A General and Low-Cost Route to Printable High-Mobility Inorganic Thin Film Transistors

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Abstract

We have developed a general and low-cost process to fabricate high mobility metal oxide semiconductors that is suitable for thin film electronics. This process uses simple metal halide precursors dissolved in an organic solvent and is capable of forming uniform and continuous thin films via digital fabrication (e.g. inkjet printing). This process has been demonstrated to deposit a variety of semiconducting metal oxides including binary oxides (ZnO, In_2O_3, SnO), ternary oxides (ZIO, ITO, ZTO) and quaternary compound IZTO. Functional thin film transistors with high field-effect mobility were fabricated successfully using channel layers deposited from this process ($\mu FE \cong 12$ cm^2/V-sec from inkjet printed IZTO channel layer). This novel synthetic pathway opens an avenue to form patterned metal oxide semiconductors through a simple and low-cost process for fabricating high performance inorganic thin film electronics via digital fabrication processes.

Introduction

Digital fabrication technologies, such as inkjet printing at atmospheric environment, offer an opportunity for the direct patterning of functional materials and provides a potential cost advantage over the amorphous and polycrystalline silicon-based technologies. Inkjet printing of inorganic materials for the formation of active devices is relatively rare compared to the research done with respect to organic materials. To date, only a handful of inorganic materials have been inkjet printed, primarily due to the difficulty in preparing inkjet printable precursors.

Current methods for the production of functional inorganic electronic devices are based on the sequential deposition, patterning, and etching of selected semiconducting, conducting, and insulating materials. These sequential processes generally involve multiple photolithography and vacuum deposition processes, which contribute to their high manufacturing costs. Solution-based and direct printing of inorganic materials offer the possibility of depositing high quality thin films at low temperature under atmospheric conditions, and the direct additive patterning processes that enable the fabrication of high-performance and ultra-low-cost electronics. Recently, high mobility (> 10 cm^2/V.s.) inorganic thin film transistors were fabricated using spin-coated $SnS_{2-x}Se_x$ [1] and In_2Se_3 [2] semiconductor thin films. Unfortunately, these devices tend to degrade (mobility and current) after exposure to the ambient atmosphere, and require storage and characterization in a nitrogen-filled dry box.

Inkjet printing of inorganic materials is relatively rare compared to the inkjet printing of organic materials, especially for semiconductor channel materials. Over the last few years, there has been tremendous progress on direct inkjet printing of polymer TFTs. Sirringhaus *et al*. have fabricated all-polymer thin film transistors with a combination of inkjet printing and spin-coating.[3] A mobility of 0.02 cm^2/V.sec was achieved from spin-coated semiconducting polymer channel layer (9,9-dioctylfluorene-co-bithiophene, P8T2). After researchers at IBM demonstrated an innovative and simple one-step synthetic pathway to a soluble pentacene precursor [4], the first inkjet-printed pentacene transistor [5] was fabricated with a maximum mobility of 0.02 cm^2/V.sec and a current on-to-off ratio of 10^5. Arias *et al* [6] reported an inkjet printed TFT using a polythiophene semiconductor channel that exhibited a field effect mobility of 0.1 cm^2/V.s. and a current on-to-off ratio of 10^7. Recently, Kawasaki *et al* [7] reported an organic TFT using an inkjet printed pentacene channel layer with a mobility of 0.15 cm^2/V.s. (the highest reported value for TFTs in which the channel is formed by inkjet printing) and a current on-to-off ratio of 10^5.

Inorganic semiconductors have the advantages of higher mobility, and better stability. However, not many inorganic materials have been inkjet printed and the majority of reports are focused on printing metal nanoparticle solutions for metallization. For example, copper nanoparticle solutions were inkjet printed for source/drain metallization of a-Si TFTs [8]; silver and gold nanoparticle solutions were inkjet printed to build active microelectromechanical systems (MEMS) [9]. The first example of "printing" inorganic semiconducting channel materials is reported by Ridley *et al* [10] who fabricated a thin film transistor with a mobility of 1 cm^2/V.s. and a current on-to-off ratio of 3.1×10^4 by casting CdSe thin films from a precursor solution of cadmium selenide nanocrystals using a micro-pipette. An extreme melting point depression enables the melting or sintering of nanocrystals into a polycrystalline film at lower temperatures. However, the device fabrication needs to be performed in a dry box and a photocurable polymer adhesive layer is required to encapsulate the active region of the TFT or no field effect could be observed. Most recently, Shimoda *et al*. [11] fabricated TFTs using an inkjetted droplet to fabricate a poly-silicon channel layer with a mobility of 6.5 cm^2/V.sec and an on/off ratio of three digits.

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This process, however, requires a special precursor and very stringent control of the oxygen level (<0.5ppm) in a dry box in addition to laser re-crystallization and thermal annealing (540°C).

Transparent conducting oxides (TCOs) like zinc oxide, tin oxide, and indium tin oxide are important for a plethora of optical and electrical applications such as flat-panel displays, organic light-emitting diodes, electromagnetic shielding, and electrochromatic windows [12,13], and more recently as channel materials for thin film transistors [14,15]. We have recently developed a general and low-cost process for inkjet printing a variety of high-mobility semiconducting metal oxides as TFT channel layers for the first time [16]. Our process uses metal halide precursors dissolved in acetonitrile which are capable of forming uniform and continuous thin films through both digital fabrication (e.g. inkjet printing) and blanket coating (e.g. spin coating) techniques. As an aprotic solvent, acetonitrile does not dissociate the metal halide precursor, which allows for a simple dissolution and drying mechanism. In addition, the high volatility of acetonitrile helps convert the printed liquid thin films into solid metal halide thin films in a short time. In contrast, metal halides tend to dissociate and form hydroxide precipitates in an aqueous solution, dry much slower, and often form poor quality films. The inkjet printed metal halide thin films were converted to high performance semiconducting metal oxides through a thermally activated substitution reaction between the metal halide film and H_2O. The mechanism of metal oxide semiconductor thin film formation is illustrated in Figure 1. The metal oxide thin film formation starts with the precursor dissolution and follows by thin liquid film formation by inkjet printing, the thin solid film formation after solvent evaporation, and finishes by a substitution oxidation reaction. This synthetic pathway opens a new avenue to fabricate a variety of patterned metal oxide semiconductors through a simple and low-cost process.

Results and Discussion

Metal halide precursor solutions for fabricating inkjet-printed oxide thin films were prepared by dissolving $ZnCl_2$, $SnCl_2$ and $InCl_3$ powders (obtained from Alfa Aesar) in acetonitrile mixed to the appropriate ratio depending on the desired product composition. All prepared solutions were treated ultrasonically to ensure complete mixing of the solutions in 30 ml pre-cleaned vial for 10 min at ambient temperature before printing.

We used a modified HP 1220C thermal inkjet printer and Microsoft PowerPoint software to print the active layer with a desired pattern. First, the metal halide precursor solution was filled into the black cartridge (HP45) by a needle syringe, sealed with a metallic ball, and then loaded into the cartridge holder. Second, the SiO_2/Si/Au substrate was cleaned with standard Acetone, Methanol and De-ionized Water (AMD) for pre-cleaning method, followed by a stream of clean dry nitrogen gas to blow it dry, before placing onto a plastic tray, and loaded into the inkjet printer. All inkjet printed thin films were annealed at 600°C for 1 hour. Our process is not only suitable for digital fabrication (inkjet printing) but also applicable for the blanket coating process such as spin coating. Spin coating provides an alternative process to evaluate our process. Precursor solutions (Acetonitrile based $ZnCl_2$, $SnCl_2$, and $InCl_3$) were spun on top of substrate at 8000 rpm for 30 seconds.

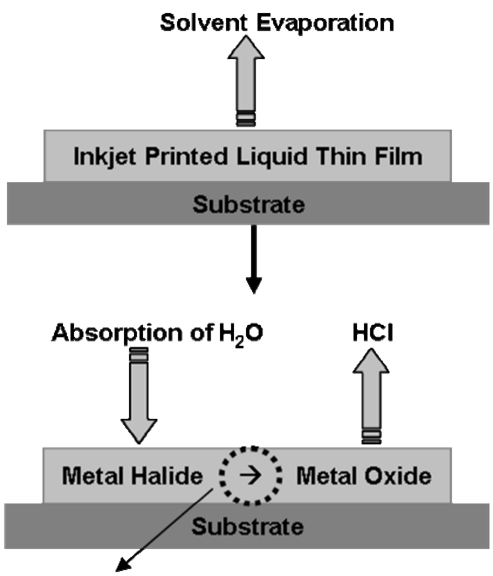
For Metal-Insulator-Semiconductor Field-Effect Transistors (MISFETs) fabrication, a heavily boron (p+) doped silicon substrate served as the gate in an inverted-gate structure. Silicon dioxide with thickness of 100 nm was thermally grown on top of the silicon substrate. The back of the substrate had the silicon dioxide etched followed by deposition of a 500 nm gold layer for the gate contact. The semiconductor channel material was printed in a strip pattern to reduce the gate leakage current. The 300 nm aluminum source and drain contacts were then evaporated on top of metal oxide layer through a shadow mask. The device characterization was performed in the dark at room temperature with a HP 4157B Semiconductor Parameter Analyzer.

The use of multi-component oxide materials provides the possibility to tailor the electrical, optical, physical and chemical properties of TCO films by altering the chemical composition [17, 18]. Our process opens a general route to achieve this goal and can be used to fabricate a variety of metal oxides. Figure 2 shows seven transparent conductive oxide thin films (ZnO, In_2O_3, SnO_2, ZnO-In_2O_3 (ZIO), In_2O_3-SnO_2 (ITO), ZnO-SnO_2 (ZTO), and In_2O_3-ZnO-SnO_2 (IZTO)) that have been fabricated in our laboratory using this new process by the combination of simple $ZnCl_2$, $SnCl_2$ and $InCl_3$ precursors in acetonitrile by both inkjet printing and spin coating.

For example, we have inkjet printed IZTO thin films using a precursor solution of $InCl_3$, $ZnCl_2$ and $SnCl_2$ in acetonitrile. Figure 3 shows the scanning electron microscope image of IZTO. Without any process optimization, the overall device performance for the inkjet printed IZTO MISFET is quite encouraging. Figure 4a shows the drain current - drain voltage (I_{DS} - V_{DS}) output characteristics for IZTO MISFET with a channel width-to-length ratio of 7 (channel length equals 200 μm) and a good gate-modulated transistor behavior. The field-effect mobility (μ_{FE}) determined by the transconductance of this device is $\mu_{FE} \cong 12$ cm^2/V-sec. Figure 4b shows the Log(I_{DS})-V_{GS} transfer characteristics at $V_{DS} = 40$ V indicating a drain current on-to-off ratio of approximately 10^6 with a turn-on voltage of -7 V. With a negative turn-on voltage, this device behaves as a depletion-mode device and the relatively large drain current on-to-off ratio indicates that it can function well as a switch. Another interesting example is the fabrication of ITO MISFET via the same process. The output characteristics of the spin-coated ITO MISFET with a channel width-to-length ratio of 7 (channel length equals 200 μm) shows a relatively high field-effect mobility (μ_{FE}) of 30.21 cm^2/V-sec, a drain current on-to-off ratio of approximately 10^5 and a turn-on voltage of -15 V. Inkjet printed ITO MISFET were also fabricated with a field effect mobility (μ_{FE}) of 2.03 cm^2/V-sec. The inkjet printed ITO TFT again showing an inferior device performance than the device fabricated from the spin coated channel layer. We believe further optimization of the inkjet printing process will lead to inkjet printed TFTs with even better performance. All electrical properties of semiconducting oxides TFTs prepared by inkjet printing and spin coating process are presented in table 1.

In conclusion, we have developed a general and low-cost process to fabricate high mobility metal oxide semiconductors that is suitable for thin film electronics. This process use simple metal halide precursors dissolved in an organic solvent and is capable of forming continuous thin films via digital fabrication (e.g. inkjet printing) and blanket coating (e.g. spin coating) techniques. This process has been demonstrated to deposit a variety of semiconducting metal oxides include binary oxides (ZnO, In_2O_3, SnO_2), ternary oxides (ZIO, ITO, ZTO) and quaternary compound IZTO. Functional thin film transistors with high field-effect mobility were fabricated successfully using channel layers deposited from this process (e.g $\mu_{FE} \cong 12.02$ cm^2/V.sec. from inkjet printed IZTO channel layer). This novel synthetic pathway opens an avenue to form patterned metal oxide semiconductors through a simple and low-cost process and to fabricate high performance inorganic thin film electronics via digital fabrication processes.

Graphics and Equations



$$M\,(Zn, In, Sn)\cdot Halides\,(Cl, Br, I) + H_2O$$
$$\xrightarrow[\Delta]{} M\cdot Oxides + H\cdot(Cl, Br, I)\uparrow$$

Figure 1.The illustration of the detail thin film deposition process.

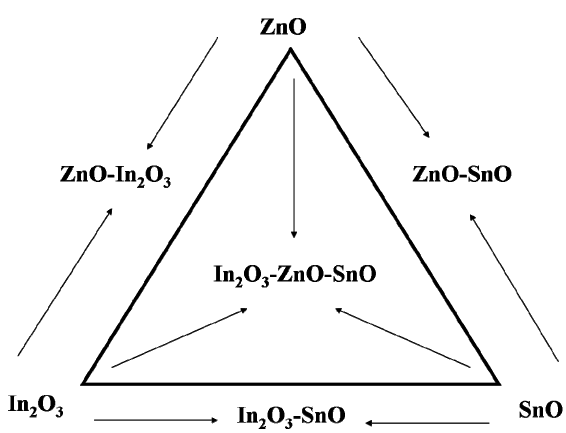


Figure 2. Seven transparent conductive oxide thin films have been fabricated by both inkjet printing and spin coating in our labs.

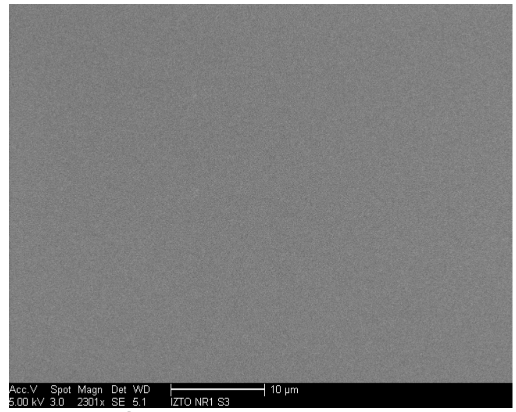


Figure 3. The Scanning electron microscope image of IZTO thin film by inkjet printing process.

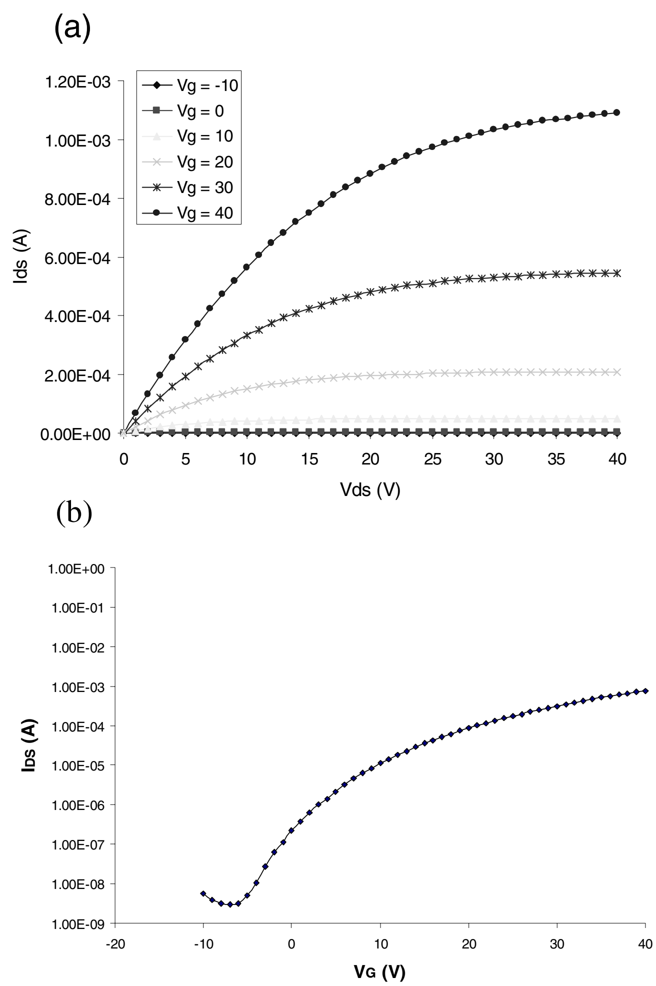


Figure 4 a, The drain current - drain voltage (I_D - V_{DS}) output characteristics and b, drain current - gate voltage (Log(I_D)-V_{GS}) transfer characteristics at V_{DS} = 40 V for IZIO MISFET.

Table 1. *Summary of Electrical Properties of Semiconducting Oxide Thin Film Transistors*

	Oxide MISFET device by Inkjet printing				
		ZIO	ZTO	ITO	IZTO
Spin-coating	Mobility (μFE) [cm^2/V-sec]	16.13	15.92	**30.21***	15.09
	On-off	1e4	1e5	1e5	1e5
	Von	-32	2	-15	-33
Inkjet printing	Mobility (μFE) [cm^2/V-sec]	7.37	1.17	2.03	**12.02****
	On-off	1e4	1e5	1e4	1e6
	Von	-25	7	-20	-7

*, ** indicate the TFT which has the highest mobility

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