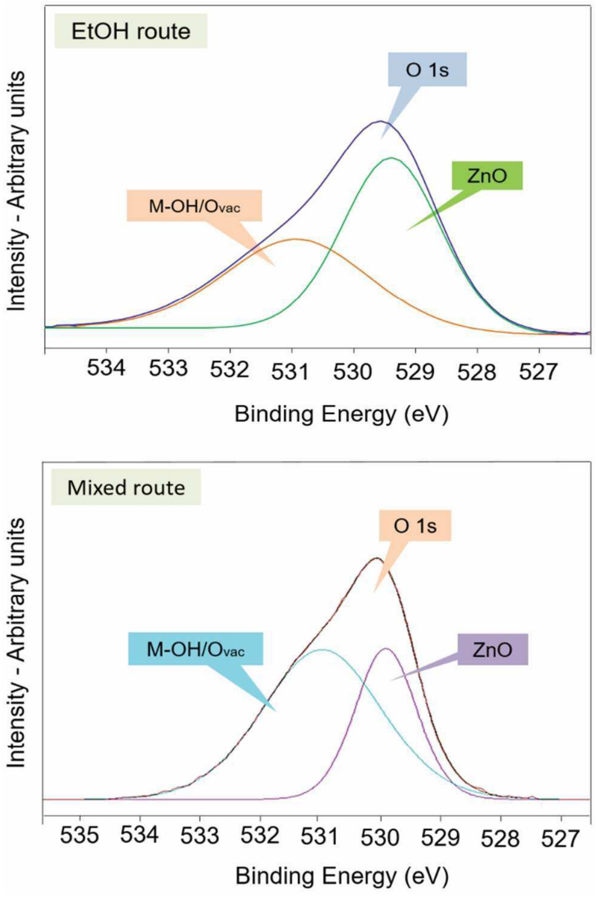

Fig. 2: XPS spectra of O1 s for ZnO films resulting from the thermal conversion of precursor, ZnAc, cast from different solvents. **Top:** ZnAc cast from EtOH, **bottom:** ZnAc cast from mixed solvent, EtOH:Acetone 1:1.

Table 1

	EtOH route		**Mixed route**	
	Position (eV)	**FWHM (eV)**	**Position (eV)**	**FWHM (eV)**
$Zn_{1/2}$	1021	1.75	1023	2.5
$Zn_{3/2}$	1045	2	1047	2.5
O 1s	529.6	2.8	530	2.2
Zn-O	529.4	1.9	529.9	1.07
M-OH	531.2	2.8	531	2.2

Table 1: Summary of observed XPS peak positions, and their FWHM, for ZnO films via ZnAc precursor route from different solvents. The (non- Gaussian) O 1s peaks have been resolved into a superposition of overlapping Gaussian Zn-O-Zn, and Metal-OH, O 1s peaks, as shown in Fig. 2.

All observed XPS peaks are in the range of what was found in previous XPS studies on ZnO

[14-19]. Overall, XPS analysis shows the chemical identity of our films as wurtzite ZnO, with Zn-OH surface groups, thus confirming successful conversion of the precursor for both casting solvents, but reveals no differences at the level of atomic binding between the different casting solvents.

However, SEM surface imaging shows morphological differences on the ~ 10nm size scale between ZnO films prepared using different solvents. In Fig. 3, we show images of ZnO surfaces resulting from the conversion of EtOH cast precursor (top), and mixed solvent cast precursor (bottom).

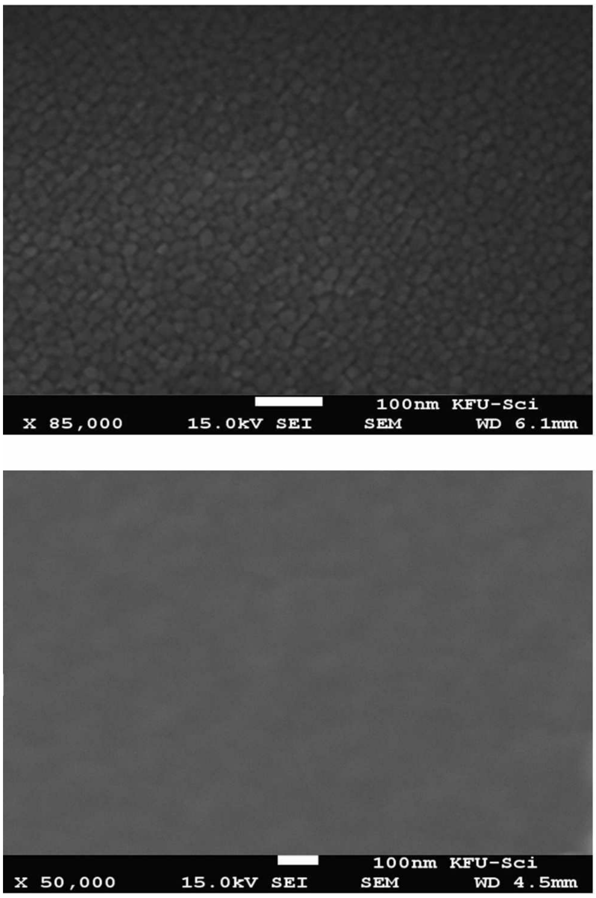

Fig. 3: SEM images of ZnO films resulting from the thermal conversion of precursor, ZnAc, cast from different solvents. **Top**: ZnAc cast from EtOH, **bottom**: ZnAc cast from mixed solvent, EtOH:Acetone 1:1.

Films from EtOH- cast precursor show recognisable small grains in the order 7 to 15 nm. However, the image of mixed solvent cast precursor films shows little contrast, grains are barely recognisable, and larger (17-20nm). The absence of clearly visible morphological features on the mixed solvent cast ZnO surface indicates a very homogeneous film.

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We believe that in the better quality mixed solvent, the precursor ZnAc forms a true solution, while in poor solvent, e.g. pure EtOH, precursor molecules will cluster into small aggregates rather than fully dissolve. On casting from such poor solution, aggregates will transfer to the substrate, priming the formation of ZnO grains with defined boundaries on thermal conversion. Grains are larger, and less clearly separated, when precursor is cast from a better solvent.

As grain boundaries often limit charge carrier mobility, the homogeneous, featureless morphology of mixed solvent cast ZnO suggests it may perform better when used as semiconductor in a thin film transistor (TFT). We therefore tested both types of ZnO films in TFTs gated by phosphate- buffered saline (PBS) as an aqueous gate medium. PBS is often used to simulate bodily fluids [2-4] and is thus a realistic medium for biosensor applications.

The surface of ZnO is hydrophilic, and PBS forms a flat ‘puddle’ with small contact angle. Resulting transistor output- and transfer characteristics are shown in Figs 4 and 5.

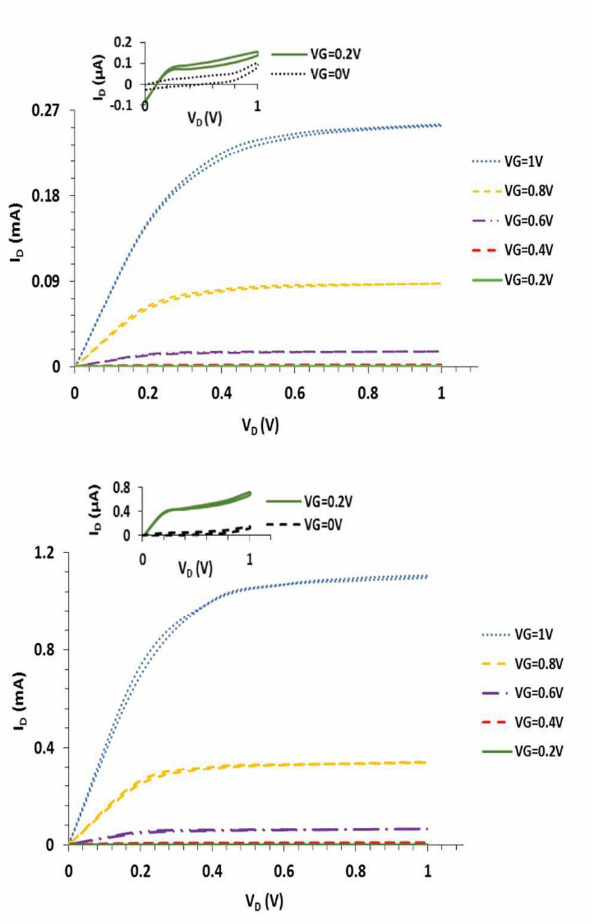

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Fig. 4: Output characteristics for Zn acetate precursor route ZnO TFTs gated by PBS electrolyte. **Top**: Precursor cast from pure EtOH. **Bottom**: Precursor cast from mixed EtOH/acetone (1:1). Insets to output characteristics show magnified characteristics at low gate voltages.

Output characteristics show that TFTs turn on for positive gate voltages, as expected for electron- transporting transistors. Electron- rather than hole type transistor action is well established for ZnO [7, 8, 14, 20], but is in contrast to organic TFTs gated with aqueous electrolytes which to date all were hole transporters. Output characteristics are near ideal, with little hysteresis, a truly linear 'linear' regime, and drain current saturation at high drain voltages. Magnified low gate voltage output characteristics (insets to Fig. 4) clearly show TFTs are 'off' at V_G = 0 V, but 'on' (above threshold) at V_G = +0.2 V. Threshold voltage is therefore between 0 and 0.2 V, similar as in previous reports on PBS- gated ZnO [14]. Low threshold is characteristic of all electrolyte- gated TFTs, due to the high specific capacitance of electrolyte gate media. In parallel, we monitored gate leakage currents; gate leakage was always small (< 5 µA at V_D = V_G = 1V for EtOH route, 0.2 µA for mixed solvent route) compared to drain current.

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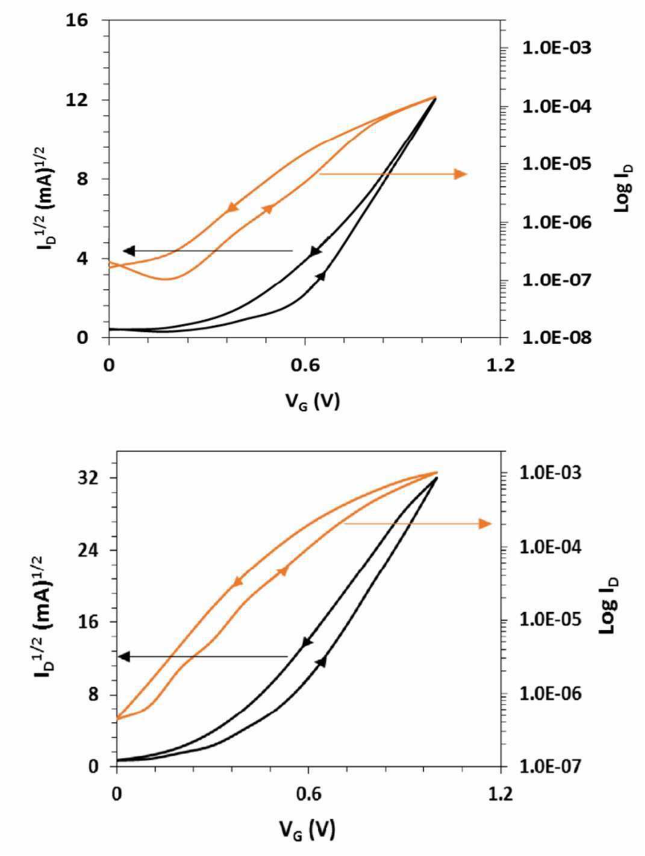

Fig. 5: Saturated transfer characteristics for Zn acetate precursor route ZnO TFTs gated by PBS electrolyte. **Top:** Precursor cast from pure EtOH. **Bottom**: Precursor cast from mixed EtOH:acetone (1:1). Transfer characteristics are shown in two different representations (on $I_D^{1/2}$ (black) and $\log I_D$ (orange) scale), as it is customary in the TFT literature.

The saturated transfer characteristics, Fig. 5, both show some hysteresis, which is also sometimes observed for ZnO TFTs under ionic liquid (IL) gate media [21]. Fig. 5, top in particular also shows a rather curved $I^{½}_{D,sat}$ *vs*. V_G plots, approaching linearity (as predicted by generic TFT theory) only at high gate voltages (above 0.8V). This may indicate increasing electrolyte capacitance or increasing carrier mobility, at high gate voltages/carrier densities in the channel. Threshold voltage is therefore better estimated from low gate voltage output characteristics, as above. Nevertheless, transfer characteristics clearly show field effect transistor action, i.e. off → on switching of drain current with gate voltage, with on/off ratios [I_D(V_G= 1V) / I_D(V_G= 0V)] 710 for EtOH route, and 2340 for mixed solvent route, which are within the range 10^2 … 10^4 reported previously for ZnO TFTs under various electrolyte gate media [14, 21].

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While characteristics are qualitatively similar between the different casting solvents, there is a remarkable quantitative difference. For our EtOH- cast TFT, saturated drain current at $V_G = V_D = 1V$ is 0.26 mA, corresponding to a sheet resistance $R_{\square}$ (1V) = W/L [V_D = 1 Volt / $I_{D,sat}$ = 0.26 mA] = 128 kΩ/▢. However, the saturated drain current for the ZnO TFT cast from ZnAc in mixed solvent is significantly higher, 1.1 mA, corresponding to a sheet resistance of only $R_{\square}$ (1V) = 30 kΩ/▢. We note that the calculation of a carrier mobility from standard transistor equations is difficult in the case of electrolyte- gating due to uncertainty on the precise figure of specific capacitance C_i [1, 7]. Instead we report the figure- of-merit μC_i that can be extracted directly from measured characteristics without assumptions on C_i [22]. When evaluating saturated transfer characteristics at high gate voltage (V_G = 0.8V … 1V), we find μC_i = 33 μAV^{-2} for EtOH- cast films, and 117 μAV^{-2} for films cast from mixed solvent, almost 5 times larger. If we assume a specific capacitance of C_i = 3 μF/cm^2 [1], this corresponds to an electron mobility of 11 cm^{2}V^{-1}s^{-1} for EtOH- cast ZnAc- precursor ZnO, and 39 cm^{2}V^{-1}s^{-1} for mixed- solvent cast ZnAc- precursor ZnO. Mobilities evaluated from electrolyte- gated transistors should be treated with caution, but the near fivefold improvement remains true regardless, as Ci will be equal in both cases.

Table 1 puts our work into context with literature results on directly comparable devices, i.e. electrolyte- gated TFTs using solution- processed ZnO as semiconductor.

Table 2

Reference	Preparation	Gate medium	$R_{\square}$ [kΩ/▢]	μC_i [μAV^{-2}]
Park *et al.[23]*	Li- doped ZnO cast from ammonia solution	Ionic liquid	110 @ 1V	8.3
Singh *et al.[14]*	ZnAc precursor cast from EtOH	PBS	5000 @ 0.5V	1.4
Singh *et al.[14]*	ZnAc precursor cast from EtOH	DI water	77000 @ 0.5V	0.23
Al Naim *et al.[7]*	ZnAc precursor cast from EtOH	DI water	180 @ 0.8V	26
Thiemann *et al.[21]*	ZnAc precursor sprayed from MetOH	Ionic liquid	50 @ 1V	48
This work	ZnAc precursor cast from EtOH	PBS	128 @1V	33

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This work	ZnAc precursor cast from EtOH : Acetone	PBS	30 @1V	117

Table 2: Performance characteristics of electrolyte- gated TFTs with solution- processed ZnO.

Data in table 1 confirm that ZnO films derived from mixed solvent route processed ZnAc precursor lead to performance in electrolyte- gated TFTs superior to any other solution-processed ZnO films. Sheet resistance is lower, and figure- of- merit higher, for mixed solvent cast precursor even compared to work using higher capacitance ionic liquid (rather than aqueous) gate medium[21], or casting dissolved (rather than precursor- route) ZnO [23].

As a further comparison, mixed solvent route ZnO also compares favourably to electrolyte- gated organic TFTs, even those using state- of- the art hole transporting polymer, Poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT). The best performing electrolyte- gated PBTTT TFTs [24] display a sheet resistance $R_{\square}(1V) = 640$ kΩ/□ for water-gated and 102 kΩ/□ for ionic liquid gated PBTTT, which is still higher than the sheet resistance we find for mixed solvent cast precursor ZnO.

The low sheet resistance and high estimated mobility we report here has so far only been matched or surpassed for conventional ‘dry’ processed ZnO TFTs. Fortunato *et al.*[8] and Zhang *et al.*[9] deposited ZnO by rf magnetron sputtering and reported carrier mobility of 70 cm^2/Vs when gated by silicon oxynitride (SiOxNy) dielectric [8], and 60 cm^2/Vs using Ta_2O_5 gate insulator [9]. Both mobilities are measured at rather high voltages though (Fortunato *et al.* : 10 V; Zhang *et al.* : 5V); Brox-Nilsen *et al.* [10] report 50 cm^2/Vs again on Ta_2O_5 at slightly lower voltage (4 V). The highest mobility to date of 110 cm^2/Vs for ZnO TFTs is reported by Bayraktaroglu *et al.* [11] who grew ZnO by pulsed laser deposition onto a substrate held at 350^{o}C. However, these direct deposition methods do not benefit from the ease of processing afforded by soluble precursor routes, and sheet resistance even in the device of Bayraktaroglu *et al.* was $R_{\square}(15V) = 25$ kΩ/□. None of Fortunato et al, Zhang *et al.*, Brox-Nilsen *et al.*, and Bayraktaroglu *et al.* report gating with an aqueous electrolyte, which would be essential for biosensor applications.

Conclusions

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It is well established that the performance of organic semiconductor devices critically depend on the choice of processing solvent [25]. Here, we report a similar observation on inorganic semiconductor devices prepared via a solution- processed precursor. We find that Zinc acetate (ZnAc), a precursor to the II-VI semiconductor zinc oxide (ZnO), dissolves significantly better in a 1:1 mix of ethanol and acetone than in either pure ethanol, acetone, or isopropanol. ZnAc cast from a better solvent will give aggregate- free precursor films that convert into more homogeneous ZnO films, as characterised by XPS and SEM. When gated by the aqueous electrolyte PBS, transistor sheet current and other performance characteristics are superior to previously reported precursor- route ZnO TFTs, and approaches performance of ZnO transistors deposited by conventional 'dry', precursor- free methods such as magnetron sputtering or laser ablation, and gated by dry dielectrics.

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