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A new precursor route to semiconducting Zinc Oxide

Talal M. Althagafi*, Abbad F. Al Baroot, and Martin Grell.

Abstract: We demonstrate a new precursor route towards solution- processed films of the II-VI semiconductor Zinc oxide (ZnO). Spray pyrolysis of aqueous solutions of the Zinc salt Zinc chloride (ZnCl_2) onto a substrate heated to at least 250°C gives films that are insoluble in water, display an absorption edge at 365 nm , and when electrically gated display thin film transistor characteristics similar to ZnO films derived via the established Zinc Acetate (ZnAc) precursor route; we therefore identify it as ZnO. Control experiments attempting spray pyrolysis of aqueous Zinc sulfate solutions, and delayed pyrolysis of cold- sprayed and dried ZnCl_2 films, do not lead to semiconducting films. Formation of ZnO from an aqueous Zinc salt requires the simultaneous presence of Zinc ions, Chloride ions, and water, at the time of pyrolysis. We therefore suggest the actual ZnO precursor is the $\text{ZnCl}_x\text{H}_2\text{O}_{(4-x)}$ species that forms when ZnCl_2 dissolves in water [The Journal of Chemical Physics 39, 3436 (1963)]. The reported process is easy to upscale for large area ZnO coatings, e.g. on window panes for thermal control, as no organic solvent vapours are released.

Index Terms: II-VI semiconductor, precursor, thin film transistor, Zinc chloride, Zinc oxide.

I. INTRODUCTION

ONE of the driving forces for developing semiconducting organic polymers has been the possibility to process them into devices from solution, opening up alternative semiconductor device manufacturing options, e.g. via printing [1]. However, organic semiconductor performance and long-term stability are limited, and the best performing semiconducting polymers are often well soluble only in environmentally unacceptable halogenated solvents [2]. Therefore, inorganic semiconductors that can be processed from solution- based precursors have recently attracted significant attention as an alternative. In 2007, Ong et al [3] have demonstrated that semiconducting films of the II-VI semiconductor Zinc oxide (ZnO) can be prepared by pyrolysis of the organic precursor, Zinc acetate (ZnAc), which dissolves in relatively benign solvents (alcohols, ketones, mixtures thereof [4]). Since water- gating of precursor- route ZnO was

demonstrated [5], it has become a popular semiconductor for application in electrolyte- gated thin film transistors (TFTs) [6]. ZnAc precursor solution now often is converted by spray pyrolysis directly onto a hot substrate [7]. However, other uses of ZnO, e.g. as window pane coating for heat management in buildings, require application of ZnO to large areas. Here, spraying ZnAc precursor would lead to plumes of organic solvent that would need containment even for relatively benign solvents. Current practical ZnO heat management solutions instead apply ZnO (or similar) to window panes using adhesive films of nanoparticles dispersed in a polymer matrix [e.g. [8]].

II. RESULT AND DISCUSSION

In Fig. 1, we show the optical transmission spectrum in the visible and near UV of a film resulting from spray pyrolysis of 0.1 M aqueous ZnCl_2 solutions onto a fused silica substrate held at 450°C on a hot plate. 0.1 M solutions had been prepared by adding 1.36 g of ZnCl_2 to 100 mL of DI water, wherein it readily dissolved. Spraying was by 3 ‘puffs’ from 15 cm distance lasting $1 \dots 2$ seconds in 20 s intervals, using a commercial GaGa Milano 134K airbrush with 0.2 mm nozzle at 1.5 bar pressure. The substrate was then kept on the hot plate for 30 more minutes.

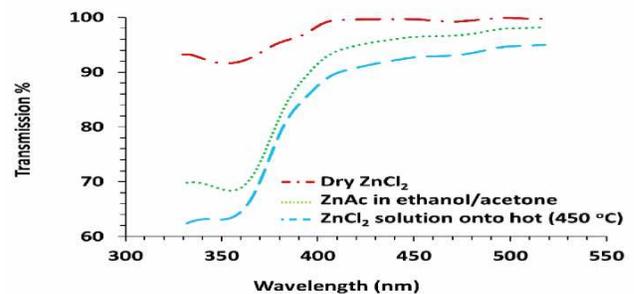


Fig. 1 Optical transmission spectra for 3 sprayed films: Aqueous ZnCl_2 solution onto hot (450°C) substrate (blue, dashed), ZnAc in ethanol/acetone 1:1 onto hot substrate (green, dotted), aqueous ZnCl_2 solution onto ambient temperature substrate, dried under vacuum, heated afterwards (red, dot dash).

At short wavelengths, optical transmission for films of spray pyrolysed aqueous ZnCl_2 (blue dashes in Fig. 1) is limited to $\sim 62\%$, but steeply rises to near fully transparent at wave-lengths above $\lambda \sim 365\text{ nm}$. For comparison, we also show the transmission spectrum for a film spray pyrolysed in the same way but from Zinc acetate (ZnAc, $\text{H}_3\text{C-CO-O-Zn-O-CO-CH}_3$) dissolved in mixed ethanol/acetone (1:1) (green dots in Fig. 1). Pyrolysis of ZnAc is well established to lead to Zinc oxide [3, 4, 6, 7]. Both films show very similar spectra, and both are no

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longer soluble in water albeit both precursors (ZnCl_2 and ZnAc) are. We therefore conclude that in both cases, spray pyrolysis has led to the same product, namely Zinc oxide (ZnO). We can exclude zinc peroxide (ZnO_2) even though it has the same elemental composition; this is discussed in more detail in the section on XPS, and in ‘conclusions’. As control experiments, we again sprayed ZnCl_2 solution in the same way but onto a substrate held at ambient temperature, dried under dynamic vacuum for 1 h, and heated to 450 °C after drying. The resulting film (red dot- dash in Fig. 1) does not show the pronounced ‘absorption edge’ at 365 nm characteristic of semiconducting ZnO , and it remained soluble in water. Similarly, we sprayed an aqueous solution of Zinc sulphate (ZnSO_4) onto hot substrate in the same way as we had done for ZnCl_2 solutions. This film also did not show an absorption edge, and remained soluble in water. We conclude neither of the latter two processes leads to ZnO .

To establish the chemical identity of spray- pyrolyzed films of waterborne ZnCl_2 beyond doubt as ZnO , we have performed XPS characterisation, using a Kratos Axis Ultra DLD instrument with monochromated aluminium source. Note we now sprayed on heated soda lime glass substrates, rather than fused silica. A wide- range XPS survey scan (0 .. 1200 eV) of a spray pyrolysed ZnCl_2 film now shows a number of peaks that can be assigned and quantified for elemental composition from their peak area, as shown in table 1:

Table 1

Approx. position(eV)	1089	1018	528	344	283	198	151
Assignment	Na 1s	Zn 2p	O 1s	Ca 2p	C 1s	Cl 2p	Si 2s
Atom%	3.2	34.0	40.5	1.0	13.8	1.7	5.9

Table 1: XPS peak positions, elemental assignments, and atom percentages calculated from peak areas, for films derived from spray pyrolysis of ZnCl_2 on soda lime glass.

This shows Zinc and Oxygen as the main components of spray pyrolysed films, in near 1:1 ratio, as expected for ZnO , but not ZnO_2 . The small excess of oxygen over Zinc, as well as the presence of Na, Ca, and Si, can be explained as contributions from the glass substrate, as these are the ingredients of soda lime glass. Chloride is likely to be a remainder from the ZnCl_2 precursor, but is present at only 1.7%, far less as in the original ZnCl_2 . Carbon from organic surface contamination is commonly found in XPS, and often used for calibration. For more detailed analysis, we resolved the O 1s and Zn 2p peaks more clearly; these are shown in Fig. 2. In parallel, we recorded the Zn LMM Auger peak at ~ 988 eV.

For O 1s (Fig. 2a), we find a broad peak that can be deconvoluted into 3 narrow, but overlapping Gaussians. The strongest is located at 530.2 eV, and two weaker peaks at slightly higher binding energies (531.5 eV, 532.7 eV). The strong peak corresponds to O 1s in metal oxide, and the ones at higher binding energy to hydroxide (-OH surface groups), or to oxygen defects, i.e. oxygen outside of the lattice structure [11]. The Zn 3p peak (Fig. 2b) is split into the Zn 2p_{3/2} and Zn 2p_{1/2} doublet at 1021 eV / 1045 eV; both O 1s and Zn 2p peaks are

very similar to the XPS signatures of ZnO derived via the Zinc acetate precursor route, e.g. [4]. However, the Zn 2p XPS doublet is rather insensitive between metallic zinc and ZnO , this is better differentiated by the Zn LMM Auger peak (inset Fig. 2b) [12]. We find this Auger peak located at 988 eV, and in location and shape it well matches the documented LMM Auger peak for Zinc in ZnO , rather than metallic Zinc or any other common Zinc compound [12]. Overall, XPS and Auger analysis confirm that spray pyrolysed ZnCl_2 forms films of ZnO , with -OH surface groups. UV/Vis, XPS, and Auger spectroscopy therefore establishes aqueous ZnCl_2 as an alternative precursor for ZnO . We cannot strictly establish the crystal structure (wurtzite vs. zincblende), but the thermodynamically stable wurtzite structure is most likely.

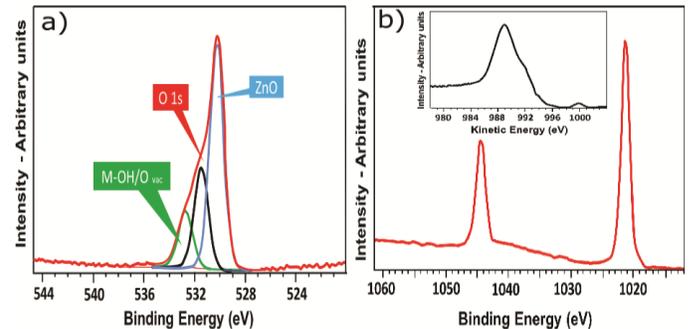


Fig. 2: Highly resolved XPS spectra of spray pyrolyzed films in the O 1s (Fig. 2a) and Zn 2p (Fig. 2b) regions (~ 530 eV region, and ~ 1015 eV ... 1050 eV, respectively). Note the splitting of Zn 2p into Zn 2p_{3/2} and Zn 2p_{1/2}. Inset to Fig. 2b: Zn LMM Auger peak at ~ 988 eV.

To test the semiconducting properties of spray pyrolysed ZnCl_2 films, we sprayed aqueous ZnCl_2 onto thin film transistor (TFT) substrates held at 450 °C. Transistor substrates consist of silica- coated glass substrates with evaporated Au / Cr adhesion layer (10 nm Cr / 120 nm Au) contact pairs of width $W = 1$ mm separated by a gap (‘channel’) of $L = 30\mu\text{m}$, $W/L = 33$; we have used same substrates previously for water- gated TFTs [4, 13]. We electrically addressed contact pairs on sprayed substrates as TFT ‘Source’ (S) and ‘Drain’ (D) and gated via a droplet of deionised water contacted with a tungsten (W) needle bent into L- shape to overlap the width of the channel, similar as in our previous work on water- gated ZnO TFTs [5]. An illustration is in Fig. 3a. The source and drain contacts have been covered by glass and only the active area is exposed to electrolyte. Electrical characterisation was with a pair of Keithley 4200 source/measure units controlled by bespoke software to apply gate- and drain voltages, and to record resulting drain current. A blank substrate displayed sheet resistance of at least 330 $\text{G}\Omega/\square$, a non- gated spray pyrolysed ZnCl_2 film still 10 $\text{G}\Omega/\square$, indicating low doping levels.

Fig. 3 shows the resulting output- and transfer characteristics for water- gated TFTs using spray pyrolysed ZnCl_2 films in their channel.

Characteristics clearly show field effect transistor action for positive drain- and gate voltage, as expected for a TFT with electron- transporting semiconducting channel, like ZnO . We find saturation for $V_D > V_G$ in the output characteristics, and

estimate a threshold voltage of $V_{th} = 0.24$ V from the (linear) transfer characteristic for W gate, similar as in previous reports [4-6]. Such low thresholds are typical for electrolyte-gated TFTs, resulting from the high capacitance of electrolytic gate media [14]. At $V_G = V_D = 0.6$ V, we find a saturated drain current $I_{D,sat} = 72$ μ A, corresponding to a sheet current I_{\square} (0.6 V) = $L/W * I_{D,sat}$ (0.6 V) = 2.16 μ A/ \square , and a sheet resistance of R_{\square} (0.6 V) = $W/L [V_D = 0.6$ Volt / $I_{D,sat} = 72$ μ A] = 278 k Ω / \square . These performance characteristics are similar to water-gated TFTs using ZnO prepared via the ZnAc precursor route, e.g. I_{\square} (0.8 V) = 4.4 μ A/ \square and R_{\square} (0.8 V) = 182 k Ω / \square in [5]. The on/off ratio taken from Fig. 3d is ~ 300 , and the inverse subthreshold slope 215 mV/decade. Our ZnCl₂-derived films perform similarly to water-gated ZnAc precursor route ZnO TFTs reported in the literature.

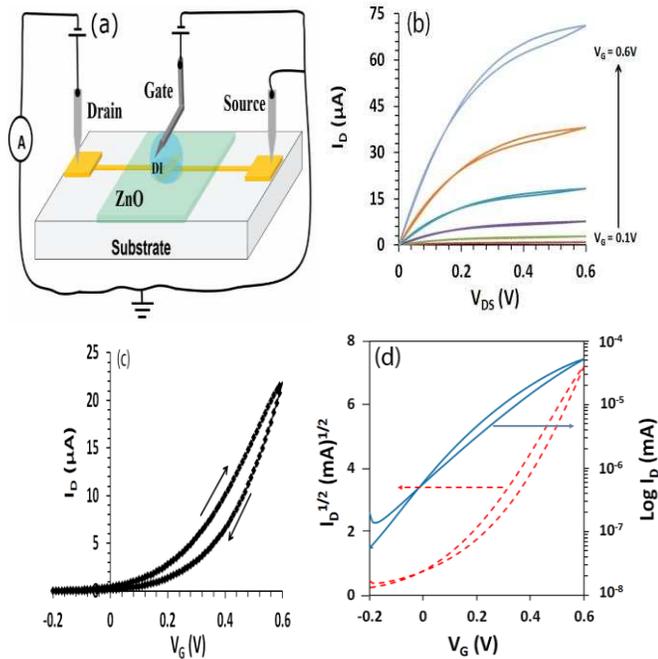


Fig. 3: (a), scheme of water-gated TFT architecture Output (b) linear transfer characteristics ($V_D = 0.1$ V) (c), and saturated transfer characteristics (d) on root (red dashed) and log (blue) drain current scales of water-gated TFTs using films of spray pyrolysed aqueous ZnCl₂ solutions in the transistor channel.

For better understanding of the process leading from waterborne ZnCl₂ to ZnO, We conducted control experiments on transistor substrates, similar as for optical characterisation: We: sprayed aqueous ZnCl₂ solutions onto TFT substrate at ambient temperature, dried under vacuum, and heated after drying. Also, we sprayed aqueous ZnSO₄ onto hot TFT substrate. Both control experiments resulted in films that were still soluble in water, and attempted gating and TFT characterisation did not lead to significant drain current, or recognisable transistor characteristics. We further determined the minimum required substrate temperature for successful spray pyrolysis of ZnCl₂. From experiments with stepwise-reduced substrate temperatures, we find that films sprayed to substrates held at 250 $^{\circ}$ C still gave TFTs with similar properties as those reported in Fig. 3, but not for substrate temperatures of

200 $^{\circ}$ C or below. Also, spraying fewer than 3 ‘puffs’ did not lead to working devices. A surface profilometer characterisation shows a film thickness of ~ 85 nm for 3 puffs, but significant surface roughness up to ~ 40 nm.

III. CONCLUSION

In conclusion, we show that films the material resulting from spray pyrolysis of aqueous ZnCl₂ displays the same insolubility in water, optical absorption edge, XPS and Auger spectra, and semiconducting properties in TFTs as ZnO. We can exclude that our films consist of Zinc peroxide (ZnO₂), despite this consisting of the same chemical elements as ZnO. ZnO₂ is unstable above 230 $^{\circ}$ C [15] hence would decompose at the pyrolysis temperature we used, and ZnO₂ has a larger (and indirect) bandgap (3.8 eV \longleftrightarrow 327 nm) than we observe in Fig. 1. Our spectra match the 100% ZnO spectra reported in a comparison of ZnO₂ vs. ZnO by Companion [16]. Further, XPS elemental proportions support ZnO over ZnO₂. We therefore identify it as ZnO. Formation of ZnO from an aqueous Zinc salt requires the simultaneous presence of Zinc ions, Chloride ions, and water, at the time of pyrolysis. This is shown by control experiments where either water or Chloride were absent at the time of (attempted) pyrolysis, which both do not lead to semiconducting films. We therefore suggest the actual ZnO precursor is the ZnCl_xH₂O_(4-x) species that forms when ZnCl₂ dissolves in water [9, 10]. This species clearly relies in the simultaneous presence of Zinc ions, Chloride ions, and water. While we cannot exactly determine the reaction mechanism leading from ZnCl_xH₂O_(4-x) to ZnO, it is interesting to note that Chen et al. [15] report the synthesis of Zinc peroxide (ZnO₂) nanoparticles from aqueous ZnCl₂ solution. ZnO₂ thermally converts into ZnO at 230 $^{\circ}$ C [15], while we find a similar minimum required substrate temperature of 250 $^{\circ}$ C for formation of semiconducting films from sprayed ZnCl₂ solution. While we can exclude ZnO₂ in the resulting film, it may transiently appear as an intermediate on the route from ZnCl_xH₂O_(4-x) to ZnO. Regardless of the precise nature of the precursor and its conversion mechanism, we demonstrate a new solution-based precursor route to a high performance inorganic semiconductor that requires only the most generic and easily available chemicals, namely ZnCl₂ and water. The required substrate temperature of 250 $^{\circ}$ C is significantly lower than for ZnO from ZnAc precursor route [3-7]. Spraying waterborne ZnCl₂ onto hot window panes immediately during manufacture could deposit a ZnO coating for thermal management without later application of heat management films. Unlike ZnAc precursor spraying, this process would release only water vapour rather than solvent fumes.

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